Appendix D

Sediment Air Emission Calculations

Foth | Envirocon Joint Venture

Memorandum

101 International Drive, P.O. Box 16655
Missoula, MT 59808

December 1, 2016

TO: Eric Ealy

CC: Denis Roznowski, Alan Buell

FR: Curt Dungey, CHMM, CIH; Brian Symons, P.E.

RE: Air Emission Estimates from Sediment Management, Stabilization, and Barge Decant Dewatering Operations

This technical memorandum summarizes an analysis of potential emissions of volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC) originating from activities occurring inside the sediment processing tent, including sediment management, stabilization, and barge decant dewatering activities taking place as part of the Phase 2 Wet Dredge Project. Results of the analysis are compared against state and federal regulatory limits. Results demonstrate that potential calculated emission rates are less than applicable state standards for air toxics and that ambient air concentrations inside the processing tent are well within workplace health standards.

This technical memorandum is organized to provide the following:

- Information and assumptions regarding the sediment handling, stabilization processes, and barge decant dewatering operations;
- Explanation of the screening level equations, parameterization, and assumptions;
- Summary of the estimated emissions; and
- Comparison of estimated emissions to Wisconsin Department of Natural Resources (WDNR) and Occupational Safety and Health Administration (OSHA) regulatory requirements.

Sediment management and stabilization will include the following steps:

1. Dredged sediments will be unloaded from scows and manually segregated with a trackhoe bucket with thumb to remove large debris.
    a. The typical dredge rate is assumed to be 1,200 cubic yards per day (cy/day).

2. Sediment will be transported to a sediment processing area located within the ventilated tent that will be installed on-site specifically for Phase 2 Wet Dredge project use (hereafter referred to as the "tent structure").

3. Sediment will then be stabilized in the sediment processing area.

    a. The feed rate is assumed to be 1,200 cy/day.
    b. Mixing will be completed over 12 hours.

4. Stabilized sediment will be transported to a holding bin located within the ventilated tent.

5. Stabilized sediment will then be loaded into haul trucks for off-site disposal.

In addition to sediment management and stabilization activities, barge decant dewatering operations will also occur in a portion of the sediment processing tent. This will include removal of solids in geobags or geotextile tubes, with remaining water collected and discharged for storage outside the building prior to final water treatment.

Emissions Basis for Each Processing Step

Material Segregation

The primary objective of the material segregation is to separate large debris from dredged material and small debris to facilitate sediment processing to meet disposal criteria. The large debris will be segregated from sediment and smaller debris on the barge for separate off-loading and management. Large debris will be manually separated from the sediment using a trackhoe bucket with thumb. Due to the limited degree of dredged material agitation and the short time required to separate large debris from the remaining sediment, the emissions rate and mass is expected to be minimal.

Dredged Material Holding

The dredged materials inside the sediment processing tent will be contained in storage areas before and after stabilization. Emissions from dredged materials are estimated based on the USEPA 450/4-90-004 guidance: *Air/Superfund National Technical Guidance Study Series* (USEPA, 1990). Section 4.1.2 (USEPA, 1990) estimates VOC emissions. The emission rate for a specific species i, M_i, from an exposed contaminated waste layer can be calculated using Equation 2 as follows:

$$M_i = 0.72 \left[\frac{K_{eq}\, D_e\, \pi^2\, t}{4d^2}\right]^{0.5} C_{oi} \quad (2)$$

where:

M_i	=	emissions rate of contaminant i (grams per cubic meter)
K_{eq}	=	partition coefficient of species i (unitless)
D_e	=	effective diffusivity of species i (centimeters squared per second)
t	=	time of exposure (seconds)
d	=	depth of soil or dredged material waste layer (centimeters)
C_{oi}	=	concentration of species i (grams per cubic centimeter dredged material) in the dredged material

The value of K_{eq} can be calculated using Equation 3 (USEPA, 1990). The partition coefficient is a function of the contaminant's vapor pressure, molecular weight, air porosity of the soil, and an organic loading. For the Phase 2 Wet Dredge project, the organic loading was based on measured total organic carbon of the sediments, and the default value for E_a from Table 3 (USEPA, 1990) was used.

$$K_{eq} = \frac{P_i^* MW_{ORG}\, E_a}{RTL} \quad (3)$$

where:

K_{eq}	=	partition coefficient of species i (unitless)
E_a	=	air porosity of soil (volume/volume)
R	=	universal gas constant; 82.1 atm*cm^3/(mol*K)
T	=	temperature (degrees Kelvin)
P_i^*	=	vapor pressure of species i (atm)
MW_{ORG}	=	molecular weight of organic constituent (g/mol)
L	=	organic waste loading (g organic/cm^3 soil)

The effective diffusivity (D_e) is calculated from Equation 4 (USEPA, 1990).

$$D_e = D_a \frac{{E_a}^{3.33}}{{E_T}^2} \quad (4)$$

where:

D_e	=	effective diffusivity (centimeters squared per second)
D_a	=	diffusivity in air (centimeters squared per second)
E_a	=	air porosity of soil (volume/volume)
E_T	=	total porosity of soil (volume/volume)

The air-filled porosity (E_a) and total porosity values (E_T) for compacted subsoils of high moisture content were used (see Table 3; USEPA, 1990).

Other constants used in estimating emission rates from the stockpile or bin during dredged material hold time were:

d = depth of dredged material (assumes USEPA default for depth of dredged material emitting emissions equals 100 centimeters)
t = time dredged materials are exposed
C_{oi} = concentration of species i, estimated based on mass balance after stabilization step

Sediment Stabilization

The USEPA's *Air/Superfund National Technical Guidance Study Series*: *Models for Estimating Air Emission Rates from Superfund Remedial Actions* (USEPA, 1993) provides a screening level model for estimating VOC emissions during solidification and stabilization of dredged materials. VOC emissions from ex situ stabilization and solidification processes for dredged materials are estimated from Equation 4-18 (USEPA, 1993), as shown in Equation 1 as follows:

$$ER_i = C_i \, F \, V_i \quad (1)$$

where:
ER_i = emission rate of contaminant i (mass per time)
C_i = concentration of contaminant i in dredged material (mass of contaminant i per mass of dredged material)
F = treatment (feed) rate of dredged material (mass per time)
V_i = fraction of contaminant i volatilized

The expected range of VOCs volatilized during stabilization and solidification of dredged material is 40 to 100% (USEPA, 1993). The recommended default value for estimating VOC volatilization during stabilization and solidification is 80% (see Table 4-5; USEPA, 1993). VOCs are generally considered organic compounds with vapor pressures greater than 1 millimeter (mm) mercury at 20 to 25 degrees Celsius (°C).

USEPA guidance (USEPA, 1993) for volatilization of contaminants during stabilization is limited to VOCs and does not include SVOCs. For example, naphthalene's vapor pressure is 0.09 mm mercury at 25°C which is an order of magnitude lower than the VOCs measured in the sediments. Other SVOCs detected in Phase 2 Wet Dredge project sediments have vapor pressures that are 2 to 10 orders of magnitude lower than VOCs. To estimate the relative volatilization of VOCs and SVOCs, the fraction of contaminant volatilized was estimated using 80% volatilization of benzene as a reference. This approach is based on USEPA guidance for VOCs. Given benzene has the highest vapor pressure for the group, this was used as a starting point. Volatilization fractions of other VOCs and SVOCs were estimated based on the proportionate relationship of:

$$Relative\ Volitilization = \left[K_{eq} \, D_e\right]^{0.5}$$

Due to low vapor pressures, evaporation of SVOCs is negligible at 20°C (NIOSH, 2013).

Values used for other variables in the equation for VOC emissions from the stabilization and solidification process include:

C_i = concentration of species i; used the 95th Percentile value calculated from Phase 2 dredge area core sample data

F = feed rate (kilograms per hour) assuming average of 1,200 cy mixed over 12 hours each day

Barge Decant Dewatering Operations

Barge decant water is directed to geobags or geotextile tubes located inside the sediment processing tent for dewatering and collection of sediment prior to filtrate being discharged outside for storage prior to further treatment. Inflow to the building is estimated to be approximately 90,000 gallons per day. The estimated incoming COC concentrations are estimated from recent laboratory data for wastewater influent. The total pounds per day of each COC through the system can then be calculated using the concentration and total daily flow. Air emissions for each COC from water management can then be estimated by taking into account certain chemical specific data for each COC, including molecular weight and vapor pressure. While estimated air emissions from this operation is small, it has been added to the estimated air emissions from sediment management and material storage.

Results

Emission rates were estimated for each step: stabilization/mixing of sediments for 12 hours for a 1,200 cy/day operation and holding for the remainder of the day before and after stabilization as shown in Table 1. In addition, emission rates from barge decant dewatering activities were added to these activities. These rates were summed for a daily emission rate. Detailed calculation sheets are provided in Attachment 1 – Calculations.

The total emission rates per the anticipated daily operation were then compared to WDNR and OSHA regulatory standards. This building volume of 2,100,000 cubic feet (see Tables 1 and 2), an exhaust fan height of 30 feet, and 4.57 air exchanges/hour resulting in 13.1 minutes per exchange. Wisconsin Administrative Code NR 445.07 provides emission thresholds, standards, and control requirements for specified hazardous air contaminants based on pounds per hour or pounds per year for specific stack heights. The emission calculations must be performed based on a potential to emit basis. For this reason, the processing rate of 1,200 cy per day was used.

The VOCs of concern for the Phase 2 Wet Dredge project are based on 24-hour averages (pounds/hour) for emissions thresholds, with the exception of benzene, which is an annual threshold. The SVOCs of concern for the Phase 2 Wet Dredge project have annual thresholds (pounds/year).

The 24-hour average rate was calculated by taking the total emissions in pounds per day and dividing it by 24 hours, as follows:

24-hour average rate (pounds/hour) = pounds per day/24 hours per day

Annual emissions were calculated by multiplying the 24-hour average rate (pounds/hour) by 24 hours per day times 110,000 cy/year (total removal) divided by 1200 cy/day as follows:

Annual emission rate (pounds/year) =
24-hour average (pounds/hour) × 24 hours × 110,000 cy/yr/1200 cy/day

The ventilation system for the building will include five individual exhaust units that each are equipped with a granular activated carbon (GAC) module to remove and treat organic vapors in the exhaust. While the primary function of the GAC is to control odors, the GAC is anticipated to remove 95% of the vapor phase emissions as part of the operation. Therefore, air emission calculations have been adjusted to include a control efficiency of 95%. Individual worksheets for each processing step show both uncontrolled and controlled air emissions from the activity.

Based on the assumptions listed above and an exhaust fan height of 30 feet, none of the emission rates exceeded Wisconsin's regulatory thresholds for the VOCs and SVOCs of concern with regulatory limits.

Air concentrations inside the building during operations were also estimated for comparison to an 8-hour OSHA or National Institute for Occupational Safety and Health (NIOSH) time-weighted average (TWA). The mass of emissions generated during 12 hours of operations from the mixing stockpile/bin; ambient emissions from a volume of stored sediments over 24 hours; plus air emissions from the barge decant dewatering operation was summed and divided by the mass of the air in the building (Table 2) to estimate the mass of contaminant in mass of ambient air. Multiplying this by 1,000,000 provides the concentration of the contaminant in parts per million (ppm). Given the air exchange provided by the exhaust fans in the tent, complete building air exchange occurs every 13.1 minutes (Table 2). Therefore, the maximum concentration of the contaminant is equal to the ppm based on total mass divided by the length of operations (12 hours) multiplied by 13.1 minutes as follows:

Concentration (ppm) = ((mass generated during operations/time of operations) +
mass from stored sediment) × time before complete air exchange =
ppm/ (12 hours × 60 min/hour) × 13.1 minutes

Table 1

Sediment Management Total Emissions Rates

Analyte	Controlled Geotube Volatilization Emissions	Controlled Stabilization Emissions	Controlled Bin Emissions	Controlled Total Emissions	Controlled Total Emissions	Comparison to Regulatory Limits		
	24-hour Average Rate (lb/hour)	24-hour Average Rate (lb/hour)	24-hour Average Rate (lb/hour)	24-hour Average Rate (lb/hour)	Annual Emissions (lb/yr)	Regulatory Limit Stacks 25 to <40 feet (NR 445.07)		Regulatory Limit Met?
Benzene[1]	4.41E-03	0.01	0.001	0.0.01	29.03	**936**	**Annual, lb/yr**	**Yes**
Toluene[1,2]	8.61E-04	0.02	0.002	0.03	59.28	**39.3**	**24 hr ave, lb/hr**	**Yes**
Ethylbenzene[1,2]	6.78E-04	0.06	0.005	0.07	143.31	**90.6**	**24 hr ave, lb/hr**	**Yes**
Xylenes, Total[1]	8.74E-04	0.07	0.005	0.07	154.13	**90.6**	**24 hr ave, lb/hr**	**Yes**
1,2,4-Trimethylbenzene[1]	9.99E-05	0.02	0.001	0.02	40.06	**25.6**	**24 hr ave, lb/hr**	**Yes**
1,3,5-Trimethylbenzene[1]	5.71E-05	0.01	0.0004	0.01	11.79	**25.6**	**24 hr ave, lb/hr**	**Yes**
Isopropylbenzene[1] (Cumene)	ND	9.75E-05	8.33E-06	1.06E-04	0.23	**51.3**	**24 hr ave, lb/hr**	**Yes**
p-Isopropyltoluene[1] (Cymene)	ND	2.81E-04	2.54E-05	3.06E-04	0.67			
Naphthalene	2.28E-08	0.08	0.01	0.08	183.56	**10.9**	**24 hr ave, lb/hr**	**Yes**
1- and 2-Methylnaphthalene	7.88E-09	0.04	0.01	0.04	87.02			
Acenaphthylene	3.62E-08	6.88E-04	0.0001	0.0008	1.66			
Acenaphthene	1.94E-06	1.08E-02	1.05E-03	0.012	26.17			
Fluorene	5.35E-08	3.16E-03	3.18E-04	0.0035	7.66			
Phenanthrene	3.38E-10	4.64E-03	4.83E-04	0.0051	11.26			
Anthracene	5.00E-11	1.24E-04	1.29E-05	0.0001	0.30			
Fluoranthene	3.12E-11	7.06E-05	7.83E-06	0.0001	0.17			
Pyrene	3.14E-11	7.19E-05	7.98E-06	7.98E-05	00.18			
Benzo(a)anthracene	3.30E-15	1.16E-06	1.37E-07	1.30E-06	2.85E-03			
Chrysene	4.73E-15	7.62E-07	8.98E-08	8.52E-07	1.87E-03			
Benzo(a)pyrene	1.78E-18	2.43E-08	3.01E-09	2.73E-08	6.00E-05	**6.64**	**Annual, lb/yr**	**Yes**
Benzo(b)fluoranthene	1.20E-15	2.80E-07	3.46E-08	3.14E-07	6.91E-04	**10**	**Annual, lb/yr**	**Yes**
Benzo(k)fluoranthene	1.71E-17	3.11E-08	3.85E-09	3.49E-08	7.68E-05	**10**	**Annual, lb/yr**	**Yes**
Dibenzo(a,h)anthracene	7.68E-19	9.44E-10	1.23E-10	1.07E-09	2.35E-06	**6.08**	**Annual, lb/yr**	**Yes**
Benzo(ghi)perylene	1.52E-17	5.09E-08	6.60E-09	5.75E-08	1.27E-04			
Indeno(1,2,3-cd)pyrene	1.37E-17	2.36E-08	3.06E-09	2.66E-08	5.86E-05	**66.4**	**Annual, lb/yr**	**Yes**

lb/hour = pounds per hour
lb/year = pounds per year
*** Wisconsin Administrative Code NR 445.07. Regulatory limit for trimethylbenzene is for all isomers and mixtures, including 1,2,4-trimethylbenzene and 1,3,5-trimethyl benzene combined.

1. volatile organic compounds (VOC) Chemicals without blue shading do not have state regulatory limits.
2. Both Toluene and Ethylbenzene also have annual regulatory limits at 292,000 and 730,000 lb/year, respectively. Annual emissions of each chemical will be well below the specified limit.

Concentration to be compared to regulatory limit.

Prepared by: CED1
Checked by: BDS1

As a further check, the air concentration of each constituent was calculated using the Occupational Safety Professional Reference (Stewart, 2007) as follows:

Concentration (ppm) = mg constituent/m^3 air × 24.45/MW

Because of the air exchange, the factor of 13.1 minutes/ (12 hours × 60 mins/hr.) is included, representing the air exchange of the building, as follows:

Concentration (ppm) =
mg constituent/m^3 air × 24.45/MWX (6minutes/12hours × 60 minutes/hr.)

Table 2

Assumptions for Estimation of Ambient Air Concentrations

Building Volume	2,100,000	ft^3
	59,465	m^3
Complete Mixing Duration	720	min.
Complete Building Air Exchange	13.1	min/exchange
Mass of Air in Building	160,326	lbs

Prepared by: CED1
Checked by: BDS1

As shown in Table 3, the values calculated from the molecular weight estimate are within the same order of magnitude with the majority of the SVOCs at 0 ppm. All estimated concentrations are well below either a regulatory limit specified by OSHA or a recommended limit set forth by NIOSH. It should be noted that while OSHA standards are regulatory limits that are enforced by OSHA, NIOSH develops recommended guidelines based on recent occupational safety and health research and studies, but are not enforceable by a regulatory agency. Note that concentrations could vary slightly if building volumes are adjusted or incoming concentrations of material change.

Table 3

Ambient Air Concentrations on Contaminants of Concern in Sediment During Stabilization

Contaminants of Concern	Mass Generated per Complete Mixing Duration and Hold		Maximum Estimated Concentration in Ambient Air (mass per mass) - Mass Balance Approach - fresh air exchange B7		8-hour TWA			Check Using Molecular Weight to Estimate Concentration ppm = (mg/m^3 x 24.45)/MW; (concentration in mg/m^3 = lbs of constituent/volume of building)		Molecular Weight (g/mol)
Benzene	5.14+00	lbs	0.58	ppm	1	ppm	OSHA	0.22	ppm	78.1
Toluene	1.23+01	lbs	1.40	ppm	200	ppm	OSHA	0.45	ppm	92.1
Ethylbenzene	3.00+01	lbs	3.41	ppm	100	ppm	OSHA	0.96	ppm	106.2
Xylenes, Total	3.22+01	lbs	3.66	ppm	100	ppm	OSHA	1.03	ppm	106.2
1,2,4-Trimethylbenzene	8.37+00	lbs	0.95	ppm	25	ppm	NIOSH	0.24	ppm	120.2
1,3,5-Trimethylbenzene	2.46+00	lbs	0.28	ppm	25	ppm	NIOSH	0.07	ppm	120.2
Isopropylbenzene (Cumene)	4.88-02	lbs	0.01	ppm	50	ppm	OSHA	0.001	ppm	120.2
p-Isopropyltoluene (Cymene)	1.41-01	lbs	0.02	ppm	--	ppm	--	0.004	ppm	134.2
Naphthalene	3.84+01	lbs	4.37	ppm	10	ppm	OSHA	1.02	ppm	128.2
2-Methylnaphthalene	1.82+01	lbs	2.07	ppm	--	ppm	--	0.43	ppm	142.2
Acenaphthylene	3.46-01	lbs	0.04	ppm	--	ppm	--	0.01	ppm	152.2
Acenaphthene	5.46+00	lbs	0.62	ppm	--	ppm	--	0.12	ppm	154.2
Fluorene	1.59+00	lbs	0.18	ppm	--	ppm	--	0.033	ppm	166.2
Phenanthrene	2.34+00	mg	5.9E-07	mg/m^3	0.2	mg/m^3	OSHA	2.35E-04	mg/m^3	178.2
Anthracene	6.27E-02	mg	1.6E-08	mg/m^3	0.2	mg/m^3	OSHA	6.29E-06	mg/m^3	178.2
Fluoranthene	3.58-02	lbs	0.004	ppm	--	ppm	--	6.01E-04	ppm	202.2
Pyrene	3.64E-02	mg	9.1E-09	mg/m^3	0.2	mg/m^3	OSHA	4.14E-06	mg/m^3	202.3
Benzo(a)anthracene	5.89-04	mg	1.5E-10	mg/m^3	0.2	mg/m^3	OSHA	7.56E-08	mg/m^3	228.3
Chrysene	3.87E-04	mg	9.7E-11	mg/m^3	0.2	mg/m^3	OSHA	4.97E-08	mg/m^3	228.3

Contaminants of Concern	Mass Generated per Complete Mixing Duration and Hold		Maximum Estimated Concentration in Ambient Air (mass per mass) - Mass Balance Approach - fresh air exchange B7		8-hour TWA			Check Using Molecular Weight to Estimate Concentration ppm = (mg/m^3 x 24.45)/MW; (concentration in mg/m^3 = lbs of constituent/volume of building)		Molecular Weight (g/mol)
Benzo(a)pyrene	1.24E-05	mg	3.1E-12	mg/m^3	0.2	mg/m^3	OSHA	1.76E-09	mg/m^3	252.3
Benzo(b)fluoranthene	1.34E-04	mg	3.6E-11	mg/m^3	0.2	mg/m^3	OSHA	2.02E-08	mg/m^3	252.3
Benzo(k)fluoranthene	1.58-05	lbs	1.8E-06	ppm	--	ppm	--	2.13E-07	ppm	252.3
Dibenzo(a,h)anthracene	4.82E-07	lbs	5.5E-08	ppm	--	ppm	--	5.89E-09	ppm	278.3
Benzo(ghi)perylene	2.60-05	lbs	3.0E-06	ppm	--	ppm	--	3.20E-07	ppm	276.3
Indeno(1,2,3-cd)pyrene	1.20E-05	lbs	1.4E-06	ppm	--	ppm	--	1.48E-07	ppm	276.3

g/mol = grams per mole (a mole being a standardized quantity of molecules)
lbs = pounds
ppm = parts per million
mg/m^3 = milligrams per cubic meter

Prepared by: CED1
Checked by: BDS1

References

NIOSH (National Institute for Occupational Safety and Health), 2013. NIOSH Pocket Guide to Chemical Hazards. Updated: August 5, 2013. Available from: www.cdc.gov/niosh/npg/npgd0145.html.

Stewart, 2007. *Occupational Safety Calculations: A Professional Reference.* James H. Stewart Ph.D.; C.I.H.; CSP, et.al. Millennium Associates, Orleans, MA.

U.S. Environmental Protection Agency, 1990. *Air/Superfund National Technical Guidance Study Series: Development of Example Procedures for Evaluating the Air Impacts of Soil Excavation Associated with Superfund Remedial Actions*. USEPA, Office of Air Quality. USEPA 450/4-90-014.

U.S. Environmental Protection Agency, 1993. *Air/Superfund National Technical Guidance Study Series: Models for Estimating Air Emission Rates for Superfund Remedial Actions.* USEPA, Office of Air Quality. USEPA 451/R-93-001.

Attachment 1

Calculations

Air Emissions Calculation Assumptions

PROBLEM STATEMENT:

Calculate Volatile and Semi-Volatile Organic Compound emissions from sediment handling and stablization inside the Remediation Cover.

Note: EPA guidance is for VOCs only - applying same emission calculations for SVOCs is extremely conservative; no EPA guidance was found on handling SVOCs.

AIR EMISSION SOURCES AND ASSUMPTIONS CALCULATIONS

1. Tent structure wil be used as designed for soil treatment. Dimensions for structure will be 157 ft wide X 377 ft long X 54 ft high X 0.66 cross-sectional area correction factor.
2. Emissions from dredging will be minimum (see EPA 1993 - Section 4); focus will be on stablization (emission rate calculated from stablization model equation 4-18) and hold of sediments.

REMEDIATION COVER DIMENSIONS AND PROCESSING PERIOD/VOLUME

12.5

Operation time: 21.3 weeks 128 days

cfm air flow	2.9.E+10
160,000	29,491,200,000

cf exhausted over operating time

Exhaust Fans, Electric (5 X 32,000 cfm). Assume 24/7 operation. Exhaust fan stack height is 30 feet.

Total Volume of Phase 2 temporary tent structure = 2,100,000 cf

Air Exchange Rate = 4.57 air exchanges/hr = 13.1 min/exchange exhaust 230,400,000 cf/day = 9,600,000 cf/hr 160000 cfm

				cy/day	hr/day	cy/hr	Total CY
Maximum Material Processing Rate =	159.00 ton/hr =	115.00 cy/hr	(12 hr/day, 6 days/week)	1200	12	100	110,000

Total material for processing = 201,135 tons 126,500 cubic yards bulked volume 1.59 ton/cy in place; 1.15 bulking factor

110,000 cubic yards in-place volume 117.77 lbs/cubic foot 1.15 bulking factor after stabilization

GENERAL TYPES OF EMISSION FACTORS

Vehicles –

Internal Combustion Engine-Diesel (assumed to be minimal - not calculated)

VOC emissions from Soil Contained in Vehicles may be minimal;

Ignore particulate emissions due to minimal wind in structure.

Stockpiles –

VOC emissions are greatest concern. USEPA 451, March 1993.

Notes: STABILIZATION STEP: VOC emissions - USEPA 451 March 1993 for Stabilization emissions

Notes: HOLD STEP: VOC emissions - compacted, high moisture soils USEPA

Assumptions: Wind to blow particulates is minimal inside the structure

Screen & Conveyor –

VOC emissions. (Assumed to be minimial - not calculated)

Internal Combustion Engine-Diesel (to power screen) (assumed to be minimal)

Particulate emissions may be minimal since soils are moist

Assume no other vehicles normally enter the Remediation Cover.

SEDIMENT CONCENTRATIONS

Average sediment concentrations calculated from data collected from cores within the Pilot Study Dredge Area. (6/2014)

Prepared by: CED1
Checked by: BDS1

Air Emissions Calculations - Volatization from Wastewater during Geotube Dewatering

Analyte	CAS NO.	Wastewater Influent Concentration (ug/L) [3]	Molecular weight	Molarity (g-mole/L)	Vapor Pressure (atm) @ 25C	Partial pressure (atm)	Emission Rate [1, 2] (lb/hr)	Uncontrolled 24-Average (lb/hr) = Emission Rate X Mixing hours/24hrs/day	Uncontrolled Annual Emission based on TOTAL cy/project at 1200 cy/day (lb/year)	Controlled 24-Average (lb/hr) = Emission Rate X Mixing hours/24hrs/day	Controlled Annual Emission based on TOTAL cy/project at 1200 cy/day (lb/year)	Regulatory Limit (NR 445.07) Thresholds for Emission Points 40 to < 75 ft Height		Regulatory Limit Met?
Benzene	71-43-2	52	78.12	6.66E-07	1.25E-01	8.34E-08	1.77E-01	0.088	194.23	4.41E-03	9.71	936	Annual, lb/yr	Yes
Toluene	108-88-3	34	92.14	3.69E-07	3.74E-02	1.38E-08	3.44E-02	0.0172	37.88	8.61E-04	1.89	39.3	24 hr ave, lb/hr	Yes
Ethylbenzene	100-41-4	80	106.16	7.54E-07	1.25E-02	9.42E-09	2.71E-02	0.014	29.82	6.78E-04	1.49	90.6	24 hr ave, lb/hr	Yes
Xylenes, Total	1330-20-7	140	106.20	1.32E-06	9.21E-03	1.21E-08	3.50E-02	0.017	38.45	8.74E-04	1.92	90.6	24 hr ave, lb/hr	Yes
1,2,4-Trimethylbenzene	95-63-6	56	120.19	4.66E-07	2.63E-03	1.23E-09	3.99E-03	0.0020	4.39	9.99E-05	0.22	25.6	24 hr ave, lb/hr	Yes
1,3,5-Trimethylbenzene	108-67-8	20	120.19	1.66E-07	4.21E-03	7.01E-10	2.28E-03	0.0011	2.51	5.71E-05	0.13			
Isopropylbenzene (Cumene)	98-82-8	ND [4]	120.19		6.05E-03							51.3	24 hr ave, lb/hr	Yes
p-Isopropyltoluene (Cymene)	99-87-6	ND [4]	134.22		1.43E-03									
Naphthalene	91-20-3	0.29	128.18	2.26E-09	1.16E-04	2.62E-13	9.10E-07	4.551E-07	1.001E-03	2.276E-08	5.01E-05	10.9	24 hr ave, lb/hr	Yes
2-Methylnaphthalene	91-57-6	0.13	142.20	9.14E-10	8.95E-05	8.18E-14	3.15E-07	1.577E-07	3.468E-04	7.88E-09	1.73E-05			
Acenaphthylene	208-96-8	1.4	152.20	9.20E-09	3.82E-05	3.51E-13	1.45E-06	7.241E-07	1.593E-03	3.62E-08	7.96E-05			
Acenaphthene	83-32-9	72	154.21	4.67E-07	3.97E-05	1.85E-11	7.75E-05	3.874E-05	8.523E-02	1.94E-06	4.26E-03			
Fluorene	86-73-7	4.8	166.22	2.89E-08	1.64E-05	4.75E-13	2.14E-06	1.070E-06	2.354E-03	5.35E-08	1.18E-04			
Phenanthrene	85-01-8	0.11	178.23	6.17E-10	4.53E-06	2.80E-15	1.35E-08	6.754E-09	1.486E-05	3.38E-10	7.43E-07			
Anthracene	120-12-7	2.2	178.24	1.23E-08	3.36E-08	4.14E-16	2.00E-09	1.000E-09	2.201E-06	5.00E-11	1.10E-07			
Fluoranthene	206-44-0	4.3	202.26	2.13E-08	1.07E-08	2.27E-16	1.25E-09	6.235E-10	1.372E-06	3.12E-11	6.86E-08			
Pyrene	129-00-0	5.3	202.26	2.62E-08	8.75E-09	2.29E-16	1.26E-09	6.286E-10	1.383E-06	3.14E-11	6.91E-08			
Benzo(a)anthracene	56-55-3	0.74	228.00	3.25E-09	6.58E-12	2.14E-20	1.32E-13	6.599E-14	1.452E-10	3.30E-15	7.26E-12			
Chrysene	218-01-9	0.68	228.30	2.98E-09	1.03E-11	3.06E-20	1.89E-13	9.459E-14	2.081E-10	4.73E-15	1.04E-11			
Benzo(a)pyrene	50-32-8	0.40	252.00	1.59E-09	6.58E-15	1.04E-23	7.14E-17	3.569E-17	7.851E-14	1.78E-18	3.93E-15	6.64	Annual, lb/yr	Yes
Benzo(b)fluoranthene	205-99-2	0.27	252.00	1.07E-09	6.58E-12	7.05E-21	4.82E-14	2.408E-14	5.297E-11	1.20E-15	2.65E-12	10	Annual, lb/yr	Yes
Benzo(k)fluoranthene	207-08-9	0.20	252.00	7.94E-10	1.26E-13	1.00E-22	6.85E-16	3.424E-16	7.533E-13	1.71E-17	3.77E-14	10	Annual, lb/yr	Yes
Dibenzo(a,h)anthracene	53-70-3	0.04	278.36	1.47E-10	2.76E-14	4.07E-24	3.07E-17	1.535E-17	3.378E-14	7.68E-19	1.69E-15	6.08	Annual, lb/yr	Yes
Benzo(ghi)perylene	191-24-2	0.17	276.34	6.15E-10	1.32E-13	8.09E-23	6.06E-16	3.032E-16	6.670E-13	1.52E-17	3.33E-14			
Indeno(1,2,3-cd)pyrene	193-39-5	0.11	276.34	3.98E-10	1.84E-13	7.33E-23	5.49E-16	2.746E-16	6.042E-13	1.37E-17	3.02E-14	66.4	Annual, lb/yr	Yes

Feed Rate (kg/hr)		
Dredge Production Rate (cy/day)		1,200.0
Hours of mixing per day (hr/day)		12.0
Gallon of Decant Water/day		90,000
Target Annual production (cy)		110,000
Maximum % Volatilized (VOCs)		80

USEPA recommended default for VOCs; 24-hr period

Notes:

1. Raoult's Law states the partial pressure of constituent i (Pi) over a solution equals the mole fraction of the constiuent in solution times the vapor pressure of the constituent. We calculate the number of moles in the gas using Dalton's Law that states the pressure exerted by a gas PiV= niRT for component i. Assuming the ventilation contacts the wastewater, the concentraton of each gas component = ni= PiV/RT, where R = . Emission rate in lb/hr = ni x molecular weight i for ventilation of 1 hour.
2. Values used in formula for emission rate
   - Building ventilation flow: 9600000 cubic feet/hour
   - Temperature: 485 ◦R (25◦C)
   - Gas Constant R: 0.7302 f3-atm/R-lb mole
3. Values are from influent water sample results for Short-Term Water Treatment System dated 06/17/2016; Test America Job ID: 490-105964-1.
4. ND = No data available

Prepared by: AKM
Checked by: CED1

Concentration to be compared to regulatory limit.

Air Emissions Calculations - Solidification Mass Balance Equation[2]

Analyte	CAS NO.	95th Percentile Phase 2 Dredge Area Sediments (ug/kg) [3]	Total Mass of Consitutent in Volume mixed per day (=dredge vol) (lb)	Volatilization Factor	Emission Rate (lb/hr) = conc X feed rate X volatilization factor	Mass Volatilized = Total Mass X % volatilized/24 hours	Uncontrolled 24-Average (lb/hr) = Emission Rate X Mixing hours/24hrs/day	Uncontrolled Annual Emission based on TOTAL cy/project at 1200 cy/day (lb/year)	Controlled 24-Average (lb/hr) = Emission Rate X Mixing hours/24hrs/day [4]	Controlled Annual Emission based on TOTAL cy/project at 1200 cy/day (lb/year) [4]	Regulatory Limit (NR 445.07) Thresholds for Emission Points 25 to < 40 ft Height		Regulatory Limit Met?
Benzene[1]	71-43-2	1,292	4.93	80%	3.29E-01	3.94	0.164	361.66	0.01	18.08	936	Annual, lb/yr	Yes
Toluene[1]	108-88-3	7,504	28.64	41%	9.71E-01	11.65	0.485	1068.08	0.02	53.40	39.3	24 hr ave, lb/hr	Yes
Ethylbenzene[1]	100-41-4	34,160	130.35	22%	2.39E+00	28.63	1.193	2625.66	0.06	131.28	90.6	24 hr ave, lb/hr	Yes
Xylenes, Total[1]	1330-20-7	38,200	145.77	21%	2.56E+00	30.73	1.281	2817.90	0.06	140.90	90.6	24 hr ave, lb/hr	Yes
1,2,4-Trimethylbenzene[1]	95-63-6	21,760	83.04	10%	6.67E-01	8.00	0.334	733.96	0.02	36.70	25.6	24 hr ave, lb/hr	Yes
1,3,5-Trimethylbenzene[1]	108-67-8	5,040	19.23	12%	1.95E-01	2.34	0.098	214.86	0.00	10.74			
Isopropylbenzene (Cumene)[1]	98-82-8	82	0.31	15%	3.90E-03	0.05	0.002	4.29	0.00	0.21	51.3	24 hr ave, lb/hr	Yes
p-Isopropyltoluene (Cymene)[1]	99-87-6	518	1.98	6.8%	1.12E-02	0.13	0.006	12.34	0.00	0.62			
Naphthalene	91-20-3	485,400	1,852.29	2.0%	3.07E+00	36.79	1.533	3373.04	0.08	168.65	10.9	24 hr ave, lb/hr	Yes
2-Methylnaphthalene	91-57-6	280,000	1,068.48	1.6%	1.45E+00	17.36	0.724	1592.28	0.04	79.61			
SVOCs													
Acenaphthylene	208-96-8	8,565	32.68	1.01%	2.75E-02	0.33	0.014	30.27	6.88E-04	1.51			
Acenaphthene	83-32-9	127,150	485.20	1.07%	4.34E-01	5.20	0.217	476.99	1.08E-02	23.85			
Fluorene	86-73-7	62,055	236.80	0.64%	1.27E-01	1.52	0.063	139.18	3.16E-03	6.96			
Phenanthrene	85-01-8	174,300	665.13	0.33%	1.85E-01	2.22	0.093	203.99	4.64E-03	10.20			
Anthracene	120-12-7	57,300	218.66	0.03%	4.97E-03	0.06	0.002	5.46	1.24E-04	0.27			
Fluoranthene	206-44-0	65,525	250.04	0.01%	2.82E-03	0.03	0.001	3.10	7.06E-05	0.16			
Pyrene	129-00-0	77,735	296.64	0.01%	2.87E-03	3.45E-02	1.44E-03	3.16	7.19E-05	0.16			
Benzo(a)anthracene	56-55-3	33,385	127.40	0.00044%	4.63E-05	5.56E-04	2.32E-05	0.05	1.16E-06	2.55E-03			
Chrysene	218-01-9	25,200	96.16	0.00038%	3.05E-05	3.66E-04	1.52E-05	3.35E-02	7.62E-07	1.68E-03			
Benzo(a)pyrene	50-32-8	24,080	91.89	0.00001%	9.71E-07	1.16E-05	4.85E-07	0.00	2.43E-08	5.34E-05	6.64	Annual, lb/yr	Yes
Benzo(b)fluoranthene	205-99-2	12,100	46.17	0.00029%	1.12E-05	1.34E-04	5.59E-06	1.23E-02	2.80E-07	6.15E-04	10	Annual, lb/yr	Yes
Benzo(k)fluoranthene	207-08-9	9,700	37.02	0.00004%	1.24E-06	1.49E-05	6.21E-07	1.37E-03	3.11E-08	6.83E-05	10	Annual, lb/yr	Yes
Dibenzo(a,h)anthracene	53-70-3	670	2.56	0.00002%	3.77E-08	4.53E-07	1.89E-08	4.15E-05	9.44E-10	2.08E-06	6.08	Annual, lb/yr	Yes
Benzo(ghi)perylene	191-24-2	10,580	40.37	0.00006%	2.04E-06	2.44E-05	1.02E-06	2.24E-03	5.09E-08	1.12E-04			
Indeno(1,2,3-cd)pyrene	193-39-5	6,650	25.38	0.00004%	9.43E-07	1.13E-05	4.71E-07	1.04E-03	2.36E-08	5.19E-05	66.4	Annual, lb/yr	Yes

Feed Rate (kg/hr)			
Dredge Production Rate (cy/day)		1,200.0	
Hours of mixing per day (hr/day)		12.0	
Bulking factor		1.00	For these calculations, we do not include a bulking factor as we are basing off incoming mass = Coi X volume dredged
Bulk density (tons/cy)		1.59	
Feed Rate (kg/hr)		144,241.6	Feed rate = dredge production rate (cy/day)/Hours of mixing per day (hr/day) X bulking factor X bulk density (tons/cy) X 2000 lbs/ton X 0.45356 kg/lb
Target Annual production (cy)		110,000	
Maximum % Volatilized (VOCs)		80	USEPA recommended default for VOCs; 24-hr period

Notes:

1. Volatile Organic Compounds (VOC)
2. Calculations were based on EPA-451/R-93-001: March 1993. Emissions from Solidification/Stabilization, Section 4.3.1: Batch operations. 70% - 90% of the volatile contaminants in treated waste eventually evaporate. Most loss occurs within 60 minutes of mixing the waste. Emission Rate (mass/time) = concentration of contaminant in soil or sediment X treatment rate of soil (mass/time) X fraction of contaminant volatilized.
3. Values are the calculated 95th percentile of Phase 2 dredge area core sample data.
4. Vapor phase emissions will be controlled using Granular Activated Carbon (GAC) treatment of the ventilated flow that is exhausted from each of the five modules used for management of flow from the tent structure. It will be assumed the control efficiency of the GAC is 95%.

Concentration to be compared to regulatory limit.

Prepared by: CED1
Checked by: BDS1

Air Emissions - Pre- and Post-Solidification Storage

Stockpile - pre-stablization: USEPA 1990 Guidance (Section 4) assuming compacted subsoils with high moisture content (total porosity = 0.35, air-filled porosity = 0.15)

Analyte	CAS NO.	95th Percentile Phase 2 Dredge Area Sediments (ug/kg) [1]	Approx Concentration after Stablization (ug/kg)	Molecular Weight (g/mol) [MW]	Henry's Law Constant (atm-m/mol)	Henry's Law Constant (dimensionless) = H/RT	Log Kow	Dw (cm2/sec)	Vapor Pressure (mm Hg) @ 25C [3]	Vapor Pressure (atm) @ 25C [Pj] [4]	Diffusivity in Air (cm2/sec) [Da] [3]	$[PxD]^{0.5}$	Volatilization Vactor	Effective Diffusivity (cm2/sec) [De] = $Da*(Ea^{3.33})/(E_T^2)$	Organic Waste Loading (g/cc) TOC x Dry Density [L]	Partition Coefficient (g.vap/g.liq) [Keq] = Pi (vapor pressure) X MW X Ea/(R*T*Loading)	Emission Rate (g/cm3) = 0.72 X (Keq*de*3.1417^2)*t}^0.5/(4d^2)^0.5}*Coi	Total Emissions from Pile (lb) [Mi x Daily Dredge Volume]	Uncontrolled 24-Average (lb/hr) = (Total Emissions from Pile/day)/24hrs/day	Uncontrolled Annual Emission based on 1200 cy/day (lb/year)	Controlled 24-Average (lb/hr) = (Total Emissions from Pile/day)/24hrs/day	Controlled Annual Emission based on 1200 cy/day (lb/year)	Regulatory Limit (NR 445.07) Thresholds for Emission Points 25 to < 40 ft Height		Regulatory Limit Met?
Benzene	71-43-2	1,292	1,282	78.12	5.50E-03	2.25E-01	2.1.E+00	9.8.E-06	95.20	1.25E-01	9.00E-02	1.06E-01	100.0%	1.62E-02	2.77E-03	5.06E-02	1.34E-07	2.70E-01	1.13E-02	24.752	0.001	1.238	936	Annual, lb/yr	Yes
Toluene	108-88-3	7,504	7,473	92.14	6.68E-03	2.73E-01	2.7.E+00	8.6.E-06	28.40	3.74E-02	7.80E-02	5.40E-02	50.8%	1.41E-02	2.77E-03	1.78E-02	4.30E-07	8.69E-01	3.62E-02	79.702	0.002	3.985	39.3	24 hr ave, lb/hr	Yes
Ethylbenzene	100-41-4	34,160	34,085	106.16	6.44E-03	2.63E-01	3.2.E+00	7.8.E-06	9.50	1.25E-02	6.80E-02	2.92E-02	27.5%	1.23E-02	2.77E-03	6.86E-03	1.14E-06	2.30E+00	9.58E-02	210.705	0.005	10.535	90.6	24 hr ave, lb/hr	Yes
Xylenes, Total	1330-20-7	38,200	38,119	106.20	5.25E-03	2.15E-01	3.3.E+00	7.8.E-06	7.00	9.21E-03	8.50E-02	2.80E-02	26.4%	1.53E-02	2.77E-03	5.06E-03	1.22E-06	2.47E+00	1.03E-01	226.195	0.005	11.310	90.6	24 hr ave, lb/hr	Yes
1,2,4-Trimethylbenzene	95-63-6	21,760	21,739	120.19	1.47E-01	6.01E+00	na	na	2.00	2.63E-03	6.22E-02	1.28E-02	12.0%	1.12E-02	2.77E-03	1.64E-03	3.39E-07	6.85E-01	2.85E-02	62.748	0.001	3.137	25.6	24 hr ave, lb/hr	Yes
1,3,5-Trimethylbenzene	108-67-8	5,040	5,034	120.19	1.47E-01	6.01E+00	na	na	3.20	4.21E-03	6.21E-02	1.62E-02	15.2%	1.12E-02	2.77E-03	2.62E-03	9.91E-08	2.00E-01	8.35E-03	18.364	0.0004	0.918			
Isopropylbenzene (Cumene)	98-82-8	82	82	120.19	6.59E-03	2.70E-01			4.60	6.05E-03	6.50E-02	1.98E-02	18.7%	1.17E-02	2.77E-03	3.76E-03	1.98E-09	4.00E-03	1.67E-04	0.366	8.33E-06	0.018	51.3	24 hr ave, lb/hr	Yes
p-Isopropyltoluene (Cymene)	99-87-6	518	518	134.22					1.08	1.43E-03	5.73E-02	9.04E-03	8.51%	1.03E-02	2.77E-03	9.90E-04	6.02E-09	1.22E-02	5.07E-04	1.115	2.54E-05	0.056			
Naphthalene	91-20-3	485,400	485,304	128.18	4.80E-04	2.00E-02			0.088	1.16E-04	6.00E-02	2.64E-03	2.48%	1.08E-02	2.77E-03	7.68E-05	1.61E-06	3.25E+00	1.35E-01	298.087	0.007	14.904	10.9	24 hr ave, lb/hr	Yes
2-Methylnaphthalene	91-57-6	280,000	279,954	142.20	7.09E-04	2.90E-02			0.068	8.95E-05	5.20E-02	2.16E-03	2.03%	9.38E-03	2.77E-03	6.58E-05	8.00E-07	1.62E+00	6.74E-02	148.211	0.003	7.411			
Acenaphthylene	208-96-8	8,565	8,565	152.20	1.15E-04	4.70E-03			0.029	3.82E-05	4.71E-02	1.34E-03	1.26%	8.50E-03	2.77E-03	3.00E-05	1.57E-08	3.18E-02	1.33E-03	2.915	0.0001	0.146			
Acenaphthene	83-32-9	127,150	127,137	154.21	9.17E-05	3.75E-03			0.030	3.97E-05	5.10E-02	1.42E-03	1.34%	9.20E-03	2.77E-03	3.17E-05	2.50E-07	5.04E-01	2.10E-02	46.236	0.001	2.312			
Fluorene	86-73-7	62,055	62,048	166.22	7.92E-05	3.24E-03			0.013	1.64E-05	4.40E-02	8.51E-04	0.801%	7.94E-03	2.77E-03	1.41E-05	7.56E-08	1.53E-01	6.37E-03	14.006	0.0003	0.700			
Phenanthrene	85-01-8	174,300	174,289	178.23	1.32E-04	5.40E-03			0.003	4.53E-06	4.35E-02	4.44E-04	0.418%	7.85E-03	2.77E-03	4.18E-06	1.15E-07	2.32E-01	9.66E-03	21.257	0.000	1.063			
Anthracene	120-12-7	57,300	57,298	178.24	1.12E-04	4.60E-03			2.55E-05	3.36E-08	3.90E-02	3.62E-05	0.034%	7.04E-03	2.77E-03	3.09E-08	3.07E-09	6.21E-03	2.59E-04	0.56948	1.29E-05	0.028			
Fluoranthene	206-44-0	65,525	65,525	202.26	9.49E-06	3.88E-04			8.13E-06	1.07E-08	3.02E-02	1.80E-05	0.017%	5.45E-03	2.77E-03	1.12E-08	1.86E-09	3.76E-03	1.57E-04	0.34469	7.83E-06	0.017			
Pyrene	129-00-0	77,735	77,735	202.26	1.12E-05	4.60E-04			6.65E-06	8.75E-09	2.72E-02	1.54E-05	0.015%	4.91E-03	2.77E-03	9.15E-09	1.89E-09	3.83E-03	1.60E-04	0.35098	7.98E-06	0.018			
Benzo(a)anthracene	56-55-3	33,385	33,385	228.00	3.40E-06	1.39E-04			5.00E-09	6.58E-12	5.10E-02	5.79E-07	0.0005%	9.20E-03	2.77E-03	7.76E-12	3.24E-11	6.56E-05	2.73E-06	0.00601	1.37E-07	3.00E-04			
Chrysene	218-01-9	25,200	25,200	228.30	1.23E-06	5.02E-05			7.80E-09	1.03E-11	2.48E-02	5.05E-07	0.0005%	4.48E-03	2.77E-03	1.21E-11	2.13E-11	4.31E-05	1.80E-06	0.00395	8.98E-08	1.98E-04			
Benzo(a)pyrene	50-32-8	24,080	24,080	252.00	6.97E-08	2.85E-06			5.00E-12	6.58E-15	4.30E-02	1.68E-08	0.00002%	7.76E-03	2.77E-03	8.58E-15	7.14E-13	1.44E-06	6.02E-08	0.00013	3.01E-09	6.62E-06	6.64	Annual, lb/yr	Yes
Benzo(b)fluoranthene	205-99-2	12,100	12,100	252.00	1.15E-06	4.70E-05			5.00E-09	6.58E-12	2.26E-02	3.86E-07	0.0004%	4.08E-03	2.77E-03	8.58E-12	8.23E-12	1.66E-05	6.93E-07	0.00152	3.46E-08	7.62E-05	10	Annual, lb/yr	Yes
Benzo(k)fluoranthene	207-08-9	9,700	9,700	252.00	1.14E-08	4.66E-07			9.60E-11	1.26E-13	2.26E-02	5.34E-08	0.0001%	4.08E-03	2.77E-03	1.65E-13	9.14E-13	1.85E-06	7.70E-08	0.00017	3.85E-09	8.47E-06	10	Annual, lb/yr	Yes
Dibenzo(a,h)anthracene	53-70-3	670	670	278.36	1.42E-07	5.82E-06			2.10E-11	2.76E-14	2.00E-02	2.35E-08	0.0000%	3.61E-03	2.77E-03	3.98E-14	2.92E-14	5.90E-08	2.46E-09	0.00001	1.23E-10	2.70E-07	6.08	Annual, lb/yr	Yes
Benzo(ghi)perylene	191-24-2	10,580	10,580	276.34	1.09E-08	4.45E-07			1.00E-10	1.32E-13	4.90E-02	8.03E-08	0.0001%	8.84E-03	2.77E-03	1.88E-13	1.57E-12	3.17E-06	1.32E-07	0.00029	6.60E-09	1.45E-05			
Indeno(1,2,3-cd)pyrene	193-39-5	6,650	6,650	276.34	1.22E-06	4.99E-05			1.40E-10	1.84E-13	1.90E-02	5.92E-08	0.0001%	3.43E-03	2.77E-03	2.63E-13	7.27E-13	1.47E-06	6.12E-08	0.00013	3.06E-09	6.73E-06	66.4	Annual, lb/yr	Yes

Fractional Organic Carbon		0.45	
Sediment Density assuming bulking factor, g/cc		1.55	Calculation: (In Place Dry Density/Bulking Factor)
In-Place Sediment Density, g/cc [2]		1.89	117.77 lb/cu.ft. (1.59 tons/cy)
Particle Density, g/cc		2.62	Calculation: Particle Density accounting for organic matter content.
Inorganic Particle Density, g/cc [2]		2.71	Unchanged: Upland Soil Physical Data; Previous Sheet
Organic Density, g/cc		1.30	Unchanged: Clark, Viessman, and Hammer, 1977, Water Supply and Pollution Control, 3rd Edition, Harper & Row, New York, NY, p. 630.
Moisture Content, % dry [2]		17.0	MTTD system requires 17% moisture (MH 5/30/2014) - not used in these calculations
Total Organic Matter		3.0	3% typical for sediment organic carbon content (EBD) -adjusts particle density slightly
Total Organic Carbon, mg/kg		1,789	Average TOC 20140530.xls (MH 5/30/2014)
Organic Loading, g/cc [L]		0.0028	Calculation: (Soil Pile Dry Density x Total Organic Carbon/1,000,000)
Soil Volume in Pile (cy)		2,886	Assumes stockpiles are full.
Stockpile Area (sq.ft.)		23,750	Inclues Sediment Processing Area and Stabilized Sediment Curing Area (Drawing 6)
Stockpile Depth [cm]		100	EPA Default (Average depth of 3.28 ft)
Loading Cycle, cy/hr		100.00	300 cy/day X 1 day/8 hours
Stockpile Residence Time, sec [t]		43,200	Cycle time (B57) converted to seconds
Void Ratio (vol/vol)		0.69	Calculation : (Particle Density/Soil Pile Dry Density) -1
Soil Porosity (vol/vol) [E_T]		0.41	Calculation : (Void Ratio)/(1 + Void Ratio)
Water Porosity (vol/vol)		0.65	Calculated from 1-air porosity
Air Porosity (vol/vol) [E_a]		0.35	Entered value from Table 3, USEPA July 1990 EPA 450/4-90-014 compacted subsoils, high moisture
Universal Gas Constant, R	82.0575	cm^3-atm/K-mol	
Temperature, Kelvin (25C)	298		
Daily Dredge Volume (cy)		1200	
Target Annual Volume (cy)		110,000	
Hold time in each bin	12	hours	

Notes:

1. Values are the calculated 95th percentile of Phase 2 dredge area core sample data.
2. Source of soil geotechnical data is the *Geotechnical Investigation Report* (FE JV, May 2013); values shown are average for SB-180
3. GSI Chemical Properties Database (http://www.gsi-net.com/en/publications/gsi-chemical-database/list.html), Vapor Pressure of Cumene at 40'C.
4. Pi (atm) = Pi (mm Hg)/760
5. H (atm.m3/mol) = H (unitless) x R x T
6. Vapor phase emissions will be controlled using Granular Activated Carbon (GAC) treatment of the ventilated flow that is exhausted from each of the five modules used for management of flow from the tent structure. It will be assumed the control efficiency of the GAC is 95%.

Volatile Organic Compounds

Prepared by: CED1
Checked by: BDS1

Sediment Management Total Emissions Rates

	Controlled Geotube Volatization Emissions	Controlled Stablization Emissions	Controlled Bin Emissions	Controlled Total Emissions	Controlled Total Emissions	Comparison to Regulatory Limits		
Analyte	24 hour average rate (lb/hr)	24 hour average rate (lb/hr)	24 hour average rate (lb/hr)	24 hour average rate (lb/hr)	Annual Emissions (lb/yr)	Regulatory Limit (NR 445.07) Thresholds for Emission Points 25 to < 40 feet		Regulatory Limit Met?
Benzene	4.41E-03	0.01	0.001	0.01	29.03	936	Annual, lb/yr	Yes
Toluene	8.61E-04	0.02	0.002	0.03	59.28	39.3	24 hr ave, lb/hr	Yes
Ethylbenzene	6.78E-04	0.06	0.005	0.07	143.31	90.6	24 hr ave, lb/hr	Yes
Xylenes, Total	8.74E-04	0.06	0.005	0.07	154.13	90.6	24 hr ave, lb/hr	Yes
1,2,4-Trimethylbenzene	9.99E-05	0.02	0.001	0.02	40.06	25.6	24 hr ave, lb/hr	Yes
1,3,5-Trimethylbenzene	5.71E-05	0.00	0.0004	0.01	11.79			
Isopropylbenzene (Cumene)	ND	9.75E-05	8.33E-06	1.06E-04	0.23	51.3	24 hr ave, lb/hr	Yes
p-Isopropyltoluene (Cymene)	ND	2.81E-04	2.54E-05	3.06E-04	0.67			
Naphthalene	2.28E-08	0.08	0.01	0.08	183.56	10.9	24 hr ave, lb/hr	Yes
1- and 2-Methylnaphthalene	7.88E-09	0.04	0.003	0.04	87.02			
Acenaphthylene	3.62E-08	6.88E-04	0.0001	0.0008	1.66			
Acenaphthene	1.94E-06	1.08E-02	1.05E-03	0.0119	26.17			
Fluorene	5.35E-08	3.16E-03	3.18E-04	0.0035	7.66			
Phenanthrene	3.38E-10	4.64E-03	4.83E-04	0.0051	11.26			
Anthracene	5.00E-11	1.24E-04	1.29E-05	0.0001	0.30			
Fluoranthene	3.12E-11	7.06E-05	7.83E-06	0.0001	0.17			
Pyrene	3.14E-11	7.19E-05	7.98E-06	7.98E-05	0.18			
Benzo(a)anthracene	3.30E-15	1.16E-06	1.37E-07	1.30E-06	2.85E-03			
Chrysene	4.73E-15	7.62E-07	8.98E-08	8.52E-07	1.87E-03			
Benzo(a)pyrene	1.78E-18	2.43E-08	3.01E-09	2.73E-08	6.00E-05	6.64	Annual, lb/yr	Yes
Benzo(b)fluoranthene	1.20E-15	2.80E-07	3.46E-08	3.14E-07	6.91E-04	10	Annual, lb/yr	Yes
Benzo(k)fluoranthene	1.71E-17	3.11E-08	3.85E-09	3.49E-08	7.68E-05	10	Annual, lb/yr	Yes
Dibenzo(a,h)anthracene	7.68E-19	9.44E-10	1.23E-10	1.07E-09	2.35E-06	6.08	Annual, lb/yr	Yes
Benzo(ghi)perylene	1.52E-17	5.09E-08	6.60E-09	5.75E-08	1.27E-04			
Indeno(1,2,3-cd)pyrene	1.37E-17	2.36E-08	3.06E-09	2.66E-08	5.86E-05	66.4	Annual, lb/yr	Yes

ND = No data available

Prepared by: CED1
Checked by: BDS1

Estimation of Ambient Air Concentrations of COCs from Tent Structure Activities

Given Data		
Building Volume	2100000	ft^3
	59465	m^3
Complete Mixing Duration	720	min
Complete Building Air Exchange	13.1	min
Mass of Air in Building	160326	lbs

References
http://www.cdc.gov/niosh/npg/npgd0145.html
https://www.osha.gov/dts/chemicalsampling/data/CH_229000.html

Calculations

COC	Mass Generated per Complete Mixing, Holding, and Dewatering		Maxiumum Estimated Concentration in Ambient Air (mass per mass) - Mass Balance Approach - fresh air exchange B7		8 Hr TWA			Check Using Molecular Weight to Estimate Concentration ppm = (mg/m^3 x 24.45)/MW or mg/m3 = (ppm x MW)/24.45 (Ref Occupational Safety Professional Reference - calculated concentration in mg/m3 = lbs of constituent/volume of building)		Molecular Weight (g/mol)
Benzene	5.14E+00	lbs	0.58	ppm	1	ppm	OSHA	0.22	ppm	78.1
Toluene	1.23E+01	lbs	1.40	ppm	200	ppm	OSHA	0.45	ppm	92.1
Ethylbenzene	3.00E+01	lbs	3.41	ppm	100	ppm	OSHA	0.96	ppm	106.2
Xylenes, Total	3.22E+01	lbs	3.66	ppm	100	ppm	OSHA	1.03	ppm	106.2
1,2,4-Trimethylbenzene	8.37E+00	lbs	0.95	ppm	25	ppm	NIOSH	0.24	ppm	120.2
1,3,5-Trimethylbenzene	2.46E+00	lbs	0.28	ppm	25	ppm	NIOSH	0.07	ppm	120.2
Isopropylbenzene (Cumene)	4.88E-02	lbs	0.01	ppm	50	ppm	OSHA	0.001	ppm	120.2
p-Isopropyltoluene (Cymene)	1.41E-01	lbs	0.02	ppm	--	ppm	--	0.004	ppm	134.2
Naphthalene	3.84E+01	lbs	4.37	ppm	10	ppm	OSHA	1.02	ppm	128.2
2-Methylnaphthalene	1.82E+01	lbs	2.07	ppm	--	ppm	--	0.43	ppm	142.2
Acenaphthylene	3.46E-01	lbs	0.04	ppm	--	ppm	--	0.01	ppm	152.2
Acenaphthene	5.46E+00	lbs	0.62	ppm	--	ppm	--	0.12	ppm	154.2
Fluorene	1.59E+00	lbs	0.18	ppm	--	ppm	--	0.033	ppm	166.2
Phenanthrene	2.34E+00	mg	5.9E-07	mg/m^3	0.2	mg/m^3	OSHA	2.35E-04	mg/m^3	178.2
Anthracene	6.27E-02	mg	1.6E-08	mg/m^3	0.2	mg/m^3	OSHA	6.29E-06	mg/m^3	178.2
Fluoranthene	3.58E-02	lbs	0.004	ppm	--	ppm	--	6.01E-04	ppm	202.2
Pyrene	3.64E-02	mg	9.1E-09	mg/m^3	0.2	mg/m^3	OSHA	4.14E-06	mg/m^3	202.3
Benzo(a)anthracene	5.89E-04	mg	1.5E-10	mg/m^3	0.2	mg/m^3	OSHA	7.56E-08	mg/m^3	228.3
Chrysene	3.87E-04	mg	9.7E-11	mg/m^3	0.2	mg/m^3	OSHA	4.97E-08	mg/m^3	228.3
Benzo(a)pyrene	1.24E-05	mg	3.1E-12	mg/m^3	0.2	mg/m^3	OSHA	1.76E-09	mg/m^3	252.3
Benzo(b)fluoranthene	1.43E-04	mg	3.6E-11	mg/m^3	0.2	mg/m^3	OSHA	2.02E-08	mg/m^3	252.3
Benzo(k)fluoranthene	1.58E-05	lbs	1.8E-06	ppm	--	ppm	--	2.13E-07	ppm	252.3
Dibenzo(a,h)anthracene	4.82E-07	lbs	5.5E-08	ppm	--	ppm	--	5.89E-09	ppm	278.3
Benzo(ghi)perylene	2.60E-05	lbs	3.0E-06	ppm	--	ppm	--	3.20E-07	ppm	276.3
Indeno(1,2,3-cd)pyrene	1.20E-05	lbs	1.4E-06	ppm	--	ppm	--	1.48E-07	ppm	276.3

Prepared by: CED1
Checked by: BDS1

Appendix E

Construction Quality Assurance Plan for Phase 2 Wet Dredge

Report

Construction Quality Assurance Plan for Phase 2 Wet Dredge

Ashland/NSP Lakefront Site

Project I.D.: 16X002

NSPW

Eau Claire, Wisconsin

December 2016

Foth | Envirocon

Joint Venture

Construction Quality Assurance Plan
for
Phase 2 Wet Dredge

Project ID: 16X002

Prepared for
NSPW
Eau Claire, Wisconsin

Prepared by
Foth Infrastructure & Environment/
Envirocon Joint Venture

December 2016

101 International Drive, P.O. Box 16655 • Missoula, MT 59808

Construction Quality Assurance Plan for Phase 2 Wet Dredge

Contents

Contents (*continued*)

Tables

Figures

List of Abbreviations, Acronyms, and Symbols

AOC	Administrative Settlement Agreement and Order on Consent
BMP	best management practice
Brennan	JF Brennan Co.
COC	contaminants of concern
CQA Officer	Construction Quality Assurance Officer
CQAP	*Construction Quality Assurance Plan for Phase 2 Wet Dredge*
EPA	Environmental Protection Agency
FE JV	Foth Infrastructure & Environment/Envirocon Joint Venture
Final Design	*Final Design for Phase 2 Wet Dredge*
GPS	global positioning system
HASP	*Health and Safety Plan for Phase 2 Wet Dredge*
Monitoring Plan	*Monitoring Plan for Phase 2 Wet Dredge*
NSP	Northern States Power Company
NSPW	Northern States Power Company – a Wisconsin Corporation
QA	quality assurance
QC	quality control
RDWP	*Remedial Design Work Plan*
Site	Ashland/NSP Lakefront Site
USEPA	U.S. Environmental Protection Agency
WDNR	Wisconsin Department of Natural Resources

1 Introduction

This *Construction Quality Assurance Plan for Phase 2 Wet Dredge* (*CQAP*) supports the implementation of the Phase 2 Wet Dredge (Wet Dredge) at the Ashland/NSP Lakefront Site (Site). The purpose of this *CQAP* is to outline the construction inspection and documentation procedures utilized before, during and after construction activities related to the implementation of the Wet Dredge. This *CQAP* identifies the responsibilities for project personnel during Wet Dredge activities and procedures for monitoring the performance of the activities in accordance with the scoping documents through a quality assurance program. This *CQAP* establishes the procedures to verify that the construction substantially meets the requirements specified in the *Final Design for Phase 2 Wet Dredge* (*Final Design*) (FE JV, 2016a).

This *CQAP* does not include environmental in-situ measurements and contaminants of concern (COC) sampling that may be conducted to verify the efficacy of the work, or confirm no adverse environmental impacts are occurring during the Wet Dredge implementation. Information and procedures pertaining to those tasks are presented in the *Monitoring Plan for Phase 2 Wet Dredge* (*Monitoring Plan*) (FE JV, 2016b), which is provided in Appendix C in the 95% Design and Section 5.6.2 of the *Phase 2 Wet Dredge 95% Design (95% Design)* (FE JF, 2016a).

Major construction activities conducted during the Wet Dredge include the following:

- Mobilization and site preparation
- Placement of barrier systems
- Debris removal and sediment dredging
- Debris and sediment management and disposal
- Water treatment and management
- Placement of a restorative layer

1.1 CQAP Organization

The remainder of this *CQAP* is organized into the following sections:

- **Section 2—Responsibility and Authority** presents the roles and responsibilities of the parties involved in the Wet Dredge, including U.S. Environmental Protection Agency (USEPA/EPA) and other agencies.

- **Section 4—Quality Assurance Program** describes the performance objectives and criteria, quality assurance measures, inspection and verification activities, and contingency actions for each Wet Dredge activity.

- **Section 4—Contingency Actions** describes contingencies that may be taken in case potential problems or issues of non-conformance arise during implementation of the Wet Dredge.

- **Section 5—Documentation and Reporting** describes the reporting requirements for Wet Dredge QA activities. These requirements include daily and weekly summary reports, inspection data sheets, problem identification and corrective measures reports, work acceptance reports, and final documentation. A description of the provisions for final records storage is also included in this section.

- **Section 6—References** presents the references cited and used to generate this document.

2 Responsibility and Authority

The responsibility and authority for the development and implementation of the construction quality assurance program for the Wet Dredge rests with the Northern States Power Company (NSPW) Contractor. The NSPW Contractor will perform activities according to this *CQAP*. Lead *CQAP* personnel are listed in Table 2-1. Additionally, a general project organization chart is provided on Figure 2-1.

Table 2-1
Project Construction Quality Assurance Personnel

Title	Name	Affiliation	Phone
Project Coordinator	Eric Ealy	Xcel Energy, Inc. (on behalf of NSPW)	612-330-2928
Construction Manager	Tom Perry	Xcel Energy, Inc. (on behalf of NSPW)	906-204-6680
Assistant Construction Manager	Pat Carr	Braun Intertec	218-343-4471
Contractor Project Manager	Denis Roznowski	FE JV	920-496-6756
Certifying Engineer	Steve Garbaciak	FE JV	630-368-3069
Contractor Deputy Project Manager	Alan Buell	FE JV	406-698-2012
Construction Manager	Brad Hay	FE JV	678-822-3568
Marine Operations Coordinator	Ken Aukerman	FE JV	920-496-6780
Land Operations Coordinator	Richard Whitman	FE JV	801-450-9667
CQA Officer	Kris Gamble	FE JV	417-861-6160
QC Officer	Dave Gehring	FE JV	509-531-4908
Project Health & Safety Supervisor	Dan Allen	FE JV	720-404-6325
Project Health & Safety Manager	David Hardy	FE JV	405 308-6115
Sediment Removal Subcontractor	Greg Smith	JF Brennan Co.	608-792-0465
Independent CQA Officer, 3rd Party	TBD	TBD	TBD
Marine Survey Lead	Mike Shaylor	FE JV	406-240-5215
Monitoring Lead	Andy Pierre	FE JV	920-609-8095

This *CQAP* is being implemented in accordance with the *Final Design*. In the event changes are necessary to this *CQAP* due to unforeseen project conditions, these potential changes will be discussed with Wisconsin Department of Natural Resources (WDNR) and USEPA prior to implementation.

2.1 Organizations Involved with Construction

Contracts for construction activities will be administered by the NSPW Contractor. The following organizations will be involved with the construction:

Project Coordinator:	Northern States Power Company d.b.a. Xcel Energy, Inc.
Engineer:	Foth Infrastructure & Environment/Envirocon Joint Venture
General Contractor:	Foth Infrastructure & Environment/Envirocon Joint Venture
Surveyor:	Foth Infrastructure & Environment/Envirocon Joint Venture
Marine Sub-Contractor:	JF Brennan Co. (Brennan)
Materials Testing:	TestAmerica (chemical) & Coleman Geotechnical (geotech)
CQA:	Foth Infrastructure & Environment/Envirocon Joint Venture
Independent CQA:	TBD

Figure 2-1 illustrates an organization chart and clear lines of communication for the NSPW Contractor, NSP/NSPW, and regulatory oversight team.

2.2 Responsibility and Authority

2.2.1 USEPA and WDNR

USEPA is the regulatory authority and is responsible for overseeing and authorizing the Wet Dredge. In this capacity, USEPA will review information described in the *Final Design* and its supporting documents (including this *CQAP*), for consistency with the Wet Dredge objectives, the *Consent Decree* (*CD*) (USEPA, 2012), and applicable state and federal laws and regulations.

USEPA is working cooperatively with the WDNR. WDNR will participate in Wet Dredge review and coordination with USEPA. When applicable, WDNR will provide their comments directly to USEPA for communication to the parties.

The USEPA Remedial Project Manager, or a designee, will exercise project oversight for USEPA, coordinate comments developed by USEPA and other agencies, and communicate agency observations with NSPW and the NSPW Contractor. The USEPA Remedial Project Manager will notify NSPW if it identifies any concerns regarding the implementation of the Wet Dredge. NSPW will propose to USEPA's Remedial Project Manager appropriate response measures or recommendations. USEPA will make final decisions to resolve such issues or problems that may change the project scope.

2.2.2 NSPW Project Coordinator and Management Team

The Wet Dredge will be overseen by the NSPW Project Coordinator and management team as having responsibility for implementing the Wet Dredge and addressing the requirements of the *CD*. The Project Coordinator will work closely with the NSPW Contractor Project Manager to ensure the goals of the Wet Dredge are met. The NSPW management team will be comprised of the Construction Manager, Assistant Construction Manager, and Environmental Compliance

Manager, who will report to the NSPW Project Coordinator. If any concerns arise regarding the implementation of the Wet Dredge, NSPW will communicate the concerns to the USEPA Remedial Project Manager, including any proposed remedies to address unforeseen conditions, if warranted.

2.2.3 NSPW Contractor Project Manager

The NSPW Contractor Project Manager will be responsible for Wet Dredge management and administration of contracts. The NSPW Contractor Project Manager, working with the Marine Sub-Contractor, will implement the Wet Dredge operations. The NSPW Contractor Project Manager will be responsible for the following:

- Maintaining the project budget and design, construction performance objectives, and overall project schedule
- Interacting with and coordinating regulatory concurrence of activities with WDNR and USEPA
- Maintaining open communications with Project Coordinator
- Reviewing activities with construction manager and operations coordinators
- Reviewing and approving deliverables
- Approving change orders internally
- Submitting change orders to Project Coordinator
- Reviewing as-built surveys and drawings
- Providing monthly progress reports for NSPW's submittal to Agencies

The NSPW Contractor Project Manager will be supported by the Deputy Project Manager who will perform the same duties as the NSPW Contractor Project Manager, as necessary. The NSPW Contractor Project Manager will focus on marine operations and coordinate with land operations. The Deputy Project Manager will focus on the land operations and coordinate with marine operations.

2.2.4 Certifying Engineer

The Wet Dredge will be designed and managed by the NSPW Contractor Project Manager and Certifying Engineer. The Certifying Engineer is responsible for designing the framework and performance standards for the Wet Dredge such that successful implementation will result in achieving the objectives of the *CD* and activity-specific objectives. Additionally, the Certifying Engineer will provide oversight, consultation, and observations during work to assist with implementation of the Wet Dredge in conformance with USEPA-approved documents. During implementation of the Wet Dredge, work activities will be observed and overseen by the Certifying Engineer, working collaboratively with the NSPW Contractor Project Manager. The

Certifying Engineer is responsible for determining whether the work activities and results are consistent with the design intent of the Wet Dredge or if any design modifications are needed. The Certifying Engineer, on behalf of NSPW, will request USEPA's approval for any modifications that are judged necessary for the Wet Dredge.

2.2.5 Construction Manager

The Construction Manager will be present during construction activities and responsible for:

- Interacting with and coordinating regulatory concurrence of activities with WDNR and USEPA
- Overseeing overall construction compliance to project field schedules, reporting requirements, and performance objectives set forth in the design plans and specifications
- Reviewing the implementation of approved changes to the plans and specifications
- Reviewing contractor personnel qualifications to verify conformance with the specifications
- Reviewing warranty submittals to verify compliance with the specified warranty requirements
- Maintaining open communication with on-site NSPW management representative
- Reviewing change orders and coordination with the NSPW Contractor and Contractor Project Manager/Deputy Project Manager

2.2.6 CQA Officer

The CQA Officer will be present during construction activities and responsible for:

- Coordinating CQA and construction data management amongst all parties
- Coordinating with the Marine and Land Operations Coordinators
- Interacting directly with Quality Control (QC) Officer
- Reviewing applicable plans, specifications and the *CQAP*
- Reviewing and recommending approval or disapproval of site-specific documentation, including contractor submittals, manufacturers' information, installer's information, and reference standards
- Issuing any required, daily non-conformance (in-situ measurement and sampling results) reports to USEPA, WDNR and NSPW
- Educating personnel on site-specific CQA requirements

- Confirming calibrations of QA/QC testing equipment are correctly performed and recorded
- Confirming that the QA/QC field in-situ measurement and sampling activities are properly performed, recorded, and results meet specified requirements
- Reporting any deviation from the *CQAP* plans and specifications
- Preparing, reviewing, and maintaining required reports, files, and logs
- Overseeing collection, marking, packaging, and shipping of conformance samples

The CQA Officer will also be responsible for identifying those field conditions that may warrant deviation from the Wet Dredge scope and/or goals. In such circumstances, the CQA Officer will report to the Certifying Engineer, who in turn, will coordinate with NSPW, USEPA, and WDNR to identify and agree upon any necessary deviations to meet the overall objectives of the work. Any agreed-upon deviations will be documented in the weekly progress reports to USEPA.

2.2.7 QC Officer

The QC Officer will be present during construction activities and responsible for:

- Tracking the progress of each individual construction task
- Observing and documenting activities performed by the Marine Sub-Contractor
- Conducting QC inspections
- Ensuring field data acquisition accuracy and completeness
- Collecting each day's records, receipts, samples, etc. for the Marine Sub-Contractor's activities
- Filing daily, monthly, and project progress reports as specified in the plans and specifications
- Notifying the CQA Officer and Marine Operations Coordination of all incidents in non-conformance, discrepancies, problems, etc.
- Ensuring the proper peer QA/QC review of project construction data, reports, and designs
- Maintaining and distributing copies of bills of lading, permits, manifests, and site reports
- Coordinating change requests with NSPW Contractor Project Manager, Certifying Engineer, USEPA, and WDNR

2.2.8 Project Health & Safety Manager

The Project Health & Safety Manager will be responsible for:

- Ensuring adequate health and safety protocols have been established for the project
- Coordinating with the Project Health & Safety Supervisor as necessary
- Coordinating with the Marine Sub-Contractor's Health & Safety Manager as necessary
- Reviewing records of training for all on-site project personnel and subcontractors
- Establishing proper decontamination procedures to be implemented at the site
- Reviewing copies of incident reports, and health and safety reports submitted to the NSPW management representative
- Verifying all subcontract activities are performed according to the site-specific *Health and Safety Plan for Phase 2 Wet Dredge* (*HASP*) (FE JV, 2016c), which is presented in Appendix G in the *95% Design*
- Supervising accident investigation and reporting

2.2.9 Project Health & Safety Supervisor

The Project Health & Safety Supervisor will be present during construction activities and responsible for:

- Conducting daily health and safety meetings
- Coordinating with the Marine Sub-Contractor's Health & Safety Manager
- Performing daily job safety hazard analysis
- Conducting safety audits where necessary
- Ensuring adequate health and safety protocols are practiced at the Site
- Verifying that project personnel have adequate training and equipment to perform assigned tasks
- Maintaining records of training for all on-site project personnel and subcontractors
- Notifying the Construction Manager of alert or alarm conditions related to on-site health and safety monitoring
- Ensuring implementation of proper decontamination procedures

- Providing copies of, incident reports, and health and safety reports to the NSPW management representative
- Ensuring all subcontract activities are performed according to the site *HASP*
- Conducting accident investigation and reporting

2.2.10 Marine Operations Coordinator

The Marine Operations Coordinator will be present during construction activities and responsible for:

- Overseeing and managing marine construction compliance to project field schedules, reporting requirements, and performance objectives set forth in the design plans and specifications
- Communicating and coordinating regulatory activities with on-site agency representative
- Verifying that the Marine Sub-Contractor is following the *CQAP*
- Responsible for implementation of approved changes to the plans and specifications
- Overseeing and managing daily marine work and crew activities
- Assist CQA Officer in reviewing and recommending approval or disapproval of site-specific documentation, including contractor submittals, manufacturers' information, installer's information, and reference standards
- Daily coordination with other site personnel to assure that project requirements are being met and the schedule maintained
- Maintaining marine site security
- Ensuring that the Marine Sub-Contractor is meeting the requirements of the marine design
- Ensuring that the Marine Sub-Contractor is meeting the requirements of the marine project plans and specifications
- Coordinating with the Monitoring Lead in-situ measurement and COC sampling activities (e.g., water, air, noise, and sediment)
- Coordinating with the Marine Sub-Contractor's on-site Health & Safety officer

2.2.11 Land Operations Coordinator

The Land Operations Coordinator will be present during construction activities and responsible for:

- Directing and supervising daily land work and crew activities
- Daily coordination with other site personnel to assure that project requirements are being met and the schedule maintained
- Maintaining land site security
- Ensuring compliance with plans, specifications, and landside procedures applicable to the field activities
- Ensuring that the NSPW Contractor is meeting the requirements of the landside design
- Ensuring that NSPW Contractor is meeting the requirements of the landside project plans and specifications
- Coordinating with the CQA Officer land in-situ measurement and sampling activities (e.g., air and noise)

2.2.12 Monitoring Lead

The Monitoring Lead will be present during construction activities and responsible for:

- Assigning appropriate field personnel to each in-situ measurement or sampling activity
- Executing site-specific CQA requirements
- Performing calibrations of QA/QC testing equipment
- Overseeing and performing collection, marking, packaging and shipping of samples
- Developing chain of custody and documentation of samples

2.2.13 Independent CQA

The Independent CQA will be present during construction activities and responsible for:

- Performing assessments of the design and construction team's adherence to the *CQAP*
- Acting as NSPW's independent oversight
- Attending required meetings
- Reporting results of assessments directly to NSPW

2.2.14 Marine Sub-Contractor

The Marine Sub-Contractor will be responsible for implementing the marine-based Wet Dredge activities. The Marine Sub-Contractor's work will comply with the Wet Dredge requirements and provide all necessary QC information.

As part of the Wet Dredge implementation, the Marine Sub-Contractor will be responsible for developing and implementing their quality management protocols, which meet or exceeds standards established in the *Monitoring Plan* and the *Final Design*. Independent of the Marine Sub-Contractor's QC program, the Certifying Engineer and the NSPW Contractor Project Manager will oversee implementation of this *CQAP* to verify that the Wet Dredge is implemented in accordance with the design.

The Marine Sub-Contractor will use key personnel to help with the tasks described above, including a Project Manager, Superintendent's Construction QC Manager, and Health & Safety Manager.

2.2.15 Other Subcontractors

Other subcontractors, if utilized by the NSPW Contractor or the Marine Sub-Contractor, are responsible for the quality of their work, protection of the environment, and adhering to the requirements of relevant *Final Design* documents. The other subcontractor's principals will designate a job foreman with responsibility to see that the work is conducted in accordance with the *Final Design* documents.

3 Quality Assurance Program

The Wet Dredge is planned and designed specifically to meet the goals described in the *Remedial Design Work Plan for Phase 2 Wet Dredge (RDWP)* (FE JV, 2016d). In-situ measurements (air, water, noise) and COC sampling (air, water, and sediment) will be performed during Wet Dredge implementation to compare activities conducted at the Site to the sediment cleanup and water/air quality goals.

This section describes the specific activities that will be undertaken to achieve QA during the Wet Dredge project. It also describes the methods used to measure compliance with clean-up and quality goals defined for the work. Specific activities to be implemented are described, along with specific objectives, criteria, QA measures, inspection and verification activities, and contingency actions.

For each Wet Dredge activity, inspection and verification activities will be implemented to confirm that sediment cleanup and water/air quality goals have been met. During the Wet Dredge activities, the QA process will progress as follows:

- The Marine Sub-Contractor and the marine monitoring crew will conduct inspection and verification activities (i.e., visual observations, COC sampling, and in-situ measurements) to determine whether sediment cleanup and water/air quality goals have been met. The NSPW Contractor Project Manager will have final approval authority for all such inspections and for verifying that corrective actions are implemented, if any are warranted.

- The Marine Sub-Contractor will provide documentation to the CQA Officer to demonstrate that specific components of the work are supported by appropriate equipment and materials, assembly and installation of support equipment is satisfactory, and the Wet Dredge has been properly implemented. The NSPW Contractor Project Manager, in consultation with the CQA Officer, will determine whether the objectives of the Wet Dredge have been met.

The remainder of this section details the Wet Dredge activities and associated performance objectives and criteria, along with QA measures and specific inspection and verification activities that will be performed to confirm that sediment cleanup and water/air quality goals have been met.

3.1 Task List

The following activities will be completed at the Site:

- Site preparation
- Install barrier systems
- Remove debris (shoreline and marine)
- Remove sediment (inventory and residual dredging)
- Post dredge and hydraulic interim sampling

- Final confirmation sampling
- Re-dredging (as a contingency)
- Placement of restorative layer
- Restorative layer thickness verification and COC sampling
- Water treatment
- Sediment stockpiling, processing, transportation, and disposal
- Post-dredge bulkhead wall cleaning
- Support activities
  - Best management practices (BMP)
  - Environmental in-situ measurements and sampling

3.2 Performance Objectives and Criteria

Performance objectives and criteria associated with Wet Dredge activities include the following:

- Contain, prevent, or otherwise mitigate to the extent practicable any environmental effects caused during the Wet Dredge activities.

- Install, erect or otherwise emplace BMPs to adequately protect the environment, project personnel, equipment materials, supplies, and the public.

- Conduct debris removal activities in such a manner that defensibly characterizes the efficacy and reproducibility of the removal methodology (or methodologies).

- Conduct wet dredging in such a manner that defensibly characterizes the efficacy and reproducibility of the dredging methodology (or methodologies).

- Collect and utilize accurate and defensible water quality data, complying with the requirements of the *Monitoring Plan*, to demonstrate that barrier systems and BMPs adequately control the transport and migration of sediment, COC, and other potential water impacts (such as surface sheens) during sediment removal and restorative layer placement activities.

- Collect and utilize accurate and defensible air and noise data to demonstrate that wet dredging and sediment management activities comply with the requirements of the *Monitoring Plan.*

- Collect and utilize accurate and defensible post mechanical and hydraulic interim and final confirmation samples, complying with the requirements of the *Monitoring Plan*, to demonstrate sediment removal activities.

- Manage, process, and treat as needed, and dispose of generated wastes (i.e., debris, sediment, water, and refuse) consistent with disposal requirements.

- Place appropriate thickness of restorative layer over the dredged surface and, as required, collect and utilize accurate and defensible COC samples, complying with the requirement of the *Monitoring Plan*.

- Restore site conditions in previously dredged areas, as well as support areas, to original or better conditions.

Certain QA activities will be conducted as described below to verify these performance standards are being met during the work.

3.3 QA Measures, Inspection, and Verification

The QA measures described below will be implemented during Wet Dredge activities to meet sediment cleanup and water/air quality goals and complete work according to the project requirements. Inspection and verification activities will be implemented, and the results of the inspection and verification activities will be compared to criteria to determine if sediment cleanup and water/air quality goals have been achieved. If these goals have not been achieved, contingency actions, as described in Section 4, will be implemented.

3.3.1 Environmental Protection and Containment Area(s)

As part of this work item, the Marine Sub-Contractor will assemble and install barrier systems, with the goal of preventing loss of suspended or dissolved constituents from the dredging area into the surrounding environment (Chequamegon Bay). The barrier systems will include oil booms, gap closures, and an arrangement (e.g., isolation, rock protection, breakwater, and gaps) of full-height curtains intended to control water column impacts that may potentially occur at the specific work location. Ancillary controls consist of absorbent booms around the dredge area, and landside BMPs such as erosion control devices and impermeable liners placed as necessary to control inadvertent spillage of solids and fluids.

The CQA Officer will observe the installation of the barrier systems and will then inspect the curtains on an ongoing basis to verify that they are constructed and are functioning as desired to mitigate potential environmental impacts. Substandard installation or performance of the barrier systems that are noted by the QC Officer will be reported immediately to the Certifying Engineer, Marine Operations Coordinator, and the Marine Sub-Contractor's Project Manager, for immediate assessment and corrective action.

3.3.2 Debris Removal

Removal of debris and wood waste is a necessary precursor to sediment removal and will be verified by continuous observation of the Marine Sub-Contractor's debris removal activities (potentially including such additional manual measures as probing the lakebed). The QC Officer will estimate the percentage and depth of debris encountered and will also observe its removal and management for disposal.

3.3.3 Sediment Removal

Sediment removal activities are planned using mechanical and hydraulic dredging methods with the goal of removing impacted sediments from the dredge management units (DMU). Evaluation of dredging effectiveness will be accomplished by performing a series of post mechanical and hydraulic and final confirmation samples to verify that sediment removal has

met the sediment cleanup goals. The results of sampling may result in additional dredging in localized areas.

The CQA Officer will also track the Marine Sub-Contractor's physical positioning throughout the dredging process to assess whether dredging is adequately reaching the targeted extents and design elevation of the DMUs. The Marine Sub-Contractor will employ real-time positioning technology that will enable regular checks on positioning adequacy. The QC Officer will report acceptable horizontal and vertical controls on a routine basis. Unacceptable horizontal and vertical controls noted by the QC Officer will be reported immediately to the Certifying Engineer, Marine Operations Coordinator, and the Marine Sub-Contractor's Project Manager for immediate assessment and corrective action.

3.3.4 Material Handling, Processing, Transportation and Disposal

Debris and dredged material generated during Wet Dredge activities will require specific handling, processing, and disposal measures. Design documents will describe specific procedures that pertain to the handling of various waste streams; treatment of those waste streams, as needed; and discharge or disposal criteria that are applicable to each waste stream.

The CQA Officer will routinely monitor the NSPW Contractor's waste handling, processing, and disposal operations to identify compliance with their methods and procedures, as well as with BMPs for minimizing impacts to the environment. Notably, the CQA Officer will monitor disposal-specific data to ensure that materials designated for a certain disposal option meet the required criteria for that option, including transportation requirements that may apply to materials identified for off-site disposal. Deviations from planned procedures or contraventions of applicable criteria noted by the CQA Officer will be reported immediately to the Construction Manager for immediate assessment and corrective action.

3.3.5 BMPs

Various BMPs will be employed during Wet Dredge activities for protection of the environment, as well as site security, health and safety, and protection of workers and the public. The CQA Officer will inspect BMPs on a routine basis to verify that the intended function of the practice is being met. Deficient BMPs will be reported immediately to the Construction Manager for immediate assessment and corrective action.

3.3.6 Placement of Clean Restorative Layer

Following confirmation of completion of Wet Dredge sediment removal, a restorative layer will be placed over the dredged area using material to specified thicknesses as defined in the *95% Design*. The CQA Officer will verify that appropriate material and sufficient and correct placement of restorative layer is being performed by reviewing the Marine Sub-Contractor's supplied depth and positioning data, as well as the tonnage of material placed.

3.3.7 Restoration of Landside Conditions

On-land areas used for material handling and sediment and water management will need to be returned to acceptable conditions at the conclusion of Wet Dredge activities. The CQA Officer

will document pre-work conditions for land areas to be used during the project and will refer to pre-work surveys to determine submerged initial conditions. The CQA Officer will visually verify that land areas have been restored to original or better conditions. Inspections and condition verification will be done in collaboration with the NSPW Contractor. Restoration efforts failing to meet original conditions will be reported immediately to the Construction Manager for immediate assessment and corrective action.

3.3.8 Project Materials

Certain Wet Dredge tasks will rely on imported materials and supplies. Noteworthy among these are materials used to construct the containment area(s) and restorative layer to be used for dredged areas. The CQA Officer will verify that imported materials meet the specifications provided in the pre-work submittal documentation and will report non-compliant conditions immediately to the Construction Manager for assessment and corrective action.

4 Contingency Actions

This section addresses contingency actions that may be undertaken in case potential problems or nonconformance issues arise during the implementation of Wet Dredge activities. The purpose of the contingency actions is to establish measures to prevent, respond to, and report such occurrences. In such events, the CQA Officer will coordinate with the respective party to implement corrective actions as soon as possible.

Possible contingency concerns include the following:

- Spillage of hazardous substances, including the unscheduled release of dredged material, project-generated water, fuel, hydraulic fluids, chemical reagents, or similar materials
- Exceedance of water quality goals
- Exceedance of air or noise quality goal
- Damage to or failure of the barrier systems
- Damage to the shoreline bulkhead wall by dredging or material transfer equipment

The CQA Officer will report any incidents requiring contingency response conditions immediately to the Construction Manager for immediate assessment and corrective action.

4.1 Spill Notification and Response

During the Wet Dredge activities, several methods for potential spillage of hazardous or otherwise unsuitable materials exist, including spills as a result of dredging, barge overflow, transfer of dredged material and debris, stabilization of dredged materials, refueling of equipment, damage to equipment, or discharge of untreated water into Chequamegon Bay (e.g., from bypass of wastewater treatment or other spillage events). All hazardous materials will be handled during Wet Dredge operations in accordance with the *95% Design* and appropriate BMPs, to limit the potential for spills to occur. Spill response equipment will be on-site at all times to be deployed in the event of a spill. All response actions will comply with the site-specific *HASP*.

In the event of a hazardous materials spill, the project team shall assess the spill to determine the appropriate response and have on-site resources safely and effectively mitigate the spill. If the appropriate trained personnel and resources are not available, the area may require evacuation, and the local fire department, Hazmat Response Team, and the EPA National Response Center shall be notified.

Following determination that the spill can be safely and effectively managed by the project team, immediate response actions shall be taken to contain and clean the spill as follows:

- The area of the spill shall be isolated, and all non-essential cleanup personnel shall be kept away.

- The source of the spill shall be located, stopped and contained.
- Proper materials and personal protective equipment necessary to address the spill shall be secured.
- Appropriate spill response materials shall be deployed as necessary. Once utilized they shall be collected and disposed of appropriately.
- The affected area and equipment that contacted the spilled material shall be decontaminated.

In the event of any emergency, the respective party shall follow measures to ensure the rapid communication of the emergency situation as described in the site-specific *HASP*.

4.2 Water Quality Contingency Measures

Water quality outside the dredge area will be monitored as described in the *Monitoring Plan*. The *Monitoring Plan* includes detailed water quality in-situ measurements and COC sampling procedures and response actions in the event of an exceedance of any of the applicable water quality goals.

- Possible contingency actions, after assessing monitors for bio-fouling and cleaning, as appropriate, could include one or more of the following:
- Installation of more aggressive BMPs
- Operational modifications (change buckets, dredging rate, etc.)
- Work-slowdown or temporary stoppage to further assess the source of exceedance, identify effective mitigation measures, and allow the water column to recover
- If necessary, and if not already deployed, deployment of an additional barriers

4.3 Air Quality Contingency Measures

Air quality in-situ measurements and COC sampling will be performed as described in the *Monitoring Plan*. In the event that air quality exceeds relevant goals, possible contingency actions could include one or more of the following:

- Operational modifications to dredge sequence on a short term basis (e.g. prevailing wind direction, COC and odor content of current sediment, etc.), offloading or stockpiling equipment, and methods
- Work-slowdown or temporary stoppage to further assess the source of impacts, identify effective mitigation measures, and allow air quality to improve
- Placing covers, tarps, etc. over stockpiled sediments

- Apply Rusmar foam to blanket odor source(s)
- Deploying additional air misters, relocating air misters based on wind direction, or increasing application rate of air misters

4.4 Barrier Systems Contingency Measures

Barrier systems will be installed to reduce the transport and migration of sediment, COCs, or other materials from the dredge area to meet applicable substantive permit requirements. The barriers systems will consist of multiple components, including breakwater curtains, gaps curtains, gaps closure, isolation curtain, and multiple oil and absorbent booms. Any damage to the barrier systems could potentially result in a release causing an exceedance in water quality goals and result in a temporary work-stoppage.

The location and arrangement of the elements of the barrier systems were selected to limit migration distance, while also allowing for sufficient space for maintenance and in-situ measurement and COC sampling activities. The barriers will be inspected regularly for damage, and repairs or replacement will be made as necessary. The Marine Sub-Contractor shall have an adequate replacement quantity of each curtain for possible deployment in the event that any particular curtain becomes damaged beyond repair.

4.5 Bulkhead Protection Contingency Measures

Dredging will occur, in part, along an existing shoreline bulkhead wall. This bulkhead wall is located between the dredge area and the entire land-based operations area, which will become an area of heavy traffic throughout Wet Dredge activities, particularly during shoreline dredging and material transfer activities. The heavy equipment that will be working around the bulkhead will utilize contingency measures to avoid striking or damaging the structure.

The bulkhead will be clearly marked with surveyors paint in the vicinity of dredge area activities, as necessary so that it will remain visible from all sides to equipment operators. Equipment operators will take precautions while working near the bulkhead wall, such as operating at low speeds to safeguard against damaging the structure. If necessary, a spotter may be located in the vicinity of the bulkhead wall, who will maintain communication with operators to inform them of any approaching dangers. Any traversing of the bulkhead with equipment will be accomplished by means of bridging the bulkhead with crane mats.

4.6 Slope Stability Contingency Measures

Stable slope angles presented on the design drawings, are based on geotechnical data collected at the Site. During dredging activities, there is the potential for material along the extents of the dredge prism to slough downward and inward, causing additional volume of material to enter the dredge area. This would increase the duration of Wet Dredge activities and increase the necessary throughput of sediment through the treatment process.

To mitigate this potential, the Marine Sub-Contractor will utilize dredging BMPs, including the following:

- Dredging progressively from the top of slopes downward.
- Use of a global positioning system- (GPS) enabled dredge bucket to properly maintain horizontal and vertical accuracy during sediment and debris removal.
- Overlap between dredge bucket "bites" for complete coverage of each DMU, and if necessary, small overlap of dredge cell borders to safeguard against material sloughing in.
- Horizontal variation of dredge bucket "bites" for each removal depth and maintaining the designed side slope of 5H: 1V.
- Controlled ascending and descending bucket speeds.
- Limit "sweeping" with the dredge bucket along the bottom of the dredge cells to identify high spots.

In the event that slope instabilities or areas of sloughing are noted, then possible contingency actions could include one or more of the following:

- Work-slowdown or temporary stoppage to further assess the source of impacts, identify effective mitigation measures, and allow sediment to stabilize.
- Lessening the inclination angle of the side slope(s).

5 Documentation and Reporting

Documentation and reporting for construction QA activities will include pre-construction documentation, construction documentation, and post-construction documentation, as detailed below. The CQA Officer and Marine Operations Coordinator will work closely on a daily basis during Wet Dredge activities to collect and generate documentation to verify that the project is being completed as required. The following sections describe documentation that will be required throughout Wet Dredge activities.

5.1 Pre-Construction Documentation

The following pre-construction documentation will be submitted for review by the Certifying Engineer.

5.1.1 Project Construction Schedule

Prior to the start of construction, a detailed Project Construction Schedule will be submitted which details each construction element. Periodic schedule updates will be submitted following progress meetings.

5.1.2 Health and Safety Plan

A detailed site-specific *HASP* presenting the minimum health and safety requirements for Site activities and the measures and procedures to be employed for protection of on-site personnel has been prepared. The plan covers the controls, work practices, personal protective equipment, and other health and safety requirements that will be implemented in connection with Wet Dredge activities.

5.2 Wet Dredge Documentation

During work activities, respective parties will be required to provide a variety of documentation to the CQA Officer, including testing results of received materials, documentation of received materials and products, weight tickets for shipments of materials imported or exported, and survey results. A daily log of activities, as described below, will be maintained. The CQA Officer will maintain a field report of daily activity and complete an internal weekly report. The contents of these reports are described below. Daily and weekly progress reports will be completed by the CQA Officer and posted to the project SharePoint Site. The records described in this section will be maintained in the project files.

All final project documentation will be stamped by licensed professionals, as appropriate. Work surveys, including as-built surveys, will be documented on drawings using the same data, unit, and scale as work plan drawings. Record drawings will allow for a direct visual assessment of the quality and completeness of work.

5.2.1 Daily Quality Control Report

During construction activities, a Daily Control Report will be prepared by QC Officer. At a minimum, the daily report will record the following:

- Identification of on-site personnel and visitors
- Daily weather conditions
- Activities completed
- Any changes to BMPs or environmental controls
- Materials delivered or used
- Equipment used
- Debris removed
- Sediment removed (either volume in cubic yards for mechanical dredging or square footage for hydraulic dredging)
- Restorative layer square footage placed
- Sediment and debris transported and disposed to landfill (tons)
- Survey data
- Results of any QC inspections, tests, or other monitoring activities
- Problems encountered or deficiencies and resolution of problems, including measures taken
- Any authorized deviations from the *Final Design*

Daily Quality Control Reports will be provided on a weekly basis as part of the Weekly Summary Report as discussed below.

5.2.2 Daily CQA Report

The CQA Officer will maintain a daily field log to record observations, measurements, inspections completed, data received, communications with other members of the project team or EPA, any water or air quality or noise level exceedances, additional environmental controls that were implemented, problems encountered, and resolutions. The daily field log will be supported by submittals received such as survey results and weight tickets, monitoring results, laboratory data inspection reports, and written communication from members of the project team or USEPA. Daily CQA reports will be posted to the project SharePoint Site.

5.2.3 Weekly CQA Report

The CQA Officer, will prepare weekly summaries of progress. The Weekly Summary Report will identify progress organized by activity and posted to the project SharePoint Site.

5.2.4 Weekly Construction Meetings

Weekly progress meetings will be coordinated with NSPW, including pre-notification of time and place of meetings. Conference call access will be provided as needed and requested by the NSPW management representative. Meeting minutes will be prepared and made available to attendees.

5.2.5 Monthly Progress Reports to Agencies

NSPW shall submit a written progress report to USEPA and WDNR on the 15th day of each month during Wet Dredge activities.

5.2.6 Import Material Characterization

Prior to any on-site placement of import materials, a Borrow Site Characterization Report shall be submitted to the CQA Officer. The characterization report will include identification of the source (including a map documenting the origin of the material), Site inspection, and material sample and characterization (physical and chemical testing, as specified) to ensure that the import material will uniformly meet the physical specifications of its intended use.

5.3 Post-Construction Documentation

NSPW will submit a Data Report to USEPA and WDNR after completion of Wet Dredge activities.

6 References

Foth Infrastructure & Environment/Envirocon Joint Venture, 2016a. *95% Design for Phase 2 Wet Dredge* – Ashland/NSP Lakefront Site. December 2016.

Foth Infrastructure & Environment/Envirocon Joint Venture, 2016b. *Monitoring Plan for Phase 2 Wet Dredge* – Ashland/NSP Lakefront Site (Appendix C in *95% Design for Phase 2 Wet Dredge*). December 2016.

Foth Infrastructure & Environment/Envirocon Joint Venture, 2016c. *Health and Safety Plan for Phase 2 Wet Dredge* – Ashland/NSP Lakefront Site (Appendix G in *95% Design for Phase 2 Wet Dredge*). December 2016.

Foth Infrastructure & Environment/Envirocon Joint Venture, 2016d. *Remedial Design Work Plan for Phase 2 Wet Dredge* – Ashland/NSP Lakefront Site. December 2016.

Figures

Organization Chart

Ashland/NSP Lakefront Site - Phase 2 Wet Dredge

Regulatory Oversight

USEPA Region 5 Tech Support
Adam Brown
Jim Burton
(Weston Solutions)

USEPA Remedial Project Manager
Scott Hansen

WDNR
Jamie Dunn

Project Coordinator NSPW
Eric Ealy

Independent CQA
TBD

NSPW Management Team
Construction Management
Tom Perry
Pat Carr

NSPW Support Team
Owner-SME-Dredging/ Sediment
Mike Palmer
Owner-Procurement-Financial Controls Management
John Voigt

Joint Venture Sr. Management
Pete Joy
Steve Laszewski
John D'Antuono
Keith Summers

Project Manager
Denis Roznowski
Deputy Project Manager
Alan Buell

Design Engineering
Stephen Garbaciak, Jr., P.E.
(Certifying Engineer)
John Starke, P.E.
(Certifying Engineer)

Project Health & Safety Manager
David Hardy

Project Health & Safety Supervisor
Dan Allen

Construction Manager
Brad Hay

CQA Officer
Kris Gamble

Monitoring Lead
(water quality, air, noise & sediment monitoring)
Andy Pierre

Marine Operations Coordinator
Ken Aukerman

QC Officer
Dave Gehring

Land Operations Coordinator
Richard Whitman

Sediment Removal & Bathymetric Survey
Tyler Lee (JF Brennan)

Marine Survey/CAD
Mike Shaylor
John Whitstone
Jim Buchberger

Material Handling
Buddy Wherley

Water Treatment System Operator
Steve Calhoun

Technical Support Team

Tara Van Hoof, Field Team Coordinator	Greg Smith, Constructability
Bob Meller, Geologist	Brian Symons, Phase 1 Engineering Coordination
Steve Lehrke, Environmental Statistician	Ron French, Permitting/Data Coordination
Brooke Lund, CQA	Craig Harley, Engineering
Allison Haus, Data Validation	TBD, Technician
Beth Schuh, Administrative Assistant	Brian Stanul, Engineering

Foth | Envirocon
Joint Venture

Appendix F

Quality Assurance Project Plan for Phase 2 Wet Dredge

Report

Quality Assurance Project Plan for Phase 2 Wet Dredge

Ashland/NSP Lakefront Site

Project I.D.: 16X002

NSPW

Eau Claire, Wisconsin

December 2016

Foth | Envirocon

Joint Venture

Quality Assurance Project Plan
for
Phase 2 Wet Dredge

Project ID: 16X002

Prepared for
NSPW

Eau Claire, Wisconsin

Prepared by
Foth Infrastructure & Environment/
Envirocon Joint Venture

December 2016

101 International Drive, P.O. Box 16655 • Missoula, MT 59808

Quality Assurance Project Plan for Phase 2 Wet Dredge

Contents

Contents (*continued*)

Contents (*continued*)

Contents (*continued*)

Appendices

List of Abbreviations, Acronyms, and Symbols

0	degrees (direction)
°C	degrees Celsius
°F	degrees Fahrenheit
%D	percent difference
%R	percent recovery
%RSD	percent relative standard deviation
AOC	Administrative Settlement Agreement and Order on Consent
ASTM	American Society for Testing and Materials
Bay	Chequamegon Bay
BMP	best management practices
Brennan	J.F. Brennan Co., Inc.
BTEX	Benzene/Toluene/Ethylbenzene/Xylene
CCC	calibration check compound
CCV	continuing calibration verification
CDOM	colored dissolved organic matter
COD	chemical oxygen demand
COC	contaminants of concern
CQAP	*Construction Quality Assurance Plan for Phase 2 Wet Dredge*
CRM	certified reference material
cy	cubic yard
DAF	dissolved air flotation
DGPS	differential global positioning system
DMU	dredge management unit
DO	dissolved oxygen
DOC	dissolved organic carbon
DQO	data quality objective
DRET	Dredging Elutriate Test
DRO	diesel range organics
EDD	electronic data deliverable
EPA	Environmental Protection Agency
FDOM	fluorescent dissolved organic matter
FE JV	Foth Infrastructure & Environment/Envirocon Joint Venture
Final Design	*Final Design for Phase 2 Wet Dredge*
ft	feet/foot
Foth	Foth Infrastructure & Environment, LLC
GC/FID	gas chromatograph/ flame ionization detector
GC/MS	gas chromatograph/mass spectrometer
GPS	global positioning system
GRO	gasoline range organics
H_2SO_4	sulfuric acid
HASP	*Health and Safety Plan for Phase 2 Wet Dredge*
HCI	hydrochloric acid
HDPE	high density polyethylene

Hg	Mercury
HNO_3	nitric acid
ICAL	initial calibration
ICV	initial calibration verification
kg/m^3	kilogram per cubic meter
LCS	laboratory control standard
LCSD	laboratory control standard duplicate
LFB	laboratory fortified blank
m	meter
MB	method blank
MDL	method detection limits
MET	Modified Elutriate Test
mg/kg	milligrams per kilogram
MGP	manufactured gas plant
mg/L	milligrams per liter
mg/m^3	milligrams per cubic meter
mL	milliliter
mm Hg	millimeter of mercury
Monitoring Plan	*Monitoring Plan for Phase 2 Wet Dredge*
MPC	measurement performance criteria
MS	matrix spike
MSD	matrix spike duplicate
NA	not applicable
NaOH	sodium hydroxide
NAPL	non-aqueous phase liquid
NAVD	North American Vertical Datum
ND	not detected
NFG	National Functional Guidelines
NSP	Northern States Power Company
NSPW	Northern States Power Company, a Wisconsin Corporation
NTU	nephelometric turbidity units
OPR	ongoing precision and recovery
ORO	oil range organics
OSHA	Occupational Safety and Health Administration
PAH	polynuclear aromatic hydrocarbons
PDWP	pre-design workplace
PE	performance evaluation
PID	photo ionization detector
PM_{10}	particulate matter 10 microns or less in size
ppm	parts per million
ppbv	parts per billion by volume
PTFE	Polytetrafluoroethylene
QA	quality assurance
QC	quality control

QL	quantitation limit
R	Recovery
RA	remedial action
RAL	remedial action level
QAPP	*Quality Assurance Project Plan for Phase 2 Wet Dredge*
RD	remedial design
RF	response factor
RI	remedial investigation
RL	reporting limit
ROD	*Record of Decision*
rpd	relative percent difference
SDG	sample delivery group
SIM	selected ion monitoring
Site	Ashland/NSP Lakefront Site
SOW	statement of work
SPCC	system performance check compound
SRM	standard reference material
SVOC	semi-volatile organic compounds
SWAC	surface-weighted average concentration
TBD	to be determined
TCLP	Toxicity Characteristic Leaching Procedure
TEC	threshold effect concentration
TOC	total organic carbon
tPAH	total polynuclear aromatic hydrocarbon
TS	total solids
TSA	technical systems audit
TSS	total suspended solids
TVOC	total volatile organic compounds
µg/kg	micrograms per kilogram
µg/L	micrograms per liter
USEPA	U.S. Environmental Protection Agency
USCG	U.S. Coast Guard
VOC	volatile organic compounds
WDNR	Wisconsin Department of Natural Resources
Work Plan	*Wet Dredge Work Plan*
ZnAC	Zinc acetate

References

Foth Infrastructure & Environment/Envirocon Joint Venture, 2016a. *Final Design for Phase 2 Wet Dredge Pilot Study* – Ashland/NSP Lakefront Site. April 2016.

Foth Infrastructure & Environment/Envirocon Joint Venture, 2016b. *Monitoring Plan for Phase 2 Wet Dredge Pilot Study* – Ashland/NSP Lakefront Site (Appendix D in *Final Design for Phase 2 Wet Dredge Pilot Study*). April 2016.

U.S. Environmental Protection Agency, 2010. *Record of Decision*. September 2010.

Wisconsin Department of Natural Resources, 2003. *Consensus-Based Sediment Quality Guidelines, Recommendations for Use & Application Interim Guidance,* WT-732 2003. December 2003.

QAPP Worksheets #1 and 2: Title and Approval Page

Site Name:	Ashland/NSP Lakefront Site	
Site Location:	Ashland, Wisconsin	
Superfund Site Identification Number:	EPA ID #WISFN0507952	
Document Title:	Quality Assurance Project Plan for Phase 2 Wet Dredge	
Lead Organization:	Northern States Power – Wisconsin (NSPW)	
Lead Organization Project Coordinator:	Eric Ealy	
	NSPW 414 Nicollet Mall, Minneapolis, MN 55401	
	Signature	Date
FE JV Project Manager:	Denis Roznowski, P.E.	
	Foth Infrastructure & Environment/Envirocon Joint Venture 2121 Innovation Court, Suite 300, De Pere, WI 54115	
	Signature	Date
Certifying Engineer:	Stephen Garbaciak, Jr., P.E.	
	Foth Infrastructure & Environment/Envirocon Joint Venture Glen Hill North Office Park, 800 Roosevelt Road, Building E, Suite 412, Glen Ellyn IL 60137	
	Signature	Date
Construction Quality Assurance Officer:	Kris Gamble	
	Foth Infrastructure & Environment/Envirocon Joint Venture 605 N. Boonville Avenue, Springfield MO 65806	
	Signature	Date

Document Preparer(s):	Allison Haus, Ph.D.	
	Foth Infrastructure & Environment/Envirocon Joint Venture 8550 Hudson Blvd #100, Lake Elmo, MN 55042	
	Signature	Date
	Beth Schuh	
	Foth Infrastructure & Environment/Envirocon Joint Venture 2121 Innovation Court, Suite 300, De Pere, WI 54115	
	Signature	Date
Federal Regulatory Agency:	United States Environmental Protection Agency (EPA)	
Federal Regulatory Agency Project Manager:	Scott Hansen	
	EPA, Region 5 77 W. Jackson Blvd, C-14J, Chicago, IL 60604	
	Signature	Date
State Regulatory Agency:	Wisconsin Department of Natural Resources (WDNR)	
State Regulatory Agency Project Manager:	Jamie Dunn	
	101 S Webster Street, Madison WI, 53707	
	Signature	Date
Other Stakeholders:	None	
Other Stakeholders Representative:	None	
Applicable Plans and Reports:	*Final Design for Phase 2 Wet Dredge* (FE JV, 2016a)	

QAPP Worksheet #3: Distribution List

QAPP Recipients	Responsibility	Organization	Telephone Number	E-mail Address
Scott Hansen	Remedial Project Manager	EPA Region 5	800-621-8431	hansen.scott@epa.gov
Jamie Dunn	Project Manager	WDNR	715-635-4049	james.dunn@wisconsin.gov
Eric Ealy	Project Coordinator	NSPW	612-330-2928	eric.j.ealy@xcelenergy.com
Tom Perry	Construction Manager	NSPW	906-204-6680	thomas.e.perry@xcelenergy.com
Pat Carr	Assistant Construction Manager	Braun Intertec	218-343-4471	Patrick.carr@xcelenergy.com
Denis Roznowski	Project Manager	FE JV	920-496-6756	Denis.Roznowski@Foth.com
Alan Buell	Deputy Project Manager	FE JV	303-215-0187	ABuell@envirocon.com
Kris Gamble	Construction Quality Assurance Officer	FE JV	417-861-6160	Kris.Gamble@Foth.com
Brad Hay	Construction Manager	FE JV	678-822-3568	bhay@envirocon.com
Ken Aukerman	Marine Operations Coordinator	FE JV	920-917-3834	Ken.Aukerman@foth.com
Stephen Garbaciak Jr.	Certifying Engineer	FE JV	630-368-3069	Steve.Garbaciak@foth.com
Richard Whitman	Land Operations Coordinator	FE JV	801-450-9667	rwhitman@envirocon.com
David Hardy	Project Health & Safety Manager	FE JV	405 308-6115	dhardy@envirocon.com
Dan Allen	Project Health & Safety Supervisor	FE JV	720-404-6325	dallen@envirocon.com
Allison Haus	Data Validator	FE JV	715-379-9019	Allison.Haus@Foth.com
Sandie Fredrick	Laboratory Project Manager	TestAmerica	920-261-1660	Sandie.fredrick@testamericainc.com
Amelia Kennedy	Laboratory Manager	TestAmerica	615-369-3717	Amelia.kennedy@testamericainc.com

Note:

1. Additional QAPP recipients may be identified prior to finalizing the document.

QAPP Worksheets #4, 7, and 8: Personnel Qualifications and Sign-off Sheet

Name	Project Title/Role	Organizational Affiliation	Telephone Number	Signature	Date QAPP Read
Eric Ealy	Project Coordinator/Overall responsibility for project implementation	NSPW	612-330-2928		
Tom Perry	Owner's Representative	NSPW	906-204-6680		
Steve Laszewski	FE JV Management Committee Member	FE JV	920-496-6823 920-562-0321 (cell)		
Keith Summers	FE JV Management Committee Member	FE JV	920-496-6805 920-562-0328(cell)		
Pete Joy	FE JV Management Committee Member	FE JV	406-523-1157 406-544-5825 (cell)		
Denis Roznowski	Project Manager	FE JV	920-496-6756 920-819-3513 (cell)		
Alan Buell	Deputy Project Manager	FE JV	303-215-0187 406-698-2012 (cell)		
Stephen Garbaciak Jr.	Certifying Engineer	FE JV	630-368-3069 708-793-2354 (cell)		
Brad Hay	Construction Manager	FE JV	303-215-0187 678-822-3568 (cell)		
Ken Aukerman	Marine Operations Coordinator	FE JV	920-496-6780 920-917-3834 (cell)		
Brian Bell	Dredging Expert	FE JV	219-548-0042 630-240-9496 (cell)		
David Hardy	Project Health & Safety Manager	FE JV	405-308-6115 (cell)		

Name	Project Title/Role	Organizational Affiliation	Telephone Number	Signature	Date QAPP Read
Dan Allen	Project Health & Safety Supervisor	FE JV	720-404-6325 (cell)		
Andy Pierre	Monitoring Lead	FE JV	920-496-6727 920-609-8095 (cell)		
Brian Symons	Staff Engineer	FE JV	913-401-3341 913-940-0081 (cell)		
Brian Hanks	Staff Engineer	FE JV	913-401-3343 913-991-0341 (cell)		
Jim Hutchison	Staff Engineer	FE JV	920-496-6813 920-819-8015 (cell)		
Steve Lehrke	Data Statistician	FE JV	920-496-6894 920-562-0329 (cell)		
Nick Azzolina	Project Hydrogeologist	FE JV	920-857-6032 (cell)		
Curt Dungey	Air Quality Technician	FE JV	920-496-6918 920-606-6093 (cell)		
Beth Schuh	Administrative Assistant	FE JV	920-496-6730 920-858-9193 (cell)		
Lori Kurowski	Work Plan Coordinator	FE JV	920-496-6858		
John Whitstone	GIS/CAD Specialist	FE JV	920-496-6845		
Dan Tilly	GIS/CAD/SharePoint Specialist	FE JV	920-496-6924 920-246-6883 (cell)		
Mike Nimmer	Technical Staff	FE JV	920-496-6764 920-619-5905 (cell)		
Mike Mason	Technical Staff	FE JV	913-401-3344 913-302-7392 (cell)		
Kris Gamble	Construction Quality Assurance Officer	FE JV	417-836-3630 417-861-6160 (cell)		
Allison Haus	Data Validator	FE JV	651-288-8554		

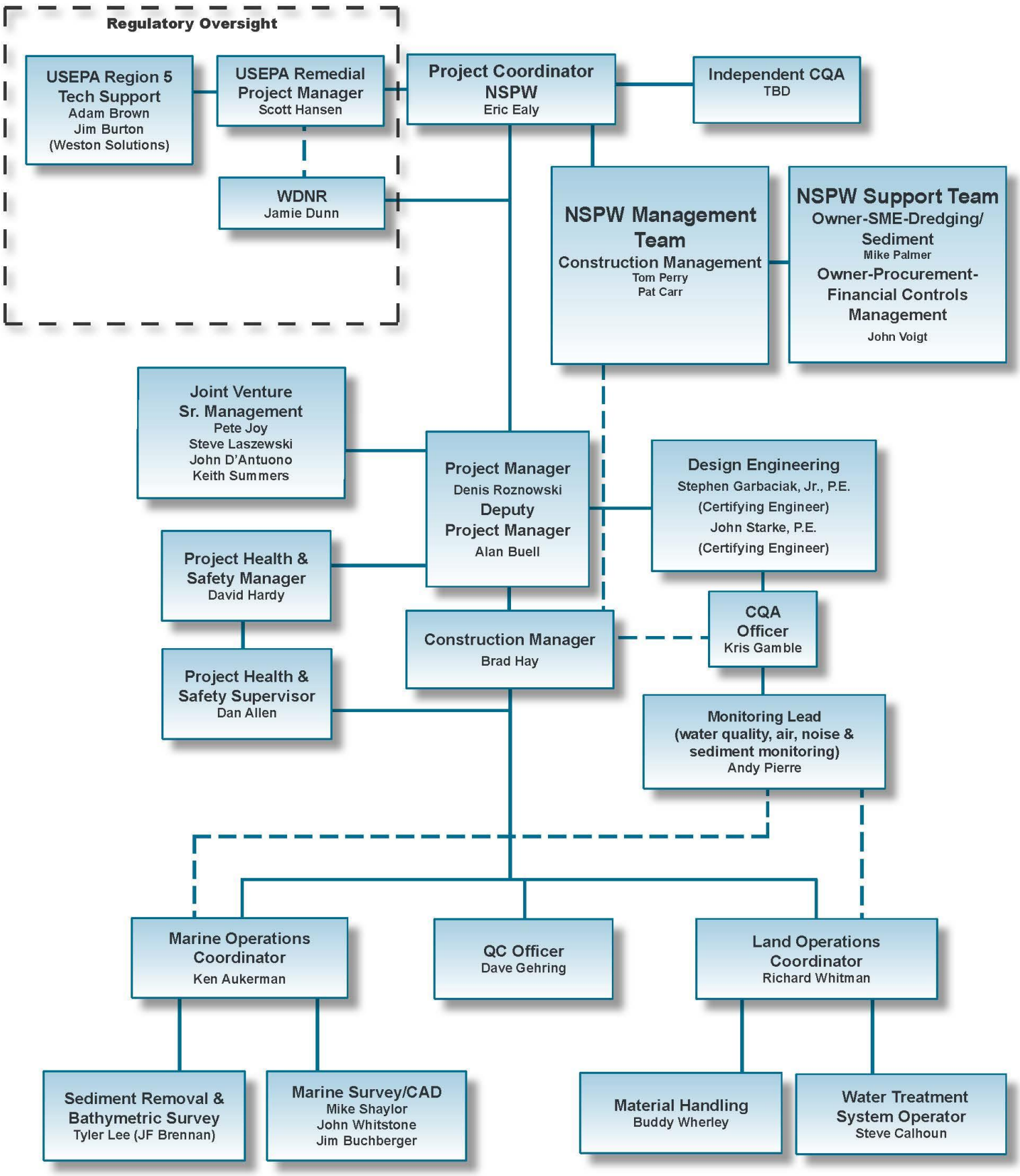
Name	Project Title/Role	Organizational Affiliation	Telephone Number	Signature	Date QAPP Read
			715-379-9019 (cell)		
Marty Sturzl	Technical Advisor	FE JV	920-496-6888 920-619-1978 (cell)		
Dave Gehring	Quality Control Officer	FE JV	509 531-4908 (cell)		
Greg Smith	Sediment Removal	JF Brennan Co.	608-792-0465 (cell)		
Tyler Lee	Project Manager	JF Brennan Co.	608-792-0815 (cell)		
Mitch Evenson	O&M Manager	Cedar Corporation	920-496-6792 416-579-5859 (cell)		
Sandie Fredrick	Laboratory Project Manager	TestAmerica	920-261-1660		
Amelia Kennedy	Laboratory Manager	TestAmerica	615-369-3717		

Note:

1. Additional personnel and roles may be identified prior to finalizing the document.

Organization Chart

Ashland/NSP Lakefront Site - Phase 2 Wet Dredge



Technical Support Team

Tara Van Hoof, Field Team Coordinator	Greg Smith, Constructability
Bob Meller, Geologist	Brian Symons, Phase 1 Engineering Coordination
Steve Lehrke, Environmental Statistician	Ron French, Permitting/Data Coordination
Brooke Lund, CQA	Craig Harley, Engineering
Allison Haus, Data Validation	TBD, Technician
Beth Schuh, Administrative Assistant	Brian Stanul, Engineering

Foth | Envirocon
Joint Venture

QAPP Worksheet #6: Communication Pathways

Communication Driver	Organization	Name	Contact Information	Procedure (timing, pathway, documentation, etc.)
Regulatory agency interface and point of contact	NSPW	Eric Ealy	See Worksheet 3 for contact information.	All communication with agencies will be made by NSPW unless otherwise delegated to others.
Project reporting requirements (i.e., monthly progress reports)	FE JV	Denis Roznowski/ Alan Buell	See Worksheet 3 for contact information.	FE JV will provide reports on behalf of NSPW electronically to EPA and WDNR.
Ensure compliance with the QAPP requirements	FE JV	Kris Gamble	See Worksheet 3 for contact information.	Construction Quality Assurance Officer or designee to provide guidance on QAPP requirements and implementation to all personnel engaged in activities outlined herein.
Identify contractors selected to perform field activities outlined in this document	NSPW	Eric Ealy	See Worksheet 3 for contact information.	NSPW will notify EPA and WDNR via email of the selected contractor(s) and appropriate qualifications 7 days prior to commencing field activities.
Timing of field in-situ measurements and sampling activities	FE JV	Ken Aukerman	See Worksheet 3 for contact information.	Notification will be made via e-mail to NSPW regarding the field in-situ measurement and sampling schedule as soon as possible.
Identification of field non-conformance issues and corrective action measures	FE JV	Steve Garbaciak	See Worksheet 3 for contact information.	Notification will be made via email to NSPW and the Construction Quality Assurance Officer regarding non-conformance and suggested corrective action within 1 business day of identification.

Communication Driver	Organization	Name	Contact Information	Procedure (timing, pathway, documentation, etc.)
Reporting and releases or spills	FE JV	Denis Roznowski/ Alan Buell	See Worksheet 3 for contact information.	Depending on the event, notification will be made to the National Response Center within 24 hours of an event. All events will be reported to NSPW (for reporting to EPA and WDNR) within 24 hours of occurrence.
Reporting laboratory quality control variances or issues and corrective action measures	TestAmerica	Sandie Fredrick	See Worksheet 3 for contact information.	QA/QC issues with project field samples or analytical testing and suggested corrective action(s) will be reported to the Construction Quality Assurance Officer within 1 business day of identification.
Release of in-situ measurements and analytical data results	FE JV	Steve Garbaciak	See Worksheet 3 for contact information.	Upon approval of its release by the Construction Quality Assurance Officer, final validated data will be provided to EPA and WDNR in the agreed upon format.
QAPP	NSPW	Eric Ealy	See Worksheet 3 for contact information.	Any changes requested by NSPW will be provided via an addendum (or addenda) and must be approved by EPA, in consultation with WDNR, before changes can be implemented.

Note:

1. Additional communication drivers, personnel and procedures may be identified prior to finalizing the document.

QAPP Worksheet #9: Project Planning Session Summary

Project Name: Phase 2 Wet Dredge Pilot Study	**Site Name:** Ashland/NSP Lakefront Site
Projected Date(s) of Field Efforts: Spring 2017 – Fall 2018	**Site Location:** Ashland, Wisconsin
Lead Organization Project Coordinator: Eric Ealy	

Date of Session: A series of technical conversations were held in November 2013 through present. This list reflects the participants in discussions held from September 2015 to the present.

Scoping Session Purpose: Discuss elements of the Phase 2 Wet Dredge which is the subject of this program, ultimately documented in the *Final Design for Phase 2 Wet Dredge* (FE JV, 2016a) and this document.

Name	Organization	Telephone Number	E-mail Address	Project Role
Eric Ealy	NSPW	612-330-2928	eric.j.ealy@xcelenergy.com	Project Coordinator
Tom Perry	NSPW	906-204-6680	thomas.e.perry@xcelenergy.com	Construction Manager
Pat Carr	Braun Intertec	218-343-4471	Patrick.carr@xcelenergy.com	Assistant Construction Manager
Denis Roznowski	FE JV	920-496-6756	Denis.roznowski@foth.com	Project Manager
Alan Buell	FE JV	406-698-2012	abuell@envirocon.com	Deputy Project Manager
Brad Hay	FE JV	678-822-3568	bhay@envirocon.com	Construction Manager
Steve Garbaciak	FE JV	630-368-3069	Steve.Garbaciak@foth.com	Certifying Engineer
Scott Hansen	EPA	800-621-8431	hansen.scott@epa.gov	Remedial Project Manager
Craig Melodia	EPA	(312)-353-8870	melodia.craig@epa.gov	Regional Counsel
Jamie Dunn	WDNR	715-635-4049	james.dunn@wisconsin.gov	Project Manager
Bill Fitzpatrick	WDNR	608-266-9267	william.fitzpatrick@wisconsin.gov	Technical Lead
Scott Inman	WDNR	608-264-9201	scott.inman@wisconsin.gov	Technical Lead

Notes/comments: None

Consensus decisions made: Details provided in the *Final Design for Phase 2 Wet Dredge* (FE JV, 2016a).

QAPP Worksheet #10: Conceptual Site Model

The site has historically had several industrial uses including as a manufactured gas plant (MGP). Coal tars and oils were a by-product of the manufactured gas process, including PAHs. Additional information about sources of PAHS at the site can be found in the ROD (Section 5.1), RI/FS, Phase 1 RD/RA and other documents found in the administrative record. In 2014 and 2015, Northern States Power Company (NSPW) conducted source removal and source control remedial activities at the Site to meet the selected remedy for Phase 1, thereby removing contaminated pathways of PAHs to Chequamegon Bay. The remedial activities performed during the Phase 1 work was discussed in the Pilot Study Design. In 2015, a Breakwater was constructed for wave attenuation during the Pilot Study sediment removal and Phase 2 Full Scale Sediment Removal. The remedial completed during the Pilot Study activities are as follows:

1. Installation of a multi-barrier system consisting of a primary, secondary, and tertiary curtain system along with a rock protection and gap curtain system;
2. Mechanical dredging, management, and disposal of impacted inventory sediment and wood debris in the Pilot Study Dredge Area (PSDA) and Extended Pilot Study Dredge Area (EPSDA);
3. Hydraulic dredging, dewatering, management and disposal of impacted residual sediment in the PSDA and EPSDA;
4. Treatment of carriage water generating during dredge operation and any direct contact storm water;
5. Water quality monitoring consisting of hand-held and real-time in-situ measurements as well as chemical of concern (COC) sampling;
6. Air quality monitoring consisting of hand-held and real-time in-situ measurements as well as COC sampling;
7. and
8. Implementation of storm water management best management practices (BMP).

Site Description

The Site is located in the city of Ashland (City), Wisconsin, along the southeast shoreline of Chequamegon Bay (Bay), which is part of southwestern Lake Superior. The Site was historically industrialized and encompasses several upland properties, including the sites of a former manufactured gas plant, former lumber operations, a former wastewater treatment plant, and several acres of impacted sediment offshore. The Site has known contamination of upland soils, groundwater, and Bay sediments, and has been divided into two remedial areas: the Phase 1 upland area, where soil removal is completed and groundwater treatment is currently being addressed; and the Phase 2 sediment area, which is further divided into nearshore and offshore areas. Several performance standards must be met for the Phase 2 Wet Dredge project as listed in Section 12.3 of the ROD.

The ROD identified a select set of volatile organic compounds (VOC), semi-volatile organic compounds (SVOC) including polynuclear aromatic hydrocarbons (PAH), NAPL, and metals as COCs for human and ecological receptors. Recreational receptor exposures to COCs in sediments were below USEPA's target risk levels, with the exception of iron (USEPA, 2010). EPA established a remedial goal for tPAHs for ecological receptors, as discussed in the ROD. Total PAH was calculated as the sum of 18 individual listed PAHs: 2-methylnaphthalene, acenaphthene, acenaphthylene, anthracene, fluorene, naphthalene, phenanthrene, benzo(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene, dibenzo(a,h)anthracene, fluoranthene, indeno(1,2,3-c,d)pyrene, and pyrene. Drawing No. 11 of the *95% Design* shows the current estimate of the extent of tPAH-impacted sediment in the Phase 2 Wet Dredge area.

The local offshore subsurface environment consists of impacted fill materials consisting primarily of wood waste and impacted offshore soft sediments which directly underlie the free water of the Bay. The most abundant PAH compounds include benzene and naphthalene and also free phase hydrocarbons (free product) present as NAPL. The free product, or NAPL, is present in underground pockets of materials that do not readily mix with water. NAPL has also been found in subsurface sediments in the near shore area. Much of the impacted sediment is covered with a layer of wood waste.

Wood waste is thickest near the shoreline and the East and West Peninsulas. The wood debris layer is up to 7 feet thick in areas, with an average thickness of 9 inches. Wood debris overlays approximately 95% of the impacted sediments. The Feasibility Study (FS Study) (URS, 2008) estimated that the entire area of impacted sediments encompasses approximately 16 acres based upon a preliminary remediation goal (PRG) for sediment, expressed as a surface-weighted average concentration (SWAC), of 9.5 parts per million (ppm) tPAH. The underlying sand unit is typically impacted with PAHs increasing with depth below the sediment/surface water interface. The deeper silt/clay unit is generally un-impacted and forms an interface between contaminated sediment and clean lakebed material. (

QAPP Worksheet #11: Project/Data Quality Objectives

Who will use the data?

FE JV, NSPW, EPA, and WDNR will use the data to plan, implement, and evaluate the Phase 2 Wet Dredge.

What will the data be used for?

The data collected as part of this study will be used to evaluate the physical and chemical properties of Site sediment, air and water quality, and noise, in relation to the proposed Phase 2 Wet Dredge. The *Monitoring Plan for Phase 2 Wet Dredge*(*Monitoring Plan*) (FE JV, 2016b) outlines in greater detail the data needs for planning and implementation purposes.

What types of data are needed (matrix, target analytes, analytical groups, field screening, on-site analytical or off-site laboratory techniques, sampling techniques)?

The following types of data will be required:

- Water quality sentinel location monitoring in-situ measurement and contaminants of concern (COC) sampling in between the dual barrier curtain system (Section 2.3 of the *Monitoring Plan*);
- Water quality compliance location monitoring continuous measurements and COC sampling outside the breakwater and gap closures (Sections 2.4 of the *Monitoring Plan*);
- Post-construction water quality monitoring in-situ measurements and COC sampling (Section 2.6 of the *Monitoring Plan*);
- Data for wastewater generated during Phase 2 Wet Dredge activities to verify compliance with monitoring requirements (Section 3 of the *Monitoring Plan*);
- Sediment data for COCs to verify the effectiveness of dredge sequencing and equipment (Section 4.1 of the *Monitoring Plan*) and to verify Remedial Action Levels (RALs) on Figure 5-1 of the *Final Design* meet performance standards in *Record of Decision* (USEPA, 2010) (Section 4.2 of the *Monitoring Plan*);
- Restorative layer placement thickness verification and COC sampling (Section 4.3 of the *Monitoring Plan*);
- Dredged material characterization data for dredged material for evaluating disposal/treatment options (Section 4.4 of the *Monitoring Plan*);
- Noise monitoring for evaluation against city of Ashland Noise Ordinance 202 (Section 6 of the *Monitoring Plan*); and
- Air quality monitoring for evaluation against specified alert and action levels (Section 7 of the *Monitoring Plan*).

How "good" do the data need to be in order to support the environmental decision?

The collected data must be of a known quality consistent with recognized standards of environmental and technical design practice to be able to support the planning and implementation of the Phase 2 Wet Dredge. The specific performance standards are discussed in detail within Table 2-1 of the *Final Design*. The collected data must be representative, complete, accurate, and defendable. Collected data and field logs will be reviewed for completeness, accuracy, and reasonableness. Discrepancies will be accordingly noted and reported within the Phase 2 Wet Dredge Remedial Action Report. For samples used to determine compliance with permit equivalency or for assessing whether sediment clean up and water quality standards specified in the *ROD* have been met, analytical testing must be sufficiently sensitive for comparison against the applicable limits.

How much data are needed (number of samples for each analytical group, matrix, and concentration)? Refer to the *Monitoring Plan* for details on the amount of data, numbers of samples, etc., planned to support this program.
Where, when, and how should the data be collected/generated? Data will be collected/generated from the proposed sampling locations within the Wet Dredge Area. The *Monitoring Plan* provides figures of specific in-situ measurement and sample locations and survey areas. These sample locations have been selected using ”lessons learned” during the Pilot Study and the Extended Pilot Study. Field activities will be initiated after ice thaw in April 2017, and will occur through the implementation of the program, expected to be completed in December 2017.
Who will collect and generate the data? As described in Worksheets #4, 7, and 8, FE JV, working on behalf of Northern States Power Company, will provide the field in-situ measurements and sampling coordination and the field team staff required to conduct the investigation, laboratory coordination and support, and other subcontractor coordination (e.g., boat crews, drilling crew, and survey crews).
How will the data be reported? Updates of in-situ measurement and sample location and collection progress during field activities will be communicated as described in Worksheet #6. Following the completion of the field investigation, a Remedial Action Report will be prepared. This report will summarize the data quality, field activities, laboratory results, and any deviations. Subcontracted laboratories will submit a data package report to FE JV for review and incorporation into the data report after completion of all testing.
How will the data be archived? The data will be managed daily and archived accordingly in the project file. Additional details regarding the management and storage of data is provided in Worksheet #29.

QAPP Worksheet #12a: Measurement Performance Criteria – Sediment/Restorative Layer PAHs

Matrix	Sediment/Restorative Layer	
Analytical Group[a]	Polynuclear aromatic hydrocarbons (PAHs; 8270D/SIM; 8270D)	
Concentration Level	Low or High	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias/ Sensitivity-Contamination	Equipment Rinsate Blanks	No target compound >QL[c]
Accuracy/Bias	LCS	50%-150% R
Accuracy/Bias	MS	50%-150% R
Accuracy/Bias	PE Sample or SRM	50%-150% R
Accuracy/Precision	MSD	50%-150% R; RPD ≤35%
Accuracy/Bias	Surrogates	Laboratory specified
Precision	Field Duplicate	RPD ≤50% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Completeness	Data Completeness Check	≥98%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.
b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.
c Equipment blank contamination will be evaluated on an individual basis.
MB Method blank
QL Quantitation limit
LCS Laboratory control standard
R Recovery
MS Matrix spike
PE Performance evaluation
SRM Standard reference material
MSD Matrix spike duplicate
RPD Relative percent difference

QAPP Worksheet #12b: Measurement Performance Criteria – Sediment/Restorative Layer TOC

Matrix	Sediment/Restorative Layer	
Analytical Group[a]	Total organic carbon (TOC; 9060A)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias	LCS	80%-120% R
Accuracy/Bias	MS	70%-130% R
Precision	Lab Duplicate	RPD ≤25% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Precision	Field Duplicate	RPD ≤50% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.
b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.
c Equipment blank contamination will be evaluated on an individual basis.
MB Method blank
QL Quantitation limit
LCS Laboratory control standard
R Recovery
MS Matrix spike

QAPP Worksheet #12c: Measurement Performance Criteria – Sediment/Restorative Layer Total Solids

Matrix	Sediment/Restorative Layer	
Analytical Group[a]	Total solids (TS; 8000C)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Precision	Lab Duplicate	RPD ≤20% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Precision	Field Duplicate	RPD ≤20% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

RPD Relative percent difference

QL Quantitation limit

QAPP Worksheet #12d: Measurement Performance Criteria – Dredged Material pH

Matrix	Dredged Material	
Analytical Group[a]	pH (9045D)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias	LCS	± 1% true for pH 7, 0.05 pH unit of known
Precision	Laboratory Duplicate	RPD ≤20%
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

LCS Laboratory control standard

RPD Relative percent difference

QAPP Worksheet #12e: Measurement Performance Criteria – Dredged Material Ignitability

Matrix	Dredged Material	
Analytical Group[a]	Ignitability (1010A)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/Sensitivity-Contamination	Water blank	No flash
Accuracy/Bias	LCS/LCSD	p-Xylene: 81° ± 5°F; Undecane: 155° ± 7°F
Precision	Laboratory Duplicate	RPD ≤20%
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.
LCS Laboratory control standard
LCSD Laboratory control standard duplicate
MB Method blank
QL Quantitation limit
RPD Relative percent difference

QAPP Worksheet #12f: Measurement Performance Criteria – Dredged Material Cyanide

Matrix	Dredged Material	
Analytical Group[a]	Cyanide (9014)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias	LCS	80%-120% R
Accuracy/Bias	MS	70%-130% R
Accuracy/Bias	PE Sample or SRM	Supplier Certified Limits
Precision	Laboratory Duplicate	RPD ≤20% if both results are >5x QL Difference ≤ QL if results are ≤5x QL
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet No. 15 for a complete list of analytes for each analytical group.
b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.
MB Method blank
QL Quantitation limit
LCS Laboratory control standard
R Recovery
MS Matrix spike
PE Performance evaluation
SRM Standard reference material
RPD Relative percent difference

QAPP Worksheet #12g: Measurement Performance Criteria – Dredged Material TCLP

Matrix	Dredged Material	
Analytical Group[a]	TCLP (1311), MET, DRET	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	Prep blank	No target compound >QL[b]
Precision	Lab Duplicate	RPD ≤30% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

QL Quantitation limit

RPD Relative percent difference

TCLP Toxicity characteristic leaching procedure

QAPP Worksheet #12h: Measurement Performance Criteria – Dredged Material Metals

Matrix	Dredged Material	
Analytical Group[a]	Metals (6020A; 7470A)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias/ Sensitivity-Contamination	Equipment Rinsate Blanks	No target compound >QL[c]
Accuracy/Bias	LCS	80%-120% R
Accuracy/Bias	MS	75%-125% R
Precision	Lab Duplicate	RPD ≤20% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Precision	Field Duplicate	RPD ≤50% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.

c Equipment blank contamination will be evaluated on an individual basis.

MB Method blank

QL Quantitation limit

LCS Laboratory control standard

R Recovery

MS Matrix spike

MSD Matrix spike duplicate

RPD Relative percent difference

QAPP Worksheet #12i: Measurement Performance Criteria – Dredged Material VOCs

Matrix	Dredged Material	
Analytical Group[a]	Volatile organic compounds (VOCs: 8260B)	
Concentration Level	Low or high	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias/ Sensitivity-Contamination	Equipment Rinsate Blanks	No target compound >QL[c]
Accuracy/Bias	LCS	70%-130% R
Accuracy/Bias	MS	50%-150% R
Accuracy/Precision	MSD	50%-150% R; RPD ≤35%
Accuracy/Bias	Surrogates	Laboratory specified
Precision	Field Duplicate	RPD ≤50% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.
b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.
c Equipment blank contamination will be evaluated on an individual basis.
VOC Volatile organic compounds
MB Method blank
QL Quantitation limit
LCS Laboratory control standard
R Recovery
MS Matrix spike
MSD Matrix spike duplicate
RPD Relative percent difference

QAPP Worksheet #12j: Measurement Performance Criteria – Dredged Material PAHs

Matrix	Dredged Material	
Analytical Group[a]	Polynuclear aromatic hydrocarbons (PAHs: 8270D/SIM; 8270D)	
Concentration Level	Low or High	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias/ Sensitivity-Contamination	Equipment Rinsate Blanks	No target compound >QL[c]
Accuracy/Bias	LCS	50%-150% R
Accuracy/Bias	MS	50%-150% R
Accuracy/Bias	PE Sample or SRM	50%-150% R
Accuracy/Precision	MSD	50%-150% R; RPD ≤35%
Accuracy/Bias	Surrogates	Laboratory specified
Precision	Field Duplicate	RPD ≤50% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Completeness	Data Completeness Check	≥98%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.
b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.
c Equipment blank contamination will be evaluated on an individual basis.
MB Method blank
QL Quantitation limit
LCS Laboratory control standard
R Recovery
MS Matrix spike
PE Performance evaluation
SRM Standard reference material
MSD Matrix spike duplicate
RPD Relative percent difference

QAPP Worksheet #12k: Measurement Performance Criteria – Surface Water VOCs

Matrix	Surface Water	
Analytical Group[a]	Volatile organic compounds (VOCs: 8260B)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias/ Sensitivity-Contamination	Equipment Rinsate Blanks	No target compound >QL[c]
Accuracy/Bias	LCS	70%-130% R
Accuracy/Bias	MS	60%-140% R
Accuracy/Precision	MSD	60%-140% R; RPD ≤30%
Accuracy/Bias	Surrogates	Laboratory specified
Precision	Field Duplicate	RPD ≤40% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.
b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.
c Equipment blank contamination will be evaluated on an individual basis.
MB Method blank
QL Quantitation limit
LCS Laboratory control standard
R Recovery
MS Matrix spike
MSD Matrix spike duplicate
RPD Relative percent difference

QAPP Worksheet #12l: Measurement Performance Criteria – Wastewater (WPDES/POTW) VOCs

Matrix	Wastewater (WPDES/POTW)	
Analytical Group[a]	Volatile organic compounds (VOCs: 624)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias	LCS	Laboratory specified
Accuracy/Bias	Surrogates	Laboratory specified
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.

MB Method blank

QL Quantitation limit

LCS Laboratory control standard

R Recovery

MS Matrix spike

MSD Matrix spike duplicate

RPD Relative percent difference

QAPP Worksheet #12m: Measurement Performance Criteria – Surface Water PAHs

Matrix	Surface Water	
Analytical Group[a]	Polynuclear aromatic hydrocarbons (PAHs: 8270D SIM)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias/ Sensitivity-Contamination	Equipment Rinsate Blanks	No target compound >QL[c]
Accuracy/Bias	LCS	60%-140% R
Accuracy/Bias	MS	60%-140% R
Accuracy/Precision	MSD	60%-140% R; RPD ≤30%
Accuracy/Bias	Surrogates	Laboratory specified
Precision	Field Duplicate	RPD ≤40% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.
b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.
c Equipment blank contamination will be evaluated on an individual basis.
MB Method blank
QL Quantitation limit
LCS Laboratory control standard
R Recovery
MS Matrix spike
MSD Matrix spike duplicate
RPD Relative percent difference

QAPP Worksheet #12n: Measurement Performance Criteria – Wastewater (WPDES/POTW) PAHs

Matrix	Wastewater (WPDES/POTW)	
Analytical Group[a]	Polynuclear aromatic hydrocarbons (PAHs: 625 SIM)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias	LCS	Laboratory specified
Accuracy/Precision	LCSD	Laboratory specified; RPD ≤30%
Accuracy/Bias	Surrogates	Laboratory specified
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.

MB Method blank

QL Quantitation limit

LCS Laboratory control standard

LCSD Laboratory control standard duplicate

R Recovery

RPD Relative percent difference

QAPP Worksheet #12o: Measurement Performance Criteria – Wastewater (WPDES) SVOCs

Matrix	Wastewater (WPDES)	
Analytical Group[a]	Semi-volatile organic compounds (SVOCs: 625)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias	LCS	Laboratory specified
Accuracy/Precision	LCSD	Laboratory specified RPD ≤30%
Accuracy/Bias	Surrogates	Laboratory specified
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.

MB Method blank

QL Quantitation limit

LCS Laboratory control standard

LCSD Laboratory control standard duplicate

R Recovery

RPD Relative percent difference

QAPP Worksheet #12p: Measurement Performance Criteria – Wastewater (POTW) WI-DRO

Matrix	Wastewater (POTW)	
Analytical Group[a]	Diesel Range Organics (DRO) (WI-DRO)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/Sensitivity-Contamination	MB	No target compounds >QL[b]
Accuracy/Bias	LCS	75%-115% R
Accuracy/Precision	LCSD	75%-115% R; RPD ≤30%
Accuracy/Bias	Surrogates	19%-150% R
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.

MB Method blank

QL Quantitation limit

LCS Laboratory control standard

LCSD Laboratory control standard duplicate

R Recovery

RPD Relative percent difference

QAPP Worksheet #12q: Measurement Performance Criteria – Wastewater (POTW) WI-GRO

Matrix	Wastewater (POTW)	
Analytical Group[a]	Gasoline Range Organics (GRO) (WI-GRO)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/Sensitivity-Contamination	MB	No target compounds >Q[b]
Accuracy/Bias	LCS	80%-120% R
Accuracy/Precision	LCSD	60%-140% R; RPD ≤30%
Accuracy/Bias	Surrogates	Laboratory specified
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.

MB Method blank

QL Quantitation limit

LCS Laboratory control standard

LCSD Laboratory control standard duplicate

R Recovery

RPD Relative percent difference

QAPP Worksheet #12r: Measurement Performance Criteria – Wastewater (WPDES/POTW) Metals

Matrix	Wastewater (WPDES/POTW)	
Analytical Group[a]	Metals (200.7; 200.8; 245.1)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias	LCS	85%-115% R
Accuracy/Bias	MS	70%-130% R
Accuracy/Precision	MSD	70%-130% R; RPD ≤20%
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.

MB Method blank

QL Quantitation limit

LCS Laboratory control sample

R Recovery

MS Matrix spike

MSD Matrix spike duplicate

RPD Relative percent difference

QAPP Worksheet #12s: Measurement Performance Criteria – Surface Water

Matrix	Surface Water	
Analytical Group[a]	Total suspended solids (TSS: SM 2540D)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Precision	Lab Duplicate	RPD ≤20% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Precision	Field Duplicate	RPD ≤40% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

RPD Relative percent difference

QL Quantitation limit

QAPP Worksheet #12t: Measurement Performance Criteria – Wastewater (WPDES/POTW) TSS

Matrix	Wastewater (WPDES/POTW)	
Analytical Group[a]	Total suspended solids (TSS: SM 2540D)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias	LCS	90%-110% R
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

RPD Relative percent difference

QL Quantitation limit

QAPP Worksheet #12u: Measurement Performance Criteria – Surface Water DOC

Matrix	Surface Water	
Analytical Group[a]	Dissolved organic carbon (DOC: 9060A)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias	LCS	80%-120% R
Accuracy/Bias	MS	75%-125% R
Precision	Lab Duplicate	RPD ≤25% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Precision	Field Duplicate	RPD ≤40% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.
b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.
MB Method blank
MS Matrix spike
QL Quantitation limit
LCS Laboratory control standard
R Recovery
RPD Relative percent difference

QAPP Worksheet #12v: Measurement Performance Criteria – Wastewater (POTW) Oil and Grease

Matrix	Wastewater (POTW)	
Analytical Group[a]	Oil and Grease (EPA 1664A)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias	OPR	78%114% R
Precision	Lab Duplicate	RPD ≤20% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.

MB Method blank

QL Quantitation limit

OPR Ongoing precision and recovery

R Recovery

RPD Relative percent difference

QAPP Worksheet #12w: Measurement Performance Criteria – Surface Water Sulfide

Matrix	Surface Water	
Analytical Group[a]	Sulfide (SM4500S2-D)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias/ Sensitivity-Contamination	Equipment Rinsate Blanks	No target compound >QL[c]
Accuracy/Bias	LCS	80%-120% R
Accuracy/Bias	MS	70%-130% R
Precision	Lab Duplicate	RPD ≤35% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Precision	Field Duplicate	RPD ≤40% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.

c Equipment blank contamination will be evaluated on an individual basis.

MB Method blank

QL Quantitation limit

LCS Laboratory control standard

R Recovery

MS Matrix spike

RPD Relative percent difference

QAPP Worksheet #12x: Measurement Performance Criteria – Wastewater (POTW) Phosphorus

Matrix	Wastewater (POTW)	
Analytical Group[a]	Total Phosphorus (EPA 365.4)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias	LCS	90%-110% R
Accuracy/Bias	LCSD	90%-110% R; RPD≤20%
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.

MB Method blank

QL Quantitation limit

LCS Laboratory control standard

LCSD Laboratory control standard duplicate

R Recovery

RPD Relative percent difference

QAPP Worksheet #12y: Measurement Performance Criteria – Surface Water and Wastewater (WPDES/POTW) pH

Matrix	Surface Water and Wastewater (WPDES/POTW)	
Analytical Group[a]	pH (MCAWW 150.1)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias	LCS	± 1% true for pH 7, 0.05 pH unit of known
Precision	Laboratory Duplicate	RPD ≤20%
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

LCS Laboratory control standard

RPD Relative percent difference

QAPP Worksheet #12z: Measurement Performance Criteria – Wastewater (WPDES) COD

Matrix	Wastewater (WPDES)	
Analytical Group[a]	Chemical Oxygen Demand (COD: SM 5220 D)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/Instrument Blank	No target compound >QL[b]
Accuracy/Bias	LCS	95%-105% R
Accuracy/Bias	LCSD	95%-105% R
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

b If MB exceedances are widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced.

MB Method blank

QL Quantitation limit

LCS Laboratory control standard

LCSD Laboratory control standard duplicate

R Recovery

RPD Relative percent difference

QAPP Worksheet #12aa: Measurement Performance Criteria – Surface Water Turbidity

Matrix	Surface Water	
Analytical Group[a]	Turbidity (Field Measurement)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Precision	Duplicate Measurement between continuous and manual monitoring	RPD ≤30% if both results are >5x background concentration

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.

RPD Relative percent difference

QAPP Worksheet #12bb: Measurement Performance Criteria – Air VOCs

Matrix	Air	
Analytical Group[a]	Volatile organic compounds (VOCs: TO-15)	
Concentration Level	Low	
DQIs	**QC Sample and/or Activity Used to Assess Measurement Performance**	**Measurement Performance Criteria**
Accuracy/Bias/ Sensitivity-Contamination	MB/System Blank	No target compound >0.2 ppbv
Accuracy/Bias	LCS	60%-140% R
Accuracy/Bias	Surrogates	60%-140% R
Precision	Field Duplicate	RPD <25% for target compounds greater than 5X RL
Completeness	Data Completeness Check	≥95%

Notes:

a Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group.
MB Method blank
RPD Relative percent difference
ppbv Parts per billion volume
LCS Laboratory control sample
R Recovery
RL Reporting limit

QAPP Worksheet #13: Secondary Data Uses and Limitations

Data type	Source	Data uses relative to current project	Factors affecting the reliability of data and limitations on data use
Facility records, surveys, etc.	NSPW Records	Detailed information on outfalls, topography, and property extent	Reports and survey data are available. No known limitations.
COC concentrations	NSPW Records	Estimate removal depth of Pilot dredge area	Spatial variability and limited vertical resolution.
Geotechnical Properties of Sediment	NSPW Records	Physical properties and characteristics of sediment within Pilot dredge area	Data spatially limited
Bathymetry Survey	NSPW Records	Establish water depths and mudline elevations within Pilot dredge area	Missing data from shallow water areas adjacent to shoreline.

Notes:
COC Contaminants of concern

QAPP Worksheet #14/16: Project Tasks & Schedule

Activity	Responsible Party	Planned Start Date	Planned Completion Date	Deliverable(s)	Deliverable Due Date
Dredging	JF Brennan	May 2017	December 2017	Subcontractor notes	TBD
Restorative layer placement	JF Brennan	May 2018	August 2018	Subcontractor notes	TBD
Water quality in-situ measurements and COC sampling	FE JV	May 2017	August 2018	Field and lab data	TBD
Air quality and noise in-situ measurements and sampling	FE JV	May 2017	August 2018	Field and lab data	TBD
Final confirmation sampling	FE JV	August 2017	October 2017	Field and lab data	TBD
Data validation	FE JV	May 2017	August 2018	Validation report	TBD
Remedial Action Report	FE JV	September 2018	November 2018	Remedial Acton Report	TBD

Notes:
TBD To be determined

QAPP Worksheet #15a: Sediment Project Action Levels and Laboratory-Specific Quantitation and Detection Limits

Analyte	Method	TEC	Pilot Study Cleanup Standard	Reference	Reporting Limit[a]	Method Detection Limit[a]
General Chemistry Analytes						
TOC (mg/kg)	9060M	--	--	--	1000	600
Total solids (%)	8000C - Modified	--	--	--	0.1	0.1
PAHs (µg/kg)						
2-Methylnaphthalene	8270D SIM / 8270D	25	--	WDNR 2003	3.33 / 67	1.6/16
Acenaphthene	8270D SIM / 8270D	6.7	--	WDNR 2003	3.33 / 67	0.5/10
Acenaphthylene	8270D SIM / 8270D	5.9	--	WDNR 2003	3.33 / 67	0.7 / 9
Anthracene	8270D SIM / 8270D	57	--	WDNR 2003	3.33 / 67	1.2 / 9
Fluorene	8270D SIM / 8270D	77	--	WDNR 2003	3.33 / 67	0.7 / 12
Naphthalene	8270D SIM / 8270D	176	--	WDNR 2003	3.33 / 67	1.2 / 9
Phenanthrene	8270D SIM / 8270D	204	--	WDNR 2003	3.33 / 67	1 / 9
Benzo[a]anthracene	8270D SIM / 8270D	108	--	WDNR 2003	3.33 / 67	1.2 / 15
Benzo[a]pyrene	8270D SIM / 8270D	150	--	WDNR 2003	3.33 / 67	1.8 / 12
Benzo[e]pyrene	8270D SIM / 8270D	150	--	WDNR 2003	3.33 / 67	1.5 / 12
Benzo[b]fluoranthene	8270D SIM / 8270D	240	--	WDNR 2003	3.33 / 67	1.5 / 12
Benzo[k]fluoranthene	8270D SIM / 8270D	240	--	WDNR 2003	3.33 / 67	1 / 14
Benzo[g,h,i]perylene	8270D SIM / 8270D	170	--	WDNR 2003	3.33 / 67	1.9 / 9
Chrysene	8270D SIM / 8270D	166	--	WDNR 2003	3.33 / 67	1.8 / 9
Dibenzo[a,h]anthracene	8270D SIM / 8270D	33	--	WDNR 2003	3.33 / 67	1.9 / 7
Dibenzofuran	8270D SIM / 8270D	150	--	WDNR 2003	3.33 / 333	1.5 / 41
Fluoranthene	8270D SIM / 8270D	423	--	WDNR 2003	3.33 / 67	1.8 / 9
Indeno[1,2,3-c,d]-pyrene	8270D SIM / 8270D	200	--	WDNR 2003	3.33 / 67	1.8 / 10
Pyrene	8270D SIM / 8270D	195	--	WDNR 2003	3.33 / 67	1.8 / 12
Total PAHs[b]	--	1,610	9,500 (SWAC[c]); 22,800 (individual sample[d])	WDNR 2003	--	--

Notes:

a Achievable method detection limits (MDL) and reporting limits (RL) are limits that the selected laboratory can achieve when performing the analytical methods specified in QAPP Worksheet #23 with nominal sample volumes in the absence of interferences. Actual MDLs and RLs will vary based on sample-specific factors. If a method with higher reporting limits is used (e.g., 8270D for PAHs) and there are no detected results, the lab must reanalyze using a method with lower detection limits (e.g., 8270D SIM). PAH detection limits are critical for post-dredge confirmation sampling used to determine sediment clean-up standards. Detection limits may be sacrificed for samples that exceed 9.5 mg/kg tPAH. Sample moisture needs to be considered along with sample size.

b Total polynuclear aromatic hydrocarbon (PAH) will be the sum of 18 of the 19 individual listed PAHs. Dibenzofuran results will not be included in the total PAH calculation. Totals will be summed using 1/2 MDL value for results below detection.

c Surface weighted average concentration across entire remedial footprint (USEPA 2010).

d No sample to exceed this concentration; also known as the "not-to-exceed threshold" (USEPA 2010).

µg/kg Micrograms per kilogram

mg/kg Milligrams per kilogram

SIM Selected ion monitoring

SWAC Surface weighted average concentration

TEC Threshold effect concentration

TOC Total organic carbon

WDNR 2003 – *Consensus-Based Sediment Quality Guidelines*

EPA 2010 – *Record of Decision*

QAPP Worksheet #15b: Dredged Material Project Action Levels and Laboratory-Specific Quantitation and Detection Limits

Analyte	Method	TEC	Pilot Study Cleanup Standard	Reference	Reporting Limit[a]	Method Detection Limit[a]
General Chemistry Analytes						
Corrosivity (pH)	9045D	--	--	--	--	--
Ignitability (flashpoint)	1010	--	--	--	--	--
Reactive Cyanide	9014	--	--	--	--	--
TCLP	1311	--	--	--	--	--
Metals						
Arsenic	6020A	--	--	--	--	--
Barium	6020A	--	--	--	--	--
Cadmium	6020A	--	--	--	--	--
Chromium	6020A	--	--	--	--	--
Lead	6020A	--	--	--	--	--
Mercury	7470A	--	--	--	--	--
Selenium	6020A	--	--	--	--	--
Silver	6020A	--	--	--	--	--
VOCs						
1,2,4-Trichlorobenzene	8260B	--	--	--	--	--
1,2,4-Trimethylbenzene	8260B	--	--	--	--	--
Benzene	8260B	--	--	--	--	--
Chloroform	8260B	--	--	--	--	--
Chloromethane	8260B	--	--	--	--	--
Ethylbenzene	8260B	--	--	--	--	--
Methylene Chloride	8260B	--	--	--	--	--
n-Butylbenzene	8260B	--	--	--	--	--
Styrene	8260B	--	--	--	--	--
Toluene	8260B	--	--	--	--	--
Xylenes, Total	8260B	--	--	--	--	--

Analyte	Method	TEC	Pilot Study Cleanup Standard	Reference	Reporting Limit[a]	Method Detection Limit[a]
PAHs (µg/kg)						
2-Methylnaphthalene	8270D SIM / 8270D	--	--	--	--	--
Acenaphthene	8270D SIM / 8270D	--	--	--	--	--
Acenaphthylene	8270D SIM / 8270D	--	--	--	--	--
Anthracene	8270D SIM / 8270D	--	--	--	--	--
Fluorene	8270D SIM / 8270D	--	--	--	--	--
Naphthalene	8270D SIM / 8270D	--	--	--	--	--
Phenanthrene	8270D SIM / 8270D	--	--	--	--	--
Benzo[a]anthracene	8270D SIM / 8270D	--	--	--	--	--
Benzo[a]pyrene	8270D SIM / 8270D	--	--	--	--	--
Benzo[e]pyrene	8270D SIM / 8270D	--	--	--	--	--
Benzo[b]fluoranthene	8270D SIM / 8270D	--	--	--	--	--
Benzo[k]fluoranthene	8270D SIM / 8270D	--	--	--	--	--
Benzo[g,h,i]perylene	8270D SIM / 8270D	--	--	--	--	--
Chrysene	8270D SIM / 8270D	--	--	--	--	--
Dibenzo[a,h]anthracene	8270D SIM / 8270D	--	--	--	--	--
Dibenzofuran	8270D SIM / 8270D	--	--	--	--	--
Fluoranthene	8270D SIM / 8270D	--	--	--	--	--
Indeno[1,2,3-c,d]-pyrene	8270D SIM / 8270D	--	--	--	--	--
Pyrene	8270D SIM / 8270D	--	--	--	--	--

Notes:

a Achievable method detection limits (MDL) and reporting limits (RL) are limits that the selected laboratory can achieve when performing the analytical methods specified in QAPP Worksheet #23 with nominal sample volumes in the absence of interferences. Actual MDLs and RLs will vary based on sample-specific factors. If a method with higher reporting limits is used (e.g., 8270D for PAHs) and there are no detected results, the lab must reanalyze using a method with lower detection limits (e.g., 8270D SIM).

µg/kg Micrograms per kilogram

mg/kg Milligrams per kilogram

PAH Polynuclear aromatic hydrocarbon

SIM Selected ion monitoring

TEC Threshold effect concentration

TOC Total organic carbon

QAPP Worksheet #15c: Surface Water Screening Levels and Laboratory-Specific Quantitation and Detection Limits

Analyte	Method	Project Water Quality Standard	Reference	Reporting Limit[a]	Laboratory-Specific Method Detection Limit[a]
General Chemistry Analytes (mg/L)					
TSS	SM 2540D	--	--	1.0	0.7
DOC	9060A	--	--	1.0	0.5
Sulfide	SM 4500S2D	--	--	0.10	0.05
Volatile Organics (µg/L)					
1,2,4-Trimethylbenzene	8260B	12.3	EPA 2010	1	0.17
1,3,5-Trimethylbenzene	8260B	12.3	EPA 2010	1	0.17
Benzene	8260B	0.34	EPA 2010	1	0.2
Ethylbenzene	8260B	14	EPA 2010	1	0.19
Toluene	8260B	--	EPA 2010	1	0.17
m+p-Xylene	8260B		--		
Xylenes (Total)	8260B	27	EPA 2010	3	0.58
PAHs (µg/L)					
1-Methylnaphthalene	8270D SIM	433	EPA 2010	0.1	0.02
2-Methylnaphthalene	8270D SIM	24.3	EPA 2010	0.1	0.03
Acenaphthene	8270D SIM	38	EPA 2010	0.1	0.02
Acenaphthylene	8270D SIM	--	--	0.1	0.03
Anthracene	8270D SIM	0.035	EPA 2010	0.1	0.03
Fluorene	8270D SIM	--	--	0.1	0.02
Naphthalene	8270D SIM	6.2	EPA 2010	0.1	0.02
Phenanthrene	8270D SIM	3.6	EPA 2010	0.1	0.03
Benzo[a]anthracene	8270D SIM	0.025	EPA 2010	0.1	0.02
Benzo[a]pyrene	8270D SIM	0.003*	EPA 2010	0.1[C]	0.02[C]
Benzo[b]fluoranthene	8270D SIM	0.003*	EPA 2010	0.1[C]	0.02[C]
Benzo[e]pyrene	8270D SIM	--	--	0.1	0.05
Benzo[g,h,i]perylene	8270D SIM	7.64	EPA 2010	0.1	0.02
Benzo[k]fluoranthene	8270D SIM	0.14	EPA 2010	0.1	0.02

Analyte	Method	Project Water Quality Standard	Reference	Reporting Limit[a]	Laboratory-Specific Method Detection Limit[a]
Chrysene	8270D SIM	0.07	EPA 2010	0.1	0.02
Dibenzo[a,h]anthracene	8270D SIM	0.003*	EPA 2010	0.1[C]	0.02[C]
Dibenzofuran	8270D SIM	--	--	--	--
Fluoranthene	8270D SIM	1.9	EPA 2010	0.1	0.03
Indeno[1,2,3-c,d]-pyrene	8270D SIM	0.03	EPA 2010	0.1	0.02
Pyrene	8270D SIM	0.3	EPA 2010	0.1	0.02
Total PAHs[b]	--	--	--	--	--

Notes:

a Achievable method detection limits (MDL) and reporting limits (RL) are limits that the selected laboratory can achieve when performing the analytical methods specified in Worksheet #23 with nominal sample volumes in the absence of interferences. Actual MDLs and RLs will vary based on sample-specific factors. Samples must report to the detection limits per Wisconsin requirements. For data sets used to assess compliance with water quality standards (i.e., compliance locations CL-1, CL-2, CL-3 and CL-4), detection limits must not exceed the standard except as identified in the table (*).

b Total polynuclear aromatic hydrocarbons (PAH) will be the sum of 18 of the 20 individual listed PAHs. Dibenzofuran and 1-methylnaphthalene results will not be included in the total PAH calculation. Totals will be summed using 1/2 MDL value for results below detection.

c May be revised in discussions with the laboratory.

µg/L Micrograms per liter

MDL Method detection limits

mg/L Milligrams per liter

SIM Selected ion monitoring

RL Reporting limits

TSS Total suspended solids

DOC Dissolved organic carbon

USEPA 2010 – Levels listed are lowest of screening levels listed on Table 4-4 of *Record of Decision*.

QAPP Worksheets #18 and #20: Sampling Numbers and Methods

Field Task	Matrix	No. of Locations	Field Instrument Used	Parameter	Method	Estimated No. of Field Samples/Frequency[a]	Field Duplicates	Matrix Spikes	Matrix Spike or Lab Duplicate	Field Blanks	Equipment Blank	Trip Blanks	Estimated Total No. of Samples
Sentinel Location Monitoring	Water	5	-	DOC	9060A	20	1	1	1	-	-	-	23
				TSS	SM 2540D	20	1	1	1	-	-	-	23
				VOCs	8260B	20	1	1	1	-	-	-	23
				PAHs	8270D SIM	20	1	1	1	-	-	-	23
				Sulfide	SM4500S2D	20	1	1	1	-	-	-	23
			Water Quality Meter	Turbidity	Field Measurement	Three times per day. Twice per day on days of Compliance Location COC sampling.	-	-	-	-	-	-	TBD
				Temperature	Field Measurement		-	-	-	-	-	-	TBD
				pH	Field Measurement		-	-	-	-	-	-	TBD
				DO	Field Measurement		-	-	-	-	-	-	TBD
				Conductivity	Field Measurement		-	-	-	-	-	-	TBD
Compliance Location Monitoring	Water	5	-	DOC	9060A	708	35	35	35	-	-	-	813
				TSS	SM 2540D	708	35	35	35	-	-	-	813
				VOCs	8260B	708	35	35	35	-	-	-	813
				PAHs	8270D SIM	708	35	35	35	-	-	-	813
				Sulfide	SM4500S2D	708	35	35	35	-	-	-	813
			Water Quality Meter	Turbidity	Field Measurement	Continuous	-	-	-	-	-	-	TBD
				Temperature	Field Measurement		-	-	-	-	-	-	TBD
				pH	Field Measurement		-	-	-	-	-	-	TBD
				DO	Field Measurement		-	-	-	-	-	-	TBD
				Conductivity	Field Measurement		-	-	-	-	-	-	TBD
Post-Construction Monitoring	Water	3	-	DOC	9060A	24	2	2	2	-	1	-	30
				TSS	SM 2540D	24	2	2	2	-	1	-	30
				VOCs	8260B	24	2	2	2	-	1	-	30
				PAHs	8270D SIM	24	2	2	2	-	1	-	30
				Sulfide	SM4500S2D	24	2	2	2	-	1	-	30
			Water Quality Meter	Turbidity	Field Measurement	Prior to removing barriers	-	-	-	-	-	-	TBD
				Temperature	Field Measurement	Prior to removing barriers	-	-	-	-	-	-	TBD
				pH	Field Measurement	Prior to removing barriers	-	-	-	-	-	-	TBD
				DO	Field Measurement	Prior to removing barriers	-	-	-	-	-	-	TBD
				Conductivity	Field Measurement	Prior to removing barriers	-	-	-	-	-	-	TBD
Final Confirmation and Restorative Layer Sampling	Restorative Layer/Sediment	84	-	PAHs	8270D SIM	252	13	13	13	-	13	-	304
				Total Solids	8000C	252	13	13	13	-	13	-	304
				TOC	9060A	252	13	13	13	-	13	-	304
		TBD	-	PAHs	8270D SIM	65	-	-	-	-	-	-	65

Field Task	Matrix	No. of Locations	Field Instrument Used	Parameter	Method	Estimated No. of Field Samples/Frequency[a]	Field Duplicates	Matrix Spikes	Matrix Spike or Lab Duplicate	Field Blanks	Equipment Blank	Trip Blanks	Estimated Total No. of Samples
Dredged Material Characterization	Dredged Material			Total Solids	8000C	65	-	-	-	-	-	-	65
				TOC	9060A	65	-	-	-	-	-	-	65
				TCLP	1311	65	-	-	-	-	-	-	65
				Cyanide	9014	65	-	-	-	-	-	-	65
				Ignitability	1010	65	-	-	-	-	-	-	65
				Corrosivity (pH)	9045D	65	-	-	-	-	-	-	65
				VOCs	8260B	65	-	-	-	-	-	-	65
				SVOCs	8270D	65	-	-	-	-	-	-	65
				Metals	6020A, 7470A	65	-	-	-		-		65
Ashland POTW Wastewater Monitoring	Water	2	-	VOCs (BETX/PVOCs)	624	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				PAHs	625 SIM	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				DRO	WI-DRO	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				GRO	WI-GRO	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				Metals	200.7; 245.1	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				Oil and Grease	1664A	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				Phosphorus, Total	365.4	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				TSS	SM2540D	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				BOD, 5-Day	SM5210B BOD	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				pH	MCAWW 150.1	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
WPDES Wastewater Monitoring	Water	2	-	VOCs	624	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				PAHs	625 SIM	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				SVOCs	625	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				Arsenic, Total	200.8	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				Cyanide, Total	4500CN-E	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				TSS	SM2540D	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				COD	SM 5220 D	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
				pH	MCAWW 150.1	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
Perimeter Air Monitoring	Air	5	Field Gas Chromatograph	TVOCs	Field Measurement	Continuous[a]	-	-	-	-	-	-	-
		5	Area Dust Monitor	PM_{10}	Field Measurement	Continuous[a]	-	-	-	-	-	-	-
		2	Summa Canister	VOCs	TO-15	144	8	-	-	-	-	-	152
		2	PID/Dust Monitor	TVOCs/PM_{10}	Field Measurement	TBD							

Notes:

a Sampling methods and locations are further described in the *Monitoring Plan for Phase 2 Wet Dredge* (FE JV, 2016b).

TOC Total organic carbon

TBD To be determined

VOC Volatile organic compound

PAH Polynuclear aromatic hydrocarbons

SIM Selected ion monitoring

TCLP Toxicity characteristic leaching procedure

SVOC Semi-volatile organic compound

TPH Total petroleum hydrocarbon

DRO Diesel range organics

QAPP Worksheet #15d: City of Ashland POTW Wastewater Project Action Levels and Laboratory-Specific Quantitation and Detection Limits

Analyte	Method	Discharge Limit[5e]	Reference	Reporting Limit[1a]	Method Detection Limit[1a]
General Chemistry Analytes					
pH	MCAWW 150.1	5.5 – 9.5 s.u.	Ashland POTW	0.1	NA
Oil and Grease	1664A	50 mg/L	Ashland POTW	4.0	1.4
BOD, 5 Day	SM5210B BOD	--	Ashland POTW	2.0	1.4
Solids, Total Suspended (TSS)	SM2540D	--	Ashland POTW	1.0	0.7
Phosphorus, Total	365.4	5 mg/L	Ashland POTW	0.1	0.05
VOCs					
1,2,4-Trichlorobenzene	624	--	--	1.0	0.35
1,2,4-Trimethylbenzene	624	--	--	1.0	0.28
1,3,5-Trimethylbenzene	624	--	--	1.0	0.22
Benzene	624	--	--	1.0	0.15
Chloroform	624	--	--	1.0	0.20
Chloromethane	624	--	--	1.0	0.45
Ethylbenzene	624	--	--	1.0	0.19
Methylene Chloride	624	--	--	5.0	1.0
Styrene	624	--	--	1.0	0.23
Toluene	624	--	--	1.0	0.12
Xylenes (Total)	624	--	--	3.0	0.45
MTBE	624	--	--	1.0	0.20
Total BTEX[2b]	--	1 mg/L	Ashland POTW	--	--
PVOC[3c]	--	1 mg/L	Ashland POTW	--	--
PAHs					
1-Methylnaphthalene	625 SIM	--	--	0.1	0.02
2-Methylnaphthalene	625 SIM	--	--	0.1	0.03
Acenaphthene	625 SIM	--	--	0.1	0.02
Acenaphthylene	625 SIM	--	--	0.1	0.03

Analyte	Method	Discharge Limit[5e]	Reference	Reporting Limit[1a]	Method Detection Limit[1a]
Anthracene	625 SIM	--	--	0.1	0.03
Fluorene	625 SIM	--	--	0.1	0.02
Naphthalene	625 SIM	--	--	0.1	0.02
Phenanthrene	625 SIM	--	--	0.1	0.03
Benzo[a]anthracene	625 SIM	--	--	0.1	0.02
Benzo[a]pyrene	625 SIM	--	--	0.1	0.02
Benzo[e]pyrene	625 SIM	--	--	0.1	0.05
Benzo[b]fluoranthene	625 SIM	--	--	0.1	0.02
Benzo[k]fluoranthene	625 SIM	--	--	0.1	0.02
Benzo[g,h,i]perylene	625 SIM	--	--	0.1	0.02
Chrysene	625 SIM	--	--	0.1	0.02
Dibenzo[a,h]anthracene	625 SIM	--	--	0.1	0.02
Fluoranthene	625 SIM	--	--	0.1	0.03
Indeno[1,2,3-c,d]-pyrene	625 SIM	--	--	0.1	0.02
Pyrene	625 SIM	--	--	0.1	0.02
Total PAHs[4d]	--	100 µg/L	Ashland POTW	--	--
Metals					
Cadmium	200.7	110 µg/L	Ashland POTW	1.0	0.4
Chromium	200.7	2500 µg/L	Ashland POTW	2.0	0.5
Copper	200.7	2000 µg/L	Ashland POTW	2.0	1.0
Lead	200.7	100 µg/L	Ashland POTW	2.0	0.2
Mercury	245.1[6f]	0.5 µg/L	Ashland POTW	0.2	0.1
Diesel Range Organics / Gasoline Range Organics					
Gasoline range organics	WI-GRO	50000 µg/L	Ashland POTW	100	50
Diesel range organics	WI-DRO	50000 µg/L	Ashland POTW	100	26

Notes:

1a Achievable MDLs and RLs are limits that the selected laboratory can achieve when performing the analytical methods specified in Worksheet #23 with nominal sample volumes in the absence of interferences. Actual MDLs and RLs will vary based on sample-specific factors.

2b Total BTEX will be the sum of benzene, toluene, ethylbenzene, and xylenes (total). Totals will be summed using 1/2 MDL value for results below detection.

3c Petroleum volatile organic compounds (PVOC) will be the sum of all volatile organic compounds (VOC).

4d Total polynuclear aromatic hydrocarbon (PAH) will be the sum of the individual listed PAHs.

5e Discharge Limits are daily maximum values unless noted otherwise.

6f If multiple positive detections of mercury occur, the analytical Method will be switched to 1631E after consultation with the USEPA and WDNR.

µg/L Micrograms per liter

mg/L Milligrams per liter

SIM Selected ion monitoring

GRO Gasoline range organics

DRO Diesel range organics

Ashland POTW City of Ashland Wastewater Treatment Plant Permit for Nonresidential Wastewater Discharge (City POTW)

QAPP Worksheet #15e: WPDES Permit Equivalency Wastewater Project Action Levels and Laboratory-Specific Quantitation and Detection Limits

Analyte	Method	Discharge Limit	Reference	Reporting Limit[1a]	Method Detection Limit[1a]
General Chemistry Analytes					
pH	MCAWW 150.1	6.0 – 9.0 s.u.	WPDES	0.1	NA
Solids, Total Suspended (TSS)	SM2540D	40,000 µg/L (daily max)	WPDES	1.0	0.7
Cyanide, Total	4500-CN-E	45 µg/L (daily max)	WPDES	10.0	7.0
Chemical Oxygen Demand (COD)	SM 5220 D	--	WPDES	20	4.0
VOCs					
1,2,4-Trimethylbenzene	624	--	--	1.0	0.28
1,3,5-Trimethylbenzene	624	--	--	1.0	0.22
Benzene	624	--	--	1.0	0.15
Ethylbenzene	624	--	--	1.0	0.19
Styrene	624	--	--	1.0	0.23
Toluene	624	--	--	1.0	0.12
Xylenes (Total)	624	--	--	3.0	0.45
Total BTEX[2b]	--	750 µg/L (monthly avg)	WPDES	--	--
PAHs					
1-Methylnaphthalene	625 SIM	--	--	0.1	0.02
2-Methylnaphthalene	625 SIM	--	--	0.1	0.03
Acenaphthene	625 SIM	220 µg/L (monthly avg)	WPDES	0.1	0.02
Acenaphthylene	625 SIM	--	--	0.1	0.03
Anthracene	625 SIM	0.71 µg/L (daily max) 0.21 µg/L (weekly avg)	WPDES	0.1	0.03
Fluorene	625 SIM	36 µg/L (weekly avg)	WPDES	0.1	0.02
Naphthalene	625 SIM	70 µg/L (monthly avg)	WPDES	0.1	0.02
Phenanthrene	625 SIM	--	--	0.1	0.03
Benzo[a]anthracene	625 SIM	--	--	0.1	0.02
Benzo[a]pyrene	625 SIM	0.24 µg/L (weekly avg) 0.054 µg/L (monthly avg)	WPDES	0.1	0.02
Benzo[e]pyrene	625 SIM	--	--	0.1	0.05

Analyte	Method	Discharge Limit	Reference	Reporting Limit[1a]	Method Detection Limit[1a]
Benzo[b]fluoranthene	625 SIM	--	--	0.1	0.02
Benzo[k]fluoranthene	625 SIM	--	--	0.1	0.02
Benzo[g,h,i]perylene	625 SIM	--	--	0.1	0.02
Chrysene	625 SIM	--	--	0.1	0.02
Dibenzo[a,h]anthracene	625 SIM	--	--	0.1	0.02
Fluoranthene	625 SIM	--	--	0.1	0.03
Indeno[1,2,3-c,d]-pyrene	625 SIM	--	--	0.1	0.02
Pyrene	625 SIM	--	--	0.1	0.02
Total PAHs[3c]	--	0.1 µg/L (monthly avg)	WPDES	--	--
SVOCs					
2-Methylphenol	625	--	--	10.0	2.3
3&4-Methylphenol	625	--	--	10.0	2.2
Phenol	625	3300 µg/L (monthly avg)	WPDES	10.0	1.5
METALS					
Arsenic, Total	200.8	--	WPDES	2.0	0.5

Notes:

1a Achievable MDLs and RLs are limits that the selected laboratory can achieve when performing the analytical methods specified in Worksheet #23 with nominal sample volumes in the absence of interferences. Actual MDLs and RLs will vary based on sample-specific factors.

2b Total BTEX will be the sum of benzene, toluene, ethylbenzene, and xylenes (total). For the purposes of reporting a calculated result, average or a mass discharge value, the permittee may substitute a 0 (zero) for any pollutant concentration that is less than the limit of detection. However, if the effluent limitation is less than the limit of detection, the department may substitute a value other than zero for results less than the limit of detection, after considering the number of monitoring results that are greater than the limit of detection and if warranted when applying appropriate statistical techniques.

3c Total polynuclear aromatic hydrocarbon (PAH) will be the sum of the individual listed PAHs. For the purposes of reporting a calculated result, average or a mass discharge value, the permittee may substitute a 0 (zero) for any pollutant concentration that is less than the limit of detection. However, if the effluent limitation is less than the limit of detection, the department may substitute a value other than zero for results less than the limit of detection, after considering the number of monitoring results that are greater than the limit of detection and if warranted when applying appropriate statistical techniques.

µg/L Micrograms per liter

SIM Selected ion monitoring

WPDES Chequamegon Bay under authority of WPDES Permit Equivalency

QAPP Worksheet #15f: Surface Water Screening Levels and Laboratory-Specific Quantitation and Detection Limits

Analyte	Method	Project Water Quality Standard	Reference	Reporting Limit[a]	Laboratory-Specific Method Detection Limit[a]
General Chemistry Analytes (NTU)					
Turbidity – Sentinel Locations	Field Measurement	34 NTU above background/20 mg/L TSS (Alert Level) 71 NTU above background/40 mg/L TSS (Action Level) 182 NTU above background/100 mg/L TSS (Not-to-Exceed Level)	--	Field Measurement	Field Measurement
Turbidity – Compliance Locations	Field Measurement	25 NTU above background/20 mg/L TSS (Alert Level) 50 NTU above background/40 mg/L TSS (Action Level) 127 NTU above background/100 mg/L TSS (Not-to-Exceed Level)	--	Field Measurement	Field Measurement
Temperature	Field Measurement	--	--	Field Measurement	Field Measurement
pH	Field Measurement	--	--	Field Measurement	Field Measurement
Dissolved Oxygen	Field Measurement	--	--	Field Measurement	Field Measurement
Conductivity	Field Measurement	--	--	Field Measurement	Field Measurement
Fluorescence	Field Measurement	--	--	Field Measurement	Field Measurement

Notes:

a Field measurement taken by FE JV personnel.
NTU Nephelometric turbidity units
TSS Total Suspended Solids
TBD To be determined
mg/L Milligrams per liter

QAPP Worksheet #15g: Air Screening Levels and Laboratory-Specific Quantitation and Detection Limits

Analyte	Method	Project Screening/ Action Criteria	Reference	Reporting Limit[a]	Laboratory-Specific Method Detection Limit[a]
Total Volatile Organic Compounds (ppm)					
TVOC	Field Gas Chromatograph	> 0.5 ppm (15-min avg conc) Site Condition 2 Alert Level > 0.5 ppm (15-min avg) and BTEX > one of following 15-min concentrations: Benzene (0.5 ppm), Toluene (15 ppm), Ethylbenzene (30 ppm), Xylene (15 ppm) Site Condition 3 Action Level	--	Field Measurement	Field Measurement

Notes:

a Field measurement taken by FE JV personnel.
TVOC Total volatile organic compounds
ppm Parts per million
BTEX Benzene/Toluene/Ethylbenzene/Xylene

QAPP Worksheet #15h: Air Screening Levels and Laboratory-Specific Quantitation and Detection Limits

Analyte	Method	Project Screening/ Action Criteria	Reference	Reporting Limit[a]	Laboratory-Specific Method Detection Limit[a]
Particulate Matter (mg/m^3)					
PM_{10}	Area Dust Monitor	> 0.50 mg/m^3 Site Condition 2 Alert Level > 1.0 mg/m^3 Site Condition 3 Action Level	--	Field Measurement	Field Measurement

Notes:

a Field measurement taken by FE JV personnel.

PM_{10} Particulate Matter up to 10 micrometers in size

mg/m^3 Milligrams per cubic meter

QAPP Worksheet #15i: Air Screening Levels and Laboratory-Specific Quantitation and Detection Limits

Analyte	Method	Project Screening/ Action Criteria	Reference	Reporting Limit[a]	Laboratory-Specific Method Detection Limit[a]
Volatile Organic Compounds (ppbv)					
Benzene	TO-15	--	--	0.20	0.056
Ethylbenzene	TO-15	--	--	0.20	0.068
Naphthalene	TO-15	--	--	0.50	0.090
Styrene	TO-15	--	--	0.20	0.058
Toluene	TO-15	--	--	0.20	0.12
Xylenes, Total	TO-15	--	--	0.40	0.061

Notes:

a Achievable method detection limits (MDL) and reporting limits (RL) are limits that the selected laboratory can achieve when performing the analytical methods specified in QAPP Worksheet #23 with nominal sample volumes in the absence of interferences. Actual MDLs and RLs will vary based on sample-specific factors. Samples must report to the detection limits per Wisconsin requirements.

ppbv Parts per billion by volume

QAPP Worksheet #17: Sampling Design and Rationale

To assess water quality performance standards during dredging activities within the Wet Dredge Project Area, a monitoring and sampling program will be implemented that meets the requirements of Wisconsin Department of Natural Resources (WDNR) Chapter 30 Permit Equivalency. As discussed within the *Final Design for Phase 2 Wet Dredge* (*Final Design*) (FE JV, 2016a), barrier systems will be utilized in conjunction with operational controls and other best management practices (BMPs) to control water quality (including dissolved parameters). Details regarding the barrier systems, including type, placement, and layout are provided in Section 4 of the *95% Design*.

The goals and objectives of water quality monitoring and sampling program are to do the following:

- Provide procedures and protocols for compliance locations, sentinel locations, and post-construction water quality in-situ measurements and sampling during on-the-water activities of the Phase 2 Wet Dredge project.

- Evaluate alternative response actions in the event that water quality goals are not met.

These goals and objectives will be met by implementing an in-situ measurement and sampling program.

As part of the Wet Dredge evaluation to meet clean-up goals, sediment/restorative layer samples will be collected at various times. The Wet Dredge Project Area will follow the same protocols in the *Monitoring Plan for Phase 2 Wet Dredge* (FE JV, 2016b). Specifically, sediment samples will be collected for the following purposes.

- Post-mechanical interim visual
- Post-hydraulic interim visual
- Dredged material characterization
- Final confirmation COC
- Restorative layer thickness verification and COC

Noise monitoring will be conducted throughout the Wet Dredge project to evaluate noise levels immediately adjacent to the Site to assure these levels are in compliance with applicable local, state, and federal requirements. Noise monitoring locations have been selected (NMP-01, NMP-02, NMP-03, NMP-04, and NMP-05) based on proximity to potential sensitive receptors near the Site. During the project, the noise monitoring program will focus on sources of potential noise-generating equipment.

Air quality during on-the water activities and processing of sediment will be evaluated during the Wet Dredge project. The program provides an integrated approach that combines manual and real-time in-situ measurements for total volatile organic compounds (TVOC), certain indicator organic compounds and particulate matter (PM_{10}) at five stations (AMP-01, AMP-02, AMP-03, AMP-04, AMP-05) surrounding the Site. Selection of stations was based on proximity to sensitive off-site receptors, such as residences, church, school, hotel, and other businesses near the Site.

Details regarding in-situ measurements and sampling activities are presented in the *Monitoring Plan*.

DOC	Dissolved organic carbon
DO	Dissolved oxygen
TSS	Total suspended solids
TVOC	Total volatile organic compounds
PM_{10}	Particulate matter 10 microns or less in size
PID	Photo ionization detector

QAPP Worksheets #19 & 30: Sample Containers, Preservation, and Hold Times

Laboratory (Name, sample receipt address, point of contact, e-mail, and phone numbers): TestAmerica, 2960 Foster Creighton Drive, Nashville, TN 37204, Sandie Fredrick, Sandie.Fredrick@testamericainc.com, 920.261.1660
List any required accreditations/certifications: NELAC, WDNR
Back-up Laboratory: NA
Sample Delivery Method: Courier/Commercial Shipping Company

Analyte/ Analyte Group	Matrix	Method	Accreditation Expiration Date	Container(s) (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround[a]
PAHs	Sediment	8270D SIM	8/31/16	8-oz. glass	< 6 °C	14 days	40 days	Quick
TOC	Sediment	9060A	8/31/16	4-oz. glass	< 6°C	--	14 days	Quick
Total Solids	Sediment	8000C	8/31/16				6 months	Quick
Corrosivity	Dredged Material	9045D	8/31/16	4-oz. glass	< 6 °C	--	None	Standard
Ignitability	Dredged Material	1010	8/31/16					Standard
Cyanide	Dredged Material	9014	8/31/16	4-oz. glass	< 6 °C	--	14 days	Standard
Metals	Dredged Material	6020A, 7470A	8/31/16	8-oz. glass	< 6 °C	--	180 days	Standard
VOCs	Dredged Material	8260B	8/31/16	2 x 40 ml VOA Vial and Terracore, if required	< 6 °C	--	14 days	Standard
PAHs	Dredged Material	8270D SIM	8/31/16	8-oz. glass	< 6 °C	14 days	40 days	Standard
VOCs	Surface Water	8260B	8/31/16	3 x 40-mL VOA vial	< 6 °C; HCl to pH < 2	--	14 days	Quick
VOCs	Wastewater	624	8/31/16	3 x 40-mL VOA vial	< 6 °C; HCl to pH < 2	--	14 days	Standard
PAHs	Surface Water	8270D SIM	8/31/16	2 x 1L-Amber glass	< 6 °C	7 days	40 days	Quick

Analyte/ Analyte Group	Matrix	Method	Accreditation Expiration Date	Container(s) (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround[a]
PAHs	Wastewater	625 SIM	8/31/16	2 x 1L-Amber glass	< 6 °C	7 days	40 days	Standard
SVOCs	Wastewater	625	8/31/16	2 x 1L-Amber glass	< 6 °C	7 days	40 days	Standard
TSS	Surface Water; Wastewater	SM 2540D	8/31/16	1L-HDPE	< 6 °C	--	7 days	Standard (WW) Quick (SW)
Sulfide	Surface Water	SM 4500S2D	8/31/16	500 mL	ZnAC and NaOH to pH > 9	--	7 days	Quick
DOC	Surface Water	9060A	8/31/16	500 mL-HDPE	< 6 °C	48 hours to filtration and preservation	28 days	Quick
DRO	Wastewater	WI-DRO	8/31/16	1L Amber glass	< 6 °C	--	7 days	Standard
GRO	Wastewater	WI-GRO	8/31/16	3 x 40ml VOA vial	< 6 °C	--	14 days	Standard
Metals	Wastewater	200.7; 200.8; 245.1	8/31/16	500 mL HDPE	< 6 °C; HNO_3 to pH < 2	--	6 months	Standard
Cyanide, Total	Wastewater	4500CN-E	8/31/16	250 mL HDPE	< 6 °C; NaOH to pH>12	--	14 days	Standard
Phosphorus, Total	Wastewater	365.4	8/31/16	250 mL HDPE	< 6 °C; H_2SO_4 to pH < 2	--	28 days	Standard
Oil and Grease	Wastewater	1664A	8/31/16	1L Amber glass	< 6 °C; H_2SO_4 to pH < 2	--	28 days	Standard
COD	Wastewater	SM 5220 D	8/31/16	250 mL HDPE	< 6 °C; H_2SO_4 to pH < 2	--	28 days	Standard
BOD, 5-Day	Wastewater	SM5210B BOD	8/31/16	500 mL HDPE	< 6 °C	--	48 hours	Standard
VOCs	Air	TO-15	8/31/16	SUMMA® canister	-10 to zero inches Hg	--	30 days	3 day

Notes:

a	Preliminary data will be provided on an expedited basis as indicated on the chain of custody form.
°C	degrees Celsius
BOD	Biological oxygen demand
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
DRO	Diesel range organics
GRO	Gasoline range organics
HDPE	High-density polyethylene
Hg	Mercury
mL	Milliliter
NA	Not applicable
PAH	Polynuclear aromatic hydrocarbon
PTFE	Polytetrafluoroethylene
SOP	Standard Operating Procedure
SVOC	Semi-volatile organic compound
TOC	Total organic carbon
TSS	Total suspended solids
VOA	Volatile organic analysis
VOC	Volatile organic compound
HCl	Hydrochloric acid
ZnAC	Zinc acetate
NaOH	Sodium hydroxide
H_2SO_4	Sulfuric acid
HNO_3	Nitric acid

QAPP Worksheet #21: Field SOPs[a]

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	SOP option or Equipment Type (if SOP provides different options)	Modified for Project? Y/N	Comments
SOP-01	Field Records	FE JV	NA	Y	None
SOP-02	Equipment Decontamination	FE JV	Decontamination equipment	Y	None
SOP-03	Navigation and Positioning	FE JV	Digital global positioning system	Y	None
SOP-04	Core Collection	FE JV	Sediment sampling device	Y	None
SOP-05	Core Processing	FE JV	Sample processing gear	Y	None
SOP-06	Conductivity, Temperature, pH, DO, and Turbidity Data Collection and Water Sampling	FE JV	Water quality meter/water sampler	Y	None
SOP-07	Multi-Parameter Water Quality Data Collection Meter Calibration and Operation	FE JV	Water quality meter	Y	None
SOP-08	Sample Custody	FE JV	NA	Y	None
SOP-09	Sample Packaging and Shipping	FE JV	NA	Y	None
SOP-10	Investigation Derived Waste Handling and Disposal	FE JV	NA	Y	None
SOP-11	Effluent Sampling	FE JV	ISCO sampler	Y	None

Notes:

a Field SOPs are provided in Appendix A of the *Monitoring Plan for Phase 2 Wet Dredge Pilot Study* (FE JV, 2016b).

NA Not applicable

SOP Standard Operating Procedure

QAPP Worksheet #22: Field Equipment Calibration, Maintenance, Testing, and Inspection

Field Equipment	Activity	SOP Reference[a]	Title or Position of Responsible Person	Frequency	Acceptance Criteria	Corrective Action
Real time kinematic positioning system	Calibration, Maintenance, Testing, and Inspection	Operations Manual and SOP-03	Field Personnel	Daily and in accordance with Operations Manual as needed.	In accordance with Operations Manual	Calibrate in accordance with Operations Manual or replace unit.
Digital global positioning system	Calibration, Maintenance, Testing, and Inspection	Operations Manual and SOP-03	Field Personnel	Daily and in accordance with Operations Manual as needed.	Operating within 1 meter of known benchmark	Calibrate in accordance with Operations Manual or replace unit.
Water quality meter	Calibration, Maintenance, Testing, and Inspection	Operations Manual and SOP-07	Field Personnel	Weekly	In accordance with Operations Manual	In accordance with Operations Manual
Field gas chromatograph	Calibration, Maintenance, Testing, and Inspection	Operations Manual	Field Personnel	Daily	In accordance with Operations Manual	In accordance with Operations Manual
Area dust monitor	Calibration, Maintenance, Testing, and Inspection	Operations Manual	Field Personnel	Daily	In accordance with Operations Manual	In accordance with Operations Manual

Notes:

a Field SOPs are provided in Appendix A of the *Monitoring Plan for Phase 2 Wet Dredge Pilot Study* (FE JV, 2016b).

SOP Standard Operating Procedure

QAPP Worksheet #23: Analytical SOPs

SOP #[a]	Title, Revision Date, and/or Number	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project Work? (Y/N)[b]
8260/NV05-77.18b	*Method 8260B/C: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); 11/29/13; Rev. 18c*	Definitive	Dredged Material/Organics	GC/MS	Y
8260/624/SM6200 B/NV05-77.20	*Method 8260B/624/SM6200B: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); 8/31/2015; Rev. 20a*	Definitive	Water/Organics	GC/MS	Y
8270/NV04-22-15b	*Method 8270C/D: Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); 8/6/13; Rev. 15c*	Definitive	Sediments/ Restorative Layer/Dredged Material/ Organics	GC/MS	Y
8270/625/NV04-22.17	*Method 8270C/D/625: Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); 12/14/2015; Rev. 17a.*	Definitive	Water/Organics	GC/MS	Y
WI DRO/NV04-38	*Wisconsin Method of Determining Diesel Range Organics (DRO) Method WI DRO; 7/31/13; Rev. 8*	Definitive	Water/Organics	GC/FID	Y
6020/NV06-215.6	*Method 6020/6020A: Metals Analysis by Inductively Coupled Plasma- Mass Spectrometry; 11/29/13; Rev. 6a*	Definitive	Dredged Material/ Metals	ICP/MS	N
6020/200.7/200.8/NV06-215.8b	*Methods 6020/6020A, 200.7, and 200.8: Metals Analysis by Inductively Coupled Plasma – Mass Spectrometry; 12/31/2015; Rev. 8c*	Definitive	Water/Metals	ICP/MS	N
7470/245.1/SM3112B/ NV06-41.18a	*Method 7470A/245.1/245.2(SC)/SM3112B: Mercury in Liquid Waste (Manual Cold Vapor Technique); 1/31/2016; Rev. 18b*	Definitive	Water/Metals	CVAA	N

SOP #[a]	Title, Revision Date, and/or Number	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project Work? (Y/N)[b]
1631E/NC-MT-001	*Method 1631E: Preparation and Analysis of Mercury in Aqueous and Solid Samples by Cold Vapor Atomic Fluorescence; 1/9/15; Rev. 7*	Definitive	Water/Metals	CVAF	N
9060A/NV07-79.11	*Total Organic Carbon, Total Inorganic Carbon, and Total Carbon, SW-846 Method 9060A; 3/29/13; Rev. 11*	Definitive	Sediments/Restorative Layer/Dredged Material/Conventionalism	Carbon Analyzer	Y
SM2540D/NV07-63.9	*Residue, Non-Filterable (Gravimetric, Dried at 103°C-105°C (Total Suspended Solids, TSS) Method SM2540D; 12/31/12; Rev. 9*	Definitive	Water/Conventionals	Analytical Balance and Drying Oven	Y
410.4/SM5220D/ NV07-08.7a	*Method EPA 410.4/SM5220D: Chemical Oxygen Demand By Manual Colorimetry; 10/31/14; Rev. 7b*	Definitive	Water/Conventionals	Spectrophotometer	Y
SM5210 B/NV07-05.17b	*Method SM5210 B: Biochemical Oxygen Demand and Carbonaceous Biochemical Oxygen Demand*	Definitive	Water/Conventionals	BOD Analyzer	N
365.4 SM4500-P B, H/NV07-82	*Total Phosphorus by Colormetric, Automated, Block Digester AA II EPA Method 365.4 and SM4500-P B, H*	Definitive	Water/Conventionals	Lachat	Y
9014/NV07-137.10b	*Total and Amenable Cyanide (Automated Colorimetric, with Off-line Distillation); Method 9014; 9/30/13; Rev. 10b*	Definitive	Dredged Material/Waters/ Conventionals	Lachat and distillation system	Y
SM4500-S^{-2} D/NV07-180	*Sulfide (Colorometric, Methylene Blue) Methods SM4500S^2D and SM4500-S^2B*	Definitive	Sediments/Waters/ Conventionals	Lachat	Y
8000/NV03-172.8	*Determination of % Dry Weight; Method SW-846 8000C; 5/31/13; Rev. 8*	Definitive	Sediments/Restorative Layer/Conventionals	Analytical Balance and Drying Oven	Y
9045/NV03-54.8	*Soil and Waste pH, Corrosivity; Method 9045 C/D: 10/13/13; Rev. 8*	Definitive	Dredged Material/Waters/ Conventionals	pH probe	Y

SOP #[a]	Title, Revision Date, and/or Number	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project Work? (Y/N)[b]
1010/NV07-30	*Pensky-Martens Closed-Cup for Determining RCRA Ignitability and Flash Point (Liquids) SW-846 Method 1010A, ASTM D93 and Cleveland Open Cup Method for Flash Points (Soils/Solids) ASTM D92; 2/28/14; Rev. 9*	Definitive	Dredged Material / Conventionals	Cleveland Open-Cup Tester	N
1664 9070/NV03-112.11	*n-Hexane Extractable Material and Silica Gel Treated n-Hexane Extractable Material by Extraction and Gravimetry, Method 1664/9070A; 11/9/2015; Rev. 11a*	Definitive	Water/Organics	NA	N
3510/NV03-24.14	*Separatory Funnel Liquid-Liquid Extraction; SW-846; Method 3510C; 2/28/14; Rev. 14*	Definitive	Water/Organics	NA	N
3541/NV03-231.4	*Preparation of Soil/Sediment by automated SOXHLET for the Analysis of Semi-volatile Organic Compounds; SW-846; Method 3541; 1/31/14; Rev. 4*	Definitive	Sediments/Restorative Layer/Dredged Material/Organics	NA	N
3546/NV03-247.0	*Microwave Extraction; SW-846; Method 3546; 12/9/13; Rev. 0*	Definitive	Sediments/Restorative Layer/Dredged Material/Organics	NA	N
3550/NV03-23.16	*Ultrasonic Extraction; SW-846; Method 3550B/C; 7/31/13; Rev.16*	Definitive	Sediments/Restorative Layer/Dredged Material/Organics	NA	N
3580/NV03-106.8	*Waste Dilution; SW-846; Method 3580A; 1/31/14; Rev.8*	Definitive	Dredged Material/Water/Organics	NA	N
WI GRO/NV05-204.5a	*Wisconsin DNR Modified GRO Method for Determining Gasoline Range Organics; Method WI GRO; 3/31/14; Rev. 5a*	Definitive	Water/Organics	NA	N
3005/NV06-103.12	*Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by ICP Spectroscopy, SW-846 Method 3005A, SM3030C; 7/31/13; Rev. 12*	Definitive	Water/Metals	NA	N

SOP #[a]	Title, Revision Date, and/or Number	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project Work? (Y/N)[b]
3010/NV06-18.10	*Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by ICP Spectroscopy, SW-846 Method 3010A; 7/31/13; Rev. 10*	Definitive	Water/Metals	NA	N
3051/NV06-94.14b	*Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils; Method 3051; 2/3/14; Rev 14b*	Definitive	Sediments/Restorative Layer/Metals	NA	N
NV02-01.13	*Sample Receiving; 3/29/13; Rev. 13*	Definitive	NA	NA	N
NV10-169.9	*Handling of Soils Regulated by USDA; 12/31/13 Rev. 9*	Definitive	NA	NA	N
NV10-83.10	*Waste Disposal; 11/30/12; Rev. 10*	Definitive	NA	NA	N
1311/NV03-70	*Toxicity Characteristic Leaching Procedure SW-846 Method 1311; 11/29/13; Rev. 8*	Definitive	Dredged Material/Water	NA	N
EPA - 823-B-98-004	*Inland Testing Manual - EPA-823-B-98-004*	Definitive	Dredged Material/Water	NA	N
KNOX – MS – 0022	*Canister Cleaning and Preparation; 10/28/14; Rev. 3*	Definitive	Air	Canisters	N
KNOX – MS – 001	*VOA Canister Analysis; 5/19/14; Rev. 15*	Definitive	Air	GC/MS	N

Notes:

a Analytical SOPs are contained in Appendix A of this *QAPP*.

b Modifications to SOPs are project-specific criteria outlined in QAPP Worksheet #28.

GC/MS Gas chromatograph/mass spectrometer

GC/FID Gas chromatograph/flame ionization detector

CVAA Cold-vapor atomic absorption

CVAF Cold vapor atomic fluorescence

COD Chemical oxygen demand

NA Not applicable

QAPP Worksheet #24: Analytical Instrument Calibration

Instrument	Calibration Procedure	Calibration Range	Frequency	Acceptance Criteria	Corrective Action	Title/Position Responsible for Corrective Action	SOP Reference[a]
GC/MS (VOC)	Bromofluoro-benzene tune; initial and continuing calibration as required in SOP	See Appendix A	Verify tuning every 12 hours; ICAL after instrument set up, after major instrument changes, and when continuing calibration criteria are not met	ICAL %RSD ≤20% or linear curve r ≥0.995, or r2 >0.990 or quadratic curve r2 >0.990 (minimum average RFs must comply with method) CCV %D ≤20%D ICV %D ±30%D	Inspect system, correct problem, rerun calibration and affected samples	Analyst	8260/NV05-77.18b; 8260/624/SM6200 B/NV05-77.20
GC/MS (SVOC)	Decafluorotriphenyl-phosphine tune; initial and continuing calibration as required in SOP	See Appendix A	Verify tune every 12 hours; ICAL after instrument set up, after major instrument changes, and when continuing calibration criteria are not met	ICAL %RSD ≤30% for CCCs; ICAL %RSD <15% or linear curve recovery ® ≥ 0.995, or r2 >0.990 or quadratic curve r2 >0.990 CCV %D ≤20% for CCCs; SPCC minimum average RF	Inspect system, correct problem, rerun calibration and affected samples	Analyst	8270/NV04-22-15b; 8270/625/NV04-22.17
GC/MS-SIM (PAH)	Perfluorotributylamine tune; initial and continuing calibration as required in SOP	See Appendix A	Verify tune every 12 hours; ICAL after instrument set up, after major maintenance, and/or after instrument changes have occurred	ICAL %RSD ≤25%; no more than 10% of compounds between 25 and 30% CCV %D ≤30%; no more than 10% of compounds between 25 and 30%	Inspect system, correct problem, rerun calibration and affected samples	Analyst	8270/NV04-22-15b; 8270/625/NV04-22.17

Instrument	Calibration Procedure	Calibration Range	Frequency	Acceptance Criteria	Corrective Action	Title/Position Responsible for Corrective Action	SOP Reference[a]
GC/FID (DRO)	Initial and continuing calibration as required in SOP	See Appendix A	ICAL after instrument set up, after major instrument changes, and when continuing calibration criteria are not met; calibration verification every 24 hours	ICAL %RSD ≤25% for individual compounds and ≤20% for fuel products; CCV ≤25% for individual compounds and no more than 10% of compounds between 25 to 30%; <20% for fuel products	Inspect system, correct problem, rerun calibration and affected samples	Analyst	WI DRO/NV04-38
ICP/MS (metals)	Daily performance check; initial and continuing calibration per SOP	See Appendix A	Performance check daily; ICAL daily or per batch; CCV every ten samples	Daily performance check per manufacturer; background mass 220 <30 cps; Ba+/Ba++ <3%; Ce/CeO <3%; ICAL r ≥0.995; CCV ±10%	Inspect system, correct problem, rerun calibration and affected samples	Analyst	6020/NV06-215.6; 6020/200.8/200.7/NV06-215.8b
CVAA (mercury)	Daily performance check; initial and continuing calibration per SOP	See Appendix A	Performance check daily; ICAL daily or per batch; CCV every ten samples and end of batch	ICAL %R 95-105%; CCV %R 90-110%	Inspect system, correct problem, rerun calibration and affected samples	Analyst	7470/245.1/SM 3112B/ NV06-41.18a
CVAF (mercury)	Initial and continuing calibration per SOP	See Appendix A	ICAL may be performed daily, but is required only when indicated by instrument and preparation QC problems; CCV at the end of the analytical sequence or every 12 hours	ICAL must have < 15% RSD and low standard within ±25% of true value; CCV %R 77-123%	Inspect system, correct problem, rerun calibration and affected samples	Analyst	NC-MT-001

Instrument	Calibration Procedure	Calibration Range	Frequency	Acceptance Criteria	Corrective Action	Title/Position Responsible for Corrective Action	SOP Reference[a]
Carbon Analyzer (DOC, TOC)	Initial and continuing calibration per SOP	See Appendix A	ICAL daily; CCV every ten burns	CCV 80-120%	Inspect system, correct problem, rerun calibration and affected samples	Analyst	9060/NV07-79.11
Lachat (cyanide, sulfide)	Initial and continuing calibration per SOP	See Appendix A	ICAL daily; CCV every ten samples	ICAL r ≥0.995, cyanide ICV/CCV and sulfide CCV ±10%; sulfide ICV ±15%	Inspect system, correct problem, rerun calibration and affected samples	Analyst	9012/NV07-137.10b and SM4500-S^{-2} D/NV07-180
Spectrophoto-meter	Initial and continuing calibration per SOP	See Appendix A	Each new lot of COD Reagent Vials, every 6 months, or if CCV fails	RSD ± 10% or use first-order linear regression with r ≥ 0.995 or r2 > 0.990; All standards ± 10% of true (except RL standard at ± 25%) when re-fitted against initial calibration	Re-prepare standards and re-run	Analyst	410.4/SM5220D /NV07-08.7a
Analytical balance (particle size, total solids, TSS)	Daily	See Appendix A	Weigh and record NIST traceable standard weight in range of interest	±5% of certified weight	Inspect system, correct problem, rerun calibration and affected samples	Analyst	SM2540D/NV07-63.9 and 8000/NV03-172.8
Cleveland Open-Cup Tester	None	Up to 250°F	NA	NA	NA	NA	1010 / NV07-30

Notes:

a	Refer to the Analytical SOP Reference Table in QAPP Worksheet #23.
GC/MS	Gas chromatograph/mass spectrometer
VOC	Volatile organic compound
ICAL	Initial calibration
%RSD	Percent relative standard deviation
RF	Response factor
CCV	Continuing calibration verification
%D	Percent difference
ICV	Initial calibration verification
SVOC	Semi-volatile organic compound
CCC	Calibration check compound
SPCC	System performance check compound
SIM	Selected ion monitoring
PAH	Polynuclear aromatic hydrocarbons
DRO	Diesel range organics
DOC	Dissolved organic carbon
TOC	Total organic carbon
TSS	Total suspended solids
NA	Not applicable

QAPP Worksheet #25: Analytical Instrument and Equipment Maintenance, Testing, and Inspection

The selected laboratory (TestAmerica) is operating under a quality system that conforms to ISO 17025:2005. The activities documented in this table are documented in the TestAmerica Quality Assurance Manual Document 0001, Rev. 22 (TestAmerica, 2014).

QAPP Worksheet #26 & 27: Sample Handling, Custody, and Disposal

Sampling Organization: Foth Infrastructure & Environment/Envirocon Joint Venture (FE JV)
Laboratory: TestAmerica, Inc.
Method of sample delivery (shipper/carrier): Courier/Commercial Shipping Company
Number of days from reporting until sample disposal: Varies[a]

Activity	Organization and title or position of person responsible for the activity	SOP Reference[b]
Sample labeling	FE JV	SOP-09
Chain-of-custody form completion	FE JV	SOP-08
Packaging	FE JV	SOP-09
Shipping coordination	FE JV	SOP-09
Sample receipt, inspection, & log-in	TestAmerica	NV02-01.13
Sample custody and storage	TestAmerica	NV10-169.9
Sample disposal	TestAmerica	NV10-83.10

Notes:

a Samples will be stored at the laboratory as directed. No samples will be disposed of without prior approval by the FE JV Project Manager.

b Analytical SOP acceptance criteria is found in Appendix A of this *QAPP*. Field SOPs are provided in Appendix C of the *Monitoring Plan for Phase 2 Wet Dredge* (FE JV, 2016b).

QAPP Worksheet #28a: Analytical Quality Control and Corrective Action – Dredged Material VOCs

Matrix: Dredged Material
Analytical Group: Volatile Organic Compounds (VOCs)
Analytical Method/SOP: 8260B/8260_NV05-77.18b

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	No target compounds >QL; no common lab contaminants >5x QL	Identify source and attempt to eliminate. Re-extract and/or re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Laboratory Supervisor/Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Equipment Rinsate Blank	1 per collection method per event	No target compounds >QL; no common lab contaminants >5x QL	Evaluate impacts on data on a case-by-case basis.	Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Surrogates	Every sample	See Appendix A	Check calculations and instrument performance; recalculate, re-analyze.	Laboratory Analyst/Laboratory Supervisor	Laboratory specified
LCS	1 per batch (up to 20 samples)	See Appendix A	If sufficient sample is available, re-prepare and/or re-analyze samples. Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	70%-130% R
MS/MSD[b]	1 per batch (up to 20 samples)	See Appendix A	Flag data. Discuss in narrative. Re-prepare and re-analyze to verify matrix interference for recoveries <10%.	Laboratory Analyst/Laboratory Supervisor	50%-150% R; RPD ≤35%

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Trip Blank	One per cooler containing samples for VOC analyses	No target compounds >QL; no common lab contaminants >5x QL	Evaluate impacts on data on a case-by-case basis.	Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Field Duplicate[b]	1 per 20 field samples	RPD ≤50% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.	Evaluate during data validation.	Data Validator	RPD ≤50% if both results are >5x QL. Difference ≤2x QL if results are ≤5x QL.

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP*.

b Sample duplicates may be performed in lieu of MS/MSDs to obtain meaningful precision information. Sample duplicates should be aliquots from a single homogenization as it will be used to assess laboratory precision and bias.

QC Quality control

SOP Standard Operating Procedure

MB Method blank

QL Quantitation limit

DQO Data quality objective

ND Not detected

LCS Laboratory control standard

R Percent Recovery

MS/MSD Matrix spike/matrix spike duplicate

RPD Relative percent difference

QAPP Worksheet #28b: Analytical Quality Control and Corrective Action – Sediment PAHs/SVOCs

Matrix: Sediment; Dredged Material
Analytical Group: Poly Aromatic Hydrocarbons (PAHs)/Semi-Volatile Organic Compounds (SVOCs)
Analytical Method/SOP: 8270D, 8270D-SIM/8270/NV04-22-15b

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	No target compounds >QL; no common lab contaminants >5x QL	Identify source and attempt to eliminate. Re-extract and/or re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Laboratory Supervisor/Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Equipment Rinsate Blank	1 per collection method per event	No target compounds >QL; no common lab contaminants >5x QL	Evaluate impacts on data on a case-by-case basis.	Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Surrogates	Every sample	See Appendix A	Check calculations and instrument performance; recalculate, re-analyze.	Laboratory Analyst/Laboratory Supervisor	Laboratory specified
LCS	1 per batch (up to 20 samples)	See Appendix A	If sufficient sample is available, re-prepare and/or re-analyze samples. Qualify data as needed. Notify FE JV project manager if sufficient sample mass is unavailable, or if corrective action does not resolve.	Laboratory Analyst/Laboratory Supervisor	50%-150% R
MS/MSD[b]	1 per batch (up to 20 samples)	See Appendix A	Flag data. Discuss in narrative. Re-prepare and re-analyze to verify matrix interference for recoveries <10%.	Laboratory Analyst/Laboratory Supervisor	50%-150% R; RPD ≤35%

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Field Duplicate[b]	1 per 20 field samples	RPD ≤50% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL	Evaluate during data validation.	Data Validator	RPD ≤50% if both samples are >5x QL; difference ≤2x QL if results are ≤5x QL

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP*.

b Sample duplicates may be performed in lieu of MS/MSDs to obtain meaningful precision information. Sample duplicates should be aliquots from a single homogenization as it will be used to assess laboratory precision and bias.

QC Quality control

SOP Standard Operating Procedure

MB Method blank

QL Quantitation limit

DQO Data quality objective

ND Not detected

LCS Laboratory control standard

R Recovery

MS/MSD Matrix spike/matrix spike duplicate

RPD Relative percent difference

QAPP Worksheet #28c: Analytical Quality Control and Corrective Action – Dredged Material Metals

Matrix:	Dredged Material
Analytical Group:	Metals
Analytical Method/SOP:	6020A/6020/NV06-215.6

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	No Target Analytes >QL	Identify source and attempt to eliminate. Re-extract and/or re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Laboratory Supervisor/Data Validator	No Target Analytes >QL
Equipment Rinsate Blank	1 per collection method per event	No target compounds >QL	Evaluate impacts on data on a case-by-case basis.	Data Validator	No target compounds >QL
LCS or QC Standard	1 per batch (up to 20 samples)	See Appendix A	Re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	80%-120% R
Laboratory Duplicates	1 per batch (up to 20 samples)	See Appendix A	Re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	RPD ≤20% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL
MS/MSD[b]	1 per batch (up to 20 samples)	See Appendix A	Flag data. Discuss in narrative. Analyze post-spike if recoveries <30%.	Laboratory Analyst/Laboratory Supervisor	75%-125% R

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Serial Dilution	If MS fails	See Appendix A	Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	RPD ≤10% if analyte > 50x MDL; no criteria if ≤50x MDL
Field Duplicate[b]	1 per 20 field samples	RPD ≤50% if both samples are >5x QL. Difference ≤2x QL if results are ≤5x QL.	Evaluate during data validation.	Data Validator	RPD ≤50% if both samples are >5x QL Difference ≤2x QL if results are ≤5x QL

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP*.

b Sample duplicates may be performed in lieu of MS/MSDs to obtain meaningful precision information. Sample duplicates should be aliquots from a single homogenization as it will be used to assess laboratory precision and bias.

QC Quality control

SOP Standard Operating Procedure

MB Method blank

QL Quantitation limit

DQO Data quality objective

ND Not detected

LCS Laboratory control standard

R Recovery

MS/MSD Matrix spike/matrix spike duplicate

RPD Relative percent difference

QAPP Worksheet #28d: Analytical Quality Control and Corrective Action – Sediment TOC

Matrix: Sediment
Analytical Group: Total Organic Carbon
Analytical Method/SOP: 9060A/9060/NV07-79.11

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	No Target Analytes >QL	Identify source and attempt to eliminate. Re-extract and/or re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Section Supervisor/ FE JV Data Validation Coordinator	No Target Analytes >QL
Equipment Rinsate Blank	1 per collection method per event	No Target Analytes >QL	Evaluate impacts on data on a case-by-case basis.	Data Validation Staff	No Target Analytes >QL
LCS	1 per batch (up to 20 samples)	80%-120% R	Re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/Section Supervisor	80%-120% R
Laboratory Duplicates	1 per batch (up to 20 samples)	RPD ≤20%	Re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	RPD ≤25% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MS[b]	1 per batch (up to 20 samples)	80%-120% R; RPD ≤20%	Flag data. Discuss in narrative. Re-prepare and/or re-analyze if recoveries are <30% to verify matrix interference.	Laboratory Analyst/Section Supervisor	70%-130% R RPD ≤30%
Field Duplicate[b]	1 per 20 field samples	RPD ≤50% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL	Evaluate during data validation.	Data Validation Staff	RPD ≤50% if both samples are >5x QL; difference ≤2x QL if results are ≤5x QL
PE Sample	1 per method per year; SRM/CRM may be analyzed in lieu of PE samples	Supplier certified limits	PE Sample: Lab re-analyzes another PE sample or utilizes a different laboratory with acceptable PE sample results. SRM/CRM: Qualify data, re-prepare and/or re-analyze as needed.	Project Chemist/ Laboratory Staff	Supplier certified limits

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP.*

b Sample duplicates may be performed in lieu of MS/MSDs to obtain meaningful precision information. Sample duplicates should be aliquots from a single homogenization as it will be used to assess laboratory precision and bias.

QC Quality control
SOP Standard Operating Procedure
MB Method blank
QL Quantitation limit
DQO Data quality objective
ND Not detected
LCS Laboratory control standard
R Recovery
MS/MSD Matrix spike/matrix spike duplicate
RPD Relative percent difference
PE Performance evaluation
SRM/CRM Standard reference material/certified reference material

QAPP Worksheet #28e: Analytical Quality Control and Corrective Action – Sediment Total Solids

Matrix:	Sediment
Analytical Group:	Total Solids
Analytical Method/SOP:	8000C/8000/NV03-172.8

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Laboratory Duplicates	1 per batch (up to 20 samples)	RPD ≤20%	Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	RPD ≤20%
Field Duplicate	1 per 20 field samples	RPD ≤50% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL	Evaluate during data validation.	Data Validation Staff	RPD ≤20% if both samples are >5x QL; difference ≤2x QL if results are ≤5x QL

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP.*
QC Quality control
SOP Standard Operating Procedure
QL Quantitation limit
RPD Relative percent difference

QAPP Worksheet #28f: Analytical Quality Control and Corrective Action – Dredged Material Cyanide

Matrix:	Dredged Material
Analytical Group:	Cyanide
Analytical Method/SOP:	9014/NV07-137.10b

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	≤QL	Identify source and attempt to eliminate. Re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Section Supervisor/FE JV Data Validation Coordinator	≤QL
LCS	1 per batch (up to 20 samples)	85%-115% R	Re-prepare and/or re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/ Section Supervisor	80%-120% R
Laboratory Duplicates	1 per batch (up to 20 samples)	RPD ≤35%	Re-prepare and/or re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/ Section Supervisor	RPD ≤35% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL
MS	1 per batch (up to 20 samples)	69%-135% R	Flag data. Discuss in narrative. Re-prepare and/or re-analyze if recoveries are <30% to verify matrix interference.	Laboratory Analyst/ Section Supervisor	70%-130% R

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
PE Sample	1 per method per year; SRM/CRM may be analyzed in lieu of PE samples.	Supplier certified limits	PE Sample: Lab re-analyzes another PE sample or utilizes a different laboratory with acceptable PE sample results. SRM/CRM: Qualify data, re-prepare and/or re-analyze as needed.	Project Chemist/ Laboratory Staff	Supplier certified limits

Notes:

a	SOP acceptance criteria is provided in Appendix A of this *QAPP*.
QC	Quality control
SOP	Standard Operating Procedure
MB	Method blank
QL	Quantitation limit
DQO	Data quality objective
ND	Not detected
LCS	Laboratory control standard
%R	Percent recovery
MS/MSD	Matrix spike/matrix spike duplicate
RPD	Relative percent difference
PE	Performance evaluation
SRM/CRM	Standard reference material/certified reference material

QAPP Worksheet #28g: Analytical Quality Control and Corrective Action – Dredged Material pH

Matrix:	Dredged Material
Analytical Group:	pH
Analytical Method/SOP:	9045D/NV03-54.8

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
LCS	1 per batch (up to 20 samples)	+/-1% true	Re-prepare and/or re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/ Section Supervisor	+/-1% true
Laboratory Duplicates	1 per batch (up to 20 samples)	RPD ≤20%	Re-prepare and/or re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/ Section Supervisor	RPD ≤20%

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP*.

QC Quality control

SOP Standard Operating Procedure

LCS Laboratory control standard

RPD Relative percent difference

QAPP Worksheet #28h: Analytical Quality Control and Corrective Action – Dredged Material TCLP, MET, and DRET

Matrix:	Dredged Material
Analytical Group:	TCLP, MET, DRET
Analytical Method/SOP:	1311/NV03-70, EPA - 823-B-98-004, ACOE - D-95-1

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	No target compounds >QL	Identify source and attempt to eliminate. Re-extract and/or re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Section Supervisor/FE JV Data Validation Coordinator	No target compounds >QL
Laboratory Duplicates	1 per batch (up to 20 samples)	See Appendix A per analytical method	Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	RPD ≤30%

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP*.
QC Quality control
SOP Standard Operating Procedure
MB Method blank
QL Quantitation limit
DQO Data quality objective
ND Not detected
RPD Relative percent difference

QAPP Worksheet #28i: Analytical Quality Control and Corrective Action – Dredged Material Ignitability

Matrix:	Dredged Material
Analytical Group:	Ignitability
Analytical Method/SOP:	1010A/1010 / NV07-30

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Water blank	1 per batch (up to 20 samples)	No flash	Correct problem, re-analyze blank and all samples processed with the contaminated blank.	Laboratory Analyst/Laboratory Supervisor	No flash
LCS/LCSD	1 per batch (up to 20 samples)	p-Xylene: 81° ± 5°F; Undecane: 15°° ± 7°F	Re-prep, perform maintenance as needed, and re-analyze all affected samples.	Laboratory Analyst/Laboratory Supervisor	p-Xylene: 81° ± 5°F; Undecane: 15°° ± 7°F
Laboratory Duplicates	1 per batch (up to 20 samples)	RPD ≤20%	Repeat. Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	RPD ≤20%

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP*.
QC Quality control
SOP Standard Operating Procedure
LCS Laboratory control standard
LCSD Laboratory control standard duplicate
RPD Relative percent difference

QAPP Worksheet #28j: Analytical Quality Control and Corrective Action – Surface Water VOCs

Matrix:	Surface Water
Analytical Group:	Volatile Organic Compounds (VOCs)
Analytical Method/SOP:	8260B/8260/NV05-77.18b

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	No target compounds >QL; no common lab contaminants >5x QL	Identify source and attempt to eliminate. Re-extract and/or re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Laboratory Supervisor/Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Equipment Rinsate Blank	1 per collection method per event	No target compounds >QL; no common lab contaminants >5x QL	Evaluate impacts on data on a case-by-case basis.	Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Surrogates	Every sample	See Appendix A	Check calculations and instrument performance; recalculate, re-analyze.	Laboratory Analyst/Laboratory Supervisor	Laboratory specified
LCS	1 per batch (up to 20 samples)	See Appendix A	If sufficient sample is available, re-prepare and/or re-analyze samples. Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	70%-130% R
MS/MSD	1 per batch (up to 20 samples)	See Appendix A	Flag data. Discuss in narrative. Re-prepare and re-analyze to verify matrix interference for recoveries <10%.	Laboratory Analyst/Laboratory Supervisor	60%-140% R; RPD ≤30%

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Trip Blank	One per cooler containing samples for VOC analyses	No target compounds >QL; no common lab contaminants >5x QL	Evaluate impacts on data on a case-by-case basis.	Data Validator	No target compounds >QL; no common lab contaminants >5x QL

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP*.
QC Quality control
SOP Standard Operating Procedure
MB Method blank
QL Quantitation limit
DQO Data quality objective
ND Not detected
LCS Laboratory control standard
R Recovery
MS/MSD Matrix spike/matrix spike duplicate
RPD Relative percent difference

QAPP Worksheet #28k: Analytical Quality Control and Corrective Action – Wastewater (WPDES/POTW) VOCs

Matrix:	Wastewater (WPDES/POTW)
Analytical Group:	Volatile Organic Compounds (VOCs)
Analytical Method/SOP:	8260/624/SM6200B/NV05-77.20

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	No target compounds >QL; no common lab contaminants >5x QL	Identify source and attempt to eliminate. Re-extract and/or re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Laboratory Supervisor/Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Equipment Rinsate Blank	1 per collection method per event	No target compounds >QL; no common lab contaminants >5x QL	Evaluate impacts on data on a case-by-case basis.	Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Surrogates	Every sample	See Appendix A	Check calculations and instrument performance; recalculate, re-analyze.	Laboratory Analyst/Laboratory Supervisor	Laboratory specified
LCS	1 per batch (up to 20 samples)	See Appendix A	If sufficient sample is available, re-prepare and/or re-analyze samples. Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	70%-130% R
MS/MSD	1 per batch (up to 20 samples)	See Appendix A	Flag data. Discuss in narrative. Re-prepare and re-analyze to verify matrix interference for recoveries <10%.	Laboratory Analyst/Laboratory Supervisor	60%-140% R; RPD ≤30%

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Trip Blank	One per cooler containing samples for VOC analyses	No target compounds >QL; no common lab contaminants >5x QL	Evaluate impacts on data on a case-by-case basis.	Data Validator	No target compounds >QL; no common lab contaminants >5x QL

Notes:

a	SOP acceptance criteria is provided in Appendix A of this *QAPP*.
QC	Quality control
SOP	Standard Operating Procedure
MB	Method blank
QL	Quantitation limit
DQO	Data quality objective
ND	Not detected
LCS	Laboratory control standard
R	Recovery
MS/MSD	Matrix spike/matrix spike duplicate
RPD	Relative percent difference

QAPP Worksheet #28I: Analytical Quality Control and Corrective Action – Surface Water PAHs

Matrix:	Surface Water
Analytical Group:	Polynuclear Aromatic Hydrocarbons (PAHs)
Analytical Method/SOP:	8270D-SIM/8270/NV04-22-15b

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	No target compounds >QL; no common lab contaminants >5x QL	Identify source and attempt to eliminate. Re-extract and/or re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Laboratory Supervisor/Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Equipment Rinsate Blank	1 per collection method per event	No target compounds >QL; no common lab contaminants >5x QL	Evaluate impacts on data on a case-by-case basis.	Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Surrogates	Every sample	See Appendix A	Check calculations and instrument performance; recalculate, re-analyze.	Laboratory Analyst/Laboratory Supervisor	Laboratory specified
LCS	1 per batch (up to 20 samples)	See Appendix A	If sufficient sample is available, re-prepare and/or re-analyze samples. Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	60%-140% R
MS/MSD[b]	1 per batch (up to 20 samples)	See Appendix A	Flag data. Discuss in narrative. Re-prepare and re-analyze to verify matrix interference for recoveries <10%.	Laboratory Analyst/Laboratory Supervisor	60%-140% R; RPD ≤30%

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Field Duplicate[b]	1 per 20 field samples	RPD ≤40% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL	Evaluate during data validation.	Data Validator	RPD ≤40% if both samples are >5x QL; difference ≤2x QL if results are ≤5x QL

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP.*

b Sample duplicates may be performed in lieu of MS/MSDs to obtain meaningful precision information. Sample duplicates should be aliquots from a single homogenization as it will be used to assess laboratory precision and bias.

QC Quality control

SOP Standard Operating Procedure

MB Method blank

QL Quantitation limit

DQO Data quality objective

ND Not detected

LCS Laboratory control standard

R Recovery

MS/MSD Matrix spike/matrix spike duplicate

RPD Relative percent difference

QAPP Worksheet #28m: Analytical Quality Control and Corrective Action – Wastewater (WPDES/POTW) PAHs

Matrix: Wastewater (WPDES/POTW)
Analytical Group: Polynuclear Aromatic Hydrocarbons (PAHs)
Analytical Method/SOP: 8270/625/NV04-22.17

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	No target compounds >QL; no common lab contaminants >5x QL	Identify source and attempt to eliminate. Re-extract and/or re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Laboratory Supervisor/Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Equipment Rinsate Blank	1 per collection method per event	No target compounds >QL; no common lab contaminants >5x QL	Evaluate impacts on data on a case-by-case basis.	Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Surrogates	Every sample	See Appendix A	Check calculations and instrument performance; recalculate, re-analyze.	Laboratory Analyst/Laboratory Supervisor	Laboratory specified
LCS	1 per batch (up to 20 samples)	See Appendix A	If sufficient sample is available, re-prepare and/or re-analyze samples. Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	60%-140% R
MS/MSD[b]	1 per batch (up to 20 samples)	See Appendix A	Flag data. Discuss in narrative. Re-prepare and re-analyze to verify matrix interference for recoveries <10%.	Laboratory Analyst/Laboratory Supervisor	60%-140% R; RPD ≤30%

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Field Duplicate[b]	1 per 20 field samples	RPD ≤40% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL	Evaluate during data validation.	Data Validator	RPD ≤40% if both samples are >5x QL; difference ≤2x QL if results are ≤5x QL

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP.*

b Sample duplicates may be performed in lieu of MS/MSDs to obtain meaningful precision information. Sample duplicates should be aliquots from a single homogenization as it will be used to assess laboratory precision and bias.

QC Quality control

SOP Standard Operating Procedure

MB Method blank

QL Quantitation limit

DQO Data quality objective

ND Not detected

LCS Laboratory control standard

R Recovery

MS/MSD Matrix spike/matrix spike duplicate

RPD Relative percent difference

QAPP Worksheet #28n: Analytical Quality Control and Corrective Action – Wastewater (WPDES) SVOCs

Matrix:	Wastewater (WPDES)
Analytical Group:	Semi-volatile organic compounds (SVOCs)
Analytical Method/SOP:	8270/625/NV04-22.17

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	No target compounds >QL; no common lab contaminants >5x QL	Identify source and attempt to eliminate. Re-extract and/or re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Laboratory Supervisor/Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Equipment Rinsate Blank	1 per collection method per event	No target compounds >QL; no common lab contaminants >5x QL	Evaluate impacts on data on a case-by-case basis.	Data Validator	No target compounds >QL; no common lab contaminants >5x QL
Surrogates	Every sample	See Appendix A	Check calculations and instrument performance; recalculate, re-analyze.	Laboratory Analyst/Laboratory Supervisor	Laboratory specified
LCS	1 per batch (up to 20 samples)	See Appendix A	If sufficient sample is available, re-prepare and/or re-analyze samples. Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	60%-140% R
MS/MSD[b]	1 per batch (up to 20 samples)	See Appendix A	Flag data. Discuss in narrative. Re-prepare and re-analyze to verify matrix interference for recoveries <10%.	Laboratory Analyst/Laboratory Supervisor	60%-140% R; RPD ≤30%

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Field Duplicate[b]	1 per 20 field samples	RPD ≤40% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL	Evaluate during data validation.	Data Validator	RPD ≤40% if both samples are >5x QL; difference ≤2x QL if results are ≤5x QL

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP.*

b Sample duplicates may be performed in lieu of MS/MSDs to obtain meaningful precision information. Sample duplicates should be aliquots from a single homogenization as it will be used to assess laboratory precision and bias.

QC Quality control

SOP Standard Operating Procedure

MB Method blank

QL Quantitation limit

DQO Data quality objective

ND Not detected

LCS Laboratory control standard

R Recovery

MS/MSD Matrix spike/matrix spike duplicate

RPD Relative percent difference

QAPP Worksheet #28o: Analytical Quality Control and Corrective Action – Wastewater (POTW) Metals

Matrix: Wastewater (POTW)
Analytical Group: Metals
Analytical Method/SOP: 6020/200.7/NV06-215.8b; 7470/245.1/SM3112B/NV06-41.18a; 1631E/NC-MT-001

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	No Target Analytes >QL	Identify source and attempt to eliminate. Re-extract and/or re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Laboratory Supervisor/Data Validator	No Target Analytes >QL
Equipment Rinsate Blank	1 per collection method per event	No target compounds >QL	Evaluate impacts on data on a case-by-case basis.	Data Validator	No target compounds >QL
LCS or QC Standard	1 per batch (up to 20 samples)	See Appendix A	Re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	80%-120% R
Laboratory Duplicates	1 per batch (up to 20 samples)	See Appendix A	Re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	RPD ≤20% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL
MS[b]	1 per batch (up to 20 samples)	See Appendix A	Flag data. Discuss in narrative. Analyze post-spike if recoveries <30%.	Laboratory Analyst/Laboratory Supervisor	75%-125% R

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Serial Dilution	If MS/MSD fails	Appendix A	Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	RPD ≤10% if analyte > 50x MDL; no criteria if ≤50x MDL
Field Duplicate[b]	1 per 20 field samples	RPD ≤50% if both samples are >5x QL. Difference ≤2x QL if results are ≤5x QL.	Evaluate during data validation.	Data Validator	RPD ≤40% if both samples are >5x QL Difference ≤2x QL if results are ≤5x QL

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP.*

b Sample duplicates may be performed in lieu of MS/MSDs to obtain meaningful precision information. Sample duplicates should be aliquots from a single homogenization as it will be used to assess laboratory precision and bias.

QC Quality control

SOP Standard Operating Procedure

MB Method blank

QL Quantitation limit

DQO Data quality objective

ND Not detected

LCS Laboratory control standard

R Recovery

MS/MSD Matrix spike/matrix spike duplicate

RPD Relative percent difference

QAPP Worksheet #28p: Analytical Quality Control and Corrective Action – Wastewater (POTW) WI-GRO

Matrix:	Wastewater (POTW)
Analytical Group:	Gasoline Range Organics (GRO)
Analytical Method/SOP:	WI GRO/NV05-204.5a

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	No target compounds >QL	Identify source and attempt to eliminate. Re-extract and/or re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Section Supervisor/ FE JV Data Validation Coordinator	No target compounds >QL
Equipment Rinsate Blank	1 per sampling method (i.e., sediment sampling device) 1 per 20 samples or 1 per day, whichever is least	No target compounds >QL No target analyte >QL	The analytes reported in this group are unlikely to be introduced from sampling equipment. Equipment contamination will be evaluated by analyzing one equipment blank at the beginning of the sampling program. If initial results indicate equipment contamination of this analytical group, it will become a monitored sensitive analysis. Equipment blanks for sensitive analytes will be analyzed at a frequency of 1 per 20 or 1 per day (whichever is least frequent). Evaluate impacts on data on a case-by-case basis.	Data Validation Staff	No target compounds >QL

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Surrogates	Every sample	≥ 80% R	Check calculations and instrument performance; recalculate, re-analyze.	Laboratory Analyst/Section Supervisor	≥ 80% R
LCS	1 per batch (up to 20 samples)	80%-120% R	Re-prepare and/or re-analyze samples. Qualify data as needed.	Laboratory Analyst/Section Supervisor	80%-120% R
MS/MSD	1 per batch (up to 20 samples)	44%-166% R; RPD ≤20%	Flag data. Discuss in narrative. Re-prepare and re-analyze to verify matrix interference for recoveries <10%.	Laboratory Analyst/Laboratory Supervisor	60%-140% R; RPD ≤30%
PE Sample	1 per method per year; SRM/CRM may be analyzed in lieu of PE samples	Supplier certified limits	PE Sample: Lab re-analyzes another PE sample or utilizes a different laboratory with acceptable PE sample results. SRM/CRM: Qualify data, re-prepare and/or re-analyze as needed.	Project Chemist/ Laboratory Staff	Supplier certified limits

Notes:

a	SOP acceptance criteria is provided in Appendix A of this *QAPP.*
QC	Quality control
SOP	Standard Operating Procedure
MB	Method blank
QL	Quantitation limit
DQO	Data quality objective
ND	Not detected
LCS	Laboratory control standard
R	Recovery
MS/MSD	Matrix spike/matrix spike duplicate
RPD	Relative percent difference
PE	Performance evaluation
SRM/CRM	Standard reference material/certified reference material

QAPP Worksheet #28q: Analytical Quality Control and Corrective Action – Wastewater (POTW) WI-DRO

Matrix:	Wastewater (POTW)
Analytical Group:	Diesel Range Organics (DRO)
Analytical Method/SOP:	WI DRO/NV04-38.8

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	No target compounds >QL	Identify source and attempt to eliminate. Re-extract and/or re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Section Supervisor/ FE JV Data Validation Coordinator	No target compounds >QL
Equipment Rinsate Blank	1 per sampling method (i.e., sediment sampling device) 1 per 20 samples or 1 per day, whichever is least	No target compounds >QL No target analyte >QL	The analytes reported in this group are unlikely to be introduced from sampling equipment. Equipment contamination will be evaluated by analyzing one equipment blank at the beginning of the sampling program. If initial results indicate equipment contamination of this analytical group, it will become a monitored sensitive analysis. Equipment blanks for sensitive analytes will be analyzed at a frequency of 1 per 20 or 1 per day (whichever is least frequent). Evaluate impacts on data on a case-by-case basis.	Data Validation Staff	No target compounds >QL

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Surrogates	Every sample	19%-150% R	Check calculations and instrument performance; recalculate, re-analyze.	Laboratory Analyst/Section Supervisor	19%-150% R
LCS	1 per batch (up to 20 samples)	75%-115% R	Re-prepare and/or re-analyze samples. Qualify data as needed.	Laboratory Analyst/Section Supervisor	70%-120% R
MS/MSD	1 per batch (up to 20 samples)	52%-154% R; RPD ≤20%	Flag data. Discuss in narrative. Re-prepare and re-analyze to verify matrix interference for recoveries <10%.	Laboratory Analyst/Laboratory Supervisor	60%-140% R; RPD ≤30%
PE Sample	1 per method per year; SRM/CRM may be analyzed in lieu of PE samples	Supplier certified limits	PE Sample: Lab re-analyzes another PE sample or utilizes a different laboratory with acceptable PE sample results. SRM/CRM: Qualify data, re-prepare and/or re-analyze as needed.	Project Chemist/ Laboratory Staff	Supplier certified limits

Notes:

a	SOP acceptance criteria is provided in Appendix A of this *QAPP.*
QC	Quality control
SOP	Standard Operating Procedure
MB	Method blank
QL	Quantitation limit
DQO	Data quality objective
ND	Not detected
LCS	Laboratory control standard
R	Recovery
MS/MSD	Matrix spike/matrix spike duplicate
RPD	Relative percent difference
PE	Performance evaluation
SRM/CRM	Standard reference material/certified reference material

QAPP Worksheet #28r: Analytical Quality Control and Corrective Action – Surface Water Sulfide

Matrix:	Surface Water
Analytical Group:	Sulfide
Analytical Method/SOP:	SM4500-S^{-2} D/NV07-180

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	≤QL	Identify source and attempt to eliminate. Re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Section Supervisor/FE JV Data Validation Coordinator	≤QL
LCS	1 per batch (up to 20 samples)	90%-110% R	Re-prepare and/or re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/ Section Supervisor	80%-120% R
Laboratory Duplicates	1 per batch (up to 20 samples)	RPD ≤50%	Re-prepare and/or re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/ Section Supervisor	RPD ≤35% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL
MS	1 per batch (up to 20 samples)	70%-130% R	Flag data. Discuss in narrative. Re-prepare and/or re-analyze if recoveries are <30% to verify matrix interference.	Laboratory Analyst/ Section Supervisor	70%-130% R

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP.*

QC	Quality control	SOP	Standard Operating Procedure
MB	Method blank	QL	Quantitation limit
DQO	Data quality objective	ND	Not detected
LCS	Laboratory control standard	R	Recovery
MS	Matrix spike	RPD	Relative percent difference

QAPP Worksheet #28s: Analytical Quality Control and Corrective Action – Wastewater (POTW) Oil and Grease

Matrix:	Wastewater (POTW)
Analytical Group:	Oil and Grease
Analytical Method/SOP:	EPA 1664A

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	≤QL	Identify source and attempt to eliminate. Re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Section Supervisor/FE JV Data Validation Coordinator	≤QL
OPR	1 per batch (up to 20 samples)	78%-114% R	Re-prepare and/or re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/ Section Supervisor	78%-114% R
Laboratory Duplicates	1 per batch (up to 20 samples)	RPD ≤50%	Re-prepare and/or re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/ Section Supervisor	RPD ≤35% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL
MS	1 per batch (up to 20 samples)	70%-130% R	Flag data. Discuss in narrative. Re-prepare and/or re-analyze if recoveries are <30% to verify matrix interference.	Laboratory Analyst/ Section Supervisor	70%-130% R

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP.*

QC	Quality control	SOP	Standard Operating Procedure
MB	Method blank	QL	Quantitation limit
DQO	Data quality objective	ND	Not detected
OPR	Ongoing precision and recovery	R	Recovery
MS	Matrix spike	RPD	Relative percent difference

QAPP Worksheet #28t: Analytical Quality Control and Corrective Action – Surface Water DOC

Matrix:	Surface Water
Analytical Group:	Dissolved Organic Carbon (DOC)
Analytical Method/SOP:	9060A/9060/NV07-79.11

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
MB	1 per batch (up to 20 samples)	No Target Analytes >QL	Identify source and attempt to eliminate. Re-extract and/or re-analyze blank and affected samples (if sufficient sample remains). Alert Project Team if repeated or widespread exceedances impact project DQOs. Qualify data as needed. Report results if sample results >5x blank result or sample results ND. If contamination is widespread or reoccurring, analyses must stop and the source of contamination must be eliminated or reduced before analyses can continue.	Laboratory Analyst/Section Supervisor/FE JV Data Validation Coordinator	No Target Analytes >QL
LCS	1 per batch (up to 20 samples)	90%-120% R	Re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/Section Supervisor	80%-120% R
Laboratory Duplicates	1 per batch (up to 20 samples)	RPD ≤20%	Re-analyze affected samples. Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	RPD ≤30% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL
MS	1 per batch (up to 20 samples)	75%-122% R; RPD ≤20%	Flag data. Discuss in narrative. Re-prepare and/or re-analyze if recoveries are <30% to verify matrix interference.	Laboratory Analyst/Section Supervisor	75%-125% R RPD ≤25%

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Field Duplicate	1 per 20 field samples	RPD ≤40% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL	Evaluate during data validation.	Data Validation Staff	RPD ≤40% if both samples are >5x QL; difference ≤2x QL if results are ≤5x QL
PE Sample	1 per method per year; SRM/CRM may be analyzed in lieu of PE samples	Supplier certified limits	PE Sample: Lab re-analyzes another PE sample or utilizes a different laboratory with acceptable PE sample results. SRM/CRM: Qualify data, re-prepare and/or re-analyze as needed.	Project Chemist/ Laboratory Staff	Supplier certified limits

Notes:

a	SOP acceptance criteria is provided in Appendix A of this *QAPP*.
QC	Quality control
SOP	Standard Operating Procedure
MB	Method blank
QL	Quantitation limit
DQO	Data quality objective
ND	Not detected
LCS	Laboratory control standard
R	Recovery
MS/MSD	Matrix spike/matrix spike duplicate
RPD	Relative percent difference
PE	Performance evaluation
SRM/CRM	Standard reference material/certified reference material

QAPP Worksheet #28u: Analytical Quality Control and Corrective Action – Surface Water and Wastewater (WPDES/POTW) TSS

Matrix:	Surface Water and Wastewater (WPDES/POTW)
Analytical Group:	Total Suspended Solids (TSS)
Analytical Method/SOP:	SM2540D/ SM2540D/NV07-63.9

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Laboratory Duplicates	1 per batch (up to 20 samples)	RPD ≤20%	Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	RPD ≤20%
Field Duplicate	1 per 20 field samples	RPD ≤40% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL	Evaluate during data validation.	Data Validation Staff	RPD ≤40% if both samples are >5x QL; difference ≤2x QL if results are ≤5x QL

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP.*

QC Quality control

SOP Standard Operating Procedure

QL Quantitation limit

RPD Relative percent difference

QAPP Worksheet #28v: Analytical Quality Control and Corrective Action – Wastewater (POTW) BOD

Matrix:	Wastewater (POTW)
Analytical Group:	Biological Oxygen Demand, 5-Day (BOD)
Analytical Method/SOP:	SM5210B BOD

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Laboratory Duplicates	1 per batch (up to 20 samples)	RPD ≤20%	Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	RPD ≤20%
Field Duplicate	1 per 20 field samples	RPD ≤40% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL	Evaluate during data validation.	Data Validation Staff	RPD ≤40% if both samples are >5x QL; difference ≤2x QL if results are ≤5x QL

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP.*

QC Quality control

SOP Standard Operating Procedure

QL Quantitation limit

RPD Relative percent difference

QAPP Worksheet #28w: Analytical Quality Control and Corrective Action – Wastewater (WPDES) COD

Matrix:	Wastewater (WPDES)
Analytical Group:	Chemical Oxygen Demand (COD)
Analytical Method/SOP:	SM5220D COD

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Laboratory Duplicates	1 per batch (up to 20 samples)	RPD ≤20%	Qualify data as needed.	Laboratory Analyst/Laboratory Supervisor	RPD ≤20%
Field Duplicate	1 per 20 field samples	RPD ≤40% if both results are >5x QL; difference ≤2x QL if results are ≤5x QL	Evaluate during data validation.	Data Validation Staff	RPD ≤40% if both samples are >5x QL; difference ≤2x QL if results are ≤5x QL

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP.*

QC Quality control

SOP Standard Operating Procedure

QL Quantitation limit

RPD Relative percent difference

QAPP Worksheet #28x: Analytical Quality Control and Corrective Action – Turbidity

Matrix:	Water
Analytical Group:	Turbidity
Analytical Method/SOP:	Multi-Parameter Water Quality Data Collection Meter Calibration and Operation/SOP-07

QC Sample	Number/ Frequency	Method/SOP Acceptance Criteria[a]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific Measurement Performance Criteria (MPC)
Field Duplicate	See *Monitoring Plan*	None	Recalibrate instruments	Field Staff	RPD ≤30% if both results are >5x background

Notes:

a SOP acceptance criteria is provided in Appendix A of this *QAPP*.

b Refer to the *Monitoring Plan for Phase 2 Wet Dredge* (FE JV, 2016b).

QC Quality control

SOP Standard Operating Procedure

RPD Relative percent difference

QAPP Worksheet #29: Project Documents and Records

Sample Collection and Field Records			
Record	Generation	Verification	Storage location/archival
Field Log Book or data collection sheets	Field Team Personnel	Monitoring Lead	Project file/electronic storage
Chain of Custody Forms	Field Team Personnel	Monitoring Lead	Project file/electronic storage
Shipping or Air Bills	Field Team Personnel	Monitoring Lead	Project file/electronic storage
Contractor Daily QC Reports	Field Team Personnel	Monitoring Lead	Project file/electronic storage
Deviations	Field Team Personnel	Monitoring Lead	Project file/electronic storage
Corrective Action Reports	Field Team Personnel	Monitoring Lead	Project file/electronic storage
Correspondence	Field Team Personnel	Monitoring Lead	Project file/electronic storage

Project Assessments			
Record	Generation	Verification	Storage location/archival
Field audit checklists	Construction Quality Assurance Officer or Designee	Construction Quality Assurance Officer or Designee	Project file/electronic storage
Data verification checklists	Data Validator	Construction Quality Assurance Officer	Project file/electronic storage
Data validation report	Data Validator	Construction Quality Assurance Officer	Project file/electronic storage
Data usability assessment report	Construction Quality Assurance Officer or Designee	Construction Quality Assurance Officer or Designee	Project file/electronic storage

Laboratory Records			
Record	Generation	Verification	Storage location/archival
Laboratory Data Deliverables	Analyst/Data Reporting Group	Lab QA Manager	Lab project file/electronic storage
Internal Audit Reports	Lab Manager	Lab QA Manager	Lab project file/electronic storage
Standard Operating Procedures	Analyst/Department Manager	Lab QA Manager	Lab project file/electronic storage
Corrective Action Reports	Analyst/Department Manager	Lab QA Manager	Lab project file/electronic storage

Laboratory Data Deliverables				
Record	**Organics**	**Metals**	**Conventionals**	**Geotech**
Narrative	X	X	X	X
Chain of Custody Forms	X	X	X	X
Summary Results	X	X	X	X
QC Results	X	X	X	X

Data Report Deliverable
Results Summary Tables
Laboratory Data Deliverables
Chain of Custody Forms
QC Summary

QAPP Worksheet #31, 32, & 33: Assessments and Corrective Action

Assessments:					
Assessment Type	**Responsible Party and Organization**	**Number/ Frequency**	**Estimated Dates**	**Assessment Deliverable**	**Deliverable Due Date**
Safety Audit	Project Health & Safety Supervisor	As needed	As needed	Written Audit Report	Within one month of audit
Technical Audit of Field Activities	Construction Quality Assurance Officer[a]	As needed	As needed	Written Audit Report	Within one month of audit
Internal Lab Audits	Laboratory Manager	Per laboratory QA Manual; at least annually	Per laboratory QA Manual; at least annually	Written Audit Report	As required per laboratory QA Manual
Technical Audit of Project Activities	Construction Quality Assurance Officer[a]	As needed	As needed	Written Report	Within one month of audit

Notes:
a Or designee
QA Quality assurance

Assessments Response and Corrective Action:					
Assessment Type	**Responsibility for Responding to Assessment Findings[a]**	**Assessment Response Documentation**	**Timeframe of Notification**	**Responsibility for Implementing Corrective Action**	**Responsible for Monitoring Corrective Action Implementation**
Readiness Assessment prior to Mobilization	Construction Quality Assurance Officer[b]	Readiness Review Assessment and Response Checklist	Immediately	Marine Operations Coordinator	Marine Operations Coordinator
Safety Audit	Project Health & Safety Supervisor	Memo	Verbal summary of major findings within 24 hours; written report within one month	Marine and Land Operations Coordinator	Project Health & Safety Manager
Technical Audit of Field Activities	Construction Quality Assurance Officer[b]	Memo	Verbal summary of major findings within 24 hours; written report within one month	Marine and Land Operations Coordinator	QC Officer
Internal Laboratory Audits	Construction Quality Assurance Officer[b]	Memo or as required by laboratory QA Manual	Major deficiencies within 24 hours; written report as required by laboratory QA Manual	Laboratory Manager	Lab Quality Manager and Laboratory Manager
Technical Audit of Project Activities	Construction Quality Assurance Officer[b]	Memo	Verbal summary of major findings within 24 hours; written report within one month	Marine and Land Operations Coordinator	QC Officer

Notes:

a Quality assessment activities will measure the effectiveness of the project implementation and associated quality assurance/quality control (QA/QC) activities. Audits are used as a means of monitoring the performance of field and laboratory activities and are conducted by the Project Health & Safety Supervisor (safety audits), Construction Quality Assurance Officer (technical systems audit [TSA]), or a qualified alternate. Audits will include systems audits that are more qualitative in nature and will be made at appropriate intervals to ensure that all aspects of the QA program are operative. Performance audits are quantitative audits that are conducted to assess the accuracy of measurement systems; this would include the use of PE samples. With the exception of internal laboratory audits, audits will only be performed if deemed necessary by the Project Health & Safety Supervisor or Construction Quality Assurance Officer.

b Or designee

QAPP Worksheet #34: Data Verification and Validation Inputs

Item	Description	Verification (completeness)	Validation (conformance to specifications)
Planning Documents/Records			
1	*QAPP*	X	
2	Contract	X	
3	Field SOPs	X	
4	Laboratory SOPs	X	
Field Records			
5	Chain of Custody forms	X	
6	Sample collection forms	X	
7	Equipment calibration records	X	
8	*Monitoring Plan*/SOP deviations	X	
9	Field audit and corrective action reports	X	
Analytical Data Package			
10	Cover sheet	X	X
11	Case narrative	X	X
12	Laboratory internal Chain of Custody forms	X	X
13	Sample receipt records	X	X
14	Sample prep logs	X	X
15	Analytical logs	X	X
16	Sample results forms	X	X
17	Standards traceability	X	X
18	Instrument performance checks		
19	Instrument calibration forms	X	X
20	QC sample results	X	X
21	Raw data	X	X
22	Electronic data deliverable	X	X

Notes:

QAPP Addendum 2	*Quality Assurance Project Plan for Phase 2 Wet Dredge*
Monitoring Plan	*Monitoring Plan for Phase 2 Wet Dredge* (FE JV, 2016b)
SOP	Standard Operating Procedures
QC	Quality control

QAPP Worksheet #35: Data Verification Procedures

Records Reviewed	Requirement Documents	Description	Responsible Person, Organization
Field records	*QAPP*/ Field SOP	Verify conformance to approved sampling and field measurement procedures; ensure that activities met performance criteria; and verify that deviations from procedures or criteria were documented.	Construction Quality Assurance Officer or designee, FE JV
Analytical data deliverables, contractual documents	*QAPP*	Verify the required deliverables, analytes lists, method holding times, analytical procedures, laboratory qualifiers, measurement criteria, and project QLs conform to specifications. Verify that deviations from procedures or criteria were documented.	Construction Quality Assurance Officer or designee, FE JV
Field records, database output	*QAPP*/ Field SOP	Verify transcription of field data from field forms to database.	Construction Quality Assurance Officer or designee, FE JV
Custody records, analytical data reports	*QAPP*	Review traceability from sample collection through reporting.	Construction Quality Assurance Officer or designee, FE JV
Laboratory EDDs, analytical data reports, database output	*QAPP*	Verify a subset of EDD entries against hard copy or PDF analytical reports.	Construction Quality Assurance Officer or designee, FE JV
Data validation reports, database output	*QAPP*	Verify that entry of qualifiers was correct and complete.	Data Validator, FE JV
Analytical data reports	*QAPP*	Verify that reported analytes, holding times, analytical procedures, measurement criteria, and project QLs conform to the QAPP. Verify that deviations from procedures or criteria were documented.	Data Validator, FE JV
Analytical data reports	*QAPP*/ NFG	One hundred percent of the laboratory data will be validated (see details below).	Data Validator, FE JV
Analytical data reports	*QAPP*/ NFG	Verify that the qualifiers applied during validation were in conformance with the QAPP and specified validation guidance.	Data Validator, FE JV

Records Reviewed	Requirement Documents	Description	Responsible Person, Organization
Data validation reports	*QAPP*/ NFG	Verify that data validation was performed in accordance with the QAPP specifications and that all required peer reviews were conducted. If validation actions deviated from the QAPP specifications and/or regional validation guidance based on professional judgment, verify that rationale was documented.	Data Validator, FE JV

Notes:

EDD	Electronic data deliverable
NFG	National Functional Guidelines
QA	Quality Assurance
QAPP	*Quality Assurance Project Plan for Phase 2 Wet Dredge*
Monitoring Plan	*Monitoring Plan for Phase 2 Wet Dredge* (FE JV, 2016b)
QL	Quantitation limit
SOP	Standard Operating Procedure

Data Validation

All Sample Delivery Groups (SDG) will receive Stage 2A validation. Stage 2A validation is based on information summarized by the laboratory on its quality control forms but includes no raw data review. At a minimum, Stage 2A validation will include the following data elements:

- Agreement of analyses conducted with Chain of Custody requests
- Holding times and sample preservation
- Results of laboratory, equipment, field, and trip blanks
- Surrogate recoveries
- Laboratory control sample/laboratory control sample duplicate (LCS/LCSD) results
- Matrix spike/matrix spike duplicate (MS/MSD) results
- Laboratory duplicate results
- Field duplicate results
- Total solids

Qualifiers will be applied based on the criteria in this *QAPP*, EPA National Functional Guidelines for data review (EPA 1999, 2004, 2008), or professional judgment.

Reports summarizing data qualification as a result of the validation effort will be prepared.

QAPP Worksheet #36: Data Validation Procedures

Data Validator: Foth Infrastructure & Environment/Envirocon Joint Venture (FE JV) or designated external validator

Analytical Group/Method	VOCs (8260B, 624)	PAHs, SVOCs (8270D, 8270D-SIM, 625, 625 SIM)	GRO, DRO (WI-GRO, WI-DRO)	Metals (6020A, 200.7, 200.8, 245.1, 1631E)	TOC, DOC, CN, pH, Sulfide (9060A; 9012, 4500CN-E, 9045D, SM4500S2D)	TS, (SM 2540B)	COD (SM5220D), TSS (SM2540D)	Phosphorus, Oil & Grease (365.4, 1664A)
Data Deliverable Requirements	Level II	Level II	Level II	Level II	Level II	Level II	Level II	Level II
Analytical Specifications[a]	Appendix A	Appendix A	Appendix A	Appendix A	Appendix A	Appendix A	Appendix A	Appendix A
Measurement Performance Criteria	WS-12	WS-12	WS-12	WS-12	WS-12	WS-12	WS-12	WS-12
Percent of Data Packages to be Validated	100%	100%	100%	100%	100%	100%	100%	100%
Validation Procedure	EPA Stage 2A/ Stage 4	EPA Stage 2A/ Stage 4	EPA Stage 2A/ Stage 4	EPA Stage 2A/ Stage 4	EPA Stage 2A/ Stage 4	EPA Stage 2A/ Stage 4	EPA Stage 2A/ Stage 4	EPA Stage 2A/ Stage 4

Notes:

a Analytical specifications are found in Appendix A of this *QAPP Addendum 2.*

QAPP Worksheet #37: Data Usability Assessment

Personnel (organization and position/title) responsible for participating in the data usability assessment: Quality Control (QC) Officer

Describe how the usability assessment will be documented: Results from the assessment will be summarized in the final project report.

Summarize the data usability assessment process:

Step 1	**Review the Project's Objectives and Sampling Design** Review the key outputs defined during planning (DQOs) to make sure they are still applicable. Review the sampling design for consistency with stated objectives.
Step 2	**Review the data verification and data validation outputs** Review available quality assurance (QA) reports, including data validation and verification reports. Perform basic calculations and summarize the data (using graphs, maps, tables, etc.). Look for patterns, trends, and anomalies. Review deviations from planned activities and determine their impacts on data usability. Evaluate implications of unacceptable QC sample results.
Step 3	**Verify the assumptions of the selected statistical method** Verify whether the underlying assumptions for selected statistical methods are valid. If serious deviations from assumptions are discovered, another statistical method may be used.
Step 4	**Implement the statistical method** Implement the specified statistical procedures for analyzing the data and review underlying assumptions.
Step 5	**Document data usability and draw conclusions** Determine if the data can be used as intended, considering deviations and corrective actions. Evaluate data quality indicators. Assess the performance of the sampling design and identify limitations on data use.

Appendix A

Laboratory Standard Operating Procedures

Appendix A

Laboratory Standard Operating Procedures

Title: PENSKY-MARTENS CLOSED-CUP FOR DETERMINING RCRA IGNITABILITYAND FLASH POINT (LIQUIDS) SW-846 METHOD 1010A, ASTM D93 AND CLEVELAND OPEN CUP METHOD FOR FLASH POINTS (SOILS/SOLIDS) ASTM D92

Approvals (Signature/Date)			
Sessily Overton-Gray	2/17/14	Johnny Davis	1/27/14
Sessily Overton-Gray Department Manager	Date	Johnny Davis Health & Safety Manager / Coordinator	Date
Steve Miller	1/25/14	Michael H. Dunn	1/23/14
Steve Miller Quality Assurance Manager	Date	Michael H. Dunn Technical Director	Date

1.0 Scope and Application

1.1 Analyte, Matrices: This procedure uses the Pensky-Martens closed-cup tester and the Cleveland open-cup tester to determine the flash point of liquids and solids.

1.2 Reporting Limits: The reporting range is up to 200°F.

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

The sample is heated at a slow, constant rate with continual stirring for liquids. If required by the client for soil/solids samples, remove the paddle from the stirrer. A small flame or electric igniter is directed into or across the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame ignites the vapor above the sample.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

Sample homogeneity and drafts can affect flash point values.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- The testers should always be used in a hood to minimize solvent vapors from entering the laboratory. **Note: Do not operate exhaust fan during the test.**
- Caution should be exercised in the presence of a flame and electricity.
- In the event a sample ignites in the test apparatus, do not attempt to remove the sample. Turn off the apparatus and flame. The flame should go out when the cup is closed. If this does not happen, the flame may be extinguished by covering the sample with a non-flammable material. After the apparatus has cooled, the sample may be removed.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Undecane	Flammable Irritant	NA	If inhaled, remove to fresh air; give oxygen if necessary. In case of skin or eye contact, flush with copious amounts of water; remove contaminated clothing, life eyelids. If ingested, contact poison center immediately.
p-Xylene	Flammable Irritant	100 ppm-TWA	Inhalation of vapors may be irritating to the nose and throat. Inhalation of high concentrations may result in nausea, vomiting, headache, ringing in the ears, and severe breathing difficulties, which may be delayed in onset. High vapor concentrations are anesthetic and central nervous system depressants. Skin contact results in loss of natural oils and often results in a characteristic dermatitis. May be absorbed through the skin. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Pensky-Martens Closed-Cup Flash Tester.
- Cleveland Open-Cup Tester.
- Temperature sensor and thermometer on the tester. The sensor detects to 250°F.

6.2 Supplies

None.

7.0 Reagents and Standards

7.1 Purity of Reagents. Reagent-grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 **p-Xylene:** Purchased from a commercial supplier, purity 98% or better. Flash point of 81 ± 5°F (closed cup). Use for the Laboratory Control Sample.

7.3 **Undecane:** Purchased from a commercial supplier, purity 99%. Flash point 155 ± 7°F (closed cup). Use for the LCS open cup.

7.4 See SOP Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214 for shelf-life and storage requirements for reagents and standards.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Liquid waste, Soil, Solid	Glass or Metal	4 oz. glass or metal container	None.	Not applicable	SW-846 Section 3.0

9.0 Quality Control

Refer to TestAmerica Nashville's QA Manual for specific quality control (QC) procedures. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC for Open Cup and Closed Cup

The following quality control samples are prepared with each batch of no more than 20 samples.		
Quality Controls	**Acceptance Criteria**	**Corrective Action**
Water Blank	No flash	Correct problem, re-analyze blank and all samples processed with the contaminated blank.
Laboratory Control Sample (LCS) and LCS Duplicate (LCSD), p-Xylene for Closed Cup, Undecane for Open Cup	See Sections 7.2, 7.3	Re-prep, perform maintenance as needed, and re-analyze all affected samples.
Sample Duplicate	Same result as original sample	Repeat.

- A **Water Blank** is run with each analytical batch; it should not flash. Record the result.
- A **Laboratory Control Sample (LCS) and LCS Duplicate (LCSD)** are run as positive controls every 20 samples for closed cup and open cup. p-Xylene has a flash point of 81 ± 5°F using closed cup or 110 ± 7°F using open cup.
- **Sample Duplicate**: Run a second aliquot of at least one client sample per group of 10 samples.

9.2 Instrument QC
None.

10.0 Procedure
10.1 Sample Preparation
- Sample size:

Matrix	Sample Size
Liquid waste	100 mL
Soil/Solid	50 g

- Set up the tester according to the manufacturer's instructions. Contact the Nashville airport (www.flightstats.com/go/airport/BNA/weather) for sea-level pressure. Calculate the lab pressure as shown in Section 11. Enter the corrected barometric pressure into the tester.
- Bring the sample to near room temperature. It is acceptable to start the test with samples slightly under room temperature.
- Refer to SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

10.2 Calibration Verification

1	Determine the corrected flash point of the p-Xylene (81 ± 5°F) standard before analyzing samples in closed-cup or Undecane (155 ± 7°F) for open cup.
2	If the flash points obtained for Undecane and p-Xylene are not within the limits, check the condition and operation of the apparatus, especially with regard to the rightness of the lid, stirrer presence, location of both large and small propellers phased 90° apart, the location of the action of the shutter, the position of size of the test flame and sensor, and/or the condition of the electric element. After adjustment, repeat the test of affected samples. All samples must be bracketed by acceptable controls, i. e., LCS and LCSD.
3	Sensors are calibrated quarterly against an NBS or ASTM certified thermometer, or equivalent. Confirm the probe (thermistor) calibration quarterly or when major maintenance

	has occurred.
4	Once a standard has been successfully analyzed, sample analysis may begin.

10.3 Sample Analysis

1	Thoroughly clean and dry all parts of the cup and accessories between determinations. Be sure to remove any solvent, which had been used to clean the apparatus. The cup can be cleaned with acetone followed by soapy water to remove any traces of residue remaining from a previous test. If any traces of carbon or other material are present, rinse the cup with chloroform until clean. Flush the cup with cold water and thoroughly dry with a paper towel before continuing sample analysis.
2	Thoroughly mix the sample to be tested by inverting the container and fill the cup with the sample to the level indicated inside the cup.
3	Set the cup in the heating unit. Place the lid on the cup for Pensky-Martens, making sure the locking device is properly engaged. Carefully put probe in place. Place unit head in proper position on Pensky-Martens. If analyzing a soil per client request, remove the paddles from the stirrer. Generate a Non-conformance (NCM) indicating 1010A modified for soil/solid.
4	Initiate program A for distillate fuels, i. e., kerosene, diesel, heating oil, new lube oils, etc. Initiate program B for residual fuel oils, used lube oils, petroleum liquids with solids, etc.
5	Record the detected flash point to the nearest integer as the temperature read on the display at the time the test flame application causes a distinct flash in the interior of the cup. The characteristics of a distinct flash are a quick white light inside the cup that should cause flames to rise out of the three openings in the lid. Do not confuse the true flash point with the bluish halo that sometimes surrounds the test flame at applications preceding the one that causes the actual flash.
6	If the sample boils and repeated introductions of the igniter result in the igniter's being immediately extinguished each time, discontinue analysis and report sample as having a flash point >X°F. It is also acceptable to cool the sample prior to the initiation of the tester.
7	If the sample does flash, a duplicate analysis is performed. If the result is not confirmed, corrective action should be initiated to determine the cause of the discrepancy. A sample having a flash point less than 140°F is considered hazardous.

10.4 Example Analysis Queue / Sequence*

1	Method Blank
2	LCS
3	Samples 1-20
4	LCSD

11.0 Calculations / Data Reduction

11.1 Accuracy: Not applicable.

11.2 Precision (RPD)

$$RPD = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(orig. sample value + dup. sample value)}/2}$$

11.3 Correction for Barometric Pressure:

Enter in tester each day of use.

Corrected mm Hg in the lab = (Nashville Barometric Pressure* (in. Hg) – 0.64) x 25.4.

*www.flightstats.com/go/airport/BNA/weather

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): Not applicable.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four pairs of sample duplicates with identical results for each pair are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- If the sample flashes, place in the flammable solvent drum in the waste disposal area. If the sample does not flash, place in the trash or sanitary sewer.

15.0 References / Cross-References

15.1 SW-846 Method 1010A, Update IIIB, November 2004, ASTM D92-02b, and D93-80 (Annual Book of ASTM Standards)

15.2 TestAmerica Nashville's Quality Assurance Manual.

15.3 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.4 SOPs: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Determination of Method Detection Limits / NV08-202, Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

15.5 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

Item	Modification
1	Electric igniter is used.

17.0 Attachment

None.

18.0 Revision History

- Revision 5, dated 24 April 2009
  - Integration for TestAmerica and STL operations.
  - Added more information on flash point temperatures.
  - Added more information on LCS(s) for closed cup versus open cup.
- Revision 6, dated 31 January 2011
  - Addition of QAF-45, Section 14.2, "(closed cup)" to Undecane flash point temperature.
- Revision 7, dated 31 October 2012
  - Organizational changes.
  - Add reference to Sample Homogenization, Sub-sampling, and Compositing / NV08-229 (Amendment 6a).
  - Distinguish between the standards used for LCS and CCV.
  - Determine the corrected pressure in the lab from the barometric pressure at the Nashville airport instead of from the lab barometer.
  - OK and WY no longer limit batch size to 10 samples.
  - Remove closed cup technique.
- Revision 8, dated 29 March 2013
  - TEI-Ford audit item1: Clarify % acceptance and definitions for flash point and ignitability.
  - Modified for soil/solid by removing the paddle from the stirrer.
  - Remove the need for a CCV.
- Revision 9, dated 28 February 2014
  - Organizational changes.
  - Addition of ATM D93 to title.
  - Add more instruction for the tester check.
  - Describe the use of tester's programs A and B.

Title: TOXICITY CHARACTERISTIC LEACHING PROCEDURE SW-846 METHOD 1311

Approvals (Signature/Date)

10/28/13	
Rodney Street Department Manager	
10/14/13	9/16/13
Jacolby Robinson Department Supervisor	Johnny Davis Health & Safety Manager / Coordinator Department Manager
11/5/13	11/5/13
Steve Miller Quality Assurance Manager	Michael H. Dunn Technical Director

1.0 Scope and Application

1.1 This method is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multi-phasic wastes, including oils.

1.2 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run, i. e., Total divided by 20.

1.3 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

1.5 For oily waste, rather than performing the leaching on the unfiltered portion of oily waste, assume it is 100% liquid and perform a totals analysis (EPA Memorandum #35, page 10). Oily waste may be leached if required by the client/program.

1.6 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 µm glass fiber filter, is defined as the TCLP extract.

2.2 For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. Oils that do not filter are considered 100% solids. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 um glass fiber filter.

2.3 Oily wastes are analyzed as totals unless the client specifies leaching.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This method may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- Be sure to wear disposable gloves, safety glasses, and a lab coat when performing this method. Nitrile gloves are used when performing this extraction. Latex and vinyl gloves provide no significant protection against organic solvents.
- Use caution in the handling and storing of strong acids and bases.
- Some of the samples may be designated "hazardous waste." Therefore, all are handled as if they are hazardous.
- Use the hood whenever the samples are odorous or a light powder.
- Be aware of safety measures in the manipulation of pressure and compressed gases.
- Check the vacuum filtration for micro-cracks and discard apparatus if cracks are found. The use of a vacuum system during sample filtration presents the risk of imploding glassware. All glassware used during vacuum operations must be thoroughly inspected prior to each use. Glass that is chipped, scratched, cracked, rubbed or marred in any manner must not be used under vacuum. It must be removed from service and replaced. Ensure that the vacuum exhaust hose is vented to a fume hood so vapors are not pumped into the working environment.
- The rotary extraction device is checked daily before use. Pressure may build up in the extraction vessel. Vent into a hood if needed.
- Kevlar gloves must be worn when handling VOA vials.

5.2 Primary Materials Used: There are no materials used in this method that have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetic acid	Corrosive Poison Flammable	10 ppm-TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
Hydro-chloric acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sodium Hydro-xide	Corrosive	2 mg/m^3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Agitation apparatus: The agitation apparatus is capable of rotating the extraction vessel(s) in an end-over-end fashion at 30 ± 2 rpm, e.g., 48-vessel device (Model 3740-48-BRE) by Associated Design and Manufacturing Company, Alexandria, VA (703-549-5999) and 4-ZHE extractor (Model YT300RAHW) by Millipore Corp., Bedford, MA (800-225-3384), or equivalent.

6.2 Extraction Vessels

6.2.1 **Zero-Headspace Extraction Vessel (ZHE)** - This device is for use only when the waste is being tested for the mobility of volatile analytes. The ZHE allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see Section 6.3.1). The vessels have an internal volume of 500-600 mL, and are equipped to accommodate a 90-110 mm filter. The devices contain VITON^R 1 O-rings which are replaced as needed.

The ZHE is checked for leaks before every extraction. Pressurize the device to about 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If bubbles are visible, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, take the device out of service.

The ZHEs use gas pressure to actuate the ZHE piston. Use Model YT30090HW, Gas Pressure Device by Millipore Corp. (Bedford, MA, 800-225-3384) or equivalent.

VITON^R is a trademark of DuPont.

Use the following procedure to clean the ZHE:

- If organic residue is visibly coating the inside of the vessel, break down the ZHE, and rinse the parts with reagent-grade Methylene chloride.
- Wash with hot, soapy water.
- Rinse with reagent water.
- Place in an oven at 350°C for one (1) hour.
- Allow the device to cool to room temperature prior to use.

6.2.2 **Bottle Extraction Vessel** - When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is used. Headspace is allowed in this vessel.

The extraction bottles are constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Section 6.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when organics are of concern. Plastic bottles, other than PTFE, are not used if organics are to be investigated.

6.3 Filtration Devices:

6.3.1 **Zero-Headspace Extractor Vessel (ZHE)** - When the waste is evaluated for volatiles, the zero-headspace extraction vessel described in Section 6.2.1 is used for filtration. The device is capable of supporting and keeping in place the glass fiber filter and is able to withstand the pressure needed to accomplish separation (50 psi).

[NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.]

6.3.2 **Filter Holder** - When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Section 6.3.3). These have a minimum internal volume of 300 mL and are equipped to accommodate a minimum filter size of 47 mm Vacuum filtration is used.

6.3.3 **Materials of Construction** - Extraction vessels and filtration devices are made of inert materials which do not leach or absorb waste components. Glass, PTFE, or type 316 stainless steel equipment is used when evaluating the mobility of both organic and inorganic components. Devices made of high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) are used only when evaluating the mobility of metals.

6.3.4 **Positive pressure filtration device** - stainless steel.

6.4 Filters: Filters are made of borosilicate glass fiber and contain no binder materials and have an effective pore size of 0.6 to 0.8 µm. Pre-filters are not used. When evaluating the mobility of metals, filters are acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with reagent water (a minimum of 1 L per rinse is recommended) or purchased pre-cleaned from a commercial source (0.7 µm pore size, Catalog Number FG77090MM, Environmental Express, MT. Pleasant, SC, or equivalent) and certified as metal free. Glass fiber filters are fragile and are handled with care.

6.5 pH Meters: A meter accurate to ± 0.05 units at 25°C is used (Fisher Scientific with Accumet flat surface polymer-body electrode or equivalent).

6.6 ZHE Extract Collection Devices: glass, PTFE, or HDPE, gas-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions:

6.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1% of total waste), a 60 mL syringe is used to collect and combine the initial liquid and solid extract.

6.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1% of total waste), the syringe may be used for both the initial solid/liquid separation and the final extract filtration.

6.6.3 If the waste contains no initial liquid phase (is 100% solid) or has no significant solid phase (is 100% liquid), the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

6.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e. g., a gas tight syringe, pressure filtration unit (see Section 6.3.2), or other ZHE device).
6.8 Laboratory Balance: A laboratory balance accurate to within ± 0.01 grams is used (all weight measurements are to be within ± 0.1 grams).
6.9 Beaker or Erlenmeyer flask, glass, 1000 – 2000 mL.
6.10 Magnetic stirrer.

7.0 Reagents and Standards

7.1 Reagent grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.
7.2 Reagent water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest.
7.3 Hydrochloric acid (1N), HCl, made from ACS reagent grade. Prepare by diluting 83.3 mL of 37% HCl to 1 liter with reagent water.
7.4 Sodium hydroxide (1N), NaOH, made from ACS reagent grade, 40 g to 1 L reagent water. A commercial solution is acceptable.
7.5 Glacial acetic acid, CH_3CH_2OOH, ACS reagent grade.
7.6 Extraction fluids

7.6.1 **Extraction Fluid #1**: Add 5.7 mL glacial CH_3CH_2OOH to about 500 mL of reagent water and add 64.3 mL of 1.0N NaOH, and dilute to a volume of 1.0 liter with reagent water. When correctly prepared, the pH of this fluid is 4.93 ± 0.05. Check pH each day of use and record pH in LIMS.

Note: When making 20 liters of Extraction Fluid #1: Add 114 mL of glacial CH_3CH_2OOH to about 2 liters to water and add 1286 mL of 1 N NaOH and dilute to 20 liters with reagent water.

7.6.2 **Extraction Fluid #2**: Dilute 114.0 mL glacial CH_3CH_2OOH with reagent water (See Section 7.2) to a volume of 20 liters. When correctly prepared, the pH of this fluid is 2.88 ± 0.05. Check and record the pH in LIMS.

Note: These extraction fluids are monitored frequently for impurities. The pH is checked daily prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid is discarded and fresh extraction fluid is prepared.

7.8 Refer to SOP Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214 for shelf-life and storage requirements. Refer to benchsheets, logbooks, and LIMS.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 The TCLP may place requirements on the minimal size of the field sample, depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure. Another aliquot is needed to actually conduct the nonvolatile extraction. (See Section 1.4 concerning the use of this extract for volatile organics.) If volatile organics are of concern, another aliquot is needed. Quality control measures may require additional aliquots.
8.2 Preservatives are not added to samples before extraction, i. e., TCLP leaching.

8.3 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) is leached.

8.4 When the waste is to be evaluated for volatile analytes, care is taken to minimize the loss of volatiles. Samples are collected and stored in a manner intended to prevent the loss of volatile analytes.

8.5 TCLP extracts are prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations are acidified with nitric acid to a pH < 2 after matrix spiking, unless precipitation occurs (see Section 10.2.14 if precipitation occurs). Extracts are preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for volatile organic analyte determinations are not allowed to come into contact with the atmosphere (i. e., no headspace) to prevent losses.

8.6 Samples must undergo TCLP extraction within the following time periods:

Sample Maximum Holding Times (Days): Holding times must be continuous with no gap during the TCLP leaching process.

	From: Field collection	From: Leaching End (Must not exceed 4 hours)	From: Preparative extraction	
	To: Beginning of TCLP Leaching	To: Preparative extraction	To: Determinative analysis	Total Elapsed Time
Volatiles	14	NA	14	28
Semivolatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA = Not Applicable

If sample holding times are exceeded, the values obtained are considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time does not invalidate characterization if the waste exceeds the regulatory level.

9.0 Quality Control

Refer to the quality control section of TestAmerica-Nashville's QA Manual for specific quality control (QC) procedures. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC

The following quality control samples are prepared with each batch of samples, not to exceed 20 samples:

Quality Controls	Control Limit	Corrective Action
TCLP Batch Blank	< Report Limit	Re-prep samples and repeat
Matrix Spike	LIMS	Report

- TCLP batch blank: Prepare at least one TCLP batch blank for each leaching fluid type **and** each ultimate analysis type (i. e., semivolatiles (glass), metals (plastic), volatiles (VOA)). Each container lot number must be checked for cleanliness.

- Each container type and fluid type combination requires a blank.
- A **matrix spike** is performed for each waste type (e. g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data are being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike is analyzed for each analytical batch per waste.
  - Matrix spikes are to be added after filtration of the TCLP extract and **before** preservation by the relevant department. Matrix spikes are not added prior to TCLP extraction of the sample.
  - In order to avoid differences in matrix effects, the matrix spikes are added to the same nominal volume of TCLP extract by the appropriate department (i. e., extraction, metals, inorganics, and volatiles) as that which was analyzed for the unspiked sample.
  - The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the TCLP extract when the recovery of the matrix spike is below the expected analytical method performance.
  - All quality control measures described in the appropriate analytical methods are followed.
    - The use of standard addition quantitation **must** be employed for a **metallic** contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50% and the concentration does not exceed the regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.
      - The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.
      - The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amount of standard to three of these aliquots. The fourth aliquot in unknown. Preferably, the first addition is prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions are prepared so that the concentrations are approximately 100% and 150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.
      - Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentration as the dependent variable (y-axis) versus concentrations of the additions of standard as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.
      - Alternately, subtract the instrumental signal or external-calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected interment signals or external-calibration-derived concentrations as the dependent variable versus the independent variable. Derive concentrations for unknown using the internal calibration curve as if it were an external calibration curve.

9.2 Instrument QC: Not applicable.

10.0 Procedure: See Sample Subsampling, Homogenization and Compositing / NV08-229.

10.1 Preparing a representative sample: See SOP Sample Sub-sampling, Homogenization and Compositing / NV08-229. If possible, shake/mix the entire sample contents and pour it into a shallow pan. Take random, representative sample portions to generate a representative sub-sample. If volatiles are requested, minimize the shaking and handling time.

10.2 Preliminary Evaluations: Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. This aliquot must not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids (Section 10.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Sections 10.1.1.9-10.1.1.12); (3) determination of whether the solid portion of the waste requires particle size reduction (Section 10.1.2); and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste (Section 10.1.3). Oils are treated as being 100% solids if leaching is performed.

10.2.1 **Organic/aqueous Determination:** Add a few drops of each phase to an individual test tube containing water. The phase is organic if it does not dissolve in the water.

10.2.2 **Determination of % volume of each phase:** Using a metric ruler, obtain the height of each phase in cm and the total height in cm. Calculate each phase % volume: (cm phase x 100)/cm total sample.

10.2.3 **Preliminary determination of percent solids**: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

10.2.3.1 If the waste obviously yields no liquid when subjected to pressure or vacuum filtration (i. e., is 100% solids), proceed to Section 10.1.2.

10.2.3.2 If the sample is liquid or multi-phasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Section 6.3.2 and is outlined in Sections 10.1.1.3 through 10.1.1.10. Oils that do not filter are treated as 100% solids.

10.1.1.3	Pre-weigh the filter and the container that receives the filtrate.
10.1.1.4	Assemble the filter holder and filter following the manufacturer instructions. Place the filter on the support screen and secure.
10.1.1.5	Weigh out a subsample of the waste (100 gram minimum) and record the weight.
10.1.1.6	Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid is decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.
10.1.1.7	Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering. Note: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 10.1.1.5 to determine the weight of the waste sample that is filtered. Gradually apply vacuum of 1-10 psi, until air moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in

	any 2 minute interval and there is still visible liquid, then transfer to a positive pressure filtration device. Slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i. e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration. Note: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.
10.1.1.8	The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. NOTE: Some wastes, such as oily wastes and some paint wastes, obviously contain some material that appears to be a liquid. Even after applying vacuum, as outlined in Section 10.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.
10.1.1.9	Remove the solid phase and filter from the filtration apparatus.
10.1.1.10	Dry the filter and solid phase at 100 ± 20°C until two successive weighings (record both) yield the same value within ± 1%. Record the final weight. Do not dry oily waste; it is considered to be 100% solid.

10.1.1.11 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{(Wt. of dry waste + filter) - tared wt. of filter}}{\text{Initial wt. of waste (Section 10.1.1.5 or 10.1.1.7)}} \times 100$$

10.1.1.12 If the percent dry solids is less than 0.5%, then proceed to Section 10.2.9 if the nonvolatile TCLP is to be performed, and to Section 10.3 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section (10.1) and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 10.1.2) and determine the appropriate extraction fluid (Section 10.1.3). If only the volatile TCLP is to be performed, see the note in Section 10.1.3.

10.1.2 **Determination of whether the waste requires particle size reduction**: Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension. If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Section 10.3.6).

Note: Surface area criteria are meant for filamentous (e. g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample specific

methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

10.1.3 **Determination of appropriate extraction fluid:** If the solid content of the waste is greater than or equal to 0.5% and if the sample is extracted for nonvolatile constituents (Section 10.2), determine the appropriate fluid (Section 10.7) for the nonvolatiles extraction as follows:

NOTE: **TCLP extraction for volatile constituents uses only Extraction Fluid #1** (Section 10.7.1). Therefore, if TCLP extraction for non-volatiles is not required, proceed to Section 10.3.

10.1.3.1	Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask. Record the weight used.
10.1.3.2	Add 96.5 mL of reagent water to the beaker and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use Extraction Fluid #1. Proceed to Section 10.2.
10.1.3.3	If the pH from Section 10.1.3.2 is >5.0, add 3.5 mL 1N HCl, slurry briefly, but do NOT stir continuously. Heat to 50 ± 1°C, and hold at 50 ±1°C for 10 ± 1 minutes.
10.1.3.4	Let the solution cool to room temperature and record the pH. Do NOT stir during pH determination. If the pH is <5.0, use Extraction Fluid #1. If the pH is >5.0, use Extraction Fluid #2. Proceed to Section 10.2.

10.1.4 If the aliquot of the waste used for the preliminary evaluation (Sections 10.1.1) was determined to be 100% solid at Section 10.1.1.1, then it can be used for the Section 10.2 extraction (assuming at least 100 grams remain), and the Section 10.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Section 10.1.1.7, then another aliquot is used for the volatile extraction procedure in Section 10.3. The aliquot of the waste subjected to the procedure in Section 10.1.1.7 might be appropriate for use for the Section 10.2 extraction if an adequate amount of solid (as determined by Section 10.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract is produced to support the analyses. If an adequate amount of solid remains proceed to Section 10.2.10 of the nonvolatile TCLP extraction.

10.2 Procedure When Volatiles Are Not Involved

A minimum sample size of 100 grams (solid and liquid phases) is used unless insufficient sample is supplied. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Section 10.1.1), whether the initial liquid phase of the waste is miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids are generated for extraction such that the volume of TCLP extract is sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP extraction is not sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis. If 100 grams is not available, then reduce the fluid volume to maintain a 20:1 ratio and comment on the worklist and in LIMS.

10.2.1 If the waste **obviously** yields no liquid when subjected to vacuum filtration (i. e., is 100% solid, see Section 10.1.1), weigh out a subsample of the waste (100 gram minimum) and proceed to Section 10.2.9.

10.2.2 If the sample is liquid or multi-phasic, liquid/solid separation is required. This involves the filtration device described in Section 6.3.2 and is outlined in Sections 10.2.3 to 10.2.8.

10.2.3	Pre-weigh the container that receives the filtrate.
10.2.4	Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 6.4) or certified, metal free commercial filter. NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.
10.2.5	Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains <0.5% dry solids (Section 10.1.1), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample is filtered so that the amount of filtered liquid supports all of the analyses required of the TCLP extract. For wastes containing >0.5% dry solids (Sections 10.1.1), use the percent solids information obtained in Section 10.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids are generated by filtration to support the analyses to be performed on the TCLP extract.
10.2.6	Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid is decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.
10.2.7	Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see Section 6.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 10.2.5, to determine the weight of the waste sample that is filtered. Gradually apply vacuum of 1-10 psi, until air moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval and there is still visible liquid, then transfer to the positive pressure filtration device. Slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration. NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.
10.2.8	The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (See Section 10.2.12) or stored at 4°C until time of analysis. NOTE: Some wastes, such as oily wastes and some paint wastes, obviously contain

	some material that appears to be a liquid. Even after applying vacuum, as outlined in Section 10.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.
10.2.9	If the waste contains <0.5% dry solids (see Section 10.1.1), proceed to Section 10.2.13.
	If the waste contains >0.5% dry solids (see Section 10.1.1), and if particle size reduction of the solid was needed in Section 10.1.2, proceed to Section 10.2.10.
	If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Section 10.2.11.

10.2.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Section 10.1.2. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e. g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon™ coated sieve is used to avoid contamination of the sample. If unavailable, it is acceptable to use a stainless steel sieve.

10.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

Weight of Extraction Fluid =

$$\frac{20 \times \%\ \text{solids (Sec. 10.1.1)} \times \text{weight of waste filtered (Sec. 10.2.5 or 10.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Section 10.1.3) to the extractor vessel. Close the extractor bottle tightly, secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Record these details. Ambient temperature (i. e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2°C during the extraction period. Record. If outside of range, speed, time, and temperature, re-extraction of fresh sample is required. If insufficient sample is available, report with narrative clearly stating "results may not be usable for compliance with 40 CFR Part 261 toxicity characteristic."

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e. g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e. g., after 15 minutes, 30 minutes, and 1 hour) and vented.

10.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Section 10.2.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) are acid-washed or certified metal-free (see Section 6.4) if evaluating the mobility of metals.

10.2.13 Prepare the TCLP extract as follows:

10.2.13.1	If the waste contained no initial liquid phase, the filtered liquid material obtained from Section 10.2.12 is defined as the TCLP extract. Proceed to Section 10.2.14.
10.2.13.2	If compatible (e. g., multiple phases do not result on combination), combine the filtered liquid resulting from Section 10.2.12 with the initial liquid phase of the waste obtained in Section 10.2.10. This combined liquid is defined as the TCLP extract. Proceed to Section 10.2.14.
10.2.13.3	If the initial liquid phase of the waste, as obtained from Section 10.2.7, is not or may not be compatible with the filtered liquid resulting from Section 10.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the TCLP extract, and combine the results mathematically, as described in Section 10.2.14.

10.2.14 Following collection of the TCLP extract, the pH of the extract is determined and recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots **must** be acidified with nitric acid to pH <2 after matrix spike is added. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses is not acidified and the extract is analyzed as soon as possible. All other aliquots are stored under refrigeration (0-6°C) until analyzed. The TCLP extract is extracted and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals are acid-digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ± 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

V_1 = the volume of the first phase (L).
C_1 = the concentration of the analyte of concern in the first phase (mg/L).
V_2 - the volume of the second phase (L).
C_2 = the concentration of the analyte of concern in the second phase (mg/L).

10.2.15 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 9.0 for quality assurance requirements.

10.3 Procedure When Volatiles Are Involved

Use the ZHE device to obtain TCLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE is not used to evaluate the mobility of nonvolatile analytes (e. g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psi) due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary.

10.3.1	Pre-weigh the (evacuated) filtrate collection container (See Section 6.6) and set aside. The containers listed in Section 6.6 are recommended for use under the conditions stated in Sections 6.6.1 - 6.6.3.
10.3.2	Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that minimizes the distance the piston has to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 10.3, Section 10.1.1). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.
10.3.3	If the waste is 100% solid (see Section 10.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Section 10.3.5.
10.3.4	If the waste contains < 0.5% solids (Section 10.1.1), the liquid portion of waste, after filtration, is defined as the TCLP extract. Filter enough of the sample so that the amount of filtered liquid supports all of the volatile analyses required. For wastes containing ≥ 0.5% solids, use the percent solids information obtained in Section 10.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows: 7.3.4.1 For wastes containing < 0.5% solids (see Section 10.1.1), weigh out a 500 gram subsample of waste and record the weight. 7.3.4.2 For wastes containing ≥ 0.5% solids (see Section 10.1.1), determine the amount of waste to charge into the ZHE as follows: Weight of waste to charge ZHE = $\frac{25 \times 100}{\text{Percent solids (Section 10.1.1)}}$ Weigh out a subsample of the waste of the appropriate size and record the weight.
10.3.5	• If particle size reduction of the solid portion of the waste was required in Section 10.1.2, proceed to Section 10.3.6. • If particle size reduction was not required in Section 10.1.2, proceed to Section 10.3.7.
10.3.6	Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Section 10.1.2. Wastes and appropriate reduction equipment are refrigerated, if possible, to 0-6°C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere is avoided to the extent possible. NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e. g., paper, cloth) and similar waste materials. Actual measurement of surface area is not used.

	When the surface area or particle size has been appropriately altered, proceed to Section 10.3.7.
10.3.7	Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.
10.3.8	Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate. NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Section 10.3.4 to determine the weight of the waste sample that is filtered.
10.3.9	Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 0-6°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100% solid (see Section 10.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Section 10.3.12.
10.3.10	Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container. NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.
10.3.11	The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase. NOTE: Some wastes, such as oily wastes and some paint wastes, obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material does not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid. If the original waste contained <0.5% dry solids (see Section 10.1.1), this filtrate is defined as the TCLP extract and is analyzed directly. Proceed to Section 10.3.15.

10.3.12	The liquid phase may now be either analyzed immediately (See Sections 10.3.13 through 10.3.15) or stored at 0-6°C under minimal headspace conditions until time of analysis. Determine the weight of Extraction Fluid #1 to add to the ZHE as follows: Weight of extraction fluid = $\frac{20 \times \%\ \text{solids (Sec. 10.1.1)} \times \text{weight of waste filtered (Sec. 10.3.4 or 10.3.8)}}{100}$
10.3.13	The following sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction Fluid #1 is used in all cases (See Section 10.7). 10.3.13.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used contains fresh extraction fluid and is pre-flushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device. 10.3.13.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced due to the addition of extraction fluid. This bleeding is done quickly and is stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed. 10.3.13.3 Place the ZHE in the rotary agitation apparatus (if it is not already there) and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 ± 2°C during agitation. Record speed, time and temperature. If outside of range, speed, time, and temperature, re-extraction of fresh sample is required. If insufficient sample is available, report with narrative.
10.3.14	Following the 18 ± 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i. e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in Section 6.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Section 10.3.9. All extract shall be filtered and collected, if the extract is multi-phasic, or if the waste contained an initial liquid phase (see Sections 6.6 and 10.3.1). NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it

	is suspected that the glass fiber filter has been ruptured.
10.3.15	If the original waste contained no initial liquid phase, the filtered liquid material obtained from Section 10.3.13 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Section 10.3.13 and the initial liquid phase (Section 10.3.9) are collectively defined as the TCLP extract.
10.3.16	Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at 0-6°C until analyzed. Analyze the TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i. e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average: Final Analyte Concentration = $\frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$ V_1 = the volume of the first phases (L). C_1 = the concentration of the analyte of concern in the first phase (mg/L). V_2 = the volume of the second phase (L). C_2 = the concentration of the analyte of concern in the second phase (mg/L). SEE SECTION 17.3 FOR AN EXAMPLE OF PROPORTIONAL RECOMBINATION.
10.3.17	Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 9.0 for quality assurance requirements.

11.0 Calculations / Data Reduction

See the determinative method.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency. Water MDLs are used for TCLP.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in compliance with federal, state, and local laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Unused or excess leaching fluids are discharged into the sanitary sewer.
- Leached samples are disposed of in a trash receptacle.

15.0 References / Cross-References

15.1 SW-846 Method 1311, Update I, Revision 0, July 1992.

15.2 Technical Assistance Document for Complying with the TC Rule and Implementing the Toxicity Characteristic Leaching Procedure (TCLP), EPA-902-B-94-001, Revised May, 1994.

15.3 TestAmerica Nashville's Quality Assurance Manual.

15.4 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.5 SOPs: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Reagent and Standard Purchase, Preparation, Control, and Documentation / NV08-214, Sample Sub-sampling, Homogenization and Compositing / NV08-229.

15.6 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachments

17.1 Step by Step Procedure Summary

Determine pH and appropriate extraction fluid:

1. Particle-size reduce and weigh out 5.0 grams of sample into an Erlenmeyer flask. Record the weight.
2. Add 96.5 mL DI water to 5.0 gram sample and stir for 5 minutes. Record initial pH of sample.
3. If the pH is <5.0, use Fluid #1.
4. If the pH is >5.0, add 3.5mL of 1N HCl, slurry briefly and heat for 10 minutes at 50°C.
5. Bring sample back down to room temperature and record secondary pH.
6. If the pH is <5.0, use Fluid #1. If the pH is >5.0, use Fluid #2. The amount of extraction fluid is equal to 20 times the weight of the solid.

Determine % solids of sample by filtration.

Determine appropriate extraction vessel (GLASS for semi-volatiles, PLASTIC for inorganics).

If sample is <0.5% solids, the original filtrate ***is*** the TCLP/ZHE extract, and this prep date must be entered into LIMS (still no charge to client per management).

If bi-phasic, filter sample (saving filtrate) until 100.0 grams of solid is obtained.

Oils that do not filter are treated as 100% solid.

Procedure when volatiles *are not* involved: **3 options**:

1. If sample is obviously 100% solids, no initial filtration is necessary.
   a. Weigh out 100.0 ± 0.1 grams of sample and record weight. Reduce particle size if necessary.
   b. Use 2L extraction fluid. Perform rotary extraction (30 ± 2 rpm for 18 ± 2 hours at 23 ± 2°C).
   c. Filter and record final pH. This is the final TCLP extract.
2. If sample is <0.5% solids (determined by filtration), *the filtrate is the TCLP extract* and enough sample is filtered to support all analysis.
3. If sample is >0.5% solids (determined by filtration), filter sample and retain filtrate for recombination and analysis. Weigh solids portion and determine amount of extraction fluid to use.

   Weight of extraction fluid = (20 x %solids x grams of waste filtered) / 100

   a. Perform rotary extraction. (30 ± 2 rpm for 18 ± 2 hours at 23 ± 2°C)
   b. Filter. Combine original filtrate with rotated filtrate. This is the final TCLP extract.

When performing ZHE extraction for volatiles, samples are exposed to the atmosphere as little as possible. Also, the ZHE extractor may only be charged with sample once.

Procedure when volatiles *are* involved (**3 options**):

1. If the sample is obviously 100% solids, no initial filtration necessary.
   a. Weigh out 25 g ± 0.1 grams and record weight. Reduce particle size if necessary.
   b. Use 500 mL Extraction Fluid #1. Perform rotary extraction using ZHE extractors (30 ± 2 rpm for 18 ± 2 hours at 23 ± 2°C).
   c. Following the 18 ± 2 hour extraction, check the ZHE for pressure. If pressure has been maintained, collect the filtrate. This is the final ZHE extract.
2. If sample is <0.5% solids (determined by filtration), weigh out 500g and add to the ZHE extraction vessel. Assemble apparatus and filter. *The filtrate is the ZHE extract*.
3. If sample is >0.5% solids (determined by filtration), determine the amount of sample to charge the ZHE extractor with:

   Grams of sample to charge ZHE = (25 / % solids) x 100

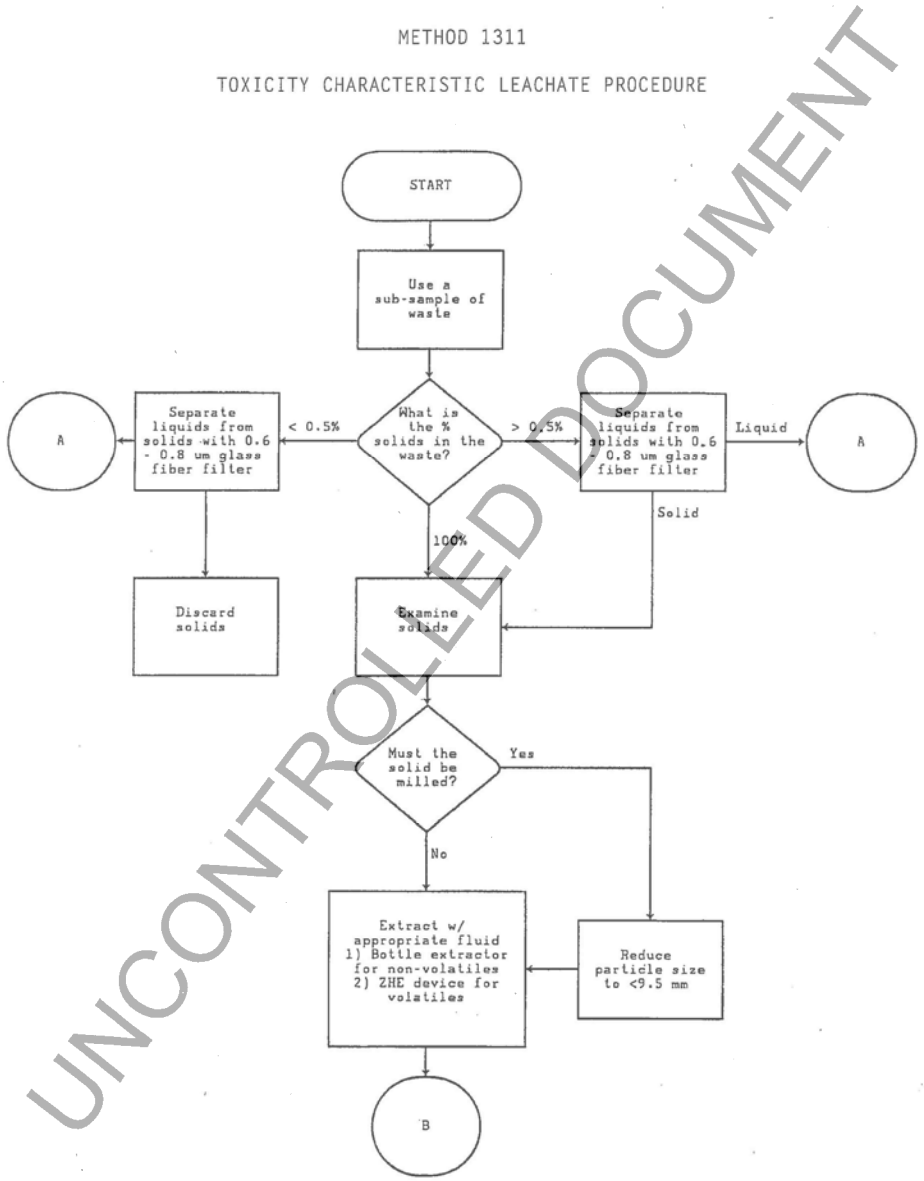
   a. Assemble apparatus and filter. Collect and weigh initial filtrate. Retain filtrate for recombination and analysis. Weight of solids remaining in ZHE extractor is the difference between the initial grams charged into the ZHE and the grams of filtrate obtained.
   b. Determine amount of Extraction Fluid #1 to add to ZHE extractor

   Weight of extraction fluid = (20 x %solids x grams of solids in ZHE) / 100

   c. Perform ZHE rotary extraction. (30 ± 2 rpm for 18 ± 2 hours at 23 ± 2°C)
   d. Following the 18 ± 2 hour extraction, check the ZHE for pressure. If pressure has been

maintained, collect the filtrate.
Filter. Combine original filtrate with rotated filtrate. This is the final ZHE extract.

17.2 TCLP Flowchart



17.3 Example: Proportional Recombination

1. Separate solids from liquid.
2. Particle size reduction of solids.
3. TCLP leaching with 100 g, out of 300 g total solids, produces 200 mL leachate.
4. Original sample liquid is miscible with leachate.
5. Only used 1/3 of total solids, so combine leachate with 1/3 of original 800 mL sample filtrate.
6. TCLP sample volume for analysis = 2000 mL leachate + 1/3 (800mL) = 2,267 mL.

Volume used for Recombination = A x B x C

A = total volume free liquid in sample as received.
B = weight solids leached / weight total wet solids.
C = volume leach fluid recovered / volume added

- If the liquid phases are not miscible, then both phases are tested separately.
- Results are mathematically recombined using partial fractions, just as is done physically in the above example.

Example problem:
Aqueous phase = 5 ppm
Organic phase = <1,000 ppm
What value is reported? "<1,000 ppm" with footnote giving positive result for aqueous phase.

17.4 TCLP Regulatory Limits

EPA Hazardous Waste Code	Contaminant	Regulated Level (mg/L)
D004	Arsenic (As)	5.0
D005	Barium (Ba)	100.0
D018	Benzene	0.5
D006	Cadmium (Cd)	1.0
D019	Carbon Tetrachloride	0.5
D020	Chlordane	0.03
D021	Chlorobenzene	100.0
D022	Chloroform	6.0
D007	Chromium (Cr)	5.0
D023	o-Cresol	200.0
D024	m-Cresol	200.0
D025	p-Cresol	200.0
D026	Cresol	200.0
D016	2,4-D	10.0
D027	1,4-Dichlorobenzene	7.5
D028	1,2-Dichloroethane	0.5
D029	1,1-Dichloroethylene	0.7
D030	2,4-Dinitrotoluene	0.13
D012	Endrin	0.02
D031	Heptachlor	0.008
D032	Hexachlorobenzene	0.13

EPA Hazardous Waste Code	Contaminant	Regulated Level (mg/L)
D033	Hexachlorobutadiene	0.5
D034	Hexachloroethane	3.0
D008	Lead (Pb)	5.0
D013	Lindane	0.4
D009	Mercury (Hg)	0.2
D014	Methoxychlor	10.0
D035	Methyl ethyl ketone	200.0
D036	Nitrobenzene	2.0
D037	Pentachlorophenol	100.0
D038	Pyridine	5.0
D010	Selenium (Se)	1.0
D011	Silver (Ag)	5.0
D039	Tetrachloroethylene	0.7
D015	Toxaphene	0.5
D040	Trichloroethylene	0.5
D041	2,4, 5-Trichlorophenol	400.0
D042	2,4,6-Trichlorophenol	2.0
D017	2,4,5-TP (Silvex)	1.0
D043	Vinyl Chloride	0.2

18.0 Revision History

- Revision 6, dated 30 April 2010
  - Integration for TestAmerica and STL operations.
  - Addition of Sections 14.2, 17.3, 17.4, QAF-45.
  - Addition of sieve composition.
  - For oils, use total analysis, rather than TCLP.
  - Clarified holding time table.
- Revision 7, dated 30 April 2012
  - Organizational changes.
  - Addition of Change Forms 6a and 6b.
  - Addition of language to address oily samples.
- Revision 8, dated 29 November 2013
  - Organizational changes.
  - Addition of amendments 7a, 7b, 7c.
  - Change description of the method blank to a TCLP batch blank with the requirement for one method blank for each container type (i. e., ultimate analysis category). Each container lot number must be checked for cleanliness. Each container type and fluid type combination requires a blank.
  - Add the procedure for cleaning the ZHE.

Title: ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY ICP SPECTROSCOPY SW-846 METHOD 3005A, SM3030 C

Approvals (Signature/Date)

Rodney Street Department Manager	7/15/13 Date
Michael H. Dunn Technical Director Quality Assurance Manager	7/3/13 Date
Johnny Davis Health & Safety Manager / Coordinator Extractions Operations Manager	7/15/13 Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method is an acid digestion procedure used to prepare surface and groundwater samples for analysis, by inductively coupled argon plasma spectroscopy (ICP). The procedure is appropriate for the following metals:

Analyte	CAS #		Analyte	CAS #:
Aluminum; Al	7429-90-5		Magnesium; Mg	7439-95-4
Antimony; Sb	7440-36-0		Manganese; Mn	7439-96-5
Arsenic; As	7440-38-2		Molybdenum; Mo	7439-98-7
Barium; Ba	7440-39-3		Nickel; Ni	7440-02-0
Beryllium; Be	7440-41-7		Potassium; K	7440-09-7
Cadmium; Cd	7440-43-9		Selenium; Se	7782-49-2
Calcium; Ca	7440-70-2		Silver; Ag	7440-22-4
Chromium; Cr	7440-47-3		Sodium; Na	7440-23-5
Cobalt; Co	7440-48-4		Thallium; Tl	7440-28-0
Copper; Cu	7440-50-8		Vanadium; V	7440-62-2
Iron; Fe	7439-89-6		Zinc; Zn	7440-66-6
Lead; Pb	7439-92-1			

1.2 Reporting Limits: See the determinative method (6010 / NV06-44 or 6020 / NV06-215) and the Control Limits Manual.

1.3 When analyzing for total dissolved metals filter the sample, at the time of collection, **prior** to acidification with nitric acid.

1.4 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor/Manager or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 Total recoverable metals: The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

2.2 Dissolved metals: The sample is filtered through a 0.45-µm PTFE filter at the time of collection, and the liquid phase is then acidified at the time of collection with nitric acid. Note: If lab filtered, acidify the filtrate, return to the original container, and wait at least twenty-four (24) hours before digestion.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the

responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochlo-ric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

None.

6.2 Supplies

Labware: All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. Polymeric or glass volumetric ware and storage containers must be cleaned by leaching with more dilute acids (approximately 10% v/v) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. To avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels. Certified, clean containers are acceptable.

- Plastic digestion vessels, certified, with caps, or equivalent.
- Graduated cylinder or equivalent, 50 or 100-mL, Class A.
- Watch glasses or equivalent.
- Hot plate or equivalent heating source (hot block), adjustable and capable of maintaining a temperature of 90-95°C.
- Volumetric flasks and pipets of suitable precision and accuracy (Class A).

- Syringe filter, 25 mm with 0.45 µm, PTFE membrane, VWR International 28145-497, or equivalent.
- .

7.0 Reagents and Standards

7.1 **Reagent water**, analyte-free.

7.2 Spectroscopic grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.3 **Hydrochloric acid**, concentrated, HCl. If the method blank is less than the MDL, the acid is acceptable.

7.4 **Nitric acid**, concentrated, HNO_3. If the method blank is less than the MDL, the acid is acceptable.

7.5 **Laboratory Control /Matrix Spike /Matrix Spike Duplicate (LCS/MS/MSD) Standards:** See the determinative method for the standard, its preparation, and its spike amount.

7.6 See Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214 for shelf-life and storage requirements for reagents and standards. Additional information is found in LIMS.

8.0 Sample Collection, Preservation, Shipment and Storage

Total or Dissolved	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Total Recoverable Metals	HDPE[1]	50 mL	HNO_3 to pH < 2 **at time of collection**	6 months	SW846 Section 2.0, Standard Methods for the Analysis of Water and Wastes SM3030 C.
Dissolved Metals	HDPE[1]	50 mL	Filter **in the field** through a 0.45-µm filter prior to acidification, then acidify with HNO_3 to pH < 2		SW846 Section 2.0

[1]All sample containers must be pre-washed with detergents, acids and water. Plastic, certified-clean containers are used if the containers are supplied by TestAmerica Nashville. Temperature preservation is not required.

For the determination of the dissolved elements, the sample **must** be filtered prior to acid preservation through a 0.45-µm pore diameter, PTFE membrane filter at the time of collection or as soon thereafter as practically possible. If filtered in the lab, return the filtrate to the original sample container and preserve. Hold for 24 hours prior to analysis.

9.0 Quality Control

Refer to the quality control section of TestAmerica Nashville's QA Manual for specific quality control (QC) policies. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 **Sample QC**: The following quality control samples are prepared with **each batch of no more than 20 samples.**

Quality Controls	Frequency	Control Limit
Method Blank	1 per batch	See determinative method.
Laboratory Control Sample (LCS), second source	1 per batch	See determinative method.
Matrix Spike (MS)	1 per batch	See determinative method.
Matrix Spike Duplicate (MSD)	1 per batch	See determinative method.

- **Method blank:** Prepare and analyze at least one blank using reagent water with each batch.
- A **Laboratory Control Sample (LCS)** is analyzed with every batch. See the determinative method for the spike amount.
- **Matrix Spike (MS) / Matrix Spike Duplicate (MSD):** Prepare a MS/MSD for each batch. In each case the MS/MSD aliquots must be duplicates of the aliquot used for sample analysis and spiked prior to sample preparation. The added analyte concentration must be the same as that used in the LCS.
  - The sample must be spiked **prior** to sample digestion.

9.2 Instrument QC: See the determinative method.

10.0 Procedure

10.1 Sample Digestion

Matrix	Sample Size
Water	50.0 mL

CAUTION: The addition of hydrochloric acid must be in the form of concentrated hydrochloric acid and not from a premixed combination of acids as a buildup of chlorine gas, as well as other gases, will result form a premixed acid solution. These gases may be violently released upon heating. This is avoided by adding the acid in the described manner.

CAUTION: Toxic nitrogen oxide and chlorine fumes may be evolved; therefore all work must be performed in a properly operating ventilation system. Be aware of the potential for a vigorous reaction. If a vigorous reaction occurs, allow cooling before capping the vessel.

1	Transfer a 50.0-mL representative aliquot of the well-mixed sample to a digestion tube. Also, prepare LCS, MS, and MSD QC samples. If the samples are filtered in the lab, all QC must also be filtered with the same lot of filters as the samples. Record filter lot LIMS number on benchsheet.
2	Add 1.0 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl.
3	Cover with a watch glass (for hot plate) or other suitable cover (plastic for hot block) and heat on a hot plate or other heating source (hot block) at 90 to 95°C until the volume has been reduced to 10-15 mL. Record preparation date and temperature. CAUTION: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.
4	Remove the vessel and allow to cool.
5	Wash down the container walls and adjust the final volume to 50.0 mL with reagent water in a certified, centrifuge tube.
6	Allow any undissolved material to settle overnight, filter using a PTFE membrane, or centrifuge a portion of the prepared sample until clear. Record the filter lot number. The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted sample cannot be characterized, all analyses are performed as soon as possible after the completed preparation. If any sample is filtered, the Method Blank and LCS must also be filtered.

11.0 Calculations / Data Reduction

Not applicable.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in accordance with all federal and state regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Waste Streams Produced by the Method:

- Digestates are taken to the waste disposal area for neutralization and discharge to the sanitary sewer.

15.0 References / Cross-References

15.1 SW-846 Method 3005A, Update 1, July 1992.

15.2 Method 3030C - 1998, Standard Methods for the Analysis of Water and Wastewater, on-line edition, 2011 editorial revisions. North Carolina Memo on Aquifer Protection Section Policy for Metals Determinations Required by 15A NCAC 2L, January 7, 2011.

15.3 TestAmerica Nashville's Quality Assurance Manual.

15.4 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.5 SOPs: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Determination of Method Detection Limits / NV08-202, 6010 / NV06-44, 6020 / NV06-215, 200.7 /NV06-17, 200.8 / NV06-216.
15.6 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modification

Item	Modification
1	If SM 3030C digestion is specified, see the attachment of this method for that procedure.

17.0 Attachment

Standard Method 3030C:

- Maintain constant sample volume, acid volume, and contact time. **Digestion and filtration must be completed within 72 hours of collection.**

1	Transfer 50.0 mL of sample to a 50 mL digestion vessel, add 2.5 mL of 1:1 HCl, heat on digestion block at 95°C for 15 minutes. Allow time for the sample to reach temperature.
	Wash down the container walls and adjust the final volume to 50.0 mL with reagent water in a certified centrifuge tube.
2	Cool, filter through 0.45 µm, PTFE membrane filter. Filter all QC with the same lot of filters as the samples. Record the filter lot number in LIMS.

18.0 Revision History

- Revision 8, dated 10 September 2008
  - Integration for TestAmerica and STL operations.
  - Change ppm to µg/mL.
- Revision 9, dated 29 June 2010
  - Addition of QAF-45.
  - Addition of Section 14.2.
  - Incorporation of Change 8a.
  - Update to current vendor standards and preparation
- Revision 10, 31 March 2011
  - Add the need to record the LIMS filter ID.
  - If samples are filtered, QC samples must also be filtered with the same lot of filters.
- Revision 11, 29 March 2013
  - Organizational changes.
  - OK no longer limits batch size to 10 samples.
  - Addition of Amendment 10a.
  - Clarify field filtration procedure.
- Revision 12, dated 31 July 2013
  - Addition of a PTFE filter syringe. Removal of standard information with reference to the determinative method.
  - Re-order the last steps of the sample digestion process.

Title: ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS FOR ANALYSIS BY ICP SPECTROSCOPY SW-846 METHOD 3010A

Approvals (Signature/Date)

	7/15/13		7/15/13
Rodney Street Metals Department Manager	Date	Johnny Davis Health & Safety Manager / Coordinator	Date
	7/3/13		
Michael H. Dunn Technical Director Quality Assurance Manager	Date		

1.0 Scope and Application

1.1 Analyte, Matrices: This method is used for the preparation of aqueous samples, mobility-procedure (TCLP, SPLP) extracts, and wastes that contain suspended solids for analysis, by inductively coupled argon plasma spectroscopy (ICP or ICP/MS). It is not applicable to dissolved metals. The procedure is appropriate for the following total metals:

Analyte	CAS #
Aluminum, Al	7429-90-5
Antimony, Sb	7440-36-0
Arsenic, As	7440-38-2
Barium; Ba	7440-39-3
Beryllium; Be	7440-41-7
Bismuth, Bi	7440-69-9
Boron, B	7440-42-8
Cadmium; Cd	7440-43-9
Calcium; Ca	7440-70-2
Chromium; Cr	7440-47-3
Cobalt; Co	7440-48-4
Copper; Cu	7440-50-8
Iron; Fe	7439-89-6
Lead; Pb	7439-92-1
Lithium, Li	7439-93-2

Analyte	CAS #:
Magnesium, Mg	7439-95-4
Manganese, Mn	7439-96-5
Molybdenum, Mo	7439-98-7
Nickel, Ni	7440-02-0
Potassium, K	7440-09-7
Selenium, Se	7782-49-2
Silver, Ag	7440-22-4
Sodium, Na	7440-23-5
Strontium, Sr	7440-24-6
Sulfur, S	7704-34-9
Tin, Sn	7440-31-5
Titanium, Ti	7440-32-6
Thallium, Tl	7440-28-0
Vanadium, V	7440-62-2
Zinc, Zn	7440-66-6

1.2 Reporting Limits: See the determinative method (6010 / NV06-44 or 6020 / NV06-215) and the Laboratory Information Management System (LIMS).

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor/Manager or the Laboratory Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

A mixture of nitric acid and the sample is refluxed in a covered hot block digestion vessel. This step is repeated with additional portions of nitric acid, if necessary, until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it **must** be discarded and the sample re-digested.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

Interferences are discussed in the determinative analytical method.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health

practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.
- All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease causative agents.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors causes breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms include coughing, choking, and irritation of the nose, throat, and respiratory tract. Causes redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and cause damage to the eyes. Contact causes severe burns and permanent eye damage.
Hydrochlo-ric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Causes redness, pain, and severe skin burns. Vapors are irritating and cause damage to the eyes. Contact causes severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

None.

6.2 Supplies

Labware: All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. Polymeric or glass volumetric ware and storage containers must be cleaned by leaching with more dilute acids (approximately 10% v/v) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. To avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels. Commercial, certified-clean containers are acceptable.

- Certified, plastic digestion vessel with caps.
- Graduated cylinder or equivalent, 50 or 100-mL, Class A.
- Funnel or equivalent.
- Hot block, or equivalent, adjustable and capable of maintaining a temperature of 90-95°C.
- Volumetric flasks and pipets of suitable precision and accuracy (Class A)
- Watch glass, ribbed or non-ribbed (plain).

- Syringe filter, PTFE membrane. The filter diameter and pore size are not significant.

7.0 Reagents and Standards

7.1 **Reagent water**, analyte-free (< MDL).

7.2 Spectroscopic grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.3 **Hydrochloric acid**, 1:1: HCl. If the method blank is less than the MDL, the acid is acceptable.

7.4 **Nitric acid**, concentrated: HNO_3. If the method blank is less than the MDL, the acid is acceptable.

7.5 **Stock Element Solution for Method 6010**, commercial, certified, for LCS and Matrix Spikes. See the determinative method for the standard, its preparation, and its spike amount.

7.6 **Stock Element Solution for Method 6020**, commercial, certified, for LCS and Matrix Spikes. See the determinative method for the standard, its preparation, and its spike amount. ,

7.7 See SOP Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214 for shelf-life and storage requirements for reagents and standards.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	HDPE or Glass[1]	50 mL	HNO_3 to pH < 2	6 months	SW846 Section 2.0

[1]All sample containers must be pre-washed with detergents, acids and water. Plastic, certified containers are used if the containers are supplied by TestAmerica Nashville. Temperature preservation is not required.

If samples are preserved at the lab, wait 24 hours after preservation before digestion.

9.0 Quality Control

The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 **Sample QC**

The following quality control samples are prepared with **each batch of no more than 20 samples.**		
Quality Controls	**Frequency**	**Acceptance Criteria**
Method Blank	1 per batch	See the determinative method.
Laboratory Control Sample (LCS)[1], second source		
Matrix Spike		
Matrix Spike Duplicate		

[1]For AZ, TX, WV samples, a LCS duplicate is required.

- **Method Blank:** The laboratory prepares and analyzes a method blank with each batch of the same matrix. Blank data are used to assess contamination from the laboratory environment.
- A **Laboratory Control Sample (LCS)** is analyzed with every batch; it is made from a standard **different** from the calibration standard. See the determinative method for the spike amount.
- **Matrix Spike/Matrix Spike Duplicate:** Sample homogeneity and the chemical nature of the

sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect. Unless otherwise specified by the data user, the matrix spike (MS) / matrix spike duplicate (MSD) procedure is required. Prepare a MS/MSD each batch. The MS/MSD aliquots must be duplicates of the aliquot used for sample analysis and spiked prior to sample preparation. The added analyte concentration must be the same as that used in the LCS.

9.2 Instrument QC: See the determinative method.

10.0 Procedure

10.1 Sample Digestion

Matrix	Sample Size
Water	50.0 mL

Refer to SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

Note: If running dissolved metals, use SOP 3005 / NV06-103.

CAUTION: The addition of hydrochloric acid must be in the form of concentrated hydrochloric acid and not from a premixed combination of acids as a buildup of chlorine gas, as well as other gases, will result from a premixed acid solution. These gases may be violently released upon heating. This is avoided by adding the acid in the described manner.

CAUTION: Toxic nitrogen oxide and chlorine fumes may be evolved; therefore all work must be performed in a properly operating ventilation system. Be aware of the potential for a vigorous reaction. If a vigorous reaction occurs, allow cooling before capping the vessel.

1	Transfer a 50.0-mL representative aliquot of the well-mixed sample to a certified digestion tube and add 1.5 mL of concentrated HNO_3. • For the method blank, use 50.0 mL of reagent water. • For LCS, use 50.0 mL reagent water, and spike with the appropriate amount of spike. • For MS and MSD, spike 50.0 mL of a sample with the appropriate amount of spike.
2	Cover the digestion tube with the watch glass. Place the vessel in hot block and cautiously evaporate to a low volume (about 5 mL), making certain that the sample does not boil and that no portion of the bottom of the container is allowed to go dry.
3	Cool the container and add additional 1.5 mL portion of concentrated HNO_3. Cover the container with a watch glass and return to the hot block. Adjust the temperature of the hot plate so that a gentle reflux action occurs. Note: If a sample is allowed to go to dryness, low recoveries result. Should this occur, discard the sample and re-digest. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing)
4	Uncover the container, and evaporate to a low volume (about 5 mL), not allowing any portion of the bottom of the container to go dry. Cool.
5	Add 5.0 mL of 1:1 HCl, cover, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation. .

6	Wash down the container walls and adjust the final volume to 50.0 mL with reagent water in a certified centrifuge tube.
7	Allow any undissolved material to settle overnight, filter using a PTFE membrane, or centrifuge a portion of the prepared sample until clear. Record the filter lot number. The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted sample cannot be characterized, all analyses are performed as soon as possible after the completed preparation. If any sample is filtered, the Method Blank and LCS must also be filtered

11.0 Calculations / Data Reduction

Not applicable.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

12.5 Control Charts: Laboratory method performance can be shown with the use of control charts, available from the QA department.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes must be stored, managed, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Digestates are taken to the waste disposal area for neutralization and discharge to the sanitary sewer.

15.0 References / Cross-References

15.1 SW-846 Method 3010A, Rev. 1, July 1992.
15.2 TestAmerica Nashville's Quality Assurance Manual.
15.3 Corporate Environmental Health and Safety Manual (CW-E-M-001)
15.4 SOPs: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Determination of Method Detection Limits / NV08-202, 6010 / NV06-44, 6020 / NV06-215, Standard Purchase, Preparation, Control, Documentation / NV08-214, Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
15.5 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachments

None.

18.0 Revision History

- Revision 6, dated 10 September 2008
  - Integration for TestAmerica and STL operations.
  - Change ppm to µg/mL.
- Revision 7, dated 25 September 2009
  - Addition of OH VAP requirements.
  - Included new stock standard concentrations and final digestate concentrations.
- Revision 8, dated 29 July 2011
  - Organizational changes.
  - Addition of QAF-45 and Section 14.2.
  - Addition of Bismuth, Lithium, and Sulfur, standardization of element lists.
- Revision 9, dated 31 July 2012
  - Add SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
  - Specify that this method is not applicable to dissolved metals.
  - Update 6010 standards and preparations. Add 6020 standards and preparations.
- Revision 10, dated 31 July 2013
  - Organizational changes.
  - Addition of a PTFE filter. Removal of standard information with reference to the determinative method.
  - Re-order the last steps of the digestion process.

Title: ACID DIGESTION OF WIPES, FILTERS, AND AGRICULTURAL SOILS SW-846 METHOD 3050B

Approvals (Signature/Date)	
2/26/14	2/25/14
Rodney Street Department Manager — Date	Johnny Davis Health & Safety Manager / Coordinator — Date
2/21/14	2/27/14
Steve Miller Quality Assurance Manager — Date	Michael H. Dunn Technical Director — Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method describes the digestion procedure for the preparation of wipes, filters, and soils, including agricultural, for analysis by inductively coupled plasma atomic emission spectrometry and mass spectroscopy (ICP-AES, ICP-MS) for the analytes listed below. Other elements and matrices may be analyzed by this method of performance if demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest.

Analyte	CAS #
Aluminum; Al	7429-90-5
Antimony; Sb	7440-36-0
Arsenic; As	7440-38-2
Barium; Ba	7440-39-3
Beryllium; Be	7440-41-7
Boron; B	7440-42-8
Cadmium; Cd	7440-43-9
Calcium; Ca	7440-70-2
Chromium; Cr	7440-47-3
Cobalt; Co	7440-48-4
Copper; Cu	7440-50-8
Iron; Fe	7439-89-6
Lead; Pb	7439-92-1
Lithium	7439-93-2
Magnesium; Mg	7439-95-4

Analyte	CAS #:
Manganese; Mn	7439-96-5
Molybdenum; Mo	7439-98-7
Nickel; Ni	7440-02-0
Phosphorus	7723-14-0
Potassium; K	7440-09-7
Selenium; Se	7782-49-2
Silver; Ag	7440-22-4
Sodium; Na	7440-23-5
Sulfur	7704-34-9
Thallium; Tl	7440-28-0
Tin	7440-31-5
Titanium	7440-32-6
Vanadium; V	7440-62-2
Zinc; Zn	7440-66-6

1.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that dissolves almost all elements that could become "environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure, as they are not usually mobile in the environment.

1.3 Reporting Limits: See the determinative method.

1.4 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

Samples are generally digested with additions of Nitric acid , Hydrogen peroxide, and Hydrochloric acid. The digestate is then diluted to a final volume of 50 mL for wipes/filters or 100 mL for soils.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

See the determinative method.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health

practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.
- All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease causative agents.
- Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.
- The inductively coupled plasma should only be viewed with proper eye protection from the ultraviolet emissions.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrogen peroxide (30%)	Oxidizer Flamma-ble Corrosive	1ppm TWA; 1.4 mg/m^3 TWA, 75 ppm IDLH	Strong oxidizer. Contact with other material may cause a fire. Eye contact may result in permanent eye damage. May cause central nervous system effects, eye and skin irritation, possible burns, severe respiratory tract irritation with possible burns, severe digestive tract irritation with possible burns. May cause blood abnormalities. **Target Organs:** Blood, central nervous system.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Analytical balance, with capability to measure to 0.01 g.
- Centrifuge.
- Heating source, adjustable and able to maintain a temperature of 90±5°C (e. g., hot plate, hot block, or equivalent).

6.2 Supplies

- Volumetric flasks, 100 to 500 mL, Class A.
- Pipettors, various µL, with metal-free, disposable plastic tips.
- Graduated Cylinders, 50 mL, 250 mL, 500 mL, Class A.
- Beakers, 150 mL.
- Calibrated, digestion tubes, plastic, 50 mL, graduated, with screw caps.
- Temperature measurement device capable of measuring to at least 100°C with suitable precision and accuracy (e. g., thermometer, thermocouple, thermistor, etc.)
- Watch glass, ribbed (for use with the centrifuge tubes).
- Plastic centrifuge tube racks.
- Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125 mL to 1-L capacities.
- pH test strips, 0-14, wide-range.
- 50-mL HDPE digestion tubes.
- 2" x 2" x 2" sterile cotton gauze or ashless filter paper (mixed cellulose ester, 0.8 µm pore size) or Ghost wipe (4" x 4" 1000/cs wet with reagent water (Environmental Express, Mt. Pleasant, SC, SC4250, or equivalent) for LCS and blank matrix.
- Sieve, 100 mesh.
- Erlenmeyer flask, 500 mL.
- Hot plate.

7.0 Reagents and Standards

7.1 **Reagent water**, analyte-free.

7.2 Spectroscopic grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

7.3 **Hydrochloric acid**, concentrated, HCl. If the method blank is less than the MDL, the acid is acceptable.

7.4 **Nitric acid**, concentrated, HNO_3. If the method blank is less than the MDL, the acid is acceptable.

7.5 **Hydrogen peroxide**, 30%. If the method blank is less than the MDL, the reagent is acceptable.

7.6 **Stock Element Solution**, commercial, certified, for LCS and Matrix Spikes, purchased from Environmental Express, Cat. No. HP3594, or equivalent, with the following concentrations:

Analyte	Stock Std Concentration (µg/mL)	Analyte	Stock Std Concentration (µg/mL)
Aluminum	200	Lead	5
Antimony	10	Lithium	100
Arsenic	5	Magnesium	500
Barium	200	Manganese	50
Beryllium	5	Molybdenum	50
Bismuth	100	Nickel	50
Boron	100	Potassium	500
Cadmium	5	Silver	5
Calcium	500	Sodium	500

Analyte	Stock Std Concentration (µg/mL)	Analyte	Stock Std Concentration (µg/mL)
Chromium	20	Thallium	5
Cobalt	50	Titanium	100
Copper	25	Vanadium	50
Iron	100	Zinc	50

7.7 See SOP Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214 for shelf-life and storage requirements for reagents and standards. Also, refer to benchsheets, logbooks, and LIMS.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time from Collection	Reference
Wipe	HDPE or Glass[1]	One wipe	None	6 months	NA
MCE filter	Cassette	One filter	<6°C	6 months	NA
Soil	Glass, plastic	10 g	<6°C upon receipt in lab	N/A	SW-846 Ch. 3, LDNR (2011

[1]All sample containers must be pre-washed with detergents, acids and water. Plastic, certified-clean containers are used if the containers are supplied by TestAmerica Nashville.

8.1 Wipe Sampling Using Gauze Pad

1	Using a new pair of disposable, latex gloves, remove a gauze pad from its protective package. Moisten the gauze pad with approximately 1 to 2 mL reagent water. Apply no more water than that necessary to moisten approximately the central 80% of the area of the gauze pad. Excess water may cause sample loss due to dripping from the gauze pad. If using the pre-moistened Wash'n Dri™, omit the water.
2	Place the template (10 cm x 10 cm, plastic, or other known size) over the area to be sampled. Wipe the surface to be sampled with firm pressure, using 3 to 4 vertical S-strokes. Fold the exposed side of the pad in and wipe the area with 3 to 4 horizontal S-strokes. Fold the pad once more and wipe the area with 3 to 4 vertical S-strokes.
3	Fold the pad, exposed side in, and place it in a new plastic bag. Seal and label the bag clearly. Discard the gloves.
4	Clean the template in preparation for the net wipe sample.
5	Include the two blank pads (moistened and placed in individual bags) with each sample set.

8.2 Wipe Sampling Using Filter Paper

1	Wear clean, impervious, disposable gloves when taking wipe samples to prevent sample contamination. Change gloves between samples to reduce the possibility of cross contamination.
2	Moisten Smear Tabs and Whatman filters with reagent water prior to use. Wipe a 10 cm x 10 cm area by starting at the outside edge of the surface, applying firm pressure, wipe the surface and progress towards the center by making concentric squares of decreasing size. If possible wipe the area at least 3 times.

3	If using a Ghost Wipe, remove it from its package and unfold it. Next fold the Ghost Wipe in half and wipe a 10 cm x 10 cm area by starting at the outside edge of the surface applying firm pressure, wipe the surface and progress towards the center by making concentric squares of decreasing size. Fold wipe in half, with contaminant side in, and wipe the surface again by making concentric squares of decreasing size. Fold the wipe in half, contaminant side in,and wipe the surface a third time.
4	Fold the wipe sample with exposed side in.
5	Transfer the wipe sample into a 2-ounce jar and seal.

9.0 Quality Control

Refer to TestAmerica-Nashville's QA Manual for specific quality control (QC) policies. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Batch QC

Quality Controls	Frequency	Control Limit
Method Blank	1 per batch	See determinative method.
Laboratory Control Sample (LCS), second source	1 per batch	See determinative method.
Matrix Spike	1 per batch	See determinative method.
Matrix Spike Duplicate	1 per batch	See determinative method.

- **Method blank** - The laboratory prepares and analyzes at least one blank with each batch of samples of the same matrix.
- A **Laboratory Control Sample (LCS)** is analyzed with every batch; it is prepared from a second-source standard.
- **Matrix Spike (MS) / Matrix Spike Duplicate (MSD)**: Use a separate wipe/filter for the MS/MSD and spike as for the LCS.

9.2 Instrument QC: See the determinative method.

9.3 QC for MCE filters and Ghost Wipes

Order in Sequence	QC Check	Acceptance Criteria
Initial Performance	ICV	90-110% recovery
	CCV	90-110% recovery
	RLV	75-125% recovery
	ICS	85-115% recovery
	IB	< Reporting Limit
Continuing Performance	CCV	90-110% recovery
	RLV	75-125% recovery
	IB	< Reporting Limit
Termination Performance	CCV	90-110% recovery
	RLV	75-125% recovery
	IB	< Reporting Limit

10.0 Procedure

10.1 Sample Preparation

Matrix	Sample Size
Wipe, filter	One wipe/filter per sampled area
Soil	10 g (dried)

Note: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. The use of an acid vapor scrubber system for waste minimization is encouraged.

10.2 Digestion for a Wipe or Filter

1	Rinse the beakers several times with reagent water and allow them to dry.
2	Place each wipe/filter in a separate, washed beaker.
3	Add 5 mL reagent water, followed by 2.5 mL concentrated HNO_3 to each vessel. Cover with a watch glass. Place the vessel on the hotplate. Heat to 95 ± 5°C for 10 to 15 minutes. Record. Cool, add 5 mL concentrated HCl, and reflux for 30 minutes.
4	
5	After vessels have cooled to room temperature, dilute digested wipe solutions to 50 mL. Transfer to a centrifuge tube and cap.

10.3 Digestion for True Total Barium (TTB) (29B)

1	Grind a 10 g, dried sample to pass a 100-mesh sieve.
2	Weigh 100 mg of sample to the nearest tenth of a milligram.
3	Place the subsample into a 50-mL digestion tube, add 35 mL reagent water, and 15 mL of concentrated Nitric acid.
4	Reflux on a hot plate until the volume is approximately 30 mL.
5	Transfer to a 50-mL digestion tube, and bring to the mark with reagent water.
6	Analyze by SOP 6010 / NV06-44. Report as dry weight.

10.4 Digestion for Soil (Non-TTB Metals, LDNR 29B)

1	Place 0.5 to 1.0 g soil in a digestion tube
2	Add 10 mL 1:1 HNO_3, mix, and cover. Heat to 95 ± 5°C and reflux for 10-15 minutes. Cool and add 5 mL concentrated HNO_3; cover and reflux 30 minutes. Repeat. Cover with a ribbed cover and evaporate to about 5-10 mL or heat at 95 ± 5°C for two hours. Do not allow to go dry.
3	Cool and add 2 mL reagent water and 3 mL 30% H_2O_2. Cover and heat to start the reaction. Heat until effervescence subsides and cool. Continue to add 1 mL 30% H_2O_2 until the reaction ceases or the appearance remains unchanged. Do not add more than 10 mL 30% H_2O_2.
4	Add 5 mL concentrated HCl and 10 mL reagent water. Cover and reflux for 15 minutes. Cool and dilute to 100 mL with reagent water.

11.0 Calculations / Data Reduction

Not applicable.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses

performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required; each matrix must be represented.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

12.5 Control Charts: Laboratory method performance can be shown with the use of control charts, available from the QA department.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method: See the determinative method.

15.0 References / Cross-References

15.1 SW-846 Method 3050B, Update III, Rev. 2, December 1996.

15.2 LDNR 29B, **Laboratory Procedures for Analysis of Exploration and Production Waste**, Louisiana Department of Natural Resources, Injection and Mining Division, 2011.

15.3 TestAmerica Nashville's Quality Assurance Manual.

15.4 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.5 SOPs: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Method Start-up / SA08-203, Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214, 6010 / NV06-44.

15.6 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachments

None.

18.0 Revision History

- Revision 6, dated 10 September 2008
  - Integration for TestAmerica and STL operations.
  - Removal of GFAA procedure and references.
- Revision 7, dated 30 September 2010
  - Addition of NIOSH 9100 and OSHA ID-125G.
  - Addition of QAF-45 and Section 14.2.
  - Addition of SOP references.
- Revision 8, dated 29 June 2012
  - Organizational changes.
  - Reduce scope to wipes and filters only.
- Revision 9, dated 28 September 2012
  - Organizational changes.
  - Addition of agricultural soils.
- Revision 10, dated 28 February 2014
  - Organizational changes.
  - Addition of change forms 9a and 9b.
  - Require sample preservation at <6^{o}C for solids and MCE filters.
  - Add Lithium, Phosphorus, Strontium, Sulfur, Tin, and Titanium to the method.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP)
Change Form

SOP Number/Revision No.: 3051 / NV06-94.14b Effective Date: **2/3/2014**

Last Mod. Date: **9/30/2013**

SOP Title: **Method 3051 / 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils**

Affected SOP Section Number(s): Section 10.0, Procedure for Sample Digestion

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 06

Revision Number with Mod ID: **14c**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add underlined text. Delete crossed-out text.

Section 10.0, Procedure for Sample Digestion, Step 3.

3	Place the carousel in the microwave unit. Load and run the 3051 program: Tthe temperature of each sample **must** rise to 175 ± 5°C in approximately 5.5 ± 0.25 minutes and remain at 175 ± 5°C for 4.5 minutes or the remainder of the 10-minute digestion period. ~~**Print/scan the temperature profile information for each batch.**~~

1/24/14	
Department Manager Approval Date	
Steve Shilley 1/24/13	Michael A. Brown 1/24/14
Quality Manager Approval	Technical Director Approval Date

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP)
Change Form

SOP Number/Revision No.: 3051 / NV06-94.14a Effective Date: **9/30/2013**

Last Mod. Date: 6/28/13

SOP Title**: Method 3051 / 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils**

Affected SOP Section Number(s): Section 10.0, Procedure for Sample Digestion

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 06

Revision Number with Mod ID: **14b**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add bold text.

Section 10.0, Procedure for Sample Digestion, Step 6.

6	Dilute the digest to a known volume (100 mL) in a Class A volumetric flask ensuring that the samples and standards are matrix matched. The digest is now ready for analysis for the elements of interest. **Record the lot number of the 50-mL, centrifuge tubes.**

9/6/13	9/6/13
Department Manager Approval Date	Technical Director Approval Date Quality Manager Approval

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP)
Change Form

SOP Number/Revision No.: 3051 / NV06-94.14 Effective Date: **6/28/2013**

Last Mod. Date: 4/30/13

SOP Title**: Method 3051 / 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils**

Affected SOP Section Number(s): Sections 6.2 and 10.0

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 06

Revision Number with Mod ID: **14a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add underlined text.

Section 6.2, Supplies

- Syringe filter, PTFE membrane.

Section 10.0 Procedure for Sample Digestion, step 5, add third bullet:

- Filter using a PTFE membrane. Record the filter ID and lot number. If a sample in the batch is filtered, the Method Blank and LCS must also be filtered.

6/21/13	6/21/13
Department Manager Approval Date	Technical Director Approval Date Quality Manager Approval

Title: MICROWAVE-ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS SW-846 METHOD 3051/3051A

Approvals (Signature/Date)			
	4/11/13		
Rodney Street Department Manager	Date		
	4/9/13		4/11/13
Michael H. Dunn Technical Director Quality Assurance Manager	Date	Johnny Davis Health & Safety Manager / Coordinator Extractions Operations Manager	Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method is applicable to the microwave-assisted acid digestion of sludges, sediments, soils, and oils for the following metals:

Analyte	CAS #
Aluminum; Al	7429-90-5
Antimony; Sb	7440-36-0
Arsenic; As	7440-38-2
Barium; Ba	7440-39-3
Beryllium; Be	7440-41-7
Bismuth, Bi	7440-69-9
Boron; B	7440-42-8
Cadmium; Cd	7440-43-9
Calcium; Ca	7440-70-2
Chromium; Cr	7440-47-3
Cobalt; Co	7440-48-4
Copper; Cu	7440-50-8
Iron; Fe	7439-89-6
Lead; Pb	7439-92-1

Analyte	CAS #:
Magnesium; Mg	7439-95-4
Manganese; Mn	7439-96-5
Molybdenum; Mo	7439-98-7
Nickel; Ni	7440-02-0
Potassium; K	7440-09-7
Selenium; Se	7782-49-2
Silver; Ag	7440-22-4
Sodium; Na	7440-23-5
Strontium; Sr	7440-24-6
Sulfur, S	7704-34-9
Thallium; Tl	7440-28-0
Vanadium; V	7440-62-2
Zinc; Zn	7440-66-6

1.2 Reporting Limits: See the determinative method.

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor/Manager or the Technical Director. All abnormalities must be noted on the data or the benchsheet and in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

A representative sample of up to 0.5 g is digested in 9 mL of concentrated nitric acid and 3 mL of concentrated hydrochloric acid using microwave heating with a laboratory microwave unit. The sample and acid are placed in a fluorocarbon (PFA or TFM) microwave vessel. The vessel is capped and heated in the microwave unit. After cooling, the vessel contents are centrifuged, or allowed to settle and then diluted to volume and analyzed by the appropriate method. Digestates produced by the method are suitable for analysis by inductively coupled plasma emission spectroscopy (ICP-ES) or inductively coupled plasma mass spectroscopy (ICP-MS).

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

None.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples must be done in a fume hood.
- The inductively coupled plasma must only be viewed with proper eye protection from the ultraviolet emissions.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochlo-ric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Causes redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Microwave apparatus requirements (Mars Xpress, or equivalent)
  - The microwave unit provides programmable power.
  - The microwave unit cavity is corrosion resistant as well as ventilated.
  - All electronics are protected against corrosion for safe operation.
  - The system requires fluorocarbon (PFA or TFM) digestion vessels (120 mL capacity) capable of withstanding high pressures. Vessels use controlled, self-sealing, pressure relief at pressures exceeding their rating.
  - An oscillating turntable is employed to insure homogeneous distribution of microwave radiation within the unit.
- Analytical balance, with capability to measure to 0.01 mg and 300 g.

6.2 Supplies

All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. Polymeric or glass volumetric ware and storage containers must be cleaned by leaching with more dilute acids (approximately 10% v/v) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. To avoid precipitation of silver,

ensure that all HCl has been rinsed from the vessels.

- Volumetric flasks, 25 mL, 100 mL, 200 mL, Class A.
- Automatic pipettors, 50 µL, 100 µL, 250 µL, 500 µL, 1000 µL, with disposable plastic tips.
- Disposable serological pipettes, 1 mL, 5 mL, 10 mL.
- Graduated Cylinders, 50 mL, 250 mL, 500 mL, Class A.
- Certified, centrifuge tubes, plastic, 50 mL, graduated, with screw caps.
- Watch glass, plastic, ribbed (for use with the centrifuge tubes).
- Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125 mL to 1-L capacities.
- pH test strips, 0-14.
- Teflon™ boiling chips for soil blank matrix and LCS.

7.0 Reagents and Standards

7.1 **Reagent water**, analyte-free.

7.2 Reagents may contain elemental impurities, which might affect analytical data. All acids used for this method **must be** of ultra high-purity grade or equivalent. Suitable acids are available from a number of manufacturers. Acids are acceptable when the following criteria are met:

7.3 **Hydrochloric acid**, concentrated, HCl. If the method blank is less than the MDL, the acid is acceptable.

7.4 **Nitric acid**, concentrated, HNO_3. If the method blank is less than the MDL, the acid is acceptable.

7.5 **Stock Element Solutions:** See the determinative method for standards, spike amounts and concentrations.

7.6 See SOP Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214 for shelf-life and storage requirements for reagents and standards.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Soil	HDPE or Glass[1]	2 oz. glass	none	6 months from collection to analysis	SW846 Section 2.0

[1]All sample containers must be pre-washed with detergents, acids and water. Plastic, certified containers are used if the containers are supplied by TestAmerica Nashville. Temperature preservation is not required.

9.0 Quality Control

The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC

The following quality control samples are prepared with **each batch of no more than 20 samples.**		
Quality Controls for Each Batch	**Frequency**	**Acceptance Limit**
Method Blank	1 per batch	See the determinative method.
Laboratory Control Sample (LCS)[1], second source		
Matrix Spike		
Matrix Spike Duplicate		

[1]For AZ, TX, WV samples, a LCS duplicate is required.

- **Method or Preparation blank:** The laboratory prepares and analyzes a method blank with each batch of the same matrix. Use Teflon™ boiling chips for the blank matrix.
- A **Laboratory Control Sample (LCS)** is analyzed with every batch. The standard used must be different than the calibration standard.
  - Add 2000 µL of stock standard/0.5 g Teflon™ boiling chips to a final volume of 100 mL.

Analyte	Final Concentration of Digestate (µg/mL)	Analyte	Final Concentration of Digestate (µg/mL)
Aluminum	4.0	Magnesium	10.0
Antimony	0.2	Manganese	1.0
Arsenic	0.1	Molybdenum	1.0
Barium	4.0	Nickel	1.0
Beryllium	0.1	Potassium	10.0
Boron	2.0	Silver	1.0
Cadmium	0.1	Sodium	10.0
Calcium	10.0	Strontium	0.5
Chromium	0.4	Sulfur	2.0
Cobalt	1.0	Thallium	0.1
Copper	0.5	Titanium	2.0
Iron	2.0	Vanadium	1.0
Lead	0.1	Zinc	1.0
Lithium	2.0		

- **Matrix Spike/Matrix Spike Duplicate:** Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect. Add a known amount of each analyte to a minimum of 5% of the routine samples. In each case the MS aliquot must be a duplicate of the aliquot used for sample analysis and must be added prior to sample preparation. The added analyte concentration must be the same as that used in the LCS (2000 µL/0.5 gram sample).

9.2 Instrument QC:

The microwave may be used in one of two modes: temperature control or power mode.

- **Microwave Temperature Validation:** If using temperature feedback, the accuracy of the temperature measurement system is periodically, i. e., quarterly, validated at an elevated temperature by an external, calibrated temperature measurement system. Heat a liquid, i. e., oil, to about 150°C in the microwave; record the microwave sensor temperature. Check with a thermometer; record the result. If the measured temperatures vary by more than 2°C, calibrate the microwave temperature measurement system. Consult the microwave manufacturer's instructions about the specific temperature sensor calibration procedure.
- **Microwave Power Validation:** If using the power control program, **weekly** validate the accuracy of the system per MARS 5 Express Revision 1 instructions (see Attachment 1). Calibration is the normalization and reproduction of the microwave field strength to permit reagent and energy coupling in a predictable and reproducible manner. It balances reagent heating and heat loss from the vessels and is equipment dependent due to the heat retention and loss characteristics of the specific vessel. Use of this calibration to control this reaction requires balancing output power, coupled energy, and heat loss to reproduce the temperature heating profile. Record check and power output. The conditions for each acid mixture and each batch containing the same specified number of vessels are determined individually.

Only identical acid mixtures and vessel models and specified numbers of vessels are used in a given batch.

10.0 Procedure for Sample Digestion: See SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

Matrix	Sample Size
Soil, sediment, sludge, oil	0.50 gram

1	Weigh a well-mixed sample to the nearest 0.01 gram into the fluorocarbon sample vessel equipped with a single ported cap and a pressure relief valve. For soils, sediments, and sludges, nominally use 0.50 g. Use no more than 0.5 grams for oil samples. For the method blanks and LCS, start with Teflon™ boiling chips and the addition of acid (add spike to LCS). For MS and MSD, spike a sample. See Section 9.1 for spike amounts.
2	Add 9 ± 0.1 mL concentrated nitric acid and 3 ± 0.1 mL of concentrated HCl in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and hand-tighten the cap. Place the vessels in the microwave carousel. Do not digest more than 24 vessels per run. **If using the power mode, balance system with blank vessels.** Set the microwave to Method 3051 (soils).
3	Place the carousel in the microwave unit. The temperature of each sample **must** rise to 175 ± 5°C in approximately 5.5 ± 0.25 minutes and remain at 175 ± 5°C for 4.5 minutes or the remainder of the 10-minute digestion period. **Print/scan the temperature profile information for each batch.**
4	At the end of the digestion stage, allow the vessels time to cool down at least 5 minutes prior to removing them from the microwave unit. When the vessels have cooled to near room temperature, align and check vessel pressure seals and compare volumes. Visual comparison of each vessel is made against a designated vessel marked at the initial vessel volume height and at a 1% volume loss height. Make a visual comparison check. For each sample that has the appearance of a volume loss of more than 1%, prepare a new volume of sample for digestion.
5	Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Transfer the sample to a clean, centrifuge tube and cap if sample needs to have particulates removed. If the digested sample contains particulates, which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, or allowed to settle. • Centrifugation for 10 minutes is usually sufficient to clear the supernatant. • Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge the sample.
6	**Dilute the digest to a known volume (100 mL)** in a Class A volumetric flask ensuring that the samples and standards are matrix matched. The digest is now ready for analysis for the elements of interest.

11.0 Calculations / Data Reduction
See the determinative method.

12.0 Method Performance
12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL

procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required; each matrix must be represented.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

12.5 Control Charts: Laboratory method performance can be shown with the use of control charts, available from the QA department.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are managed, stored and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method: See the determinative method.

15.0 References / Cross-References

15.1 SW-846 Method 3051A, Update IV, Rev. 1, February 2007.

15.2 TestAmerica Nashville's Quality Assurance Manual.

15.3 Corporate Environmental Health and Safety Manual (CW-E-M-001)

15.4 SOPs: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Determination of Method Detection Limits / NV08-202, Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

15.5 CEM Mars 5 Express Instrument Manual.

15.6 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachments

Attachment 1
Microwave Actual Power Output at 400, 800, 1600 Watts
(from MARS 5, Rev. 1, Instrument Manual)

1	Install the turntable in the microwave cavity.
2	With the main menu displayed, highlight "Load Method." Press the "SELECT" key. The "Directory Menu" screen will appear.
3	Use the "+" and/or "-" keys to highlight "CEM Directory." Press the "SELECT" key. The "CEM Menu" screen will appear.
4	Use the "+" and/or "-" keys to highlight "400W Power Test." Press the "SELECT" key to return to the main menu.
5	Place 1000 mL of ambient temperature (18-22^{o}C) reagent water in a 1000 mL Teflon™ or polypropylene beaker.
6	Using a thermometer with 0.1^{o}C gradations, measure and record the initial water temperature, T_i. Ensure that the thermometer is immersed to its indicated immersion line prior to reading the temperature.
7	Remove the thermometer from the beaker. Carefully place the beaker in vessel #1 position on the turntable. Gently close the door to avoid spilling any of the water.
8	Press "Start."
9	At the end of the programmed time (2 minutes), remove the beaker from the microwave cavity. Stir the water thoroughly for 30 seconds, then measure and record the peak temperature reading. This is the final temperature, T_f. The microwave power output is calculated as follows: Power in Watts = $35 (T_f - T_i)$
10	If the measured power is below 340W, repeat the microwave power measurement. If the power remains less than 340W, the instrument is not producing adequate microwave power at the 400W selection.
11	Repeat steps 2 through 9 for the 800W and 1600W power tests.
12	If the measured power is below 680W for the 800W power test, repeat the power measurement. If the power remains less than 680W, the instrument is not producing adequate microwave power at the 800W selection.
13	If the measured power is below 1360W for the 1600W power test, repeat the power measurement. If the power remains less than 1360W, the instrument is not producing adequate microwave power at the 1600W selection.
14	If the instrument is not producing sufficient wattage, refer to the Troubleshooting Guide, page 78 (of the MARS 5 instruction manual).

18.0 Revision History

- Revision 9, dated 31 December 2007
  - Integration for TestAmerica and STL operations.
  - Addition of power output procedure for CEM MARS 5 microwaves and deletion of short version description.
- Revision 10, dated 5 December 2008
  - Removal of unnecessary QC text.
  - Addition of Microwave Temperature Validation and change of previous "Microwave Temperature Validation" to "Microwave Power Validation."
  - Clarify/simplify previous 10.2.3, 10.2.4 (now Steps 3, 4 in digestion procedure).

  - Change Attachment 1 from 300, 900, 1200 W to 400, 800, 1600 W.
- Revision 11, dated 25 September 2009
  - Addition of OH VAP requirements.
  - Included new stock standard concentrations and final digestate concentrations.
- Revision 12, dated 31 August 2010
  - Addition of QAF-45 and Section 14.2.
  - Addition of Amendment 11a, changing the aliquot mass of the oil matrix sample.
  - Clarification of duration of samples in the microwave.
  - Change volume loss height from 10% to 1%.
- Revision 13, dated 31 May 2012
  - Organizational changes.
  - Oklahoma and Wyoming no longer limit batch size to 10 samples.
  - Provide instruction for oil samples.
  - Update year of method reference.
  - Add Sulfur.
- Revision 14, dated 30 April 2013
  - Organizational changes.
  - Refer stock element standards to the determinative method.
  - Change oil sub-sample mass to 0.5 g.

Title: SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION SW-846 METHOD 3510C

Approvals (Signature/Date)			
Jacolby Robinson Department Supervisor	Date 2/27/14	Johnny Davis Department Manager Health & Safety Manager / Coordinator	Date 2/25/14
Steve Miller Quality Assurance Manager	Date 2/10/14	Michael H. Dunn Technical Director	Date 2/28/14

1.0 Scope and Application

1.1 Analyte, Matrices: This method predominantly describes a procedure for extracting water-insoluble and slightly water-soluble organic compounds from aqueous samples and concentrating them for injection onto a gas chromatograph set up for an appropriate determinative method.

1.2 Reporting Limits: Results are dependent on the volume used, degree of contamination, ability to concentrate, and the sensitivity of the determinative method.

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

A measured volume of sample, nominally 1000, 250, or 125 mL, at a specified pH, is serially extracted with Methylene chloride using a separatory funnel. The extract is dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method to be used.

3.0 Definitions

3.1 Reduced Volume Extraction / Large Volume Injection (RVE/LVI): The option to use a reduced sample volume for extraction combined with a larger volume extract injection on the instrument. Volumes for this option are shown in this document as LVI.

3.2 See TestAmerica Nashville's QA Manual for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

Interferences are often due to contamination from solvents or extraction glassware.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: Use the hoods to evacuate solvent vapors from the building and dispose of solvent wastes appropriately.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Sodium hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3	This material causes burns in contact with the skin or eyes. Inhalation of Sodium Hydroxide dust causes irritation of the nasal and respiratory system.
Sulfuric acid (1)	Corrosive Oxidizer Dehydrator	1 mg/m^3	This material causes burns if comes into contact with the skin or eyes. Inhalation of vapors causes irritation of the nasal and respiratory system.
Acetonitrile	Flammable Poison	40 ppm TWA	Early symptoms may include nose and throat irritation, flushing of the face, and chest tightness. Prolonged exposure to high levels of vapors may cause formation of cyanide anions in the body.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Kuderna-Danish (K-D) apparatus.
  - Concentrator tube, 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.
  - Evaporation flask, 250 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.
  - Snyder column, Three-ball macro (Kontes K-503000-0121 or equivalent).
  - Snyder column, 3 chamber micro (Kontes K-569001-0219 or equivalent).
  - Clamps
- Nitrogen Evaporator: N-Evap Model #116 by Organomation, or equivalent.

6.2 Supplies

- Separatory funnel, 2 liter, 500 mL, or 250 mL, Teflon™ with polytetrafluoroethylene (PTFE) stopcock.
- Funnel, Teflon™. Put a plug of glass wool in a funnel and fill about 2/3 full with sodium sulfate. Rinse funnel and Sodium sulfate with 5-10 mL of Methylene chloride before use.
- Boiling chips, solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).
- Water bath, heated, capable of temperature control (± 5°C). The bath is used in a hood.
- Vials, glass with PTFE-lined screw-caps.
- pH indicator paper, 0 – 14 pH range.
- Erlenmeyer flask, Teflon™250 mL or 500 mL.
- Graduated cylinder, glass, Class A, 1 liter, or equivalent.
- Volumetric flasks, Class A, at 1, 5, and 10 mL.
- Centrifuge, capable of approximately 2000 rpm.
- Nitrogen, compressed gas, high purity.

7.0 Reagents and Standards

7.1 Reagent grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the America Chemical Society, where such specifications are available. Other grades may be used, however, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents are stored in glass or Teflon™ to prevent the leaching of contaminants from plastic containers.

7.2 **Reagent water**, analyte-free.

7.3 **Sodium hydroxide** solution (10 N), NaOH, commercial source.

7.4 **Sodium sulfate** (granular, anhydrous), Na_2SO_4. Sodium sulfate must be solvent rinsed. A commercially rinsed product is acceptable.

7.5 **Sulfuric acid** solution, H_2SO_4, commercial source. Make a 1:1 dilution with reagent water.

7.6 **Extraction/exchange solvents**: All solvents are pesticide quality or equivalent and from commercial sources: **Methylene chloride,** CH_2Cl_2, **Hexane**, C_6H_{14}, **Acetonitrile**, CH_3CN.

7.7 **Sodium chloride** (NaCl), commercial source, granular.

7.8 **Acetone**, CH_3COCH_3, commercial source.

7.9 **Spiking Solutions**: See the determinative method and LIMS for information. These are purchased ready for use or prepared in the analysis department.

7.10 See SOP Reagent and Standard Purchase, Preparation, control, Documentation / NV08-214 for information on shelf-life and storage requirements for standards and reagents.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time from Collection	Reference
Water	Amber Glass, 1 L, 250 mL, or 125 mL Teflon™-lined cap	varies	0-6°C	7 days until extraction, 40 days until analysis	SW846 Chapter 2

For South Carolina samples, a 1-liter sample is required.

9.0 Quality Control

Refer to TestAmerica Nashville's QA Manual for specific quality control (QC) policies. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

The following quality control samples are prepared with each batch of no more than 20 samples.

Quality Controls	Frequency
Method Blank	1 in 20 or fewer samples
Laboratory Control Sample (LCS)[1], second source	1 in 20 or fewer samples
Matrix Spike	1 in 20 or fewer samples
Matrix Spike Duplicate	1 in 20 or fewer samples

[1]For AZ, MA, and TX samples, a LCS duplicate is required.

- **Method blank:** The laboratory prepares and analyzes a method blank (reagent water) with each batch.
- A **Laboratory Control Sample (LCS)**, reagent water spiked with a source different from the calibration standard, is analyzed with every batch. Use the same sample preparations,

analytical methods, and QA/QC procedures employed for the test samples.

- **Matrix Spike/Matrix Spike Duplicate:** Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect. Unless otherwise specified by the data user, the MS/MSD procedure is required.
  - The laboratory must add a known amount of each analyte to be reported to a minimum of 5% of the routine samples. In each case the MS/MSD aliquot must be a duplicate of the aliquot used for sample analysis and added **prior** to sample extraction.

10.0 Procedure

10.1 Sample Preparation

Matrix	Sample Size
Water	1000, 250 , or 125 mL

1	Generally, the **entire** contents of the sample bottle are to be extracted. Mark the level of sample on the outside of the bottle and measure against a calibrated bottle of the same size and shape. (Bottles are calibrated quarterly using Class A volumetric flasks. See Section 17.3.) Alternatively, using a Class A, graduated cylinder, measure the required amount of sample. If high analyte concentrations are anticipated, a smaller sample volume may be taken and diluted to 1 L with organic-free reagent water, or samples may be collected in smaller sample bottles and the whole sample used. Shake the sample container well and transfer to a separatory funnel that has been pre-rinsed with about 10 mL of Methylene chloride.
2	For TCLP: 500 mL of the TCLP extract is used for semivolatile (BNA) extraction, 100 mL is used for pesticide extraction. Reagent water is used to bring the volume to about 1 L. Add surrogates (Table 2) to all samples and QC. • For TCLP BNA, spike the LCS, MS/MSD with 1 mL of the TCLP BNA spike. • For TCLP Pesticides, spike with 0.5 mL TCLP Pesticides spike and surrogate and 1 mL of Toxaphene.
3	Mixing by shaking is sometimes ineffective as solids settle during the time required to secure the sub-sample aliquot for analysis. Usually decantation prior to shaking or after initial settling following mixing (in order to preserve the suspended solids) is not an appropriate homogenization procedure. However, if decantation is used, documentation of the process must be made in the preparation or analysis logbook or benchsheet. If the inclusion of solid material adversely affects the extraction or analysis procedure, notify the project manager. The project manager must contact the client to verify if they would like the lab to extract only the aqueous portion. In this case, pour out only the liquid portion into a graduated cylinder and note the volume decanted and the approximate percentage of sediment present on the benchsheet.
4	Using a glass syringe, add the surrogate spiking solution into each sample in the graduated cylinder or sample bottle and mix well. (See Table 2 for details on the surrogate standard solution. This addition of surrogate must be made into both client and QC samples.)
5	Using a glass syringe, add the matrix spike/LCS spiking solution into the appropriately designated graduated cylinder or sample bottle and mix well. (See Table 2, the determinative method, and LIMS for details on the matrix spike/LCS solution.)
6	Check the pH of the sample by immersing a glass or Teflon™ rod tip or a pipet in the sample and touch to wide-range pH paper and adjust the pH, if necessary, to the pH indicated in **Table 1**, using 1:1 (v/v) Sulfuric acid or 10 N Sodium hydroxide. Rinse the glass or Teflon™

	rod with Methylene chloride into the separatory funnel. Other strengths of acid or base solution may be employed, provided that they do not result in a significant change (< 1%) in the volume of sample extracted.
7	For Method 8270 BNA, always adjust to acid pH first. If only PAHs are being analyzed by Method 8270, then only the base extraction needs to be done. In order to extract only the base-neutral, all samples within the batch must be PAH only, and the QC **must** be treated the same as the samples.

10.2 Sample Extraction

1	Use Methylene chloride to rinse the graduated cylinder (or sample container) and transfer this rinse solvent to the separatory funnel containing the sample. **Record** the sample volume on the benchsheet. For 1 L sample volume, use 60 mL Methylene chloride. For 250 mL sample volume, use 15 mL Methylene chloride. For 125 mL sample volume use 8 mL Methylene chloride.
2	Seal and shake the separatory funnel vigorously for 1 - 2 minutes with periodic venting to release excess pressure. Methylene chloride creates excessive pressure very rapidly; therefore, initially vent **immediately** after the separatory funnel has been sealed and shaken once. Vent the separatory funnel into a hood to avoid exposure of the analyst to solvent vapors.
3	Allow the organic layer to clearly separate from the water phase for at least 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation at approximately 2000 rpm for about 5 minutes, or other physical methods. Collect the solvent extract in an Erlenmeyer flask. Add a comment on the benchsheet and NCM in the LIMS indicating that the sample formed an emulsion.
4	Repeat the extraction **two** more times using fresh portions of solvent. Combine the three solvent extracts.
5	If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH indicated in **Table 1 (Section 17)**. Serially extract three times with proportional volumes of Methylene chloride. Collect and combine the extracts and label the combined extract appropriately.
6	If performing GC/MS analysis (Method 8270), the acid/neutral and base extracts are combined prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts may be preferable (e. g., if for regulatory purposes the presence or absence of specific acid/neutral or base compounds at low concentrations must be determined, separate extract analyses may be warranted).
7	Dry the extract by passing it through a Teflon™ funnel filled to about 2/3 full with pre-rinsed, anhydrous sodium sulfate. Collect the dried extract in a clean Erlenmeyer flask. Rinse the funnel with 20 - 30 mL of Methylene chloride and add it to the flask to complete the quantitative transfer. Perform the concentration using the Kuderna-Danish Technique.
8	Extracts may be held prior to concentration if stored covered; in addition, 8310, 8270, and 8081 extracts when held are stored at 0-6^{o}C and in the dark. Proceed to sample concentration.

10.3 Sample Concentration by Kuderna-Danish Technique

1	Assemble a K-D concentrator by attaching a 10-mL concentrator tube to a 250-mL, or smaller, evaporation flask.
2	Add one or two clean boiling chips to the KD flask. Quantitatively transfer extract to the KD. Rinse the flask with approximately 10-20 mL solvent. Attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of Methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15 – 20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the temperature and/or flask position to complete the concentration in 10 - 20 minutes. Record the temperature. At the proper rate of distillation, the balls of the column actively chatter, but the chambers do not flood. When the apparent volume of liquid reaches about 10 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.
3	If a solvent exchange is required (as indicated in Table 1), remove the Snyder column and KD, and using nitrogen blow-down technique, reduce the volume to about 2 mL. To 4 mL of Hexane or 2 mL of Acetonitrile, whichever is the appropriate exchange solvent, add a new boiling chip, and attach the 3-chamber micro-Snyder column to the concentrator tube. Concentrate the extract and alter the temperature of the water bath, if necessary, to maintain proper distillation.
4	Remove the Snyder column and rinse it and its lower joints into the concentrator tube with 1 - 2 mL of Methylene chloride or exchange solvent. The extract is further concentrated by using the technique outlined in Section 10.3.6 or adjusted in a Class A volumetric to 1.0 - 10.0 mL with the solvent last used.
5	If further concentration is indicated in Table 1, use the nitrogen blow-down technique to adjust the extract to the final volume required.
Nitrogen blow-down technique	
6	Place the concentrator tube in a warm bath (35°C) and evaporate the solvent to the just below final volume indicated in Table 1, using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).
7	The internal wall of the tube must be rinsed several times with Methylene chloride or appropriate solvent during the operation. During evaporation, the tube must be positioned to avoid water condensation (i. e., the solvent level is below the level of the water bath). Under normal procedures, the extract must not be allowed to become dry.
8	The sample is then transferred to a Class A volumetric flask and adjusted to the final volume by using the rinsate from the tube.
9	Transfer the sample to a vial with a PTFE-lined cap and label appropriately. Individual states may require silica gel clean-up. Refer to Table 1, state-specific SOPs and/or 8015 / NV05-31 for details. The extract may now be analyzed for the target analyses using the appropriate determinative technique(s). Store refrigerated.

10.4 Example Analysis Queue / Sequence

See the determinative method.

11.0 Calculations / Data Reduction

Enter sample volume and final extract volume in LIMS.

12.0 Method Performance

12.1 Method Detection Limits (MDLs): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99%

confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes must be stored, managed, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.1 Wastestreams produced by this method:

- Extracted aqueous samples are collected, neutralized to a pH between 2.0 and 10.0, and discharged to the sanitary sewer.
- Used sodium sulfate and glass wool or filter paper contaminated with Methylene chloride from the extract drying step are placed in a hood overnight, then discarded in the trash.
- Assorted flammable solvent waste from various rinses is collected in the flammable waste drums.

15.0 References / Cross-References

15.1 SW-846 Method 3510C, Update III, Revision 3, December 1996.
15.2 CA LUFT Manual, Version 2.0, October 4, 2010.
15.3 TestAmerica Nashville's Quality Assurance Manual.
15.4 Corporate Environmental Health and Safety Manual (CW-E-M-001).
15.5 SOPs: Waste Disposal / NV10-83, 8270 / NV04-22, 8081 / NV04-16, 8082 / NV04-105, 8015 / NV05-31, 8310 / NV04-57, FL PRO / NV04-78, WI DRO / NV04-38, MADEP-EPH / NV04-168, NWTPH-Dx / NV04-190, NWTPH-EPH / NV04-191, OA-2 / NV04-188, OK DRO / NV04-74, TN EPH / NV04-187, CT ETPH / NV04-86, Training Procedures for Environmental Technical Staff

/ NV08-199, Balance Calibration / NV08-213, Reagent and Standard Purchase, Preparation, control, Documentation / NV08-214.

15.6 Controlled Documents: PF-1, Prep Lab Summary Chart, QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

16.0 Method Modifications

Item	Modification
1	Use of reduced sample volumes.

17.0 Attachments

17.1

Table 1. Specific Extraction Conditions for Various Determinative Methods

Determinative Method	Initial Extraction pH	Secondary Extraction pH	Exchange Solvent Req. for Analysis	Exchange Solvent Required for Cleanup	Volume of Extract Required for Cleanup (mL)	Final Extract Volume for Analysis (mL)[a]
8081	5-9	None	Hexane	Hexane	5.0	5.0
8082	5-9	None	Hexane	Hexane	5.0	5.0
8270[a]	<2	>11	None	-	-	1.0
8310	As rec'd	None	Acetonitrile	Acetonitrile	-	1.0
8015	None	None	None	-	-	1.0
CA TPH (LUFT)	<2	None	None			1.0[b]
CT-ETPH	<2	None	None	None		1.0
FL PRO	<2	None	None	-	2.0	2.0[b]
MA-EPH	<2	None	None	Hexane	1.0	1.0[b]
NWTPH-Dx	<2	None	None		1.0	1.0[b]
NWTPH-EPH	<2	None	None	Hexane	2.0	2.0[b]
OA-2	<2	None	None	-	-	1.0
TN-EPH	<2	None	None	-	-	1.0
WI/OK-DRO	<2	None	None	-	-	1.0

[a] If only PAHs are being analyzed by Method 8270, then only the base extraction needs to be done. In order to do this, all samples within the batch must be PAH only and the QC **must** be treated the same as the samples.

[b] Silica gel cleanup required.

17.2

Table 2. Surrogate and Matrix Spike/LCS Amounts

Method	Surrogate Spike Amount	MS/LCS Spike Amount	Sample Volume
8081	1.0 mL of Pest/PCB surrogate	1.0 mL Pest spike, 1.0 mL Toxaphene/Technical Chlordane spike	1 L
8081	1.0 mL of Pest/PCB LVI surrogate	1.0 mL Pest LVI spike, 1.0 mL Toxaphene/Technical Chlordane LVI spike	125 mL
8082	1.0 mL of Pest/PCB surrogate	1.0 mL PCB spike	1 L
8082	1.0 mL of Pest/PCB LVI surrogate	1.0 mL PCB LVI spike	125 mL

Method	Surrogate Spike Amount	MS/LCS Spike Amount	Sample Volume
8270	1.0 mL of BNA surrogate	500 µL of BNA spike	1 L
8270	1.0 mL of BNA LVI surrogate	500 µL of BNA LVI spike	250 mL
8310	1.0 mL of HPLC surrogate	1.0 mL of HPLC spike	1
8015	1.0 mL of o-Terphenyl surrogate	1.0 mL DRO spike	1 L
8015	1.0 mL of o-Terphenyl LVI surrogate	1.0 mL DRO LVI spike	250 mL
CA TPH (LUFT)	1.0 mL of o-Terphenyl surrogate	1.0 mL DRO spike	1 L
CT ETPH	1.0 mL of o-Terphenyl surrogate	2.0 mL of FL/WI spike	1 L
FL PRO	2.0 mL of o-Terphenyl surrogate 2 mL of C_{35} surrogate	2.0 mL of FL/WI spike	1 L
MA-EPH	1 mL of MA surrogate 1 mL fractionation surrogate	1 mL of MA spike	1 L
NWTPH-Dx	1.0 mL of o-Terphenyl surrogate	1 mL of DRO spike	1 L
NWTPH-EPH	2 mL of MA surrogate	2 mL MA spike	1 L
OA-2	1 mL o-Terphenyl surrogate	1 mL DRO spike	1 L
OK-DRO	1 mL of o-Terphenyl surrogate	2.0 mL of FL/WI spike	1 L
TN-EPH	1 mL o-Terphenyl surrogate	1 mL TN EPH spike	1 L
WI/OK-DRO	1.0 mL of C_{35} surrogate	2.0 mL of FL/WI spike	1 L
See individual SOPs for information on compounds, concentrations, and how to make the surrogate and spike solutions. Also, see the Prep Summary Chart for additional spike and surrogate information.			

17.3 Calibration of Bottles: Representative bottles, of varying size and shape, are calibrated using 100 mL, 50 mL, and 10 mL Class A volumetric flasks. Graduation marks are made accordingly, and bottles are then ready to be used as measuring guides for liquid samples. Date of calibration is noted on the bottle. The calibrated bottles are verified for accuracy quarterly and the verification recorded in a logbook.

18.0 Revision History

- Revision 8, dated 30 April 2008
  - Integration for TestAmerica and STL operations.
- Revision 9, dated 25 September 2009

  - Ohio VAP requirements
- Revision 10, dated 29 January 2010.
  - Addition of centrifuge to Section 6.2.
  - Define acronyms, abbreviations and/or refer to QAF-45.
  - Add Section 14.2 to document.
  - Change sample volume to 1000 mL.
- Revision 11, dated 30 June 2011.
  - Addition of Nitrogen to list of supplies (Amendment 10a).
  - Change sample volume for 8081/8082 to 1 Liter.
  - Clarify TCLP 8151 spike amounts.
  - Remove vertical adjustment of the apparatus in the water bath from sample concentration procedure description.
  - Distinguish Hexane and Acetonitrile volume additions when solvent exchange is required.
  - Organizational changes.
  - Change glass funnels to Teflon™ funnels.
- Revision 12, dated 30 April 2012
  - Organizational changes.
  - Addition of change form 11a, removing C35 surrogate from NWTPH-EPH.
  - Add considerations for samples with large amounts of solids, and revise sequence of steps for sample preparation.
  - Noted bottle calibration quarterly frequency in Section 10. Added date of calibration noted on bottle in section 17.3.
- Revision 13, dated 31 December 2012
  - Organizational changes.
  - Add information for Reduced Volume Extraction / Low Volume Injection.
- Revision 14, dated 28 February 2014
  - Organizational changes.
  - Addition of change forms 13a, b, c.
  - WV no longer requires an LCS duplicate. SC does not allow LVI.
  - Section 10.2, Step 3: Add “for at least 10 minutes” to the first sentence.
  - Change to different NWTPH EPH surrogate (Table 2).

Title: PREPARATION OF SOIL/SEDIMENT BY AUTOMATED SOXHLET FOR THE ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS SW-846 METHOD 3541

Approvals (Signature/Date)

Jacolby Robinson — 1/30/14	Johnny Davis — 1/15/14
Jacolby Robinson — Date	Johnny Davis — Date
Department Supervisor	Health & Safety Manager / Coordinator
Steve Miller — 1/17/14	Michael H. Dunn — 12/30/13
Steve Miller — Date	Michael H. Dunn — Date
Quality Assurance Manager	Technical Director

1.0 Scope and Application

1.1 This method describes a procedure for isolating and concentrating organic compounds from solid/sediment samples.

1.2 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

A nominally 10 g portion of soil/sediment is mixed until it forms a free-flowing powder with anhydrous Sodium sulfate. The samples are then spiked with the appropriate spike solutions. In the initial extraction stage, the sample-loaded extraction thimble is immersed into the boiling solvent. This insures very rapid intimate contact between the specimen and solvent and rapid extraction of the organic analytes. In the second stage, the thimble is elevated above the solvent and is rinse-extracted. In the third stage, the solvent is evaporated. The extract is exchanged, as necessary, into a solvent compatible with the cleanup or determinative method being employed. (See Table 1 for appropriate exchange solvents.)

3.0 Definitions

3.1 Surrogate standards: A surrogate is added to each sample, blank, laboratory control sample (LCS) and matrix spike sample prior to extraction.

3.2 See TestAmerica Nashville's Quality Assurance Manual for other laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

Interferences may be caused by contaminants in solvents, reagents, and glassware. It is vital to prevent the addition of these contaminants by using proper techniques to prep glassware and aliquot sample masses. Gloves can also be a source of contamination. Therefore it is necessary to prevent contact between gloves and samples or solvent.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- Use nitrile gloves when performing this extraction. Latex and vinyl gloves provide no significant protection against the organic solvents used in this method.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material[1]	Hazards	Exposure Limit [2]	Signs and symptoms of exposure

Material[1]	Hazards	Exposure Limit [2]	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Methylene chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
1 – Always add acid to water to prevent violent reaction.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Analytical balance; capable of accurately weighing ± 0.01 g. Balances are calibrated per SOP Balances / NV08-213.
- Gerhardt Soxtherm, automated Soxhlet apparatus, or equivalent.

6.2 Apparatus, Reagents, Standards, and Supplies

- Stainless steel funnel.
- Filter paper, Whatman No. 41 or equivalent.
- Glass wool; pesticide grade or equivalent.
- Pasteur pipettes, disposable.
- Aluminum foil; clean, unused.
- Gas tight syringe, 1.0 mL volume and 0.5 mL volume.
- Stainless steel spatula or scoopula.
- Soxtherm beaker.
- Brinkman 50 mL solvent dispenser.
- 4-mL amber screw-top vials and 20-mL scintillation vials.
- Weigh boats.

7.0 Reagents and Standards

7.1 Sodium sulfate ($NaSO_4$): Anhydrous powdered reagent grade. Purify by heating at 400°C for 4 hours in a shallow tray. Commercially baked material is acceptable. Store in sealed glass container.

7.2 Methylene chloride (CH_2Cl_2), chromatography residue grade or equivalent.

7.3 Extraction/exchange solvents. All solvents must be pesticide quality or equivalent.

- Hexane, C_6H_{14}.
- Acetonitrile, CH_3CN.

7.4 Acetone, chromatography residue grade or equivalent.

- Acetone rinse for Pesticides/PCBs: 1:1 volume to volume Acetone:Hexane.
- Acetone rinse for Other Semi-volatiles: 1:1 volume to volume Acetone:Methylene chloride.

7.5 Sand, Ottawa or equivalent.

8.0 Sample Collection, Preservation, Shipment and Storage

Samples must be collected, preserved, shipped and stored according to the appropriate regulatory requirements governing the samples being collected. Soils must be stored at <6°C and extracted within 14 days. See the appropriate determinative method SOP.

9.0 Quality Control

9.1 Samples are prepared and analyzed in batches. A batch is defined as environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A batch is composed of one to 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing/analyzing of the first and last sample in the batch to be 24 hours.

- A LCS and method blank must be included with every preparation batch. Samples in a prep batch (20 field samples, blank, MS, MSD, LCS) must be prepared within a 24 hour time frame.
- The method blank, Sodium sulfate or Ottawa sand, is analyzed to insure the preparation process and instrument are contamination free. The preparation process and instrument must be considered contaminant-free prior to analyzing any samples.
- A LCS is Sodium sulfate or Ottawa sand to which target compounds at known concentrations are spiked to determine if the preparation and/or analytical process are in control.
- Matrix spike compounds at known concentrations are spiked into a sample and duplicated to determine the matrix effects of the sample on recovery of the compounds.
- Batch QC

Quality Controls	Frequency
Method Blank (MB)	1 in 20 or fewer samples
Laboratory Control Sample (LCS)[1]	1 in 20 or fewer samples
Matrix Spike (MS)[2]	1 in 20 or fewer samples
MS Duplicate (MSD)	1 in 20 or fewer samples
Surrogates	Every sample[3]
[1]LCSD is only required for AZ, MA, TX samples or when requested by the client/project/contract.	
[2]The sample selection for MS/MSD is randomly selected, unless specifically requested by a client or predetermined by the extraction lab.	
[3]Analytical and QC samples (MB, LCS, MS/MSD).	

9.2 Instrument QC

Not Applicable.

10.0 Procedure

10.1 Sample Preparation

10.1.1 Decant and discard any water layer on the sediment sample. Mix sample thoroughly. Discard any foreign objects such as sticks, leaves and rocks. See SOP Sample Sub-sampling, Homogenization and Compositing / NV08-229.

10.1.2 The following steps are performed rapidly to avoid loss of the more volatile compounds:

10.1.2.1 Weigh nominally 10 g of sample (see Table 1) into a properly cleaned weigh boat. Record the weight to the nearest 0.01 g.

10.1.2.2 Mix enough powdered $NaSO_4$ into each sample aliquot until the sample has a dry, sandy, free-flowing texture. Use Sodium sulfate as the matrix for the blank and LCS.

10.1.2.3 Transfer the dried sample into the extraction thimble.

10.1.2.4 Place the thimble and sample into the wire holder and place in the Soxtherm beaker.

10.1.2.5 Add the proper volumes of the appropriate spiking solutions to each sample. Add surrogate spike to each sample. Add matrix spike standard to only the Matrix Spike, Matrix Spike Duplicate (MS/MSD) and Laboratory Control Sample (LCS). See Table 2 for information on surrogate/spike solutions and amounts.

10.1.2.6 Immediately add 125-150 mL of Methylene chloride rinse to Soxtherm beaker.

10.2 Soxtherm Extraction

10.2.1 The Soxtherm beaker with sample and solvent is placed in the Soxtherm unit. Record the unit ID in LIMS.

10.2.2 The unit(s) to be used for extraction is chosen on the Soxtherm Controller and the correct method highlighted and entered:

- 200°C temperature limit
- 150°C extraction temperature
- 60-minute boiling time
- 5 x 15 mL solvent reduction A
- 60-minute extraction time
- 1.4 x 15 mL solvent reduction B
- 10-minute solvent cooling
- 5.0-minute solvent reduction interval
- 5-second solvent reduction pulse

10.2.3 Cooling water and air are “on” to the unit(s).

10.2.4 Press the “RUN” button on each unit.

NOTE: Each individual unit may be set to run a separate program.

10.2.5 The Soxtherm unit turns off at the end of the extraction program. The cooling water and gas need not be turned off at the end of the program.

10.2.6 Remove the beaker and sample from the Soxtherm. Discard the sample in the appropriate container and remove the wire rack. Transfer the extract, if needed, to a concentrator tube. Also, make sure to rinse the extraction vessels with solvent and add to the extract. If extracts are held, cover and store at 0-6°C in the dark.

10.3 Extract concentration: Nitrogen blowdown technique

10.3.1 If a solvent exchange is required (as indicated in Table 1), remove the Snyder column and KD, and using the nitrogen blow-down technique, reduce the volume to 2 mL. Add 4 mL of the exchange solvent and a new boiling chip, and attach the 3 chamber micro-Snyder column to the concentrator tube. Concentrate the extract raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches about 1-2 mL, remove the KD apparatus and allow it to drain and cool for at least 10 minutes.

10.3.2 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

10.3.3 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i. e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analyses may be lost.

10.3.4 The sample is taken to a volume of less than the required final volume. The sample is the transferred to a Class A volumetric flask and adjusted to the final volume using the last solvent used.

10.3.5 Transfer the sample to a vial with a PTFE-lined cap and labeled appropriately. Individual states may require silica gel clean-up. Refer to state-specific SOPs and/or 8015 / NV05-31 (its attachments contain information on various state DROs).

11.0 Calculations / Data Reduction / Documentation / Review

See the determinative method.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure which is in accordance with the TestAmerica Quality Assurance Manual and SOP MDL / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: See the Quality Assurance Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration, initially and on an ongoing basis.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the Quality Assurance Manual and SOP Waste Disposal / NV10-83 and USDA Disposal of Soils/ NV10-162.

14.2 Wastestreams Produced by the Method:

- Soil is disposed in the trash receptacle after allowing to sit in fume hood overnight.

15.0 References / Cross References

15.1 Method 3541, SW846 Update II, Revision 0, September 1994.
15.2 TestAmerica Nashville's Quality Assurance Manual.
15.3 Corporate Environmental Health and Safety Manual (CW-E-M-001).
15.4 SOPs:

- Organochlorine Pesticides by Gas Chromatography, 8081 / NV04-53
- Polychlorinated Biphenyls (PCBs) by Gas Chromatography, 8082/ NV04-105.

- Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), 8270 / NV04-168.
- Massachusetts Method for the Determination of Extractable Petroleum Hydrocarbons, MADEP-EPH / NV04-168.
- Procedure for the Determination of Method Detection Limits, MDL / NV08-202.
- Training Procedures for Environmental Technical Staff Training / NV08-199.
- Waste Disposal / NV10-83
- Disposal of Soils Regulated by USDA, USDA Disposal of Soils / NV10-162.
- Separatory Funnel Liquid-liquid Extraction, 3510 / NV03-24.
- Balance Calibration, Balances / NV08-213.
- Sample Sub-sampling, Homogenization and Compositing / NV08-229.

15.6 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachments

Table 1. Specific Extraction Conditions for Various Determinative Methods
Table 2. Surrogate and Spike Amounts

Table 1
Specific Extraction Conditions for Various Determinative Methods

Determinative Method	Sample Weight (g)	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)[a]	Final extract vial size(mL)
8015B/C/D	25	As received	none	none	-	1.0	1.0	20.0
FLPRO	25	As received	none	none	-	2.0	2.0	4.0
EPH (NC & MA)	10	As received	none	none	-	1.0	1.0	4.0
8081A/8081B	10	5-9	none	Hexane	Hexane	10.0	10.0	20.0
8082/8082A	10	5-9	none	Hexane	Hexane	10.0	10.0	20.0
8270C/8270D[b,c]	10	<2	>11	none	-	-	1.0	4.0

[a] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced as low as 1.0 mL to achieve lower detection limits.
[b] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.
[c] Extraction pH sequence may be reversed to better separate acid and neutral waste components. Excessive pH adjustments may result in the loss of some analytes.

Table 2
Surrogate and Spike Amounts

Method	Surrogate	Spike
8081A/8081B	1.0 mL of Pest/PCB surrogate	1.0 mL Pest Spike; 1.0 mL Chlordane/Toxaphene
8082/8082A	1.0 mL of Pest/PCB surrogate	1.0 mL of Pest/PCB spike
8270C/8270D	1.0 mL of BNA surrogate	500 µL of BNA spike
8310	1.0 mL of HPLC surrogate	1.0 mL of HPLC spike
8015B/C/D	1.0 mL of o-Terphenyl surrogate	1.0 mL DRO spike
CT ETPH	1.0 mL of C_{35} surrogate	2.0 mL of FL/WI spike
FL PRO	2.0 mL of o-Terphenyl and 2 mL of C_{35} surrogates.	2.0 mL of FL/WI spike
MA EPH	1 mL MA surr., 1 mL Fractionation surr.	1 mL of Mass Spike
OA-2	1 mL of o-Terphenyl surrogate	1 mL DRO spike
TN EPH	1 mL of o-Terphenyl surrogate	1 mL TN EPH spike
OK DRO	1.0 mL of C_{35} surrogate	2.0 mL of FL/WI Spike
See individual SOPs for information on compounds, concentrations, and how to make the surrogate and spike solutions. Also, see current Document PF-1, Prep Lab Summary Chart.		

18.0 Review History

- Revision 0, dated 2/29/2008, new Soxtherm equipment
- Revision 1, dated 20 June 2008
  - Replace “should” where appropriate.
  - Insert holding time and preservation information.
  - Update temperature range for KD.
- Revision 2, dated 29 June 2010
  - Removal of Method 8141.
  - Addition of Section 14.2, QAF-45.
  - Deletion of unnecessary documentation and data review steps in Section 11.
  - Change in duration of boiling and extraction times, solvent reduction B setting.
  - Addition of Acetone rinse preparation depending upon determinative method.
- Revision 3, dated 30 April 2012
  - Organizational changes.
  - Change nominal sample mass to 10 grams.
  - Remove KD procedure except for solvent exchange; note how concentration is obtained by instrument/equipment.
  - Remove requirement for batches of 10 in OK and WY.
  - Provide information on how to store the extracts if unable to complete concentration the same shift as extraction.
- Revision 4, dated 31 January 2014
  - Organizational changes.
  - MA added as a state requiring LCSDs. WV no longer requires LCSDs.

Title: MICROWAVE EXTRACTION SW-846 METHOD 3546

Approvals (Signature/Date)			
Jacolby Robinson	12/4/13 Date	Johnny Davis	12/3/13 Date
Department Supervisor		Health & Safety Manager / Coordinator	
Steve Miller	12/9/13 Date	Michael H. Dunn	11/14/13 Date
Quality Assurance Manager		Technical Director	

1.0 Scope and Application

1.1 This method is a procedure for extracting water insoluble or slightly water soluble organic compounds from soils, clays, sediments, sludges, and solid wastes. This method is only applicable to solid samples with small particle sizes.

1.2 This method is applicable to the extraction of semivolatile organic compounds, organophosphorus pesticides, organochlorine pesticides, chlorinated herbicides, phenoxyacid herbicides, substituted phenols, and PCBs. This method may also be applicable for the extraction of additional target analytes, provided that the analyst demonstrates adequate performance for the intended application.

1.3 This method is also applicable to classes of analytes, to fuel types, and to petroleum fractions.

NOTE: Mention of the analyses of other fuel types and petroleum fractions does *not* imply a regulatory requirement for such analyses, using this or any other method.

1.4 Use of this method is restricted to use by, or under supervision of, appropriately experienced and trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.5 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 Samples are prepared for extraction by grinding them to a powder and loading them into the extraction vessel. The total mass of material to be prepared depends on the specifications of the determinative method and the sensitivity needed for the analysis, but an amount of 2 - 20 g of material is usually necessary and can be accommodated by this extraction procedure.

2.2 This method has been validated using a solvent mixture of Hexane and Acetone (1:1), Methylene chloride and Acetone (1:1), and Methylene chloride only. This solvent system or other solvent systems may be employed, provided that adequate performance is demonstrated for the analytes of interest.

2.3 The extraction vessel containing the sample and solvent system is heated to the extraction temperature and extracted for 10 minutes (or as recommended by the instrument manufacturer).

2.4 The appropriate solvent system is added to the vessel and sealed.

2.5 The mixture is allowed to cool. The vessel is opened and the contents are filtered. The solid material is rinsed and the various solvent fractions are combined.

2.6 The extract may be concentrated, if necessary, and, as needed, exchanged into a solvent compatible with the cleanup or determinative procedure to be employed.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each determinative method to be used for specific guidance on quality control procedures.

4.2 If necessary, cleanup procedures may be employed. See the determinative method.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- The use of organic solvents, elevated temperatures, and high pressures in this method present potential safety concerns in the laboratory. Common sense laboratory practices can be employed to minimize these concerns. The sections to follow describe additional steps that should be taken.
- The extraction vessels are at elevated temperatures and pressure after the extraction stage. Allow the vessels to cool before opening (the use of a water bath is recommended for this purpose) and always monitor the temperature and pressure by reconnecting the control vessel to the apparatus prior to opening the vessels.
- During the heating step, some solvent vapors may escape through the vessel liner/seal cover. Follow the manufacturer's directions regarding the vessel assembly and instrument setup to prevent release of solvent vapors to the laboratory atmosphere.
- The instrument may contain flammable vapor sensors and should be operated with all covers in place and doors closed to ensure proper operation of the sensors. If so equipped, follow the manufacturer's directions regarding replacement of extraction vessel seals when frequent vapor leaks are detected.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Methylene chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
1 – Always add acid to water to prevent violent reaction.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Milestone Ethos EX Microwave-Assisted Extractor: Microwave solvent extraction apparatus capable of sensing the temperature to within ± 2.5 EC and automatically adjusting the microwave field output power within 2 seconds of sensing. Temperature sensors are accurate to ± 2 EC. Temperature feedback control provides the primary performance mechanism for this method.
  - Pressure rotor: supports and rotates pressure reactors during microwave extraction
  - Pressure reactor: hard case shell with screw-on pressure cap in which extraction vessel is placed. Includes pressure relief valve activated when pressure exceeds 30 bar.
  - Glass insert: Disposable glass thimble fits inside extraction vessel. Recommended container for sample and reagents/solvents as alternative to direct sample contact with extraction vessel. Minimizes cleaning, reduces carryover, prevents active site development and extends lifetime of extraction vessel.
  - Extraction vessel cover: Teflon™ cap designed to seal snugly against the interior of the extraction vessel. Cover requires 'flaring' initially and as needed to ensure snug fit with wall of extraction vessel.

  - Optimize the conditions, as needed, according to the manufacturer's instructions. In general, the pressure is not a critical parameter, since it is a result of the solvent system vapor pressure at the elevated temperature.
  - Once established, the same procedure is used for all samples extracted for the same type of analysis.
- Analytical balance; capable of accurately weighing 15 ± 0.1 g. Balances are calibrated per SOP Balances / NV08-213.

6.2 Apparatus, Reagents, Standards, and Supplies

- Extraction vessel-Teflon™ thimble (~ 75 ml volume) to contain sample and reagents/solvents during extraction.
- Apparatus for grinding, capable of reducing particle size to < 1 mm.
- Apparatus for separating sample from solvent extract.
- Glass, Teflon™, or metal funnels.
- Filter paper.
- Pasteur pipettes.
- Filter paper, Whatman No. 41 or equivalent.
- Glass wool; pesticide grade or equivalent.
- Aluminum foil; clean, unused.
- Gas tight syringe, 1.0 mL volume and 0.5 mL volume.
- Stainless steel spatula or scoopula.
- Erlenmeyers flasks.
- Brinkman 50 mL solvent dispenser.
- 4-mL amber screw-top vials and 20-mL scintillation vials.
- Weigh boats.

7.0 Reagents and Standards

7.1 Reagent water, analyte-free.

7.2 Drying agents:

7.2.1 Sodium sulfate: Anhydrous powdered reagent grade, solvent rinsed. Commercially cleaned is acceptable.

7.3 Methylene chloride, chromatography residue grade or equivalent.

7.4 Extraction/exchange solvents. All solvents, Hexane, Acetone, must be pesticide quality or equivalent. No single solvent is universally applicable to all analyte groups. Whatever solvent

system is employed, *including* those specifically listed in this method, the analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest.

7.5 Sand, Ottawa or equivalent.

8.0 Sample Collection, Preservation, Shipment and Storage

See the determinative method.

9.0 Quality Control

9.1 Sample QC: Samples are prepared and analyzed in batches. A batch is defined as environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A batch is composed of one to 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing/analyzing of the first and last sample in the batch to be 24 hours.

- The method blank, Sodium sulfate or Ottawa sand, is analyzed to insure the preparation process and instrument are contamination free. The preparation process and instrument must be considered contaminant-free prior to analyzing any samples.
- An LCS is Sodium sulfate or Ottawa sand to which target compounds at known concentrations are spiked to determine if the preparation and/or analytical process are in control.
- Matrix spike compounds at known concentrations are spiked into a sample and duplicated to determine the matrix effects of the sample on recovery of the compounds.
- Batch QC

Quality Controls	Frequency
Method Blank (MB)	1 in 20 or fewer samples
Laboratory Control Sample (LCS)[1]	1 in 20 or fewer samples
Matrix Spike (MS)[2]	1 in 20 or fewer samples
MS Duplicate (MSD)	1 in 20 or fewer samples
Surrogates	Every sample[3]
[1]LCSD is only required for AZ, MA, TX, WV samples or when requested by the client/project/contract.	
[2]The sample selection for MS/MSD is randomly selected, unless specifically requested by a client or predetermined by the extraction lab.	
[3]Analytical and QC samples (MB, LCS, MS/MSD).	

9.2 Instrument QC

See the determinative method.

10.0 Procedure

10.1 Sample Preparation: The sample preparation steps vary with the type of sample to be extracted, as described below. Where practical, samples are air-dried and ground to a fine powder before extraction.

10.1.1 **Sediment/soil samples:** Decant and discard any water layer on a sediment sample. Discard any foreign objects such as sticks, leaves, and rocks. Mix the sample thoroughly, especially composited samples. When practical, air dry the sample at room temperature for 48 hrs in a glass tray or on Hexane-rinsed aluminum foil. Alternatively, mix the sample with an equal volume of anhydrous Sodium sulfate or pelletized diatomaceous earth until a free-flowing powder is obtained.

CAUTION: Dry, finely-ground soil/sediment allows the best extraction efficiency for nonvolatile, nonpolar organics, e.g., 4,4'-DDT, PCBs, etc. Air-drying may not be appropriate for the analysis of the more volatile organochlorine pesticides (e.g., the

BHCs) or the more volatile of the semivolatile organics because of losses during the drying process. Oven-drying during this step is not recommended for any analytes.

CAUTION: Drying should always be performed in a hood, to avoid contamination of the laboratory.

10.1.2 **Waste samples:** *This extraction procedure is for solids only. For waste samples, see SOP 3580 / NV03-106.*

10.2 Sample Grinding

10.2.1 Dry sediment/soil and dry waste samples amenable to grinding: Grind or otherwise reduce the particle size of the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Disassemble grinder between samples, according to manufacturer's instructions, and decontaminate with soap and water, followed by Acetone and Hexane rinses.

10.2.2 Gummy, fibrous, or oily materials not amenable to grinding: Cut, shred, or otherwise reduce in size these samples to allow mixing and maximum exposure of the sample surfaces for the extraction. The analyst may add anhydrous Sodium sulfate, pelletized diatomaceous earth, sand, or other clean, dry reagents to the sample to make it more amenable to grinding.

10.3 Sample extraction

1	Ensure that walls of pressure reactor, extraction vessel, glass inserts, caps, and covers are all clean and dry.
2	Place magnetic stir bar inside glass insert. Identify the glass inserts for use as extraction batch QC (MB, LCS, LCSD) as required.
3	Homogenize and sub-sample solid samples according to laboratory SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
4	Weigh out nominally 15 ± 0.1 g of sample into each glass insert.
5	For the MB/LCS/LCSD aliquots, add approximately 15 g Ottawa sand to the appropriate glass inserts.
6	Mix contents of glass inserts using a spatula. It is recommended that glass inserts be placed inside extraction vessels prior to mixing to provide structural support that helps to reduce breakage of glass inserts. Alternatively, samples and QC can be covered with extraction vessel covers and mixed manually or vortexed on a small orbital shaker.
7	Add the appropriate surrogate and analyte spike volumes to the contents of the extraction vessels
8	Immediately add 30 mL of appropriate solvent to each sample and QC aliquot a. For 8270 extractions, use 1:1 Hexane/Acetone. b. For 8082, use 1:1 Hexane/Acetone. c. For 8015, use Methylene chloride. d. For 8081, use Hexane.
9	Add flared extraction vessel covers to each extraction vessel containing sample and QC aliquots. a. It is important that each cover fits snugly to ensure a proper seal. The cover should not slide easily or loosely inside the extraction vessel, but should require some finger pressure to insert firmly. Whole hand pressure (or tools) are not required and should not be utilized. b. A cover flaring tool is provided by Milestone and should be used as needed. c. For the representative sample that will be used as the temperature control reference, add the Thermowell liner into the extraction vessel cover.

10	Place each extraction vessel into a pressure reactor. Screw on the pressure cap/safety valve lid. The pressure cap should be hand tightened until the sealing valve tip (white) is flush with the top of the cap. For the sample with the Thermowell liner, add the protection foil and appropriate safety lid so that the ATC temperature sensor can be inserted into the extraction vessel.
11	Place all the extraction vessels into the rotor so that the pressure-release valve is facing outside of the rotor on the outside ring and inside toward the center on the inside ring.
12	Place the rotor in the microwave oven and insert the ATC temperature sensor into the reference vessel. Note: the temperature sensor is fragile. Use caution when handling.
13	Close the microwave oven and start the appropriate extraction profile For 8270/8081/8082, use a 10 minute ramp to 110 ^{o}C, hold for 10 minutes, followed by 15 minute cool-down. For 8015, use a 10 minute ramp to 110^{o}C, hold for 10 minutes, followed by 15 minutes cool-down.
14	After the extraction period and cool-down, pressure reactors should be at ambient temperature prior to removal from the rotor and opening.
15	Once ambient temperature is achieved (not to exceed 40 degrees C) remove pressure reactor from the rotor, and remove pressure cap and reaction vessel. a. Set up clean dry filter funnels with 5-10 g Sodium sulfate in filter paper or glass wool (for 8270). b. Remove the extraction vessel cover and decant the extract solvent through Sodium sulfate. c. Remove and rinse contents of glass insert with ~ 8 mL of fresh solvent into the Sodium sulfate, and then likewise rinse the surfaces of the insert, extraction vessel, and cover with ~8 mL of solvent. Rinse the Sodium sulfate bed with an additional 8 mL of solvent. d. Recover these solvent rinses as part of the extract.
16	Clean and concentrate extract as needed.
17	Discard the glass insert and solvent-rinse the pressure reactors, extraction vessels, caps, covers, liners, and probes to clean. Allow to air dry prior to reuse. If glass inserts are not used, more rigorous cleaning using soap and water may be required, per laboratory SOP for cleaning of reusable glassware/Teflon™ containers.

10.4 Sample Concentration by Kuderna-Danish Technique

1	Assemble a K-D concentrator by attaching a 10-mL concentrator tube to an evaporation flask.
2	Add one or two clean boiling chips to the KD flask. Quantitatively transfer extract to the KD. Rinse the flask with approximately 10-20 mL solvent and transfer to the KD. Attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of Methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15 – 20^{o}C above the boiling point of the solvent; see Section 7.4) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the apparatus and the water temperature, as required, to complete the concentration in 10 - 20 minutes. At the proper rate of distillation the balls of the column actively chatters, but the chambers do not flood. When the apparent volume of liquid reaches about 10 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for

	at least 10 minutes.
3	If a solvent exchange is required (as indicated in Table 1), remove the Snyder column and KD, and using nitrogen blow-down technique, reduce the volume to about 2 mL. Add about 5 mL of the exchange solvent, a new boiling chip, and attach the 3-chamber micro-Snyder column to the concentrator tube. Concentrate the extract, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches about 1-2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.
4	Remove the Snyder column and rinse it and its lower joints into the concentrator tube with 1 - 2 mL of Methylene chloride or exchange solvent. The extract may be further concentrated by using the nitrogen blowdown technique or adjusted in a Class A volumetric to 1.0 - 10.0 mL with the solvent last used.
5	If further concentration is indicated in Table 1, use the nitrogen blow-down technique to adjust the extract to the final volume required.
Nitrogen blow-down technique	
6	Place the concentrator tube in a warm bath (35°C) and evaporate the solvent to the just below final volume indicated in Table 1, using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).
7	The internal wall of the tube must be rinsed several times with concentrated extract, Methylene chloride or appropriate solvent during the operation. During evaporation, the tube must be positioned to avoid water condensation (i. e., the solvent level should be below the level of the water bath). Under normal procedures, the extract must not be allowed to become < 0.5 mL.
8	The sample is then transferred to a Class A volumetric flask and adjusted to the final volume by using the rinsate from the tube.
9	Transfer the sample to a vial with a PTFE-lined cap and label appropriately. The extract may now be analyzed for the target analyses using the appropriate determinative technique(s). Store refrigerated at 0-6 C.

11.0 Calculations / Data Reduction / Documentation / Review

See the determinative method.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure which is in accordance with the TestAmerica Quality Assurance Manual and SOP MDL / SA08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: See the Quality Assurance Manual and SOP Training / SA08-199 for information on how to accomplish this demonstration, initially and on an ongoing basis.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the Quality Assurance Manual and SOP Waste Disposal / NV10-83 and USDA Disposal of Soils/ NV10-162.

14.2 Wastestreams Produced by the Method:

- Soil is disposed in the trash receptacle after standing in the fume hood overnight.

15.0 References / Cross References

15.1 Method 3546, SW846, Revision 0, February 2007.

15.2 TestAmerica Nashville's Quality Assurance Manual.

15.3 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.4 SOPs:

- Massachusetts Method for the Determination of Extractable Petroleum Hydrocarbons, MADEP-EPH / NV04-168.
- Procedure for the Determination of Method Detection Limits, MDL / NV08-202.
- Training Procedures for Environmental Technical Staff, Training / NV08-199.
- Waste Disposal / NV10-83
- Disposal of Soils Regulated by USDA, USDA Disposal of Soils / NV10-162.
- Balance Calibration, Balances / NV08-213.
- Sample Subsampling, Homogenization and Compositing / NV08-229.
- 3580 / NV03-106.

15.6 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachments

Table 1. Specific Extraction Conditions for Various Determinative Methods
Table 2. Surrogate and Spike Amounts

Table 1
Specific Extraction Conditions for Various Determinative Methods

Determinative Method	Sample Weight (g)	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)[a]	Final extract vial size(mL)
8015 -	15	As received	none	none	-	1.0	1.0	2.0
FLPRO	15	As received	none	none	-	2.0	2.0	2.0
MA EPH	10	As received	none	none	-	1.0	1.0	2.0
8081	15	As received	none	none	none	5.0	5.0	20.0
8082	15	As received	none	Hexane	Hexane	5.0	5.0	20.0
8270[b]	15	As received	None	Methylene Chloride	-Methylene Chloride	-	1.0	2.0

[a] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced as low as 1.0 mL to achieve lower detection limits.
[b] The specificity of GC/MS may make cleanup of the extracts unnecessary

Table 2
Surrogate and Spike Amounts

Method	Surrogate	Spike
8081	1.0 mL of Pest/PCB surrogate	1.0 mL Pest Spike; 1.0 mL Chlordane/Toxaphene
8082	1.0 mL of Pest/PCB surrogate	1.0 mL of Pest/PCB spike
8270	1.0 mL of BNA surrogate	500 µL of BNA spike
8310	1.0 mL of HPLC surrogate	1.0 mL of HPLC spike
8015	1.0 mL of o-terphenyl surrogate	1.0 mL DRO spike
CT ETPH	1.0 mL of C_{35} surrogate	2.0 mL of FL/WI spike
FL PRO	2.0 mL of o-terphenyl and 2 mL of C_{35} surrogates.	2.0 mL of FL/WI spike
MA EPH	1 mL MA surr., 1 mL Fractionation surr.	1 mL of Mass Spike
OA-2	1 mL of o-terphenyl surrogate	1 mL DRO spike
TN EPH	1 mL of o-terphenyl surrogate	1 mL TN EPH spike
OK DRO	1.0 mL of C_{35} surrogate	2.0 mL of FL/WI Spike
See individual SOPs for information on compounds, concentrations, and how to make the surrogate and spike solutions. Also, see current Document PF-1, Prep Lab Summary Chart.		

18.0 Review History

None.

Title: ULTRASONIC EXTRACTION
SW-846 METHOD 3550B/C

Approvals (Signature/Date)

Jacolby Robinson 5/29/13	Johnny Davis 6/21/13
Jacolby Robinson Date	Johnny Davis Date
Department Supervisor	Health & Safety Manager / Coordinator
Michael H. Dunn 7/3/13	Organic Extractions Department Manager
Michael H. Dunn Date	
Technical Director	
Quality Assurance Manager	

1.0 Scope and Application

1.1 Analyte, Matrices: This method describes a procedure for extracting semi-volatile organic compounds from solids such as soils, shredder fluffs, sludges, and wastes.

1.2 Reporting Limits: See the determinative method, 8015/NV05-31, 8081/NV04-53, 8082/NV04-105, 8270/NV04-22, and TestAmerica Nashville's Control Limits Manual (CLM).

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

A measured weight of sample, 25-30 grams, is mixed with anhydrous Sodium sulfate to form a free-flowing powder and serially extracted with Methylene chloride using ultrasonic extraction. The extract is dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method to be used.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: Use the hoods to evacuate solvent vapors from the building and dispose of solvent wastes appropriately.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Causes coughing, dizziness, dullness, and headache.
Methylene chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. Absorbable through skin.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure causes lightheadedness, nausea, headache, and blurred vision. Vapors cause irritation to the skin and eyes.
n-Pentane	Flammable Irritant	600 ppm TWA 120 ppm TWA 350 mg/m^3 TWA 1500 ppm IDLH	Extremely flammable; vapor may cause flash fire. Breathing vapors may cause drowsiness and dizziness. Causes eye and skin irritation. Repeated exposure may cause skin dryness or cracking. Aspiration hazard if swallowed. Targets central nervous system, respiratory system, eyes, skin.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Ultrasonic Liquid Processor, with a minimum power wattage of 300 watts with pulsing capability. This is a horn-type device equipped with a titanium tip, or a device that will give equivalent performance.
  - ¾" horn for low-concentration method.
  - Settings: 100% amplitude, 1.5 seconds on, 1.5 seconds off, for three minutes.
- Kuderna-Danish (K-D) apparatus.
  - Concentrator tube. 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.
  - Evaporation flask, 250 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.
  - Snyder column, Three-ball macro (Kontes K-503000-0121 or equivalent).
  - Snyder column, 3-chamber micro (Kontes K-569001-0219 or equivalent).
  - Clamps
- Nitrogen Evaporator: N-Evap Model #116 by Organomation, or equivalent.
- Balance, top-loading, capable of accurately weighing to the nearest 0.01 g.

6.2 Supplies

- Filter paper, Whatman No. 41 or equivalent. DO NOT USE FOR 8270.
- Boiling chips, solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).
- Water bath, heated, capable of temperature control (± 5°C). The bath is used in a hood.
- Vials, glass, with Polytetrafluoroethylene (PTFE)-lined screw caps.
- Spatula, stainless steel or wooden tongue depressors.
- Funnel, glass, Teflon™ or metal. Use a plug of glass wool in a funnel and fill with a little Sodium sulfate. Rinse funnel, glass wool, and Sodium sulfate with about 5-10 mL of Methylene chloride before use.
- Syringe, 1.0 mL.
- Beaker, thick-walled, glass or Teflon™.
- Volumetric flasks, Class A.
- Nitrogen, compressed gas, high purity.

7.0 Reagents and Standards

7.1 Reagent grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of

the America Chemical Society, where such specifications are available. Other grades may be used, however, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents are stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 **Reagent water**, analyte-free.

7.3 **Sodium sulfate**, granular, anhydrous. Purify by heating to about 400°C for about 4 hours in a shallow tray or pre-cleaned with Methylene chloride. Store in a sealed, glass container. A commercially cleaned product is acceptable.

7.4 **Extraction/exchange solvents**: All solvents are pesticide quality or equivalent and from commercial sources: **Methylene chloride, Hexane**, **Acetonitrile, Pentane.**

7.5 **Acetone**, commercial source.

7.6 **Spiking Solutions**: See Table 2. In addition, refer to the determinative method and LIMS for additional information. These may be purchased ready to use or prepared in the analysis department.

7.7 See SOP Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214 for shelf-life and storage requirements for reagents and standards. Also, refer LIMS.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Soil/Solid	Glass, 4 oz.Teflon™-lined cap	25-30 g	0-6°C	14 days from collection until extraction, 40 days from extraction until analysis	SW-846 Chapters 2 and 4

9.0 Quality Control

Refer to the quality control section of TestAmerica Nashville's QA Manual for specific quality control (QC) policies. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

QC Check	Frequency
Method Blank	One per batch
Laboratory Control Sample (LCS)	One per batch
Matrix Spike	One per batch
Matrix Spike Duplicate	One per batch

- **Method blank:** The laboratory prepares and analyzes a method blank (Sodium sulfate, 25-30 grams) with each batch not to exceed 20 samples.
- A **Laboratory Control Sample (LCS),** 25-30 g Sodium sulfate, is spiked with a source different from the calibration standard, is analyzed with every batch not to exceed 20 samples. Use the same sample preparations, analytical methods and QA/QC procedures employed for the test samples.
- **Matrix Spike/Matrix Spike Duplicate:** Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect. Unless otherwise specified by the data user, the MS/MSD procedure is required. See SOP Sample Homogenization, Subsampling, and Compositing/NV08-229.
  - The laboratory adds a known amount of each analyte to be reported per batch of the

routine samples. In each case, the MS/MSD aliquot must be a duplicate of the aliquot (25-30 g) used for sample analysis and added **prior** to sample extraction.

10.0 Procedure

10.1 Sample Preparation

Matrix	Sample Size
Soil	25 g DRO; 30 g Other Methods
Fluff	25 g

1	Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.
2	Dry waste samples amenable to grinding: Grind or otherwise subdivide the waste so that it either passes through a 1 mm sieve or can be extruded through a 1 mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 100 g after grinding.
3	Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction.
4	See SOP Sample Homogenization, Subsampling, and Compositing / NV08-229 (not applicable to fluffs).

10.2 Equipment Set-up and Tuning

- It is critical that the method be followed explicitly to achieve the maximum extraction efficiency. This procedure requires that:
  - The extraction device must have a minimum of 300 watts of power and be equipped with appropriate disrupter horn.
  - The horn must be properly maintained, including tuning according to the manufacturer's instructions prior to use, and inspection of the horn tip for excessive wear.
  - The extraction is performed in the specified pulse mode, and the horn tip is positioned just below the surface of the solvent yet above the sample.
  - Very active mixing of the sample and the solvent must occur when the ultrasonic pulse is activated.
- To tune the sonicator:

1	Power on the sonicator.
2	Set amplitude to 80%.
3	Press “tune” button and proceed to adjust the “tuner knob” clockwise or counterclockwise for a minimum “output watts.” A minimum is usually less than 35 which is displayed on the power monitor bar graph.
4	Repeat Step 3 if a minimum is not reached during the first attempt. **Note:** Do not tune sonicator when sonicator tip is in contact with a sample, solvent, or body part. **Note:** If an overload occurs during Step 3, power off sonicator and repeat Steps 1-3. **Note:** Do not attempt to tune the sonicators that are “self-tuning.”
5	Record the tuning event in the tune log.

10.3 Sample Extraction (non-fluff)

1	Weigh 25-30 g of sample into a 400 mL, thick-walled glass or Teflon™ beaker by taking portions of a well mixed sample. More than 25-30g may need to be used based on the

	samples dry weight. Record the weight to the nearest 0.1 g. See Document PF-1, Prep Lab Summary Chart, for specific gram amounts for each method.
2	Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture are mixed with anhydrous Sodium sulfate to obtain a free-flowing powder. Use as little Sodium sulfate as possible.
3	Add the surrogate standard solution to all samples, spiked samples and QC samples. See Table 2 for information on surrogate solutions and amounts. For the blank and LCS, use Sodium sulfate for the solid matrix, 25-30 g. For the LCS, add the amount of standard solution noted in Table 2.
4	For the sample in each batch selected for spiking, add the matrix spiking solution. See Table 2 for information on spike solutions and amounts. Add surrogates and spike before adding solvent.
5	Immediately add about 100 mL Methylene chloride or enough to adequately cover the sample by about an inch.
6	Place the bottom surface of the tip of the ¾" disrupter horn about ½ inch below the surface of the solvent, but above the sediment layer.
7	Extract ultrasonically for **3** minutes, with output control knob set at 80% amplitude and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent - duty cycle knob set at 50%, 1.5 seconds on and 1.5 seconds off (energy on 50% of time and off 50% of time). Do not use microtip probe.
8	Decant the extract and filter it using folded filter paper or a small amount of glass wool in a funnel into a clean Erlenmeyer flask. Rinse the funnel and contents with about 20 mL Methylene chloride.
9	Repeat the extraction **two** times with two additional 100 mL portions of solvent or enough to cover the sample. Decant off the solvent after each ultrasonic extraction into the Erlenmeyer flask. After the final ultrasonic extraction, pour the entire sample into the funnel and rinse the beaker with about 20 – 30 mL of Methylene chloride and add it to the funnel to complete the quantitative transfer. Let the funnel drain until all visible solvent is removed from the funnel, do not attempt to dry.
10	If samples are not concentrated the day they are extracted, then samples must be sealed. Method 8081, 8270, and 8310 samples must be sealed and stored at 0-6°C in the dark until concentration. Proceed to concentration.

10.4 Sample Concentration by Kuderna-Danish Technique

1	Assemble a K-D concentrator by attaching a 10-mL concentrator tube to an evaporation flask.
2	Add one or two clean boiling chips to the KD flask. Quantitatively transfer extract to the KD. Rinse the flask with approximately 10-20 mL solvent and transfer to the KD. Attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of Methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15 – 20°C above the boiling point of the solvent; see Section 7.4) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the apparatus and the water temperature, as required, to complete the concentration in 10 - 20 minutes. At the proper rate of distillation the balls of the column actively chatters, but the chambers do not flood. When the apparent volume of liquid reaches about 10 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.
3	If a solvent exchange is required (as indicated in Table 1), remove the Snyder column and KD, and using nitrogen blow-down technique, reduce the volume to about 2 mL. Add about 5 mL of the exchange solvent, a new boiling chip, and attach the 3-chamber micro-Snyder

	column to the concentrator tube. Concentrate the extract, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches about 1-2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.
4	Remove the Snyder column and rinse it and its lower joints into the concentrator tube with 1 - 2 mL of Methylene chloride or exchange solvent. The extract may be further concentrated by using the nitrogen blowdown technique or adjusted in a Class A volumetric to 1.0 - 10.0 mL with the solvent last used.
5	If further concentration is indicated in Table 1, use the nitrogen blow-down technique to adjust the extract to the final volume required.
Nitrogen blow-down technique	
6	Place the concentrator tube in a warm bath (35°C) and evaporate the solvent to the just below final volume indicated in Table 1, using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).
7	The internal wall of the tube must be rinsed several times with concentrated extract, Methylene chloride or appropriate solvent during the operation. During evaporation, the tube must be positioned to avoid water condensation (i. e., the solvent level should be below the level of the water bath). Under normal procedures, the extract must not be allowed to become < 0.5 mL.
8	The sample is then transferred to a Class A volumetric flask and adjusted to the final volume by using the rinsate from the tube.
9	Transfer the sample to a vial with a PTFE-lined cap and label appropriately. The extract may now be analyzed for the target analyses using the appropriate determinative technique(s). Store refrigerated at 0-6 C.

11.0 Calculations / Data Reduction

Enter the sample weight and final extract volume in LIMS.

12.0 Method Performance

12.1 Method Detection Limits (MDLs): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes must be stored, managed, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Used Sodium sulfate and glass wool or filter paper and sample contaminated with Methylene chloride from the extract drying step are placed in a hood overnight and then discarded in the trash.
- Assorted flammable solvent waste from various rinses is collected in flammable solvent waste containers and transferred to waste disposal and placed in the flammable solvent drum.

15.0 References / Cross-References

15.1 SW-846 Method 3550B, Update III, Revision 2, December 1996, and **Method 3550C**, Update IV, Revision 3, February 2007.

15.2 TestAmerica Nashville's Quality Assurance Manual.

15.3 Corporate Environmental Health and Safety Manual (CW-E-M-001)

15.4 SOPs: Waste Disposal / NV10-83, 8270 / NV04-22, 8082 / NV04-105, 8081 / NV04-16, 8082 / NV04-105, 8015 / NV05-31, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213, Sample Homogenization, Sub-sampling and Compositing / NV08-229.

15.5 Controlled Documents: PF-1, Prep Lab Summary Chart, QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

16.0 Method Modifications

Item	Modification
1	See the attachments for extraction procedures for fluffs and wipes.

17.0 Attachments

17.1

Table 1. Specific Extraction Conditions for Various Determinative Methods

Determinative Method	Initial Extraction pH	Exchange Solvent Req. for Analysis[a]	Exchange Solvent Required for Cleanup	Volume of Extract Required for Cleanup (mL)	Final Extract Volume for Analysis (mL)[a]
8081	As received	Hexane	Hexane	10	10[b]
8082	As received	Hexane	Hexane	10	10[b]
8270	As received	None	-	-	1.0
8015	As received	None	-	-	1.0
[a]For TRPH on shredder fluff, see Section 17.3, 17.4.					

Determinative Method	Initial Extraction pH	Exchange Solvent Req. for Analysis[a]	Exchange Solvent Required for Cleanup	Volume of Extract Required for Cleanup (mL)	Final Extract Volume for Analysis (mL)[a]
[b]For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.					

17.2

Table 2. Surrogate and Matrix Spike/LCS Amounts

Determinative Method	Surrogate Spike	MS/LCS Spike Amount
8081	1.0 mL of Pest/PCB surrogate	1.0 mL Pest spike, 1.0 mL Toxaphene/Total Chlordane spike
8082	1.0 mL of Pest/PCB surrogate	1.0 mL PCB spike
8270	1.0 mL of BNA surrogate	500 µL of BNA spike
8015	1.0 mL of o-terphenyl surrogate	1.0 mL DRO spike
See individual SOPs for information on compounds, concentrations, and how to make the surrogate and spike solutions. Also, see the Prep Summary Chart for additional spike and surrogate information.		

17.3 Procedure summary for the extraction of Fluffs for PCBs: Place 50.0 grams or the entire contents of sample in a wide-mouth jar and add surrogate. Add 125 mL of Hexane and cap. Place in a mechanical shaker for 30 minutes. Place in the ultrasonic water bath for 30 minutes. Pipet about 10 mL into a vial and transfer to the analytical group for clean-up and analysis.

17.4 Procedure summary for the extraction of Fluffs for TRPH: Place 25 g in a 125-mL, wide-mouth, glass container. Add 100 mL of Pentane; cap and place in a mechanical shaker for 30 minutes, then in an ultrasonic water bath for 30 minutes. The extract is ready for analysis by GC-FID (SOP 8015 / NV05-31).

17.5 Procedure summary for the extraction of Wipes for PCBs: Add 1.0 mL surrogate. Add 9 mL hexane to sample container. Seal and place in mechanical shaker for 30 minutes. Place in the ultrasonic water bath for 30 minutes. Reduce the volume to less than 10 mL by blowing down with nitrogen if needed. Bring to 10.0 mL final volume with hexane. Transfer to the analytical group for clean-up and analysis.

18.0 Revision History

- Revision 11, dated 25 September 2008
  - Integration for TestAmerica and STL operations.
- Revision 12, dated 31 August 2009
  - Addition of OH VAP requirements.
- Revision 13, dated 29 June 2009
  - Addition of spiking of clay-like samples
  - Addition of PF-1, QAF-45, SOP Sample Homogenization, Subsampling and Compositing / NV08-229.
  - Addition of Section 14.2.
- Revision 14, dated 31 May 2011
  - Organizational changes in signature block.
  - Changed order of spiking back to after adding drying agent per EPA August 5, 2010 memo.

  - Addition of Pentane and Nitrogen.
  - Addition of instructions for shredder fluff extraction for TRPH.
- Revision 15, dated 30 April 2012
  - Organizational changes.
  - Add provision of holding the extracts in the dark if unable to complete the sample concentration step during the same shift as when extracted.
- Revision 16, dated 31 July 2013
  - Organizational changes.
  - Addition of Amendment 15a.
  - Added clarity on supply specification, cleaned Sodium sulfate, and non-fluff sample extraction,

Title: WASTE DILUTION
SW-846 METHOD 3580A

Approvals (Signature/Date)			
	9/26/13		
Cory Spry Department Manager	Date		
	12/30/13		1/7/14
Jacolby Robinson Department Supervisor	Date	Johnny Davis Health & Safety Manager / Coordinator Department Manager	Date
	12/26/13		11/11/13
Steve C. Miller Quality Assurance Manager	Date	Michael H. Dunn Technical Director	Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method describes a solvent dilution of a non-aqueous waste sample prior to cleanup and/or analysis. It is designed for wastes that may contain organic chemicals that are soluble in the dilution solvent.

1.2 Reporting Limits: Results are dependent on the volume used, degree of contamination, ability to concentrate, and the sensitivity of the determinative method.

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

One gram of sample is weighed into a 10-mL volumetric flask, and the sample is diluted to 10.0 mL with an appropriate solvent. Diluted samples are injected into the GC or GC/MS for analysis.

3.0 Definitions

See Appendix 5 of TestAmerica Nashville's QA Manual for laboratory definitions. Also, refer to Controlled Document, QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

4.0 Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method or reagent blanks.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This method may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: Use the hoods to evacuate solvent vapors from the building and dispose of solvent wastes appropriately.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and causes skin to become dry and cracked. Skin absorption can occur; symptoms parallel inhalation exposure. Irritant to the eyes.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Balance, capable of weighing 100 g to the nearest 0.01 g.

6.2 Supplies

- Glass scintillation vials: About 10-20 mL, with Teflon™ lined screw-cap, or equivalent.
- Spatula, metal, or equivalent.
- Disposable pipettes: Pasteur.
- Pyrex glass wool.
- Volumetric flasks, Class A, 10 mL.

7.0 Reagents and Standards

7.1 Reagent grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the America Chemical Society, where such specifications are available. Other grades may be used, however, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents are stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 **Extraction/exchange solvents**: All solvents are pesticide quality or equivalent and from commercial sources: Methylene chloride, Hexane, or Methanol. Alternates may be used, if needed.

7.3 See SOP Reagent and Standard Purchase, Preparation, control, Documentation / NV08-214 for information on shelf-life and storage requirements for standards and reagents.

8.0 Sample Collection, Preservation, Shipment and Storage

See the determinative method SOP.

9.0 Quality Control

See the determinative method SOP.

10.0 **Procedure:** See SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

Matrix	Sample Size
Waste	1 g

1	Transfer approximately 1.0 g of each phase of the sample to separate 10 mL, Class A, volumetric flasks. (Record weight to the nearest 0.1 g.)

2	Add surrogate solution to all samples, LCSs, and blanks. Add spike to LCSs. See Table 1 for information on surrogate and spike standards.
3	Immediately dilute to 10.0 mL with the appropriate solvent. Cap and shake for about two minutes. For compounds to be analyzed by GC/ECD, e.g., organochlorine pesticides and PCBs, use Hexane. For base/neutral and acid semivolatile priority pollutants, use Methylene chloride. For TPH use Methylene chloride.
4	Transfer the extract to a 10-20 mL vial and cap it. If turbid, centrifuge or filter through a small glass wool plug. Store refrigerated.
5	The extract is ready for cleanup or analysis.

Note: For GC/MS volatiles, also refer to SOP 5035 / NV05-108.

11.0 Calculations / Data Reduction

11.1 Accuracy. Not applicable.

11.2 Precision (RPD). Not applicable.

11.3 Calculations: Enter sample volume and final dilution volume in LIMS, as described in the determinative method.

12.0 Method Performance

12.1 Method Detection Limits (MDLs): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information regarding this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information regarding this demonstration.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes must be stored, managed, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

- **Waste Streams Produced by the Method:** See the determinative method.

15.0 References / Cross-References

15.1 **SW-846 Method 3580A**, Update I, July 1992.
15.2 **TestAmerica Nashville's Quality Assurance Manual.**
15.3 **Corporate Environmental Health and Safety Manual (CW-E-M-001).**
15.4 **SOPs**: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213, Reagent and Standard Purchase, Preparation, control, Documentation / NV08-214, 5035 / NV05-108, Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
15.5 **Controlled Document**: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachment

Table 1. Surrogate and Spike Amounts

Method	Surrogate Spike Amount
8081	1.0 mL of Pest/PCB surrogate, 1.0mL of Pest spike, 1.0mL of Chlor/Tox spike
8082	1.0 mL of Pest/PCB surrogate, 1.0mL of PCB spike
8270	2.0 mL of BNA surrogate, 2.0mL of BNA spike
8310	1.0 mL of HPLC surrogate, 1.0mL of HPLC spike
8015	1.0 mL of o-Terphenyl surrogate, 1.0mL of DRO wipe/oil spike
CA TPH	1.0 mL of o-Terphenyl surrogate,1.0mL of DRO wipe/oil spike
CT ETPH	1.0 mL of o-Terphenyl surrogate,1.0mL of DRO wipe/oil spike
FL PRO	2.0.0 mL of o-Terphenyl surrogate, 2.0mL of DRO wipe/oil spike 2.0 mL of C_{35} surrogate
MA-EPH	1.0 mL of o-Terphenyl/chloro-octadecane solution, 1.0mL of MA spike 1.0 mL of 2-Fluorobiphenyl / 2-Bromonaphthalene solution
NWTPH-Dx	1.0.0 mL of o-Terphenyl surrogate, 1.0mL of DRO wipe/oil spike
NWTPH-EPH	2.0 mL o-Terphenyl surrogate, 1.0mL of WA spike
OA-2	1.0 mL o-Terphenyl surrogate, 1.0mL of DRO wipe/oil spike
OK-DRO	1.0 mL of o-Terphenyl surrogate, 1.0mL of DRO wipe/oil spike
TN-EPH	1.0 mL o-Terphenyl surrogate, 1.0mL of DRO wipe/oil spike
OK-DRO	1.0 mL o-Terphenyl surrogate, 1.0mL of DRO wipe/oil spike
WI DRO	1.0 mL of C_{35} surrogate, 1.0mL of DRO wipe/oil spike
See individual SOPs for information on compounds, concentrations, and how to make the surrogate and spike solutions. Also, see the Prep Summary Chart for additional spike and surrogate information.	

18.0 Revision History

- Revision 6, dated 26 February 2010

  - Integration for TestAmerica and STL operations.
- Revision 7, dated 30 November 2011
  - Organizational changes.
  - Addition of Methanol and references to Methods 3585 and 5035.
- Revision 8, dated 31 January 2014
  - Organizational changes.
  - Remove references to Methods 3585 and 5035.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP)
Change Form

SOP Number/Revision No.: **6020 / NV06-215.6** Effective Date: **11/29/2013**

Last Mod. Date: 8/30/2013

SOP Title: **Method 6020/6020A: Metals Analysis by Inductively Coupled Plasma – Mass Spectrometry**

1.1 Affected SOP Section Number(s): **Section 10.2, Instrument Setup**

.

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 06

Revision Number with Mod ID: **6a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add bold text.

Section 10.2, Instrument Setup, Step 6

6	Use the average of least three integrations for both calibration and sample analyses. **The relative standard deviation for instrument QC must be <5%. The RSD for samples with concentrations greater than two times the reporting limit is <20%.**

2/17/14	
Department Manager Approval Date	
Steve Miller 11/1/13	Michael A. Brown 2/17/14
Quality Manager Approval Date	Technical Director Approval Date

Title: METALS ANALYSIS BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY SW-846 METHOD 6020/6020A

Approvals (Signature/Date)			
	8/20/13		8/28/13
Rodney Street Metals Operations Manager	Date	Johnny Davis Health & Safety Manager / Coordinator	Date
	8/13/13		
Michael H. Dunn Technical Director Quality Assurance Manager	Date		

1.0 Scope and Application

1.1 Analyte, Matrices: Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of concentrations of a large number of elements in water samples and in waste extracts or digests. When dissolved constituents are required, samples are filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples (SOP 3005 / NV06-103). Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total acid-leachable elements are required (SOPs 3010 / NV06-18, 3050 / NV06-93, 3051 / NV06-3051). The 6020 elements are:

Element	CAS #*	Reporting Limit (ug/L)	Element	CAS #*	Reporting Limit (ug/L)
Aluminum	7429-90-5	20	Manganese	7439-96-5	2
Antimony	7440-36-0	2	Molybdenum	7439-98-7	2
Arsenic	7440-38-2	2	Nickel	7440-02-0	2
Barium	7440-39-3	2	Potassium	7440-09-7	1000
Beryllium	7440-41-7	2	Selenium	7782-49-2	2
Cadmium	7440-43-9	1	Silver	7440-22-4	2
Calcium	7440-70-2	1000	Sodium	7440-23-5	1000
Chromium	7440-47-3	2	Thallium	7440-28-0	2
Cobalt	7440-48-4	2	Tin	7440-31-5	2
Copper	7440-50-8	2	Titanium	7440-32-6	2
Iron	7439-89-6	25	Vanadium	7440-62-2	2
Lead	7439-92-1	2	Zinc	7440-66-6	25
Magnesium	7439-95-4	1000			

*Chemical Abstract Service

1.2 Reporting Limits: RLs are shown in the table above.

1.3 If this method is used to determine any analyte not listed above, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the same manner as the listed elements and matrices.

1.4 Use of this method is relegated to spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS.

1.5 An appropriate internal standard is used for each analyte determined by ICP-MS. The internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{72}Ge, ^{159}Tb, ^{165}Ho, ^{209}Bi. The Lithium internal standard has an enriched abundance of ^{6}Li, so that interference from lithium native to the sample is minimized.

1.6 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 This method describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted

according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences are assessed and valid corrections applied or the data flagged to indicate problems. Interference correction includes compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

2.2 When analyzing groundwater or other aqueous samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid-preserved prior to analysis.

3.0 Definitions

3.1 **Instrument Detection Limits (IDLs)** are the concentrations equivalent to the analytes' signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the same wavelength. IDLs are useful tool to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with MDLs or report limits. It may be helpful to compare the calculated IDL to the MDL and RL; however, it should be understood that the RL must be verified. Each measurement must be performed as though it were a separate analytical sample (i. e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples).

- IDLs should be determined at least every three months. Analyze seven consecutive reagent blank solutions on three non-consecutive days; calculate the average of the standard deviation of each element.

3.2 **Internal Standard:** Pure analyte added to a sample, in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.3 **Linear Dynamic Range (LDR):** The concentration range over which the instrument response to an analyte is linear.

3.4 **Spectral Interference Check (SIC) Solution:** Used to prepare ICSA and ICSAB. A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting inter-element spectral interferences with respect to a defined set of method criteria.

3.5 **Report Limit Verification (RLV):** The RLV is a report limit concentration, primary standard to verify the RL.

3.6 See TestAmerica Nashville's QA Manual Appendix 5 for other laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). The data system and collision cell are used to correct for these interferences. This involves reaction with Helium and/or determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal.

Isobaric molecular and doubly charged ion interferences are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature. The Agilent 7500ce/cx addresses these interferences by using He as the reactive gas within a collision cell.

Common Background Molecular Ion Interferences in ICP-MS					
Molecular Ion	Mass	Element Interference	Molecular Ion	Mass	Element Interference
NH^+	15		$^{38}ARH^+$	39	
OH^+	17		$^{40}ARH+$	41	
OH_2^+	18		CO_2^+	44	
C_2^+	24		CO_2H^+	45	Sc
CN^+	26		ArC+, ArO^+	52	Cr
CO^+	28		ArN^+	54	Cr
N_2^+	28		$ArNH^+$	55	Mn
N^2H^+	29		ArO^+	56	
NO^+	30		$ArOH^+$	57	
NOH^+	31		$^{40}Ar^{36}Ar^+$	76	Se
O_2^+	32		$^{40}AR^{38}Ar^+$	78	Se
O_2H^+	33		$^{40}AR_2^+$	80	Se
$^{36}ARH^+$	37				

Matrix Molecular Ion Interferences		
Molecular Ion	Mass	Element Interference
Bromide		
$^{81}BRH^+$	82	Se
$^{79}BrO^+$	95	Mo
$^{81}BrO^+$	97	Mo
$^{81}BrOH^+$	98	Mo
$Ar^{81}Br^+$	121	Sb
Chloride		
$^{35}ClO^+$	51	V
$^{35}ClOH^+$	52	Cr
$^{37}ClO^+$	53	Cr
$^{37}ClOH^+$	54	Cr
$Ar^{35}Cl^+$	75	As
$Ar^{37}Cl^+$	75	As
Sulfate		
$^{32}SO^+$	48	
$^{32}SOH^+$	49	
$^{34}SO^+$	50	V, Cr
$^{34}SOH^+$	51	V
SO_2^+, S_2^+	64	Zn
$Ar^{32}S^+$	72	
$Ar^{34}S^+$	74	
Phosphate		
PO^+	47	
POH^+	48	
PO_2^+	63	Cu
ArP^+	71	
Group I, II Metals		
$ArNa^+$	63	Cu
ArK^+	79	
$ArCa^+$	80	

Matrix Molecular Ion Interferences		
Molecular Ion	**Mass**	**Element Interference**
Matrix Oxides		
TiO	62-66	Ni, Cu, Zn
ZrO	106-112	Ag, Cd
MoO	108-116	Cd

Possible Polyatomic Interferences in Typical Environmental Samples and the ORS Mode Used to Eliminate Them		
Analyte Isotope	**Principal Interferences**	**Corrective ORS Mode**
^{24}Mg	$^{12}C^{12}C$	He
^{27}Al	$^{12}C^{14}N^{1}H$	He
^{51}V	$^{35}Cl^{16}O$	He
^{52}Cr	$^{40}Ar^{12}C$, $^{35}Cl^{16}O^{1}H$, $^{36}Ar^{16}$)	He
^{55}Mn	$^{40}Ar^{16}O$, $^{40}Ca^{16}$)	He
^{56}Fe	$^{40}Ar^{16}O$, $^{23}Na^{37}Cl$, $^{43}Ca^{16}O^{1}H$, ArS	He
(63,65)Cu	$^{40}Ar^{23}Na$, SO_2	He
(64,66,68)Zn	SO_2, ArS	He
^{75}As	$^{40}Ar^{35}Cl$, $^{40}Ca^{35}Cl$	He
$^{(78,80)}Se$	$^{40}Ar^{38}Ar$, SO_3	He

4.2 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total dissolved solid levels below 0.1% (1,000 mg/L) have been currently recommended to minimize solid deposition. Internal standards are used to correct for physical interferences. When intolerable physical interferences are present in a sample, a significant suppression of the internal standard signals (to less than 70% of the signals in the calibrations standard) is observed. Dilution of the sample usually eliminates the problem i.e. Internal standard >70% of ICAL.

4.3 Memory interferences can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples is long enough to reduce significant memory interference.

4.4 If there is poor relative standard deviation (precision) on standards and sample:

4.4.1 Check that the interface cones are in good condition and that the orifices of both cones are round and of the proper size.

4.4.2 Evaluate the nebulizer to see if it is operating properly by checking the aerosol with the plasma off and the spray chamber removed. If the aerosol is not forming properly clean or replace the gem tips.

4.4.3 Check that the peristaltic pump tubing is in good condition. Follow air bubbles through the tubing to insure that the flow is smooth and not pulsating.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This method may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the

responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.
- The inductively coupled plasma should only be viewed with proper eye protection from the ultraviolet emissions.
- The ICP-MS uses high voltage.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS/SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS/SDS for each material before using it for the first time or when there are major changes to the MSDS/SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydro-chloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors causes coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Causes redness, pain, and severe skin burns. Vapors are irritating and cause damage to the eyes. Contact causes severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors causes breathing difficulties and leads to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Causes redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and cause damage to the eyes. Contact causes severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- **Inductively coupled plasma mass spectrometer:** Agilent 7500ce/cx is capable of providing resolution, better than or equal to 0.9 amu at 10% peak height. The system has a mass range from 6 to 240 amu and a collision cell and data system that allows corrections for isobaric interferences and the application of the internal standard technique. A mass-flow controller for the nebulizer Argon and Helium and peristaltic pumps for the sample solution are used.

Tune Adjustment Variables		
Instrument Parameter	**Normal Mode**	**Helium Mode**
RF Power	1500	1500
Carrier gas	~1.1 L/min	Same as Normal
Makeup gas	0.0	Same as Normal
Sample Depth	87-10mm	Same as Normal

Tune Adjustment Variables		
Persitaltic Pump Speed	0.1 rps	Same as Normal
Spray Chamber	2°C	Same as Normal
Extract 1	0 V	Same as Normal
Extract 2	-120 to -150 V	Same as Normal
Omega bias	-15 to -40 V	Same as Normal
Omega lens	5 to -5 V	Same as Normal
Cell entrance	-30 to -10 V	-25 V
QP focus	3 V	-10 V
Cell exit	-30 to -8 V	-45 V
OctP RF	160 to 200 V	Same as Normal
OctP bias	-10 to -3 V	-18 V
QP bias	-7 to -0.5 V	-15 V

- Set up the Instrument with the proper operating parameters according to the instrument manufacturer's instructions. Load tunes: normal.U and He.U (see examples in Section 17). Load "60202008" method and calibration.
- Operating conditions. Follow the instructions provided by the instrument manufacturer. Allow at least 30 minute for the instrument to equilibrate before analyzing any samples. Verify by analyzing a tuning solution at least **five integrations** with relative standard deviations of ≤ 5% for the analytes contained in the tuning solution.

6.2 Supplies

- Helium: High-purity grade (99.99%).
- Argon gas supply: high purity grade (99.99%).
- Macropipettes and micropipettes with disposable tips.
- Autosampler tubes.
- disposable Centrifuge Tubes: 50 mL with caps.
- Teflon™ boiling chips for solid matrix blank (Chemware P/N D1069103, or equivalent).
- Syringe filter, 25 mm with 0.45 µm PTFE membrane, VWR International 28145-497, or equivalent.

7.0 Reagents and Standards

7.1 Reagent water, analyte-free.

7.2 Acids used in the preparation of standards and for sample processing are of ultra high purity. Concentrations of antimony and silver between 50-500 µg/L require 0.5% (v/v) HCl for stability. For concentrations above 500 µg/L Ag, additional HCl may be needed.

7.3 Stock Standard Solutions: Each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Take care when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon or polyethylene bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging.

- **Primary Calibration Stock Standard:** Purchase: Inorganic Ventures TA-40 Custom Solution, or equivalent: All element concentrations are 100.0µg/mL.
- Environmental Express HP10M31-1, or equivalent, containing 10,000 µg/mL Na.
- Environmental Express HP10M41-1, or equivalent, containing 10,000 µg/mL Mg.
- Environmental Express HP10M52-1, or equivalent, containing 10,000 µg/mL K.

- Environmental Express HP10M9-1, or equivalent, containing 10,000 µg/mL Ca.
- Ultra Scientific IAA-213-5, or equivalent, containing 1,000 µg/mL Al.
- Ultra Scientific IAA-256-5, or equivalent, containing 1,000 µg/mL Ba.
- Environmental Express HP100026-1, or equivalent, containing 1,000 µg/mL Fe.
- Ultra Scientific IAA-225-5, or equivalent, containing 1,000 µg/mL Mn.
- Ultra Scientific IAA-230-5, or equivalent, containing 1,000 µg/mL Zn.

- **Secondary Spiking Stock Standard:** Purchase the following:
  - Inorganic Ventures TA-41 Custom Solution, or equivalent, containing
    - 10 µg/mL As, Cr^{+3}, Co, Cu, Pb, Mn, Ni, V, Zn, Se, Ba, Be, Cd, Tl
    - 100 µg/mL Al, Fe
    - 1000 µg/mL Ca, Mg, K, Na
  - Inorganic Ventures TA-42 Custom Solution, or equivalent, containing
    - 10 µg/mL Ag, Mo, Sn, Ti, Sb

7.4 Mass Spectrometer Tuning Standards. A solution containing elements representing all of the mass regions of interest is analyzed to verify that the resolution and mass calibration of the instrument are within the required specifications. This solution is also used to verify that the instrument has reached thermal stability.

- **Instrument Tuning Standard:** Purchase the following:
  - Agilent Tuning Solution 5184-3566, or equivalent, containing 10 µg/L Li, Co, Y, Ce, Tl.
- **Tune Check Standard:** Prepare solution of 100 µg/L Be, Mg, Co, Y, In, and Pb by adding the following to 250 mL mixed acid diluent
  - 25 µL Ultra Scientific IAA-204-5, or equivalent, containing 1,000 µg/mL Be
  - 2.5 µL Environmental Express HP10M31-1, or equivalent, containing 10,000 µg/mL Mg
  - 25 µL Ultra Scientific IAA-227-5, or equipment, containing 1,000 µg/mL Co
  - 25 µL Environmental Express, or equivalent, containing 1,000 µg/mL Y
  - 25 µL Environmental Express, or equivalent, containing 1,000 µg/mL In
  - 25 µL Ultra Scientific IAA-282-5, or equivalent, containing 1,000 µg/mL Pb

7.5 The **interference check solution (ICS)** is prepared to contain known concentrations of interfering elements that demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate chemical corrections for chloride-related interferences such as $^{35}Cl^{16}O^{+}$ on $^{51}V^{+}$ and $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system or collision cell within quality control limits.

NOTE: The ICS solutions in Table 1 are intended to evaluate corrections for known interferences on only the analytes in Section 1.1. If this method is used to determine an element not listed in Table 1, it is the responsibility of the analyst to modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of correction of interferences on the unlisted element (see Section 8.4).

These solutions are prepared from ultra-pure reagents, obtained commercially (Inorganic Ventures, or equivalent).

- **Working ICS Solution A** (6020ICS-A) is prepared by adding 5.0 mL of Inorganic Ventures 6020ICS-0A, or equivalent, plus 45 mL mixed acid diluent. ICS solution A must be prepared fresh weekly. 6020ICS-0A contains 10,000 µg/mL chloride, 2,000 µg/mL carbon, 1,000 µg/mL each aluminum, calcium, iron, potassium, magnesium, phosphorus,

sodium, and sulfur, and 20 µg/mL each molybdenum and titanium.

- **Working ICS Solution B** (6020ICS-B) is prepared by adding
  - 0.5 mL of Inorganic Ventures TA-STD-1 (contains all targets), or equivalent. TA-STD-1 contains 2.0 µg/mL each Arsenic, Barium, Beryllium, Cadmium, Cobalt, Chromium, Copper, Lead, Manganese, Nickel, Selenium, Silver, Tin, Thallium, Vanadium, and Zinc.
  - 50 µL of a 20 µg/mL solution of Ultra Scientific IAA-251, or equivalent, containing 1,000 µg/mL Sb.
  - plus 49.5 mL mixed acid diluent.
  - ICS solution B must be prepared fresh weekly.
- **ICS AB:** Add 5 mL of 6020ICS-0A to ICS B (50 mL).

Recommended Interference Check Sample Components and Concentrations			
Solution Component (mg/L)	**ICS A Concentration 1:10 (mg/L)**	**ICS B Concentration 1:100 (mg/L)**	**ICS AB Concentration (mg/L)**
Al	100		100.0
Ca	100		100.0
Fe	100		100.0
Mg	100		100.0
Na	100		100.0
P	100		100.0
K	100		100.0
S	100		100.0
C	200		200.0
Cl	1000		1000
Mo	2.0		2.0
Ti	2.0		2.0
As	0	0.02	0.02
Cd	0	0.02	0.02
Cr	0	0.02	0.02
Co	0	0.02	0.02
Cu	0	0.02	0.02
Mn	0	0.02	0.02
Ni	0	0.02	0.02
Ag	0	0.02	0.02
Zn	0	0.02	0.02
Ba	0	0.02	0.02
Sb	0	0.02	0.02
Be	0	0.02	0.02
Pb	0	0.02	0.02
Se	0	0.02	0.02
Tl	0	0.02	0.02
Sn	0	0.02	0.02
V	0	0.02	0.02

7.6 Internal Standards: Purchase Inorganic Ventures 6020ISS, or equivalent; it contains 10 µg/mL ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, ^{209}Bi. Purchase Environmental Express HP100020-1, or equivalent; it contains 1000 µg/mL ^{72}Ge.

- Prepare a 1 µg/mL solution by diluting 50 mL 6020ISS and 0.5 mL HP100020-1 to 500 mL

mixed acid diluent. When added to the sample or standard by the instrument at 1:20, the resulting concentration is 50 ug/L. Generally, an internal standard is no more than 50 amu removed from the analyte.

Isotopes, Internal Standards, and Reaction Gas for Selected Elements			
Element of Interest	**Mass**	**IS**	**Reaction Gas**
Aluminum	27	45	Helium
Antimony	121	103	No gas
Arsenic	75	72	Helium
Barium	137	159	No gas
Beryllium	9	45	Helium
Bismuth (IS)	209		No gas, Helium
Cadmium	111	103	Helium
Calcium	40	45	Helium
Chromium	52	45	Helium
Cobalt	59	72	Helium
Copper	65	72	Helium
Germanium (IS)	72		No gas, Helium
Holmium (IS)	165		No gas, Helium
Indium (IS)	115		No gas, Helium
Iron	56	89	Helium
Lead	(206) (207) 208	209	No gas
Lithium (IS)	6[a]		No gas, Helium
Magnesium	24	45	Helium
Manganese	55	72	Helium
Molybdenum	95	103	Helium
Nickel	60	72	Helium
Potassium	39	45	Helium
Rhodium (IS)	103		No gas, Helium
Scandium (IS)	45		No gas, Helium
Selenium	78	72	Helium
Silver	107	103	Helium
Sodium	23	45	Helium
Terbium (IS)	159		No gas, Helium
Thallium	205	209	No gas
Tin	118	103	No gas
Titanium	47	72	Helium
Vanadium	51	72	Helium
Yttrium (IS)	89		No gas, Helium
Zinc	66	72	Helium

[a]Internal standard must be enriched in the ^{6}Li isotope. This minimizes interference from indigenous Lithium.

7.7 Hydrochloric acid (HCl), concentrated. To prepare a 5% solution, add 10 mL concentrated HCl to 200 mL reagent water.

7.8 Nitric acid (HNO_3), concentrated. To prepare a 5% solution, add 10 mL concentrated HNO_3 to 200 mL reagent water.

7.9 Mixed Acid Diluent: A mixture of 1% HNO_3 and 0.5% HCl (volume/volume) in reagent

water is used to prepare standards and blanks.

- Add 2 mL HNO_3 and 1 mL HCl to 200 mL reagent water.

7.10 See SOP Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214 for additional shelf-life and storage requirements for reagents and standards.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water, TCLP Extract	HDPE or Glass	125 mL	HNO_3 to pH ≤ 2[1]	6 months	SW-846 Chapter 3
Soil	HDPE or Glass	50 grams	No requirement	6 months	SW-846 Chapter 3

[1]If water samples are preserved in the lab, they should be held for at least 24 hours before analysis; record acidification start/stop time and pH. Temperature preservation is not required.

For the determination of dissolved elements, the sample **must** be filtered prior to acid preservation through a 0.45-µm pore diameter, PTFE membrane filter at the time of collection or as soon thereafter as practically possible.

9.0 Quality Control

Refer to the quality control section of TestAmerica-Nashville's QA Manual for specific quality control (QC) policies. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC: The following quality control samples must be prepared with each batch:

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Method Blank	1 per 20 samples	< ½ RL or MDL, whichever is greater.	Correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank.
Laboratory Control Sample (LCS)[1], second source	1 per 20 samples	80-120[2]% recovery	Correct problem then re-prep and analyze the LCS and all affected targets in the affected analytical batch. If high and ND, OK to report.
Matrix Spike	1 per 20 samples	75-125[2]% recovery	Run post-digestion spike.
Matrix Spike Duplicate	1 per 20 samples	<20[2]% RPD	Run post-digestion spike.
Dilution test	If MS/MSD fail.	If concentration is high enough, at least 10 times RL, run 1:4 fold dilution, must agree within 10% of the original determination.	Report and qualify
Post digestion spike addition	When dilution test fails	Recovery with 20% of the expected results	Re-run, report, and qualify.

[1]AZ, MA, TX, WV require an LCS duplicate in each batch.
[2]If historical limits are calculated, they cannot exceed these limits.

- **Method blank:** For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation, including pre-filtering, digestion, dilution,

filtering, and analytical process.
  - Use the same volume of reagent water or weight of Teflon™ boiling chips as the samples.
- **Laboratory Control Sample (LCS):** For each batch of samples processed, at least one LCS must be carried throughout the **entire sample preparation and analytical process**. Spike equivalent aliquots of reagent water for water batches or Teflon™ boiling chips for soil batches with each analyte of interest at the approximate mid-point of the linear dynamic range.
  - Prepare the LCS by diluting 500 µL of each of the **second-source** standards to 50 mL mixed acid diluent.
- **Matrix Spike / Matrix Spike Duplicate:** Take separate, identical aliquots from a sample for replicate and spiked analyses to assess the effect and document the bias and precision of a method in a given sample matrix. See SOP Sample Homogenization, Subsampling, and Compositing / NV08-229.
  - Prepare and analyze a matrix spike and matrix spike duplicate at a frequency of one per matrix batch up to 20 samples. In each case the MS aliquot must be a duplicate of the aliquot used for sample analysis and added prior to sample preparation.
  - The added analyte concentration and standard source must be the same as that used in the LCS.
  - Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unspiked sample, and compare these values to the designated MS recovery range
  - If less than acceptable accuracy and precision are obtained, additional tests are required:
    - If MS/MSD is outside the QC limits, the same sample from which the MS/MSD aliquots were prepared is also spiked with a **post-digestion spike**. Otherwise, another sample from the same preparation is used as an alternative. The spike addition produces a minimum level of 10 times the RL. If this spike fails, an interference effect is suspected, and the dilution test is run on this sample. If both the MS/MSD and the post-digestion spike fail, then matrix effects are confirmed. Report and qualify.
  - **Dilution test**: If the analyte concentration is sufficiently high (minimally, a factor of 10 times the report limit), an analysis of a 1:4 (5X) dilution should agree within 10% of the original determination. If not, a chemical or physical interference effect is suspected. Report and qualify.

9.2 Instrument QC

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Tune	Daily, prior to analysis of samples.	Adjust sensitivity with a stability ≤5% RSD.	Adjust instrument setting and re-run.
Pulse/Analog Check Standard	Immediately after Tune	0.05 or greater for targets	Adjust concentration, re-run.
Tune Check Standard	Each day	5% RSD, 10% amu	Adjust and re-run
Calibration Standards	Each day	Linear regression: r 0.998, r^2 ≥ 0.996. Mid and Upper ± 10% true; low ± 30% true.	Clean, adjust, and re-calibrate.
Calibration Blank	Each day	≤ MDL or ½ RL, whichever is greater.	Re-run calibration.
Spectral Interference Check Solutions, A and AB	Beginning of analytical run or once every 12 hours, whichever is more frequent	Target ± 2 times RL or ± 20% true.	Terminate analysis; correct problem; re-analyze ICS; re-analyze all affected samples.

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Linear Range Standard (LRS)	Once daily	> 90% true	Re-run calibration or decrease Linear Dynamic Range to highest calibration point.
Instrument Detection Limits (IDL)	Quarterly	±3 standard deviations of the average response.	
Independent Calibration Verification Sample (ICV), second source	Immediately after calibration	90-110 % recovery	Correct problem then repeat initial calibration.
Independent Calibration Blank (ICB)	Immediately after ICV	No target analytes above RL.	
Continuing Calibration Verification Sample (CCV)	Every 10 samples and at the end of the run	90-110% recovery	Repeat calibration and re-analyze all samples since last successful calibration.
Undigested Low Level Continuing Calibration Verification (LLCCV)	Beginning and end of each batch.	70-130% true	Re-calibrate.
Continuing Calibration Blank	Following the CCV	≤ RL	Correct problem then analyze calibration blank and previous 10 samples.
Digested Lower Limit of Quantitation Check (LLQC) or Report Limit Verification (RLV)	Once daily	70-130% recovery	Re-calibrate.
Internal Standards	All samples, standards, QC	70-130% recovery	Dilute and re-run. For blank and LCS, correct problem and re-run batch.
MDL Verification (digested)	Yearly	Detected	Re-evaluate MDL standard used and MDL; see Technical Director.

- **Tune**: See Section 6.1.
- **Pulse/Analog Check Standard**: This standard contains 100 µg/L of all targets.
  - Prepare by taking about 0.25 mL of 100 µg/mL primary calibration standard and 12.5 mL of 1 µg/mL internal standard solution to 250 mL mixed acid diluent.
- **Tune Check Standard:** Verify that the instrument has reached thermal stability, is aligned correctly, and is properly tuned. Use the Tune Check Standard to perform this check. Target analytes must have <5% RSD, <0.1 amu true resolution, and <0.9 amu at 10% peak height.
- **Calibration**: See Section 10.
- **Calibration Blank:** This blank is used in establishing the calibration curve. It consists of the mixed acid diluent (1% HNO_3 and 0.5% HCl (volume/volume) in reagent water) and the selected concentrations (50 µg/mL, added on-line) of internal standards such that there is an appropriate internal standard element for each of the analytes.
- **Rinse Blank Solution**: After calibration, flush the system with the rinse blank solution until the signal levels return to the method's levels of quantitation (usually about 75 seconds) before the analysis of each sample.
  - The rinse blank consists of 4% HNO_3 and 4% HCl (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.
- **Spectral Interference Check Solution (ICS A and ICS AB):** The laboratory must periodically verify the inter-element correction (IEC) routine by analyzing SIC solutions. The spectral interference check solution is run at the beginning of the analytical sequence or every

12 hours, whichever is more frequent. If the SIC does not meet criteria, then the SICs are re-analyzed.

- Ensure that the analytical results of ICS A fall within the control limit of ± 2 times the RL of the analyte's true value or ± 20% of the analyte's true value, whichever is greater (the true value is zero unless otherwise stated) in the ICSA. For example, if the analysis result(s) for Arsenic (RL = 10 µg/L, ICSA true value = 0 µg/L) in the ICSA analysis during the run is 19 µg/L, then the analytical result for Arsenic falls within the ± 2 times the RL window for Arsenic in the ICSA. If the analytical results of the ICS A do not fall within the control limits, terminate the analysis, correct the problem, re-calibrate the instrument, and re-analyze the analytical samples analyzed since the last compliant ICS A was performed.
- Ensure that the results for the ICS AB during the analytical runs fall within the control limit of ± 2 times the RL of the true value or ± 20% of the true value, whichever is greater, for the analytes included in the ICS AB. If the analytical results of the ICS AB do not fall within the control limits, terminate the analysis, correct the problem, re-calibrate the instrument, and re-analyze the analytical samples analyzed since the last compliant ICS AB was performed.

- **Linear Range Standard (LRS):** For single-point and/or multi-point calibration, run at the beginning of the analytical sequence. Run the highest standard level, to show linearity to that concentration. All samples exceeding **90%** this concentration are diluted. The LRS concentrations are Na, Mg, Al, K, Ca, Fe at 100 µg/mL; all other elements at 1.00 µg/mL. The standard must be within 10% of the true values to continue.
- **Instrument Detection Limits (IDL):** On a quarterly basis, analyze seven consecutive reagent blanks per day on three non-consecutive days; calculate the average of the standard deviations.
- **Independent Calibration Verification (ICV and ICB):** The laboratory analyzes a mid-level and an ICB immediately following daily calibration. Analysis of the I ICV must verify that the instrument is **within ± 10%** of the known concentration. The ICB must not contain target analytes above the MDL.
  - Weekly, prepare the 100 µg/mL ICV by diluting 500 µL of each of the 100 µg/mL **second-source** standards to 50 mL 1% HNO_3:0.5% HCl (mixed acid diluent).
- **Continuing Calibration Verification (CCV and CCB):** Analyze after every 10th sample and at the end of the analytical sequence.
  - For the CCV, add 50 µL of the primary calibration stock standard and 450 µL of the 100 µg/mL of the Al, Fe cation spike to 50 mL mixed acid diluent.
  - If the calibration cannot be verified within the specified limits, reanalyze either or both the CCV and the CCB. If the second analysis of the CCV or the CCB confirm calibration to be outside the limits, sample analysis must be discontinued, the cause determined, corrected and/or the instrument recalibrated. All samples following the last acceptable CCV must be reanalyzed. All samples **must be bracketed** by acceptable CCVs and CCBs.
  - The CCB (prepared by acidifying reagent water to the same concentrations of the acids as used for the standards) must not contain target analytes above the RL. If it does, repeat the analysis one more time. If the CCB is still not less than the RL, terminate the analysis, correct the problem, re-calibrate, and re-analyze the previous 10 samples.
- **Report Limit Verification (RLV):** %D must be ± 30%. Run at the beginning and end of each batch.
  - Prepare a 2 µg/L LLCCV (however, Al is 20 µg/L; Fe is 25 µg/L; Zn is 25 µg/L, Minerals are 1000 µg/L):
  - Add 10 mL of 10 µg/L primary standard solution.
  - Add 0.9 mL of 1 µg/mL Al primary standard (Ultra Scientific IAA-213-5, or equivalent, 1000 µg/mL).

- Add 1.2 mL of 1 µg/mL Fe primary standard (Ultra Scientific IAA-226-5, or equivalent, 1000 µg/mL).
- Add 1.2 mL of 1 µg/mL Zn primary standard (Ultra Scientific IAA-230-5, or equivalent, 1000 µg/mL).
- Add 49.9 µL of the 1000 µg/mL Minerals spiking solution (5 µL TA-9/50 mL reagent water).

- **Lower Limit of Quantitation Check Sample (LLQC):** The LLQC is analyzed once daily to confirm the lowest quantitation limit. Ideally, this check sample and the low-level calibration verification standard are prepared at the same concentrations with the only difference being the LLQC sample is carried through the **entire preparation and analytical procedure including digestion**. See Section 10 for preparation.
- **Internal Standards:** Use the internal standard technique by adding one or more elements (not in the samples and verified not to cause an uncorrected inter-element spectral interference) at the same concentration (which is sufficient for optimum precision) to the prepared samples (blanks and standards) that are affected the same as the analytes by the sample matrix. Use the ratio of analyte signal to the internal standard signal for calibration and quantitation. Internal standards are automatically added to all calibration standards, samples, and QC, by the instrument.

  The intensities of all internal standards must be monitored for every analysis. If the intensity of any internal standard in a sample falls below **70%** of the intensity of that internal standard in the initial calibration standard, a significant matrix effect must be suspected. Use the following procedure:

1	Make sure the instrument has not drifted by observing the internal standard intensities in the nearest clean matrix (calibration blank).
2	If the low internal standard intensities are also seen in the nearest calibration blank, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.
3	If drift has not occurred, matrix effects need to be removed by dilution of the affected sample. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards.
4	If the first dilution does not eliminate the problem, this procedure must be repeated until the internal-standard intensities rise to the minimum **70%** limit. Correct all reported results for all dilutions.

- **MDL Verification:** A solution containing all target analytes at 2-3 times the MDL must be **digested** and analyzed after the completion of the MDL study and on an annual basis. Detection limits are verified when all analytes in the MDL check solution are detected.

10.0 Procedure

10.1 Sample Preparation

Use metal digestion SOPs 3005 / NV06-103, 3010 / NV06-18, or 3051 / NV06-94.

Matrix	Sample Size	Matrix	Sample Size
Water	50 mL of sample	Soil	0.5 gram of sample

10.2 Instrument Setup

1	Initiate appropriate operating configuration of the instrument's computer, according to the instrument manufacturer's instructions. Click "Instrument Control" and turn plasma "ON,"
2	Load tunes "normal.U" and "He.U." Load "60202008" method and calibration.

10.2 Calibration: Refer to SOP Selection of Calibration Points / CA-T-P-002 and Calibration Curves (General) / CA-Q-S-005. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

1	Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. Verify by analyzing the Tuning solution at least **five integrations** with relative standard deviations of ≤ 5% for the analytes contained in the tuning solution.
2	Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution is verified to be less than 0.9 amu full width at 10 percent peak height. The tune limits are:

Tune	m/z	Criteria	Tune	m/z	Criteria
Normal	7	<5% RSD	He	59	<5% RSD
	89	<5% RSD		51	low counts
	205	<5% RSD		52	low counts
	156/140	m/z ratio <3%		75	low counts
	70/140	m/z ratio <3%			

At least four integrations are required.

3	Run P/A (Pulse/Analog) check standard daily using the P/A standard.
4	Run the Tune Check daily using the Tuning solution.
5	Calibrate the instrument for the analytes of interest (recommended isotopes for the analytes in Section 1 are provided in Section 4), using the calibration blank and at least three calibration standards. For the calibration standards, serially dilute the 100 µg/mL calibration standard as follows:

mL of 100 µg/mL Calibration Standard	Final Volume (mL) of 1% HNO_3: 0.5% HCl.	Calibration Standard Concentration (µg/L)
0	50	0
0.5	50	1
5.0	50	10
0.050	50	100

PREPARE FRESH WEEKLY.

To prepare the 1000 µg/L calibration standard for Al, Ca, Fe, K, Mg, Na dilute 50 µL Al, and Fe primary standards (1,000 µg/mL) and 50 µL Cation Spike (1,000 µg/mL) to 50 mL reagent water.

To prepare the 10000 µg/L standard for Al, Ca, Fe, K, Mg, Na, dilute 0.5 mL each of the Al and Fe primary standards (1,000 µg/mL) and 0.5 mL Cation Spike (1,000 µg/mL) to 50 mL reagent water.

To prepare the Linear Range Standard, dilute 500 µL of TA-40 primary standard (100 µg/mL)

	and 1000 µL TA-13 (5,000 µg/mL) to 50 mL reagent water. NOTE: Improved performance in calibration stability may be obtained if the instrument is exposed to the interference check solution after cleaning sampler and skimmer cones. Improved performance is also realized if the instrument is allowed to rinse for 5 or 10 minutes before the calibration blank is run.
6	**Use the average of at least three integrations for both calibration and sample analyses.**
7	Prepare a standard curve by calculating the counts per second (cps) of standards versus the corresponding target concentrations using first-order linear regression. The correlation coefficient r must be greater than or equal to 0.998 ($r^2 \geq 0.996$), or re-calibrate.
8	Monitor all masses which could affect data quality to determine potential effects from matrix components on the analyte peaks.
9	After initial calibration, the calibration curve must be immediately verified by use of an initial calibration verification (ICV) standard.
10	The calibration curve must be verified at the end of each analysis batch and after every 10 samples by use of a continuing calibration verification (CCV) standard and a continuing calibration blank (CCB).
11	The calibration curve must also be verified prior to the analysis of any samples by use of a low-level continuing calibration verification (LLCCV) standard.
12	Verify the inter-element correction factors at the beginning of the daily sequence or every 12 hours, whichever is more frequent.
13	Flush the system with the rinse blank solution until the signal returns to ≤ RL.

10.3 Sample Analysis

1	Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Use at least three integrations.
2	Dilute and re-analyze samples that are more concentrated than the upper calibration standard for an analyte (or species needed for a correction) or measure an alternative less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration.

10.4 Example Analysis Queue / Sequence*

1	Tune
2	P/A Standard
3	Tune Check Standard
4	ICAL
5	ICV
6	ICB
7	Digested RLV
8	LRS
9	ICS A
10	ICS AB
11	Rinse x 2-4
12	CCV
13	CCB
14	Undigested RLV
15	Method Blank

16	LCS*
17	Samples (up to 20 samples)
18	Matrix Spike
19	Matrix Spike Duplicate
20	CCV
21	CCB
22	Undigested RLV

*AZ, MA, TX, WV require an LCS duplicate in each batch.

11.0 Calculations / Data Reduction

11.1 Relative Standard Deviation (RSD)

RSD = (SD / $\overline{x_i}$) x 100

$$SD = \sqrt{\sum_{i=1}^{n} \frac{\left(x_i - \overline{x_i}\right)^2}{n-1}}$$

11.2 Accuracy

% Recovery = Measured concentration x 100
Known concentration

11.3 Precision (RPD)

RPD = Absolute value (orig. sample value - dup. sample value) x 100
(Orig. sample value + dup. sample value)/2

11.4 Response Factor

RF = Intensity
Concentration

11.5 % Drift

% Drift = (Result - True Value) x 100
True Value

11.6 Linear Calibration Using a Least Squares Regression: This is most easily achieved by performing a first-order linear regression of the instrument response versus the concentration of the standards. Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). This is a statistical requirement and is not simply a graphical convention.

The regression produces the slope and intercept terms for a linear equation in the form:

$y = ax + b$

y = instrument response (peak area)
a = slope of the line

x = concentration of the calibration standard
b = the intercept

The acceptance criteria for the calibration standard recovery should be ± 10% of its true value for all standards except the lowest concentration. A recovery of ± 30% of its true value should be achieved for the lowest concentration standard.

11.7 Coefficient of Determination **Correlation Coefficient**

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2} \qquad r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response ratio; x = Concentration

11.8 Concentration Calculation: Sample data are reported in units of µg/L for aqueous samples, µg/kg for solid samples. LIMS calculates the concentration from the raw data provided by the analyst. Include appropriate interference corrections, internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundance of these isotopes between samples and standards.) All results are reported with up to **three significant figures**.

$$\text{Concentration (µg/L or µg/kg)} = \frac{\text{(µg/mL* from instrument)(digest volume, mL)(Dilution factor)}}{\text{Sample Volume, mL, or Mass, g}}$$

µg/mL from instrument = Intensity/RF

***average of at least three integrations**

11.9 If solid results are needed on a dry weight basis, calculate as follows: Perform a separate determination of % solids. The concentrations determined in the digest are reported on the basis of the dry weight of the sample:

$$\text{Conc. (µg/kg dry weight basis)} = \frac{\text{(µg/mL from instrument)(digest volume, mL)(Dilution factor)}}{\text{(Wet Sample Mass, g)(\% Solids/100)}}$$

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency. Compare the MDL to the IDL. The MDL must be ≥ the IDL or adjust.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of

TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

12.5 Control Charts: Laboratory method performance can be shown with the use of control charts, available from LIMS or the QA department.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are managed, stored, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Acidic aqueous wastes are taken to the waste disposal area, neutralized, and discharge to the sanitary sewer.

15.0 References / Cross-References

15.1 Method 6020, SW-846 Update II, Revision 0, September 1994 and **Method 6020A**, SW-846 Update IV, Revision 1, February 2007.

15.2 TestAmerica Nashville's Quality Assurance Manual.

15.3 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.4 SOPs: Selection of Calibration Points / CA-T-P-002, Calibration Curves (General) / CA-Q-S-005, Method 3005 / NV06-103; Method 3010 / NV3010, Method 3050 / NV06-93; Method 3051 / NV06-94; Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213, Determination of Method Detection Limits / NV08-202, Sample Homogenization, Subsampling, and Compositing / NV08-229.

15.5 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

Item	Modification
1	If 3030C digestion is specified, see the attachment in SOP 3005 / NV06-103 for that procedure.

17.0 Attachments

Example Tune File for Normal.U

Sensitivity

Tune File : NORMAL.U

Integration Time: 0.1000 sec
Sampling Period: 0.7200 sec
n: 61

m/z	Range	Count	Mean	RSD%
7	100,000	15994.0	16213.0	2.20
89	100,000	53785.0	51687.8	2.39
205	100,000	16676.0	16220.7	2.48
59	100,000	35117.0	36280.9	2.08
156/140	2	1.235%	1.217%	6.32
70/140	5	1.839%	1.711%	4.89

Tuning Parameters

===Plasma Condition===			===Ion Lenses===			===Q-Pole Parameters===		
RF Power	1550	W	Extract 1	0	V	AMU Gain	125	
RF Matching	1.76	V	Extract 2	-145	V	AMU Offset	126	
Smpl Depth	8	mm	Omega Bias	-30	V	Axis Gain	0.9989	
Torch-H	-0.1	mm	Omega Lens	-1.4	V	Axis Offset	-0.03	
Torch-V	0.1	mm	Cell Entrance	-30	V	QP Bias	-3	V
Carrier Gas	0.8	L/min	QP Focus	3	V			
Makeup Gas	0.1	L/min	Cell Exit	-30	V	===Detector Parameters===		
Optional Gas	---	%				Discriminator	8	mV
Nebulizer Pump	0.1	rps	===Octopole Parameters===			Analog HV	2100	V
Sample Pump	---	rps	OctP RF	150	V	Pulse HV	1360	V
S/C Temp	2	degC	OctP Bias	-6	V			

===Reaction Cell===								
Reaction Mode	OFF							
H2 Gas	---	mL/min	He Gas	0	mL/min	Optional Gas	---	%

Generated : Jul 15, 2013 13:06:03
Printed : Jul 15, 2013 13:06:08

Example Tune File for He.U

Sensitivity

Tune File : HE.U

Integration Time: 0.1000 sec
Sampling Period: 0.7200 sec
n: 60

m/z	Range	Count	Mean	RSD%
89	20,000	3993.0	4250.3	2.89
205	20,000	6693.0	6657.7	2.75
59	20,000	7657.0	7513.1	2.61
51	20	2.0	5.0	46.98
52	200	164.0	173.1	8.27
75	20	17.0	14.2	28.67
78	20	0.0	1.2	104.94

Tuning Parameters

===Plasma Condition===			===Ion Lenses===			===Q-Pole Parameters===		
RF Power	:	1550 W	Extract 1	:	0 V	AMU Gain	:	125
RF Matching	:	1.76 V	Extract 2	:	-145 V	AMU Offset	:	126
Smpl Depth	:	8 mm	Omega Bias-ce	:	-30 V	Axis Gain	:	0.9989
Torch-H	:	-0.1 mm	Omega Lens-ce	:	-1.4 V	Axis Offset	:	-0.03
Torch-V	:	0.1 mm	Cell Entrance	:	-30 V	QP Bias	:	-16 V
Carrier Gas	:	0.8 L/min	QP Focus	:	-10 V			
Makeup Gas	:	0.1 L/min	Cell Exit	:	-40 V	===Detector Parameters===		
Optional Gas	:	--- %				Discriminator	:	8 mV
Nebulizer Pump	:	0.1 rps	===Octopole Parameters===			Analog HV	:	2100 V
Sample Pump	:	--- rps	OctP RF	:	150 V	Pulse HV	:	1360 V
S/C Temp	:	2 degC	OctP Bias	:	-18 V			

===Reaction Cell===								
Reaction Mode	:	ON						
H2 Gas	:	--- mL/min	He Gas	:	5.6 mL/min	Optional Gas	:	--- %

Generated : Jul 15, 2013 13:14:12
Printed : Jul 15, 2013 13:14:17

18.0 Revision History

- Revision 3, dated 30 December 2009
  - Integration for TestAmerica and STL operations.
  - Updated to 6020A.
- Revision 4, dated 31 August 2011
  - Organizational changes.
  - Addition of QAF-45 and Section 14.2.
  - Addition of corporate SOPs Selection of Calibration Points / CA-T-P-002 and Calibration Curves (General) / CA-Q-S-005.
  - Update ICS A and ICS B concentrations and vendor, with concentration changes to ICS AB. Remove 20 mg/L mineral standard.
  - Addition of Tune Check to Section 9.
  - Addition of a 1 µg/L calibration standard.
  - Deletion of repetitive language.
  - Remove requirement to run batches of 10 for WY samples.
- Revision 5, dated 30 November 2011
  - Add minerals to list of analytes, changing primary, secondary standard, Working ICS Solution B, LCS, ICV, LLCCV, and calibration standard preparations; Isotopes, Internal Standards, and Reaction Gases for Selected Elements.
  - Add preparation of mixed acid diluent.
  - Change some tune criteria.
  - Remove system flushing between each standard solution in the calibration instructions.
  - Modify the analytical sequence with the mention of a rinse instead of a memory check.
- Revision 6, dated 30 August 2013
  - Organizational changes
  - Addition of filter information.
  - Update standard identification, source, related preparations.
  - Update Reporting Limits (RLs).
  - Addition of Agilent 7500cx.
  - Remove use of Hydrogen (H_2) as reaction gas from literature, tables, attachments, etc.
  - Update Isotopes, Internal Standards, and Reaction Gas for Selected Elements.
  - Change frequency of Matrix Spike / Matrix Spike Duplicate.
  - Change some tune criteria.
  - Modify the analytical sequence with the mention of Digested RLV before analysis of ICS A and ICS AB and Undigested RLV after analysis of CCB at beginning and end of batch.
  - Remove the requirement to run batches of 10 for OK samples.

Title: MERCURY IN LIQUID WASTE (MANUAL COLD VAPOR TECHNIQUE) METHOD 7470A

Approvals (Signature/Date)			
Rodney Street Department Manager	1/29/14 Date	Johnny Davis Health & Safety Manager / Coordinator	1/27/14 Date
Steve Miller Quality Assurance Manager	1/25/14 Date	Michael H. Dunn Technical Director	1/24/14 Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method uses cold-vapor atomic absorption for determining the concentration of mercury (CAS # 7439-97-6) in mobility-procedure extracts, aqueous wastes, and ground waters.

1.2 Reporting Limits: The typical detection limit for this method is 0.0002 mg/L.

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

This method is a cold-vapor atomic absorption technique and is based on the absorption of radiation at 253.7-nm, by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 Potassium permanganate is added to eliminate possible interference from sulfide.

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

4.3 Seawaters, brines, and industrial effluents high in chlorides **require** additional permanganate because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 ηm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by using an excess of hydroxylamine sulfate reagent, or by dilution of the original sample.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This method may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: Perform the digestion in an operational fume hood.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury	Oxidizer Corrosive Poison	0.1 mg/m^3 Ceiling (Mercury Com-pounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. Can cause burns. Can cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. Can affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; can cause serious and permanent eye damage.
Nitric acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which can be fatal. Other symptoms can include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and can cause damage to the eyes. Contact can cause severe burns and permanent eye damage.
Hydro-chloric acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and can cause damage to the eyes. Contact can cause severe burns and permanent eye damage.
Potassium perman-ganate	Oxidizer	5 mg/m^3 for Mn Com-pounds	Causes irritation to the respiratory tract. Symptoms can include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Sulfuric acid	Corrosive Oxidizer Dehydra-tor Poison Carcino-gen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Potassium persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Leeman Mercury Cold Vapor Analyzer Hydra AA: Instrument settings recommended by the particular manufacturer are followed.
- Recorder: Data acquisition by PC running Leeman software.
- Air pump: Any peristaltic pump capable of delivering 1 liter air/minute is used.
- Flowmeter: Capable of measuring an air flow of 1 liter/minute.

- Hot water bath or digestion block. - Adjustable and capable of maintaining a temperature of 90-95°C.

6.2 Supplies

- Volumetric flasks and pipettes of suitable precision and accuracy (Class A).
- Certified, centrifuge tubes, 50-mL.

7.0 Reagents and Standards

7.1 Reagent water, analyte-free.

7.2 Hydrochloric acid, HCl, concentrated, commercial.

7.3 Nitric acid (HNO_3), concentrated: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to change lots of the Nitric acid.

7.4 Sulfuric acid, concentrated, commercial, reagent grade.

7.5 Stannous chloride: Add 100 g Stannous chloride to 100 mL HCl, dilute to 1000 mL with reagent water in a 1-L container.

7.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 120 g of Sodium chloride and 120 g of Hydroxylamine sulfate in reagent water and dilute to 1000 mL with reagent water in a 1-L container. (Hydroxylamine hydrochloride may be used in place of Hydroxylamine sulfate.)

7.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 50 g of Potassium permanganate in 1000 mL of reagent water in a 1-L container.

7.8 Potassium persulfate, 5% solution (w/v): Dissolve 50 g of Potassium persulfate in 1000 mL of reagent water in a 1-L container.

7.9 Stock mercury solution: Stock solutions are purchased at 1000 µg/mL from CPI and Ultra Scientific. Use caution in handling mercury solutions.

7.10 Mercury intermediate working standard: Make dilution of the stock mercury solution to obtain a working standard containing 1.0 µg/mL. Dilute 0.05 mL 1000 µg/mL stock to 50.0 mL with 1% HNO_3 in a Class A, volumetric flask. Prepare monthly.

7.11 Initial Calibration Verification/Laboratory Control Sample (ICV/LCS): Prepare from a **different** source than the calibration standards.

7.12 See SOP Reagent and Standard Purchase, Preparation, Control, and Documentation / NV08-214 for shelf-life and storage requirements for reagents and standards.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	HDPE or Glass	30.0 mL	HNO_3 to pH ≤ 2	28 days from collection	SW-846 Chapter 2

Temperature preservation is not used. Certified cleaned containers are used, if the containers are supplied by TestAmerica Nashville.

9.0 Quality Control

Refer to the QA Manual for quality control (QC) policies. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC

The following quality control samples are prepared with **each batch of no more than 20 samples.**			
Quality Controls	**Frequency**	**Acceptance Limits**	**Corrective Action**
Method Blank	1 per batch	< ½ RL	Correct problem, then re-prep and analyze method blank, all samples, and QC processed with the contaminated blank.
Laboratory Control Sample[1] (LCS), second source	1[1,2] per batch	80-120% recovery	Correct problem, then re-prep and analyze the LCS, all samples, and QC in the affected analytical batch. If high and sample is ND, it is OK to report.
Matrix Spike	1 per batch	75-125% recovery	If both MS and MSD are similarly outside acceptable limits and the LCS is within acceptable limits, the batch is acceptable. If one analysis of the MS/MSD pair is within acceptable limits and the other is outside acceptable limits, repeat the analysis exhibiting unacceptable results.
Matrix Spike Duplicate	1 per batch[2]	75-125% recovery, < 20% RPD	
Dilution Test	1 per batch	5X dilution sample result must be 90-110% of the undiluted sample result.	Perform post-digestion spike.
Post-digestion Spike	If results of dilution test do not agree.	80-120%	Dilute and reanalyze

1 All AZ, MA, and TX samples require a LCS duplicate in each batch.

- **Method blank:** The laboratory prepares and analyzes at least one blank (30 mLs reagent water) with each batch.
- A **Laboratory Control Sample (LCS):** To evaluate the ability of analyzing a clean matrix of known concentration, prepare one LCS per batch exactly as client samples, and compare the % recovery to the control limits.
  - Add 30 µL of 1.0 µg/mL standard to 30.0 mL reagent water for the LCS in a certified, centrifuge tube for a final concentration of 1.0 µg/L.
- A **Matrix Spike/Matrix Spike Duplicate (MS/MSD)** are analyzed every batch. If the recovery for the MS/MSD cannot be determined, due to the high concentration (4 times greater than the spike level) of the sample used for spiking, then run a dilution test.
  - Prepare the spike solution by adding 30 µL of 1.0 µg/mL standard to 30.0 mL reagent water for the MS/MSD in a certified, centrifuge tube for a final concentration of 1.0 µg/L.
- **Dilution Test:** Dilute the sample by a minimum of five fold and re-analyze. Agreement within 10% between the concentration for the undiluted sample and five times the concentration for the diluted sample indicates the absence of interferences. If the results do not agree, run a post-digestion spike.
- **Post-Digestion Spike:** If the post-digestion spike is not within 80-120%, dilute the original sample and re-run.

9.2 Instrument QC

Quality Controls	Frequency	Control Limit	Corrective Action
Initial Calibration Verification Sample (ICV), second source	Immediately after calibration	90-110% recovery. Replicates >RL: <10% RPD. Replicates < RL: <30% RPD.	Correct problem, then repeat initial calibration. If the RPD fails for a concentration level, run two new replicates.
Initial Calibration Blank	Beginning of each batch	< MDL	Correct problem, then re-digest and re-analyze calibration and entire digestion batch.
Continuing Calibration Verification Sample (CCV)	Every 10 samples and end of batch	90-110%	If CCV falls outside of range low rerun once and if still out of range, correct problem, recalibrate and rerun all affected samples. If high and sample is ND, OK to report.
Continuing Calibration Blank	Following the CCV	< ½ RL	Rerun affected samples.
Control Report Limit Atomic Absorption (CRA) / Report Limit Verification (RLV)	Beginning of each batch	0.14-0.26 µg/L, ± 30% true	Correct problem, re-run, re-calibrate.

- **Initial Calibration Verification (ICV)** and **Initial Calibration Blank (ICB):** A verification standard made from a **different** source than the calibration standards is run immediately after calibration.
  - Prepare ICV by adding 75 µL of the 1.0 µg/mL second-source standard to 30.0 mL acidified reagent water in a certified, centrifuge tube for a final concentration of 2.5 µg/L.
  - The ICB contains the same acid and reagent water as the calibration standards. They are digested.
- **Continuing Calibration Verification** (CCV) and **Continuing Calibration Blank (CCB)**: Every 10 samples and at the end of the sequence, a mid-level standard (2.0 µg/L) is analyzed. If the CCV is outside of range, rerun once and, if still out of range, correct problem, recalibrate and rerun all affected samples.
  - Prepare CCV by adding 60 µL of the 1.0 µg/mL primary source standard to 30.0 mL acidified reagent water in a certified, centrifuge tube for a final concentration of 2.0 µg/L.
  - The CCB contains the same acid and reagent water as the calibration standards. They are digested.
- **Control Report Limit Atomic Absorption (CRA)**, **Report Limit Verification (RLV):** Daily, analyze a low calibration verification at 0.2 µg/L at the beginning of the analytical sequence. If the percent recovery falls outside the limits, the CRA/RLV must be re-analyzed immediately. If it fails again, correct the problem, re-calibrate. The CRA/RLV is also used as the MDL verification and establishes the report limit.
  - Prepare by diluting the 2.0 µg/L CCV standard by 10x (3.0 mL to 30.0 mL). The acceptance range is 0.14 µg/L to 0.26 µg/L.

10.0 Procedure

10.1 Sample Preparation: Refer to SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

Matrix	Sample Size
Water	30 mL of sample

1	Transfer 30.0 mL of sample into a 50-mL, certified, centrifuge tube. Record the centrifuge tube lot number. For the LCS, add 30.0 mL reagent water to a 50-mL, certified, centrifuge tube.
2	Prepare the spiked QC samples as described in Section 9.1.
3	Add 1.5 mL of H_2SO_4 and 0.75 mL of concentrated HNO_3, mixing after each addition.
4	Add 4.5 mL of 5% Potassium permanganate solution to each sample bottle. Ensure that equal amounts of permanganate are added to standards and blanks.
5	Add 2.4 mL of Potassium persulfate to each bottle, mark liquid level, and cap. Heat for 120 ± 10 minutes in a water bath maintained at 95 ± 2°C. Record start and stop time and temperature.
6	If Potassium permanganate is reduced during sample preparation, remove the sample from the batch, and re-prepare as a dilution that allows permanganate to persist throughout all of the sample preparation.
7	Cool, if needed, bring to mark with reagent water, and add 1.8 mL of Sodium chloride hydroxylamine sulfate to reduce the excess permanganate. Additional hydroxylamine solution may be needed to complete de-colorization. Place in autosampler and start analysis.

10.2 Calibration: Refer to SOP Selection of Calibration Points / CA-T-P-002 and Calibration Curves (General) / CA-Q-S-005. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

1	Start-up the instrument computer, using "WinHg runner," the software: Go to the control tab and turn the pump on at 5 mL/minute. Turn lamp and gas on. The instrument turns on and goes through a warm-up period. Because of instrument variation refer to the manufacturer's recommended operating conditions when using this method. Allow the instrument to proceed through a warm-up period before beginning the calibration sequence.
2	Standard preparation: **Daily**, prepare calibration standards from 1.0 µg/mL working standard in 30.0 mL of 1% HNO_3.
3	Transfer into a 50-mL**,** certified, centrifuge tube. Record the centrifuge tube lot number.
4	Mix thoroughly and add 1.5 mL of concentrated H_2SO_4 and 0.75 mL of concentrated HNO_3 to each bottle.
5	Add 4.5 mL of $KMnO_4$ solution to each bottle.
6	Add 2.4 mL of Potassium persulfate to each bottle, mark liquid level, and cap. Heat for 120 ± 10 minutes in a water bath maintained at 95 ± 2°C. Record start and stop time and

mL Standard/30.0 mL final volume	Final Concentration, µg/L
0.0	0.0
0.006	0.2
0.015	0.5
0.030	1.0
0.060	2.0
0.075	2.5
0.150	5.0

	temperature.
7	Cool, if needed, bring to mark with reagent water, and add 1.8 mL of Sodium chloride hydroxylamine sulfate to reduce the excess permanganate. Additional hydroxylamine solution may be needed to complete de-colorization. Place in autosampler and start analysis.
8	After computer start-up (see Sample Analysis below), put the appropriate standards for the method selected in the standard rack. Click on standard tab.
9	Depress standard buttons for standards 1, 2, 3, 4, 5, and 6.
10	Depress Rep 1 and Rep 2 buttons, then click standard Auto. The instrument begins calibration, using a linear calibration curve model. Only linear models are allowed.
10	To view first order linear regression curve, click data base button and the cal curve tab. The new curve is displayed. If its correlation coefficient $r \geq 0.995$ (or $r^2 \geq 0.990$), then check the accepted box and the new curve is stored.
11	Ensure the control limits in Section 9.2 for initial calibration are achieved.

10.3 Sample Analysis

1	Replenish the stannous chloride reservoir for automated addition of reagent.
2	Running samples: • Click rack editor button to open appropriate rack file (1 or 2), then enter sample ID into appropriate cup position. • Save information before returning to WinHg runner. • Return to runner and click sample tab. • Choose rack number to be run, start cup number and end cup number. • To begin, click run auto button; the instrument begins the sequence. Spiked samples and check standards are analyzed.
3	Shut-down procedure: • Return to control tab. Turn gas and pump off, and loosen tubes. • Turn off the power to the lamp if the instrument is not used for 24 hours or longer.

10.4 Example Analysis Queue / Sequence*

1	Initial Calibration (daily)
2	ICV (daily)
3	ICB (daily)
4	CRA/RLV (daily)
5	Method Blank
6	LCS
7	Matrix Spike
8	Matrix Spike Duplicate
9	Samples 1-10
10	CCV
11	CCB
12	Samples 11-20
13	CCV
14	CCB

*May be up to 20 samples.

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\text{LCS \% Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 % Drift

$$\text{\% Drift} = \frac{(\text{Result - True Value}) \times 100}{\text{True Value}}$$

11.4 Linear calibration using a least squares regression

Perform a linear regression of the instrument response versus the concentration of the standards. Non-linear equations are not allowed for this analysis. Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). This is a statistical requirement and is not simply a graphical convention.

The regression produces the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

y = instrument response (peak area)
a = slope of the line
x = concentration of the calibration standard
b = the intercept

Do not force the line through the origin, but have the intercept calculated from the data points. The use of a linear regression is not used as a rationale form reporting results below the lowest calibration standard. The regression calculation generates a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.995 or $r^2 \geq 0.990$.

11.4 Coefficient of Determination

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2}$$

Correlation Coefficient

$$r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response or Response ratio
x = Concentration

11.5 Sample Concentrations: Record metal concentrations directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account.

Concentration (µg/L) = (µg/L from instrument) (dilution factor)

Dilution factor = 1 if there is no dilution.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required for each matrix.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are managed, stored, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Acid waste: transfer to the waste disposal area for neutralization.
- Mercury waste: dispose in Mercury waste drum.

15.0 References / Cross-References

15.1 EPA Method 7470A, SW-846 Revision 1, September 1994.
15.2 EPA Method 7000B, SW-846 Revision 2, February 2007.
15.3 TestAmerica Nashville's Quality Assurance Manual.
15.4 Corporate Environmental Health and Safety Manual (CW-E-M-001)
15.5 SOPs: Selection of Calibration Points / CA-T-P-002, Calibration Curves (General) / CA-Q-S-005, Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff /

NV08-199, Determination of Method Detection Limits / NV08-202, Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
15.6 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications
None.

17.0 Attachments
None.

18.0 Revision History
- Revision 10, 15 May 2009
  - Integration of STL and TestAmerica formats.
  - Correction of acid addition volumes to samples based on 50-mL final volume.
- Revision 11, 25 September 2009
  - Incorporation of OH VAP requirements.
  - Revision of preparation of LCS, MS/MSD, ICV, CCV, and standards due to change of pipettors.
- Revision 12, dated 31 October 2011
  - Organizational changes.
  - Incorporation of amendments 11a and 11b.
  - Addition of QAF-45 and Section 14.2.
  - Addition of reference to the corporate SOPs Selection of Calibration Points / CA-T-P-002 and Calibration Curves (General) / CA-Q-S-005.
  - OK is now the only state requiring batches of no more than 10 samples.
  - Add % drift equation.
  - Change volume additions of Sulfuric acid, Nitric acid, Potassium permanganate, Potassium persulfate, and Hydroxylamine.
- Revision 13, dated 30 November 2011
  - Modification of Sample Preparation steps 4 and 5, Calibration steps 6 and 7.
- Revision 14, dated 29 February 2012
  - Correction of reagent additions in Section 10.
  - Revised instruction on reduction of Potassium permanganate.
- Revision 15, dated 31 July 2012
  - OK no longer limits batch size to 10 samples.
  - ICV and CCV are digested.
  - Clarification of sample preparation and calibration sections.
- Revision 16, dated 31 January 2014
  - Organizational change.
  - Addition of Changes 15a, b, c. Return CCV limits to 90-110%.
  - WV no longer requires a LCSD.
  - Specify that $r^2 \geq 0.990$.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP)
Change Form

SOP Number/Revision No.: **7471 / NV06-100.13a** Effective Date: **11/29/2013**

Last Mod. Date: 9/30/13

SOP Title: **Method 7471A/B: Mercury in Solid or Semisolid Waste (Manual Cold Vapor Technique)**

Affected SOP Section Number(s): Section 9.2, Instrument QC

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 06

Revision Number with Mod ID: **13b**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Delete crossed-out text.

Section 9.2, Instrument QC, Change the following rows:

Quality Controls	Frequency	Control Limit	Corrective Action
~~Instrument Detection Limits (IDL)~~	~~Quarterly~~	~~±3 times standard deviation of the average response of blanks.~~	~~Update MDL/IDL comparison. If IDL > MDL, correct problem and rerun IDL.~~

- ~~**Instrument Detection Limits (IDL):** On a quarterly basis, analyze 10 CCBs consecutively. Calculate the average response and standard deviation. The IDL is ± 3SD of the average response. Update LIMS with new information. IDL must be ≤ MDL.~~

11/5/13	
Department Manager Approval Date Steve Shilley 11/1/13	Michael A. Brown 11/5/13
Quality Manager Approval Date	Technical Director Approval Date

SOP Number/Revision No.: **7471 / NV06-100.13** Effective Date: **9/30/2013**

Last Mod. Date: 5/31/12

SOP Title: **Method 7471A/B: Mercury in Solid or Semisolid Waste (Manual Cold Vapor Technique)**

Affected SOP Section Number(s): Section 9.2, Instrument QC, Section 10.1, Sample Preparation; Section 10.2, Calibration

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 06

Revision Number with Mod ID: **13a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add bold text; ~~delete~~ crossed-out text.

Section 9.2, Instrument QC, Change the following rows:

Quality Controls	Frequency	Control Limit	Corrective Action
Control Report Limit Atomic Absorption (CRA) / Report Limit Verification (RLV)	Beginning of each batch	0.14-0.26 µg/L, ± 30% true	Correct problem, re-run, re-calibrate.
~~MDL Verification~~	~~Minimum annually~~	~~Detect~~	~~Re-evaluate MDL standard used and MDL; see Technical Manager.~~

- **Control Report Limit Atomic Absorption (CRA),** Report Limit Verification (RLV): Daily analyze a standard at the RL standard, prepared like the samples. If the percent recovery falls outside the control limits, the **CRA/**RLV must be re-analyzed immediately. If it fails again, correct problem, re-calibrate. The RLV may also be used as the MDL verification (1-3 X MDL) and establishes the report limit.

Section 10.1, Sample Preparation, Step 1

1	Weigh a 0.6-g portion of a well homogenized sample (three 0.2 g portions) and place in the bottom of a clean, certified, ~~polypropylene~~ tube. **Record the centrifuge tube lot number.** See SOP Sample Homogenization, Subsampling, and Compositing / NV08-229.

Section 10.2, Calibration, Add to section title: **Document the preparation of calibration standards,**

the ICV standard, and the CRA standard in a preparation batch in LIMS.

Section 10.2, Calibration, Step 2

2	**Each day of analysis**, prepare a fresh set of the following calibration standards in clean, certified, centrifuge tubes. **Record the centrifuge tube lot number.**

9/6/13	9/6/13
Department Manager Approval Date	Technical Director Approval Date Quality Manager Approval

Title: MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE) SW-846 METHOD 7471A/B

Approvals (Signature/Date)

Rodney Street Metals Operations Manager	5-8-12 Date	Johnny Davis Health & Safety Manager / Coordinator	5-18-12 Date
Eric S. Smith Quality Assurance Manager	5/30/12 Date	Michael H. Dunn Technical Director	5-18-12 Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method is used for measuring total Mercury (organic and inorganic) in soils, sediments, and sludge-type materials.

1.2 Reporting Limit (RL): The nominal laboratory RL is 0.1 mg/kg.

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor/Manager or the Laboratory Technical Director. All abnormalities must be noted on the data or the benchsheet and in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

This method is based on cold-vapor atomic absorption at the 253.7-nm wavelength. The Mercury is reduced to the elemental state and aerated from solution in a closed system. The Mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of Mercury concentration.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 Potassium permanganate is added to eliminate possible interference from sulfide.

4.2 Copper has also been reported to interfere; however, Copper concentrations as high as 10 mg/kg had no effect on recovery of Mercury from spiked samples.

4.3 Samples high in chlorides require additional permanganate because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the Mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent or by dilution of the sample.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury	Oxidizer Corrosive Poison	0.1 mg/m^3 Ceiling (Mercury Com-pounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. Can cause burns. Can cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. Can affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; can cause serious and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which can be fatal. Other symptoms can include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and can cause damage to the eyes. Contact can cause severe burns and permanent eye damage.
Hydro-chloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and can cause damage to the eyes. Contact can cause severe burns and permanent eye damage.
Potas-sium Perman-ganate	Oxidizer	5 mg/m^3 for Mn Com-pounds	Causes irritation to the respiratory tract. Symptoms can include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Leeman Mercury Analyzer PS-200 II, or equivalent. Instrument settings recommended by the particular manufacturer are followed.
- Data Acquisition, Leeman software.
- Air pump: Any peristaltic pump capable of delivering 1 L/minute air is used.
- Flowmeter, capable of measuring an air flow of 1 L/minute.
- Hot water bath or digestion block, adjustable and capable of maintaining a temperature of 92-98°C.

6.2 Supplies

- Volumetric flasks and pipets of suitable precision and accuracy (Class A).
- Teflon™ boiling chips (Mercury-free blank matrix).
- Polypropylene, certified, centrifuge tubes, 50 mL.

7.0 Reagents and Standards

7.1 Reagent water, analyte-free.

7.2 **Hydrochloric acid**, HCl, concentrated, commercial.
7.3 **Nitric acid**, HNO_3, concentrated, commercial.
7.4 **Aqua regia**: Prepare immediately before use by carefully adding **three** volumes of concentrated HCl to **one** volume of concentrated HNO_3.
7.5 **Stannous chloride** (10% weight to volume): Add 100 g stannous chloride to 100 mL HCl, dilute to 1000 mL with reagent water in a 1-L container.
7.6 **Sodium chloride-hydroxylamine sulfate solution**: Dissolve 120 g of Sodium chloride and 120 g of Hydroxylamine sulfate in reagent water and dilute to 1000 mL with reagent water in a 1-L container.
7.7 **Potassium permanganate**, Mercury-free, 5% solution (w/v): Dissolve 50 g of Potassium permanganate in 1000 mL of reagent water in a 1-L container.
7.8 **Mercury stock solution:** Certified commercial source (1000 µg/mL).

- **Mercury intermediate working standard**: Make dilution of the stock Mercury solution to obtain a working standard containing 1.0 µg/mL. Dilute 0.05 mL stock to 50.0 mL with 1% HNO_3 (10 mL concentrated acid to 1 L reagent water) in a Class A, volumetric flask. Prepare monthly.

7.7 See SOP Reagent and Standard Purchase, Preparation, Control, and Documentation / NV08-214 for shelf-life and storage requirements for reagents and standards.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Solid	HDPE or Glass	1-10 g	Less than or equal to 6 degrees C.	28 days from collection	SW-846 Chapter 2

9.0 Quality Control

Refer to the quality control section of TestAmerica Nashville's QA Manual for specific quality control (QC) policies. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC

The following quality control samples are prepared with **each batch of no more than 20 samples.**			
Quality Controls	**Frequency**	**Control Limit**	**Corrective Action**
Method Blank	1 each batch	< RL	Correct problem, re-prep and analyze the MB, all samples, and QC in the affected analytical batch.
Laboratory Control Sample[1] (LCS), second source	1[1] each batch	80-120% recovery	Correct problem, then re-prep and re-analyze the LCS, all samples, and QC in the affected analytical batch. If high and target is ND, OK to report.
Matrix Spike (MS), second source	1 each batch	7471A: 75-125% recovery 7471B: 80-120% recovery	Report and qualify

The following quality control samples are prepared with **each batch of no more than 20 samples.**			
Quality Controls	**Frequency**	**Control Limit**	**Corrective Action**
Matrix Spike Duplicate (MSD), second source	1 each batch	7471A: 75-125% recovery 7471B: 80-120% recovery RPD< 20%	Report and qualify
Dilution Test	Diluted samples	5X sample result must be 90-110% of the undiluted sample result.	Run post-digestion spike
Post-digestion Spike	If MS/MSD fails	80-120% recovery	Dilute and re-analyze.

[1]For AZ, TX, WV samples, a LCS duplicate is required.

- **Method blank:** The method blank starts with the addition of 50 mL reagent water and aqua regia to 0.6 g boiling chips.
- A **Laboratory Control Sample (LCS):** To evaluate the ability of analyzing a clean matrix of known concentration, prepare one LCS per batch exactly as client samples, as follows:
  - Add 0.100 mL of the intermediate secondary working solution to 0.6 gram Teflon™-boiling chips. Dilute to 100 mL in a Class A volumetric flask with reagent water for a 1.0 µg/L final concentration in the digestate.
- **Matrix Spike/Matrix Spike Duplicate Pair:** To evaluate the effect of the matrix on the analysis, analyze two, identical, 0.6 gram aliquots of a client sample.
  - Spike each aliquot with 0.100 mL of the intermediate secondary standard. Digest and dilute to 100 mL in a Class A volumetric flask with reagent water for a 1.0 µg/L final concentration in the digestate
  - If the recovery for the MS/MSD cannot be determined, due to the high concentration (about four times greater than the spike level) of the sample used for spiking, then run a dilution test.
  - If the MS/MSD % recovery is not met, perform the following:
- **Dilution Test:** If there is a sample in the batch greater than 5.0 µg/kg, dilute the sample by a minimum of five-fold and reanalyze. If results do not agree, run a post-digestion spike.
- **Post-digestion Spike:** If the post-digestion spike does not meet the QC criteria, dilute the original sample and re-run.

9.2 Instrument QC

Quality Controls	**Frequency**	**Control Limit**	**Corrective Action**
Initial Calibration Verification Sample (ICV), second source	Immediately after calibration	90-110% recovery	Correct problem, then repeat initial calibration.
Initial Calibration Blank (ICB)	Immediately after ICV	< MDL	Correct problem then re-digest and reanalyze calibration and entire digestion batch.
Continuing Calibration Verification Sample (CCV), primary source	Every 10 samples	7471A: 90-110% recovery 7471B: 80-120% recovery	Correct problem; repeat all QC and samples since last successful CCV. If high and target is ND, OK to report.
Continuing Calibration Blank (CCB)	Following each CCV	< RL	Correct problem, repeat all QC and samples associated with that CCB.

Quality Controls	Frequency	Control Limit	Corrective Action
Instrument Detection Limits (IDL)	Quarterly	±3 times standard deviation of the average response of blank.	Compare with MDL and re-run if IDL > MDL. If the IDL is still > MDL, elevate the MDL to the IDL. Update LIMS.
Report Limit Verification (RLV)	Daily	Required percent recovery is ±30%.	Perform maintenance, recalibrate.
MDL Verification	Minimum annually	Detect	Re-evaluate MDL standard used and MDL; see Technical Director.

- **Initial Calibration Verification (ICV) and Initial Calibration Blank (ICB):** The laboratory analyzes an ICV and an ICB immediately following daily calibration.
  - For the ICV, add 250 µL of the secondary intermediate standard to 100 mL of reagent water in a Class A volumetric flask for a 2.5 µg/L final concentration.
  - The ICB contains the same acid and reagent water as the calibration standards; it is not digested.
- **Instrument Detection Limit (IDL):** - On a quarterly basis, analyze 10 CCBs consecutively. Calculate the average response and standard deviation. The IDL is ± 3SD of the average response. Compare to the MDL.
- **Continuing Calibration Verification (CCV and CCB):** Analyze after every 10th sample and at the end of the analytical sequence.
  - Prepare the CCV at 2.0 µg/L by adding 200 µL of the primary Mercury standard to 100 mL reagent water in a Class A volumetric flask. Digest the CCV in the same manner as the samples.
  - The CCB contains the same acid and reagent water as the calibration standards; it is digested.
- **Report Limit Verification (RLV):** Daily analyze a standard at the RL standard, prepared like the samples. If the percent recovery falls outside the control limits, the RLV must be re-analyzed immediately. If it fails again, correct problem, re-calibrate. The RLV may also be used as the MDL verification (1-3 X MDL) and establishes the report limit.

10.0 Procedure

10.1 Sample Preparation

Matrix	Sample Size
Solid	0.6 gram

1	Weigh a 0.6-g portion of a well homogenized sample (three 0.2 g portions) and place in the bottom of a clean, certified, polypropylene tube. See SOP Sample Homogenization, Subsampling, and Compositing / NV08-229.
2	Prepare the spiked QC samples as described in Section 9.1.
3	Add 5.0 mL of reagent water and 5.0 mL of aqua regia to all samples and QC.
4	Heat 2 minutes in a hot block at 95 ±3°C. Record time and temperature. Vary the location of the thermometer weekly and record the position.
5	Cool; then add 10.0 mL reagent water and 15.0 mL potassium permanganate solution to each sample bottle.
6	Mix thoroughly, cap, and place in the hot block for 30 minutes at 95 ± 3°C. Record.
7	Cool and add 6.0 mL of sodium chloride-hydroxylamine sulfate to reduce the excess

	permanganate.
8	Dilute to 100 mL in a Class A volumetric flask. Transfer an aliquot to a centrifuge tube for storage.

10.2 Calibration: Refer to SOPs Calibration Curves (General) / CA-Q-S-005 and Selection of Calibration Points / CA-T-P-002. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

1	Start-up the instrument computer, using "WinHg runner," the software: Go to the control tab and turn the pump on at 5 mL/minute. Turn lamp and gas on. The instrument turns on and goes through a warm-up period. Because of instrument variation refer to the manufacturer's recommended operating conditions when using this method. Allow the instrument to proceed through a warm-up period before beginning the calibration sequence.
2	**Each day of analysis**, prepare a fresh set of the following calibration standards in clean, certified, centrifuge tubes:

µL of 1.0 µg/mL Primary Standard to 100 mL Reagent Water	Calibration Standard Concentration (µg/L)
0	0
20	0.2
50	0.5
100	1.0
200	2.0
250	2.5
500	5.0

	Note: The lowest non-zero calibration standard is at or below the RL. Run each in replicate.
3	Add 5.0 mL reagent water to each.
4	Add 5.0 mL aqua regia and heat 2 minutes in a water bath at 95 ±3°C. Record. Allow the sample to cool.
5	Add 10.0 mL reagent water and 15.0 mL $KMnO_4$ solution to each tube, and return to the water bath for 30 minutes at 95 ± 3°C. Record. Cool.
6	Add 6.0 mL sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate.
7	Dilute to 100 mL reagent water in a Class A volumetric flask.
8	Place the appropriate standards for the method selected in the standard rack. Click on the standard tab.
9	Depress standard buttons for standards #1, #2, #3, #4, #5, #6, and #7.
10	Depress Rep 1 and Rep 2 buttons, then click standard Auto. The instrument will begin calibration.
11	To view first-order linear regression curve, click database button and the cal curve tab. The new curve is displayed. If its correlation coefficient, r, is greater than or equal to 0.995 ($r^2 \geq 0.99$), the new curve is stored. Higher order, nonlinear models are not allowed.
12	If the correlation coefficient requirement is not met, prepare the calibration standards again and repeat calibration.
13	When calibrating replicates > RL, RPD must be <10. For the blank and RL standard replicates, RPD must be <30. If the RPD fails for a concentration level, run two new replicates.

10.3 Sample Analysis

1	Replenish the stannous chloride reservoir for automated addition of reagent.
2	Click rack editor button open appropriate rack file (1 or 2), then enter sample ID into appropriate cup position.
3	Save information before returning to "WinHg runner."
4	Return to " WinHg runner" and click sample tab.
5	Choose rack number to be run, start cup number and end cup number.
6	To begin click run auto button, the instrument will begin the sequence. Print the raw absorbance and concentration for each sample and QA/QC.
7	To shutdown the procedure, return to the control tab. Turn gas and pump off and loosen tubes. Turn off the power to the lamp if the instrument will not be used for 24 hours or longer.

10.4 Example Analysis Queue / Sequence

1	Initial Calibration (daily)
2	ICV (daily)
3	ICB (daily)
4	RLV (daily)
5	Method Blank
6	LCS
7	LCSD, if needed
8	Sample 1
9	Matrix Spike
10	Matrix Spike Duplicate
11	Samples 2-10
12	CCV
13	CCB
14	Samples 11-20
15	CCV
16	CCB

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\textbf{LCS \% Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\textbf{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 Linear calibration using a least squares regression

Perform a first-order linear regression of the instrument response versus the concentration of the standards. Non-linear equations are not allowed for this analysis. Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). This is a statistical requirement and is not simply a graphical convention.

The regression produces the slope and intercept terms for a linear equation in the form:

$y = ax + b$

y = instrument response (peak absorbance)
a = slope of the line
x = concentration of the calibration standard
b = the intercept

The analyst must not force the line through the origin, but have the intercept calculated from the data points. The use of a linear regression is not used as a rationale for reporting results below the calibration range demonstrated by the analysis of the standards. The regression calculation generates a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.995 or $r^2 \geq 0.99$. Re-fit the calibration points. Each point must be within 10% of true or re-calibrate.

11.4 Coefficient of Determination **Correlation Coefficient**

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2} \qquad r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response
x = Concentration

11.5 Record and print metal concentrations directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account.

$$\textbf{Concentration (µg/g)} = \frac{(\text{µg/L from instrument})\,(\text{dilution factor})}{\text{grams of sample}}$$

If no dilution, the dilution factor is 1.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless the method requires a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average %

recovery within the control limits and a precision less than the quality control maximum are required for each matrix.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are managed, stored, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Digestates are disposed of in the Mercury waste drum in the waste disposal area.

15.0 References / Cross-References

15.1 SW-846 Methods 7471A, Update III, September 1994, and 7471B, Revision 2, February 2007.

15.2 TestAmerica Nashville's Quality Assurance Manual.

15.3 TestAmerica Nashville's Control Limits Manual.

15.4 Corporate Environmental Health and Safety Manual (CW-E-M-001)

15.5 SOPs: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213, Determination of Method Detection Limits / NV08-202, Sample Homogenization, Subsampling, and Compositing / NV08-229, Selection of Calibration Points / CA-P-T-002, Calibration Curves (General) / CA-Q-S-005.

15.6 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachments

None.

18.0 Revision History

- Revision 10, dated 30 September 2008
  - Integration of TestAmerica and STL operations.
  - Update to 7471B.
- Revision 11, dated 25 September 2009
  - Addition of OH VAP requirements.
- Revision 12, dated 31 August 2010
  - Addition of QAF-45, Section 14.2, and SOP Selection of Calibration Points / CA-P-T-002.
  - Distinguish QC requirements for 7471A and 7471B.

- Refer to hot block rather than water bath. Add instruction to vary the location of the thermometer in the hot block weekly and record the thermometer's position.
- Delete redundant information and add standardized text.
- Add instruction to print the raw absorbance and concentration information.

- Revision 13, dated 31 May 2012
  - Organizational changes.
  - Oklahoma and Wyoming no longer limit batch size to 10 samples.
  - Addition of SOP Calibration Curves (General) / CA-Q-S-005.
  - Clarify calibration procedure, accuracy for calibration standards, and example analysis queue.

Title: DETERMINATION OF % DRY WEIGHT METHOD SW-846 8000C

Approvals (Signature/Date)

Jacolby Robinson	5/24/13	Johnny Davis	5/28/13
Department Manager	Date	Health & Safety Manager / Coordinator	Date
Michael H. Dunn	5/22/13	Extractions Operations Manager	
Technical Director Quality Assurance Manager	Date		

1.0 Scope and Application

1.1 If sample results are to be reported on a dry weight basis, the % dry weight or % moisture of the sample is calculated using the following method.

1.2 Analyte, Matrices: This method is typically performed on non-aqueous matrices, i. e., soils/sludge.

1.3 Reporting Limits: Results are reported to the nearest integer dry weight.

1.4 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor/Manager or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

A sample aliquot is weighed and dried in an oven to constant weight.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

Oily matrices may not achieve a constant weight.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: Use caution while operating near a hot oven and handling hot pans.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 Equipment and Supplies

6.1 Instrumentation

- Oven, capable of maintaining a temperature of 105 ± 5ºC.
- Balance, top-loading, capable of accurately weighing to the nearest 0.1 g.

6.2 Supplies

- Aluminum weight pan or equivalent.
- Spatulas, wooden tongue depressors
- 100-mL beakers
- Desiccator (optional)
- Anhydrous desiccant, Drierite, or equivalent.

7.0 Reagents and Standards

None.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Non-aqueous	HDPE or Glass, 2 or 4 oz. glass	10 grams	None	None specified	SW-846 8000C, ASTM D2974-00

9.0 Quality Control

Refer to the quality control section of TestAmerica Nashville's QA Manual for specific quality control (QC) procedures. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

Quality Controls	Frequency	Control Limit
Sample Duplicate	1 in 20 or fewer samples	≤ 20% RPD

- Run one sample in duplicate per batch.

10.0 Procedure

10.1 Weigh the aluminum pan and record the weight to the nearest gram on the worklist.

10.2 Weigh a 10-plus gram aliquot (if available) of the sample from the sample container into the pan and record the weight in grams) on the worklist. Record the date and time the samples are placed into the 105 ± 5°C oven. See SOP Sample Sub-sampling, Homogenization, and Compositing / NV08-229 for information on how to take a representative sample.

10.3 Dry overnight at 105 ± 5° C.

10.4 Remove from the oven and allow it to cool.

10.5 Re-weigh each sample after drying and record the weight in grams. If less than overnight drying is used, repeat until constant weight (≤ 0.1%) is achieved.

10.6 Example Analysis Queue / Sequence*

1	Constant Weight Confirmation, if dried less than overnight.
2	Samples 1-20*
3	Sample Duplicate

*May be up to 20 samples

11.0 Calculations / Data Reduction

11.1 Accuracy: Not applicable.

11.2 Precision (RPD)

$$RPD = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 Calculate the **% moisture** as follows:

$$\% \text{ Moisture} = \frac{\text{(g of sample – g of dry sample)*} 100}{\text{g of sample}}$$

11.4 Calculate the **% dry weight** as follows:

% Dry Weight = 100 - % Moisture

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): Not applicable.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: Not applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are managed, stored, and disposed of in accordance with applicable federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Dried samples are disposed of into the trash receptacle.

15.0 References / Cross-References

15.1 SW-846 Method 8000C, Revision 3, March 2003.

15.2 TestAmerica Nashville's Quality Assurance Manual.

15.3 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.4 SOPs: Waste Disposal / NV10-83, Sample Subsampling, Homogenization, and Compositing / NV08-229, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213.

15.5 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachment

None.

18.0 Revision History

- Revision 5, dated 29 February 2008
  - Integration for TestAmerica and STL operations.
  - Addition of constant weight change criteria evaluations per batch.
  - Addition of a sample duplicate per batch.
  - Addition of % moisture calculation.
- Revision 6, dated 16 July 2010
  - Addition of desiccator and desiccant.
  - Change to 110 ± 5°C for the drying temperature.
  - Change to longer drying time from one hour.
  - Change in constant weight change to 0.1%.
  - Simplify dry weight calculation.
  - Addition of ASTM D2216-05 reference.
- Revision 7, dated 31 August 2011
  - Organizational changes.
  - Change overnight drying to “about 8 hours.”
  - Remove references to ASTM D2974-00 and SOP identification number from Dry Weight / NV03-172 to 8000 / NV03-172.
- Revision 8, dated 31 May 2013
  - Organizational changes.
  - Change in precision requirements for the weighings and drying time. Remove constant weight confirmation.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP) Change Form

SOP Number/Revision No.: **8260 / NV05-77.18b** Effective Date: **2/3/2014**

Last Mod. Date: 11/29/13

SOP Title: **METHOD 8260B/C: VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY / MASS SPECTROMETRY (GC/MS)**

Affected SOP Section Number(s): Section 10.5.4, Library Searches

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 05V

Revision Number with Mod ID: **18c**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

☐ Procedural Changes (Define Below) – Re-Training Required.

■ Other

2. Summary of Procedure Change: Add underlined text, remove crossed-out text.

Section 3.0, Definitions, Add the following definition:

Q-value: Tentatively Identified Compound (TIC) quality value of spectra match to library spectra expressed as a percent.

Section 10.5, Qualitative Analysis, 8th bullet:

- For samples containing components not associated with the calibration standards or the requested target list, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines do not use normalization routines that would misrepresent the library or unknown spectra when compared to each other
  - For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Evaluate the "Q-value." If Q > 80, report. If Q< 80, evaluate by the following g~~G~~uidelines for tentative identification ~~are~~:
    1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) are present in the sample spectrum.
    2) The relative intensities of the major ions agree within ±20%. **Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.**
    3) Molecular ions present in the reference spectrum are present in the sample spectrum.
    4) Ions present in the sample spectrum but not in the reference spectrum are reviewed for possible background contamination or presence of co-eluting compounds.
    5) Ions present in the reference spectrum but not in the sample spectrum are reviewed for possible subtraction from the sample spectrum because of background contamination or

co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.	

John Kelley 1/31/14	Glen L. Norton 1/28/14
Department Supervisor Approval Date	Department Manager Approval Date
Steve Miller 1/19/14	Michael A. Burns 1/24/14
Quality Assurance Manager Approval Date	Technical Director Approval Date

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville Standard Operating Procedure (SOP) Change Form

SOP Number/Revision No.: **8260 / NV05-77.18a, 624 / NV05-66.9, 524.2 / NV05-10, SM6200 B / NV05-236.3** Effective Date: **11/29/2013**
Last Mod. Date: 9/30/13, 10/31/13, 10/31/12, 3/29/13

SOP Title: **Method 8260B: Volatile Organic compounds by Gas Chromatography / Mass Spectrometry (GC/MS)**
Affected SOP Section Number(s): Section 9.2, Instrument QC

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 05V

Revision Number with Mod ID: **8260-18b, 624-9a, 524.2-10a, SM6200 B-3a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add bold text.
Section 9.2, Instrument QC, BFB Tuning and Breakdown Check

BFB (4-Bromofluorobenzene) Mass Intensity Criteria

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50%, **but less than or equal to 120%,** of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101 % of m/z 174
177	5 to 9% of m/z 176

John Kelley 1/26/13	Glen L. Norton 11/27/13
Department Supervisor Approval Date	Department Manager Approval Date
Steve Shilley 11/27/13	Michael A. Brown 11/26/13
Quality Assurance Approval Date	Technical Approval Date

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure
(SOP) Change Form

SOP Number/Revision No.: **8260 / SA/NV05-77.18** Effective Date: **9/30/2013**

Last Mod. Date: 8/30/13

SOP Title: **Method 8260B: Volatile Organic compounds by Gas Chromatography / Mass Spectrometry (GC/MS)**

Affected SOP Section Number(s): Section 16.0, Method Modifications: TPH-GRO by Method 8260B

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 05V

Revision Number with Mod ID: **18a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add underlined, delete crossed-out. *(Italics are for 8260C.*

- Section 1.2, Reporting Limits

Compound	Retention Time (minutes)	Typical Reporting Limits: Water Standard Level (µg/L)	Water Low-Level (µg/L)	Soil Wet Weight (µg/kg)
tert-Amyl-alcohol (TAA)[3]	2.914	20	20	20 ~~2~~
Isopropyl alcohol	3.836	50 ~~20~~	50	50
Allyl chloride (3-Chloro-1-propene)	4.026	2	2 ~~10~~	10
3,3-Dimethyl-1-butanol	5.021	10	10	NA ~~0~~

- Section 9.2: Instrument QC Table, ICAL acceptance criteria

QC Check	Frequency	Acceptance Criteria[1]	Corrective Action[2]
Minimal five-point initial calibration for all target analytes. Single-point surrogate calibration	Initial calibration prior to sample analysis. Perform instrument re-calibration once per year minimum.	8260B: SPCCs average RF ≥ 0.30 or 0.1 depending on the compound, ~~and~~ %RSD ~~for RFs~~ for CCCs ≤ 30% and all other target analytes %RSD ~~for RF~~ ≤ 15%~~.~~ or correlation coefficient r^2 ≥ 0.990 or r ≥ 0.995. Re-calculate low point; must be within 30% true. *8260C: Minimum RF for initial and continuing calibration varies by analyte (see Calibration standards below). RSD ≤ 20% each target or correlation coefficient r^2 ≥ 0.990 r ≥ 0.995. Up to 10% of targets may exceed these*	Correct problem then repeat initial calibration.

		criteria. If using linear regression, re-fit lowest calibration point. It must be <u>within</u> ± 30% <u>of true</u> ~~or re-calculate~~.	

- Section 9.2: Instrument QC, **Initial Calibration Check Compounds (CCCs):**

  - *For 8260C, the minimum RF for initial and continuing calibration <u>must be</u> ~~is~~:*

RF	For These Compounds
<u>0.05</u>	*<u>1,2-Dichloro-3-propane</u>*
0.1	*<u>RF may be lower if data is used for screening: Acetone, Bromoform, Bromomethane, 2-Butanone, Carbon disulfide, Carbon tetrachloride, Chloroethane, Chloromethane, Cyclohexane, Dibromochloromethane, Dichlorodifluoromethane, 1,2-Dichloroethane, 1,1-Dichloroethene, cis-1,2-Dichloroethene, trans-1,2-Dichloroethene, 1,2-Dichloropropane, trans-1,3-Dichloropropene, Ethylbenzene, Ethylene dibromide, 2-Hexanone, Isopropylbenzene, Methyl acetate, 4-Methyl-2-butanone, Methylene chloride, Methyl cyclohexane, Methyl tert-butyl ether, m & p-Xylene, 1,1,1-trichloroethane, 1,1,2-Trichloroethane, 1,1,2-Trichloro-1,2,2-trifluoroethane</u>*
0.2	*1,1-Dichloroethane, Chloroform, Trichlorethene, Bromodichloromethane, cis-1,3-Dichloropropene, Tetrachloroethane, and 1,2,4-Trichlorobenzene*
0.3	*o-Xylene, Styrene, 1,1,2,2-Trichloroethane*
0.4	*Toluene, 1,2-Dichlorobenzene*
0.5	*Benzene, Chlorobenzene, 1,4-Dichlorobenzene*
0.6	*1,3-Dichlorobenzene*

    - ~~*For 8260C, the must be less than or equal to 20% for each target analyte with up to 10% of compounds meeting the 40% criterion.*~~

- Section 9.2: Instrument QC, **Initial Calibration Verification (ICV),** second bullet for 8260B:

  - The ICV of each target must be within 30% of the expected value, with the exception of the following poor purge efficiency analytes that may be within 40% of the expected value ~~for up to 20% of targets:~~. <u>No more than 20% of analytes are allowed to fail this criterion.</u>

Acrolein	Ethanol	2-Methylnaphthalene
t-Amyl alcohol (TAA)	t-Butyl formate (TBF)	Vinyl acetate
t-Butyl alcohol (TBA)	1-Methylnaphthalene	

- Section 9.2: Instrument QC, **Continuing Calibration Verification (CCV),** 8260C bullet:
  - *For 8260C, ~~see ICAL and ICV information.~~<u>the CCV % difference for each target must be ≤ 20% with only up to 20% of the targets of interest allowed to exceed 20% difference. The minimum RF must also be achieved.</u>*

John Kelley 9/17/13	Glen L. Norton 9/26/13
Department Manager Approval Date	Operations Manager Approval Date
Michael A. Burns 9/16/13	
Technical Director, Quality Manager Approval Date	

Title: VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) SW-846 METHOD 8260B/C

Approvals (Signature/Date)

John Haley	8/7/13	Glenn L. Norton	8/5/13
John Haley Department Supervisor	Date	Glenn Norton Volatiles Operations Manager	Date
Michael H. Dunn	8/30/13	Johnny Davis	8/15/13
Michael H. Dunn\ Technical Director Quality Assurance Manager	Date	Johnny Davis Health & Safety Manager / Coordinator	Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method is used to determine volatile organic compounds in a variety of matrices; it is applicable to nearly all types of samples, regardless of water content, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

CAS No. (a)	Compound	CAS No. (a)	Compound
630-20-6	1,1,1,2-Tetrachloroethane[1, 2, 6, 7]	156-59-4	cis-1,2-Dichloroethene[1, 2, 5, 6, 7]
71-55-6	1,1,1-Trichloroethane[1, 2, 5, 6]	10061-01-5	cis-1,3-Dichloropropene[1, 2, 5, 6, 7]
79-34-5	1,1,2,2-Tetrachloroethane[1, 2, 5, 6, 7]	110-82-7	Cyclohexane[4, 5]
76-13-1	1,1,2-Trichloro-1,2,2-trifluoroethane[5,6,7]	108-94-1	Cyclohexanone[4]
79-00-5	1,1,2-Trichloroethane[1, 2, 5, 6]	74-95-3	Dibromomethane[1, 2, 6, 7]
75-34-3	1,1-Dichloroethane[1, 2, 5, 6, 7]	75-27-4	Dichlorobromomethane[1,2, 6, 7]
75-35-4	1,1-Dichloroethene[1, 2, 5, 6, 7]	75-71-8	Dichlorodifluoromethane[1, 2, 5, 7]
563-58-6	1,1-Dichloropropene[1, 7]	75-43-4	Dichlorofluoromethane[4]
87-61-6	1,2,3-Trichlorobenzene[1]	64-17-5	Ethanol[3]
96-18-4	1,2,3-Trichloropropane[1, 2, 6, 7]	141-78-6	Ethyl acetate [4]
526-73-8	1,2,3-Trimethylbenzene	140-88-5	Ethyl acrylate
120-82-1	1,2,4-Trichlorobenzene[1, 2, 5]	60-29-7	Ethyl ether (Diethyl ether)[4]
95-63-6	1,2,4-Trimethylbenzene[1, 9]	97-63-2	Ethyl methacrylate[2, 7]
96-12-8	1,2-Dibromo-3-chloropropane[1, 2, 5, 7]	100-41-4	Ethylbenzene[1, 2, 5, 6, 7, 8, 9]
95-50-1	1,2-Dichlorobenzene[1, 2, 5, 6, 7]	106-93-4	Ethylene dibromide (EDB, 1,2-Dibromoethane)[2]
107-06-2	1,2-Dichloroethane[1, 2, 5, 6, 7, 8]	87-68-3	Hexachlorobutadiene[1, 2]
78-87-5	1,2-Dichloropropane[1, 2, 5, 6, 7]	110-54-3	Hexane[4]
176-02-8	1,3,5-Trichlorobenzene[4]	74-88-4	Iodomethane[2, 6, 7]
108-67-8	1,3,5-Trimethylbenzene[1, 9]	78-83-1	Isobutyl alcohol [2, 7]
541-73-1	1,3-Dichlorobenzene[1, 2, 5, 7]	67-63-0	Isopropy alcohol[4]
142-28-9	1,3-Dichloropropane[1, 7]	180-20-3	Isopropyl ether (IPE, Di-isopropyl ether)[3]
106-46-7	1,4-Dichlorobenzene[1, 2, 5, 6, 7]	98-82-8	Isopropylbenzene (Cumene)[1, 5, 9]
123-91-1	1,4-Dioxane[2, 8]	126-98-7	Methacrylonitrile[2, 7]
590-20-7	2,2-Dichloropropane[1, 7]	79-20-9	Methyl acetate[5]
78-93-3	2-Butanone (MEK)[1, 2, 5, 6, 7, 8]	80-62-6	Methyl methacrylate[2, 7]
126-99-8	2-Chloro-1,3-butadiene (Chloroprene)[2, 7]	1634-04-4	Methyl-t-butyl ether[1, 3, 4, 5, 9]
110-75-8	2-Chloroethyl vinylether[4]	108-87-2	Methylcyclohexane[5]
95-49-8	2-Chlorotoluene[1]	75-09-2	Methylene chloride[1, 2, 5, 6, 7]
591-78-6	2-Hexanone[1, 2, 5, 6, 7]	108-38-3	m-Xylene [9]
75-65-0	2-Methyl-2-propanol (tert-Butyl Alcohol)[3]	91-20-3	Naphthalene[1, 2, 9]

CAS No. (a)	Compound	CAS No. (a)	Compound
91-57-6	2-Methylnapthalene[4]	71-36-3	n-Butanol (n-Butyl Alcohol)[4]
79-46-9	2-Nitropropane[4]	123-86-4	n-Butyl acetate[4]
624-95-3	3,3-Dimethyl-1-butanol[3]	104-51-8	n-Butylbenzene[1, 9]
107-05-1	3-Chloro-1-propene (Allyl chloride)[2,7]	142-82-5	n-Heptane[4]
106-43-4	4-Chlorotoluene[1]	103-65-1	n-Propylbenzene[1, 9]
99-87-6	4-Isopropyltoluene (p-Isopropyltoluene)[1, 9]	95-47-6	o-Xylene[9]
108-10-1	4-Methyl-2-pentanone (MIBK)[1, 2, 5, 6, 7]	76-01-7	Pentachloroethane
67-64-1	Acetone[1, 2, 5, 6, 7]	107-12-0	Propionitrile[2, 7]
75-05-8	Acetonitrile[2, 7]	135-98-8	sec-Butylbenzene[1, 9]
107-02-8	Acrolein (Propenal)[2, 7]	100-42-5	Styrene[1, 2, 5, 6, 7]
107-13-1	Acrylonitrile[2, 6, 7]	75-85-4	tert-Amyl-alcohol (TAA)[3]
71-43-2	Benzene[1, 2, 5, 6, 7, 8, 9]	994-05-8	tert-Amyl-methyl-ether (TAME)[3]
100-44-7	Benzyl chloride[4]	637-92-3	tert-Butyl ethyl ether (Ethyl-tert-butyl-ether, ETBE)[3]
108-86-1	Bromobenzene[1]	762-75-4	tert-Butyl-formate (TBF)[3]
75-25-2	Bromoform[1, 2, 5, 6, 7]	98-06-6	tert-Butylbenzene[1, 9]
74-83-9	Bromomethane[1, 2, 5, 6, 7]	127-18-4	Tetrachloroethene[1, 2, 5, 6, 7]
106-99-0	Butadiene	109-99-9	Tetrahydrofuran[4]
STL00350	C4-C12	108-88-3	Toluene[1, 2, 5, 6, 7, 8, 9]
80006-61-9	C6-C10	156-60-5	trans-1,2-Dichloroethene[1, 2, 5, 6, 7]
75-15-0	Carbon disulfide[1, 2, 5, 6, 7, 8]	10061-02-6	trans-1,3-Dichloropropene[1, 2, 5, 6, 7]
56-23-5	Carbon tetrachloride[1, 2, 5, 6, 7]	110-57-6	trans-1,4-Dichloro-2-butene[2, 6, 7]
108-90-7	Chlorobenzene[1, 2, 5, 6, 7, 8]	79-01-6	Trichloroethene[1, 2, 5, 6]
74-97-5	Chlorobromomethane[1, 6, 7]	75-69-4	Trichlorofluoromethane[1, 2, 5, 6, 7]
124-48-1	Chlorodibromomethane[1, 2, 5, 6, 7]	108-05-4	Vinyl acetate[2, 6, 7]
75-00-3	Chloroethane[1, 2, 5, 6, 7]	75-01-4	Vinyl chloride[1, 2, 5, 6, 7]
67-66-3	Chloroform[1, 2, 5, 6, 7, 8]	1330-20-7	Xylene (total)[1, 2, .5, 6, 7, 8, 9]
74-87-3	Chloromethane[1, 2, 5, 6, 7]		

[1] - Laboratory normal 8260 compound
[2] - Appendix IX compound
[3] - Oxygenate
[4] - Additional compounds by request only
[5] TCL list (OLM 04.2 list)
[6] - Appendix I compound
[7] -Appendix II compound
[8] - Skinner list
[9] - NY Stars List
a = Chemical Abstract Service Registry Number0

1.2 Reporting Limits: The RL for an individual compound is instrument-dependent and also dependent on the choice of sample preparation/introduction method. The RL analyte concentration is defined by the lowest non-zero standard in the calibration curve. Using standard quadrapole instrumentation and the purge-and-trap technique, RLs, though highly matrix-dependent, are provided in the table below for guidance and may not be achievable. RLs listed

for soil are based on wet weight. When reported on a dry weight basis, RLs are higher, based on the percent dry weight in each sample. For the most current RL, refer to LIMS.

Chromatographic Retention Times and Typical Reporting Limits

Compound	Retention Time (minutes)	Typical Reporting Limits		
		Water Standard Level (µg/L)	Water Low-Level (µg/L)	Soil Wet Weight (µg/kg)
Dichlorodifluoromethane	1.884	1	0.5	2
Chloromethane	2.095	1	0.5	2
Vinyl chloride	2.222	1	0.5	2
Butadiene	2.264	1	0.5	2
Bromomethane	2.601	1	0.5	2
tert-Butyl-formate (TBF)[3]	2.609	20	20	20
Chloroethane	2.718	1	0.5	2
tert-Amyl-alcohol (TAA)[3]	2.914	20	20	2
Dichlorofluoromethane	2.950	1	0.5	2
Trichlorofluoromethane	3.013	1	0.5	2
Ethanol	3.235	100	100	200
Ethyl ether (Diethyl ether)	3.351	5	5	10
1,1-Dichloroethene	3.364	1	0.5	2
Acrolein	3.488	50	50	20
1,1,2-Trichloro-1,2,2-trifluoroethane	3.615	1	0.5	2
Acetone	3.667	5	5	50
Iodomethane	3.783	10	10	20
Isopropyl alcohol	3.836	20	50	50
Carbon disulfide	3.857	1	0.5	2
Acetonitrile	4.016	20	20	20
Allyl chloride (3-Chloro-1-propene)	4.026	2	10	10
Methyl acetate	4.047	10	10	10
Methylene chloride	4.163	5	5	10
2-Methyl-2-propanol	4.311	10	10	50
Acrylonitrile	4.448	10	10	10
trans-1,2-Dichloroethene	4.480	1	0.5	2
MTBE	4.490	1	0.5	2
Hexane	4.807	2	0.5	10
1,1-Dichloroethane	4.976	1	0.5	2
3,3-Dimethyl-1-butanol	5.021	10	10	0
Vinyl acetate	5.050	10	10	20
Isopropyl ether (IPE, Di-isopropyl ether)	5.071	2	0.5	2
2-Chloro-1,3-butadiene (Chloropopene)	5.092	5	5	5
tert-Butyl ethyl ether (Ethyl-tert-butyl-ether, ETBE)[3]	5.514	1	0.5	5
2,2-Dichloropropane	5.683	1	0.5	2

Compound	Retention Time (minutes)	Typical Reporting Limits		
		Water Standard Level (µg/L)	Water Low-Level (µg/L)	Soil Wet Weight (µg/kg)
cis-1,2-Dichloroethene	5.683	1	0.5	2
2-Butanone	5.715	50	50	50
Ethyl acetate	5.788	5	5	50
Propionitrile	5.788	10	10	50
Methacrylonitrile	5.968	20	20	50
Chlorobromomethane	5.978	1	0.5	2
Tetrahydrofuran	6.063	5	5	20
Chloroform	6.084	1	0.5	2
1,1,1-Trichloroethane	6.327	1	0.5	2
Cyclohexane	6.390	5	1	10
1,1-Dichloropropene	6.527	1	0.5	2
Carbon tetrachloride	6.538	1	0.5	2
Isobutyl alcohol	6.696	50	50	100
Benzene	6.801	1	0.5	2
1,2-Dichloroethane	6.823	1	0.5	2
tert-Amyl-methyl-ether (TAME)	6.960	1	0.5	2
n-Heptane	7.150	2	2	4
n-Butanol	7.582	100	20	100
Trichloroethene	7.656	1	0.5	2
Ethyl acrylate	7.815	5	5	10
1,2-Dichloropropane	7.973	1	0.5	2
Methylcyclohexane	7.973	5	0.5	10
Dibromomethane	8.131	1	0.5	2
Methyl methacrylate	8.142	5	5	10
1,4-Dioxane	8.184	200	200	200
Dichlorobromomethane	8.353	1	0.5	2
2-Nitropropane	8.680	5	5	10
2-Chloroethylvinyl ether	8.796	10	10	20
cis-1,3-Dichloropropene	9.007	1	0.5	2
4-Methyl-2-pentanone	9.239	5	5	50
Toluene	9.503	1	0.5	2
trans-1,3-Dichloropropene	9.830	1	0.5	2
Ethyl methacrylate	9.988	10	10	10
1,1,2-Trichloroethane	10.115	1	0.5	5
Tetrachloroethene	10.337	1	0.5	2
1,3-Dichloropropane	10.368	1	0.5	2
2-Hexanone	10.516	5	5	50
Chlorodibromomethane	10.727	1	0.5	2
n-Butyl acetate	10.738	10	10	40

Compound	Retention Time (minutes)	Typical Reporting Limits		
		Water Standard Level (µg/L)	Water Low-Level (µg/L)	Soil Wet Weight (µg/kg)
Ethylene dibromide (EDB, 1,2-Dibromo-ethane)	10.907	1	0.5	2
Chlorobenzene	11.698	1	0.5	2
1,1,1,2-Tetrachloroethane	11.835	1	0.5	2
Ethylbenzene	11.888	1	0.5	2
m & p-Xylene	12.088	1	0.5	2
o-Xylene	12.743	1	0.5	2
Styrene	12.774	1	0.5	2
Bromoform	13.080	1	0.5	2
Isopropylbenzene (Cumene)	13.418	1	0.5	2
Cyclohexanone	13.555	50	50	50
Bromobenzene	13.914	1	0.5	2
1,1,2,2-Tetrachloroethane	13.925	1	0.5	2
1,2,3-Trichloropropane	13.988	1	0.5	2
trans-1,4-Dichloro-2-butene	14.030	5	5	10
n-Propylbenzene	14.115	1	0.5	2
2-Chlorotoluene	14.241	1	0.5	2
1,3,5-Trimethylbenzene	14.410	1	0.5	2
4-Chlorotoluene	14.421	1	0.5	2
tert-Butylbenzene	14.917	1	0.5	2
Pentachloroethane	14.927	5	5	10
1,2,4-Trimethylbenzene	14.990	1	0.5	2
1,3-Dichlorobenzene	15.391	1	0.5	2
4-Isopropyltoluene (p-Isopropyltoluene)	15.476	1	0.5	2
sec-Butylbenzene	15.524	1	0.5	2
1,4-Dichlorobenzene	15.529	1	0.5	2
1,2,3-Trimethylbenzene	15.613	1	0.5	2
Benzyl chloride	15.729	10	5	20
1,2-Dichlorobenzene	16.056	1	0.5	2
n-Butylbenzene	16.056	1	0.5	2
1,2-Dibromo-3-chloropropane	17.101	10	5	5
1,3,5-Trichlorobenzene	17.375	1	0.5	2
1,2,4-Trichlorobenzene	18.135	1	0.5	2
Hexachlorobutadiene	18.346	1	0.5	2
Naphthalene	18.431	5	5	5
1,2,3-Trichlorobenzene	18.716	1	0.5	2
2-Methylnaphthalene	19.729	10	5	5
INTERNAL STANDARDS/SURROGATES				
Dibromofluoromethane	6.284			
1,2-Dichloroethane-d_4	6.717			

Compound	Retention Time (minutes)	Typical Reporting Limits		
		Water Standard Level (µg/L)	Water Low-Level (µg/L)	Soil Wet Weight (µg/kg)
Fluorobenzene	7.160			
Toluene-d_8	9.408			
Chlorobenzene-d_5	11.656			
4-Bromofluorobenzene	13.671			
1,4-Dichlorobenzene-d_4	15.486			

1.2 There are various techniques by which these compounds may be introduced into the GC/MS system. Purge-and-trap, by Methods 5030 /NV05-107 (aqueous samples or Methanol extracts of bulk containers) and 5035 / NV05-108 (solid and waste oil samples), is used for volatile organic analytes.
1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor/Manager or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method. The analytes are introduced directly to a capillary column for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) directly interfaced to the gas chromatograph (GC).
2.2 Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major ion relative to an internal standard using at least a five-point calibration curve.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components are avoided, since such materials out-gas organic compounds which are concentrated in the trap during the purge operation. Analyses of blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, perform maintenance. **Subtracting blank values from sample results is not permitted**.
4.2 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. A technique to prevent this problem is to rinse the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. Re-analyze any suspect samples.
4.3 Special precautions are taken to analyze for Methylene chloride. The analytical and sample storage areas are isolated from all atmospheric sources of Methylene chloride. Otherwise, random background levels result. Since Methylene chloride permeates through PTFE tubing, all

gas chromatography carrier gas lines and purge gas plumbing is constructed from stainless steel or copper tubing.

4.4 Samples can be contaminated by diffusion of volatile organics (particularly Methylene chloride and Fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage. A trip blank, prepared from organic-free reagent water and carried through the sampling, handling, and storage, serve as a check on such contamination.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and should cool them to room temperature prior to working on them.
- The mass spectrometer is under vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.
- There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.
- Kevlar gloves must be worn when opening and closing VOA vials.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Sodium bisulfate	Irritant	None	Causes mild to severe irritation to the eyes. Prolonged exposure causes burn if not flushed with water. Causes mild irritation to skin. Prolonged exposure causes burn if not flushed with water.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Hydro-chloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors causes coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and cause damage to the eyes. Contact causes severe burns and permanent eye damage.
Trisodium phosphate		None listed	Keep in closed container; avoid high temperatures and strong acids.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Purge-and-trap device for aqueous samples at ambient temperature, described in Method 5030 / NV05-107.
- Purge-and-trap device for solid samples at 40°C, described in Method 5035 / NV05-108.
- The trap is VOCARB 3000 – 10.0-cm Carbopack™ B/6.0-cm Carboxin™ 1000/1.0-cm Carboxin 1001. The amount of thermal decomposition products formed must be routinely tracked by daily monitoring of the formation of Chloromethane and Bromomethane.
- Gas chromatography/mass spectrometer/data system
  - Gas chromatograph (HP): Analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection with appropriate interface for sample introduction device. The system includes all required accessories, including syringes, analytical columns, and gases.

Injector temperature:	250°C
MS interface temperature:	260°C
Carrier gas (He) flow rate:	Constant flow of 1.0 mL/minute.
Initial temperature:	45°C hold for 6 minutes.
Temperature program:	13°C/minute to 150°C; 18°C/minute to 220°C
Final temperature:	220°C, hold until all expected compounds have eluted (2 minutes)
Split ratio (min.)	1:10

May vary by instrument; see maintenance log for current program.

- The capillary column is directly coupled to the source.
- Gas chromatographic column: DB-624, 20 m x 0.18 mm with 1.0 µm film thickness, or equivalent.
- Mass spectrometer: Capable of scanning from 35 to 300 amu every 1 second or less using 70 volts (nominal) electron energy in the electron impact ionization mode. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.
- Data system (HP Chem Station with Enviroquant and CHROM): A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer has software that allows searching the GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software is used that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library is also available.

6.2 Supplies

- Microsyringes, 10, 25, 100, 250, 500, and 1,000 µL.
- Syringes, 5, 10, or 25 mL.
- Balance, analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.
- Glass scintillation vials, 20 mL, with PTFE-lined screw-caps or glass culture tubes with PTFE-lined screw-caps.
- Disposable pipets, Pasteur.
- Volumetric flasks, Class A, 10 mL, 50 mL and 100 mL, with ground-glass stoppers.
- Spatula, stainless steel, or wooden tongue depressor.
- Helium for carrier gas.
- Nitrogen for purge-and-trap gas.
- Narrow-range pH paper.
- Residual chlorine test strips.
- Sea or Ottawa sand for blank and LCS soil matrix.

7.0 Reagents and Standards

7.1 Reagent grade chemicals are generally used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. See the QA Manual and SOP Reagent and Standard Purchase / NV08-214 for more information on reagent chemicals, such as shelf-life and storage.

7.2 Reagent water, analyte-free.

7.3 Methanol, CH_3OH: Purge-and-trap grade or equivalent, demonstrated to be free of analytes at the MDL. Store apart from other solvents.

7.4 Hydrochloric acid (1:1 v/v), HCl: Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

7.5 Stock solutions: Stock solutions are prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in Methanol, using assayed liquids. Any specific standards or procedure for making standards mentioned in this SOP may be substituted with equivalent standards or procedures. See standard log for specific standard information.

7.5.1 **Primary Standards**

		For Working Standard		
Name of standard	**Vendor[2]/Conc (µg/mL)**	**Volume used (mL)**	**Final Volume (mL)**	**Conc. (µg/mL)**
Full List Non-gas Standard				
Custom 8260 VOC mega-mix[1] without gases	Restek 567641/2000, 4000, 10000,-20000, 40000	2.5	50	100 – 2000
Megamix additions	Restek 567647/2000, 4000,20000, 50000, 100000	2.5	50	100-5000
Ketones	Restek 567642/10000	2.5	50	500
Acrolein	Restek 567644 /5000	2.5	50	250
Cyclohexanone	567648/20000	2.5	50	1000
Vinyl acetate	Restek 567646/4000	2.5	50	200
2-Chloroethyl vinyl ether	Restek 567643 /2000	2.5	50	100
List 2: Pentachloroethane, 2-Methylnaphthalene	Restek 567719 / 2000	2.5	50	100

		For Working Standard		
Name of standard	**Vendor[2]/Conc (µg/mL)**	**Volume used (mL)**	**Final Volume (mL)**	**Conc. (µg/mL)**
1-Methylnaphthalene	Restek 31283/1000	0.1	2	50
Full List Gas Standard				
Gas Mix	Restek 567645/2000	1.0	20	100
Short List				
Short List Mix	Ultra CUS-7011/100-1000	5	10	50-500
3,3-Dimethyl-1-butanol	Restek 563892/20000	0.25	10	500
1 Custom 8260 VOC mix has variable concentrations. See the standard log for exact compound concentrations.				
2 The vendors/catalog numbers are recommended; equivalent products are acceptable.				

7.5.1.1 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store, with minimal headspace and protected from light, at ≤ 6°C or less or as recommended by the standard manufacturer. Return standards to storage as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of target compounds.

7.5.1.2 **Frequency of Standard Preparation**

7.5.1.2.1 Monitor standards for the permanent gases frequently by comparison to the initial calibration curve. Prepare fresh standards if this check exceeds a 20% drift. **Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented**. Dichlorodifluoromethane and Chloromethane are usually the first compounds to evaporate from the standard and, therefore, are to be monitored very closely when standards are held beyond one week.

7.5.1.2.2 Monitor standards for the non-gases frequently by comparison to the initial calibration. Prepare fresh standards if this check exceeds a 20% drift. Undiluted standards for non-gases usually need to be replaced after **one month for working standards and three months for opened stock standard** or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-Chloroethyl vinyl ether and Styrene may need to be prepared more frequently.

7.5.1.3 **Secondary dilution standards:** Using stock standard solutions, prepare secondary dilution standards in Methanol containing the compounds of interest, either singly or mixed together. Secondary dilution standards are stored with minimal headspace and, except for gases, are good for 2-4 weeks unless acceptability is demonstrated. Replace secondary standards for gases after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. Handle and store standards as stated above and return them to the refrigerator or freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

7.5.1.3.1 The working calibration standard for the Non-Gas mixture is made by adding 2.5 mL of each of the first six standards in the Primary Standard table above in 50.0 mL Methanol in a Class A volumetric. The Gas

Standard is added right before use as described in the calibration section.

7.5.2 **Internal Standard/Surrogate Standard Mix (IS/SS)**

7.5.2.1 The internal standards are Fluorobenzene, Chlorobenzene-d_5, and 1,4-Dichlorobenzene-d_4. Prepare internal standard stock and secondary dilution standards in Methanol. Stock standard is 250 µg/mL, Restek 567649, or equivalent.

7.5.2.2 The surrogates are Toluene-d_8, 4-Bromofluorobenzene (the GC/MS Tuning Standard), 1, 2-Dichloroethane-d_4, and Dibromofluoromethane. Stock standard is 2500 µg/mL, Restek 567650, or equivalent.

7.5.2.3 Prepare a 250 µg/mL IS/SS standard by diluting 5.0 mL of stock internal standard (250 µg/mL) and 5.0 mL stock surrogate standard (2500 µg/mL) to a final volume of 50.0 mL of Methanol in a Class A volumetric.

7.5.3 **Bromoform Breakdown Check:** Purchase 50 g neat Bromoform from Sigma-Aldrich 241032-50G, or equivalent.

7.5.3.1 Prepare a 20 µg/L standard by adding 0.02 g of the neat Bromoform standard to 1000 mL reagent water.

7.5.4 **Second-Source Standards for Initial Calibration Standard (ICV):** The ICV is a **second-source** standard that contains all the 8260 compounds. Prepare as for the primary standard with the only difference being that the vendor numbers have a ".sec" on the end of the number.

7.6 Sodium bisulfate or Trisodium phosphate for soil sample preservation. See SOP 5035 / NV05-108.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time From Collection to Analysis	Reference
Water[2]	3 x 40-mL VOAs (Optional: TSP)	40 mL	pH < 2 with Hydrochloric acid. Cool 0-6°C, No headspace. Keep in dark. If Chlorine residual present, add 0.008% $Na_2S_2O_3$.	14 days, 7 days if not acidified.	SW846 Chapters 2 and 4
Low-concentration Soil	2 pre-weighed vials, stirring bar	5 g	0-6°C, 5 mL preservative[1]		
	2 EnCores™		0-6°C, Add 5 g sample and 5 mL preservative to pre-weighed vial with stirring bar within 48 hours of collection		
High concentration Soil	2-oz. glass[3] or 25 g Encore™	5g or 25 g	0-6°C, Add 1 mL Methanol/gram soil	Transfer to VOA within 48 hours, then 14 days	

[1]0.2 gram sodium bisulfate or Trisodium phosphate/mL reagent water

[2]2-Chloroethyl vinyl ether degrades in acid-preserved samples; its analysis requires a non-preserved vial. If analyzing a sample for combined purgeable halocarbons, aromatics, Acrolein, and Acrylonitrile, analyze the sample within 7 days. Alternatively, collect at least 2 separate vials for analysis: one vial preserved to pH 4-5 with HCl for Acrolein and Acrylonitrile, and a second vial for the other analytes preserved to pH <2 with HCl.

[3]See SOPs 5030 / NV05-107 for waters and 5035 / NV05-108 for soils/solids, including the soil freezing option, with or without water.

Analysis Method	Sample Storage	Holding Times from Date and Time of Collection			
		MeOH Addition	Shipping	Extraction	Analysis
Wisconsin VOC Soils	VOC vial	Immediately	4 days	21 days	21 days
	Brass Tube	within 2 hours	4 days	21 days	21 days
	EnCore™	within 48 hours	40 hours	21 days	21 days

9.0 Quality Control

The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC: The following QC is run **every batch of no more than 20 samples:**

QC Check	Frequency	Acceptance Criteria[1]	Corrective Action[2]
Method blank	One per analytical prep batch and after calibration (see Section 9.2)	No analytes detected ≥ ½ RL or MDL, whichever is greater	Correct problem then re-prep[3] and analyze method blank and all samples processed with the contaminated blank. If target > 10x blank, report but qualify.
LCS[4] for all analytes using the primary standard.	One[6] per prep batch	See LIMS[5]	Re-prep[3] and analyze the LCS and all samples in the affected analytical batch. If high and samples are ND, report. If low, re-prep. If the LCS exceeds the upper control limit AND a sample from that batch is greater than the RL, re-prep and re-analyze the batch. If the LCS exceeds the upper control limit AND the sample from that batch is less than the RL, the data is acceptable to report.
MS/MSD using the primary standard	One per batch per matrix, if insufficient sample for MS/MSD, then analyze a LCS/LCSD.	See LIMS	None (LCS is used to determine if data is acceptable).
Surrogate	Every sample, spike, standard, and blank.	See LIMS	Check system, re-analyze, re-prep[3], may qualify. If %recovery is high and the sample is ND, it is acceptable to report. If low, re-prep and rerun. If the surrogate % recovery exceeds the upper control limit AND a sample is greater than the RL, re-prepare and re-analyze the sample. If the surrogate % recovery exceeds the upper control limit AND the sample is less than the RL, data is acceptable to report. If the surrogate % recovery is lower than the lower control limit, re-prepare the sample. OH VAP requires all surrogates to be in control; otherwise, the samples must be re-prepared and re-analyzed
pH check	All water samples.	pH ≤2or ≥ 11	If the pH is > 2 but less than 11, comment the data and LIMS.
Residual chlorine check (North Carolina samples only)	Each sample.	Residual chlorine must be negative.	If the residual chlorine is positive, then comment the data, and LIMS.

[1]This is a summary of the acceptance criteria.
[2]All abnormalities must be noted in LIMS.
[3]If unable to re-prep the samples because of insufficient sample volume or holding time has expired, place a comment in LIMS.

[4] All AZ, MA, TX, and WV samples require a LCS duplicate in each batch.
[5].See Section 16 for South Carolina LCS acceptance criteria and Minnesota Ethanol acceptance criteria.

- A **Method Blank** is run with each analytical batch. The blank is carried through all stages of the sample preparation and measurement using the appropriate blank matrix (reagent water or sand).
- A **Laboratory Control Sample (LCS)** is included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix (reagent water or sand) similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes from the primary source.

Matrix	LCS Preparation	Final Concentration
Water	Add 50 µL of the primary source standard to 50.0 mL reagent water in a Class A volumetric flask.	50 – 5000 µg/L
Low-concentration Soil	Add 5 µL of the primary source standard to a VOA vial containing 5.0 g sand and 5 mL preservative and a stirring bar.	50 - 5000 µg/kg
High-concentration Soil (analyzed as waters)	Add 50 µL of the primary source standard to 50.0 mL reagent water in a Class A volumetric flask.	50 - 5000 µg/kg

- **Matrix Spike/Matrix Spike Duplicate:** Documenting the effect of the matrix includes the analysis of at least one matrix spike/matrix spike duplicate pair for each batch.

Matrix	MS/MSD Preparation	Final Concentration
Water Batch	Add 43 µL of the primary source standard to the client's sample in VOA vials.	50 – 5000 µg/L
Low-concentration Soil Batch	Add 5 µL of the primary source standard to a VOA vial containing 5 g preserved client sample (with stirring bars).	50 - 5000 µg/kg
High-concentration Soil Batch (analyzed as waters)	Add 1.0 mL of the Methanol-extract-of-client-sample and 50 µL of the primary source standard and dilute with reagent water in a 50-mL, Class A volumetric.	50 - 5000 µg/kg

- **Surrogate standards**: The analyst monitors both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, QA/QC standard, and blank with surrogate compounds which are not expected to be affected by method interferences. The surrogate and internal standards are prepared together as described in Section 7.
  - The IS/SS standard mix (250 µg/mL each) is added by the autosampler (nominally 1 µL) during all analyses with the exception of the calibration.

Purge Volume, mL	Concentration of IS/SS Standards in Sample, µg/L
5	50
10	25

- **pH Check:** The analyst must document that each sample has a pH ≤ 2 or ≥ 11 by checking with narrow-range pH paper. The pH check is performed after sample analysis to avoid

contamination and creation of a headspace in the sample vials. Record as pH <2 or >2 or > 11.

- **Residual Chlorine Check:** The analyst must document the presence/absence of residual chlorine in North Carolina samples by checking with residual chlorine test strips.

9.2 Instrument QC

Italicized information is unique to 8260C.

QC Check	Frequency	Acceptance Criteria[1]	Corrective Action[2]
a. Check of mass spectral ion intensities, i. e., BFB Tune	Prior to initial calibra-tion or Continuing calibration verification, every 12 hours.	Refer to criteria for Tune criteria	Retune the instrument and verify (instrument maintenance may be needed).
b. Bromoform Break-down Check	At beginning of daily sequence.	≤ 0.5 µg/L Bromomethane; ≤ 0.5 µg/L Chloromethane	Re-condition or replace trap. Re-calibrate.
Minimal five-point initial calibration for all target analytes. Single-point surrogate calibration	Initial calibration prior to sample analysis. Perform instrument re-calibration once per year minimum.	8260B: SPCCs average RF ≥ 0.30 or 0.1 depending on the compound and %RSD for RFs for CCCs ≤ 30% and all other target analytes %RSD for RF ≤ 15%. $r^2 \geq 0.990$ or $r \geq 0.995$. Re-calculate low point; must be within 30% true. *8260C: Minimum RF for initial and continuing calibration varies by analyte (see Calibration standards below). RSD ≤ 20% each target.* $r^2 \geq 0.990$ or $r \geq 0.995$. *Up to 10% of targets may exceed these criteria. If using linear regression, re-fit lowest calibration point. It must be ± 30% or re-calculate.*	Correct problem then repeat initial calibration.
Initial calibration verification (ICV), must be from a second source	Immediately following each initial calibration.	All analytes within 30% of expected value. Problematic compounds may be within 40%.	Correct problem then repeat initial calibration. ICV must be run prior to reporting samples.
Continuing Calibration Verification (CCV)	Daily, before sample analysis and every 12 hours of analysis time.	8260B: CCCs: ≤20% difference (when using RFs) or drift (when using least squares regression). SPCCs: minimum RF. All other target compounds ≤ 30%, except for specific compounds which may have a % difference ≤ 40%. *8260C: All targets of interest ≤ 20%. Up to 20% of targets may exceed this criterion. Common targets meet minimum RF.*	Correct problem then repeat CCV (re-calibrate if necessary) and re-analyze any samples processed with that CCV. If the CCV is high and the sample is ND, it is acceptable to report.[3]
Continuing Calibration Blank	After each CCV.	< ½ RL or MDL, whichever is greater.	Correct problem, repeat.
Internal Standards[3]	Every sample, standard and blank.	Retention time ±30 seconds from retention time of the mid-point std. in the ICAL. EICP area within -50% to +100% of most recent ICAL mid-point std.	Inspect mass spectrometer and GC for malfunctions; mandatory re-analysis of samples analyzed while system was malfunctioning.
Retention time window calculated for	Each sample.	Relative retention time (RRT) of the analyte within 0.06 RRT units of the RRT of the internal standard.	Correct problem then re-analyze all samples analyzed since the last retention time

QC Check	Frequency	Acceptance Criteria[1]	Corrective Action[2]
each analyte			check.
MDL verification (MDLV)	Minimum yearly.	Detectible.	Re-evaluate MDL standard used and MDL; see Technical Director.

[1] This is a summary of the acceptance criteria.
[2] All abnormalities must be noted in LIMS.
[3]Target compounds associated with failed internal standards must be re-analyzed (undiluted if possible) if additional sample is available; if not available, qualify data in LIMS.

- **BFB Tuning and Breakdown Check**:
  - **BFB Tuning**: At the beginning of each 12-hour analytical shift and **prior** to the analysis of samples or calibration standards, inject 50 ηg or less of the 4-Bromofluorobenzene standard into the GC/MS system (1 µL of 250 µg/mL standard /50 mL reagent water, purged at a 1:10 split for a 25 ηg on the column). (BFB is one of the surrogate compounds.) The resultant mass spectra for the BFB **must** meet the tuning criteria below before sample analysis begins.

BFB (4-Bromofluorobenzene) Mass Intensity Criteria

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101 % of m/z 174
177	5 to 9% of m/z 176

  - Three options are available for acquiring the spectra for reference to meet the BFB tuning requirements:

Option 1 It is recommended that each initial tune verification utilize the "Autofind" function and be set up to look at the apex ± 1 scan and average the three scans. Background correction is required prior to the start of the peak but no more than 20 scans before. Background correction **cannot** include any part of the target peak. Sometimes the instrument does not always correctly identify the apex on some peaks when the peak is not perfectly shaped. It is acceptable to manually identify and average the apex peak ± 1 scan and background correct.

Option 2 The scan across the peak at one half peak height may be averaged and background-corrected.

Option 3 A single scan at the apex (only) may also be used for the evaluation of the tune. Background correction is still required.

Note: It is acceptable to adjust parameters within the specifications set by the manufacturer or the analytical method to properly tune the instrument. If the tune verification does not pass it may be necessary to clean the source or perform additional maintenance. Document any maintenance in the instrument log. **Excessive adjusting (more than two tries) without clear documentation is not allowed. No more than two consecutive tunes may be attempted. Perform necessary maintenance.**

- Note: All subsequent standards, samples, controls, and blanks associated with a BFB tune **must** use identical mass spectrometer instrument conditions.

- **Bromoform Breakdown Check**: The daily BFB Tune/Breakdown Check containing surrogates, internal standards, BFB, and 20 µg/L Bromoform must be analyzed prior to the analysis of the Continuing Calibration Verification (CCV). If levels of Chloromethane or Bromomethane exceed 0.5 µg/L, then the trap may be too contaminated with salts or tightly bound contamination for analysis to continue. The trap must be replaced, and the system re-calibrated.

- **Calibration standards**: See Section 10.2.

SPCCs and CCCs are unique to 8260B. ***Italicized text is unique to 8260C.***

- **Initial System Performance Check Compounds (SPCCs)**: A system performance check is made before the calibration curve is used. Five compounds (the System Performance Check Compounds) are checked for a minimum average response factor, compound instability, and degradation caused by contaminated lines or active sites in the system. These compounds are Chloromethane, 1,1-Dichloroethane, Bromoform, Chlorobenzene, And 1,1,2,2-Tetrachloroethane. The minimum mean response factors for the volatile SPCCs must be met and are as follows:

Chloromethane	0.10
Bromoform	0.10
1,1,2,2-Tetrachloroethane	0.30
1,1-Dichloroethane	0.10
Chlorobenzene	0.30

Example problems include:

- Chloromethane is the most likely compound to be lost if the purge flow is too fast.
- Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve Bromoform response.
- Tetrachloroethane and 1,1-Dichloroethane are degraded by contaminated transfer lines or active sites in trapping materials.

- **Initial Calibration check compounds (CCCs):** The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites in the system. Meeting the CCC criteria is **not** a substitute for successful calibration of the target analytes. The CCCs are:

1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene
1,2-Dichloropropane	Vinyl chloride

- Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for **all** target analytes from the initial calibration with the equations in Section 11.
- The RSD must be less than or equal to **15% for each target analyte**; however, the

RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%. If an RSD of greater than 30% is measured for any CCC, then corrective action to eliminate a system leak or contamination and/or column reactive sites is necessary before re-attempting calibration. The CCCs may not be in the project target list. If that is the case, each target must have a RSD < 15% or a correlation coefficient $r \geq 0.995$ ($r^2 \geq 0.990$) as calculated by the equations in Section 11. When using linear regression, re-calculate the low calibration point. It must be within 30% true.

- *For 8260C, the minimum RF for initial and continuing calibration is:*

RF	*For These Compounds*
0.1	*Critical compounds*
0.2	*1,1-Dichloroethane, Chloroform, Trichlorethene, Bromodichloromethane, cis-1,3-Dichloropropene, Tetrachloroethane, and 1,2,4-Trichlorobenzene*
0.3	*o-Xylene, Styrene, 1,1,2,2-Trichloroethane*
0.4	*Toluene, 1,2-Dichlorobenzene*
0.5	*Benzene, Chlorobenzene, 1,4-Dichlorobenzene*
0.6	*1,3-Dichlorobenzene*

  - *For 8260C, the must be less than or equal to 20% for each target analyte with up to 10% of compounds meeting the 40% criterion.*

- **Initial Calibration Verification (ICV)** is verified immediately after calibration using the introduction technique used for samples. Analyze a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS.
  - The ICV is made from the **second-source** standards, one at a time, as needed, to be run after an initial calibration: Add 25 µL of the second-source, non-gas, working standard to 50 mL reagent water in a 50-mL, Class A volumetric. Add 25 µL of the Gas Mix working standard to the Class A volumetric for a final concentration of 50-5000 µg/L.
  - The ICV of each target must be within 30% of the expected value, with the exception of the following poor purge efficiency analytes that may be within 40% of the expected value for up to 20% of targets:

Acrolein	Ethanol	2-Methylnaphthalene
t-Amyl alcohol (TAA)	t-Butyl formate (TBF)	Vinyl acetate
t-Butyl alcohol (TBA)	1-Methylnaphthalene	

  - If ICV criterion is not met, correct the problem and re-calibrate.
- **Continuing Calibration Verification (CCV):** Run every 12 hours of sample analysis, CCVs are often made each day for several instruments in the following proportions, always from the **primary** calibration standards:
  - Add 25 µL of the working calibration Non-Gas Standard and 25 µL of the primary Gas Mix to a 50-mL, Class A volumetric and dilute to the mark with reagent water. The final concentration is 50-5000 µg/L.
  - Area counts of the internal standards must be between 50 - 100% of the areas of the internal standards in the mid-point calibration standard. If not, inspect the GCMS for possible maintenance issues and then re-analyze. Contact the department supervisor for assistance in determining the appropriate course of action. **Do not report data from a failing internal standard associated with target compounds.**
  - **For 8260B Only: Continuing System Performance Check Compounds (SPCCs)**
    - A System Performance Check **must** be made during every 12-hour analytical shift. Each SPCC compound in the calibration verification standard **must** meet its minimum

response factor. This is the same check that is applied during the initial calibration.
    - If the minimum response factors are not met, the system **must** be evaluated, and corrective action **must** be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.
- **For 8260B Only: Continuing Calibration Check Compounds (CCCs)**
    - After the system performance check is met, the CCCs are used to check the validity of the initial calibration, if present in the target list. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. See Section 11 for equations.
    - If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i. e., greater than 20% difference or drift), for any one CCC, then corrective action **must** be taken prior to the analysis of samples. **If the CCCs are not included in the list of analytes for a project and therefore not processed in the calibration standards, then all analytes must meet the 20% difference or drift criterion.**
    - Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new five-point initial calibration must be generated. The CCC or target criteria **must** be met before sample analysis begins.
- **For 8260B Only: Continuing Evaluation of Non CCC/SPCC compounds** – The percent difference or drift for each of the non-CCC analytes is less than or equal to 30%. Recovery for some compounds with poor purge efficiency may exceed this 30% requirement and still be deemed acceptable provided all of the following criteria are met:
    - Poor performing analytes are one of the following: Acrolein, tert-Amyl alcohol (TAA), tert-Butyl alcohol (TBA), tert-Butyl formate (TBF), Ethanol, 2-Methylnaphthalene, Vinyl acetate.
    - The percent difference or drift is less than or equal to 40%.
- *For 8260C, see ICAL and ICV information.*
- **Continuing Calibration Blank (CCB):** The CCB is reagent water or sand.
- **Internal Standards** are used to evaluate the effect of the sample matrix. Any samples that do not meet the internal standard criteria must be evaluated for validity. If the change in sensitivity is a matrix effect, the sample is re-analyzed to confirm. If the change in sensitivity is due to instrumental problems, all affected samples must be re-analyzed after the problem is corrected.
    - The retention times of the internal standards in the calibration verification standard are evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required. Note any maintenance in the logbook.
    - Internal standards permit most of the components of interest in a chromatogram to have retention times of 0.80 - 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Attachment 1). If interferences are noted, use the next most intense ion as the quantitation ion.
    - **Internal standard response** - If the EICP area for any of the internal standards in the calibration verification standard and samples changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made.

When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required. Note any maintenance in the logbook.

- The laboratory re-analyzes any sample where the internal standard fails and there is no evidence of matrix interference. If there is no matrix interference, the sample must be reanalyzed at the original dilution.
  - If the internal standard is within criteria, report the second analysis.
  - If the internal standard is still outside of criteria, the sample must be analyzed at a second dilution.
  - If the internal standard still does not meet criteria, the sample must be diluted until the internal standard meets criteria. Multiple runs may be required.
- See Attachment 2 for the analytes corresponding to each internal standard.

- **Retention time windows**: Target analytes are identified on the basis of retention time windows.
  - Before establishing retention time windows, make sure that the chromatographic system is functioning reliably and that the operating parameters have been optimized for the target analytes and surrogates in the sample matrix to be analyzed.
  - Establish the retention time windows for target analytes.
  - The relative retention times of each target analyte in each calibration standard must agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.
- **Method Detection Limit Verification (MDLV):** Annually verify that the MDL is detectible; if not, re-evaluate the MDL.

10.0 Procedure

10.1 Sample Preparation

Matrix	Sample Size
Water	VOA vial
Low-concentration Soil	5 grams
High-concentration Soil	1 mL Methanol extract of soil

- All samples and standard solutions are allowed to warm to ambient temperature before analysis.
- Refer to SOP 5030 / NV05-107 for waters and 5035 / NV05-108 for soils/solids.
- For Wisconsin VOC soils, the following procedure must be performed for Methanol extraction of Soil/Sediment:

1	Hand-shake the sample in its vial containing Methanol vigorously for 2 minutes. Sonicate for 20 minutes.
2	Allow sediment to settle until a layer of Methanol is apparent.
3	Withdraw an appropriate aliquot of the Methanol extract for sparging and add to a VOA vial.
4	Analyze all reagent blanks and QC samples on the same instrument as that used for the samples.
5	If the responses exceed the calibration or linear range of the systems, use a smaller aliquot of Methanol extract or dilute the aqueous sample.

10.2 Initial Calibration: Refer to SOP Acceptable Manual Integration Practices / CA-Q-S-002, Selection of Calibration Points / CA-T-P-002 and Calibration Curves (General) / CA-Q-S-005. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

1 Evaluate the **BFB tuning criteria.**

2 Prepare the **Initial calibration standards** at a minimum of five different concentrations from the secondary dilution of stock standards or from a premixed certified solution in organic-free reagent water. **At least one of the calibration standards corresponds to a concentration at or below the laboratory reporting limit.** This low standard must have valid ion abundances for all monitored ions. The remaining standards define the working range of the system. Initial calibration standards are mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

Initial Calibration (5-point)

Primary Working Standard	Final Volume (mL)	Concentration (µg/L)
1	100	0.5-2.5
2	100	1 - 5
4	100	2 - 10
20	100	10 - 50
40	100	20 - 100
100	100	50 - 250
200	100	100 - 500
400	100	200 - 1000

1 µL of IS/SS Standard at 250 µg/mL is added by the autosampler to 5 mL for a 50-µg/L concentration in the standards and samples with a 5-mL purge; 1 µL/10 mL for a 25 µg/L concentration. See Section 9.1 for make-up and final concentrations for other purge volumes. The surrogate calibration is a single-point.

- All target analytes for a particular analysis must be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes for which the method has been demonstrated. **However, the laboratory must not report a quantitative result for a target analyte that was not included in the calibration standard(s).**
- **Internal Standards:** The calibration standards must also contain the internal standards chosen for the analysis. Calibration standards for soils must also contain the preservative Na_2SO_4. See Method 5035 / NV05-108 for how to accomplish the preservation.
- **Surrogates**: Historically the surrogate compounds have been included in the multi-point initial calibration at variable concentrations in order to evaluate the linear response as with any target analyte. With improvements in instrumentation and more reliance on the autosampler, an option is available allowing the autosampler to spike the initial calibration standards with surrogates in the same manner as the samples are spiked. With this option, the surrogate standards in the initial calibration can be averaged to develop a response factor and an effective one-point calibration with the sole purpose to measure the surrogate recovery using the same concentration for each sample analysis. For this calibration option, the surrogate linear response is less important, since multiple concentrations of surrogates are not being measured. Instead, the surrogate concentration remains constant throughout, and the recovery of this known concentration can easily be attained without demonstrating if the response is linear.
- **Technique:** To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a Class A, volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection and stopper. Mix by inverting the flask three times. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and are prepared daily. Transfer each standard to separate VOA vials.

	• **Water or Soil Samples:** A different calibration curve is necessary for Methods 5030 / NV05-107 and 5035 / NV05-108. Calibration **must** be performed using the same sample introduction technique that is used for samples. For Method 5030, the purging efficiency varies with purge volume; therefore, develop the standard curve with whichever volume of sample that is to be analyzed.
3	**Calibration sequence**: 1 BFB Tuning Criteria 2 ICAL 3 ICV 4 ICB
4	**Tabulate the area response of the characteristic ions** (see Attachment 1) against the concentration for each target analyte and each internal standard. Calculate response factors (RF) for each target analyte relative to one of the internal standards.
5	• Evaluate the RSD or linearity.
6	For 8260B: evaluate the SPCC and CCC compounds for the initial calibration criteria. For 8260C: evaluate each target.
7	Evaluate the retention times and minimum response factors.
8	Evaluate the success of the initial calibration by immediately running an Initial Calibration Verification (ICV).
9	Evaluate the Initial Calibration Blank to be sure it is free of contaminants.

10.3 Daily GC/MS Calibration Verification

1	Evaluate the BFB tuning and Breakdown Check criteria.
2	Evaluate the CCV and CCB.
3	For 8260B, evaluate the SPCC and CCC compounds for the continuing calibration criteria. For 8260C: evaluate each target.

10.4 Example Analysis Queue / Sequence (based on 12 hours)

1	Tune/Breakdown Check
2	CCV, for daily and ongoing calibration check
3	LCS
4	Blank
5	Samples
6	Matrix Spike
7	Matrix Spike Duplicate
When 12 hours have passed, run a 2nd tune and CCV before running more samples, no more than 20 samples in a 12-hour batch.	

- **Dilutions**: If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the upper calibration standard, the sample must be reanalyzed at a higher dilution. **Secondary ion quantitation is allowed only when there are sample interferences with the primary ion**.
  - When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of an organic-free, reagent water blank or the repeating of suspected samples. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is

demonstrated to be free of interferences. Repeat all affected samples.

- Prepare dilutions such that the response of the major constituents (previously saturated peaks) is in the upper half of the linear range of the curve.
- The following procedure is used to dilute aqueous samples for analysis of volatiles. All steps must be performed without delays.

1	Dilutions are made in Class A, volumetric flasks (50 to 100 mL). Select the volumetric flask that allows for the necessary dilution. Intermediate dilution steps may be necessary for extremely large dilutions.
2	Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask, and add slightly less than this quantity of organic-free reagent water to the flask.
3	Inject the appropriate volume of the original sample from the syringe into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, three times. Repeat above procedure for additional dilutions.
4	Fill a VOA vial with the diluted sample and cap.

- For high concentration samples, see SOP 5035 / NV05-108.

10.5 Qualitative analysis

The qualitative identification of each compound determined by this method is based on relative retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be kept up to date and obtained through analysis of known standards on the instrument using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. See Attachment 1 for primary and secondary ions for each compound. Compounds are identified as present when the following criteria are met:

- The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time is accepted as meeting this criterion.
- The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.
- The relative intensities of the characteristic ions agree with 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%). When two or more analytes that co-elute share secondary ions, and all the characteristic secondary ions for the target analyte are present but outside the ± 30 % relative intensity, report the compound as positive if there is no interference with the primary quantitation ion. If co-eluting peaks share the primary ion, the analyte may only be reported as a co-eluting pair.
- Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i. e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.
- Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes co-elute (i. e., only one

chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum might contain extraneous ions contributed by the co-eluting compound. If all of the ions associate with the reference spectrum for the target analyte are present and within the ± 30% criteria, a positive result must be assumed even in the presence of extraneous ion fragments without presumptive evidence for a negative identification. (All ions associated with the target analyte are also present in the interfering peak.) The analyst must carefully weigh the background spectrum and the spectrum of any co-eluting analytes whenever assessing a potential hit. Analyst experience in interpreting mass spectral data and the above specified guidelines are used together to interpret difficult matrices. Add appropriate qualifiers in Element (ID2).

- Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.
- For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification is determined by the purpose of the analyses being conducted. Data system library search routines are not to use normalization routines that would misrepresent the library or unknown spectra when compared to each other.
- For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:
  - Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) must be present in the sample spectrum.
  - The relative intensities of the major ions must agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).
  - Molecular ions present in the reference spectrum must be present in the sample spectrum.
  - Review ions present in the sample spectrum but not in the reference spectrum for possible background contamination or presence of co-eluting compounds.
  - Review ions present in the reference spectrum but not in the sample spectrum for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

10.6 Quantitative analysis

- Once a compound has been identified, the quantitation of that compound is based on the integrated abundance from the EICP of the **primary** characteristic ion. The internal standard used is the one nearest the retention time of that of a given analyte. See Attachment 1.
- If the RSD of a compound's response factors is 15% or less, then the concentration is determined using the average response factor (*RF*) from initial calibration data.
- Where applicable, the concentration of any non-target analyte identified in the sample may be estimated. The same formulae are used with the following modifications: The areas A_x and A_{is} are from the total ion chromatograms, and the RF for the compound must be assumed to be 1.
- The resulting concentration is reported indicating:
  - that the value is an estimate, and

- in Level 4 data packages, which internal standard was used to determine the concentration. Use the nearest internal standard free of interferences.

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\% \text{ Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 Response Factor

$$RF = \frac{A_s x C_{is}}{A_{is} x C_s}$$

A_s = Peak area of the analyte or surrogate.
A_{is} = Peak area of the internal standard.
C_s = Concentration of the analyte or surrogate.
C_{is} = Concentration of the internal standard

11.4 Standard Deviation, Relative Standard Deviation

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_i - RF_{mean}\right)^2}{n-1}} \qquad RSD = \frac{SD \times 100}{RF_{mean}}$$

RF_i = RF for each of the calibration standards
RF_{mean} = mean RF for each compound from the initial calibration
n = Number of calibration standards, e. g., 5

11.5 % Difference, % Drift

$$\% \text{ Difference} = \frac{(RF_v) - (\text{Avg. RF}) \times 100}{\text{(Avg. RF)}}$$

RF_v = RF from verification standard
Avg. RF = Average RF from Initial Calibration.

$$\% \text{ Drift} = \frac{\text{Result - True Value} \times 100}{\text{True Value}}$$

11.6 Linear Calibration Using a Least Squares Regression: A linear calibration model based on a least squares regression may only be employed if RSD does not meet the acceptance criteria.

For calibration, x is the mass of the analyte in the sample aliquot introduced into the instrument and y is the area (or height) or the response, as in:

$x = C_s$ and $y = A_s$

A linear least squares regression attempts to construct a linear equation of the form:

$y = ax + b$

by minimizing the differences between the observed results (y_i, the instrument response) and the predicted results (y_i', the response calculated from the constructed equation). The regression equation is:

$y_i' = ax_i + b$

a = regression coefficient or the slope of the line.
b = the y-intercept.
y_i' = predicted (or calculated) response for the i^{th} calibration standard.
x_I = mass of analyte in the i^{th} calibration standard aliquot introduced into the instrument.

The sum of the squares of the differences is minimized to obtain a and b:

$$\sum_{i=1}^{n}(x_i - x_i')^2$$

n = total number of calibration points. The regression calculations attempt to minimize this sum of the squares, hence the name "least squares regression."

Weighting the sum of the square of the differences may significantly improve the ability of the least squares regression to fit the linear model to the data. The general form of the sum of the squares of the differences containing the weighting factor is:

$$\sum_{i=1}^{n} w_i(x_i - x_i')^2$$

w_i = weighting factor for the i^{th} calibration standard (w=1 for unweighted least squares regression).
x_i – observed instrument response (area) for the i^{th} calibration standard.
x_i' = predicted (or calculated) response for the i^{th} calibration standard.
n = total number of calibration standards.

The mathematics used in least squares regression has a tendency to favor numbers of larger value over numbers of smaller value. Thus the regression curves that are generated tend to fit points that are at the upper calibration levels better than those points at the lower calibration levels. To compensate for this, a weighting factor which reduces this tendency can be used.

Examples of allowed weighting factors which place more emphasis on numbers of smaller value are:

$w_i - 1/x_i$ or $w_i = 1/x_i^2$

Do not include the origin (0, 0) as an extra calibration point. The use of a linear regression may NOT be used as a rationale for reporting results below the calibration range demonstrated by the analysis of the standards. If it is necessary to report results at lower concentrations, then the analyst must run a calibration that reaches those lower concentrations.

The regression calculation generates a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.995 or $r^2 \geq 0.990$.

11.7 Coefficient of Determination **Correlation Coefficient**

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2} \qquad r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response ratio
x = Concentration

11.8 Concentration Calculation

Concentration = (µg/L from instrument) (dilution factor)

12.0 <u>Method Performance</u>

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes must be stored, managed, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Aqueous waste generated from analysis may have a pH of less than 2.0. Transfer to waste disposal for neutralization and then dump into the sanitary sewer.
- Solid waste generated from analysis is placed in the trash.

15.0 References / Cross References

15.1 EPA Method 8260B, SW-846 Update III, Revision 2, December 1999, **Method 8260C**, Update.IV, Rev. 3, August 2006.

15.2 Method 8000B, SW-846, Revision 2, December 1996, **Method 8000C**, Revision 3, March 2003.

15.3 Method TPH-GRO by Method 8260B, MRBCA (Missouri) Guidance Document, Final Draft, February 24, 2004.

15.4 California GRO, CA LUFT 8015.

15.5 TestAmerica Nashville's Quality Assurance Manual.

15.6 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.7 SOPs: Acceptable Manual Integration Practices / CA-Q-S-002, Selection of Calibration Points / CA-T-P-002, Calibration Curves (General) / CA-Q-S-005, Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Determination of Method Detection Limits / NV08-202, Reagent and Standard Purchase / NV08-214, Sample Homogenization, Sub-sampling & Compositing / NV08-229, 5030 / NV05-107, 5035 / NV05-108.

15.8 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

State	Modification
Ohio specific criteria	Only those compounds in EPA Method 8260B may be reported (superscript 1 in the table in Section 1.1). Some compounds in this SOP are not part of the original 8260B method. The method blank must be less than the RL for Ohio samples. See SOP 8260/NVOH05-77.
Missouri GRO	Prepare 1:1 mixture of unleaded gasoline and #2 diesel fuel in Methanol as GRO is defined by setting retention time window from 0.1 minutes before C_6 to 0.1 minutes after C_{10}. Verify RT window with the standard daily (every 24 hours).
California	California LUFT GRO uses gasoline and the retention time window of C_4 (t-Butanol) to

GRO	C_{12}.
Michigan GRO	See the Michigan GRO requirements below.
South Carolina	See the special LCS acceptance criteria and special state PQL requirements below.
Minnesota	See the special Ethanol analysis requirements below for water samples.

TPH-GRO by Method 8260B

Standards

- C4-C12 Standards
  - Primary: Restek 30096, 5000 µg/mL, or equivalent.
  - Secondary: O2SI 020246-S6, 10,000 µg/mL, or equivalent.
- C6-C10 Standards
  - Primary: Restek 31484, 20,000 µg/mL, or equivalent.
  - Secondary: Ultra CUS-8324, 10,000 µg/mL, or equivalent.

Sample Introduction

- Samples are purged onto the GC/MS system using all protocols specified in SW-846 Method 5030 and 5035.
- Surrogates and internal standards specified by Method 8260B are added to water and soil samples prior to purging.

Sample Analysis

- The BC/MS system is tuned to BFB tune criteria listed in Method 8260B at the frequency specified in Method 8260B.
- A 5-point standard curve is used to quantitate TPH-GRO by the internal standard technique.
- For **Missouri** GRO, the stock standard solution is a mixture of unleaded gasoline and Number 2 diesel fuel.
- For **Californi**a GRO, the stock standard is unleaded gasoline.
- The lowest calibration standard should be at or below the reporting limit of the method.
- For **Missouri,** retention time windows are defined for TPH-GRO by analyzing a standard containing C_6 and C_{10}. The retention time window is defined as $>C_6$ to C_{10}. The standard containing C_6 and C_{10} must be analyzed every day samples are analyzed in order to verify that the retention time windows are constant.
- For **California**, the retention time window are defined as $>C_4$ to C_{12}.
- For **Michigan**,
  - Use unleaded gasoline for calibration.
  - The retention time window is defined as C_6 (hexane) to C_{10} (n-decane).
  - The holding time for water and soil is 14 days.
  - For soil preparation, shake the Methanol and sample for 2 minutes, then sonicate in a water bath for 20 minutes.
  - For oil samples, add 2 g sample to 40 mL Methanol; wait 24 hours before analysis.
  - Use the internal calibration technique, summing the range.
  - Use only linear regression; $r \geq 0.990$, $r^2 \geq 0.981$.
  - ICV and CCV must be ± 20% true.
- Because the retention time window is several minutes wide for TPH-GRO, the GC/MS data system may not accurately or appropriately establish the proper baseline for calibration or quantitation. The analyst **must** visually examine the computer-generated baseline for every analytical run and manually adjust the baseline when needed. A properly drawn baseline must extend over the entire retention time window and include

the area under the entire TPH-GRO series of peaks. It is not appropriate to draw the baseline "peak to peak."

- The total ion chromatogram (TIC) **must** be used to calculate the area under the peak for TPH-GRO calibration and quantitation determinations over the entire retention time window.
- Area counts for the internal standards and surrogates added during sample preparation **must** be subtracted from the total area count for TPH-GRO. This is accomplished by subtracting the area count of the method blank from all subsequent calibration and analytical runs.
- The %RSD for the calibration curve for TPH-GRO must be less than or equal to 20%, so that linearity through the origin can be assumed and an average calibration factor used for calculations.
- A continuing calibration verification standard (CCV) must be analyzed at the beginning of each batch. The standard concentration should be at the mid-point of the calibration curve. If the %RSD exceeds 20%, a new curve must be generated.
- A method blank must be analyzed once per day to insure the analytical system is free of background contamination.

South Carolina LCS Acceptance Criteria and Special State PQL Requirements

- All routinely reported analytes require 70-130% LCS recovery. The following exceptions of poor-performing analytes require 60-140% LCS recovery:

Acetonitrile	Dichlorodifluoromethane
Acrolein	2,2-Dichloropropane
Acrylonitrile	3,3-Dimethyl-1-butanol
t-Amyl alcohol	1,4-Dioxane
Bromomethane	Ethanol
t-Butyl alcohol	2-Hexanone
t-Butyl formate	Isopropyl alcohol
Chloroethane	4-Methyl-2-pentanone
Chloromethane	Vinyl chloride
1,2-Dibromo-3-chloropropane	

- Instrumentation used for South Carolina samples must be able to achieve and report the following South Carolina PQLs when those compounds are requested:
  - Acrolein 5 ug/L
  - Acrylonitrile 5 ug/L
  - 2-Chloroethyl vinyl ether 5 ug/L
  - Methylene chloride 2 ug/L

Minnesota Ethanol Analysis Requirements for Water Samples

- The calibration standard used for Ethanol must be a water-based standard and not a Methanol-based standard. Ethanol water-based standards must be stored at <4°C.
- Initial calibration: The recovery (accuracy) for each point in the curve must be 70-130% except for the lowest point in the curve which must be 60-140%.
- Continuing calibration verification: Analyze one low-level Ethanol standard at the report level (RL) and one mid-level Ethanol calibration verification standard at approximately 500 µg/L prior to the samples. %R for Ethanol in the low-level standard must be 60-140% of the true

value. %R for Ethanol in the mid-level standards must be 70-130% of the true value and a % difference of ≤ 30%.

- For samples, absolute areas of the quantitation ions for the internal standard and surrogate must not decrease by more than 50% from the initial calibration.
- %R for Ethanol for the MS/MSD must be 70-130% with a relative percent difference (RPD) of ≤30%. %R for the LCS/LCSD must be 70-130% with a RPD ≤ 30%.
- The quantitation ion for Ethanol is 45 atomic mass units (AMU). Confirmation ions are 46 and 47 AMU. Ethanol standards must be analyzed separately from the normal VOC list due to the interference from Ethyl ether.

17.0 Attachments

17.1 Attachment 1, Characteristic Masses (m/z) for Purgeable Organic Compounds.

17.2 Attachment 2, Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation.

Attachment 1, Characteristic Masses (m/z) for Purgeable Organic Compounds

Compound	Primary Characteristic Ion	Secondary Characteristic Ion
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,1-Trichloroethane	97	99, 61
1,1,2,2-Tetrachloroethane	83	131, 85
1,1,2-Trichloro-1,2,2-trifluoroethane	101	151, 103, 153
1,1,2-Trichloroethane	97	83, 85
1,1-Dichloroethane	63	65, 83
1,1-Dichloroethene	96	61, 63
1,1-Dichloropropene	75	110, 77
1,2,3-Trichlorobenzene	180	182, 145
1,2,3-Trichloropropane	110	75, 77
1,2,3-Trimethylbenzene	0	105
1,2,4-Trichlorobenzene	180	182, 145
1,2,4-Trimethylbenzene	105	120
1,2-Dibromo-3-chloropropane (DBCP)	157	155, 75
1,2-Dichlorobenzene	146	111.148
1,2-Dichloroethane	62	98
1,2-Dichloropropane	63	112
1,3,5-Trichlorobenzene	180	145, 182
1,3,5-Trimethylbenzene	105	120
1,3-Dichlorobenzene	146	111, 148
1,3-Dichloropropane	76	78
1,4-Dichlorobenzene	146	111, 148
1,4-Dioxane	88	58, 43, 57
2,2-Dichloropropane	77	97
2-Butanone (MEK)	72	43
2-Chloro-1,3-butadiene (Chloroprene)	53	88, 90, 51
2-Chloroethyl vinyl ether	63	65, 106
2-Chlorotoluene	91	126
2-Hexanone	58	43, 57, 100
2-Methyl-2-propanol (t-butyl alcohol)	59	41, 43
2-Methylnaphthalene	142	141, 115
2-Nitropropane	43	41, 39
3,3-Dimethyl-1-butanol	57	69, 41
3-Chloro-1-propene (Allyl chloride)	76	78

4-Chlorotoluene	91	126
4-Isopropyltoluene (p-Isopropyltoluene)	119	134, 91
4-Methyl-2-pentanone (MIBK)	58	43, 100, 85
Acetone	58	43
Acetonitrile	41	40, 39
Acrolein	56	55
Acrylonitrile	53	52, 51
Benzene	78	--
Benzyl chloride	91	126, 65, 128
Bromobenzene	77	156, 158
Bromoform	173	175, 254
Bromomethane	96	94
Butadiene	0	54
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chlorobenzene	112	77, 114
Chlorobromomethane	130	49, 128
Chlorodibromomethane	127	129
Chloroethane	64	66 (51*)
Chloroform	83	85
Chloromethane	50	52 (51*)
cis-1,2-Dichloroethene	61	96, 98
cis-1,3-Dichloropropene	75	77, 39
Cyclohexane	56	84, 41, 69
Cyclohexanone	55	42, 98
Dibromomethane	93	95, 174
Dichlorobromomethane	83	85, 127
Dichlorodifluoromethane	85	87
Dichlorofluoromethane	67	69
Ethanol	45	46
Ethyl acetate	43	45, 61, 88
Ethyl acrylate	0	55
Ethyl ether (Diethyl ether)	59	45, 74
Ethyl methacrylate	69	41, 99, 86
Ethylbenzene	91	106
Ethylene dibromide (EDB, 1,2-Dibromoethane)	107	109, 188
Hexachlorobutadiene	225	223, 227
Hexane	57	41, 43, 56
Iodomethane	142	127, 141
Isobutyl alcohol	43	41, 42, 74
Isopropyl alcohol	45	59
Isopropylbenzene	105	120
Isopropylether (IPE, Diisopropyl ether))	45	87, 59
m, p-Xylene	91	106
Methacrylonitrile	41	67, 39, 52
Methyl acetate	43	74, 59
Methyl methacrylate	41	69, 100, 39
Methylcyclohexane	83	55, 98, 41
Methylene chloride	84	86, 49
Methyl-t-butyl ether (MTBE)	73	57, 43
Naphthalene	128	-
n-Butanol (n-Butyl alcohol)	56	41, 43

n-Butyl acetate	43	56, 73, 61
n-Butylbenzene	91	92, 134
n-Propylbenzene	91	120
o-Xylene	91	106
Pentachloroethane	167	165, 169, 117, 83
Propionitrile (ethyl cyanide)	54	52, 55
sec-Butylbenzene	105	134
Styrene	104	78
tert-Amyl alcohol	59	55, 73, 43
tert-Amyl ethyl ether (TAME)	73	55, 87, 43
tert-Butyl ethyl ether (ETBE)	59	87, 41
tert-Butyl formate (TBF)	59	57, 41
tert-Butylbenzene	119	91, 134
Tetrachloroethene	166	129, 131, 164
Tetrahydrofuran	42	41, 71, 72
Toluene	91	92
trans-1,2-Dichloroethene	61	96, 98
trans-1,3-Dichloropropene	75	77, 39
trans-1,4-Dichloro-2-butene	53	88, 89
Trichloroethene	130	97, 95, 132
Trichlorofluoromethane	101	103, 105
Vinyl acetate	43	86
Vinyl chloride	62	84
Internal Standards/Surrogates:		
Fluorobenzene	96	70
Chlorobenzene-d_5	117	82
1,4-Dichlorobenzene-d_4	152	115, 78
4-Bromofluorobenzene	95	174, 176
Dibromofluoromethane	111	113
1,2-Dichloroethane-d_4	65	67, 51
Toluene-d_8	98	100

Attachment 2, Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Fluorobenzene	**Chlorobenzene-d_5**	**1,4-Dichlorobenzene-d_4**
1,1,1-Trichloroethane	1,1,1,2-Tetrachloroethane	1,1,2,2-Tetrachloroethane
1,1,2-Trichloro-1,2,2-trifluoroethane	1,1,2-Trichloroethane	1,2,3-Trichlorobenzene
1,1-Dichloroethane	1,3-Dichloropropane	1,2,3-Trichloropropane
1,1-Dichloroethene	2-Chloroethylvinylether	1,2,3-Trimethylbenzene
1,1-Dichloropropene	2-Hexanone	1,2,4-Trichlorobenzene
1,2-Dichloroethane	3,3-Dimethyl-1-butanol	1,2,4-Trimethylbenzene
1,2-Dichloroethane-d_4 (s)	4-Methyl-2-pentanone (MIBK)	1,2-Dibromo-3-chloropropane (DBCP)
1,2-Dichloropropane	Benzyl chloride	1,2-Dichlorobenzene
1,4-Dioxane	Bromoform	1,3,5-Trichlorobenzene
2,2-Dichloropropane	Chlorobenzene	1,3,5-Trimethylbenzene
2-Butanone	Chlorodibromomethane	1,3-Dichlorobenzene

Fluorobenzene	Chlorobenzene-d_5	1,4-Dichlorobenzene-d_4
2-Chloro-1,3-butadiene (Chloroprene)	cis-1,3-Dichloropropene	1,4-Dichlorobenzene
2-Methyl-2-propanol (tert-Butyl alcohol)	Ethyl methacrylate	2-Chlorotoluene
2-Nitropropane	Ethylbenzene	2-Methylnaphthalene
3-Chloro-1-propene (Allyl chloride)	Ethylene dibromide (1,2-Dibromoethane)	4-Chlorotoluene
Acetone	Isopropylbenzene	4-Isopropyltoluene (p-Isopropyltoluene)
Acetonitrile	m,p-Xylene	Bromobenzene
Acrolein	o-Xylene	Bromofluorobenzene (s)
Acrylonitrile	Styrene	Hexachlorobutadiene
Benzene	Tetrachoroethene	Naphthalene
Butadiene	Toluene	n-Butylbenzene
Chlorobromomethane	Toluene-d8 (s)	n-Propylbenzene
Bromomethane	trans-1,3-Dichloropropene	Pentachloroethane
Carbon disulfide		sec-Butylbenzene
Carbon tetrachloride		tert-Buylbenzene
Chloroethane		trans-1,4-Dichloro-2-butene
Chloroform		
Chloromethane		
cis-1,2-Dichloroethene		
Cyclohexane		
Cyclohexanone		
Dibromofluoromethane (s)		
Dibromomethane		
Dichlorobromomethane		
Dichlorodifluoromethane		
Dichlorofluoromethane		
Isopropyl ether (IPE, Diisopropyl ether)		
Ethanol		
Ethyl acetate		
Ethyl acrylate		
Ethyl ether (Diethyl ether)		
Hexane		
Iodomethane		
Isobutyl alcohol (Isobutanol)		
Isopropyl alcohol (Isopropanol)		
Methacrylonitrile		
Methyl acetate		
Methyl cyclohexane		
Methyl methacrylate		
Methylene chloride		
Methyl-tert-butyl ether (MTBE)		
n-Butanol (n-Butyl alcohol)		
n-Butyl acetate		
n-Heptane		
Propionitrile		

Fluorobenzene	Chlorobenzene-d_5	1,4-Dichlorobenzene-d_4
t-Amyl alcohol		
tert-Amyl methyl ether (TAME)		
tert-Butyl ethyl ether (ETBE)		
tert-Butyl formate		
Tetrahydrofuran		
trans-1,2-Dichloroethene		
Trichloroethene		
Trichlorofluoromethane		
Vinyl acetate		
Vinyl chloride		

18.0 Revision History

- Revision 12, 10 October 2008
  - Integration for TestAmerica and STL operations.
  - Insert corrective action procedures
- Revision 13, 25 September 2009
  - Move QC summary table and QC sample preparation instructions into Section 9.
  - Addition of new analytes: 3,3-Dimethyl-1-butanol (SC) and 1,3,5-Trichlorobenzene (NH).
  - Addition of Attachment 3 for South Carolina.
- Revision 14, 6 November 2009
  - Corporate review.
  - Addition of single-point surrogate calibration.
  - Incorporate Michigan GRO requirements.
- Revision 15, 30 October 2010
  - Addition of Amendments a (SC PQLs, Attachment 3), b (characteristic ions for 1,2,3-Trichloropropane), and c (WI soil extraction procedure).
  - Addition of new analytes: 1-Methylnaphthalene (New Mexico), Pentane, Octane, Nonane (Paraffin group).
  - Addition of QAF-45 and Section 14.2.
- Revision 16, 30 September 2011
  - Organizational changes.
  - Addition of requirement for non-preserved sample if 2-Chloroethyl vinyl ether is analyzed.
  - Addition of Minnesota Ethanol analysis requirements to Section 16.0.
  - Addition of reference to SOPs Calibration Curves (General) and Acceptable Manual Integration Practices / CA-Q-S-002.
  - Addition of 2-Chloroethyl vinyl ether, Acrolein, and Acrylonitrile preservation information.
- Revision 17, 29 February 2012
  - Organizational changes.
  - Addition of Bromoform Breakdown Check.
  - Remove paraffin standard reference.
  - TPH-GRO: change CCC frequency.
  - Corrected weighting equations.
- Revision 18, dated 30 August 2013
  - Organizational changes.
  - Specify that $r^2 \geq 0.990$.
  - OK no longer limits batch size to 10 samples.
  - Add Amendment a.

- Add 8260C.
- Add new standards and new analytes.
- Change the LCS, MS, MSD to use the primary standard.
- MA also requires LCSD.
- Addition of GRO standards

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP) Change Form

SOP Number/Revision No.: **625 / NV04-27.13, 8270 / NV04-22-15b** Effective Date: **12/31/2013**

Last Mod. Date: 10/31/13, 8/6/13

SOP Title: **METHOD 625: BASE/NEUTRAL AND ACID EXTRACTABLE ORGANICS COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS); METHOD 8270C/D: SEMIVOLATILE ORGANIC COMPUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)**

Affected SOP Section Number(s): Section 17.0, Attachment

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 03P, 04B

Revision Number with Mod ID: **13a, 15c**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

☐ Procedural Changes (Define Below) – Re-Training Required.

■ Other

2. Summary of Procedure Change: Add underlined text, remove crossed-out text.

Section 17.0, Attachment, SIM Mass Groups, Add note, remove dwell times column:

Mass Group	**Compound**	~~**Dwell Time**~~

Note: For dwell times, see Chemstation AutoSIM.

Jessica Freeman 12/27/13	12/18/13
Department Supervisor Approval Date	Department Manager Approval Date
Steve Shilley 12/19/13	Michael A. Brown 12/17/13
Quality Assurance Manager Approval Date	Technical Director Approval Date

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure
(SOP) Change Form

SOP Number/Revision No.: **8270 / NV/SA04-22.15a** Effective Date: **8/6/2013**

Last Mod. Date: **3/29/2013**

SOP Title: **Method 8270C/D: Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS)**

Affected SOP Section Number(s): Section 16.0, Modifications; Section 17.0, Attachments

CONTROLLED DISTRIBUTION
ISSUED TO: QA Server, 04B

Revision Number with Mod ID: **15b**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add bold text, delete crossed-out text.

Section 16.0, Method Modification: Add a last sentence to item 4:

Item	Modification
4	SIM is not allowed for South Carolina samples unless pre-approved by the state on a project-specific basis. **SC has not approved RVE/LVI.**

Section 17.0, Attachments, Attachment 1, Characteristic Ions for Semivolatile Compounds: Modify the characteristic ions for the following compounds:

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
o,o,o-Triethylphosphorthioate	5.302	198	**121, 97** ~~80, 53, 54164, 63~~
1,4-Phenylenediamine	5.734	**108** ~~198~~	80, **107** ~~53, 54, 52~~
n-Octadecane	7.586	**57** ~~58~~	71~~, 85~~
Hexachlorophene	9.070	**196** ~~185~~	**198, 209** ~~209, 406~~

Michael A. Brum 8/6/13	8/6/13
Technical and Quality Assurance Approval Date	Operations Manager Approval Date

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure
(SOP) Change Form

SOP Number/Revision No.: **8270 / NV/SA04-22.15** Effective Date: **3/29/2013**

Last Mod. Date: 12/31/12

SOP Title: **Method 8270C/D: Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS)**

Affected SOP Section Number(s): Section 3.0, Definitions; Section 7.0, Reagents and Standards, Section 9.1, Sample QC, Section 10.2, Calibration, Section 16.0, Method Modification

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 04B

Revision Number with Mod ID: **15a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add bold text, delete crossed-out text.

Section 3.0, Definitions: Add a last sentence to 3.1 Reduced Volume Extraction / Large Volume Injection (RVE/LVI)**: Generally, reduce all concentrations by a factor of RVE/LVI, i. e., 5.**

Section 7.0, Reagents and Standards

7.6 GC/MS Tuning Standard: Add to the first sentence: "A Methylene chloride solution containing 50 µg/mL **[RVE/LVI: 10 µg/L]** of Decafluorotriphenylphosphine (DFTPP) is prepared.

7.7 Surrogate Standards: To the bullet item, add a last sentence: **Dilute by five for RVE/LVI.**

Section 9.1, Sample QC, Surrogate recoveries: Delete the phrase: The limits for surrogate recoveries are updated biannually ~~(see TestAmerica Nashville's current Control Limits Manual (CLM))~~.

Section 10.2, Calibration, Initial Calibration, Steps 1 and 2: Add bold column.

- Prepare calibration standards at five (minimum) different concentrations.

Traditional Volume Concentration (µg/mL)	**RVE/LVI Concentration (µg/mL)**	µL of 200 µg/mL standard/500 µL (1 µL injection)	RVE/LVI: µL of 200 µg/mL standard/500 µL (5 µL injection)
2	**0.4**	5	1

10	**2**	25	5
20	**4**	50	10
50	**10**	125	25
80	**16**	200	40
100	**20**	250	50

For SIM, calibration standards are diluted from the intermediate standard solution to give the following concentrations:

Concentration (µg/mL)	**RVE/LVI Concentration (µg/mL)**	µL of 10 µg/mL standard/500 µL (1 µL injection)	RVE/LVI: µL of 10 µg/mL standard/500 µL(5 µL injection)
0.05*	**0.01**	2.5	0.5
0.1	**0.02**	5	1
0.5	**0.1**	25	5
1	**0.2**	50	10
5	**1.0**	250	50
10	**2.0**	500	100

*The lowest calibration ~~0.05 µg/mL~~ standard must be used for low-level SIM analysis on samples from Wisconsin.

Section 16.0, Method Modification: Add item 5 to the table:

Item	Modification
5	**RVE/LVI**

Michael A. Brown 3/11/13	3/11/13
Technical and Quality Assurance Approval Date	Operations Manager Approval Date

SOP Number/Revision No.: **8270 / NV/SA04-22.15** Effective Date: **3/29/2013**

Last Mod. Date: 12/31/12

SOP Title: **Method 8270C/D: Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS)**

Revision Number with Mod ID: **15a**

Title: SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) EPA METHOD 8270C/D

Approvals (Signature/Date)			
	12/28/12		12/28/12
Cory Spry Extractables Operations Manager	Date	Johnny Davis Health & Safety Manager / Coordinator	Date
	12/28/12		
Michael H. Dunn Technical Director Quality Assurance Manager	Date		

Analyze and report by 8270D for Canadian, **NJ, NC, OK, SC, and WV** samples.

1.0 Scope and Application

1.1 Analyte, Matrices: This method is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of oily wastes, soils/sediments, concrete, and water samples. The following compounds can be determined by this method:

Analyte	CAS #	Analyte	CAS #
Acenaphthene[1, 2, 5]	83-32-9	Hexachlorocyclopentadiene[1, 2]	77-47-4
Acenaphthene-d_{10} (IS)		Hexachloroethane[1, 2]	67-72-1
Acenaphthylene[1, 2, 5]	208-96-8	Hexachlorophene[2]	70-30-4
Acetophenone[2]	98-86-2	Hexachloropropene[2]	1888-71-7
2-Acetylaminofluorene[2]	53-96-3	Indeno(1,2,3-cd)pyrene[1, 2, 5]	193-39-5
4-Aminobiphenyl[2]	92-67-1	*Indene*[4]	
Aniline[2]	62-53-3	Isodrin[2]	465-73-6
Anthracene[1, 2, 4, 5]	120-12-7	Isophorone[1, 2]	78-59-1
Aramite[2]	140-57-8	*cis-Isosafrole*[2]	17627-76-8
Azobenzene[3]	103-33-3	*trans-Isosafrole*[2]	4043-71-4
Benzidine[3]	92-87-5	Kepone[2]	143-50-0
Benzoic acid[3]	65-85-0	Methapyrilene[2]	91-80-5
Benz(a)anthracene[1, 2, 4, 5]	56-55-3	3-Methylcholanthrene[2]	56-49-5
Benzo(b)fluoranthene[1, 2, 4, 5]	205-99-2	*6-Methylchrysene*[4]	1705-85-7
Benzo(j)fluoranthene[4]		4,4'-Methylenebis(2-chloroaniline) (MOCA)[3]	101-14-4
Benzo(k)fluoranthene[1, 2, 4, 5]	207-08-9	Methyl methanesulfonate[2]	66-27-3
Benzo(g,h,i)perylene[1, 2, 5]	191-24-2	*2-Methylnaphthalene*[3, 4, 5]	90-12-0
Benzo(a)pyrene[1, 2, 4, 5]	50-32-8	2-Methylnaphthalene[1, 2, 5]	91-57-6
Benzyl alcohol[2]	100-51-6	Methyl parathion[2]	298-00-0
Bis(2-chloroethoxy)methane[1, 2]	111-91-1	2-Methylphenol[1, 2, 4]	95-48-7
Bis(2-chloroethyl)ether[1, 2]	111-44-4	3-Methylphenol[1, 2, 4]	108-39-4
Bis(2-chloroisopropyl)ether[1, 2]	108-60-1	4-Methylphenol[1, 2, 4]	106-44-5
Bis(2-ethylhexyl)adipate[3]	103-23-1	Naphthalene[1, 2, 4, 5]	91-20-3
Bis(2-ethylhexyl)phthalate[1, 2, 4]	117-81-7	Naphthalene-d_8 (IS)	
Bisphenol A[3]	80-05-7	1,4-Naphthoquinone[2]	130-15-4
4-Bromophenyl phenylether[1, 2]	101-55-3	1-Naphthylamine[2]	134-32-7
Butyl benzyl phthalate[1, 2, 4]	85-68-7	2-Naphthylamine[2]	91-59-8
Carbazole[1]	86-74-8	2-Nitroaniline[1, 2]	88-74-4
4-Chloroaniline[1, 2]	106-47-8	3-Nitroaniline[1, 2]	99-09-2
Chlorobenzilate[2]	510-15-6	4-Nitroaniline[1, 2]	100-01-6
4-Chloro-3-methylphenol[1, 2]	59-50-7	Nitrobenzene[1, 2]	98-95-3
1-Chloronaphthalene[3]	90-13-1	Nitrobenzene-d_5 (surr)	
2-Chloronaphthalene[1, 2]	91-58-7	2-Nitrophenol[1]	88-75-5
2-Chlorophenol[1, 2]	95-57-8	4-Nitrophenol[1, 2]	100-02-7
2-Chlorophenol-d_4 (surr)		5-Nitro-o-toluidine[2]	99-55-8
4-Chlorophenyl phenylether[2]	7005-72-3	Nitroquinoline-1-oxide[2]	56-57-5
Chrysene[1, 2, 4, 5]	218-01-9	n-Nitrosodi-n-butylamine[2]	924-16-3
Chrysene-d_{12} (IS)		n-Nitrosodiethylamine[2]	55-18-5
n-Decane[3]	124-18-5	n-Nitrosodimethylamine[2]	62-75-9
Diallate (cis and trans)[2]	2303-16-4	n-Nitrosomethylethylamine[2]	10595-95-6
Dibenz(a,h)acridine[4]	226-36-8	n-Nitrosodiphenylamine[1, 2] and Diphenylamine	86-30-6 and 122-39-4
Dibenz(a,j)acridine[3]	224-42-0	n-Nitrosodi-n-propylamine[1, 2]	621-64-7
Dibenz(a,h)anthracene[1, 2, 4, 5]	53-70-3	n-Nitrosomorpholine[2]	59-89-2
Dibenzofuran[1, 2]	132-64-9	n-Nitrosopiperidine[2]	100-75-4
2,3-Dichloroaniline[3]	608-27-5	n-Nitrosopyrrolidine[2]	930-55-2

1,2-Dichlorobenzene[1, 2, 4]	955-50-1	*n-Octadecane*[3]	593-45-3
1,2-Dichlorobenzene-d_4(surr)		Parathion[2]	56-38-2
1,3-Dichlorobenzene[1, 2, 4]	541-73-1	Pentachlorobenzene[2]	608-93-5
1,4-Dichlorobenzene[1, 2, 4]	106-46-7	*Pentachloroethane*[2]	76-01-7
1,4-Dichlorobenzene-d_4(IS)		Pentachloronitrobenzene[2]	82-68-8
3,3'-Dichlorobenzidine[1, 2]	91-94-1	Pentachlorophenol[1, 2]	87-86-5
2,4-Dichlorophenol[1, 2]	120-83-2	Perylene-d_{12} (IS)	
2,6-Dichlorophenol[2]	87-65-0	Phenacetin[2]	62-44-2
Diethyl phthalate[1, 2, 4]	84-66-2	Phenanthrene[1, 2, 4, 5]	85-01-8
Dimethoate[2]	60-51-5	Phenanthrene-d_{10} (IS)	
Dimethylaminoazobenzene[2]	60-11-7	Phenol[1, 2, 4]	108-95-2
7,12-Dimethylbenz(a)anthracene[2, 4]	57-97-6	Phenol-d_5 (surr)	
3,3'-Dimethylbenzidine[2]	119-93-7	1,4-Phenylenediamine[3]	106-50-3
2,4-Dimethylphenol[1, 2, 4]	105-67-9	Phorate[2]	298-02-2
a,a- Dimethylphenethylamine[2]	122-09-8	2-Picoline (2-Methylpyridine)[2]	109-06-8
Dimethyl phthalate[1, 2, 4]	131-11-3	Pronamide[2]	23950-58-5
Di-n-butyl phthalate[1, 2, 4]	84-74-2	Pyrene[1, 2, 4, 5]	129-00-0
1,3-Dinitrobenzene[2]	99-65-0	Pyridine[2, 4]	110-86-1
4,6-Dinitro-2-methylphenol[1, 2]	534-52-1	*Quinoline*[3]	91-22-5
2,4-Dinitrophenol[1, 2, 4]	51-28-5	Safrol[3]	94-59-7
2,4-Dinitrotoluene[1, 2, 5]	121-14-2	Terphenyl-d_{14}(surr)	1718-51-0
2,6-Dinitrotoluene[1, 2, 5]	606-20-2	*Alpha-Terpineol*[3]	7785-53-7
Dinoseb[2]	88-85-7	1,2,4,5-Tetrachlorobenzene[2]	95-94-3
1,4-Dioxane	123-91-9	2,3,4,6-Tetrachlorophenol[2]	58-90-2
1,2-Diphenylhydrazine[3]	122-66-7	*Tetraethyl dithiopyrophosphate (Sulfotepp)*[2]	3689-24-5
Di-n-octyl phthalate[1, 2, 4]	117-84-0	Tetraethylpyrophosphate[3]	107-49-3
Disulfoton[2]	298-04-4	Thionazine[2]	297-97-2
Ethyl methanesulfonate[2]	62-50-0	Thiophenol[4]	108-98-5
Famphur[3]	52-85-7	o-Toluidine[2]	95-53-4
Fluoranthene[1, 2, 4, 5]	206-44-0	2,4,6-Tribromophenol (surr)	118-79-6
Fluorene[1, 2, 5]	86-73-7	1,2,4-Trichlorobenzene[1, 2]	120-82-1
2-Fluorobiphenyl(surr)	321-60-8	2,4,5-Trichlorophenol[1, 2]	95-95-4
2-Fluorophenol (surr)	367-12-4	2,4,6-Trichlorophenol[1, 2]	88-06-2
Hexachlorobenzene[1, 2]	118-74-1	o,o,o-Triethylphosphorothioate[2]	126-68-1
Hexachlorobutadiene[1]	87-68-3	1,3,5-Trinitrobenzene[2]	99-35-4
Compounds in italics are not present in the EPA method.			
[1] – Normal laboratory 8270 compounds. ***For OH VAP projects, report only compounds designated by a 1 superscript; see Attachment 5.***			
[2] - Appendix IX compounds (by request only)			
[3] - additional compounds available by this method (by request only)			
[4] - Skinner List for Refinery Waste compounds (by request only)			
[5] - Compounds that are available by GC/MS-SIM (by request only)			
IS = These compounds are used as internal standards.			
surr = These compounds are used as surrogates.			

This method is used to quantitate neutral, acidic, and basic organic compounds that are soluble in Methylene chloride and capable of being eluted, without derivatization, from a gas chromatographic fused-silica capillary column coated with a slightly polar methyl silicone phase. This method is not appropriate for the quantitation of multi-component analytes, e. g., Aroclors, Toxaphene, Chlordane, etc., because of limited sensitivity for those analyses. This method is appropriate for confirmation of the presence of these analytes when concentration in the extract

permits. However, it is appropriate for the multi-component analyte, Diesel Range Organics (DRO), as requested by Missouri and California; see Attachment 6.

1.2 Reporting Limits: The laboratory typical report limit (RL) is approximately 2 - 100 µg/L for water samples, 67 - 670 µg/kg (wet weight) for soil/sediment samples, and 10 - 1000 mg/kg for wastes (dependent on matrix and method of preparation). See the following table for typical RLs for each compound. For the most current analyte RLs, refer to LIMS.

Typical Reporting Limits for 8270 Compounds

Analyte	Water RL µg/L	Soil RL mg/kg	Analyte	Water RL µg/L	Soil RL mg/kg
♦**Acenaphthene**	10	0.333	♦*Isosafrole*	50	1.67
♦**Acenaphthylene**	10	0.333	♦*Kepone*	10	0.333
♦*Acetophenone*	10	0.333	♦*Methapyrilene*	50	0.333
♦*2-Acetylaminofluorene*	10	0.333	♦*3-Methylcholanthrene*	10	0.333
♦*4-Aminobiphenyl*	10	0.333	♣*6-Methylchrysene*	10	0.333
♦*Aniline*	10	0.333	♦*Methyl methanesulfonate*	10	0.333
♦♣**Anthracene**	10	0.333	♣*1-Methylnaphthalene*	10	0.333
♦*Aramite*	50	1.67	♦**2-Methylnaphthalene**	10	0.333
Atrazine	10	0.333	♦*Methyl parathion*	10	1.67
Azobenzene	10	0.333	♦♣**2-Methylphenol**	10	0.333
Benzaldehyde	10	1.67	♦♣**3,4-Methylphenol**	10	0.333
Benzidine	100	1.67	♦♣**Naphthalene**	10	0.333
Benzoic acid	50	1.67	♦*1,4-Naphthoquinone*	10	1.67
♦♣**Benzo(a)anthracene**	10	0.333	♦*1-Naphthylamine*	10	0.333
♦♣**Benzo(a)pyrene**	10	0.333	♦*2-Naphthylamine*	10	0.333
♦♣**Benzo(b)fluoranthene**	10	0.333	♦**2-Nitroaniline**	25	0.833
♦**Benzo(g,h,i)perylene**	10	0.333	♦**3-Nitroaniline**	25	0.833
♣*Benzo(j)fluoranthene*	10	0.333	♦**4-Nitroaniline**	25	0.833
♦♣**Benzo(k)fluoranthene**	10	0.333	♦**Nitrobenzene**	10	0.333
♦*Benzyl alcohol*	10	0.333	♦*5-Nitro-o-toluidine*	10	1.67
Biphenyl	10	0.333	♦**2-Nitrophenol**	10	0.333
♦**Bis(2-chloroethoxy) methane**	10	0.333	♦♣**4-Nitrophenol**	25	0.833
♦**Bis(2-chloroethyl) ether**	10	0.333	♦*Nitroquinoline-1-oxide*	10	0.333
♦**Bis(2-chloroisopropyl) ether**	10	0.333	♦*n-Nitrosodiethylamine*	10	0.333
♦♣**Bis(2-ethylhexyl) phthalate**	10	0.333	♦*n-Nitroso-dimethylamine*	10	0.333
♦**4-Bromophenylphenyl ether**	10	0.333	♦*n-Nitrosodi-n-butylamine*	10	1.67
♦♣**Butyl benzyl phthalate**	10	0.333	♦**n-Nitroso-di-n-propylamine**	10	0.333
Caprolactum	10	0.333	♦**n-Nitroso-diphenylamine and Diphenylamine**	10	0.333
Carbazole	10	0.333	♦*n-Nitrosomethylethylamine*	10	0.333
♦**4-Chloro-3-methylphenol**	10	0.333	♦*n-Nitrosomorpholine*	10	1.67
♦**4-Chloroaniline**	10	0.333	♦*n-Nitrosopiperdine*	10	1.67
♦*Chlorobenzilate*	10	0.333	♦*n-Nitrosopyrrolidine*	10	1.67
1-Chloronaphthalene	10	0.333	*Octadecane*	50	0.333

Analyte	Water RL µg/L	Soil RL mg/kg	Analyte	Water RL µg/L	Soil RL mg/kg
♦**2-Chloronaphthalene**	10	0.333	♦*Parathion*	10	1.67
♦**2-Chlorophenol**	10	0.333	♦*Pentachlorobenzene*	10	1.67
♦**4-Chlorophenylphenyl ether**	10	0.333	♦*Pentachloroethane*	10	0.333
♦♣**Chrysene**	10	0.333	♦*Pentachloronitroben-zene*	10	1.67
♦*cis-Diallate*	10	0.333	♦**Pentachlorophenol**	25	0.833
♦*trans-Diallate*	10	0.333	♦*Phenacetin*	10	1.67
♦**Dibenzofuran**	10	0.333	♦♣**Phenanthrene**	10	0.333
♣*Dibenz(a,h)acridine*	10	0.333	♦♣**Phenol**	10	0.333
Dibenz(a,j)acridine	10	0.333	♦*1,4-Phenylenediamine*	50	0.333
♦♣**Dibenzo(a,h)anthracene**	10	0.333	♦*Phorate*	10	0.333
♦♣**1,2-Dichlorobenzene**	10	0.333	♦*2-Picoline*	10	0.333
♦♣**1,3-Dichlorobenzene**	10	0.333	♦*Pronamide*	10	1.67
♦♣**1,4-Dichlorobenzene**	10	0.333	♦♣**Pyrene**	10	0.333
♦**3,3'-Dichlorobenzidine**	10	0.333	♦♣**Pyridine**	10	0.67
♦**2,4-Dichlorophenol**	10	0.333	♣*Quinoline*	10	0.333
♦*2,6-Dichlorophenol*	20	0.333	♦*Safrole*	10	0.333
3,4-Dichlorophenol	10	0.333	*Terbufos*	50	167
♦♣**Diethyl phthalate**	10	0.333	♦*1,2,4,5-Tetrachloro-benzene*	10	1.67
♦*Dimethoate*	10	1.67	♦*2,3,4,6-Tetrachloro-phenol*	10	0.333
♦*p-Dimethylaminoazobenzene*	10	1.67	♦*Tetraethylpyrophos-phate, Sulfotep*	10	1.67
♦*3,3'-Dimethylbenzidine*	50	0.333	♦*Thionazine*	10	1.67
♦♣*7,12-Dimethylbenz(a)an-thracene*	10	0.333	♣*Thiophenol*	50	1.67
♦*a,a-Dimethylphenethylamine*	50	1.67	♦*o-Toluidine*	10	1.67
♦♣**2,4-Dimethylphenol**	10	0.333	♦**1,2,4-Trichloroben-zene**	10	0.333
♦♣**Dimethyl phthalate**	10	0.333	♦**2,4,5-Trichlorophenol**	10	0..667
♦♣**Di-n-butyl phthalate**	10	0.333	♦**2,4,6-Trichlorophenol**	10	0.333
♦*1,3-Dinitrobenzene*	10	1.67	♦*o,o,o-Triethylphospho-rothioate*	10	1.67
♦**4,6-Dinitro-2-methylphenol**	25	0.833	♦*1,3,5-Trinitrobenzene*	10	0.333
♦♣**2,4-Dinitrophenol**	25	0.833	Acenaphthene, SIM	0.10	0.00333
♦**2,4-Dinitrotoluene**	10	0.333	Acenaphthylene, SIM	0.10	0.00333
♦**2,6-Dinitrotoluene**	10	0.333	Anthracene, SIM	0.10	0.00333
♦♣**Di-n-octyl phthalate**	10	0.333	Benzo(a)anthracene, SIM	0.10	0.00333
♦*Dinoseb*	10	0.333	Benzo(a)pyrene, SIM	0.10	0.00333
1,4-Dioxane	10	0.333	Benzo(b)fluoranthene, SIM	0.10	0.00333
1,2-Diphenylhydrazine	10	0.333	Benzo(g,h,i)perylene, SIM	0.10	0.00333
♦*Disulfoton*	10	1.67	Benzo(k)fluoranthene, SIM	0.10	0.00333
♦*Ethyl methanesulfonate*	10	0.333	Chrysene, SIM	0.10	0.00333
♦*Famphur*	10	0.333	Dibenzo(a,h)anthracene, SIM	0.10	0.00333
♦♣**Fluoranthene**	10	0.333	2,4-Dinitrotoluene, SIM	0.2	0.0067

Analyte	Water RL µg/L	Soil RL mg/kg	Analyte	Water RL µg/L	Soil RL mg/kg
♦**Fluorene**	10	0.333	2,6-Dinitrotoluene, SIM	0.2	0.0067
♦**Hexachlorobenzene**	10	0.333	Fluoranthene, SIM	0.10	0.00333
♦**Hexachlorobutadiene**	10	0.333	Fluorene, SIM	0.10	0.00333
♦**Hexachlorocyclopentadiene**	10	0.333	Indeno(1,2,3-cd)pyrene, SIM	0.10	0.00333
♦**Hexachloroethane**	10	0.333	1-Methylnaphthalene, SIM	0.10	0.00333
♦*Hexachlorophene*	50	3.33	2-Methylnaphthalene, SIM	0.10	0.00333
♦*Hexachloropropene*	50	3.33	Naphthalene, SIM	0.10	0.00333
♦**Indeno(1,2,3-c,d)pyrene**	10	0.333	Phenanthrene, SIM	0.10	0.00333
♣*Indene*	10	1.67	Pyrene, SIM	0.10	0.00333
♦*Isodrin*	10	0.333	California / Missouri DRO	500	20
♦**Isophorone**	10	0.333	Calilfornia / Missouri ORO	500	20

♦ indicates Appendix IX compound ♣Skinner List compound
Bold compounds are reported in a standard list.
Italicized compounds are only available upon special request by this method.
SIM = Selective Ion Monitoring

1.3 The following compounds may require special treatment when being determined by this method:

- Benzidine may be subject to oxidative losses during solvent concentration, and its chromatographic behavior is poor.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- n-Nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.
- n-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.
- Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
- Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. Use caution if modifying the injection port temperature as the performance of other analytes may be adversely affected.

1.4 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor or the Technical Director. All abnormalities must be noted on the data or the benchsheet and in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation. See SOPs 3510 / NV03-24 for waters, 3550 / NV03-23 and 3541 / NV03-231 for soils and concrete, and 3580 / NV03-106 for oils, and, if necessary, sample cleanup procedures.

2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass

spectrometer (MS) connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using at least a multi-point calibration curve.

3.0 Definitions

3.1 Reduced Volume Extraction / Large Volume Injection (RVE/LVI): The option to use a reduced sample volume for extraction combined with a larger volume extract injection on the instrument. Volumes for this option are shown in this document as RVE/LVI in brackets.

3.2 See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe is rinsed with solvent between sample injections.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This method may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. Be aware of the locations of those zones, and cool them to room temperature prior to working on them.
- The mass spectrometer is under high vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.
- There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Gas chromatography/mass spectrometer/data system
  - Gas chromatograph (HP or Agilent): Analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column is directly coupled to the source.
  - Column: 30 m x 0.25 mm ID with a 0.25 µm film thickness silicone-coated fused-silica capillary column (Phenomenex ZB-5, or equivalent) [RVE/LVI: and a 5 m x 0.32 mm ID guard column (Phenomenex 7CG-G000-000-GZ0, or equivalent].
  - Mass spectrometer capable of scanning from 35 to 500 amu every 1 second less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer is capable of producing a mass spectrum for Decafluorotriphenylphosphine (DFTPP) which meets the criteria in Table 2 when 1µL of the GC/MS tuning standard is injected (50 ηg or less of DFTPP).
  - Data system (Chemstation with Enviroquant): A computer system is interfaced to the mass spectrometer. The system allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer has software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software is also available that allows integrating the abundances in any EICP between specified time or scan-number limits. The EPA/NIST Mass Spectral Library is also available.
  - Suggested operating conditions (may vary by instrument; see maintenance log for current program):

Mass range:	35-500 amu
Scan time:	1 second/scan
Initial temperature:	40°C hold for 2 minutes
Temperature program:	Rate 1: 15°C/minute to 160°C
	Rate 2: 10°C/minute to 320°C
Final temperature:	320°C hold for at least 1.5 minute.
Injector temperature:	240-250°C
Transfer line temperature:	280°C
Source temperature:	According to manufacturer's specifications (nominally 250 – 275°C)
Injector:	Grob-type, split-less
Injection volume:	1 µL [RVE/LVI: 5 µL]
Carrier gas:	Helium at 1 mL/minute

6.2 Supplies

- Microsyringe, 10 µL.
- Balance, analytical, capable of weighing 0.0001 g
- Glass vials, glass with PTFE (polytetrafluoroethylene)-lined screw-caps or crimp tops.
- Volumetric flasks, Class A, appropriate sizes with ground-glass stoppers.

7.0 Reagents and Standards

7.1 Reagent grade chemicals are used in all tests. Unless otherwise, indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water, analyte-free.

7.3 Stock Calibration Standards: Commercially prepared, certified stock standards are purchased:

- The primary standard for the typical 8270 compound list is from Ultra Scientific CUS-6150, or equivalent, with the required targets at 200 µg/mL.
- For PAHs by SIM, use Accustandard Z-014G-FL, or equivalent, with the target PAHs at 2000 µg/mL.
- For Appendix IX and miscellaneous compounds, primary source standards are purchased from NSI; equivalent substitutes are acceptable.

Analyte/Analyte Group	NSI Catalog Number	Concentration (µg/mL)
AIX Mix	C-426	2000
Acid Extractables II	C-415	2000
Amines	C-412	2000
Aramite	922-05-02	2000
a,a-Dimethylphenylamine	922-05-02	2000
Benzidines	C-411	2000
BNA II mix	C-413	2000
B/N III mix	C-414	2000
Hexachlorophene	323-03	5000
Sulfonates	C-416	2000
8270 OP Pest	C-417	2000

7.4 Matrix Spike and Laboratory Control Standard contains all targets to be reported on the samples. The same compounds mentioned in Section 7.3 are designated as the SPCCs and CCCs for 8270C.

- For both a long semivolatile list and the PAH list by SIM, purchase as the second source a 100 µg/mL standard, NSI Catalog # c-408-50x, or equivalent.
- For Appendix IX and miscellaneous compounds, these second source standards are acceptable, as well as equivalents:

Analyte/Analyte Group	RestekCatalog Number	Concentration (µg/mL)
AIX #1 Mix	31625	2000
AIX #2 Mix	31806	2000
Calibration Mix	31618	2000
OP Mix	32419	2000

7.5 Internal standard solutions: The internal standards are 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12}, and Perylene-d_{12}.

- Purchase certified, internal standard at 4000 µg/mL, NSI C-394, or equivalent.

7.6 GC/MS Tuning Standard: A Methylene chloride solution containing 50 µg/mL of Decafluorotriphenylphosphine (DFTPP) is prepared. The standard also contains 50 µg/mL each of 4, 4'-DDT, Pentachlorophenol, and Benzidine to verify injection port inertness and GC column performance.

- Purchase the tuning standard at 1000 µg/mL from Ultra Scientific, Catalog GCM-150, or equivalent.

7.7 Surrogate standards: The surrogates are Phenol-d_5, 2-Fluorophenol, 2,4,6-Tribromophenol, Nitrobenzene-d_5, 2-Fluorobiphenyl, and p-Terphenyl-d_{14}.

- Purchase the acid/base/neutral and PAH SIM surrogates from NSI, C-LIS-7070, or equivalent, at 50 µg/mL.

7.8 Acetone, Hexane, Methylene chloride, Isooctane, Carbon disulfide, Toluene, and other appropriate solvents, commercial source.

7.9 Sodium sulfate for blank and LCS soil matrix.

7.10 Transfer the stock standard solutions into bottles with PTFE-lined screw-caps. Store, protected from light, at -10°C or less or as recommended by the standard manufacturer. Stock standard solutions must be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Replace after **one year or sooner** if comparison with quality control check samples indicates a problem, or if the vendor specifies an expiration date sooner than one year.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	3 L, amber glass with Teflon®-lined cap	1 L [RWE/LVI: 250 mL]	Cool 0-6°C. Keep in dark.	7 days from collection until extraction, 40 days after extraction	SW-846 Chapter 2
Soil, Oil, Concrete	4 oz. glass jar with Teflon®-lined cap	30 g	Cool 0-6°C.	14 days from collection until extraction, 40 days after extraction	

9.0 Quality Control

The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

Certain quality control and reporting criteria may vary depending on whether SW-846 8000B or 8000C criteria are required. In these cases, both sets of criteria have been noted in this SOP. 8000C criteria are required to be applied ONLY to Arizona and Washington samples. All other samples must be processed against referenced 8000B criteria. Exceptions may be required on a project-specific basis.

9.1 Sample QC:

The following QC samples are run with each batch of no more than 20 samples.			
QC Check	Frequency	Acceptance Criteria[1]	**Corrective Action[2]**
Method blank	One per analytical prep batch	No analytes detected ≥ ½ RL or MDL, whichever is greater	Correct problem then re-prep[3] and analyze method blank and all samples processed with the contaminated blank.
LCS[6] for all analytes (2nd source)[6]	One[6] per prep batch	See LIMS and footnote 4 below.	Correct problem then re-prep[4] and analyze the LCS and all samples in the affected analytical batch.[4] If high and target is ND, OK to report.
MS/MSD (2nd source)	One per batch per matrix, if insufficient sample for MS/MSD, qualify data[3]	See LIMS.	None (the LCS is used to evaluate to determine if the batch is acceptable).
Surrogate(s)	Every sample, spike, standard, and blank	See LIMS.[5]	Check system, re-analyze, re-prep[3, 5].

[1]This is a summary of the acceptance criteria.
[2]All abnormalities must be noted on the data, the benchsheet and in LIMS.
[3]If unable to re-prep samples because of insufficient sample volume or the holding time has expired, then place a comment on the benchsheet and in LIMS.
[4]If the LCS exceeds the upper control limit AND a sample from that batch is greater than the RL, re-prep and re-analyze the batch. If the LCS exceeds the upper control limit AND the samples from that batch is less than the RL, the data is acceptable to report.
[5]If the surrogate % recovery exceeds the upper control limit AND a sample result is positive above the RL, re-prep and re-analyze the batch. If the surrogate % recovery exceeds the upper control limit AND the sample is less than the RL, data is acceptable to report. If the surrogate % recovery is lower than the lower control limit, re-prep the sample. OH VAP requires all surrogates to be in control; otherwise, the samples must be re-prepared and re-analyzed.
[6]LCSD is required for AZ, MA, TX, WV.

- A **Method blank** is extracted with every batch of samples.
- A **Laboratory Control Sample** (LCS) is included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume (reagent water for water batches, Sodium sulfate for soil batches). It is spiked with the same analytes at the same concentrations as the matrix spike. **All target analytes must meet the LCS QC criteria** (laboratory historical limits in LIMS)**.** However, if the LCS is high, and a target is ND, it is acceptable to report the result.
  - The LCS spike is from a **different source than the calibration standards**. Using the 100 µg/mL LCS/MS/MSD standard:
    - **For Non-SIM batches:**
      - Water: add 500 µL [RVE/LVI: 100 µL] of the standard per liter reagent water before extraction by Method 3510C.
      - Soil: add 500 µL of the standard per 30 gram Sodium sulfate before extraction.
      - TCLP: add 1 mL [RVE/LVI: 200 µL] of the standard/500 mL TCLP extraction fluid before extraction by Method 3510C.
      - The final concentration is 50 µg/mL on column.
    - **For SIM batches:**
      - Water: add 1 mL [RVE/LVI: 200 µL] of a 100 X dilution of the NSI standard per liter reagent water.
      - Soil: add 1 mL of a 100 X dilution of the NSI standard per 30 g Sodium sulfate.
      - The final concentration in the extracts is 1.0 µg/mL.
- **Matrix Spike / Matrix Spike Duplicate**: Documenting the effect of the matrix includes the analysis of at least one matrix spike/matrix spike duplicate pair.
  - The MS/MSD spike is from a **different source** than the calibration standards. Using the 100 µg/mL LCS/MS/MSD standard:
    - **For Non-SIM batches**:

- Water: add 500 µL [RVE/LVI: 100 µL] of the standard per liter client sample.
- Soil: add 500 µL of the standard to 30 g client sample.
- TCLP: add 1 mL [RVE/LVI: 200 µL] of the standard per 500 mL client TCLP extract.
- The final concentration is 50.0 µg/mL on column..

- **For SIM batches**:
  - Water: add 1 mL [RVE/LVI: 200 µL] of a 100 X dilution of the NSI standard per liter reagent water.
  - Soil: add 1 mL of 100 X dilution per 30 g client sample.
  - The final concentration is 1.0 µg/mL on column.

- **Surrogate recoveries:** The laboratory evaluates surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. The limits for surrogate recoveries are updated biannually (see TestAmerica Nashville's current Control Limits Manual (CLM)). If any surrogate is outside QC limits, and there is no obvious matrix interference, then re-analyze and/or re-extract the sample. If surrogates are still outside limits, flag the data in LIMS. However, if high and all results are non-detect, results are reportable. If surrogate recoveries are low, re-prep the batch.
  - **For Non-SIM**, add 1000 µL [RVE/LVI: 200 µL] of the surrogate standard at a concentration of 50 µg/mL to each sample and batch QC samples prior to extraction for a 50 µg/mL concentration.
  - **For SIM,** prepare a 1 µg/mL standard (500 µL surrogate standard) to 500 mL in methanol. Add 1.0 mL [RVE/LVI: 200 µL] to samples and QC (blanks, MS/MSD and LCS) prior to extraction. The concentration is 1.0 µg/mL.

9.2 Instrument QC

QC Check	Frequency	Acceptance Criteria[2]	Corrective Action[3]
GC/MS Tuning			
a. Check of mass spectral ion intensities[1], i.e., Tune	Prior to initial calibration or Continuing calibration verification, every 12 hours.	See below in this section for GC/MS Tuning criteria.	Retune the instrument and verify (instrument maintenance may be needed).
b. Column Breakdown	Prior to initial calibration or Continuing calibration verification, every 12 hours.	Breakdown ratio ≤ 20% (30% for 8270C).	Injector or column maintenance and re-calibration.
c. Tailing Factor	Prior to initial calibration or Continuing calibration verification, every 12 hours.	8270C 8270D Benzidine 3 2 Pentachlorophenol 5 2	Injector or column maintenance and re-calibration.
Minimum five-point initial calibration for all target analytes	Initial calibration prior to sample analysis. Perform instrument re-calibration once per year minimum.	8270C: SPCCs average RF ≥ 0.050 and %RSD for RFs for CCCs ≤ 30% and all other target analytes %RSD for RF ≤ 15% If %RSD is > 15%, linear regression $r^2 \geq 0.990$, $r \geq 0.995$. 8270D: The minimum RF for all compounds in Attachment 5 must be met[5]. All targets RSD ≤ 20% or use linear regression.	Correct problem then repeat initial calibration.

QC Check	Frequency	Acceptance Criteria[2]	Corrective Action[3]
Initial calibration verification (ICV) must be from a 2nd source.	Immediately following five-point initial calibration.	All analytes within 30% of expected value.	Correct problem then repeat initial calibration.
Initial calibration blank	Immediately after ICV	All analytes < MDL	Correct problem, re-calibrate.
Continuing calibration verification (CCV)	Daily, before sample analysis and every 12 hours of analysis time.	8270C: SPCCs average RF ≥ 0.050 and CCCs: ≤30% difference (when using RFs) or drift (when using least squares regression). Non-CCC < 20% true; up to 4 may be < 40%. 8270D: The minimum RF for all compounds listed in Attachment 4 must be met and the percent difference or drift for each target compound ≤ 20%.	Correct problem then repeat initial calibration and re-analyze all samples since last successful CCV.
Internal Standards	Every sample/standard and blank.	Retention time ±30 seconds from retention time of the mid-point std. in the ICAL for CCV. EICP area within -50% to +100% of ICAL mid-point std for the CCV and –50% to +100% of the prior CCV for the samples. See footnote 4 below.	Inspect mass spectrometer and GC for malfunctions; mandatory re-analysis of samples analyzed while system was malfunctioning (dilution of the sample may be required, see the supervisor or the technical manager for advice).
Relative Retention Time Window	Each sample.	Relative retention time (RRT) of the analyte within 0.06 RRT units of the RRT of the internal standard.	Correct problem then reprocess or re-analyze all samples analyzed since the last retention time check.
MDL verification (extracted)	Minimum yearly.	Detectible	Re-evaluate MDL standard used and MDL; see the technical manager.

[1]8270 requires DFTPP.
[2]This is a summary of the acceptance criteria.
[3]All abnormalities must be noted on the data, the benchsheet and in LIMS.
[4]Target compounds associated with failed internal standards must be re-analyzed (undiluted if possible) if additional sample is available; if not available, qualify data in LIMS.
[5]LLCV: If RF is not met at the low-level standard, the criterion for a passing LLCV is detection only and must be run following the CCV.

- **Tuning**

GC/MS Tuning (Full Scan)

- Prior to the analysis of samples or calibration standards, the GC/MS system is hardware-tuned using a 50 ng or less injection of DFTPP (in the GC/MS Tuning Standard).
- The 50 µg/mL standard is prepared by adding 2.8 mL of 1000 µg/mL stock standard to 56 mL Methylene chloride . [RVE/LVI: Use a 5X dilution of this solution.]
- Analyses **must** not begin until the tuning criteria are met, and these criteria must be demonstrated at the beginning of each 12-hour shift. Three options are available for acquiring the spectra for reference to meet the DFTPP tuning requirements:

Option 1 It is recommended that each initial tune verification utilize the "Autofind" function and be set up to look at the apex ±1 scan and average the three scans. Background correction is required prior to the start of the peak but no more than 20 scans before. Background correction **cannot** include any part of the target peak. Sometimes the instrument does

not always correctly identify the apex on some peaks when the peak is not perfectly shaped. It is acceptable to manually identify and average the apex peak ± 1 scan and background correct

Option 2 The entire peak may be averaged and background-corrected. Average scans from 0.1 minute before to 0.1 minute after peak.

Option 3 A single scan at the apex (only) may also be used for the evaluation of the tune. Background correction is required.

Note: It is acceptable to adjust parameters within the specifications set by the manufacturer or the analytical method to properly tune the instrument. If the tune verification does not pass, it may be necessary to clean the source or perform additional maintenance. Document any maintenance in the instrument log. **Excessive adjusting (more than two tries) without clear documentation is not allowed. No more than two consecutive tunes may be attempted. Perform necessary maintenance**.

- All subsequent standards, samples, controls, and blanks associated with a DFTPP tune must use the identical mass spectrometer instrument conditions.
- Use the DFTPP mass intensity criteria as follows as tuning acceptance criteria.

DFTPP Key Ions and Ion Abundance Criteria

Mass	m/z Abundance criteria
51	30-60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	40-60 percent of mass 198.
197	Less than 1 percent of mass 198.
198	Base peak, 100 percent relative abundance.
199	5-9 percent of mass 198.
275	10-30 percent of mass 198.
365	Greater than 1 percent of mass 198.
441	Present but less than mass 443.
442	Greater than 40 percent of mass 198.
443	17-23 percent of mass 442.

- **Breakdown Standard**: The GC/MS Tuning Standard is also used to assess the injection port inertness by evaluating the degradation of DDT to DDE and DDD. This ratio must **not** exceed 20%; see Section 9.2 for **percent breakdown** calculation. Perform injector or column maintenance and recalibrate if the ratio maximum is exceeded for either compound. The breakdown of DDT is measured **before** verification standards and samples are analyzed and every 12 hours throughout the sequence.
- **Tailing Factor**: To evaluate the GC column, Benzidine and Pentachlorophenol (in the GC/MS Tuning Standard) must be present at their normal responses and evaluated for peak tailing. The Benzidine and Pentachlorophenol tailing factors are calculated by the following equation:

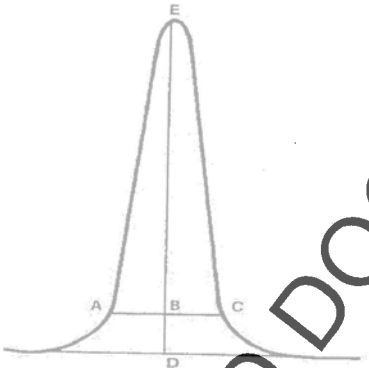
Tailing factor = BC/AB

Maximum Tailing Factor Ratios

Tailing Factor Compounds	8270C	8270D
Benzidine	3	2
Pentachlorophenol	5	2

where the peak is defined as follows: AC is the width at 10% height. DE is the height of peak and B is the height at 10% DE. This equation compares the width of the back half of the peak to the width of the front half of the peak at 10% of the height. (See Figure 1 for an example tailing factor calculation.)

FIGURE 1
TAILING FACTOR CALCULATION



TAILING FACTOR = $\frac{BC}{AB}$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm
Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

8270D - 72

Revision 4
February 2006

If all of the specified criteria are met, generate a hardcopy of the spectrum, the mass abundance data and the parameters under which the scans were acquired. This data is filed in the batch for documentation.

GC/MS Tuning (SIM)

- The objective of tuning for conventional full scan analysis is to produce a balanced mass spectrum over the range of interest. The DFTPP tune is, by necessity, done in the full scan mode. However, because the instrument is then immediately switched to the SIM mode, the DFTPP results have limited quality control value. In short, the DFTPP is not analyzed under the same conditions as the calibration, QC, and field samples. In the case of Selective Ion Monitoring (SIM) analysis, there are no comparisons between spectra; instead the instrument is optimized for the relative intensities of the pre-selected analyte ions of interest. For SIM analysis, the laboratory prints out a copy of the autotune (PFTBA) prior to analysis to demonstrate good mass assignment and peak width. No BFB tune is possible while in SIM mode. A printout of the instrument autotune (PFTBA) is included with the data for each day that SIM analyses are run in order to demonstrate good mass assignment and peak width.

- **Calibration**: See Section 10.2.
- **Initial Calibration System Performance Check Compounds (SPCCs)**: A system performance check is performed to ensure that minimum average RFs are met before the calibration curve is used.
  - **For 8270C**: The SPCCs are

System Performance Check Standards (SPCCs)	
Base/Neutral Fraction	**Acid Fraction**
n-Nitrosodi-n-propylamine	2,4-Dinitrophenol
Hexachlorocyclopentadiene	4-Nitrophenol

The **minimum acceptable average RF for the SPCCs is 0.050**. They typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

  - **For 8270D**, see Attachment 4 for required minimum response factor criteria for target analytes.
  - If the minimum response factors are not met, the system must be evaluated, and corrective action is taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. **This check must be met before sample analysis begins.** An option is to run a LLCCV to show sensitivity.
- **Initial Calibration Calibration Check Compounds (CCCs) for 8270C only**: The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes. The CCCs are:

Calibration Check Compounds (CCC)	
Base/Neutral Fraction	**Acid Fraction**
Acenaphthene*	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Diphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene*	2,4,6-Trichlorophenol
Benzo(a)pyrene*	

*For PAH SIM standard

  - Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte.

Initial Calibration RSD Differences	
8270C	**8270D**
The RSD must be less than or equal to **15%** for each target analyte; if not, see the section on linearity of target analytes in Section 10.2. However, the RSD for each individual CCC must be less than or equal to 30%.	The RSD must be less than or equal to **20%** for each target analyte; if not, see the section on linearity of target analytes in Section 10.2. If not, check

If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure.	errors in standard preparation, the possible presence of active sites in the GC system, poor chromatographic behaviors for analytes.

- The **Initial Calibration Verification (ICV)** is a second-source standard run immediately after the initial calibration. The acceptance limits are **70-130%** recovery.
  - Add 250 µL of the second-source standard to 250 µL Methylene chloride in an amber vial to prepare an ICV standard at 50 µg/mL.
  - For PAHs by SIM, use the second-source standard with the target PAHs at 2000 µg/mL. A 10 µg/mL intermediate is made by taking 50 µL of the stock standard along with 20 µL of the base/neutral surrogates. The ICV at 1 µg/mL is made by taking 50 µL of intermediate into 450 µL of Methylene chloride in an amber vial.
  - If ICV acceptance criterion is not met, correct the problem and re-calibrate.
- **Initial Calibration Blank**: a reagent/solvent blank analyzed after the ICV to ensure the system is free of contaminants (< MDL). If not contaminant-free, re-run and/or perform system maintenance.
- The **Continuing Calibration Verification standard (CCV)** is evaluated each day (or every 12 hours) that analysis is performed to determine if the chromatographic system is operating properly.
  - Prepare a daily CCV at 50 µg/mL by adding 100uL of the primary stock solution to 300 µL Methylene chloride in an amber vial. [RVE/LVI: 20 µL to a final volume of 400uL Methylene chloride].
  - For PAHs by SIM, use the primary stock standard with the target PAHs at 2000 µg/mL. A 10 µg/mL intermediate is made by taking 50 µL of the stock standard along with 20 µL of the base/neutral surrogates. A daily CCV at 1 µg/mL is made by taking 50 µL of intermediate into 450 µL of Methylene chloride in an amber vial. [RVE/LVI: 5 µL to a final volume of 500uL of Methylene Chloride].
  - The calibration verification standard is prepared at least weekly and stored at 4°C or less.
  - For 8270C, each **SPCC** in the calibration verification (CCV) standard must meet a **minimum response factor of 0.050**.. **For 8270D**, see Attachment 4 for required minimum response factor criteria for target analytes.
  - After the system performance check is met, the **CCCs** are used for 8270C only to check the ongoing validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model.

CCC % Difference Evaluation Criteria	
8270C	**8270D**
CCCs ≤ 30% and all other target compounds require an RF ≤ 20%; however, up to 5 non-CCC target compounds may be ≤ 40%.	If the percent difference for each target compound is less than or equal to **20%**, then the initial calibration is assumed to be valid. If the criterion is not met (i. e., greater than 20% difference or drift) for any target, then corrective action is taken prior to the analysis of samples. All targets are considered as CCCs.

  - If the CCV criteria cannot be met, a new initial calibration must be generated.
- **Continuing Calibration Blank (CCB):** The CCB is run after each CCV. If the result is not ≤ MDL or ½ RL, correct the problem and re-run.
- **Internal standards** are added to every sample, standard, and QA/QC.

- **Retention time** - The retention times of the internal standards in the continuing calibration verification (CCV) standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than **30 seconds** from that in the mid-point standard level of the **most recent initial calibration** sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.
- **Response** - If the EICP area for any of the internal standards in the continuing calibration verification (CCV) standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the **most recent initial calibration sequence**, the mass spectrometer must be inspected for malfunctions and corrections must be made. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.
- The laboratory re-analyzes any sample where the internal standard fails and there is no evidence of matrix interference. If there is no matrix interference, the sample must be reanalyzed at the original dilution.
  - If the internal standard is within criteria, report the second analysis.
  - If the internal standard is still outside of criteria, the sample must be analyzed at a second dilution.
  - If the internal standard still does not meet criteria, the sample must be diluted until the internal standard meets criteria. Multiple runs may be required.
- The target analytes are quantitated with specific internal standards as shown in this table:

Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation

1,4-Dichlorobenzene-d_4	**Naphthalene-d_8**	**Acenaphthene-d_{10}**
Aniline	Benzoic acid	Acenaphthene
Benzyl alcohol	Bis(2-chloroethoxy) methane	Acenaphthylene
Bis(2-chloroethyl) ether	4-Chloroaniline	2-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
2-Chlorophenol	2,4-Dichlorophenol	Dibenzofuran
1,3-Dichlorobenzene	2,4-Dimethylphenol	Diethyl phthalate
1,4-Dichlorobenzene	Hexachlorobutadiene	Dimethyl phthalate
1,2-Dichlorobenzene	Isophorone	2,4-Dinitrophenol
2-Fluorophenol (surr)	2-Methylnaphthalene	2,4-Dinitrotoluene
Hexachloroethane	Naphthalene	2,6-Dinitrotoluene
2-Methylphenol	Nitrobenzene	Fluorene
3,4-Methylphenol	Nitrobenzene-d_8 (surr)	2-Fluorobiphenyl (surr)
n-Nitrosodimethylamine	2-Nitrophenol	Hexachlorocyclopentadiene
n-Nitroso-di-n-propyl- amine	1,2,4-Trichlorobenzene	2-Nitroaniline
Phenol	1-Methylnapthalene	3-Nitroaniline
Phenol-d_5 (surr)	Hexachloropropene	4-Nitroaniline
Pyridine	2,6-Dichlorophenol	4-Nitrophenol
2-Chlorophenol-d_4 (surr)	n-Nitrosodi-n-butylamine	2,4,6-Trichlorophenol
1,2-Dichlorobenzene-d_4 (surr)	1,4-Phenylenediamine	2,4,5-Trichlorophenol
1,4-Dioxane	trans-Isosafrole	1,2-Diphenylhydrazine
Pyridine	1,2,4,5-Tetrachlorobenzene	1,3-Dinitrobenzene
2-Picoline	cis-Isosafrole	Pentachlorobenzene
N-Nitrosomethylethylamine	Safrole	1-Naphthaleneamine
Methyl-methoanesulfonate	1-Chloronaphthalene	2-Naphthaleneamine
n-Nitrosodiethylamine	1,4-Naphthoquinone	2,3,4,6-Tetrachlorophenol
Ethylmethanesulfonate	**Quinoline**	Diphenylamine

1,4-Dichlorobenzene-d_4	**Naphthalene-d_8**	**Acenaphthene-d_{10}**
Pentachloroethane	**Chrysene-d_{12}**	5-Nitro-o-Toluidine
Acetonphenone	**6-Methylchrysene**	trans-Diallate
n-Nitrosopyrrolidine	**Dibenz(a,h)acridine**	cis-Diallate
2-Toluidine	**7,12-Dimethylbenz(a)anthracene**	1,3,5-Trinitrobenzene
n-Nitrosomorpholine		Phenacetin
n-Nitrosopiperidine		4-Aminobiphenyl
2-Butoxyethanol		
Indene		
Thiophenol		
Phenanthrene-d_{10}	**Chrysene-d_{12}**	**Perylene-d_{12}**
Anthracene	Benzidine	Benzo(b)fluoranthene
4-Bromophenyl phenyl ether	Benzo(a)anthracene	Benzo(k)fluoranthene
Di-n-butyl phthalate	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)perylene
4,6-Dinitro-2-methylphenol	Butyl benzyl phthalate	Benzo(a)pyrene
Diphenylamine	Chrysene	Dibenz(a, h)anthracene
Fluoranthene	3,3'-Dichlorobenzidine	Di-n-octyl phthalate
Hexachlorobenzene	Pyrene	Indeno(1,2,3-cd)pyrene
n-Nirosodiphenylamine	Terphenyl-d_{14} (surr)	Dibenz(a,j)acridine
Pentachlorophenol	4,4'Methylenebis(2-chloroaniline)	
Phenanthrene	Aramite	
Carbazole	3-Methylcholanthrene	
Bis (2-ethylhexyl)adipate		
Tribromophenol (surr)		
Thionazin		
Pronamide		
Pentachloronitrobenzene		
Dinoseb		
Sulfotepp		
Phorate		
Dimethoate		
Disulfoton		
4-Nitroquinoline-N-oxide		
Methapyrilene		
Isodrin		
Methyl Parathion		
Benzidine		
Parathion		
Hexachlorophene		
Kepone		
4-Dimethylaminoazobenzene		
Chlorobenzilate		
3,3'-Dimethylbenzidine		
2-Acetylaminofluorene		

(surr)= surrogate

- The internal standards selected permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation. If interferences are noted, use the next most intense ion as the quantitation ion (i. e., for 1, 4-Dichlorobenzene-d_4, use 152 m/z for quantitation).
- Dilute the 4000 µg/mL internal standard by 2x with Methylene chloride. The resulting

solution contains each internal standard mixture at a concentration of 2000 µg/mL. Each 0.5 mL sample extract undergoing analysis is spiked with 10 µL [RVE/LVI: 2µL] of the internal standard solution, resulting in a concentration of 40 µg/mL of each internal standard.

- For SIM, dilute the 2000 µg/mL internal standard mix by 10x with Methylene chloride for a 200 µg/mL standard. Each 0.5 mL of sample extract undergoing analysis is spiked with 10 µL [RVE/LVI: 5 µL] of internal standard solution, resulting in a concentration of 2 µg/mL of each internal standard.

- **Evaluation of target analyte retention time:** The relative retention time (RRT) of each target analyte in each calibration standard must agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement. This criterion is met with the use of a ± 0.25 minute retention time window. Representative retention times are shown in Attachments 1 and 2.
- **Method Detection Limit Verification (MDLV)**: Annually, verify that the MDL is detectible; if not, re-evaluate the MDL.

10.0 Procedure

10.1 Sample Preparation

Matrix	Sample Size
Water	1000 mL [RVE/LVI: 250 mL]
Soil, Concrete	30 grams
Oil	1 gram

- Samples are nominally prepared by one of the following methods prior to GC/MS analysis:

Matrix	Methods	SOP #
Water	3510	NV03-24
Soil/sediment/Concrete	3541, 3546, 3550	NV03-231, NV03-25
Oily Waste	3580	NV03-106

- QC samples and client samples must be extracted by the same preparation method.
- All calibration standards, QC samples, and client samples are introduced into the GC/MS using the same injection volume, IS and SS concentrations, and instrument conditions.

10.2 Calibration and Daily Continuing Calibration Verification: Refer to SOP Selection of Calibration Points / CA-P-P-002 and Calibration Curves (General) / CA-Q-S-005. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

- Initially and/or daily, evaluate the DFTPP tune criteria (Section 9.2).
- Evaluate the percent breakdown of DDT (Section 9.2).
- Evaluate the tailing factors for Benzidine and Pentachlorophenol (Section 9.2).

Initial calibration

1 Prepare calibration standards at five (minimum) different concentrations.

Concentration (µg/mL)	µL 200 µg/mL standard/500 µL (1 µL injection)	RVE/LVI: µL 200 µg/mL standard/500 µL (5 µL injection)
2	5	1
10	25	5

	20	50	10
	50	125	25
	80	200	40
	100	250	50

- At least one of the calibration standards corresponds to a sample concentration **at or below the laboratory reporting limit (RL)**. The remaining standards correspond to the working range of the GC/MS system.
- Each standard contains each analyte to be reported. These target analytes may not include the entire list of analytes for which the method has been demonstrated; however, the laboratory **must not** report a quantitative result for a target analyte that was not included in the calibration standard(s).
- Surrogates are included at the same concentrations.
- The internal standards are at a constant 40 µg/mL. Each 0.5 mL aliquot of calibration standard is spiked with 10 µL [RVE/LVI: 2 µL] of the internal standard solution prior to analysis.

2 For SIM, calibration standards are diluted from the intermediate standard solution to give the following concentrations:

Concentration (µg/mL)	µL 10 µg/mL standard/500 µL (1 µL injection)	RVE/LVI: µL 10 µg/mL standard/500 µL(5 µL injection)
0.05*	2.5	0.5
0.1	5	1
0.5	25	5
1	50	10
5	250	50
10	500	100

*The 0.05 µg/mL standard must be used for low-level SIM analysis of samples from Wisconsin.

- Surrogates are included at the same concentrations.
- The internal standards are at a constant 2 µg/mL.
- See Attachments 2 and 3 regarding SIM Mass groups.

3 Analyze 1 µL [RVE/LVI: 5 µL] of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte. See Attachment 1. **Two characteristic ions must be valid for the low standard to be used.**

4 Calculate response factors (RFs) for each target analyte relative to one of the internal standards.

5 Evaluate the **system performance check compounds (SPCCs):** The minimum acceptable average RF for these compounds is 0.050 for 8270C. For 8270D, see Attachment 4. This check must be met before sample analysis begins.

6 Evaluate the **calibration check compounds (CCCs)**: If the RSD of any CCC is greater than 8270C criteria, then correct the chromatographic system reactivity before analysis begins. For 8270D, all compounds are treated as CCCs and must be within ± 20%.

7 Evaluate the **retention times.**

8 Evaluate the **linearity of target analytes** - If the RSD (8270C ± 15%; 8270D ± 20%) of any target analytes is within acceptance limits , then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor is used for quantitation. If the RSD of any target analyte is greater than the acceptance criteria , linear

	regression is used for calibration. The correlation coefficient r^2 must be at least 0.990 ($r \leq 0.995$). If the calibration is not considered linear by either %RSD or linear regression, then correct the problem and re-calibrate. See Section 11 for equations and information on linear regression calibration.
9	Evaluate the intercept; it must be ≤ RL or re-calibrate.
10	Evaluate the success of the initial calibration by running an Initial Calibration Verification (ICV).
11	Evaluate the Initial Calibration Blank to be sure it is free of contaminants.

Initial Calibration Sequence Summary

1	DFTPP Tuning Criteria/DDT Breakdown/Tailing Factors
2	Calibration Standards
3	ICV
4	ICB

Daily continuing calibration verification - Calibration verification is performed at the beginning of **each** 12-hour analytical shift.	
1	The initial calibration for each compound of interest is verified once every 12 hours and prior to sample analysis by analyzing a continuing calibration verification (CCV) standard.
2	Evaluate the **system performance check compounds (SPCCs):** Each SPCC in the calibration verification (CCV) standard must meet the **minimum response factor criteria** for 8270C or 8270D in the initial calibration.
3	Evaluate the **minimum response factors** of each of the most common target analytes in the calibration verification standard (same as SPCCs).
4	Evaluate the **calibration check compounds (CCCs)** for method criteria. For 8270D or for shortened compound lists, all target analytes must meet ± 20% criteria. Use the initial calibration criteria.
5	Evaluate the **internal standard retention times** in the CCV.
6	Evaluate the **internal standard responses**.
7	Analyze an extraction blank after the continuing calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants.

10.3 Sample Analysis: Refer to Acceptable Manual Integration Practices / CA-Q-S-002.

1	Allow the sample extract to warm to room temperature. Just prior to analysis, add 10 µL [RVE/LVI: 2 µL] of the internal standard solution to the 0.5 mL concentrated sample extract.
2	Inject a 1 µL [RVE/LVI: 5 µL] aliquot of the sample extract into the GC/MS system. The volume to be injected contains 50 ng of base/neutral and 50 ng of acid surrogates (assuming 100% recovery).
3	The recommended sequence for a 20-sample batch is as follows:

1	DFTPP Tuning Criteria /DDT Breakdown/Tailing Factors*
2	CCV
3	Method Blank
4	LCS
5	Matrix Spike
6	Matrix Spike
7	Samples 1-20

*Not used for SIM.

4	If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed in the upper half of the calibration range. Additional internal standard must be added to the diluted extract to maintain the same concentration as in the calibration standards (40 µg/mL, unless a more sensitive GC/MS system is being used, e. g., 2 µg/mL for SIM).
5	Evaluate the specific internal standard response. Dilutions may be required to meet this criterion. Notes: Specific analytes associated with an internal standard within -50 to +100% from the last calibration verification (CCV) may be reported with approval from the supervisor or manager even if other internal standards in that analysis are outside limits. Only analytes associated with the internal standard(s) within limits may be reported from that analysis.
6	The use of selected ion monitoring (SIM) is acceptable for applications requiring detection limits below the normal range of electron impact mass spectrometry. Multiple ions are used for compound identification; see Attachment 2. Secondary ions may drop below 30% relative intensity at concentrations less than 1 µg/mL.

10.5 Qualitative analysis

- The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be kept up to date and obtained through analysis of known standards on the instrument using the conditions of this method. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. Attachments 1 and 2 list the primary and secondary ions for each analyte. Compounds are identified when the following criteria are met.
- The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time is accepted as meeting this criterion.
- The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.
- The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. **Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.** When two or more analytes that co-elute share secondary ions, and all the characteristic secondary ions for the target analyte are present but outside the ±30% relative intensity, the compound is reported as positive if there is no interference with the primary quantitation ion. If co-eluting peaks share the primary ion, the analyte may only be reported as a co-eluting pair. (See Attachment 1.)
- Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i. e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.
- Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analyses co-elute (i. e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum contains extraneous ions contributed by the co-eluting compound. The analyst must

carefully weigh the background spectrum and the spectrum of any co-eluting analytes whenever assessing a potential hit. Analyst experience in interpreting mass spectral data and the above specified guidelines are used together to interpret difficult matrices. If all of the ions associate with the reference spectrum for the target analyte are present and within the ±30% criteria, a positive result is assumed even in the presence of extraneous ion fragments without presumptive evidence (all ions associated with the target analyte are also present in the interfering peak) for a negative identification.

- Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights for 8270C and 50% of the average of the two peak heights for 8270D samples. Mathematically, the two equations used are equivalent. Verification is performed on a mid-level control each day of use. Otherwise, structural isomers are identified as isomeric pairs. (See Attachment 1.)
- For samples containing components not associated with the calibration standards or the requested target list, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines do not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.
  - For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:
    1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) are present in the sample spectrum.
    2) The relative intensities of the major ions agree within ±20%. **Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.**
    3) Molecular ions present in the reference spectrum are present in the sample spectrum.
    4) Ions present in the sample spectrum but not in the reference spectrum are reviewed for possible background contamination or presence of co-eluting compounds.
    5) Ions present in the reference spectrum but not in the sample spectrum are reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

10.6 Quantitative analysis

- Once a compound has been identified, the quantitation of that compound is based on the integrated abundance of the primary characteristic ion from the EICP.
- If the RSD of a compound's response factor is 15% for 8270C and 20% for 8270D, or less, then the concentration in the extract is determined using the average response factor (RF) from initial calibration data. If greater than the criteria , use linear regression.
- Where applicable, the concentration of any non-target compounds identified in the sample is estimated. The same formulae are used with the following modifications: The areas A_x and A_t are from the total ion chromatograms, and the RF for the compound is assumed to be 1.
- The resulting concentration is reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.
-

10.7 Instrument Maintenance

Careful examination of the standard chromatogram indicates whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. Re-calibration of the instrument must take place when the performance changes to the point that the calibration verification acceptance criteria cannot be achieved. In addition, significant maintenance activities or hardware changes may also require re-calibration. These significant maintenance activities include, changing, replacing, or reversing the column; cleaning the MS source; changing the electron multiplier; or injector port.

11.0 Calculations / Data Reduction

11.1 Accuracy

% Recovery = Measured concentration x 100
Known concentration

11.2 Precision (RPD)

RPD = Absolute value (orig. sample value - dup. sample value) x 100
(Orig. sample value + dup. sample value)/2

11.3 Breakdown Calculation:

% Breakdown of DDT = Sum of degradation peak areas (DDD + DDE) x 100
Sum of all peak areas (DDT + DDE + DDD)

1.4 Response Factor

$$RF = \frac{A_s x C_{is}}{A_{is} x C_s}$$

A_s = Peak area of the analyte or surrogate.
A_{is} = Peak area of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

11.5 Mean Response Factor, Standard Deviation, Relative Standard Deviation

$$RF_{mean} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

$$SD = \frac{\sum_{i=1}^{n} \left(RF_i - RF_{mean}\right)^2}{n-1}$$

$$RSD = \frac{SD \times 100}{RF_{mean}}$$

11.6 % Difference, % Drift

$$\% \text{ Difference} = \frac{(RF_v) - (\text{Avg. RF}) \times 100}{(\text{Avg. RF})}$$

RF_v = RF from verification standard
Avg. RF = Average RF from Initial Calibration.

$$\% \text{ Drift} = \frac{\text{Result - True Value} \times 100}{\text{True Value}}$$

11.7 Linear Calibration Using a Least Squares Regression: This approach is not used for analytes that meet the RSD limits. For calibration, x is the mass of the analyte in the sample aliquot introduced into the instrument and y is the area or the response, as in:

$x = C_s$ and $y = A_s$

A linear least squares regression attempts to construct a linear equation of the form:

$y = ax + b$

by minimizing the differences between the observed results (y_i, the instrument response) and the predicted results (y_i', the response calculated from the constructed equation). The regression equation is:

$y_i' = ax_i + b$

a = regression coefficient or the slope of the line.
b = the y-intercept.
y_i' = predicted (or calculated) response for the i^{th} calibration standard.
x_I = mass of analyte in the i^{th} calibration standard aliquot introduced into the instrument.

The sum of the squares of the differences is minimized to obtain a and b:

$$\sum_{i=1}^{n}(y_i - y_i')^2$$

n = total number of calibration points. The regression calculations attempt to minimize this sum of the squares, hence the name "least squares regression."

Weighting the sum of the square of the differences may significantly improve the ability of the least squares regression to fit the linear model to the data. The general form of the sum of the squares of the differences containing the weighting factor is:

$$\sum_{i=1}^{n} w_i (y_i - y_i')^2$$

w_i = weighting factor for the i^{th} calibration standard (w=1 for unweighted least squares regression).

y_i – observed instrument response (area) for the i^{th} calibration standard.
y_i' = predicted (or calculated) response for the i^{th} calibration standard.
n = total number of calibration standards.

The mathematics used in least squares regression has a tendency to favor numbers of larger value over numbers of smaller value. Thus the regression curves that are generated tend to fit points that are at the upper calibration levels better than those points at the lower calibration levels. To compensate for this, a weighting factor which reduces this tendency can be used. Examples of allowed weighting factors which can place more emphasis on numbers of smaller value are:

$w_i - 1/x_i$ or $w_i = 1/x_i^2$

Do not include the origin (0, 0) as an extra calibration point. Reprocess each calibration standard as an unknown to determine the best fit model. Each calibration point above the RL must be ± 15% true (8000B) or ±20% true (8000C); the RL-level standard must be ± 30% true.

The regression calculation generates a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.995 or $r^2 \geq 0.990$.

11.8 Coefficient of Determination **Correlation Coefficient**

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2} \qquad r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response or Response ratio
x = Concentration

11.9 Calculation

- For **aqueous** samples:

$$\textbf{Concentration (µg/L)} = \frac{A_x V_t D}{RF_{mean} V_s} \quad \text{or} \quad \frac{(\mu g/mL \text{ from instrument})(D)(1000)}{mL \text{ extracted}}$$

A_x = Area of the peak for the analyte in the sample.
V_t = Total volume of the concentrated extract (mL).
D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.
RF_{mean} = Mean response factor from the initial calibration (area/concentration).
V_s = Volume of the aqueous sample extracted in mL.

- For **non-aqueous** samples:

$$\textbf{Concentration (µg/kg)} = \frac{A_x V_t D}{RF_{mean} W_s} \quad \text{or} \quad \frac{(\mu g/mL \text{ from instrument})(D)(1000)}{g \text{ extracted}}$$

A_x, V_t, D, RF_{mean} are the same as for aqueous samples, and
W_s = Weight of sample extracted (g). The wet weight or dry weight may be used, depending upon the specific application of the data.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes must be stored, managed, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Dispose of waste extracts in the waste solvent drum.

15.0 References / Cross References

15.1 Method 8270C, SW-846 Update III Revision 3, December 1996 and **Method 8270D**, Update IV, Revision 4, February 2007.

15.2 Method 8000B, SW-846, Revision 2, December 1996, **Method 8000C**, Revision 3, March 2003.

15.3 TestAmerica Nashville's Quality Assurance Manual.

15.4 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.5 SOPs: Acceptable Manual Integration Practices / CA-Q-S-002, Selection of Calibration Points / CA-T-P-002, Calibration Curves (General) / CA-Q-S-005, Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Determination of Method

Detection Limits / NV08-202, Reagent and Standard Purchase / NV08-214, 3550 / NV03-23, and 3510 / NV03-24, 3541 / NV03-231, 3580 / NV03-106,8270/NVOH04-22.

15.6 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

15.7 Corporate Quality Memorandum No. CA-Q-QM-005, May 19, 2010.

16.0 Method Modifications

Item	Modification
1	See Attachment 5 for the State of Ohio specific criteria.
2	See Attachment 6 for the State of Missouri DRO, CA LUFT DRO by GC/MS.
3	Verify with state certifications the correct version of this method to report. **Analyze and report by 8270D for Canadian, NJ, NC, OK, SC, and WV samples.**
4	SIM is not allowed for South Carolina samples unless pre-approved by the state on a project-specific basis.

17.0 Attachments

Attachment 1, Characteristic Ions for Semivolatile Compounds[a]

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
1,4-Dioxane	2.568	88	58
n-Nitrosodimethylamine	2.700	74	42, 44
Pyridine	2.714	79	52
2-Picoline	3.464	93	66, 92
n-Nitrosomethylethylamine	3.558	88	42, 43, 56
2-Fluorophenol (surr)	3.687	112	64
Methyl methanesulfonate	3.764	80	79, 65, 95
n-Nitrosodiethylamine	4.009	102	42, 57, 44, 56
Ethyl methanesulfonate	4.197	79	109, 97, 45, 65
Hexachloropropene	4.261	213	211,215,117,106,141
Phenol-d_5 (surr)	4.266	99	42, 71
Aniline	4.270	93	66, 65
Bis(2-chloroethyl) ether	4.294	93	63, 95
Phenol	4.275	94	65, 66
2-Chlorophenol	4.345	128	64, 130
1,3-Dichlorobenzene	4.425	146	148, 113
1,4-Dichlorobenzene-d_4 (IS)	4.444	152	150, 115
1,4-Dichlorobenzene	4.454	146	148, 113
Pentachloroethane	4.474	117	165, 167, 119
Benzyl alcohol	4.543	79	108, 77
n-Decane	4.550	57	
1,2-Dichlorobenzene	4.571	146	148, 113
2-Methylphenol	4.628	108	107, 77, 79, 90
Bis(2-chloroisopropyl) ether	4.632	45	77, 79
N-Nitrosodi-n-propylamine	4.717	130	42, 101, 70
3, 4-Methylphenol	4.717	107	108, 77, 79, 90
Hexachloroethane	4.764	117	201, 199
Nitrobenzene-d_5 (surr)	4.806	82	128, 54
Nitrobenzene	4.816	77	123, 65
n-Nitrosopyrrolidine	4.907	102	41, 42, 68, 69
Acetophenone	4.912	105	71, 51, 120
n-Nitrosomorpholine	4.916	108	116, 86
o-Toluidine	4.940	106	107, 77, 51, 79

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
Isophorone	4.957	82	95, 138
2-Nitrophenol	5.018	139	109, 65
2,4-Dimethylphenol	5.037	122	107, 121
Bis(2-chloroethoxy)methane	5.088	93	95, 123
n-Nitrosopiperidine	5.114	114	42, 55, 56, 41
Benzoic acid	5.116	105	122, 77
2,4-Dichlorophenol	5.168	162	164, 98
1,2,4-Trichlorobenzene	5.215	180	182, 145
Naphthalene-d_8 (IS)	5.248	136	68
Naphthalene	5.257	128	129, 127
o,o,o-Triethylphosphorthioate	5.302	198	80, 53, 54164, 63
4-Chloroaniline	5.304	127	129, 65, 92
Hexachlorobutadiene	5.370	225	223, 227
a,a-Dimethylphenethylamine	5.372	58	91, 65, 134, 42
2,6-Dichlorophenol	5.523	162	
Hexachloropropene	5.556	213	211, 215, 117, 106, 141
4-Chloro-3-methylphenol	5.615	142	107, 144
2-Methylnaphthalene	5.704	142	141
n-Nitrosodi-n-butylamine	5.729	84	57, 41, 116, 158
1,4-Phenylenediamine	5.734	198	80, 53, 54, 52
1-Methylnaphthalene	5.779	142	141, 115
Hexachlorocyclopentadiene	5.854	237	235, 272
Isosafrole (trans)	5.861	162	131, 104, 77
2,4,6-Trichlorophenol	5.911	196	198, 200
2,4,5-Trichlorophenol	5.914	196	198, 97, 132, 99
2-Fluorobiphenyl (surr)	5.953	172	171
2-Chloronaphthalene	6.003	162	127, 164
Isosafrole (cis)	6.054	162	131, 104, 77
1,2,4,5-Tetrachlorobenzene	6.063	216	214,179,108,143,218
2-Nitroaniline	6.118	138	92, 65
2,3-Dichloroaniline	6.134	161	90, 63
Safrole	6.204	162	104, 77, 103, 135
Dimethyl phthalate	6.245	163	194, 164
1-Chloronaphthalene	6.284	162	127, 164
2,6-Dinitrotoluene	6.296	165	63,89, 121
Acenaphthylene	6.320	152	151, 153
1,4-Naphthoquinone	6.374	158	104, 102, 76, 50, 130
3-Nitroaniline	6.404	138	108, 92
Acenaphthene	6.447	154	153, 152
2,4-Dinitrophenol	6.470	184	63, 154
1,3-Dinitrobenzene	6.486	168	76, 50, 75, 92, 122
4-Nitrophenol	6.527	65	109, 139
Dibenzofuran	6.560	168	139
2,4-Dinitrotoluene	6.574	165	63, 89, 182
Acenaphthene-d_{10} (IS)	6.656	164	162, 160
Diethyl phthalate	6.738	149	177, 150
4-Chlorophenyl phenyl ether	6.790	204	206, 141
Fluorene	6.799	166	165,167
Pentachlorobenzene	6.806	250	252,108,248,215,254
4-Nitroaniline	6.837	138	65, 108, 92, 80, 39
1-Naphthylamine	6.844	143	115, 89, 63

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
4,6-Dinitro-2-methylphenol	6.865	198	51, 105, 182, 77
n-Nitrosodiphenylamine	6.879	169	168, 167
2-Naphthylamine	6.895	143	115, 116
2,3,4,6-Tetrachlorophenol	6.900	232	131,230,166,234,168
1,2-Diphenylhydrazine	6.903	77	105, 182
2,4,6-Tribromophenol (surr)	6.987	330	332, 141
Thionazine	7.027	107	96, 97,143, 79, 68
5-Nitro-o-toluidine	7.051	152	77, 79, 106, 94
Diphenylamine	7.107	168	169, 167
4-Bromophenyl phenyl ether	7.138	248	250, 141
Hexachlorobenzene	7.255	284	142, 249
Sulfotepp	7.276	322	97, 202
1,3,5-Trinitrobenzene	7.314	213	74, 120, 91, 63
Diallate (trans)	7.337	86	234, 43, 70
Phenacetin	7.337	108	180,179,109,137,80
Phorate	7.347	75	121, 97, 93, 260
Pentachlorophenol	7.387	266	264, 268
Diallate (cis)	7.403	86	234, 43, 70
Dimethoate	7.474	87	93, 125, 143, 229
Phenanthrene-d_{10} (IS)	7.476	188	94, 80
Phenanthrene	7.495	178	179, 176
Anthracene	7.528	178	176, 179
4-Aminobiphenyl	7.568	169	168, 170, 115
n-Octadecane	7.586	58	71, 85
Pronamide	7.619	173	175, 145, 109, 147
Carbazole	7.641	167	139, 84
Pentachloronitrobenzene	7.676	237	142,214,249,295,265
Disulfoton	7.723	88	97, 89, 142, 186
Dinoseb	7.737	211	163, 147, 117, 240
Di-n-butyl phthalate	7.914	149	150, 104
Methyl parathion	8.000	109	125, 263, 79, 93
Parathion	8.292	109	97, 291, 139, 155
4-Nitroquinoline-1-oxide	8.310	190	101, 128, 75, 116
Methapyrilene	8.371	58	50, 191, 71
Fluoranthene	8.374	202	100, 101, 203
Benzidine	8.464	184	92, 185
Isodrin	8.522	193	66, 195, 263,265,147
Pyrene	8.543	202	100, 101, 200, 203
Terphenyl-d_4 (surr)	8.652	244	122, 212
Aramite	8.870	191	319, 334, 197, 321
Dimethylaminoazobenzene	9.001	120	77, 105, 148, 42
Butyl benzyl phthalate	9.028	149	91, 206
Chlorobenzilate	9.034	139	253, 111, 141
Hexachlorophene	9.070	185	209,406
3,3'-Dimethylbenzidine	9.251	212	106, 196, 180
Bis (2-ethylhexyl) adipate	9.298	129	57, 112, 147
4,4'-Methylenebis (2-chloroaniline)	9.301	231	266, 140, 77
Kepone	9.316	272	274,237,178,143,270
3,3'-Dichlorobenzidine	9.423	252	254, 126
Benz(a)anthracene	9.446	228	229, 226
2-Acetylaminofluorene	9.453	181	180, 223, 152

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
Chrysene-d_{12} (IS)	9.456	240	120, 36
Chrysene	9.474	228	226, 229
Bis(2-ethylhexyl) phthalate	9.474	149	167, 279
Di-n-octyl phthalate	9.926	149	167, 43
Benzo(b)fluoranthene	10.292	252	253, 125
3-Methylcholanthrene	11.305	268	252,253,126,134,113
Benzo(k)fluoranthene	10.311	252	253, 125
Benzo(a)pyrene	10.579	252	253, 125
7,12-Dimethylbenz(a)anthracene	10.600	256	241, 239, 120
Perylene-d_{12} (IS)	10.631	264	260, 265
Indeno)1,2,3-c,d)pyrene	11.778	276	138, 277
Dibenz(a,h)anthracene	11.783	278	139, 279
Dibenz(a,j)acridine	11.987	279	280, 277, 250
Dibenz(a,j)acridine	11.987	279	280, 277, 250
Benzo(g,h,i)perylene	12.107	276	138, 277
IS = internal standard			
surr = surrogate			
[a]See Attachment 2 for Retention Times and Ions used with SIM			

Attachment 2, Characteristic Ions for PAH Compounds Using SIM

Compounds	RT	Primary	Secondary*
1,4-Dichlorobenzene-d_4	6.66	152	
2-Fluorophenol	5.471	112	64
Phenol-d_5	6.251	99	71.1
Naphthalene-d_8	8.24	136	
Nitrobenzene-d_5	7.32	82.1	128.1
Naphthalene	8.27	128.1	129.1
2-Methylnaphthalene	9.13	142.1	141.1
1-Methylnaphthalene	9.42	142.1	141.1
Acenaphthene-d_{10}	10.91	164.1	
2-Fluorobiphenyl	9.82	172.1	
Acenaphthylene	10.67	153	151.1
Acenaphthene	10.958	15.1	154.1
Fluorene	11.7	166.1	167.1
Phenanthrene-d_{10}	13.3	188	
2,4,6-Tribromophenol	12.167	329.8	331.8
Phenanthrene	13.33	178.2	176.2
Anthracene	13.4	178.2	176.2
Fluoranthene	15.28	202.2	101.1
Chrysene-d_{12}	17.64	240.1	
Pyrene	15.66	202.2	101.1
Terphenyl-d_{14}	15.89	244.2	
Benzo(a)anthracene	17.61	228.2	229.2
Chrysene	17.68	228.2	229.2
Perylene-d_{12}	20.2	264.2	
Benzo(b)fluoranthene	19.45	252.2	126.1
Benzo(k)fluoranthene	19.49	252.2	126.1
Benzo(a)pyrene	20.08	252.2	126.1
Indeno(1,2,3-cd)pyrene	22.69	276.2	277.2
Dibenzo(ah)anthracene	22.7	278.2	279.2

Compounds	RT	Primary	Secondary*
Benzo(ghi)perylene	23.43	276.2	277.2
Internal standards are in **bold.**			

Attachment 3, SIM Mass Groups

Mass Group	Compound	RT	Primary	Secondary	Dwell Time
1	2-Fluorophenol	5.42	112	64	25 ms
	Phenol-d_5	6.2	99	71	
	1,4-Dichlorobenzene-d_4	6.6	152		
	Nitrobenzene-d_5	7.26	82.1	128.1	
4.20 min.					
2	Naphthalene-d_8	8.17	136		50 ms
	Naphthalene	8.2	128.1	129.1	
	2-Methylnaphthalene	9.19	142	141.1	
	1-Methylnaphthalene	9.35	142.1	141.1	
	2-Fluorobyphenyl	9.75	172.1		
5.35 min.					
3	Acenaphthylene	10.6	152.1	151.1	25 ms
	Acenaphthalene-d_{10}	10.83	164.1		
	Acenaphthene	10.88	153.1	154.1	
	Fluorene	11.69	166.1	167.1	
	2,4,6-Tribromophenol	12.11	329.8	331.8	
6.55 min.					
4	Phenanthrene-d_{10}	13.21	188		50 ms
	Phenanthrene	13.25	178.2	176.2	
	Anthracene	13.32	178.2	176.2	
	Fluoranthene	15.21	202.2	101.1	
	Pyrene	15.58	202.2	101.1	
	Terphenyl-d_{14}	15.81	244.2		
7.75 min.					
5	Benzo(a)anthracene	17.52	228.2	229.2	100 ms
	Chrysene-d_{12}	17.55	240.1		
	Chrysene	17.59	228.2	229.2	
9.85 min.					
6	Benzo(b)fluoranthene	19.34	252.2	126.1	100 ms
	Benzo(k)fluoranthene	19.38	252.2	126.1	
	Benzo(a)pyrene	19.96	252.2	126.1	
	Perylene-d_{12}	20.07	264.2		
10.65 min.					
7	Indeno(1,2,3-cd)pyrene	22.5	276.2	277.2	100 ms
	Dibenzo(a,h)anthracene	22.52	278.2	279.2	
	Benzo(g,h,i)perylene	23.21	276.2	277.2	
12.20 min.					

Attachment 4, 8270D Minimum Response Factor Criteria for Initial and Continuing Calibration Verification Using the Suggested Ions from Attachments 1 and 2.

Compound	Minimum RF	Compound	Minimum RF
Benzaldehyde	0.010	4-Nitrophenol	0.010
Phenol	0.800	Dibenzofuran	0.800

Compound	Minimum RF	Compound	Minimum RF
Bis(2-chloroethyl)ether	0.700	2,4-Dinitrotoluene	0.200
2-Chlorophenol	0.800	Diethyl phthalate	0.010
2-Methylphenol	0.700	1,2,4,5-tetrachlorobenzene	0.010
2,2'-Oxybis-(1-chloropropane)	0.010	4-Chlorophenyl-phenyl ether	0.400
Acetophenone	0.010	Fluorene	0.900
4-Methylphenol	0.600	4-Nitroaniline	0.010
n-Nitroso-di-n-propylamine	0.500	4,6-Dinitro-2-methylphenol	0.010
Hexachloroethane	0.300	4-Bromophenyl-phenyl ether	0.100
Nitrobenzene	0.200	n-Nitrosodiphenylamine	0.010
Isophorone	0.400	Hexachlorobenzene	0.100
2-Nitrophenol	0.100	Atrazine	0.010
2, 4-Dimethylphenol	0.200	Pentachlorophenol	0.050
Bis(2-chloroethoxy)methane	0.300	Phenanthrene	0.700
2,4-Dichlorophenol	0.200	Anthracene	0.700
Naphthalene	0.700	Carbazole	0.010
4-Chloroaniline	0.010	Di-n-butyl phthalate	0.010
Hexachlorobutadiene	0.010	Fluoranthene	0.600
Caprolactam	0.010	Pyrene	0.600
4-Chloro-3-methylphenol	0.200	Butyl benzyl phthalate	0.010
2-Methylnaphthalene	0.400	3,3'-Dichlorobenzidine	0.010
Hexachlorocyclopentadiene	0.050	Benzo(a)anthracene	0.800
2,4,6-Trichlorophenol	0.200	Chrysene	0.700
2,4,5-Trichlorophenol	0.200	Bis-(2-ethylhexyl)phthalate	0.010
1,1'-Biphenyl	0.010	Di-n-octyl phthalate	0.010
2-Chloronaphthalene	0.800	Benzo(b)fluoranthene	0.700
2-Nitroaniline	0.010	Benzo(k)fluoranthene	0.700
Dimethyl phthalate	0.010	Benzo(a)pyrene	0.700
2,6-Dinitrotoluene	0.200	Indeno(1,2,3-cd)pyrene	0.500
Acenaphthylene	0.900	Dibenz(a,h)anthracene	0.400
3-Nitroaniline	0.010	Benzo(g,h,i)perylene	0.500
Acenaphthene	0.900	2,3,4,6-Tetrachlorophenol	0.010
2,4-Dinitrophenol	0.010		

Attachment 5, State of Ohio Specific Criteria.
Only those compounds in the original EPA Method 8270C may be reported. Any compounds in this SOP in italics in Section 1 are not part of the original 8270C method. Run Ohio VAP samples according to SOP 8270/NVOH04-22.

Attachment 6, Missouri Department of Natural Resources (and CA LUFT) require(s) that **DRO** be analyzed by GC/MS.

- Tuning and frequency requirements are the same as in 8270, omitting DDT, Pentachlorophenol, and Benzidine.
- Extract water samples per SOP 3510 / SA03-24 and solid samples per SOP 3550 / SA03-23.
- Only base/neutral surrogates are needed.
- GC/MS mass range is 35-550 ηmu.
- Use a five-point calibration curve with 1:1 unleaded gasoline and #2 diesel fuel at 1,000 µg/mL each in Methylene chloride.

- Retention time windows set using C_{10}, C_{21}, and C_{35}. For DRO, set RT 0.1 minutes after C10 to 0.1 minutes after C21. For ORO, set RT 0.1 minutes after C_{21} to 0.1 minutes after C_{35}. Verify RT daily (24 hours) by running component standard.
- Quantitative using baseline-to-baseline, not valley-to-valley. The Total Ion Chromatogram must be used to quantitate.
- The Response Factor determined for DRO (C_{10}-C_{21}) must be used for C_{21}-C_{35}.
- Subtract area from any Internal Standard and surrogates.
- % RSD ≤ 20.
- Run a CCV at the beginning and end of each batch; it must contain all targets reported, at mid-point of calibration, % D ≤ 20.
- Run a Method Blank every extraction batch, and LCS and MS/MSD per batch.
- May reprocess file to quantitate PAH if needed. For individual targets, % RSD ≤ 15.
- Quantitation of DRO must be by external standard.

18.0 Revision History

- Revision 12, 22 October 2008
  - Integration for TestAmerica and STL operations.
  - Insert corrective action procedures
  - To incorporate Update IV criteria.
- Revision 13, 9 October 2009
  - Consolidation of text, general editing.
  - Add Appendix IX and miscellaneous compound details.
  - Distinguish 8270C versus 8270D.
- Revision 14, 30 September 2011
  - Organizational changes.
  - Add amendments 13a and 13b.
  - Add reference to SOP 3541 for concrete and SOP Calibration Curves (General).
  - Add QAF-45 and Section 14.2.
  - Remove WY as a state requiring QC every 10 samples.
  - Change Attachment 5 to refer analysts to OH8270 SOP.
  - Add Attachment 7
  - Add option to run LLCCV to show sensitivity.
  - Add note about low-level calibration standard for SIM WI samples.
  - Lower several report limits.
  - Specify GC resolution between two isomer peaks for 8270C versus 8270D.
- Revision 15, 31 December 2012
  - Organizational changes.
  - Incorporation of amendments 14a, b, c.
  - OK no longer limits batch size to 10 samples.
  - Specify that $r^2 \geq 0.990$.
  - Substitute LIMS for the Control Limits Manual.
  - Distinguish between the RSD maximum for 8270C and 8270D. For 8270D, all targets are treated as CCCs.
  - Add re-fitting text to the linear calibration section.
  - Add Reduced Volume Extraction / Large Volume Injection (RVE / LVI).

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP)
Change Form

SOP Number/Revision No.: **9012/ NV07-137.10b** Effective Date: **9/30/2013**

Last Mod. Date: 6/28/13

SOP Title: **Method 9012: Total and Amenable Cyanide (Automated colorimetric, with Off-line Distillation)**

Affected SOP Section Number(s): Section 1.2, Reporting Limits

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 07

Revision Number with Mod ID: **10c**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

☐ Procedural Changes (Define Below) – Re-Training Required.

■ Other

2. Summary of Procedure Change: Add bold text, delete crossed out text.

Section 1.2**,** Reporting Limits: The reporting limit (RL) for waters is **0.01** ~~0.005~~ mg/L, for soil, 2.0mg/kg.

Sessily Overton-Gray 9/16/13	Michael A. Brown 9/16/13
Department Supervisor Approval Date	Technical Manager Approval Date Quality Assurance Approval

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP)
Change Form

SOP Number/Revision No.: **9012/ NV07-137.10a** Effective Date: **6/28/2013**

Last Mod. Date: 4/30/13

SOP Title: **Method 9012: Total and Amenable Cyanide (Automated colorimetric, with Off-line Distillation)**

Affected SOP Section Number(s): Section 10.5, Result Calculation

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 07

Revision Number with Mod ID: **10b**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

☐ Procedural Changes (Define Below) – Re-Training Required.

■ Other

2. Summary of Procedure Change: Add underlined text; delete crossed out text.

11.5 Result Calculation

Amenable Concentration (mg/L) = (A – B) * D

A = mg/L cyanide in unchlorinated aliquot
B = mg/L cyanide in chlorinated aliquot, i. e., non-amenable.
D = dilution factor

~~Note: Amenable CN = Total CN – CN Treated tube reading.~~

Sessily Overton-May 6/10/13	J D 6/10/13
Department Supervisor Approval Date	Operations Manager Approval Date
Michael A. Brown 6/10/13	
Technical Manager Approval Date	
Quality Assurance Approval	

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP)
Change Form

SOP Number/Revision No.: **9012/ NV07-137.10** Effective Date: **4/30/2012**

Last Mod. Date: 10/31/12

SOP Title: **Method 9012: Total and Amenable Cyanide (Automated colorimetric, with Off-line Distillation)**

Affected SOP Section Number(s): Title, Section 10.3

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 07

Revision Number with Mod ID: **10a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

☐ Procedural Changes (Define Below) – Re-Training Required.

■ Other

2. Summary of Procedure Change: Add underlined text.

Title: TOTAL AND AMENABLE CYANIDE (AUTOMATED COLORIMETRIC) WITH OFF-LINE DISTILLATION METHOD 9012A/B, 9013/9013A, AND 9014

15.0 References / Cross-References

15.1 EPA Method 9012A, SW-846 Update III Revision 1, December 1996; **9010B**, SW-846 Update III, Revision 2, December 1996; **9012B**, SW-846 Update IIIB, Revision 2, November 2004; **9010C**, SW-846 Update IIIB, Revision 3, November 2004; **9013**, SW-846 Update I, Revision 0, July 1992; **9013A**, Revision 1, November 2004; **9014** Revision 0, December 1996.

Department Manager Approval	4/19/13 Date	Operations Manager Approval	4/19/13 Date
Technical Manager Approval	Date		
Quality Assurance Approval			

Title: TOTAL AND AMENABLE CYANIDE (AUTOMATED COLORIMETRIC) WITH OFF-LINE DISTILLATION METHOD 9012A/B, 9013A, AND 9014

Approvals (Signature/Date)

Ronald Martin 10-22-12 Department Manager Date	Matt Ricke 10.11.12 Inorganics Operations Manager Date
Michael H. Dunn 9-27-12 Technical Director Quality Assurance Manager Date	Johnny Davis 10-22-12 Health & Safety Manager / Coordinator Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method is used to determine the concentration of inorganic cyanide in groundwaters, soils, wastes, or leachates. The method detects inorganic cyanides that are present as either soluble salts or complexes. It is used to determine values for both total cyanide and cyanide amenable to chlorination.

1.2 Reporting Limits: The reporting limit (RL) for water is 0.005 mg/L, for soil, 2.0 mg/kg.

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor or the Laboratory Technical Director. All abnormalities must be noted on the data and in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing Sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by automated UV colorimetry. If the sample contains solids or oil that cannot be fully suspended or homogeneous, then the sample is extracted with 50% weight/volume NaOH.

2.2 In the automated colorimetric measurement, the cyanide is converted to Cyanogen chloride (CNCl) by reaction with Chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of Pyridine-Barbituric acid reagent. The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilution of the original scrubber solution to obtain colors of comparable intensity.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 Interferences are eliminated or reduced by using the distillation procedure.

4.2 Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences are removed by adding an excess of sodium arsenite to the waste prior to preservation and storage of the sample to reduce the chlorine to chloride which does not interfere.

4.3 Sulfide interference can be removed by adding an excess of bismuth nitrate to the waste (to precipitate the sulfide) before distillation.

4.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite form nitrous acid, which react with some organic compounds to form oximes. Once formed, these compounds decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid before distillation.

4.5 Magnesium chloride use accelerates and frees up the cyanide ion.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: Strong acids and bases.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Sulfuric acid	Corrosive Oxidizer Dehydrator	1 mg/m^3	This material causes burns if it comes into contact with the skin or eyes. Inhalation of vapors causes irritation of the nasal and respiratory system.
Sodium hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3	This material causes burns if it comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust causes irritation of the nasal and respiratory system.
Chloramine T hydrate	Poison		May be harmful by inhalation, ingestion, or skin absorption. This material is irritating to mucous membranes and upper respiratory tract. Avoid contact and inhalation.
Pyridine	Flammable Irritant	5 ppm-TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Potassium cyanide	Poison Corrosive	5 mg/m^3 TWA as CN	**This material forms Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			
TWA = Time-weighted average			

6.0 Equipment and Supplies

6.1 Instrumentation

- Automated continuous-flow analytical instrument (i. e., Lachat Model 8000 or 8500) with autosampler, cyanide manifold, and peristaltic pump, colorimeter with a 1 cm flowcell and 570 ηm filter, Omnion data acquisition system or Discrete Analyzer (i. e., Konelab).
- Distillation system, Andrews Glass Midi-Dist, or equivalent.
- pH Meter
- Vacuum pump
- Balance, 0-160 gram capacity.

6.2 Supplies

- 100- and 250-mL volumetric flasks, Class A.
- Class A pipets.
- Sea or Ottawa sand for blank soil matrix and LCS soil matrix.
- Plastic, certified, centrifuge tubes.

- 500 mL plastic bottle, or equivalent.
- Tumbler or shaker.

7.0 Reagents and Standards

7.1 Reagent water, analyte-free.

7.2 Reagents for sample collection, preservation, and handling

7.2.1 Sodium arsenite (0.1 N), $NaAsO_2$. Dissolve 3.2 g $NaAsO_2$ in 250 mL reagent water.

7.2.2 Sodium hydroxide solution (10N), NaOH. Commercially available, or 400 g NaOH/L reagent water.

7.2.3 Acetic acid (1.6 M) CH_3COOH. Dilute one part of concentrated Acetic acid with 9 parts of water.

7.3 Reagents for cyanides amenable to chlorination

7.3.1 Calcium hypochlorite solution: Dissolve 5 g of Calcium hypochlorite ($Ca(OCl)_2$) in 100 mL of reagent water.

7.3.2 Sodium Hypochlorite: Commercial Bleach (No additives or scents), 5 to 6% hypochlorite.

7.3.3 Sodium hydroxide solution (0.25 N), NaOH. Dissolve 10 g of NaOH in 1 liter of reagent water.

7.3.4 Ascorbic acid crystals, commercial source.

7.3.5 Potassium iodide starch paper, commercial.

7.4 Reagents for distillation

7.4.1 Sodium hydroxide (0.25 N). Dissolve 10 g NaOH in 1 liter reagent water. This solution may be used to extract soil if needed (Method 9013A).

7.4.2 Bismuth nitrate (0.062 M), $Bi(NO)_3*5H_2O$. Dissolve 30 g $Bi(NO)_3*5H_2O$ in 100 mL of reagent water. While stirring, add 250 mL of glacial Acetic acid, CH_3COOH. Stir until dissolved and dilute to 1 liter with reagent water.

7.4.3 Sulfamic acid, H_2NSO_3H. Dissolve 200 g H_2NSO_3H in 1 liter of reagent water.

7.4.4 Sulfuric acid (18 N), H_2SO_4. Slowly and carefully add 500 mL of concentrated H_2SO_4 to 500 mL of reagent water or use a commercially prepared solution.

7.4.5 Magnesium chloride solution (2.5 M), $MgCl_2*6H_2O$. Dissolve 510 g of $MgCl_2*6H_2O$ in 1 liter of reagent water.

7.4.6 Lead acetate paper, commercial.

7.5 Reagents for automated colorimetric determination (Lachat)

7.5.1 Pyridine-barbituric acid reagent: Place 15 g of Barbituric acid in a 1-liter volumetric flask, add 100 mL reagent water, rinsing down the sides of the flask to wet the barbituric acid. Add 75 mL of Pyridine and mix. Add 15 mL of concentrated HCl, mix and cool to room temperature. Dilute to 1 liter with reagent water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.5.2 Chloramine-T solution: Dissolve 2.0 g of white, water-soluble Chloramine-T in 500 mL of reagent water. Prepare fresh daily.

7.5.3 Sodium hydroxide, 10 N: Commercial source.

7.5.4 Carrier: 0.25 N NaOH.

7.5.5 Buffer: In a 1-liter volumetric flask, dissolve 97 g of Potassium phosphate, monobasic anhydrous, (KH_2PO_4) in approximately 800 mL reagent water. Dilute to volume and invert to mix. Prepare fresh monthly.

7.5.6 All working standards must be prepared in 0.25 N NaOH.

7.5.7 Dilution water and receptacle wash water (NaOH, 0.25 N): Dissolve 10.0 g NaOH in 500 mL of reagent water. Dilute to 1 liter.

7.6 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of reagent water and mix. Dilute to one liter. Standardize with 0.0192 N $AgNO_3$ to appropriate

concentration. 1 mL = 1 mg CN. Purchased standards may be used in place of prepared solutions. Dilute to make a 10 µg/mL working standard. Standardize stock against silver nitrate weekly.

7.7 Reagents for automated colorimetric determination (Konelab): See Konelab Methods Manual.

7.8 See SOP Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214 for shelf-life and storage requirements for standards and reagents. Also, refer to benchsheets, logbooks, and LIMS.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	HDPE or Glass	250 mL	Cool 0-6°C, Preserve with 4 mL 10 N NaOH/L sample at the time of collection (pH ≥ 12)	14 days from collection to analysis	SW-846 Section 2.0
Soil	HDPE or Glass	30 g	Cool 0-6°C		

- All bottles must be thoroughly cleansed and rinsed to remove soluble material from containers. Certified clean containers are acceptable.
- Oxidizing agents such as chlorine decompose most of the cyanides. To determine whether oxidizing agents are present, test a drop of the sample with Potassium iodide-starch test paper (KI starch paper); a blue color indicates the need for treatment. Add 0.1 N Sodium arsenite a few drops at a time until a drop of sample produces no color on the indicator paper. Add an additional 5 mL of Sodium arsenite for each liter of sample volume.
- Distillates not analyzed immediately are stored at 0-6°C.

9.0 Quality Control

The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC

The following quality control samples are prepared with **each batch of 20 or fewer samples.**		
Quality Controls	**Acceptance Criteria**	**Corrective Action**
Method Blank	< RL	Correct problem then re-prep and analyze blank and all samples processed with the contaminated blank. If target >10x blank, report but qualify.
Laboratory Control Sample (LCS)[1], second source, distilled	85-115% recovery	If %R is low, redistill, rerun. If high, report non-detect samples, redistill and reanalyze any positive samples.
Matrix Spike	See LIMS for historical % recovery range.	Report. Qualify as needed.
Matrix Spike Duplicate	See LIMS for historical % recovery range.	Report. Qualify as needed.

[1]For AZ, TX, WV samples, a LCS duplicate is required.

- The **Method blank:** Add method reagents to 50 mL reagent water (for water batches) or to 1 gram sea sand and 50 mL reagent water (for soil batches).
- **Laboratory Control Sample (LCS)**: A **distilled LCS** is run with each batch.

- Prepare the LCS (0.1 µg/mL) by adding 50 µL of 2nd source 100 µg/mL cyanide standard to 50 mL reagent water (for water batches) or to 1 gram sea sand and 50 mL reagent water (for soil batches).

- **Matrix Spike / Matrix Spike Duplicate**: Both the matrix spike and matrix spike duplicate are brought through the entire sample preparation and analytical process.
  - A matrix spike is prepared by adding cyanide from the working standard standard to 50 mL or 1 gram of sample to ensure a concentration of approximately 100 µg/L (using 50 µL of 100 µg/mL cyanide stock standard to 10 mL 0.25N NaOH).

9.2 Instrument QC

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Initial calibration (minimum six standards)	Initial calibration prior to sample analysis.	$r^2 \geq 0.990$, $r \geq 0.995$ for first-order linear regression	Correct problem then repeat initial calibration
Initial Calibration Verification Sample (ICV), second source, not distilled	Immediately after calibration	85-115% recovery	Re-calibrate
Initial Calibration Blank (ICB)	Immediately after the ICV	< RL	Correct the problem and re-run.
Continuing Calibration Verification Sample (CCV), distilled & non-distilled	Distilled: 1/batch; Non-distilled: every 10 samples	90-110% recovery	Correct, re-calibrate, rerun samples. If high and samples are ND, it is acceptable to report the results.
Continuing Calibration Blank (CCB)	After each CCV	< RL	Correct problem, repeat samples.

- **Initial Calibration Standards**: See Section 10.2.
- **Initial Calibration Verification (ICV)**
  - Prepare a 0.2 µg/mL ICV by adding 100 µL of 100 µg/mL 2nd source standard to 50.0 mL reagent water.
- **Continuing Calibration Verification Sample (CCV)**
  - Use 100 µL 100 µg/mL cyanide standard used for calibration to 50 mL reagent water for a final concentration of 0.2 µg/mL.
- **Initial and Continuing Calibration Blank (ICB and CCB)**: Use 0.25N NaOH.

10.0 Procedure

10.1 Sample Preparation

- **Sample size**

Matrix	Sample Size
Water	50 mL
Soil	1 gram

- See SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
- **Pretreatment for cyanides amenable to chlorination**
  - This test **must** be performed in the hood, covering all containers with aluminum foil. $K_3[Fe(CN)_6]$ may decompose under UV light and hence test positive for cyanide amenable to chlorination if exposed to fluorescent lighting or sunlight. Two identical sample aliquots are required to determine cyanides amenable to chlorination.

1	To a 50.0 mL aliquot of sample, add bleach or calcium hypochlorite solution solution dropwise while agitating and maintaining the pH between 11 and 12 with 1.25 N sodium hydroxide until an excess of chlorine is present as indicated by KI-starch paper turning blue. The sample is subjected to alkaline chlorination by this step. Designate this aliquot "AM." CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is necessary that this reaction be performed in a hood.
2	Test for excess chlorine with KI-starch paper and maintain this excess for one hour with continuous agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional bleach solution.
3	After one hour, add ascorbic acid until KI-starch paper shows no residual chlorine. Add an excess ascorbic acid to ensure the presence of excess reducing agent.
4	Test for total cyanide as described below in both the chlorinated and the unchlorinated samples. The difference of total cyanide in the chlorinated and unchlorinated samples is the cyanide amenable to chlorination.
5	Prepare an amenable blank using reagent water and an amenable LCS (0.1 µg/mL) with the samples for chlorination, and run a regular total blank and a total LCS with the run for verification.

- **Distillation Procedure**

1	Use Lead acetate paper to check for sulfide. A positive result is indicated by a black color. Add Bismuth nitrate, mix, and retest. Once sulfide is ND, transfer the sample to the distillation vessel. Add additional 2 mL Bismuth nitrate solution through the air inlet tube. Connect the distillation vessel, condenser, gas scrubber and vacuum trap. If the solids are not suspended, extract per 9013A using 1 g solids / 50 mL 0.25N NaOH. Maintain the pH >10. Extract for 16 ± 2 hours. Filter and distill the filtrate.
2	Start a slow stream of air entering the distillation vessel by adjusting the vacuum valve. Adjust the vacuum so that approximately two bubbles of air per second enter the boiling flask through the air inlet tube.
3	Add 2 mL of Sulfamic acid solution through the air inlet tube. Mix for three minutes. **Keep Bismuth nitrate to Sulfamic acid ratio to 1:1.** Note: Excessive use of sulfamic acid could create method bias.
4	Slowly add 5 mL of 18 N Sulfuric acid through the air inlet tube. Rinse the tube with water and allow the airflow to mix the flask contents for three minutes. Add 2 mL of 2.5 M Magnesium chloride through the air inlet and wash the inlet tube with a stream of water.
5	Set the timer to 90 minutes (30 minutes to heat up and 60 minutes at temperature). Continue the airflow for at least 15 minutes after the 60 minutes. After cooling the boiling flask, and closing the vacuum source, disconnect the gas scrubber.
6	Transfer the solution from the scrubber into a plastic, certified, centrifuge tube and analyze on the Lachat or Konelab.

10.2 Calibration: Refer to SOP Selection of Calibration Points / CA-P-T-002 and Calibration Curves (General) / CA-Q-S-005. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

1	Prepare a series of standards by pipetting suitable volumes of working standard potassium cyanide solution in 0.25 N NaOH with a final volume of each standard being 10.0 mL. The

	low standard must be at or below the reporting limit (RL).

mL of 10.0 µg/mL Standard Solution	Final Volume (mL) with 0.25 N NaOH	Concentration (µg/mL)
0.004 mL	10.0	0.004
0.01 mL	10.0	0.01
0.02 mL	10.0	0.02
0.04 mL	10.0	0.04
0.1 mL	10.0	0.1
0.2 mL	10.0	0.2
0.4 mL	10.0	0.4

2	Place calibration standards in test tubes or cuvettes and in the sampler in order of decreasing concentration. Start the method. Obtain absorbance values for the standard curve.
3	Prepare a standard curve by plotting absorbance of standard versus the cyanide concentration. The correlation coefficient (r^2) must be ≥ 0.990 (r ≥ 0.995) or re-calibrate. See Section 11 for applicable equations. Do not use a weighted curve if SC samples are in the batch.

10.3 Automated colorimetric determination (Konelab): Use settings in this table; see SOP Konelab / NV07-141.

Full Name	Total Cyanide				
Online Name		Test In Use	YES		
Test type	Photometric		LOW	HIGH	
		Test limit	0.000	4000.000 µg/L	
Result unit	µg/L	Initial absorbance	-0.010	2.500 A	
Number of Decim.	3	Dilution limit	*	400.0000 µg/L	
		Secondary dil 1+	0.0	9.0	
		Critical limit	*	*	
		Reflex test limit	*	*	µg/L
		Reflex test			
Acceptance	Manual	Reference class	LOW	HIGH	In Use
Dilution 1+	0.0				
Sample type	Water	Correction factor	1.00		
	Raw water	Correction bias	0.00	µg/L	
	Sewage				
Calibration type	Linear				
Repeat time (d)	0	Abs error (mA)	*		
Points/cal.	Single	Rel error (%)	*		
Acceptance	Manual				
Response limit (mA)	MIN	MAX			
	*	*			
Bias correction in	NO				

use					
Cd reduction	NO				
Type of Calibrators	Series				
Calibrator	Conc.	Dil. Ratio			
Cn-400	400.000	1+99.0			
Cn-400	400.000	1+39.0			
Cn-400	400.000	1+19.0			
Cn-400	400.000	1+9.0			
Cn-400	400.000	1+99.0			
Cn-400	400.000	1+3.0			
Cn-400	400.000	1+1.0			
Cn-400	400.000	1+0.0			
Manual QC in Use	YES	Routine QC in Use	YES		
Acceptance	Manual	Interval requests		10	
		Additional condition	NO		
Control	Mean	SD	Control	Mean	SD
Cn-BLANK	0.00	3.00	Cn-BLANK	0.00	3.00
Cn-ICV	100.00	10.00	Cn-CCV	200.00	20.0
Rules in Use		1:1.0 *SD	Rules in Use		1:1.0*SD
Blank		YES	Normal cuvette		
Sample		Volume (µL)		100	
Disp. With		Extra	Add. Volume (µL)	30	
Dilution with		Special	Wash reagent	Water	
Raw Sample					
Disp. With		Extra	Add. Volume (µL)	30	
Special diluent		0.25 NaOH			
Disp. With		Extra	Add. Volume (µL)	10	
Reagent		CN-BUFFER	Volume (µL)	40	
Disp. With		Extra	Add. Volume (µL)	30	
Wash reagent		water			
Reagent wash		Before dispense			
Reagent		CN-CHLOR T	Volume (µL)	4	
Disp. With		Extra	Add. Volume (µL)	30	
Wash reagent		water			
Reagent wash		Before dispense			
Incubation			Time (sec)	60	
Measurement		End point	Blank		
Resp. Min (A)		-0.010	Resp. Max (A)	*	
Reagent		CY-PYR BAR	Volume (µL)	20	
Disp. with		Water	Add. Volume (µL)	30	

Wash reagent		water			
Reagent wash		Before dispense			
Incubation			Time (sec)	480	
Measurement		End point			
Wavelength (nm)		575 nm	Side wavel. (nm)	None	
Meas. Type		Fixed timing			

10.4 Automated Colorimetric Determination for Lachat Auto-analyzer

1	Set up the Lachat auto analyzer (See SOP Lachat / NV07-39).
2	Allow colorimeter and recorder to warm up. Run a baseline with all reagents, feeding reagent water through the sample line.
3	When the baseline becomes steady, begin the analysis.

10.5 Example Analysis Queue / Sequence

1	Initial calibration, if needed
2	ICV, 2nd source, not distilled
3	ICB
4	Method Blank
5	CCV, primary source, not distilled
6	CCB
7	LCS*, 2nd source, distilled
8	Sample 1
9	Matrix Spike
10	Matrix Spike Duplicate
11	Samples 2-10
12	CCV, primary source, not distilled
12	CCB
13	Samples 11-20 (up to 20 samples)
14	CCV, primary source, not distilled
15	CCB

*For AZ, TX, WV samples, a LCS duplicate is required.

11.0 Calculations / Data Reduction

11.1 Accuracy

LCS % Recovery = $\frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$

11.2 Precision (RPD)

RPD = $\frac{\text{Absolute value (orig. MS value - dup. MS value)} \times 100}{\text{(Orig. MS value + dup. MS value)/2}}$

11.3 Linear calibration using a least squares regression: A linear calibration model based on a least squares regression of instrument response versus the concentration of the analyte is employed. Ensure that the instrument response is treated as the dependent variable (y) and the amount as the independent variable (x). This is a statistical requirement and is not simply a graphical convention.

For external standard calibration, x is the mass of the analyte in the sample aliquot introduced into the instrument, and y is the area of the response, as in:

$x = C_s$ and $y = A_x$

A linear least squares regression constructs a linear equations of the form:

$y = ax + b$

By minimizing the differences between the observed results (y_i, the instrument response) and the predicted results (y'_i, the response calculated from the constructed equation). The regression equation is

$y'_i = ax_i + b$

a = Regression coefficient or the slope of the line.
b = the y-intercept.
y'_i = Predicted (or calculated) response for the i^{th} calibration standard.
x_i = concentration of analyte in the i^{th} calibration standard aliquot introduced into the instrument.

The sum of the squares of the differences is minimized to obtain a and b:

$$\sum_{i=1}^{n}(y_i - y'_i)^2$$

where n is the total number of calibration points. The regression calculations attempt to minimize this sum of the squares, hence the name "least squares regression."

Weighting the sum of the squares of the differences may significantly improve the ability of the least squares regression to fit the linear model to the data. The general form of the sum of the squares of the differences containing the weighting factor is:

$$\sum_{i=1}^{n}(y_i - y'_i)^2 w_i$$

w_i = Weighting factor for the i^{th} calibration standard (w = 1 for unweighted least squares regression).
y_i = Observed instrument response (area for the i^{th} calibration standard.
y'_i = Predicted (or calculated response for the i^{th} calibration standard.
n = total number of calibration standards.

The mathematics used in least squares regression has a tendency to favor numbers of larger value over numbers of smaller value. Thus the regression curves that are generated tend to fit points that are at the upper calibration levels better than those points at the lower calibration levels.

To compensate for this, a weighting factor which reduces this tendency can be used. Examples of weighting factors which can place more emphasis on numbers of smaller value are:

$w_i = 1/x_i$ or $w_i = 1/x^2$

There are numerous other ways to define weighting factors, but these are recommended if a weighting factor other than 1 ($w_i = 1$) is to be used.

11.4 Coefficient of Determination

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2}$$

Correlation Coefficient

$$r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response
x = Concentration

11.5 Result Calculation: Concentrations of samples are calculated by the instrument by comparing sample peak response with the calibration curve to determine the concentration:

Concentration (mg/L or µg/g) = $\frac{\text{(Conc. (µg/mL), instrument) x Dilution X Volume Scrubber (mL)}}{\text{Volume (mL) or Mass (gram)}}$

Dilution =1 if no dilution

Note: Amenable CN = Total CN-Treated tube reading.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average %

recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes must be stored, managed, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Aqueous alkaline material from the auto-analyzer/titrations is disposed of in the hazardous waste, toxic, corrosive drum in the waste disposal area.

15.0 References / Cross-References

15.1 EPA Method 9012A, SW-846 Update III Revision 1, December 1996; **9010B and 9012B**, SW-846 Update IIIB Revision 2, November 2004, **9013A**, Revision 1, November 2004, **9014** Revision 0, December 1996.

15.2 Lachat Method 10-204-001-A.

15.3 Konelab Methods and Instrument Manuals.

15.4 TestAmerica Nashville's Quality Assurance Manual.

15.5 TestAmerica Nashville's Control Limits Manual.

15.6 Corporate Environmental Health and Safety Manual (CW-E-M-001)

15.7 SOPs: Calibration Curves (General) / CA-Q-S-005, Selection of Calibration Points / CA-P-T-002, Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Determination of Method Detection Limits / NV08-202, Lachat / NV07-39, Konelab / NV07-141, Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214, Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

15.8 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

Item	Modification
1	Treatment for samples with sulfide interference
2	Lachat Auto-analyzer
3	Konelab Automated Analyzer

17.0 Attachment

None.

18.0 Revision History

- Revision 7, 30 June 2008
  - Integration for TestAmerica and STL operations.
- Revision 8, 23 October 2009
  - Addition of preparation of prep blank.
  - Addition of OH VAP statements for prep blank and LCS.
  - Addition of Corporate Environmental Health and Safety Manual, Lachat, Konelab, and Standard/Reagent SOPs to reference section.
- Revision 9, 29 June 2010
  - Removal of reference to EPA 335.2 CLP-M.
  - Addition of Section 14.2, QAF-45, and the use of weighted calibration curves.
- Revision 10, 31 October 2012
  - Organizational changes.
  - Add methods 9013A and 9014.
  - Add SOPs Calibration Curves (General) / CA-Q-S-005 and Sample Homogenization, Sub-sampling, and Compositing / NV08-229 (Amendment 9b).
  - Add that SC does not allow a weighted curve (Amendment 9a).
  - OK and WY no longer limit batches to 10 samples.
  - Specify that $r^2 \geq 0.990$.
  - Remove requirement for sample duplicate and for a high and low distilled standard.
  - Modify analytical sequence.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure
(SOP) Change Form

SOP Number/Revision No.: **9045 / NV03-54.8** Effective Date: 10/31/2013

Last Mod. Date: 6/29/12

SOP Title: **METHOD 9045 C/D: SOIL AND WASTE PH, CORROSIVITY**

Affected SOP Section Number(s): **Section 10.1, Sample Preparation, 10.3, Sample Analysis, Section 15.0, References / Cross-References**

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 03T

Revision Number with Mod ID: **8a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add bold text.

Title Page: Add to the title:
METHOD 9045C/D **AND LDNR 29-B.**

Section 10.1, Sample Preparation: Add a new bullet (second position):

- **For LDNR 29-B, prepare as described in SOP LDNR 29-B Soil Preparation / NV03-251.**

Section 10.3, Sample Analysis, first table For Soils: Add to step 4:
For LDNR 29-B, report the results as "pH, 1:1 aqueous."

Section 15.0, References / Cross-References: Add reference to SOP **LDNR 29-B Soil Preparation / NV03-251**.

10/31/13	10/23/13
Department Manager Approval Date	Extractions Operations Manager Approval Date
10/23/13	
Technical and Quality Assurance Approval Date	

Title: SOIL AND WASTE pH, CORROSIVITY SW-846 METHOD 9045C/D

Approvals (Signature/Date)

Jacoby Robinson 6-6-12 Department Manager	Johnny Davis 6-6-12 Health & Safety Manager / Coordinator Extractions Operations Manager
Eric S. Smith 6/27/12 Quality Assurance Manager	Michael H. Dunn 6-7-12 Technical Director

1.0 Scope and Application

1.1 Analyte, Matrices: This method is an electrometric procedure for measuring pH in soils and waste samples. Wastes may be solids, sludges, or non-aqueous liquids. If water is present, it must constitute less than 20% of the total volume of the sample.

1.2 Reporting Limits: The practical range of the determination is from 0-14 pH units.

1.3 If for any reason a part of this SOP cannot be followed, seek the guidance of the Department Supervisor or the Laboratory Technical Director. All abnormalities must be noted on the data or the benchsheet and in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

The sample is mixed with reagent water, and the pH of the resulting aqueous solution is determined electrometrically.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 The pH electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or moderate salinity.

4.2 Errors occur when the electrodes become coated. If an electrode becomes coated with an oily material that will not rinse free, the electrode can be

1) gently wiped followed by reagent water rinse;
2) cleaned with an ultrasonic bath,
3) washed with detergent, rinsed several times with water, placed in 1:10 HCl so that the lower third of the electrode is submerged, and then thoroughly rinsed with water, or
4) wiped with Acetone to clean oily residue.

4.3 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference is controlled with instruments having temperature compensation. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled; it should therefore be noted by reporting both the pH and temperature at the time of analysis.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: None.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation:

- pH meter with thermometer or temperature sensor for automatic compensation. A wide variety of instruments are commercially available with various specifications and optional equipment, Accumet or equivalent.
- Glass or polymer combination. Accumet flat surface polymer-body electrode or equivalent.

6.2 Supplies

- Magnetic stirrer and Teflon™ - coated stirring bar.
- 250-mL flasks; 150-mL beakers; disposable, plastic, centrifuge tubes.

7.0 Reagents and Standards

7.1 Reagent water, 6.85-7.15 pH range.

7.2 Standard buffers, (pH 1, 4, 7, 10 and 13) are purchased as solutions from commercial vendors. Use of these commercially available solutions, validated by comparison to NIST standards, is required for routine use. **Opened buffers are valid for one month.** Other buffers may be used provided they bracket the sample pH. Add a single pH buffer from a second-source.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Soil/ Waste	HDPE	20 grams	Cool 0-6°C;	As soon as possible but no more than 15 minutes	SW-846 Chapter 2

Chemical preservation is not used.

9.0 Quality Control

Refer to the quality control section of TestAmerica Nashville's QA Manual for specific quality control (QC) procedures. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

Quality Controls	Frequency	Control Limit
Reagent water check	1 in 20 or fewer samples	pH 6.85-7.15
Initial Calibration Verification (ICV) / Laboratory Control Sample (LCS), second-source	1 in 20 or fewer samples	±1% true; for pH 7, ± 0.05 pH unit of known.
Continuing Calibration Verification (CCV) (buffers, same source as calibration.)	1 in 10 or fewer samples and at the end of the run	± 0.1 pH units
Sample Duplicate	1 in 20 or fewer samples	± 0.1 pH units

9.1 Sample QC: Sample duplicate.

9.2 Instrument QC: The pH buffers (CCVs) serve as quality control for the pH meter.

10.0 Procedure

10.1 Sample Preparation

- See Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
- All samples and standards must be at similar temperatures.
- Electrodes must be thoroughly rinsed with reagent water between samples.

10.2 Calibration

- Each analyst must be acquainted with the operation of each system and familiar with all instrument functions.
- **For pH determination**, each instrument/electrode system must be calibrated as described in Section 17.1 at 4, 7, and 10 (and 1 and 13 pH units where necessary) in order to bracket the pH of the samples and are approximately three pH units or more apart.
- **For corrosivity determination,** the calibration must include a pH 1 buffer for acidic wastes and a pH 13 buffer for caustic wastes; also, for corrosivity characterization, the sample must be measured at 25 ± 1°C if the pH of the waste is above 11.0.
- Various instrument designs may involve use of a "balance" or "standardize" dial and/or a slope adjustments as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the buffer solutions until readings are within 0.05 pH units of the buffer solution value. If this cannot be met, clean the electrode, replace electrolyte or electrode, and record in the maintenance log. Note: This criterion establishes adequate electrode function and the acceptability of the slope. The slope should be 90-102 for acceptance.
- For detailed operating procedures, see the manufacturer's instructions.

10.3 Sample Analysis: See Section 17 flowchart.

For Soils:	
1	To 20 gram sample in a centrifuge tube or beaker, add 20 mL reagent water, cover, and continuously agitate the suspension for 5 minutes. Record the start and stop times on the benchsheet. Additional dilutions are allowed if working with hygroscopic soils, salts, or other problematic matrices.
2	Let the soil suspension stand for one hour to allow most of the suspended particles to settle out from the suspension or centrifuge off the aqueous phase for pH measurement.
3	Adjust the electrode so that, upon lowering the electrode into the container, the electrode is immersed just deep enough (approximately 1 inch) into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole.
4	Record the pH and temperature results using controlled document, IF-36, pH runlog/soil, as "Soil pH measured in water at __°C."

For Non-aqueous Waste Materials:	
1	To 20 gram sample in a centrifuge tube or beaker, add 20 mL reagent water, cover, and continuously agitate the suspension for 5 minutes. Record the start and stop times on the benchsheet. Additional dilutions are allowed if working with hygroscopic soils, salts, or other problematic matrices.
2	Let stand for about 15 minutes or centrifuge.
3	If the waste is hygroscopic and absorbs all the reagent water, begin the experiment again using 20 g of waste and 40 mL of reagent water.
4	If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode should be cleaned if it becomes coated with an oily material.

5	Adjust the electrode so that, upon lowering the electrode into the container, the electrode is immersed just deep enough (approximately 1 inch) into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole.
6	Record the pH and temperature using controlled document, IF-36, pH runlog/soil. Report the results as "Waste pH measured in water at _____°C".

10.4 Example Analysis Queue / Sequence*

1	ICV/LCS (second source)
2	Samples 1-10
3	CCV
4	Samples 11-20
5	Sample Duplicate
6	CCV

*May be up to 20 samples

11.0 Calculations / Data Reduction

11.1 Accuracy

< 0.1 pH unit difference between known pH and measured pH.

$$\% \text{ Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD): <0.1 pH units difference between two duplicate measurements.

11.3 pH meters read directly in pH units. Report pH to the nearest 0.1 unit and temperature to the nearest degree C.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): Not applicable.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must

abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes must be stored, managed, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- If the sample pH is < 5 or > 10, take sample to the waste disposal area for neutralization, then discharge into the sewer.
- If the sample pH is >5 or < 10, discharge into the sewer.

15.0 References / Cross-References

15.1 SW-846 Method 9045 C (Update IIB, January 1995) and 9045 D (Update IIIB, November 2004).
15.2 TestAmerica Nashville's Quality Assurance Manual
15.3 TestAmerica Nashville's Control Limits Manual
15.4 Corporate Environmental Health and Safety Manual (CW-E-M-001).
15.5 SOPs: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213, Determination of Method Detection Limits / NV08-202, Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
15.6 Controlled Documents: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions, IF-36, pH runlog/soil.

16.0 Method Modifications

None.

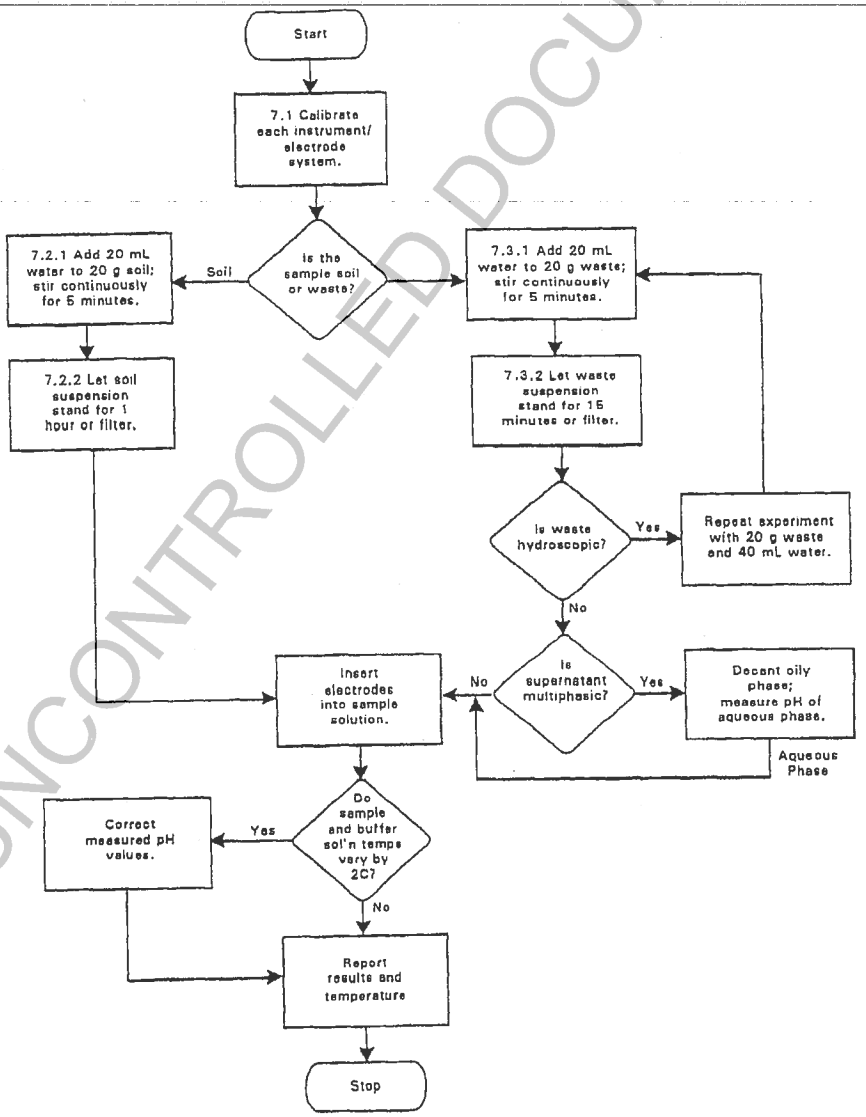
17.0 Attachment

17.1 Specific Calibration Procedures for Fisher Scientific Accumet pH Meters

	Model XL15
1	Clean electrode.
2	Replace buffer solutions with new aliquots.
3	Log buffer lot #s on the log sheets.
4	Place electrode in buffer pH 4 and let stabilize. Push the standardize button, "OK" to clear buffers.
5	Let stabilize, push "4.00, enter" and record pH.
6	Rinse probe and place in pH 7 buffer.
7	After stabilized, push "7.00, enter" and record pH.
8	Rinse probe and place in pH 10 buffer.

9	After stabilized, push "10.00, enter" and record pH.
10	Rinse probe and place in ICV; record pH.
11	If sample pH is below 4.00, recalibrate using pH buffers 1, 4 and 7.
12	If sample pH is above 10.00, recalibrate using pH buffers 7, 10, and 13.

17.2 Soil and Waste pH Flowchart (from SW-846 9045D, November 2004).



18.0 Revision History

- Revision 6, dated 30 April 2008
  - Integration for TestAmerica and STL operations.

- Further detail about calibration slope acceptability
- "but no vortex" added to description of mixing step.

- Revision 7, dated 31 March 2010
  - Addition of Section 14.1, QAF-45, Acetone to Section 5 Safety table.
  - Addition of ICV/LCS
  - Addition of %recovery and average equations.
- Revision 8, dated 29 June 2012
  - Organizational changes.
  - Removal of sample duplicate for each sample; changed to one per batch.
  - Addition of reagent water pH check.
  - Addition of SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
  - Change Section 10.3, Sample Analysis. Add reference to the controlled document, IF-36, pH runlog/soil.
  - Add second-source standard.
  - Revised calibration procedure in Section 17.
  - Add flowchart from SW-846 9045D in Section 17.
  - Change waste disposal pHs to agree with the Waste Disposal SOP.

Title: TOTAL ORGANIC CARBON, TOTAL INORGANIC CARBON, AND TOTAL CARBON SW-846 METHOD 9060A

Approvals (Signature/Date)			
Ronald Martin Department Manager	3/20/13 Date	Matt Ricke Inorganics Operations Manager	3/14/13 Date
Michael H. Dunn Technical Director Quality Assurance Manager	3/29/13 Date	Johnny Davis Health & Safety Manager / Coordinator	3/27/13 Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method determines the concentration of organic and inorganic carbon in drinking water, surface and saline waters, domestic and industrial waters, groundwaters, and organic carbon in soils, and wastes.

1.2 Reporting Limits: The reporting limit is 1.0 mg/L and 1000 mg/kg for soils.

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor or the Technical Manager. All abnormalities must be noted on the data or the benchsheet and in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 Carbon is measured using a carbonaceous analyzer. This instrument converts the organic carbon in a sample to carbon dioxide (CO_2) by catalytic combustion or chemical oxidation. The CO_2 formed is then either measured directly by an infrared detector. The amount of CO_2 in a sample is directly proportional to the concentration of carbonaceous material in the sample.

2.2 Carbonaceous analyzers are capable of measuring all forms of carbon in a sample. However, because of various properties of carbon-containing compounds in liquid samples, the manner of preliminary sample treatment as well as the instrument settings will determine which forms of carbon are actually measured. The forms of carbon that can be measured are soluble, dissolved, nonvolatile organic carbon: e.g., natural sugars.

3.0 Definitions

See the Quality Assurance Manual Appendix 5 for laboratory definitions. Also, refer to Controlled Document, QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

4.0 Interferences

Carbonate and bicarbonate carbon represent interferences under the terms of this test for Total Organic Carbon (TOC) and are removed by acidification and sparging. Removal of carbonate and bicarbonate by acidification and purging can result in the loss of volatile organic substances. This is not removed when determining Total Carbon (TC).

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous.

5.1 Specific Safety Concerns or Requirements: Be sure to wear personal protective equipment when performing this method: safety glasses, disposable gloves, and labcoat, at a minimum. Use caution in handling chemicals and hot surfaces.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Phosphoric Acid	Corrosive	1 mg/m^3 TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
Sodium Persulfate	Oxidizer Corrosive	0.1 mg/m^3-TWA as Persulfates	**STRONG OXIDIZER.** Causes irritation to the respiratory tract. Symptoms may include sore throat, shortness of breath, inflammation of nasal passages, coughing, and wheezing. Causes severe irritation or burns to the skin and eyes. Symptoms include redness, itching, pain and burns. May cause allergic skin reactions. Can cause eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Analytical system:
  - Carbon Analyzer, Shimadzu and O. I. Analytical.
  - Recording device.
- Analytical balance capable of weighing to the nearest 0.001 g.

6.2 Supplies

- Sample boats for solids samples.
- Copper beads/filaments.
- Dri-rite.
- Syringe filters, 25 mm, 0.45 µm Polyethersulfone, VWR or equivalent.
- Disposable syringes, 10 mL, Luer-lock.

7.0 Reagents and Standards

7.1 Reagent grade chemicals are used in all tests. Unless otherwise, indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. See the QA Manual and SOP Reagent and Standard Purchase / NV08-214 for more information on reagent chemicals.

7.2 Reagent water, carbon-free.

7.3 Millipore water.

7.4 Hydrochloric acid, 50% and concentrated.

- 1N: For soil sample preparation, add 167 mL of 50% HCl to 1000 mL Millipore water.
- 2N: For the Shimadzu instrument, prepare a 2N HCl by adding 83 mL concentrated HCl to 500 mL Millipore water. The shelf-life is 6 months after preparation.

7.5 Phosphoric acid (85%): For the O. I. instrument, prepare a 5% H_3PO_4 by adding 59 mL of 85% H_3PO_4 to reagent water for a total volume of 1 L. The shelf-life is 6 months after preparation.

7.6 Organic and Total Carbon Standard: Potassium hydrogen phthalate, stock solution, 1,000 µg/mL carbon: Dissolve 2.125 g of Potassium hydrogen phthalate (primary standard grade) in reagent water and dilute to 1000 mL. Commercially purchased standard is acceptable. Preserve with HCl to pH ≤ 2 pH units.

- Primary standard: SigmaUltra P1088, or equivalent, 99.95%.
- Second-source standard: Fisher P243, or equivalent, 99.99%.

7.7 Soil Organic and Total Carbon Standard: The primary standard is Ammonium oxalate, 16.9%, commercial. The second-source standard is NIST Marine Sediment 19416, or equivalent, 2.99%, or Glucose, 49%.

7.8 Carbonate-bicarbonate, stock solution (inorganic carbon standard), 1,000 µg/mL carbon: Weigh 3.50 g of Sodium bicarbonate (Mallinckrodt 7396-04, or equivalent) and 4.42 g of Sodium carbonate (EM Science SX0395-11, or equivalent) and transfer both to the same 1000 mL volumetric flask. Fill to mark with reagent water. Shake until dissolved.

- **Inorganic Performance Check Standard**: Dilute the carbonate-bicarbonate standard to a concentration of 100 µg/mL.

7.9 Sodium persulfate: Prepare a 20% solution of $Na_2S_2O_8$ by dissolving 200 g of $Na_2S_2O_8$ in reagent water for a total volume of 1 L. Stirring may be necessary, but do not heat. **WARNING: STRONG OXIDIZER**.

7.10 See SOP Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214 for information on shelf-lives and storage requirements.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water*	Amber Glass	125 mL, 40-mL VOA	For TOC: pH < 2 with sulfuric acid. Cool 0-6°C, No headspace. Keep in dark. For TIC and TC, do not acidify.	28 days	SW-846 Section 2.0.
Soil	Amber Glass	2 oz glass	Cool 0-6°C.		

*If dissolved TOC is requested, field-filter or lab-filter **prior** to acidification.

9.0 Quality Control

Refer to the quality control section of TestAmerica Nashville's QA Manual for specific quality control (QC) procedures. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

Quality Controls	Frequency	Control Limit	Corrective Action
Inorganic Performance Check	Beginning of each day	For TOC, <5.0 mg/L with proper sparging. For TC, >50% true.	Re-prep, rerun
Method Blank (MB)	Beginning of each day	< 1 µg/mL	Re-prep, rerun
Initial Calibration Verification Sample (ICV) (second source)	Immediately after initial calibration.	90-110% recovery	Re-calibrate, rerun
Laboratory Control Sample* (LCS) (second source)	1 at the beginning of each batch of 20 or fewer samples	90-110% recovery	Re-run. OK to report if high and samples ND.
Matrix Spike (water only)	1 in 10 or fewer samples	See LIMS for % recovery	Report, qualify if needed. OK to report if high and samples ND.
Sample Duplicate (soil only)	1 in every 10 or fewer samples	See LIMS for RPD	Report, qualify if needed.
Continuing Calibration	1 every 10 samples	90-110% recovery	Correct, recalibrate. OK to

Quality Controls	Frequency	Control Limit	Corrective Action
Verification Sample (CCV)			report if high and samples ND.
Continuing Calibration Blank (CCB)	Following the CCV	< RL	Re-prep, rerun.

*AZ, TX, and WV require LCS duplicates.

9.1 Sample QC: The following quality control samples are prepared with each batch of samples. A batch is no more than 20 samples,

- **System Blank**: Run one blank per batch to determine if contamination or any memory effects are occurring. Result must be less than the report limit.
- **Method Blank**: Run one per batch. The result must be less than 1.0 µg/mL and 0.1% for soils.
- **Laboratory Control Sample (LCS)**: Analyze a second-source standard each batch.
- **Matrix Spike (MS), water only**: Run a MS every 10 samples or less and bring through the entire sample preparation and analytical process. Spike with 20 µg/mL. In a batch of 10 or
- more, spike two different client samples.
- **Sample Duplicate (soil only)**: Run one soil sample duplicate every 10 samples.
- **For Dissolved TOC,** all QC samples must be filtered prior to analysis.

9.2 Instrument QC

- **Inorganic Performance Check Standard:** Analyze once per day to confirm the effectiveness of acidification and sparging, not acidified for TC.
- **Continuing Calibration Verification (CCVs)**: Analyze a mid-range CCV at the start of the batch, one every 10 samples and at the end of the batch.

10.0 Procedure

10.1 Sample Preparation

Matrix	Sample Size
Water	40 mL
Soil	5 g

- **Soil Sample Preparation**

1	Analyze every soil sample in replicate. Note: For South Carolina samples, all analysis must be in quadruplicate. For each, weigh out approximately 5 grams of soil into a 150 mL beaker or equivalent. Add about 5 mL of 1N HCl, mix well, and dry at about 103°C for about 4 hours. For Total Carbon, do not add acid.
2	Homogenize dried material.
3	Weigh up to 200 mg of sample in a ceramic boat, enter the exact weight into the analyzer, and analyze. Record weight. If the result is greater than the upper standard, reduce the weight of the sample and re-analyze.

- **TOC**: Acidify.
- **TC**: Do not acidify.
- **Dissolved TOC**: Filter non-preserved sample and QC samples through a 25 mm, 0.45-µm, Luer-lock filter. Record filter ID and lot number.

10.2 Calibration: Refer to SOP Selection of Calibration Points / CA-T-P-002. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

10.2.1 For **TOC and TC water**, prepare calibration standards as follows:

Vol. of Stock Std. (mL)	Final Volume (mL)	Concentration (µg/mL)
0	50	0
5.0 mL of 10 ppm	50	1.0
0.5	50	10
1.25	50	25
2.5	50	50

10.2.2 For **Total Inorganic Carbon Water**: Prepare a series of standards using the Carbonate-bicarbonate standard solution as follows:

Vol. of Stock Std. (mL)	Final Vol. (mL)	Concentration (µg/mL)
0.05	50	1.0
0.50	50	10
1.25	50	25
2.50	50	50

10.2.3 For **TOC or TC soil**, , prepare calibration standards using the primary soil organic carbon standard as follows:

Mass of Stock Std. (mg)	Concentration (%)
5	5
10	10
25	25
50	50

10.2.4 Correlation coefficient (r) must be ≥ 0.995 (or r^2 ≥ 0.990), or correct the problem and re-calibrate.
10.2.5 Shift through origin may be used.

10.3 Sample Analysis
10.3.1 For **Shimadzu Instrument for Water Samples**

1	Turn on oxygen gas, initiate start-up, check rotameter for flow.
2	Allow instrument to reach operating temperature. Unit is operational when “ready” light is illuminated.
3	Inject **water blank** until less than 1.0 µg/mL.
4	Using organic or inorganic working standards, calibrate using at least 3 standards per curve. The correlation coefficient (r) must ≥ 0.995 (or r^2 ≥ 0.990).
5	**Initial Calibration Verification (ICV) Standard:** Verify calibration using certified standards from 2nd source. The standard must be within 10% of the true value.
6	Daily check instrument using mid-point calibration standard (**Continuing Calibration Verification (CCV) Standard**). If the daily standard is not within 10% of the true value, recalibrate.
7	Transfer about 35 mL of sample to autosampler. Samples with significant particle content should be well mixed before removal.
8	For TOC, acidify and set Sparge to 3 minutes. For TIC or TC, do not sparge or acidify. Analyst must confirm that the instrument is sparging. Run 100 µg/mL inorganic standard

	to confirm sparging performance. Result < 5 µg/mL. For TC, >50% true.
9	Analyze water samples in quadruplicate or until <10% difference is obtained, and report average. If concentration exceeds calibration, dilute with reagent water and reanalyze. Record dilution.
10	To shut down: Initiate "finish" command from stand-by option.(main menu)
11	After cool, initiate "stand-by", turn "off" screen. Do not turn off main power switch.

10.3.2 For **Shimadzu Instrument for Soil Samples**

1	Turn on the instrument for sample measurement.
2	Select "New."
3	Scroll down to "TOC or SSM" and enter "2" (SSM), "OK," [right click], "Insert Multiple Samples."
4	Select "Calibration."
5	The calibration type is "ssmtc.cal." Enter the number of samples.
6	Enter the mg of the four standards of 16.9% for Ammonium oxalate. Verify with the second-source soil standard.
7	Open TC sample module door, place boat with sample inside; close door and tighten the handle. Note: Do not leave the sample door open.
8	Press "start"; the screen displays the message "push in sample boat."
9	Slowly and smoothly push in the sample boat, by moving the lever to the measurement mark.
10	Follow the instruction to "slowly and smoothly pull the boat back to cool."
11	Pull the lever to the cool mark and wait 30 seconds. (The screen displays a 30 second count down.) At the end of the 30 seconds, pull the lever back to the sample change mark. The screen displays the message "For additional sample measurement press start."
12	Press "start" and continue with the analysis of the calibration standards. After the last standard is analyzed. Check that the correlation r is 0.995 or greater (or $r^2 \geq 0.990$).
13	For the analysis of samples: Go back to the main menu. Select 2 "sample measurement" and press "enter." Enter the sample weight in mg." Press "start." Continue with Steps 7 through 11.
14	Run a replicate, or quadruplicate as required, analysis by pressing "start" and entering the weight of the sample. If the first analysis is above the range of the curve, analyze another portion using less weight.
15	Report the average of the analyses.

10.3.3 For the **O.I. Analytical Instrument**

1	Open WINTOC program. For TOC, select "NPOC method." For TIC, select "IC method." For TC, select "TC method."
2	Click on "Setup" and select "WINTOC Output." Enter: Month and Year for Subdirectory. Enter: Month, Day, Year for Log File Name. Enter: Month, Day for Prefix. Return counter to 1. Click [OK].
3	Click on "Instrument" and select "Calibration."
4	Click on [NEW]. Enter in calibration points (0, 1, 10, 25, 50 µg/mL), making sure to check boxes for each
5	Click [SAVE AS] and give appropriate file name to correspond with Log File Name. Click

	[OK]
6	Click on “Databases” and select “Sequences.” Click on [NEW].
7	Enter calibrators, QC, and samples in lines corresponding to positions on tray. For each, designate correct method and sample type (sample, check standard, standard) from the pull-down menus. For check standards and standards, designate standard number that corresponds to calibration table set up previously.
8	Click [SAVE AS] and give appropriate file name to correspond with Log File Name.
9	Click [OK].
10	Verify that proper calibration file name appears in “Current Calibration” window and that “Sequence Status” is “Not Running” and “current state” is “Standby.”
11	Click [START] to run tray. Verify positions to be sampled when prompted and click [OK].
12	All samples are analyzed in quadruplicate. Report the average.

10.4 Example Analysis Queue / Sequence*

1	Initial calibration, if needed.
2	ICV, if calibration needed.
3	System Blank
4	Inorganic Performance Check Standard (not used for TIC or soils)
5	CCV
6	LCS
7	Sample 1
8	Matrix Spike (water batch); Sample Duplicate (soil batch)
9	Samples 2-10
10	CCV
11	CCB
12	Sample 11
13	Matrix Spike (water batch); Sample Duplicate (soil batch)
14	Samples 12-20*
15	CCV
16	CCB

*May be up to 20 samples
*AZ, TX, and WV require LCS duplicates.

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\text{LCS \% Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 Coefficient of Determination Correlation Coefficient

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2} \qquad r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response
x = Concentration

11.4 Concentration Calculation

- For water samples µg/mL = (µg/mL instrument)(Dilution factor). Default dilution factor is 1.
- For soil samples (µg/kg) = (µg instrument)(Dilution factor)/sample weight (g).

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes must be stored, managed, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Sample and reagent wastes are taken to the neutralization tank in the disposal area; after neutralization, they are discharged to the sanitary sewer.

15.0 References / Cross References

15.1 EPA Method 9060A, SW-846 Update IIIB, November 2004.
15.2 TestAmerica Nashville's Quality Assurance Manual.
15.3 TestAmerica Nashville's Control Limits Manual.
15.4 SOPs: Selection of Calibration Points / CA-T-P-002, Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213, Determination of Method Detection Limits / NV08-202, Reagent and Standard Purchase / NV08-214.
15.5 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachment

None.

18.0 Revision History

- Revision 6, 15 May 2009
  - Integration for TestAmerica and STL operations.
  - Change in calibration curve concentrations.
  - Add interferences in Section 4.0.
  - Correct table in Section 9.0 for Inorganic Performance Check control limit.
  - Change wording about CCV in Section 9.2 to reflect current practice on CCV sequence in the batch.
  - Remove lines to be completed in Section 6.2 and add supplies.
  - Change concentration of sodium persulfate from 10% to 20%.
  - Add phosphoric acid shelf-life.
- Revision 7, 30 December 2009
  - Inclusion of changes from Amendment 6a.
  - Add preparation instructions for dissolved TOC.
  - Add filter and disposable syringe information.
- Revision 8, 30 April 2010
  - Remove separate calibration standard preparation for Shimadzu analyzer.
  - Add Section 14.2, Wastestreams.
  - Revision 9, 31 May 2011
- Revision 9, 31 May 2011
  - Add amendment 8a.
  - Organizational changes in signature block.
  - Add soil calibration.
  - Add vendor/catalog numbers of standards.
  - Change maximum concentration for inorganic performance check.
  - Modify soil sample analysis procedure.
  - Quadruplicate analysis for S.C. soils.
  - Addition of RSD for O. I. Instrument.
- Revision 10, 31 October 2012
  - Organizational changes.

- Add Total carbon.
- Specify that $r^2 \geq 0.990$.
- Require quadruplicate analysis for the Shimadzu instrument.
- Remove the need for a Report Level Verification sample.
- Modify the analytical sequence.

- Revision 11, dated 29 March 2013
  - Remove shelf life of 3 weeks for Sodium persulfate.
  - Change Sample QC to have a matrix spike for water batches and a sample duplicate for soil batches.
  - Only one curve is needed.
  - Add that all water samples are run in quadruplicate and the results averaged.
  - ICV is required only immediately after ICAL.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP)
Change Form

SOP Number/Revision No.: **9095 / NV07-52.7** Effective Date: **3/31/2014**

Last Mod. Date: 1/31/13

SOP Title: **Method 9095: Paint Filter Liquids Test**

Affected SOP Section Number(s): Various

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 07

Revision Number with Mod ID: **7a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

☐ Procedural Changes (Define Below) – Re-Training Required.

■ Other

2. Summary of Procedure Change: Make bold the underlined text

Section 1.1, Analyte, Matrices: This procedure is used to determine the presence of **free liquids** in a representative sample of waste and for determining compliance with 40 CFR 264.314 and 265.314.

Section 2.0, Summary of Method

A predetermined amount of material is placed in a paint filter. If any **liquid** portion of the material passes through and drops from the filter within the 5-minute test period, the material is deemed to contain free liquids.

Section 4.0, Interferences

Temperature can affect the test results if the test is performed below the freezing point of any **liquid** in the sample.

Section 8.0, Sample Collection, Preservation, Shipment and Storage, next to last sentence:

If any portion contains **free liquids**, the entire sample is considered to have free liquids.

Section 10.3, Sample Analysis, Step 5:

If any **liquid** portion of the test material collects in the graduated cylinder in the 5-minute period, then the material is deemed to contain free liquids for purposes of 40 CFR 264.314 and 265.314.

Sessily Overton-May 3/19/14	
Department Manager Approval Date	
Steve Shilley 3/19/14	Michael A. Brown 3/19/14
Quality Assurance Manager Date	Technical Director Approval Date

Title: PAINT FILTER LIQUIDS TEST
SW-846 METHOD 9095B

Approvals (Signature/Date)			
Ronald Martin Department Manager	11/13/12 Date	Matt Ricke Inorganics Operations Manager	1/11/13 Date
Michael H. Dunn Technical Director Quality Assurance Manager	10/15/12 Date	Johnny Davis Health & Safety Manager / Coordinator	1/22/13 Date

1.0 Scope and Application

1.1 Analyte, Matrices: This procedure is used to determine the presence of free liquids in a representative sample of waste and for determining compliance with 40 CFR 264.314 and 265.314.

1.2 Reporting Limits: The result is reported as "Free Liquids" or "No Free Liquids."

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor or the Technical Director. All abnormalities must be noted on the data or the benchsheet and in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

A predetermined amount of material is placed in a paint filter. If any portion of the material passes through and drops from the filter within the 5-minute test period, the material is deemed to contain free liquids.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

Temperature can affect the test results if the test is performed below the freezing point of any liquid in the sample. Tests are performed at room temperature of 25 ± 3°C.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: None.

5.2 Primary Materials Used: None.

6.0 Equipment and Supplies

6.1 Apparatus

- Conical paint filter: Mesh number 60 ± 5% (fine meshed size, 0.0098 inch or 0.25 mm, 250-280 µm). Available at local paint stores such as Sherwin-Williams and Glidden.

6.2 Supplies

- Glass funnel: If the paint filter, with the waste, cannot sustain its weight on the ring stand, then a fluted glass funnel or glass funnel with a mouth large enough to allow at least 1 inch of the filter mesh to protrude is used to support the filter. The funnel is fluted or has a large open-mouth in order to support the paint filter, yet not interfere with the movement, to the graduated cylinder, of the liquid that passes through the filter mesh.
- Ring stand and ring, or tripod.
- Graduated cylinder, Class A, 100 mL.

7.0 Reagents and Standards

None.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Liquid waste	Plastic or Glass	100 mL or 100 grams	None.	Not applicable	SW-846 Section 3.0

A 100 mL or 100 g representative sample is required for the test. If it is not possible to obtain a sample of 100 mL or 100 g that is sufficiently representative of the waste, the analyst may use larger size samples in multiples of 100 mL or 100 g, i.e., 200, 300, 400 mL or g. However, when larger samples are used, analysts shall divide the sample into 100 mL or 100 g portions and test each portion separately. If any portion contains free liquids, the entire sample is considered to have free liquids. If the sample is measured volumetrically, then it should lack major air spaces or voids.

9.0 Quality Control

Refer to the quality control section of TestAmerica Nashville's QA Manual for specific quality control (QC) procedures. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC

The following quality control samples are prepared with **each batch of no more than 20 samples.**.		
Quality Controls	**Acceptance Criteria**	**Corrective Action**
Sample Duplicate	Same result as original sample	Repeat.

- **Sample Duplicate**: Run a second aliquot of at least one client sample per group of 20 samples. The results should be the same.

9.2 Instrument QC: Not applicable.

10.0 Procedure

10.1 Sample Preparation

- Sample size:

Matrix	Sample Size
Waste	100 mL or 100 g

- Refer to SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
- Set up the filter and funnel.
- Bring the sample to room temperature.

10.2 Calibration

Not applicable.

10.3 Sample Analysis

1	Mix the sample well and immediately transfer 100 ± 5 g to the paint filter. **Record the weight.** A funnel may be used to provide support for the paint filter. If the sample is of such light bulk density that it overflow the filter, then the sides of the filter can be extended upward by taping filter paper to the inside of the filter and above the mesh. Settling the sample into the paint filter may be facilitated by lightly tapping the side of the filter as it is being filled.
2	In order to assure uniformity and standardization of the test, material such as sorbent pads or

	pillows which do not conform to the shape of the paint filter, should be cut into small pieces and poured into the filter. Sample size reduction may be accomplished by cutting the sorbent material with scissors, shears, knife, or other such device so as to preserve as much of the original integrity of the sorbent fabric as possible. Sorbents enclosed in a fabric should be mixed with the resultant fabric pieces. The particles to be tested should be reduced smaller than 1 cm. Grinding sorbent materials should be avoided as this may destroy the integrity of the sorbent and produce many "fine particles" which would normally not be present.
3	For brittle materials larger than 1 cm that do not conform to the filter, light crushing to reduce oversize particles is acceptable if it is not practical to cut the material. Materials such as clay, silica gel, and some polymers may fall into this category.
4	Allow sample to drain for 5 minutes into the graduated cylinder. **Record the start and stop time**.
5	If any portion of the test material collects in the graduated cylinder in the 5-minute period, then the material is deemed to contain free liquids for purposes of 40 CFR 264.314 and 265.314.

10.4 Example Analysis Queue / Sequence*

1	Sample 1
2	Duplicate
3	Samples 2 -10
4	Sample 11
5	Duplicate
6	Samples 12 -20*

*May be up to 20 samples).

11.0 Calculations / Data Reduction

11.1 Accuracy: Not applicable.

11.2 Precision (RPD): Not applicable.

11.3 Result Reporting: Report "Free Liquids" or "No Free Liquids."

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): Not applicable.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: Not applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- The samples are discarded in a trash receptacle. The liquid portion is discharged to the sanitary sewer.

15.0 References / Cross-References

15.1 SW-846 Method 9095B, Update IIIB, Revision 2, November 2004

15.2 TestAmerica Nashville's Quality Assurance Manual.

15.3 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.4 SOPs: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

15.5 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachment

None.

18.0 Revision History

- Revision 5, dated 24 April 2009
  - Integration for TestAmerica and STL operations.
  - Additional information on mesh size for filter.
- Revision 6, dated 30 December 2010
  - Addition of QAF-45 and Section 14.2.
  - Two-year review.
- Revision 7, dated 31 January 2013
  - Organizational changes.
  - Amendment 6a: Add SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
  - OK and WY no longer limit batch size to 10 samples.
  - Modify analytical sequence.

Title: STANDARD TEST METHOD FOR HEAT OF COMBUSTION BY BOMB CALORIMETER (BTUs) ASTM D240-97

Approvals (Signature/Date)			
Sessily Overton-Gray	6/19/13	James D. Carmichael	6/21/13
Sessily Overton-Gray Department Supervisor	Date	James D. Carmichael Operations Manager	Date
Michael H. Dunn	6/24/13	Johnny Davis	6/25/13
Michael H. Dunn Technical Director Quality Assurance Manager	Date	Johnny Davis Health & Safety Manager / Coordinator	Date

1.0 Scope and Application

1.1 Analytes, Matrix: This test method covers the determination of the heat of combustion of liquid hydrocarbon fuels or oily sludges.

1.2 Report Limit: The report limit is 200 BTU/lb (British Thermal Units/pound).

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted on the Controlled Document IF-4 (CALORIME.xls), the batch sheet, and in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

Heat of combustion is determined by combusting a weighed sample in an Oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations before, during and after combustion, with proper allowance for thermochemical and heat transfer corrections.

3.0 Definitions

3.1 Gross heat of combustion, Q_g (cal/g): the quantity of energy released when a unit mass of fuel is burned in a constant volume enclosure, with the products being gaseous, other than water that is condensed to the liquid state.

3.2 The following relationship may be used for converting to other units (conversion factor is exact): 1 BTU/lb = 1.8 calories/gram

3.3 Energy equivalent or the effective heat capacity of the calorimeter is the energy required to raise the temperature 1 degree expressed as calories.

3.4 See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for other laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

None.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This method may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: Stand beside the hood when igniting the bomb. Observe warnings mentioned in the method.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Benzoic Acid	Irritant	None	Eye, skin, throat irritant. Incompatible with strong oxidizers.
Oxygen, Compressed	Oxidizer	NA	Exposure to Oxygen will not result in exposure symptoms unless the individual is exposed to high levels for more than 17 hours. However, exposure of flammable or combustible materials to Oxygen can create an extremely dangerous situation and result in an explosion.

1- Exposure limit refers to the OSHA regulatory exposure limit.

6.0 Equipment and Supplies

6.1 Instrumentation

- Bomb calorimeter (Parr or equivalent) including jacket, thermometers, and ignition unit.

6.2 Supplies

Nichrome wire.

7.0 Reagents and Standards

- Benzoic acid, C_6H_6COOH, standard, commercial, 1 gram nominal pellets.
- Oxygen, commercial, 99.9%.
- Water, tap or reagent.

8.0 Sample Collection, Preservation, Shipment and Storage

This is not an environmental method and does not have regulatory limitations in this regard. No holding time is specified.

9.0 Quality Control

9.1 Sample QC: The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit
Laboratory Control Sample (Benzoic acid, one pellet)	1 in 10 or fewer samples	10236-12510 BTU/lb
Sample Duplicate[1]	1 in 10 or fewer samples	RPD ≤ 10%

[1] The aliquot must be a duplicate of the aliquot used for sample analysis.

9.2 Instrument QC

Calorimeter Standardization (when needed): Determine the Energy Equivalent of the Calorimeter (W). Use standard Benzoic acid, not less than 0.9 g and not more than 1.1 gram.

$$W = (Hm + e1 + e3) / t$$

H = heat of combustion of standard Benzoic acid.
m = mass of Benzoic acid used.
t = net temperature change.
e1 = heat formation of HNO_3.
e3 = correction for heat combustion of wire.

Currently the Energy Equivalent of Calorimeter (W) is 2469 calories/gram. Standardization is confirmed with each batch with the analysis of a Benzoic acid pellet.

10.0 Procedure

10.1 Sample Preparation

1	Mix well and quickly weigh the sample to the nearest 0.1 mg into the cup. Use 0.5 to 1.0 gram organic sample. **DO NOT EXCEED 1 GRAM.**
2	Place 10 ± 0.5 cm of nickel-chromium wire through the electrodes with a small portion of wire just contacts the top of the sample.

10.2 Sample Analysis

1	With the sample and ignition wire in place, carefully assemble top and screw tightly, slowly charge the bomb with pure Oxygen to 30 atm gauge pressure at room temperature. Do not purge the bomb to remove entrapped air. Note: **WARNING - Do not overcharge the bomb**. If, by accident, the Oxygen introduced into the bomb should exceed 35 psig, **do not** proceed with the combustion. An explosion might occur with possible violent rupture of the bomb. Detach the filling connection and exhaust the bomb in the usual manner. Discard the sample.
2	Use the same amount (2000 grams) of reagent water in the calorimeter jacket for each test. The water is measured volumetrically (1 gram = 1 milliliter).
3	Assemble the calorimeter in the jacket, attach the electrode wires, and start the stirrer. Allow 5 minutes for attainment of equilibrium; record the calorimeter temperature (see Note) at 1 - minute intervals for 5 minutes or until constant. Pull down the hood sash. Stand to one side of the hood. Fire the charge at the start of the sixth minute and record the time and temperature, $t_{initial}$. After the rapid rise period (5 minutes), record temperatures at 1 minute intervals on the minute until the difference between successive readings has been constant for 5 minutes. Record t_{final}.
4	Remove the bomb and slowly release the pressure in a hood at a uniform rate such that the operation will require not less than 1 minute. Examine the bomb interior for evidence of incomplete combustion. Repeat for verification if unburned sample or sooty deposits are found.

10.4 Example Analysis Queue

1	Benzoic acid pellet (known)
2	Samples 1-10
3	Sample Duplicate

11.0 Calculations / Data Reduction

11.1 Accuracy

Known = 10236 to 12510 BTU/lb

11.2 Precision (RPD): Run in duplicate; RPD ≤ 10%.

Sample Duplicate = $\frac{\text{Absolute value (orig. sample value - dup. sample value) x 100}}{\text{(Orig. sample value + dup. sample value)/2}}$

11.3 Calculation

Gross Heat of Combustion: Compute the gross heat of combustion by substituting in the following equation:

$Q_g = (1.8)(t \times W - 17) / g$

Q_g = gross hear of combustion, at constant volume expressed as BTU/lb. The report limit is 200 BTU/lb.
t = temperature change (^oC). Report any change > 0.05 degrees C.
W = energy equivalent of calorimeter = 2469 cal/g
1.8 is the conversion from cal/g to BTU/lb
17 is the correction for the heat of combustion for the water, wire, etc.
g = weight of sample, gram

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): Not applicable.

12.2 Demonstration of Capability: The laboratory demonstrates proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats these operations whenever new staff is trained or significant changes in instrumentation are made. See the training section of the QA Manual and SOP Training / SA08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four knowns with an average BTU/lb within the control limits or four pairs of sample duplicates resulting in an average precision less than the quality control maximum are required.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention.

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- No waste is generated.
- Non-combustible samples are disposed of in the trash.

15.0 References / Cross-References

15.1 ASTM Method D240, The American Society for Testing and Materials (re-approval 1997 with editorial changes in April 1997 and March 1999).

15.2 TestAmerica Nashville's Quality Assurance Manual.
15.3 Corporate Environmental Health and Safety Manual (CW-E-M-001).
15.4 Parr Bomb Calorimeter operating instructions, N-240M.
15.5 SOPs: Waste Disposal / NV10-83; Training of Environmental Staff / NV08-199.
15.6 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions, IF-4 (CALORIME.xls).

16.0 Method Modifications:

The volatile fuel check using 2,2,4-Trimethylpentance is not used.

17.0 Attachments

None.

18.0 Revision History

- Revision 3, dated 31 October 2007
  - Integration for TestAmerica and STL operations
  - Additional safety precaution about standing beside the hood.
  - Addition of note about ion chromatography in Sample Analysis
  - Changes of "deionized water" to "reagent water"
  - Addition of "in a hood" to the section on releasing the pressure of the bomb contents.
  - Deleted reference to Ertco-Eutechnics Model 4400 (no longer in use).
- Revision 4, dated 30 October 2009
  - Addition of reminder to pull down the hood sash and stand to one side of the hood before firing the calorimeter.
- Revision 5, dated 30 September 2011
  - Organizational changes.
  - Addition of QAF-45 and Section 14.2.
  - Addition of Nichrome wire.
  - Method modification is added.
- Revision 6, dated 28 June 2013
  - Organizational changes.
  - Add the oily sludge matrix, IF-4, and add detail to the sample preparation and analysis sections.

Title: Particle Size Analysis (ASTM D 2217 and D422-63)

Approval Signatures:

Kirstin L.Daigle
Laboratory Director

Brad W.Chirgwin
Technical Manager

Chris Callahan
Department Manager

Sara S. Goff
Quality Assurance Manager

Daniel W.Helfrich
Health & Safety Coordinator

Approval Date: February 6, 2014

Facility Distribution No. Electronic **Distributed To: Facility Intranet**

The controlled copy of this SOP is the PDF copy of the SOP that is posted to the laboratory's SOP Directory. Printed copies of this SOP or electronic copies of this SOP distributed outside the facility are considered uncontrolled.

1.0 Scope and Application

This SOP describes the laboratory procedure for the determination of particle size distribution in soils.

2.0 Summary of Method

A portion of sample is soaked in a dispersing agent then partitioned into separate portions, material retained on a #10 sieve and material passing the #10 sieve. The material retained on the #10 sieve is dried to constant weight then passed through a large size sieve stack; the material retained on each sieve is measured and recorded. Material passing the #10 sieve is subject to hydrometer analysis then passed through a small size sieve stack, the material retained on each sieve is measured and recorded. All measurements, large and small sieves and hydrometer readings and the hygroscopic moisture are used to establish the particle size distribution of the sample.

This SOP is based on the following reference methods:

- ASTM Standard D 2217 – 85 (Rapproved 1998) "Standard Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants", ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

- ASTM Standard D 422-63 (Rapproved 2007) "Standard Test Method for Particle-Size Analysis of Soils", ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

NOTE: ASTM D2217 was withdrawn without replacement by ASTM in 2007. A withdrawn standard is an ASTM standard that has been discontinued by the ASTM Sponsoring Committee responsible for the standard.

If the laboratory has modified the procedure from the reference method(s) a list of modifications will be provided in Section 16.0.

3.0 Definitions

Not Applicable

4.0 Interferences

Not Applicable

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

None

5.2 Primary Materials Used

Not Applicable

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

- Top-Loading Balance, capable of weight measurement to 0.01 g
- Mechanical Stirring Device and Dispersion Cup
- Thermometer: Accurate to 0.5℃
- Mortar and Rubber Tipped Pestle
- Sedimentation Cylinder(s) 1000 mL
- Hydrometer: ASTM 151H in specification E 100.
- Sieves, of the following size(s): Gilson Company, Inc. or equivalent
  3.0” (75.00 mm)
  2.0” (50.00 mm)
  1.5” (37.50 mm)
  1.0” (25.00 mm)
  3/4" (19.00 mm)
  3/8” (9.50 mm)
  # 4 (4.75 mm)
  #10 (2.00 mm)
  #20 (850.0 um)
  #40 (425 um)
  #60 (250.0 um)
  #80 (180.0 um)
  #100 (150.0 um)
  #200 (75.0 um)
- Drying Oven with temperature range of 60-110℃
- Stainless Steel Spatulas & Spoons
- Metal & Bristle Brushes
- Ro-Tap Sieve Shaker, W. S. Tyler or equivalent.
- Timing Device with second hand and capable of counting up to 25 hours

7.0 Reagents and Standards

- Reverse Osmosis (RO) water: In-House System
- Sodium Hexametaphosphate: ELE International or equivalent.

Sodium Hexametaphosphate Solution: Add 120 g of sodium hexametaphosphate and 2940 g of reagent water to a 1-gallon bottle. Add a stir rod to the container and place on a stir plate. Mix the solution until it is homogeneous. Assign an expiration date of 30 days from the date made unless the parent reagent expires sooner in which case use the earliest expiration date. Store the prepared solution at ambient temperature.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP. Sampling requirements may be found in the published reference method.

Listed below are minimum sample size, preservation and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time	Reference
Solid	Glass Jar w/ Teflon Lid	500 g	None	None	ASTM D422-63

Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 Quality Control

Not Applicable

10.0 Procedure

10.1 Equipment Calibration

Check the calibration of the balance on each day of use prior to use using at least 2 Class S weights that bracket the range of use. Record in the logbook designated for this purpose.

Check the temperature of the drying oven(s) each day of use, prior to use. Record in the logbook designated for this purpose.

NOTE: The QA Manager or her designee checks the calibration of liquid in glass thermometers annually against a NIST-traceable thermometer following the procedures given in laboratory SOP BR-QA-004. Electronic / digital thermometers that are battery-operated are checked quarterly using the same procedure.

Calibrate the hydrometers every two years following the procedure given in BR-GT-008.

Calibrate the sieves 6 months following the procedure given in BR-GT-008.

10.2 Hygroscopic Moisture Determination

Label an aluminum pan with the Lab ID for each sample. Tare the balance, weigh each pan and record the weight measurement in the spreadsheet.

Mix the sample with a stainless steel spatula. Measure at least 10-15 g of each sample into the labeled aluminum pan and record the weight of sample in the spreadsheet.

Place the pan + sample in an oven maintained at a temperature of 110ºC and dry the sample for at least 16 hours. Reweigh each pan and record the weight measurement in the spreadsheet.

Percent solids are calculated using the equation given in Section 11.0.

10.3 Sample Preparation

Use the calculated percent solids and the sample characteristic for each sample to determine the amount needed for analysis using Table 2. For example, if the calculated percent solids for a sample are 50% and the sample characteristic is sand, use 200 g for analysis. If there is an insufficient amount of sample available, initiate a nonconformance memo (NCM) and contact the PM for further instruction.

Place a 1000 mL plastic beaker on the balance and tare the balance. Weight the amount of sample for analysis and record the weight in the bench sheet.

Add 125 mL of sodium hexametaphosphate solution to each beaker. Stir to mix and soak the sample in this solution for 16 hours

10.4 Sample Partition

Rinse the sample slurry into a dispersion cup using reagent water. Fill the dispersion cup ½ full with reagent water and place the cup on the blender to mix for one minute.

NOTE: Some samples may not be amendable to using the blender examples include but not limited to large gravel, sands, or organic material. If the sample is not amenable, initiate a NCM to notify the PM of the anomaly and proceed to the next step without blending the sample.

Place a #10 sieve on a 1000 mL graduated cylinder. Pour the sample through the sieve. Rinse the dispersion cup with reagent water and pour the rinse through the sieve. Repeat until transfer is complete. Bring the volume in the graduated cylinder to 1000 mL with reagent water. Cover the cylinder with a rubber stopper and equilibrate the sample to ambient temperature in preparation for hydrometer analysis.

Label a medium size aluminum dish with the sample's LAB ID then transfer the sample material that was retained on the #10 sieve to the dish. Place the aluminum dish in the drying oven set at 110 ± 5° C and dry the sample material for at least 16 hours or until constant weight. Set aside for sieve analysis.

10.5 Hydrometer Analysis

Prepare a hydrometer rinse bath by adding 1000 mL of reagent water to a 1000 mL graduated cylinder

Record the hydrometer ID and start time on the worksheet. Set the timer for the elapsed time and perform each task as listed in Table 1: Hydrometer Reading Table.

To shake the cylinder, rotate the flask up and down for one minute approximating at least 60 turns. One turn down and one turn up equals two turns.

To take a hydrometer reading, gently insert the hydrometer into the graduated cylinder and wait ~ 20 seconds. Read the hydrometer from the top of the meniscus to the nearest 0.0005. Enter the reading on the worksheet. After each reading, clean the hydrometer by twisting and dropping the hydrometer into the hydrometer rinse bath.

Insert a temperature probe into the cylinder to the same depth used for the hydrometer reading. Read the temperature to the nearest 0.5℃ and enter the temperature measurement on the worksheet. Rinse the temperature probe in the hydrometer rinse bath.

Repeat the above process taking hydrometer readings every 2, 5, 15, 30, 60, 240 and 1440 minutes as per Table 1 then proceed to small sieve analysis.

10.6 Sieve Analysis

Inspect the sample material in the aluminum pan and record a description of the non-soil material (e.g.- sticks, grass, wood, plastic), hardness of material and shape of material in the worksheet.

Hardness qualifiers include hard, soft or brittle. Shape qualifiers include well rounded, rounded, subrounded, subangular, and angular.

Large Sieves

Weigh the 3/4", 3/8", #4 and #10 sieves and enter the weight measurements in the worksheet as the tare weight.

Stack the sieves then transfer the sample material from the aluminum dish to the sieve stack. If the sample material is less than 30 g, manually shake the sieve stack for 2 minutes. If the sample material is greater than 30 g, place the sieve stack into the Ro-tap machine and shake the sieve stack for 10 minutes.

Weigh each sieve and record these measurements in the worksheet.

Small Sieves

Quantatively transfer the sample from the graduated cylinder to a #200 wet wash sieve. Ensure all of the sample has been transferred to the #200 wet wash sieve by rinsing the graduated cylinder several time with RO water. Using RO water, wash the sample through the #200 sieve until the water runs clear then transfer the material retained on the sieve into a 250 mL glass beaker labeled with the sample's LAB ID.

Place the beaker in the drying oven and dry at a temperature of 110ºC for at least 16 hours. After 16 hours, remove the beaker from the oven and allow it to cool.

Gently mix the dried contents of the beaker with a rubber-tipped pestle to break any soil aggregates that may have formed during the drying stage.

Tare the balance and weigh the sieve stack sized between #20 and #200 and record the tare weights.

Transfer the sample to the sieve stack and ensure complete transfer. Use hair or wire brushes to clean the beaker. Place the sieve stack on the RoTap machine and shake for ten minutes.

Weigh each sieve and record these measurements in the worksheet.

11.0 Calculations / Data Reduction

11.1 Calculations

Sample Used (SU): Dry Preparation

$$SU = (pan + dry\ sample - pan) - (pan + non - soil\ material - pan) \otimes HMCF$$

Where:
HMCF = Hygroscopic moisture correction factor.

Sieve Analysis (Percent Finer = PF)

Large Sieves:

3 inch: PF = 100-100 (Sieve and Sample (3 inch) - Sieve (3 inch))/SU*

2 inch: PF = PF (3 inch) - 100(Sieve and Sample (2 inch) - Sieve (2 inch))/SU and so on through the #10 Sieve.*

Small Sieves:

#20: PF = PF(#10) - 100(mass passing #10/sample mass (Hyd))*(sieve and sample (#20) - sieve(#20))/sample used*

#40: PF = PF (#20) - 100(mass passing #10/sample mass (Hyd))*(sieve and sample (#40) - sieve (#40))/sample used and so on up through #10 sieve.*

Hydrometer Analysis

Particle size, Micron

1000*sqrt [930*viscosity/980*(SG-1))*(effective depth/time)]

Viscosity at sample temperature, poises
Effective Depth, cm = 16.29-264.5*(actual Hydrometer reading - 1) above equation for effective depth based on equation found with table 2 in method, in which 16.29 = 0.5*(14.0-67.0/27.8)+10.5 and 264.5 = (10.5-2.3)/0.031
Time, minutes = Time of hydrometer reading from beginning of sedimentation
Sqrt - square root
SG - Specific Gravity of soil
Viscosity - is the resistance of a liquid to flow
Percent Finer (PF):

PF = Constant*(actual hydrometer reading - hydrometer correction factor - 1)

Where:
Constant = (100,000/W)*SG/(SG-1)
W = (Total sample used *sample used for hydrometer analysis*HMCF)/Amount of total sample passing #10 sieve
Hydrometer Correction = slope*sample temperature + Intercept
Slope = ((low temp. reading -1)-(high temp. reading -1)/(low temp. - high temp.))

Intercept = (low temp. reading -1) - (low temp. * slope)

11.2 Data Reduction

11.2.1 Primary Data Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Upload the batch information into LIMS and complete the batch editor and worksheet. Initiate NCMs for any anomalies observed during the preparation process. Set the status of the batch to 1st level review.

11.2.2 Secondary Data Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements and verify those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Check the batch editor and worksheet to verify the batch is complete and any outages are documented with an NCM along with the results of any corrective actions taken. Set the status of the batch to second level review.

11.2.3 Lab Complete

Review the batch, run QC checker as appropriate and set the status to lab complete.

11.2.4 Data Reporting

Sample results are reported from the laboratory's LIMS system using the formatter specified by the Project Manager.

11.2.5 Data Archival

Data are stored in the laboratory's LIMS system.

12.0 Method Performance

Not Applicable

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001. The following waste streams are produced when this method is carried out.

- Solid Waste-Satellite Container: Solid Waste 5 Gallon Plastic Bucket (inside fume hood)
- Liquid Waste- 55 gallon poly drum

15.0 References / Cross-References

- ASTM Standard D 2217 – 85 (Reapproved 1998) "Standard Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants", ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

- ASTM Standard D 422-63 (Rapproved 2007) "Standard Test Method for Particle-Size Analysis of Soils", ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

16.0 Method Modifications

- The laboratory prepares samples for ASTM D422 using ASTM method D2217 rather then the suggested method ASTM D421.

17.0 Attachments

- Table 1: Hydrometer Reading Table (For up to 12 Sedimentation Cylinders)
- Table 2: Percent Solids Table for Weight Determination for D422.

18.0 Revision History

BR-GT-006, Revision 7:
- Title Page: Updated approval signatures and Copyright Date.
- Section 10.1: Removed calibration of RoTap machine
- Section 10.6: Updated language to better describe process to transfer sample to the #200 wet wash sieve.
- Section 16.0: Removed a modification

BR-GT-006, Revision 6:
- Title Page: Updated approval signatures
- All Sections: Removed references to dry preparation by ASTM D421; Added procedure for wet preparation.
- Attachments: Inserted Percent Solids Tab

Table 1: Hydrometer Reading Table (For up to 12 Sedimentation Cylinders)

Elapsed Time (hr:min)	Task	Cyl. No.	Actual Time (min)	Elapsed Time (hr:min)	Task	Cyl. No.	Actual Time (min)
0:00	Shake	1		1:01	Read	10	5
0:01	**Place**	**1**		**1:02**	Shake	11	
0:01	**Shake**	**2**		**1:03**	Place	11	
0:02	Place	2		1:04	Read	9	15
0:03	Read	1	2	1:05	Read	11	2
0:04	Read	2	2	1:06	Read	7	31
0:06	Read	1	5	1:07	Read	3	58
0:07	Read	2	5	1:08	Read	11	5
0:08	Shake	3		**1:09**	Shake	12	
0:09	**Place**	**3**		**1:10**	Place	12	
0:09	**Shake**	**4**		1:11	Read	10	15
0:10	Place	4		1:12	Read	12	2
0:11	Read	3	2	1:13	Read	4	63
0:12	Read	4	2	1:14	Read	8	32
0:14	Read	3	5	1:15	Read	12	5
0:15	Read	4	5	1:18	Read	11	15
0:16	Read	1	15	1:19	Read	9	30
0:17	Read	2	15	1:21	Read	5	60
0:20	Shake	5		1:25	Read	12	15
0:21	Place	5		1:26	Read	10	30
0:23	Read	5	2	1:27	Read	6	59
0:24	Read	3	15	1:33	Read	11	30
0:25	Read	4	15	1:34	Read	7	59
0:26	Read	5	5	1:41	Read	12	31
0:27	Shake	6		1:42	Read	8	60
0:28	Place	6		1:52	Read	9	63
0:30	Read	6	2	1:53	Read	10	57
0:31	Read	1	30	2:06	Read	11	63
0:32	Read	2	30	2:07	Read	12	57
0:33	Read	6	5	4:17	Read	1	256
0:34	Shake	7		4:18	Read	2	256
0:35	Place	7		4:19	Read	3	250
0:36	Read	5	15	4:20	Read	4	250
0:37	Read	7	2	4:21	Read	5	240
0:38	Read	3	29	4:22	Read	6	234
0:39	Read	4	29	5:00	Read	7	265
0:40	Read	7	5	5:01	Read	8	259
0:41	Shake	8		5:02	Read	9	253
0:42	Place	8		5:03	Read	10	247
0:43	Read	6	15	5:04	Read	11	241
0:44	Read	8	2	5:05	Read	12	235
0:47	Read	8	5	24:01	Read	1	1440
0:48	Shake	9		24:02	Read	2	1440
0:49	Place	9		24:03	Read	3	1434
0:50	Read	7	15	24:04	Read	4	1434
0:51	Read	9	2	24:05	Read	5	1424
0:52	Read	5	31	24:06	Read	6	1418
0:54	Read	9	5	24:07	Read	7	1412
0:55	Shake	10		24:08	Read	8	1406
0:56	Place	10		24:09	Read	9	1400
0:57	Read	8	15	24:10	Read	10	1394
0:58	Read	10	2	24:11	Read	11	1388
0:59	Read	6	31	24:12	Read	12	1382
1:00	**Read**	**1**	**59**				
1:00	**Read**	**2**	**58**				

Source: Laboratory Prepared Reference Document

Table 2: Percent Solids Table for Weight Determination for D422.

Percent Solid Table

Quantities of sample (in grams) to be utilized in Wet method version of ASTM D854 and D422

% Sol	Spec Grav	Hydrometer Slt/Cl	Slt/Snd	Snd	Snd/Gr
	25	**50**	**75**	**100**	**200**
1	2500	5000	7500	10000	20000
2	1250	2500	3750	5000	10000
3	833	1667	2500	3333	6667
4	625	1250	1875	2500	5000
5	500	1000	1500	2000	4000
6	417	833	1250	1667	3333
7	357	714	1071	1429	2857
8	313	625	938	1250	2500
9	278	556	833	1111	2222
10	250	500	750	1000	2000
11	227	455	682	909	1818
12	208	417	625	833	1667
13	192	385	577	769	1538
14	179	357	536	714	1429
15	167	333	500	667	1333
16	156	313	469	625	1250
17	147	294	441	588	1176
18	139	278	417	556	1111
19	132	263	395	526	1053
20	125	250	375	500	1000
21	119	238	357	476	952
22	114	227	341	455	909
23	109	217	326	435	870
24	104	208	313	417	833
25	100	200	300	400	800
26	96	192	288	385	769
27	93	185	278	370	741
28	89	179	268	357	714
29	86	172	259	345	690
30	83	167	250	333	667
31	81	161	242	323	645
32	78	156	234	313	625
33	76	152	227	303	606
34	74	147	221	294	588
35	71	143	214	286	571
36	69	139	208	278	556
37	68	135	203	270	541
38	66	132	197	263	526
39	64	128	192	256	513
40	63	125	188	250	500
41	61	122	183	244	488
42	60	119	179	238	476
43	58	116	174	233	465
44	57	114	170	227	455
45	56	111	167	222	444
46	54	109	163	217	435
47	53	106	160	213	426
48	52	104	156	208	417
49	51	102	153	204	408
50	50	100	150	200	400

% Sol	Spec Grav	Hydrometer Slt/Cl	Slt/Snd	Snd	Snd/Gr
	25	**50**	**75**	**100**	**200**
51	49	98	147	196	392
52	48	96	144	192	385
53	47	94	142	189	377
54	46	93	139	185	370
55	45	91	136	182	364
56	45	89	134	179	357
57	44	88	132	175	351
58	43	86	129	172	345
59	42	85	127	169	339
60	42	83	125	167	333
61	41	82	123	164	328
62	40	81	121	161	323
63	40	79	119	159	317
64	39	78	117	156	313
65	38	77	115	154	308
66	38	76	114	152	303
67	37	75	112	149	299
68	37	74	110	147	294
69	36	72	109	145	290
70	36	71	107	143	286
71	35	70	106	141	282
72	35	69	104	139	278
73	34	68	103	137	274
74	34	68	101	135	270
75	33	67	100	133	267
76	33	66	99	132	263
77	32	65	97	130	260
78	32	64	96	128	256
79	32	63	95	127	253
80	31	63	94	125	250
81	31	62	93	123	247
82	30	61	91	122	244
83	30	60	90	120	241
84	30	60	89	119	238
85	29	59	88	118	235
86	29	58	87	116	233
87	29	57	86	115	230
88	28	57	85	114	227
89	28	56	84	112	225
90	28	56	83	111	222
91	27	55	82	110	220
92	27	54	82	109	217
93	27	54	81	108	215
94	27	53	80	106	213
95	26	53	79	105	211
96	26	52	78	104	208
97	26	52	77	103	206
98	26	51	77	102	204
99	25	51	76	101	202
100	25	50	75	100	200

Title: Water (Moisture) Content of Soil and Rock by Mass (ASTM D2216- 05, Method B)

Approval Signatures:

Kirstin L.Daigle
Laboratory Director

Brad W.Chirgwin
Technical Manager

Chris Callahan
Department Manager

Sara S. Goff
Quality Assurance Manager

Daniel W.Helfrich
Health & Safety Coordinator

Approval Date: January 31, 2014

Facility Distribution No. Electronic **Distributed To: Facility Intranet**

The controlled copy of this SOP is the PDF copy of the SOP that is posted to the laboratory's SOP Directory. Printed copies of this SOP or electronic copies of this SOP distributed outside the facility are considered uncontrolled.

1.0 Scope and Application

This SOP describes the laboratory procedure for the determination of water (moisture) content of soil, rock, and similar materials where the reduction in mass by drying is attributed to loss of water.

The procedure is applicable to solid materials as the term is used to mean naturally occurring mineral particles of soil and read and that are not readily soluble in water. The procedure should not be used to determine water content in materials with substantial amounts of soluble solids or materials that contain extraneous matter or in marine sediments. For these types of materials, ASTM recommends special treatment or qualification of analytical results. ASTM methods for special treatment are listed in ASTM D2216-05 but are not currently offered by the laboratory. If laboratory analysis on such materials is desired, the laboratory recommends that procedures for treatment of samples and reporting specifications be specified by the customer prior to the start of analysis.

2.0 Summary of Method

A portion of sample is dried in an oven maintained at a temperature of 110 ± 5 ºC for 16 hours or until constant mass. The loss of mass due to drying is considered to be water. The water content is calculated using the difference between the mass of the wet sample and the mass of the dry sample.

This SOP is based on the following reference method:

- ASTM Standard D 2216-05, 2005, "Determination of Water (Moisture) Content of Soil and Rock by Mass", ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

If the laboratory's procedure has been modified from the reference method, a list of modifications will be provided in Section 16.0.

NOTE: Section 10.2 contains a table presenting the recommended sample volume needed to perform this test based on the size of the sample's particle size. Analysis is not always performed using the recommended sample amounts specified in the reference method because lesser sample amounts are typically received by the laboratory. When the recommended volume is not received the lab will ask for additional volume to perform the test. If additional volume is unavailable the lab will use the volume provided and create an NCM.

3.0 Definitions

- **Water Content by Mass:** The ratio of the mass of water contained in the pore spaces of soil or rock material, to the solid mass of particles in that materials, expressed as a percentage. A standard temperature of 110 ± 5℃ is used to determ ine these masses. (ASTM D2216-05)

- **Constant Mass:** The state that a water content specimen has attained when further heating causes or would cause less than 1% or 0.1% additional loss in mass. (ASTM D2216-05)

4.0 Interferences

This SOP determines moisture content in solid materials without the application of any specific treatment to account for significant amounts of either dissolved or volatile solids.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

None

5.2 Primary Materials Used

Table 1 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the SDS. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

- Drying Oven, capable of temperature measurements at 110°C (±5°C), Barnstead LC Oven Model# 3513 or equivalent.
- Top loading balance, Mettler Model# PB3002 or equivalent.
- Aluminum Pans, Fisher Scientific or equivalent.
- Stainless Steel Spatulas and Spoons, Fisher Scientific or equivalent.
- Heat shield gloves / Oven Tongs, Fisher Scientific or equivalent.

7.0 Reagents and Standards

Not Applicable

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection. The reference method specifies that soil samples should be collected and preserved in accordance with ASTM D 4220 Section 8, Groups B, C or D for soils and rock samples collected in accordance with D 5079, Section 7.5.2.

Listed below are the laboratory recommended container types, sample amount, storage conditions and required holding times for analysis:

Matrix	Sample Container	Sample Amount	Storage	Holding Time
Solid	Glass	100-200 g	0-30℃	NA

9.0 Quality Control

Not Applicable

10.0 Procedure

10.1 Calibration and Standardization

Check the calibration of the balance on each day of use prior to use using at least 2 Class S weights that bracket the range of use. Record in the logbook designated for this purpose.

Check the temperature of the drying oven(s) each day of use, prior to use. Record in the logbook designated for this purpose.

10.2 Analysis

The reference method recommends the following sample amounts for analysis based on maximum particle size.

Maximum Particle Size (mm)	Standard Sieve Size	Sample Mass for Analysis
2 or less	# 10	20 g
2 to 4.75	# 4	100 g
4.76 to 9.5	3/8 inch	500 g
9.6 to 19.0	3/4 inch	2.5 Kg
19.1 to 37.5	1 ½ inch	10 Kg
37.6 to 75.0	3 inch	50 Kg

Visually inspect the sample to identify the sieve size for which 100% of material will pass. Use a sample amount that corresponds to the to the sieve size in the chart in Section 8.0. If less than the recommended amount of sample was provided use the amount of sample available and record the anomaly with a LIMS nonconformance memo (NCM)

Mix the sample thoroughly following the homogenization procedures specified in laboratory SOP LP-QA-020. Label a clean aluminum pan with the sample ID then measure and record the weight of the pan to the nearest 0.01 g. Weigh the pre-determined sample mass into the pan and record the combined weight of the pan and the wet sample. Repeat for each sample.

Check the temperature of the drying oven(s) to ensure that the oven is within 105-115℃; then place the pans in the drying oven. Dry the samples for 16 hours or until constant mass.

Remove the pans from the oven and allow the pans to cool to room temperature or a temperature comfortable enough to handle the pans with bare hands. Measure and record the weight of the pan and dried sample.

Calculate the moisture content using the equation given in Section 11.0.

11.0 Calculations / Data Reduction

11.1 Calculation

Moisture Content

$w = [(M_{cws} - M_{cs})/(M_{cs} - M_c)]*100$

Where:
w = water content, %
M_{cws} = mass of container and wet sample, g
M_{cs} = mass of container and oven dry sample, g
M_c = mass of container, g

11.2 Data Reduction

Primary Data Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Upload the batch information into LIMS and complete the batch editor and worksheet. Initiate NCMs for any anomalies observed during the preparation process. Set the status of the batch to 1st level review.

Secondary Data Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements and verify those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Check the batch editor and worksheet to verify the batch is complete and any outages are documented with an NCM along with the results of any corrective actions taken. Set the status of the batch to second level review.

Lab Complete

Review the batch, run QC checker as appropriate and set the status to lab complete.

Data Reporting

Sample results are reported from the laboratory's LIMS system using the formatter specified by the Project Manager.

Data Archival

Data are stored in the laboratory's LIMS system.

12.0 Method Performance

12.1 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001. The following waste streams are produced when this method is carried out.

- Solid Waste- Satellite Container: 5 Gallon Plastic Bucket.

15.0 References / Cross-References

- ASTM Standard D 2216-05, 2005, "Determination of Water (Moisture) Content of Soil and Rock by Mass", ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

- TestAmerica Corporate Safety Manual, current version.

- Laboratory SOPs as referenced, current version.

16.0 Method Modifications

None

17.0 Attachments

None

18.0 Revision History

BR-GT-016, Version 7:

- Title Page: Updated Approval Signatures
- Section 2: Inserted a note referring to recommended sample size required to perform this test.
- Section 10.1: Added procedure to check oven temperature and calibration
- Section 10.2: Inserted recommended sample amount table into this Section from Section 8.
- Section 16: Removed method modification and transferred information to a note in section 2.
- Updated Material Safety Data Sheet (MSDS) to Safety Data Sheet (SDS).

BR-GT-016, Version 6:

- Updated Approval Signatures
- Converted format of SOP to company template.
- Updated the method reference

22.5 Sample Aliquots / Subsampling

Taking a representative sub-sample from a container is necessary to ensure that the analytical results are representative of the sample collected in the field. The size of the sample container, the quantity of sample placed inside the container, and the homogeneity of the sample need consideration when subsampling for sample preparation. It is the laboratory's responsibility to take a representative subsample or aliquot of the sample provided for analysis.

Each sample is handled by analysts as if it is potentially dangerous. At a minimum, safety glasses, gloves, and laboratory coats must be worn when preparing aliquots for analysis.

Refer to SOP *Sample Homogenization, Subsampling, and Compositing* / NV08-229 for specific details on taking sample aliquots and subsampling.

SECTION 23. HANDLING OF SAMPLES

Sample management procedures at TestAmerica Nashville ensure that sample integrity and custody are maintained and documented from sampling/receipt through disposal.

23.1 Chain of Custody (COC)

The COC form is the written documented history of any sample and is initiated when bottles are sent to the field or at the time of sampling. This form is completed by the sampling personnel and accompanies the samples to the laboratory where it is received and stored under the laboratory's custody. The purpose of the COC form is to provide a legal written record of the handling of samples from the time of collection until they are received at the laboratory. It also serves as the primary written request for analyses from the client to the laboratory. The COC form acts as a purchase order for analytical services when no other contractual agreement is in effect. An example of a COC form may be found in Figure 23-1.

23.1.1 Field Documentation

The information the sampler needs to provide at the time of sampling on the container label is:

- Sample identification
- Date and time
- Preservative

During the sampling process, the COC form is completed and must be legible (see Figure 24-1). This form includes information such as:

- Client name, address, phone number
- Project name and/or number
- The sample identification
- Date, time and location of sampling
- Sample collectors name

- The matrix description
- The container description
- The total number of each type of container
- Preservatives used
- Analysis requested
- Requested turnaround time (TAT)
- Any special instructions
- Purchase order number or billing information (e.g., quote number) if available
- The date and time that each person relinquished or received the sample(s), including their signed name.

When the sampling personnel deliver the samples directly to TestAmerica personnel, the samples are stored in a cooler with ice, as applicable, and remain solely in the possession of the client's field technician until the samples are delivered to the laboratory. The sample collector must assure that each container is in his/her physical possession or in his/her view at all times, or stored in such a place and manner to preclude tampering. The field technician relinquishes the samples in writing on the COC form to the sample control personnel at the laboratory or to a TestAmerica courier. When sampling personnel deliver the samples through a common carrier (Fed-Ex, UPS), the COC relinquished date/time is completed by the field personnel and samples are released to the carrier. Samples are only considered to be received by laboratory when personnel at the laboratory have physical control of the samples.

Note: Independent couriers are not required to sign the COC form. The COC is usually kept in the sealed sample cooler. The receipt from the courier is stored in Sample Control by date; it lists all receipts each date.

23.1.2 Legal / Evidentiary Chain-of-Custody

If samples are identified for legal/evidentiary purposes on the COC or by the client, Sample Control completes the custody seal and retains the shipping record with the COC. Sample movement within the laboratory as well as disposal is tracked using an internal COC included in the LIMS.

23.2 Sample Receipt

Samples are received at the laboratory by designated sample receiving personnel, and a unique laboratory project identification number is assigned. Each sample container is assigned a unique sample identification number that is cross-referenced to the client identification number such that traceability of test samples is unambiguous and documented. Each sample container is affixed with a durable sample identification label. Sample acceptance, receipt, tracking and storage procedures are summarized in the following sections and in full detail in SOP *Sample Receiving* / NV02-01.

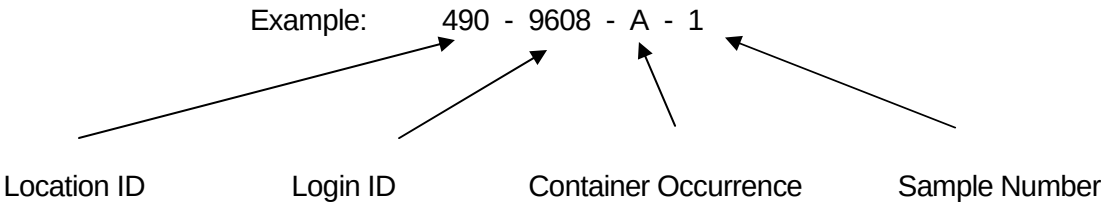
23.2.1 Laboratory Receipt

When samples arrive at the laboratory, sample receiving personnel inspect the coolers and samples. The integrity of each sample must be determined by comparing sample labels or tags with the COC and by visual checks of the container for possible damage. Any non-conformance, irregularity, or compromised sample receipt must be documented on a Cooler Receipt Form and brought to the immediate attention of the Project Manager and client. The COC, shipping documents, documentation of any non-conformance, irregularity, or comprised sample receipt, record of client contact, and resulting instructions become part of the project record and are usually scanned into LIMS.

23.2.1.1 Unique Sample Identification

All samples that are processed through the laboratory receive a unique sample identification to ensure that there can be no confusion regarding the identity of such samples at anytime. This system includes identification for all samples, subsamples and subsequent extracts and/or digestates.

The laboratory assigns a unique identification (e.g., Sample ID) code to each sample container received at the laboratory. This Primary ID is made up of the following information (consisting of 4 components):



The above example states that TestAmerica Nashville Laboratory (Location 490). Login ID is 9608 (unique to a particular client/job occurrence). The container code indicates it is the first container (“A”) of Sample #1.

If the primary container goes through a prep step that creates a “new” container, then the new container is considered secondary and gets another ID. An example of this being a client sample in a 1-Liter amber bottle is sent through a Liquid/Liquid Extraction and an extraction vial is created from this step. The vial would be a SECONDARY container. The secondary ID has 5 components.

Example: 490 - 9608 - A - 1 - A ← Secondary Container Occurrence

Example: 490-9608-A-1-A, would indicate the PRIMARY container listed above that went through a step that created the 1st occurrence of a Secondary container.

With this system, a client sample can literally be tracked throughout the laboratory in every step from receipt to disposal.

23.3 Sample Acceptance Policy

The laboratory has a written sample acceptance policy (Figure 23-3) that clearly outlines the circumstances under which samples are accepted or rejected. These include:

- A COC must be filled out completely
- Samples must be properly labeled
- Samples must be submitted in proper containers with adequate volume for the analysis and necessary QC
- Samples must be preserved according to the requirements of the requested analytical method
- Adequate sample holding times must remain for preparation and analysis
- All shipping containers including samples for water/solid volatile organic analyses should hold a trip blank
- Sample containers must be received in good condition
- The Project Manager is notified if any sample fails to meet the criteria listed in this sample acceptance policy.

Data from samples which do not meet these criteria are flagged and the nature of the variation from policy is defined. A copy of the sample acceptance policy is provided with all laboratory-supplied container shipments.

23.3.1 Inspection of samples includes a check for:

- Complete documentation to include sample identification, location (i.e., state), date and time of collection, collector's name, preservation type, sample type and any additional comments concerning the samples.
- Complete sample labels to include unique identification in indelible ink.
- Use of appropriate sample containers
- Adherence to holding times as specified in the test method and/or summarized in Section 24.
- Adequate sample volume for required analyses
- Damage or signs of contamination to sample container. Volatile vials are also inspected for headspace

23.3.2 Check and record the temperature of the samples that require thermal preservation.

- Samples are deemed acceptable if upon arrival they are not frozen (excluding VOAs) and are less than or equal to 6.0°C. Samples that are hand-delivered immediately after collection may not be at the required temperatures; however, if there is evidence that the chilling process has begun, such as the arrival on ice, the samples are considered acceptable. Condition upon receipt at the laboratory must be documented on the COC.
- If the samples were shipped in ice and solid ice is still present and in direct contact with samples, report the samples as "received on ice." Direct contact means samples must be surrounded by ice cubes or crushed ice. Ice present in a plastic bottle or other

container does not constitute direct contact. Samples shipped with only "blue ice" may not be reported as "received on ice."

23.3.3 Verify sample preservation as specified in the test method. Check for correct pH as specified in the test method. The results are documented on the Cooler Receipt Form and in LIMS. In the case of volatiles, pH is recorded after analysis on the run log and benchsheet. Chlorine is checked on samples requiring extractable organics, BOD, TOX, cyanide, fluoride, ammonia, TKN, and CBOD, and nitrate. Chlorine presence or absence is recorded for these analyses.

23.3.4 After inspecting the samples, the sample control receiving personnel sign and date the COC form, make any necessary notes of the samples' conditions on the Cooler Receipt Form, and store them in appropriate refrigerators or storage locations.

23.3.5 If samples are received without a COC, TestAmerica provides a generic COC form to be completed by the client when the samples are brought to the laboratory. The client is always provided with a copy of the completed COC form for their records.

23.3.6 If analyses with short holding times are requested, the dates and times are inspected to ensure that holding times have not already expired.

23.3.7 For samples received after normal working hours, the receipt time, date, and temperature are recorded at a minimum. The person delivering the samples signs the COC if they are the client or records their initials if they are a courier (e.g., FedEx or UPS). For samples not removed from the coolers, the coolers containing the samples are placed in a walk-in refrigerator. If samples are removed from the coolers, then the person receiving the samples must record the receipt date and time, the presence or absence of ice and custody seals, the temperature of samples, presence and type of packing material, and their initials. These samples are also placed in appropriate refrigerators.

23.3.8 Any deviations from these checks that question the suitability of the sample for analysis, or incomplete documentation as to the tests required will be resolved by consultation with the client. If the sample acceptance policy criteria are not met, the laboratory shall either:

- Retain all correspondence and/or records of communications with the client regarding the disposition of rejected samples, or
- Fully document any decision to proceed with sample analysis that does not meet sample acceptance criteria.

> **Note**: North Carolina requires that they be notified when samples are processed that do not meet sample acceptance criteria.

Once sample acceptance is verified, the samples are logged into the LIMS according SOP *Sample Receiving* / NV02-01

23.3.9 The COC, shipping documents, documentation of any non-conformance, irregularity, or compromised sample receipt, record of client contact, and resulting instructions become part of the project record.

23.4 Sample Storage

In order to avoid deterioration, contamination, or damage to a sample during storage and handling from the time of receipt until all analyses are complete, samples are stored in refrigerators, freezers, or protected locations suitable for the sample matrix. In addition, samples to be analyzed for volatile organic parameters are stored in separate refrigerators designated for volatile organic parameters only. Samples are never stored with reagents, standards, or materials that may create contamination.

To ensure the integrity of the samples during storage, refrigerator blanks are maintained in the volatile sample refrigerators and analyzed, at minimum, every two weeks.

Analysts and technicians retrieve the sample container allocated to their analysis from the designated refrigerator and place them on carts, analyze the sample, and return the remaining sample or empty container to the refrigerator from which it originally came. After all analyses are complete, samples are placed into sample storage for at least 60 days. This area is at room temperature. At the end of approximately 60 days, samples are disposed of in accordance with SOP *Waste Disposal* / NV10-83.

Access to the laboratory is controlled such that sample storage devices do not require locking mechanisms. Samples are accessible to laboratory personnel only. Visitors to the laboratory are prohibited from entering the refrigerator and laboratory areas unless accompanied by an employee of TestAmerica.

23.5 Hazardous Samples and Foreign Soils

To minimize exposure to personnel and to avoid potential accidents, hazardous and foreign soil samples are stored in designated, isolated areas designated for hazardous waste only. Any sample that is known to be hazardous at the time of receipt or after completion of analysis is placed in one of two refrigerators designated for highly contaminated samples. Foreign and U.S. soils requiring separate storage (as specified in SOP *Handling of Soils Regulated by USDA* / NV10-162) due to potential contamination with foreign organisms are tagged with an orange sticker and placed in specified locations. Foreign soils are heat-treated prior to disposal.

23.6 Sample Shipping

In the event that the laboratory needs to ship samples, the samples are placed in a cooler with enough ice to ensure the samples remain just above freezing and at or below 6.0°C during transit. The samples are carefully surrounded by packing material to avoid breakage (yet maintain appropriate temperature). For sample shipments which include water/solid volatile organic analyses, a trip blank is enclosed when required by method specifications, state requirements, or regulatory programs (see Note). The chain-of-custody form is signed by the sample control technician and attached to the shipping paperwork. Samples are generally shipped via overnight courier or hand-delivered by a TestAmerica courier to maintain sample integrity. All personnel involved with shipping and receiving samples must be trained to

maintain the proper chain-of-custody documentation and to keep the samples entact and on ice. The Environmental Health and Safety Manual contains additional shipping requirements.

Note: If a client does not request trip blank analysis on the COC or other paperwork, the laboratory will not analyze the trip blanks that were supplied. However, in the interest of good client service, the laboratory will advise the client at the time of sample receipt that it was noted that they did not request analysis of the trip blank; and that the laboratory is providing the notification to verify that they are not inadvertently omitting a key part of regulatory compliance testing.

23.7 Sample Disposal

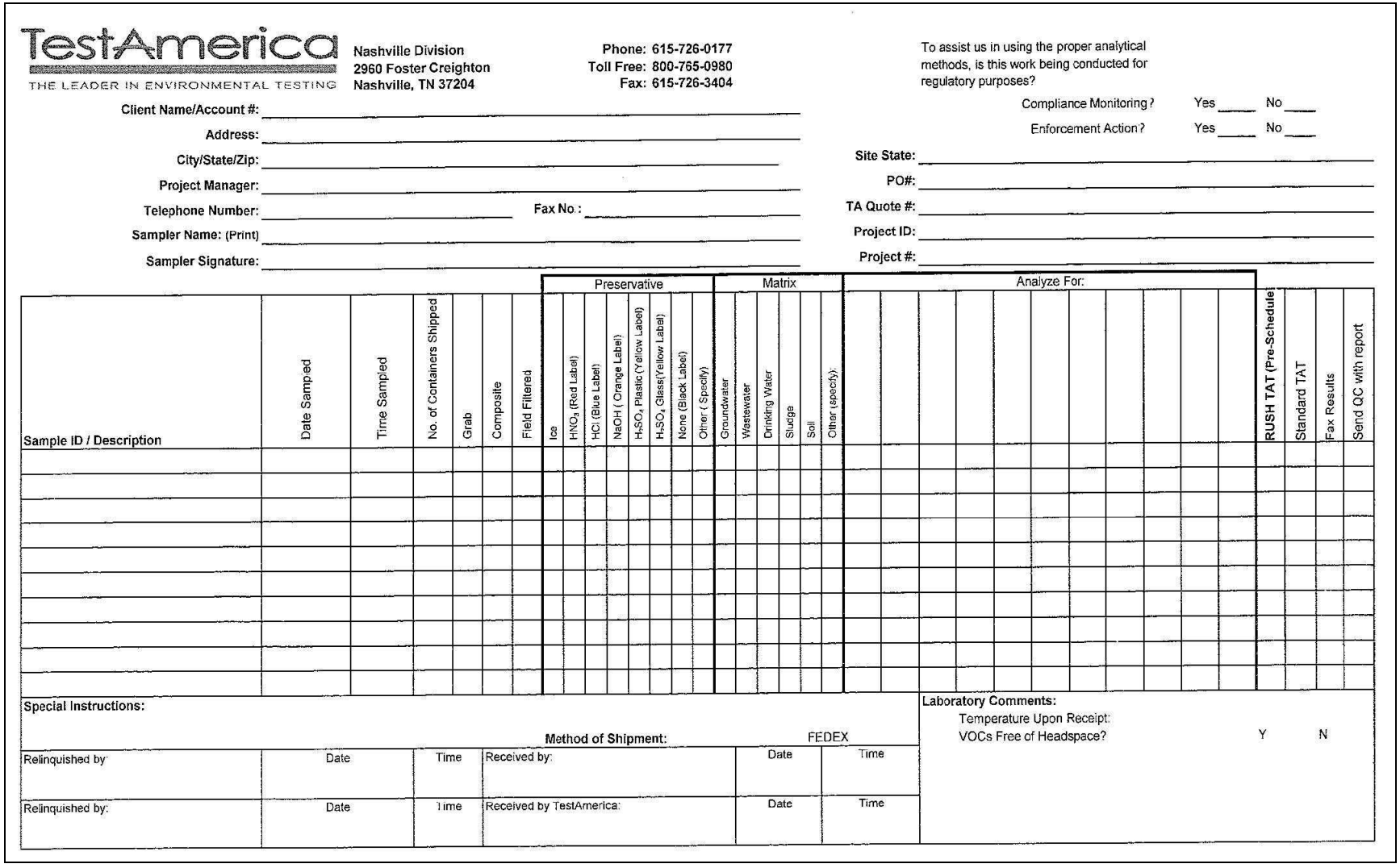
Samples are retained for a minimum of 30 days after the project report is sent; however, provisions may be made for earlier disposal of samples once the holding time is exceeded. Some samples are required to be held for longer periods based on regulatory or client requirements (e.g., 60 days after project report is sent). The laboratory must follow the longer sample retention requirements where required by regulation or client agreement.

Several possibilities for sample disposal exist: the sample may be consumed completely during analysis, the sample may be returned to the customer or location of sampling for disposal, or the sample may be disposed of in accordance with the laboratory's waste disposal procedures (SOP *Waste Disposal* / NV10-83). All procedures in the laboratory's Environmental Health and Safety Manual are followed during disposal. Samples are normally maintained in the laboratory no longer than two months from receipt unless otherwise requested. Unused portions of samples found or suspected to be hazardous according to state or federal guidelines may be returned to the client upon completion of the analytical work.

If a sample is part of a known legal action, the affected legal authority, sample data user, and/or submitter of the sample must participate in the decision about the sample's disposal. All documentation and correspondence concerning the disposal decision process must be kept on file. Pertinent information includes the date of disposal, nature of disposal (such as sample depletion, hazardous waste facility disposal, return to client), and names of individuals who conducted the arrangements and physically completed the task. The laboratory removes or defaces sample labels prior to disposal, unless this is accomplished through the disposal method (e.g., samples are incinerated). Waste disposal is tracked in the LIMS.

Waste management practices are conducted in accordance with all applicable rules and regulations. Excess reagents, samples, and method process wastes must be stored, managed, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to this document and SOP *Waste Disposal* / NV10-83.

Figure 23-1. Chain of Custody (COC)



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville Division
2960 Foster Creighton
Nashville, TN 37204

Phone: 615-726-0177
Toll Free: 800-765-0980
Fax: 615-726-3404

To assist us in using the proper analytical methods, is this work being conducted for regulatory purposes?

Compliance Monitoring? Yes ____ No ____

Enforcement Action? Yes ____ No ____

Client Name/Account #: _____

Address: _____

City/State/Zip: _____

Project Manager: _____

Telephone Number: _____ Fax No.: _____

Sampler Name: (Print) _____

Sampler Signature: _____

Site State: _____

PO#: _____

TA Quote #: _____

Project ID: _____

Project #: _____

Sample ID / Description	Date Sampled	Time Sampled	No. of Containers Shipped	Grab	Composite	Field Filtered	Preservative: Ice	Preservative: HNO_3 (Red Label)	Preservative: HCl (Blue Label)	Preservative: NaOH (Orange Label)	Preservative: H_2SO_4 Plastic (Yellow Label)	Preservative: H_2SO_4 Glass(Yellow Label)	Preservative: None (Black Label)	Preservative: Other (Specify)	Matrix: Groundwater	Matrix: Wastewater	Matrix: Drinking Water	Matrix: Sludge	Matrix: Soil	Matrix: Other (specify):	Analyze For:										RUSH TAT (Pre-Schedule)	Standard TAT	Fax Results	Send QC with report

Special Instructions:

Method of Shipment: FEDEX

Laboratory Comments:
Temperature Upon Receipt:
VOCs Free of Headspace? Y N

Relinquished by:	Date	Time	Received by:	Date	Time
Relinquished by:	Date	Time	Received by TestAmerica:	Date	Time

Figure 23-2. **Custody Seal**

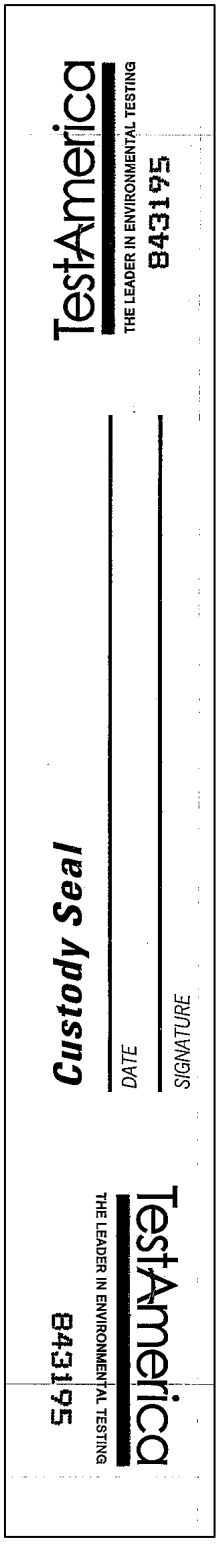


Figure 23-3. Sample Acceptance Policy

All incoming work will be evaluated against the criteria listed below. Where applicable, data from any samples that do not meet the criteria listed below will be noted on the laboratory report defining the nature and substance of the variation. In addition the client will be notified either by telephone, fax or e-mail ASAP after the receipt of the samples.

1) Samples must arrive with labels intact with a Chain of Custody filled out completely. The following information must be recorded.
   - *Client name, address, phone number and fax number (if available)*
   - *Project name and/or number*
   - *The sample identification*
   - *Date, time and location (including State) of sample collection*
   - *The collectors name*
   - *The matrix description*
   - *The container description*
   - *The total number of each type of container*
   - *Preservatives used*
   - *Analysis requested*
   - *Requested turnaround time (TAT)*
   - *Any special instructions*
   - *Purchase Order number or billing information (e.g. quote number) if available*
   - *The date and time that each person received or relinquished the sample(s), including their signed name.*
   - *The date and time of receipt must be recorded between the last person to relinquish the samples and the person who receives the samples in the lab, and they must be exactly the same.*
   - Information must be legible

2) Samples must be properly labeled.
   - Use durable labels (labels provided by TestAmerica are preferred)
   - Include a unique identification number
   - Include sampling date and time & sampler ID
   - Include preservative used.
   - Use indelible ink
   - Information must be legible

3) Proper sample containers with adequate volume for the analysis and necessary QC are required for each analysis requested. See LIMS.

4) Samples must be preserved according to the requirements of the requested analytical method (See LIMS)**.**

5) Most analytical methods require chilling samples to 4°C (other than water samples for metals analysis). For these methods, the criteria are met if the samples are chilled to below 6°C and above freezing (0°C). For methods with other temperature criteria (e.g. some bacteriological methods require ≤ 10°C), the samples must arrive within ± 2°C of the required temperature or within the method specified range. **Note:** Samples that are hand delivered to the laboratory immediately after collection may not have had time to cool sufficiently. In this case the samples will be considered acceptable as long as there is evidence that the chilling process has begun (arrival on ice).

5i.) Samples that are delivered to the laboratory on the same day they are collected may not meet the requirements of Section 5. In these cases, the samples shall be considered acceptable if the samples were received on ice.

5ii.) If sample analysis is begun within fifteen (15) minutes of collection, thermal preservation is not required.

5iii.)Thermal preservation is not required in the field if the laboratory receives and refrigerates the sample within fifteen (15) minutes of collection.

- Chemical preservation (pH) will be verified prior to analysis and documented, either in sample control or at the analyst's level. The project manager will be notified immediately if there is a discrepancy. If analyses will still be performed, all affected results will be flagged to indicate improper preservation

- For Volatile Organic analyses in drinking water (Methods 502.2 or 524.2). Residual chlorine must be neutralized prior to preservation. If there is prior knowledge that the samples are not chlorinated, state it on the COC and use the VOA vials pre-preserved with HCl. The following are other options for a sampler and laboratory where the presence of chlorine is not known:
  - 1. Test for residual chlorine in the field prior to sampling.
    - If no chlorine is present, the samples are to be preserved using HCl as usual.
    - If chlorine is present, add either ascorbic acid or sodium thiosulfate prior to adding HCl.
  - 2. Use VOA vials pre-preserved with sodium thiosulfate or ascorbic acid and add HCl after filling the VOA vial with the sample.

- **FOR WATER SAMPLES TESTED FOR CYANIDE (by Standard Methods or EPA 335)**

  - In the Field: Samples are to be tested for Sulfide using lead acetate paper prior to the addition of Sodium Hydroxide (NaOH). If sulfide is present, the sample must be treated with Cadmium Chloride and filtered prior to the addition of NaOH.

    - If the sulfide test and treatment is not performed in the field, the lab will test the samples for sulfide using lead acetate paper at the time of receipt and if sulfide is present in the sample, the client will be notified and given the option of retaking the sample and treating in the field per the method requirements or the laboratory can analyze the samples as delivered and qualify the results in the final report.

  - It is the responsibility of the client to notify the laboratory if thiosulfate, sulfite, or thiocyanate are known or suspected to be present in the sample. This notification may be on the chain of custody. The samples may need to be subcontracted to a laboratory that performs a UV digestion. If the lab does not perform the UV digestion on samples that contain these compounds, the results must be qualified in the final report.

  - The laboratory must test the sample for oxidizing agents (e.g. Chlorine) prior to analysis and treat according to the methods prior to distillation. (ascorbic acid or sodium arsenite are the preferred choice).

6) Sample Holding Times

- TestAmerica will make every effort to analyze samples within the regulatory holding time. Samples must be received in the laboratory with enough time to perform the sample analysis. Except for short holding time samples (< 48hr HT) sample must be received with at least 48 hrs (consecutive working hours) remaining on the holding time for us to ensure analysis.

- Analyses that are designated as "field" analyses (Odor, pH, Dissolved Oxygen, Disinfectant Residual; a.k.a. Residual Chlorine, and Redox Potential) should be analyzed ASAP by the field sampler prior to delivering to the lab (within 15 minutes). However, if the analyses are to be performed in the laboratory, TestAmerica will make every effort to analyze the samples within 24 hours from receipt of the samples in the testing laboratory. Samples for "field" analyses received after 4:00 pm on Friday or on the weekend will be analyzed no later than the next business day after receipt (Monday unless a holiday). Samples will remain refrigerated and sealed until the time of analysis. The actual times of all "field" sample analyses are noted on the "Short Hold Time Detail Report" in the final report. Samples analyzed in the laboratory will be qualified on the final report with an 'H' to indicate holding time exceedance.

7) All samples submitted for Volatile Organic analyses must have a Trip Blank submitted at the same time. TestAmerica will supply a blank with the bottle order.

8) The project manager will be notified if any sample is received in damaged condition. TestAmerica will request that a sample be resubmitted for analysis.

9) Recommendations for packing samples for shipment.

- Pack samples in Ice rather than "Blue" ice packs.

- Soil samples should be placed in plastic zip-lock bags. The containers often have dirt around the top and do not seal very well and are prone to intrusion from the water from melted ice.

- Water samples would be best if wrapped with bubble-wrap or paper (newspaper, or paper towels work) and then placed in plastic zip-lock bags.

- Fill extra cooler space with bubble wrap.

Figure 23-4. Cooler Receipt Form

Cooler Received/Opened On_____

1. Tracking #_____(last 4 digits, FedEx)

Courier: _____ IR Gun ID_____

2. Temperature of rep. sample or temp blank when opened:_____*Degrees Celsius*

3. If Item #2 temperature is 0°C or less, was the representative sample or temp blank frozen? YES NO…NA

4. Were custody seals on outside of cooler? YES…NO…NA

If yes, how many and where:_____

5. Were the seals intact, signed, and dated correctly? YES…NO…NA

6. Were custody papers inside cooler? YES…NO…NA

I certify that I opened the cooler and answered questions 1-6 (intial) _____

7. Were custody seals on containers: YES…NO…NA

Were these signed and dated correctly? YES…NO…NA

8. Packing mat'l used? Bubblewrap Plastic bag Peanuts Vermiculite Foam Insert Paper Other None

9. Cooling process: Ice Ice-pack Ice (direct contact) Dry ice Other None

10. Did all containers arrive in good condition (unbroken)? YES…NO…NA

11. Were all container labels complete (#, date, signed, pres., etc)? YES…NO…NA

12. Did all container labels and tags agree with custody papers? YES…NO…NA

13a. Were VOA vials received? YES…NO…NA

b. Was there any observable headspace present in any VOA vial? YES…NO…NA

14. Was there a Trip Blank in this cooler? YES…NO…NA If multiple coolers, sequence #_____

I certify that I unloaded the cooler and answered questions 7-14 (intial) _____

15a. On pres'd bottles, did pH test strips suggest preservation reached the correct pH level? YES…NO…NA

b. Did the bottle labels indicate that the correct preservatives were used YES…NO…NA

16. Was residual chlorine present? YES…NO…NA

I certify that I checked for chlorine and pH as per SOP and answered questions 15-16 (intial) _____

17. Were custody papers properly filled out (ink, signed, etc)? YES…NO…NA

18. Did you sign the custody papers in the appropriate place? YES…NO…NA

19. Were correct containers used for the analysis requested? YES…NO…NA

20. Was sufficient amount of sample sent in each container? YES…NO…NA

I certify that I entered this project into LIMS and answered questions 17-20 (intial)_____

I certify that I attached a label with the unique LIMS number to each container (intial)_____

21. Were there Non-Conformance issues at login? YES…NO Documented in LIMS? YES…NO…#_____

Title: SAMPLE RECEIVING

Approvals (Signature/Date)			
	3/4/13		2/8/13
Paul Buckingham Department Manager	Date	Andy Johnson Client Services Manager	Date
	2/18/13		2/15/13
Michael H. Dunn Technical Director Quality Assurance Manager	Date	Johnny Davis Health & Safety Manager / Coordinator Extractions Operations Manager	Date

1.0 Purpose

TestAmerica Nashville receives I samples from numerous locations for a variety of purposes. Each sample is uniquely identified upon receipt. This identification follows the sample throughout the entire system: login, storage, analysis, reporting, data archiving, invoicing, and disposal.

2.0 Scope

2.1 Generally, clients collect samples in accordance with a particular federal, state, or municipal law. The majority of samples submitted are water, wastewater, groundwater, storm water, soil, sediment, sludge, and oily waste

2.2 An essential part of any sampling/analytical scheme is ensuring sample integrity from collection to data reporting. Documentation begins when sample containers are dispatched to the field, where the collector records the collection of each sample on a Chain-of-Custody form (COC) or equivalent, the container label, the custody seal (when required) and field notebooks as each sample is collected. Each person involved in the handling of the container must sign his name, date, and time at receipt and relinquishment on the COC or equivalent.

2.3 Upon receipt of the sample in the lab and transfer of custody, Sample Receiving personnel check the samples for a variety of requirements and the associated paperwork for clarity of intended analyses. They complete documents to record these checks. If a problem exists, they create a Non-conformance Memo (NCM) and send an email to a Project Manager to call the client and determine an appropriate resolution. If everything is satisfactory, they organize the samples and enter the pertinent information into the Laboratory Information Management System (LIMS). The system assigns a job number and unique sample numbers to each sample container along with a location code. They apply a sticker with the unique sample number on the container and record the unique sample number on the COC or equivalent. The lab uses this number in every subsequent step in the laboratory.

2.4 Once the container has been labeled, the Sample Receiving specialist places the container in the proper storage location in such a manner that the analysts may readily find the sample for analysis. Samples which must be analyzed quickly are taken directly to the supervisor or analyst. After analysis, the sample is retained in a separate storage area for nominally 60 days. At the end of this time, it is disposed of properly, as prescribed by the SOPs on sample disposal.

3.0 Safety

3.1 Due to the nature of the work, a sample's origin is unknown, and the outside of the container may contain potentially harmful substances. Handle all sample containers with caution. While handling samples, wearing safety glasses and protective clothing (lab coat and gloves) is required. Kevlar or cut-resistant gloves must also be worn under nitrile or rubber gloves during cooler opening and unloading to avoid possible cuts due to sample container breakage or from cutting utensils.

3.2 If there is any suspicion or provided information about the unusual nature of a sample, it is handled under a vented hood. The supervisor and analysts are notified immediately regarding any out-of-the-ordinary problem.

3.3 Samples may contain chemicals, either as a preservative or as a component. Specific chemicals, such as H_2SO_4, HCl, HNO_3, and NaOH, are required by the regulations to preserve water samples for certain tests. If sufficiently concentrated, these chemicals are harmful to the skin on contact and sometimes harmful by inhalation and ingestion. For these reasons, protective clothing must be used when handling samples; neither eating nor drinking in the area is allowed.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors causes breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms include coughing, choking, and irritation of the nose, throat, and respiratory tract. Causes redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and cause damage to the eyes. Contact causes severe burns and permanent eye damage.
Hydrochlo-ric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Causes redness, pain, and severe skin burns. Vapors are irritating and cause damage to the eyes. Contact causes severe burns and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.
Sodium bisulfate	Irritant	None	Causes mild to severe irritation to the eyes. Prolonged exposure causes burn if not flushed with water. Causes mild irritation to skin. Prolonged exposure causes burn if not flushed with water.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and causes skin to become dry and cracked. Skin absorption can occur; symptoms parallel inhalation exposure. Irritant to the eyes.
Trisodium phosphate		None listed	Keep in closed container; avoid high temperatures and strong acids.
Ascorbic acid	(Vitamin C) Irritant	None	May cause mild irritation to the respiratory tract, gastrointestinal tract, skin, eyes. Mutagenic for somatic cells.
Sodium thiosulfate	Irritant	None	May be harmful if swallowed or inhaled. May cause irritation to skin, eyes, and respiratory tract.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

3.4 Because the samples usually arrive with a mixture of ice and ice water in their cooler, spillage onto the floor is likely. The department must attempt to minimize the amount of water on the floor, clean it up as soon as possible, and exercise caution when walking in the area.

3.5 Coolers may be heavy. Login personnel must use proper lifting techniques and ask for assistance when needed.

3.6 EH&SC must be notified immediately if a sample is labeled with Hydrofluoric Acid (HF) or asbestos. Both of these present a hazard to employees.

3.7 All relevant laboratory safety procedures must be followed.

4.0 Definitions

4.1 Bench Sheet: A list generated by LIMS showing the sample numbers needing analysis by a specific method.

4.2 Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis.
4.3 Chain of Custody (COC): An unbroken trail of accountability that ensures the physical security of samples and includes the signatures of all who handle the samples.
4.4 Composite Sample: A sample composed of more than one discrete sample. A water composite sample can be collected on a time-proportional or flow-proportional basis. Equal-volume, equal-weight, or proportional-based composites can also be submitted or requested. Do not composite VOAs. It is inappropriate to composite VOA samples.
4.5 Compromised Samples: those samples which are improperly sampled, insufficiently documented (COC and other sample records and /or labels), improperly preserved, collected in improper containers, in broken/cracked containers, or exceeding holding times when delivered to the laboratory. Under normal conditions, compromised samples are not analyzed. If the situation requires analysis, the results must be appropriately qualified.
4.6 Equipment Blank: A sample of analyte-free media, which has been used by the sample collector to rinse common sampling equipment to check the effectiveness of decontamination procedures.
4.7 Field Blank: A blank prepared in the field by filling a clean container with reagent water and appropriate preservative, if any, for the specific sampling activity being undertaken.
4.8 Field Duplicate: A sample collected at the same time and same location as the original sample in the field. Comparison of field duplicate results is an attempt to assess sampling technique and site variability.
4.9 Grab Sample: A sample collected as a discrete sample at a specific moment in time.
4.10 Headspace: An air bubble larger than pea-size (<6 mm, ¼"). Water vials with headspace are put in the box upside down to alert the analyst to avoid using it for analysis. If analysis cannot be run correctly, a NCM must be initiated.
4.11 Holding Time (Maximum Allowable Holding Time): the maximum time that a sample may be held prior to a specific analysis and still be considered valid or not compromised. The holding time begins at the time of collection, and the prep and/or analysis (depending on the method) must begin before the holding time has expired.
4.12 LIMS: Laboratory Information Management System: the software that records the status of samples in the laboratory.
4.13 Matrix: the component or substrate on which the analysis of interest is performed. Examples of matrices are aqueous (for example, wastewater, sewage, storm water, groundwater, as different from drinking water or saline/estuarine water), drinking water, saline/estuarine water, non-aqueous liquid, solid (soil, sediment, sludge), chemical waste, air, industrial hygiene filter/absorbent. Water and soil samples are typically submitted in plastic or glass containers. Soils may also arrive in baggies, envelops, etc. Air samples are often collected in Tedlar™ bags, filter cassettes, carbon tubes, or other collection media.
4.14 Preservation: the temperature mandated from and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.
4.15 Job: all samples received at one submittal from one client on one project. The job is given a unique number, called a project number or billing control number.
4.16 Trip Blank: a sample whose purpose is to determine if contamination has occurred due to improper sample container cleaning, contaminated blank source water in the laboratory, or sample contamination during storage and transportation to and from the sampling location when sampling for volatile organics. Trip blanks are prepared prior to the sampling event by the laboratory providing the sample containers. They consist of analyte-free water plus appropriate preservatives. They are transported everywhere the actual sample containers go and are not opened in the field. Trip blanks for volatile organics analysis are provided to clients requesting volatile organics.

4.17 Batch: Environmental samples which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation** batch is composed of up to 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) and /or those samples not requiring preparation, which are analyzed together as a group using the same calibration curve or factor. An **analytical** batch can include samples originating from various environmental matrices and can exceed 20 samples.
4.18 NonConformance (NCM): NonConformance memos communicate issues to the end user of the data to describe nonconformance events that may impact the data. See Nonconformance Memo Setup / CW-I-T-068 at \\corp-fs-04.tai.com\LimsUserDocs\Sample Management for how to use this module.
4.19 See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for other laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

5.0 Procedure

5.1 Sample Collection: Sample collection is the responsibility of the client. When planning the project, the client may call project management (PM) or the Technical Director to discuss the details of the sample matrix, which tests to run, and how many samples are anticipated. A PM representative generates a bottle order based on these details. The Shipping Department receives the bottle order, packs the appropriate number and type of bottles in a cooler, and ships the cooler to arrive on time at the client's address. On site, the client fills the containers, repacks them, typically adds ice, and ships them back or delivers them to TestAmerica Nashville. The client may use his own containers, coolers, and forms.
5.2 Sample Shipment: It is very important that samples be received in a timely manner, since there are holding time limitations on many tests. Samples arrive from many shipping services, by mail, and by the client's delivering them to our door, either by themselves or a courier. Daily, for most of the coolers, TestAmerica Nashville drives to the Federal Express facility, counts the coolers addressed to us, loads them onto our truck, unloads them at the laboratory, and transports them into the login area.
5.3 Preliminary Cooler Check: As soon as the coolers are in the Sample Receiving area, personnel open each cooler to determine (1) the urgency of analysis, either because the holding time is about to expire, or because the client needs the results sooner than three days and (2) if the COC or equivalent is missing.

As each cooler is checked, information is recorded on a Cooler Receipt Form. It records the temperature, the date and time received, the presence of custody seals, and who opened the cooler. It also records the packing material, coolant, and the commercial carrier tracking number if present. Any problems noted at this time, such as insufficient method information or non-compliant temperatures, are communicated to PM via email.

Only the last four digits of the FedEx tracking number are recorded. The complete tracking number can be retrieved. A list of FedEx tracking numbers is obtained daily from FedEx with the coolers. A PDF copy is generated and stored electronically in TALS/Tools/File System Shares/COCs.

If there is urgency to the analysis, the cooler is taken directly to a Sample Receiving person for login and subsequent notification of supervisor or analyst.
5.4 Temperature: Sample temperatures are checked when samples are received by the laboratory. The temperature of the samples is checked with a quarterly calibrated IR

thermometer. IR guns are verified each day of use by checking the temperature of a bottle of water at the temperature of interest that contains a calibrated thermometer. Agreement between the thermometer in the bottle and the IR gun must be within 0.5 degrees C, or the IR gun can not be used. Any IR gun not reading within 0.5°C is set aside and not used. This verification check is documented in a log.

IR Gun Temperature Guidelines

To check the temperature of samples, hold the IR gun at a perpendicular angle about six inches from the sample. Read the temperature of the attached label on the container, not the glass or plastic. Aim the IR gun straight at the label, i. e., perpendicular.

- Confirm that the IR device is within specification.
- If the temperature is 6°C or less, but not frozen, the temperature is recorded, and no further action is required.
- If a temperature is recorded between 6.0 and 6.5; then two additional containers in the same cooler must be checked, if available. All temperatures must be recorded and a NCM generated to consult with the client whether to proceed.
- If temperature is greater than 6.5°C, and the cooler is packed properly (refer to form LF-23), the Sample Receiving Tech looks to see if there is a temperature blank in the cooler. If a temperature blank is present, then take the temperature of the temp blank. The client is contacted and both the sample temp and blank temp are recorded and reported on the final report. In the event samples are received outside of the range of 0-6°C, the temperature is confirmed with a different calibrated IR thermometer. Both IR gun serial numbers and both temperatures must be recorded.
- If the temperature is less than zero (0) °C and is packed properly (refer to form LF-23), then the temperature is confirmed by a different calibrated IR thermometer, but the client is not notified. Both IR gun serial numbers and both temperatures must be recorded. The temperature is noted on the final report. If the samples are frozen, then a NCM must be initiated and the client notified for further instructions unless freezing the sample is allowable as either a state or method allowable form of preservation (i.e., Method 5035 for samples in FL, TX, and MA that are properly preserved).
- If the temperature is greater than 6.5°C, and the cooler is packed improperly (refer to form LF-23), ensure that the problem with the packing is noted by a NCM, the client contacted, and the sample temp noted on the final report.
- If the samples were shipped in ice and solid ice is still present and in direct contact with samples, report the samples as “received on ice.” Direct contact means samples must be surrounded by ice cubes or crushed ice. Ice present in a plastic bottle or other container does not constitute direct contact. Samples shipped with only “blue ice” may not be reported as “received on ice.”
- Procedures for samples that are hand delivered to the laboratory: Coolers hand-delivered by clients are typically received by Sample Receiving during normal business hours. Coolers delivered by the Test America employed courier or other carriers are typically received by Sample Receiving personnel. Coolers that are hand delivered may not be 6°C or lower at the time the samples are received. In these cases, Sample Receiving personnel must confirm that the cooling process has been started. They note that the samples were received with wet ice in the cooler. If the cooling process was not started prior to arrival at the lab, then a NCM must be generated. If samples have been collected the day prior to day of receipt, the temperature must be less than 6°C, but not frozen; otherwise, we generate a NCM and/or verify with the client that it is okay to proceed with analysis outside of the temperature requirements at the time of sample receipt.

5.5 Sample Inspection: When a job is ready for login, one of the Sample Receiving personnel carries the cooler(s) to their designated work area and LIMS computer. The containers are organized using the COC or equivalent as a guide. The Cooler Receipt Form (LF-1) and any necessary NCMs are completed and the following are inspected during the log-in process.

Note: The total amount of time the samples are removed from the cooler to the time when they are placed either in a refrigerator or delivered to the analytical departments must be kept to less than 2 hours. The initial unloading time and sample storage time must be recorded on the back of the Cooler Receipt Form (LF-1).

5.5.1 **Chain of Custody**: It is imperative that samples be accompanied by a complete COC or equivalent. It is mandatory for samples submitted for regulatory reporting of results. The COC or equivalent, in whatever format, must inform the lab about the following details:

The name, address, and phone number of the client, preferably with their account number. Preprinted COCs, with this information already on them, are available to our clients; they are prepared by project managers. The site, i. e., state, of sampling must be specified.

The name of the project is desirable. With the account number and project name, Sample Receiving can access project notes in LIMS. Project notes are created to summarize all the performance details required for a project or a client.

Also needed, a client-provided, unique sample description with the date and time it was collected and identification of its matrix. If the sample dates and times are not on the COC but are on the containers: record on Cooler Receipt Form and enter the times and dates in LIMS. If the sample dates and times are not on the containers, then determine which below applies:

The sampling date is required. Methods with holding times given in hours and the State of West Virginia also require sampling times. If this information is not on the COC, it can be obtained from the container labels, but the Cooler Receipt Form must have a note indicating that the information was taken from the label. WV requires a NCM if this information is not on the COC. If this information is neither on the COC or labels, then select the day prior to receipt as the sample date and 01:01 as the sample time, enter all analyses; and create a NCM. The PM is responsible to prevent the report from printing before this information is obtained from the client and updated in LIMS. If there is more than 3 days of holding time left for the sample, put the analysis status on HOLD. Note the 'HOLD' status on the NCM internal comment. The PM is responsible to change the status when needed.

A sample may consist of several containers, each preserved for the specific tests desired. The COC or equivalent must list the tests/methods the client desires and provide the appropriate containers with preservatives.

Each container is labeled with sample identification, date and time collected, and preservative if applicable, at a minimum. The labels are water resistant and written in indelible ink and legible. Verify that the container labels and the COC or equivalent match.

Information about potentially harmful components or high concentrations is desirable. When the lab knows this information prior to analysis, the analysis time and the analyst safety is improved.

Special instructions may be necessary. These may be written on the COC or an attachment. Example of special instructions: "Composite sample." "Only analyze the water layer in this sample."

The custody section of the COC or equivalent must be signed with the signature, date, and time of each person who has had possession of the sample since its collection. Signatures on the COC must have "-TAN" added and all information entered on the COC by Sample Receiving personnel must be legible. The "received" and "relinquished" blanks must be completed. Independent couriers are not required to sign the COC form. The COC is usually kept in the sealed sample cooler. Shipping papers or tracking numbers are used.

The COC or equivalent should indicate the turnaround time desired by the client, especially if the results are needed in less than ten days.

If there are questions about any of these issues, email the PM. The PM calls the client and resolves how to handle the problem.

5.5.2 **Condition of Containers**: While carefully removing the containers from the cooler, observe the condition of each container, i. e., whether broken or damaged, leaking, contaminated, having headspace (for volatiles containers only; see Section 4.10), presence of custody seals on individual containers, the type of packing material used, completeness of labeling, sufficient volume provided for tests requested. Record this information on the Cooler Receipt Form. Check to see if all the containers needed for the requested tests on a sample are present. If there are any problems, indicate them with an NCM so that the PM can call the client. Trip Blanks not recorded on the COC are documented on the Cooler Receipt Form.

5.5.3 **Container Material, Volume, and Preservative**: For every analysis for water and solids, there is a required container material (plastic or glass, generally), a minimum volume or mass necessary to run the test at a low detection level, and, usually, at least for waters, a chemical preservative. Consult Controlled Document LIF-3.

At Sample Receiving, each container must be checked for these three items by observing the containers submitted and the tests requested.

For water samples, note if the container material and volume matches the requirement for the test. The label tells which preservative has been added. Labels specifically state which preservative is present; also, they are color-coded. Bottles not supplied by us may be incompletely labeled.

For soil samples, note if the client submitted sufficient sample to perform the test optimally and if the container material is appropriate. Some soil analysis may have a preservative: for volatile organics analysis of soil, the sample may arrive in a VOA vial containing Sodium bisulfate, sodium phosphate, reagent water, or Methanol. Sulfide soils may have sodium hydroxide and Zinc acetate.

Record on the Cooler Receipt Form the findings from this inspection.

For preserved waters, the next step is to test the liquid in the container for its pH by using wide range pH paper. Narrow range pH paper is used if the wide range results are not clear. Only the containers used for inorganic analyses are checked in Sample Receiving, all others are checked by the analytical departments (i. e., prep, volatiles, UST, metals).

Immerse a capillary tube into the sample container. Contact the drops from the capillary tube onto the pH paper, wait for a few seconds, and check for a color change. **Do not immerse test strip into the sample.**

Wastewater samples for 200.7 metals analysis may be collected and shipped without acid preservation; however, acid must be added to the original sample container at least 24 hours before analysis to dissolve any metals that may adsorb to the container walls. This allowance is permissible for wastewater metals analysis only; it does not apply to drinking water samples. Exceptions to this wastewater rule are boron, mercury, and chromium VI, which have different preservation requirements.

Do not check the pH of VOA vials to be used for volatile organics analysis; the Volatiles Departments' analysts check the pH after analysis. Preservation compliance is recorded on the Cooler Receipt Form, and the pH of each container checked in Sample Receiving must be recorded in LIMS in the condition column for that container (example: <2, >9, >12, or =7, for a non-compliant sample). **For tests requiring an acid preservative (such as HCl, HNO_3, or H_2SO_4), the pH must be less than 2 pH units. For tests requiring an alkaline preservative (such as NaOH), the sample pH must be greater than or equal to 12 pH units for cyanide and greater than 9 pH units for sulfide.** If a sample does not meet the pH requirement for the test requested, record this information on the Cooler Receipt Form, in LIMS, and generate a NCM.

For waters on which BOD, TOX, cyanide, fluoride, ammonia, TKN, CBOD, phenolics, nitrate, nitrite and/or extractable organics analysis are requested, check the sample for residual chlorine. Extractable TRPH analysis does not require a check for residual chlorine.

Immerse a capillary tube into the sample container. Contact the drops from the capillary tube onto the free chlorine check strip, wait for a few seconds, and check for a color change.

Record the presence or absence of residual chlorine on the Cooler Receipt Form and in LIMS. If residual chlorine is present or the result is not clear due to the matrix, record on the Cooler Receipt Form and on the affected analysis comments for the analyst to "treat for residual chlorine." The container checked must be recorded in LIMS in the condition column for that container with a "c."

5.5.4 **Holding Time**: In general, each test has a holding time after which the analysis must be qualified. Also, the holding time is only valid if the sample is in a container of the appropriate material and with the correct preservative. If the holding time limit has been exceeded, record this information with an NCM so that the client can be contacted for further instructions. If the client wants us to proceed, we note the holding time problem as a footnote on the final report. "Short holds" are analysis, usually inorganic, but also formaldehydes and method 3030C, that have 72 hours or less from sampling until the hold time expires. Once all "Short Holds" are accessioned

in LIMS, an email is sent to all Nashville Users that "Short holds have been tagged". If a "Short Hold" test arrives after the email has been made or if the test is nearing expiration because of delay, the following steps are taken: Email the supervisor or group leader of the department the sample's LIMS number and what test is affected and deliver the sample to the supervisor or analyst right away.

5.5.5 **Method Selection**: The method the client wants us to run must be written definitively on the COC or equivalent. The client should know exactly what methods need to be run before containers are ordered and before sampling begins. Method numbers may vary depending upon which regulation or matrix is of concern and to which agency the analysis will be reported. There can also be more than one method by which to run a particular analyte, and each method may have a different price. Some methods can report groups of analytes, and other methods report just one result. A client may want one of the multi-analyte methods run for just a few specific analytes. If there is any question about the method to be analyzed, generate an email to the PM in order to find out. Without this degree of specificity, we cannot log in, analyze, report, and invoice properly. If there are holding time concerns, then the project may be logged in to address holding times, but questionable methods are placed on "hold" status.

5.6 Log into LIMS: Refer to Oasis \ TALS Manual \ Sample Management \ Login.pdf. After all the pertinent information from the above steps is available, login may begin. All samples received are logged into LIMS to allow the laboratory to track and evaluate sample progress. Each container has a unique designation assigned by LIMS.

5.7 Container Labeling: Labels for containers are provided to clients. These labels contain no solvent in the adhesive and are amenable to being written on; they are also water-resistant. In addition, at login, TestAmerica Nashville applies several types of labels, as warranted.

Each container base and lid (if enough room) receives a label with the sample number, generated by LIMS.

On all soils from foreign sites; sites outside the continental U.S.; and shallow depths (0 to 3 feet) quarantined sites; an orange dot is required on the sample containers. The hazard level on these must be 'foreign soil' in LIMS. Refer to USDA Soil Handling SOP.

Sample Receiving personnel apply to some containers color-coded dot labels to indicate various messages to lab personnel:

Blue signifies that the sample is held for six months or longer after all analyses are complete.

Orange signifies that the sample must be quarantined during storage because of USDA regulations.

(Red is reserved for sample storage personnel to indicate that a sample has been stored previously in the sample archive area.)

5.8 Documentation

5.8.1 **Chain-of-Custody (COC)**: The COC supplies a detailed record of the sample description, collection information, analysis requested, and any transfer of custody from sample collection through sample receipt into the laboratory. The sample collector is responsible for the care and custody of the samples until properly

dispatched to the receiving laboratory or turned over to the sample custodian or designee. Samples are delivered to the laboratory as soon as possible.

If samples are identified for legal/evidentiary purposes on the COC, Sample Receiving completes the custody seal, retains the shipping record with the COC, and initiates an internal COC for laboratory use by analysts and a sample disposal record. The internal COC is done electronically in LIMS.

At login, the project number provided by LIMS is placed on the COC. Also, the sample number for each unique sample identification is written on the COC.

5.8.2 **Cooler Receipt Form (LF-1)**: This form is completed as the cooler is unpacked and the samples within are organized according to the COC. This form is retained with the original COC. It is a checklist of all the pertinent issues with regard to sample acceptance, such as temperature upon receipt, suitable pH of sample if a preservative is required for a requested test, presence of the correct preservative for the requested test, use of proper container material (plastic, clear glass, amber glass), packing material utilized, broken or unbroken containers, completed container labels, headspace in containers for which volatile organics analysis is requested, presence of residual chlorine (when pertinent). If problems are noted at this time, an NCM is generated for the PM to contact the client for directions.

5.8.3 When login and all forms are completed, the paperwork is scanned to the server in pdf format. The paperwork includes the COC or equivalent, Cooler Receipt Form, and accompanying papers from the client.

The original is retained in the Project Management Department.

5.9 Sample Storage, Sample Holding, and Sample Distribution: The primary considerations for sample storage are temperature, light, cross-contamination, sample splitting, and security. For non-rush samples, i.e., quick turnaround due to client need or brief remaining holding time, the following protocols are routine:

If the samples are to be kept cold according to the preservation requirements, they are stored in an organized manner in one of the five walk-in coolers:

- The volatile organics samples are stored in the coolers (Walk-in Cooler #2) and refrigerators outside the Volatiles Departments.
- The inorganics bottles are stored in Walk-in Cooler #4.
- Non-volatile aqueous organics bottles are stored in Walk-in Cooler #1.
- Non-volatile solids are stored in Walk-in Cooler #3.
- Walk-in Cooler #5 is used for Inorganic bottles that are currently being used by the Inorganics Department and for the overflow from Walk-in Cooler #1.

All coolers are maintained to meet the temperature requirement of 0-6°C. The distribution of a sample depends on its matrix. Here are guidelines. These guidelines can be superseded for urgency, holding time expirations, unusual hazards, etc. If the analyst is prepared to immediately process a sample for urgency (paid rush) or holding time expirations, then it is acceptable to take the sample to the analyst or supervisor of that department. If there are unusual hazards, please consult with the Technical Director, EH&S Officer, QA Manager, and/or QA Specialist to determine best storage of samples. These guidelines must not be superseded without contacting the QA Manager, Technical Director and/or supervisors of the departments involved. The

guidelines can and are altered as needed due to Holding Blanks (refer to Holding Blank SOP) or temperature readings taken by TCLP personnel. The alterations are given to the login supervisor from the QA Department or TCLP personnel, who then passes the information to Sample Receiving personnel.

Oils Guidelines:
If the oil, pure chemical, strong odor (non gas), or drum sample has volatile methods (624, 8260, 602, 8021, 8011, 8015 alcohols, 8015 low fraction), then at least one container is placed directly in refrigerator #35 in the Volatiles Department. The location is 02.

If the oil, pure chemical, strong odor (non gas), or drum sample has extractable organic methods (BNA, DRO, HPLC, Pest/PCB/Herbs, Prep Lab) or inorganic methods **and** no VOA methods, then it is placed directly in refrigerator #34. The location is 01.

Soils Guidelines:
Never store soil vials upside down.

If the soil has volatile analysis for Florida, then the 2 reagent water vials and 1 Methanol vial are placed in the freezer above refrigerator #12. The location is FRZR1.

If the soil has TX1005 analysis, then the vials for TX1005 or at least one soil jar are/is placed in freezer #31 or #32. The locations rotate from TXS1 through TXS6; one week per location is typical. These locations are labeled in the freezer. Jars should be assigned to a soil bin: S1 through S600, and the bin put in the TX1005 freezer.

If the soil has non-Florida volatile methods, then the EnCore or prepped vials (Methanol and Sodium bisulfate vials) for the method must be placed on the Volatile Soil Cart in loginIf there are no prepped vials or only Sodium bisulfate vials, then at least one container is placed on the Volatile Soil Cart for VOA personnel to prep in Methanol. The Volatile Soil Cart is a designated metal cart kept in login during regular business hours and, if not empty, kept in Walk-in Cooler #2 overnight. During regular business hours volatile soil prep personal actively remove samples to prep them for analysis. The location is APCART except jars are assigned a location S1 through S600.

Auto shredder fluff samples for PCBs and wipes are placed on the “Fluff” shelf in Walk-in Cooler #1. The location is FLUFF.

All other soil containers, including extra containers, are placed in yellow locations bins numbered S1 through S600. The bins are organized on the shelves in Walk-in Cooler #3.

Soils with orange dots (refer to 5.7) must be stored in bins exclusive to orange doted soils.

Waters Guidelines:
In general, except for some inorganic analysis, all methods have an exclusive container. Water vials that have headspace are noted on the Cooler Receipt Form and a NCM is generated. The vials are stored upside down to make the analyst aware of the headspace.

Methods 524, 624, SM6200, and 8260 require exclusive vials and are usually preserved with Hydrochloric acid (HCl). If unpreserved, then these have a 7 day holding time. MO RBCA requires Trisodium phosphate (Na_3PO_4) preservative. Method 524 requires treatment with

Sodium thiosulfate ($Na_2S_2O_3$) in the field and transferred to Hydrochloric acid (HCl) preserved vials also in the field. These containers are placed in a box marked with a volatile location. The locations VOA1A through F and through VOA7A through F. The full box is replaced by an empty box with the next sequential number as needed. The full box is placed in the bottom section of refrigerator #12. Sample Control personnel regularly transfer full boxes to Walk-in Cooler #2 in the Volatiles Department.

PID/FID Methods 602, VPH, 8015-low fraction only for gasoline ranges-, and 8021-UST parameters only-require exclusive vials and are usually preserved with Hydrochloric acid (HCl). If unpreserved, then these have a 7 day holding time. These containers are placed in a box marked with a UST location. The full box is placed in the bottom section of refrigerator #2. Sample Control personnel regularly transfer full boxes to Walk-in Cooler #2 in the Volatiles Department.

Methods RSK 175, 504, 8011, and 8015-alcohols & acetates only- require exclusive vials and are usually preserved with Hydrochloric acid (HCl). Method 504 requires treatment with Sodium thiosulfate ($Na_2S_2O_3$) in the field and transferred to HCl preserved vials also in the field. If vials are not preserved, then the hold time is adjusted to 7 days. These containers are placed in a box marked with an RSK location. Sample Control personnel regularly transfer full boxes to the refrigerator in the Pest/PCB Department.

Texas Methods 1005 and 1006 require exclusive vials preserved with Sodium bisulfate ($NaHSO_4$) or with Hydrochloric acid (HCl) or unpreserved. If unpreserved, then these have a 7 day holding time. These containers are placed in a box marked with a TXW location. This box usually fills slowly and is on the middle shelf of refrigerator #2. Full boxes are transferred by login personnel to the TX shelves in Walk-in Cooler #1.

Metals analysis requires preservation with Nitric acid (HNO_3), but wastewater methods can be unpreserved. Unpreserved wastewater containers are preserved by Metals personnel and then held 24 hours prior to analysis. Preserved containers for methods 200.7, 3030, 6010, and 6020 are placed in red bins numbered M1 through M725 stored on shelves.

Walk-in Cooler #1 has the following shelves/areas:

"Unpreserved" shelves are marked by the weekday. Containers for method 608, 8081, 8082, 8141, and/or 8151 are placed on these shelves.

"Unpreserved" shelves are marked by the weekday. Containers for method 625, 8270, 8270 SIMS, MRBCA DRO 8270, MADEP EPH 8270 SIMS, 610, 8310, MADEP EPH 8310, 8315, and/or 8330 are placed on these shelves. Each method requires an exclusive amber liter. The liter is unpreserved. Preserved liters can be used, but it must be noted on the Cooler Receipt form.

"Preserved" shelves are marked by the weekday. Containers for Methods 8015AZ, 8015 DRO & ORO & ERO, CT-EPH, WI-DRO, OA-2, FL-PRO, FL-CWG, LA-TPH-D & O, MADEP-EPH, OK-DRO, and/or NW-TPH DX are placed on these shelves. Each method requires an exclusive amber liter. Some states require acid preservation with either Sulfuric acid (H_2SO_4) or Hydrochloric acid (HCl). Most of these states list a specific pH less than 2 is required. Some states do not list a specific pH and some do not require preservation at all. Refer to the chart at the end of this SOP. If the state does not require preservation, the liter is placed on the "unpreserved" shelves.

Containers for Methods 1664 and/or 9070 are placed on shelves marked "O/G." Each method requires an exclusive liter. The liter is preserved with Sulfuric acid (H_2SO_4), but Hydrochloric acid (HCl) is acceptable. The storage location is HEM.

Waters with glass containers for inorganics are placed on a designated shelf in locations TOC1 through TOC6.

Samples for inorganics analysis are placed in blue bins prior to storage in Walk-in Cooler #4 unless they are in glass containers: Locations are W1 to W2350.

"Problem Cart": Coolers and projects that cannot be logged due to issues with sampling, preservation, lack of information, or unclear information are placed here. The cart is only used as a last resort. Every effort is made to log in every project and not enter some analysis or enter the analysis but put it on Hold Status in LIMS. All projects on this cart must have a copy of the email sent to the PM with the paperwork. Containers for VOA methods are not stored here unless in a sealed cooler. This cart is kept in Walk-in Cooler #1, but may also be stored in Walk-in Cooler #5 if needed. The location is PROB.

"Subout": Containers for analysis for methods not performed at TA Nashville are placed here. These shelves are in Walk-in Cooler #5. The location is SUB.

Only authorized personnel may remove samples from each area.

The Soil Tracking System group is also responsible for properly compositing all samples requesting the lab to composite for the client. Sample Receiving comments compositing instructions on analysis comments and provides a labeled, empty container. See SOP Sub-sampling & Compositing / NV08-229.

All samples for organics analysis must be stored in amber-glass containers, sealed boxes (such as cardboard), or the dark.

For soil containers on which volatile organics analysis and any other analysis are requested, an analyst in the Volatiles Department must prepare a sample first to be retained in the Volatiles Department and then send the remainder on to the assigned bin for placement in Walk-in Cooler #3..

All samples are stored separately from standards and reagents used for analysis to prevent cross-contamination. A trip blank is stored with the samples from its project.

After analysis, samples are placed into sample storage for at least 60 days. This area is at room temperature. After a total of at least 75 days from receipt, they are disposed of in accordance with the Sample Disposal SOP.

Access to the laboratory is controlled such that sample storage need not be locked at all times unless a project specifically demands it. Samples are accessible to lab personnel only. Visitors to the laboratory are prohibited from entering the walk-in coolers, laboratory, or storage areas unless accompanied by an employee of TestAmerica. Samples are returned to the appropriate area after sufficient sample has been obtained to complete an analysis.

6.0 Responsibilities

6.1 Jobs are peer-reviewed or checked by the Sample Receiving Supervisor as time allows and then reviewed by Project Management personnel. Corrections are made as needed.
6.2 A sample received after normal working hours is left in the individual cooler and placed in Walk-in Cooler #1. The person receiving the samples must sign, date, record the time, temperature the cooler was received, and information about packaging and custody seals on the "Cooler Receipt Form".
6.3 TestAmerica makes every effort to contact the client for instructions whenever there is a problem or question about a sample. In the event that we cannot reach the client and there appears to be a request for a short-holding-time test, our policy is to proceed with running the test while continuing to contact the client.

7.0 References / Cross References

7.1 **40 CFR Part 136** for preservation requirements for SDWA and CWA analytes.
7.2 **Test Methods for Evaluating Solid Waste, Physical/Chemical Methods**, USEPA, SW-846.
7.3 **Standard Methods for the Examination of Water and Wastewater**, APHA-AWWA-WPCF, On-line Edition, 2011 editorial revisions.
7.4 **TDEC Division of Underground Storage Tanks Reasonable Reimbursable Guidance Document** (10/04).
7.5 **Element Data System Version 5.0 New User Tutorial.2003**
7.6 **Oasis\TALS Manual\Sample Management\Login.pdf**.)
\\corp-fs-04.tai.com\LimsUserDocs\Sample Management\Login.pdf and Non Conformance Memo Setup.pdf.
7.7 **TestAmerica Nashville's Quality Assurance Manual.**
7.8 **Corporate Environmental Health and Safety Manual / CW-E-M-001**.
7.9 **SOPs**: Sample Disposal / NV10-83 and USDA Disposal / NV10-162, Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
7.10 **Controlled Documents**: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions; LIF03, HoldingTimeAndPreservation.xls; LF-1, Cooler Receipt Form; LF-23, Hot coolers and how to prevent.doc.

8.0 Attachment

DRO Water Preservatives: This table summarizes the preservative requirements for the different DRO method and is included in this SOP.

DRO Water Preservatives

State	Method	Preservative[1]	Special Requirements or Comments
All other states	8015	none	
Arizona	8015AZ	Acid	pH < 2
Connecticut	CT ETPH	None	
Florida	FL PRO	Acid	pH < 2
Iowa	OA-2	None	
Kansas	OA-2	None	
Louisiana	MADEP EPH	Acid	pH < 2
Maine	Maine-DRO	Acid	pH < 2, may be preserved on receipt as long as it is noted on the reports
Massachusetts	MADEP EPH	Acid	pH < 2

State	Method	Preservative[1]	Special Requirements or Comments
Minnesota	WI DRO	Acid	pH < 2
Missouri	OA2	None	
Montana	MADEP EPH	Acid	pH < 2
North Carolina	MADEP EPH	Acid	pH < 2
Oklahoma	OK DRO	Acid	No pH requirement in the method
Oregon	NWTPH (Dx or EPH)	Acid	pH < 2
Tennessee	TN EPH	Acid	No pH requirement in the method
Texas	TX1005	Acid	pH < 2
Texas	TX1006	Acid	pH < 2
Washington	NWTPH (Dx or EPH)	Acid	pH < 2
Wisconsin	WI DRO	Acid	pH < 2

[1] HCl is preferred, but H_2SO_4 is acceptable.

9.0 Revision History

- Revision 8, dated 9 October 2009
  - Integration for TestAmerica and STL operations.
  - Added South Carolina daily IR gun check requirement.
- Revision 9, dated 30 June 2011
  - Organizational changes.
  - Incorporate Amendment 8a.
  - Addition of chemical hazards.
  - Addition of QAF-45 and Controlled Document references.
  - Standardization of walk-in cooler references.
  - Update use and labeling of carts.
- Revision 9, dated 30 June 2011
  - Organizational changes
  - Instructions on new walk-in coolers' use.
- Revision 10, dated 10 February 2012
  - Instructions to add "TA" to all signatures on the COC and to write legibly.
  - Describe new Walk-in Coolers #4 and #5.
  - Instructions for logging in samples with less than 24-hour holding time remaining where the client's COC is unclear.
  - Remove the use of folders.
  - Additional language to increase paperless approach.
  - File pathway update.
- Revision 11, dated 31 October 2012
  - Organizational change.
  - Modified all text to remove Element and add TALS procedures.
- Revision 12, dated 31 December 2012
  - Abbreviate NonConformance as NCM and define it. Add reference to TALS Manual describing NCMs.
  - Change Work Order to Job.
  - Move sample confirmation to Project Management SOP.
  - Modify several sections for clarity.
- Revision 13, dated 29 March 2013
  - Addition of amendment 12a and safety advice.
  - Editorial revisions.

Title: RESIDUE, FILTERABLE (TOTAL DISSOLVED SOLIDS (TDS), GRAVIMETRIC, DRIED AT 180°C) BY METHOD SM2540 C AND TOTAL SOLUBLE SALTS & SALINITY BY AGRICULTURE #60

Approvals (Signature/Date)			
Sessily Overton-Gray	7/24/13	Jamey Carmichael	7/26/13
Sessily Overton-Gray Department Supervisor	Date	Jamey Carmichael Operations Manager	Date
Michael H. Dunn	7/20/13	Johnny Davis	7/30/13
Michael H. Dunn Technical Director Quality Assurance Manager	Date	Johnny Davis Health & Safety Manager / Coordinator	Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method determines the concentration of total dissolved solids (TDS), total soluble salts, and salinity in drinking, surface, and saline waters, saturated paste or soil leachates, domestic and industrial wastes.

1.2 Reporting Limits: The reporting limit is nominally 10 mg/L.

1.3 If for any reason a part of this SOP cannot be followed, seek the guidance of the Department Supervisor/Manager or the Laboratory Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

A well mixed aliquot of the sample or leachate is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to a constant weight at 180 ± 2°C. The filtrate from Total Suspended Solids (SM2540 D / NV07-63) may be used. Leachates from soils may also be determined.

3.0 Definitions

3.1 Filterable Residue is defined as those solids capable of passing through a glass fiber filter and dried to a constant weight. TDS is considered equivalent to Total Soluble Salts and Salinity for agriculture purposes.

3.2 See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for other laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and may require prolonged drying, desiccation and rapid weighing.

4.2 Samples containing high concentrations of bicarbonate may require careful and possibly prolonged drying at 180 °C to insure that all the bicarbonate is converted to carbonate.

4.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to 200 mg, i. e., 0.2 g.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: None.

5.2 Primary Materials Used: Not applicable.

6.0 Equipment and Supplies

6.1 Instrumentation

- Analytical balance with sensitivity to 0.0001 grams.
- Drying oven for use at 180 ± 2°C.
- Low-temperature oven (94 ± 5°C) to avoid splattering.
- Dessicator
- Suction flask, 500 mL.
- Filter holder, membrane filter funnel.

- Magnetic stirrer with Teflon-coated stirring bar.

6.2 Supplies

- Volumetric flask, glass, 1 liter, Class A.
- Beakers, 150 mL.
- Class A graduated cylinder, 100 -1000 ml, or equivalent
- Glass-fiber filter discs, 4.7 cm, without organic binder, Gelman type A/E, Glass Microfibre Filter 696, or equivalent. The use of Environmental Express Pro-Weigh filters is acceptable.
- Pipets, 50-mL, wide-bore.

7.0 Reagents and Standards

7.1 Reagent water, analyte-free.

7.2 Standard Sodium chloride solution, 100 mg/L TDS: Place 0.1000 gram NaCl into a 1-liter volumetric flask, and bring to a final volume of 1000 mL with reagent water.

7.3 See SOP Reagent and Standard Purchase, Preparation, Control, Documentation for information on shelf-lives and storage requirements. Also, refer to LIMS.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	HPDE	1000 mL	Cool 0-6°C	7 days.	40 CFR Part 136.3
Soil	Plastic, glass	200 g	Not applicable	Not applicable	Agriculture Handbook #60

9.0 Quality Control

Refer to the quality control section of TestAmerica Nashville's QA Manual for specific quality control (QC) procedures. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Method Blank	1 in 20 or fewer samples	< Report Limit	Re-prep, rerun
Laboratory Control Sample (LCS)[1], second-source	1 in 20 or fewer samples	90-100% recovery	Repeat.
Sample Duplicate	1 in 10 or fewer samples	≤ 5% RPD	Report

1. For AZ, TX, WV samples, a LCS duplicate is required.

- **Method Blank:** 100 mL of reagent water processed with each batch.
- The **Laboratory Control Sample** (LCS): Use 100 mL standard Sodium chloride solution (100 mg/L) with each batch.
- **Sample Duplicate**: Run two identical aliquots of at least one sample per batch to demonstrate precision by calculating the RPD.

9.2 Instrument QC: Not applicable.

10.0 Procedure

10.1 Sample Preparation

Matrix	Sample Size
Water	100 mL, nominal

Soil	200 g

For soils, use a saturated paste leach/extract or 1:1 soil : reagent water leachate after filtration through an 0.45-micron filter. Prepare the soils using SOP LDNR 29B Soil Preparation / NV03-251.

10.2 Calibration

The balance is calibrated daily according to SOP Balance Calibration / NV08-213.

10.3 Sample Analysis

1	Preparation of glass beakers: Heat the clean glass beakers to 180 ± 2°C for one hour. Cool and store in the desiccator until needed. It is recommended to weigh in the evening or early morning due to humidity. Weigh immediately before use. **Record**.
2	Preparation of glass fiber filter: Place the filter, wrinkle-side up, on the membrane filter apparatus. While vacuum is applied, wash the disc with three successive 20-mL volumes of reagent water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard the washings. If using the Environmental Express Pro-Weigh filters, this step is not required.
3	Assemble the filtering apparatus and turn "on" the vacuum pump. Stir the sample with a magnetic stirrer or shake, and sample from ½ distance of the vortex. Rapidly transfer 100 mL to the filtration apparatus by means of a 100 mL graduated cylinder or wide-bore, 50-mL pipet.
4	Filter the sample through the glass fiber filter into a weighed glass beaker, rinse with three 10-mL portions of reagent water and continue to apply vacuum to remove as much water as possible.
5	Evaporate beaker to near dryness in an oven at 94 ± 5°C to reduce splattering of the sample.
6	Dry the evaporated sample beaker for at least one hour at 180 ± 2°C. Cool in a desiccator and weigh. **Record**. Repeat the drying cycle of drying, cooling, desiccating, and weighing until the weight change is less than 4% of previous weight or until weight loss is ≤ 0.5 mg. **Record.** If the residue weight is >200 mg, adjust the sample volume and repeat the analysis.

10.4 Example Analysis Queue / Sequence*

1	Method Blank
2	LCS
3	Samples 1-10
4	Sample Duplicate
5	Samples 11-20
6	Sample Duplicate

*May be up to 20 samples

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\% \text{ Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 Concentration calculation:

Filterable Residue (mg/L) = Total Dissolved Solids = $\frac{(A-B)\ (1{,}000{,}000)}{\text{Sample Volume, mL}}$

A = Weight of Dried (180°C) Residue + Dish (g)
B = Weight of Dish (g)

For agricultural determinations:

TDS is equal to Total Soluble Salts.

Salinity: convert TDS in mg/L to g/L. Salinity (g/L or ppt) = TDS (mg/L)/1000.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes must be stored, managed, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Solid residues are disposed of in a trash receptacle.
- Filtrate is discharged into the sanitary sewer.

15.0 References / Cross References

15.1 Method SM2540 C – 1997, Standard Methods for the Analysis of Water and Wastewater, on-line edition, 2011 editorial revisions.

15.2 Agriculture Handbook, #60.

15.3 TestAmerica Nashville's Quality Assurance Manual.

15.4 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.5 SOPs: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213, Determination of Method Detection Limits / NV08-202, Reagent and Standard Purchase / NV08-214, SM2540 D / NV07-63, LDNR 29B Soil Preparation / NV03-251.

15.6 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachment

None.

18.0 Revision History

- Revision 6, 31 March 2008
  - Integration for TestAmerica and STL operations.
- Revision 7, 15 May 2009
  - Addition of Standard Methods description of drying to a constant weight.
- Revision 8, 29 June 2010
  - Removal of reference to EPA 160.1.
  - Addition of Section 14.1 and QAF-45.
- Revision 9, 30 November 2010
  - Replace porcelain/ceramic evaporating dishes with 50-mL glass beakers. Add wide-bore pipets.
  - Change sample duplicate RPD from ≤ 20% to ≤ 5%.
  - Modify Section 10.3, Sample analysis.
- Revision 10, 31 January 2011
  - Add reference to SOP SM2540 D / NV07-63 and its filtrate.
  - Limit total residue in the evaporating dish ≤ 200 mg, not "about" 200 mg.
  - Remove "as soon as possible" from holding time; limit to 7 days.
  - Remove "½" from < RL for method blank acceptance criterion.
  - Allow weighing of clean glass beakers in the evening or early morning, not just "after 5 p.m."
  - When placing the filter on the apparatus, place "wrinkle-side up."
  - Remove time span for allowing sample to dry to near dryness at 94 ± 5°C.
  - Change temperature from 103 to 180°C in the formula for "A" in the concentration calculation.
- Revision 11, 29 June 2012
  - Organizational changes. Update SM reference.

- Modify Section 10.3, Sample Analysis to add the residue weight range for needing to repeat the analysis.
- OK and WY now allow batches of 20 samples.
- Remove shaking samples vigorously or transfer of sample using 100 mL Class A graduated cylinder.
- Addition of Total Soluble Salts and Salinity.

- Revision 12, dated 31 July 2013
  - Organizational changes.
  - Addition of Amendment 11a.

Title: RESIDUE, NON-FILTERABLE (GRAVIMETRIC, DRIED AT 103°-105°C) (TOTAL SUSPENDED SOLIDS, TSS) METHOD SM2540 D

Approvals (Signature/Date)

Sessily Overton-Gray	12/7/12		11/26/12
Sessily Overton-Gray Department Manager	Date	Matt Ricke Inorganics Operations Manager	Date
Michael H. Dunn	11/26/12	Johnny Davis	12/28/12
Michael H. Dunn Technical Director Quality Assurance Manager	Date	Johnny Davis Health & Safety Manager / Coordinator	Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method determines the concentration of total suspended residue (solids) in drinking, surface, and saline waters, domestic and industrial wastes.

1.2 Reporting Limits: The reporting limit is nominally 1.0 mg/L.

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor or the Technical Director. All abnormalities must be noted on the data or the benchsheet and in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

A well mixed sample is filtered through a standard glass fiber filter. The residue retained on the filter is dried to a constant weight at 103-105°C. The filtrate from this method may be used for Residue, Filterable (SM2540C & 160.1 / NV07-64).

3.0 Definitions

3.1 Residue, non-filterable, is defined as those solids which are retained by a glass fiber filter and dried to a constant weight at 103-105°C.

3.2 See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for other laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.

4.2 Samples high in dissolved solids, such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken so that washing of the filter and any dissolved solids in the filter minimizes this potential interference.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: None.

5.2 Primary Materials Used: Not applicable.

6.0 Equipment and Supplies

6.1 Instrumentation

- Analytical balance with sensitivity to 0.0001 grams.
- Drying oven for use at 103-105°C.
- Filter support: filtering apparatus with reservoir and a coarse (40-60 microns) fritted disc as a filter support.
- Suction flask, 300, 500 or 1,000 mL.
- Dessicator
- Filter holder, membrane filter funnel.
- Magnetic stirrer

6.2 Supplies

- Class A graduated cylinder, 10 - 1000 mL, or equivalent.
- Glass fiber filter discs, 47 mm, without organic binder, such as, Gelman type A/E, Environmental Express P/N F93447 MM, or equivalent. **Use with rough side up.**
- 50 mL wide-bore pipet. 1mL, 5mL, & 10 mL pipets.

7.0 Reagents and Standards

7.1 **Reagent water**, analyte-free.

7.2 **Standard Solution**, 100 mg/L as TSS: Dissolve 0.1000 g of Celite, Fisher Cat. No. C211-500 or equivalent in reagent water and bring to 1 L with reagent water. It is acceptable to prepare larger volumes.

7.3 See SOP Reagent and Standard Purchase, Preparation, Control, Documentation for information on shelf-lives and storage requirements.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	HPDE	1000 mL	Cool 0-6°C	As soon as possible but no more than 7 days.	40 CFR Part 136.3

- Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result (written guidance from client is required to exclude items).
- Chemical preservation of the sample is not used. Analysis should begin as soon as possible. Refrigeration or icing to 0-6°C, to minimize microbiological decomposition of solids, is recommended. Holding time is seven days.

9.0 Quality Control

Refer to the quality control section of TestAmerica Nashville's QA Manual for specific quality control (QC) policies. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC

The following quality control samples are prepared with each batch of samples.			
Quality Controls	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Method Blank (MB)	1 in 20 or fewer samples	< Report Limit	Reprep, rerun.
Laboratory Control Sample (LCS), second-source	1 in 20 or fewer samples	90-110% recovery	Repeat.
Sample Duplicate	1 in 10 or fewer samples	≤ 5% RPD	Report

1 All AZ, TX, and WV samples require a LCS duplicate in each batch.

- One **Method Blank** of 1000 mL of reagent water is processed each batch.
- The **Laboratory Control Sample** (LCS) is prepared to verify that the laboratory can perform the analysis in a clean matrix. See Section 7.2 for its preparation; use a 1000-mL aliquot. See Section 11 for the equation for accuracy.
- **Sample Duplicate**: Run two identical aliquots in each group of 10 samples. Demonstrate precision by calculating the RPD. See Section 11 for the equation.

9.2 Instrument QC: Not applicable.

10.0 Procedure

10.1 Sample Preparation

Matrix	Sample Size
Water	~1000 mL

10.2 Calibration

The balance is calibrated daily according to SOP Balance Calibration / NV08-213.

10.3 Sample Analysis

1	Place a glass fiber filter disc on the filter apparatus, rough side up.
2	Selection of Sample Volume: For a 47 mm diameter filter, filter a suitable volume of sample, nominally 1000 mL. NOTE: If during filtration of this initial volume the filtration rate drops rapidly a smaller volume of sample should be used. Do not use less than 1.0 mL. Limit sample size to yield no more than 200 mg residue on the filter. If filter residue is greater than 200 mg repeat using a smaller volume.
3	Assemble the filtering apparatus and turn "on" vacuum pump. Wet the filter with a small volume of reagent water to seat it against the fritted support.
4	If using 1000 mL, or the entire container volume shake the sample vigorously and quantitatively transfer the sample volume to the filter using a Class A graduated cylinder. If using smaller aliquots, stir with a magnetic bar on a stir plate and remove a portion, center distance between container wall and vortex, with a 1, 5, 10, or 50-mL pipet. Remove all traces of water by continuing to apply vacuum after sample has passed through.
5	With vacuum on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with **three** portions of reagent water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through.
6	Carefully remove the filter from the filter support and place it in the aluminum planchet. Dry at least one-hour at 103°-105°C. Cool in a desiccator for about an hour and weigh. Repeat the drying cycle until a constant weight is obtained of 4% or less than 0.5 mg, whichever is less. Record. If weight on filter is <0.0010 grams and less than 1000 mL was chosen, repeat steps 1-6 with a greater sample volume than initially.

10.4 Example Analysis Queue / Sequence*

1	Method Blank
2	LCS
3	Sample 1
4	Sample Duplicate
5	Samples 2- 11
6	Sample Duplicate
7	Samples 12-20

*May be up to 20 samples

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\text{LCS \% Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 Concentration calculation:

$$\textit{Non-filterable residue, mg/L} = \frac{(A-B)x(1{,}000{,}000)}{C}$$

A = weight of filter + dried residue in g
B = weight of filter in g
C = mL of sample filtered

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- The filtrate is discharged into the sanitary sewer.
- The filter with solids is disposed into a trash receptacle.

15.0 References / Cross References

15.1 Method SM2540 D - 1997, Standard Methods for the Analysis of Water and Wastewater, On-line edition, 2011 editorial revisions.

15.2 TestAmerica Nashville's Quality Assurance Manual.

15.3 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.4 SOPs: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213, Determination of Method Detection Limits / NV08-202, Reagent and Standard Purchase / NV08-214.

15.5 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachment

None.

18.0 Revision History

- Revision 7, 31 July 2009
  - Integration for TestAmerica and STL operations.
- Revision 8, 30 December 2010
  - Removal of reference to retired method EPA 160.2 (Amendment 7a).
  - Addition of QAF 45 and Section 14.2.
  - Change sample volume to nominally 1000 mL.
- Revision 9, 31 December 2012
  - Organizational changes.
  - OK and WY no longer limit batch size to 10 samples.
  - Provide instruction for aliquots smaller than 1L. Modify example sequence.
  - Reference the year of the method source and the on-line edition.

Title: HANDLING OF SOILS REGULATED BY USDA

Approvals (Signature/Date):

12/15/13	10/23/13
Andy Johnson Client Services Manager — Date	Paul Buckingham Sample Receiving Supervisor — Date
12/19/13	12/19/13
Cory Spry Department Manager — Date	Rodney Street Department Manager — Date
11/29/13	12/2/13
Winston Maupin Department Supervisor — Date	Jessica Freeman Department Supervisor — Date
12/4/13	12/5/13
John Haley Department Supervisor — Date	Glenn Norton Department Manager — Date
12/30/13	12/9/13
Jacolby Robinson Department Supervisor — Date	Johnny Davis Health & Safety Manager / Coordinator Department Manager — Date
12/24/13	12/19/13
Daniel Otero Department Supervisor — Date	Jared Knierim Department Manager — Date

Facility Distribution No. 10-162 03T, 05U, 05V, 06, 07, 10, 12

Distributed To: QA Server, 02SR, 02S, 02P, 03P,

Steve Miller	12/26/13		
Steve Miller Quality Assurance Manager	Date		
Michael H. Dunn	10/7/13	Amelia Kennedy	12/19/13
Michael H. Dunn Technical Director	Date	Amelia K. Kennedy Laboratory Director	Date

1.0 Purpose and Scope

1.1 TestAmerica Nashville receives soil samples from numerous locations. The United States Department of Agriculture (USDA) has promulgated Soil Movement Regulations to limit the spread of potentially destructive plant and animal pests and diseases into the U. S. Some of these intruders are animal and plant viruses, bacteria, fungi, nematodes, noxious weeds, and certain life stages of destructive exotic insects. For specific geographic areas, the USDA requires laboratories analyzing soil, taken from the surface down to three feet, to be permitted and to heat-treat these soils before disposal.

1.2 Regulations from EPA's Resource Conservation and Recovery Act (RCRA) also apply to these soils, if applicable. All waste is handled within the framework of TestAmerica Nashville's SOP on waste disposal (NV10-83).

1.3 This document describes the materials and procedures used to pre-treat soil samples meeting the depth limits of the Soil Movement Regulation for geographic areas designated by the USDA. After treatment, the soil must be disposed properly according to RCRA.

1.4 Solid waste is considered different from soil and does not come under the scope of this document.

1.5 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director.

2.0 Safety

2.1 Every employee is directly responsible for complete awareness of all health hazards associated with every sample and chemical that they use. The employee is aware of these hazards and all associated personal protective equipment (PPE) and spill clean-up procedures should be taken, *prior to the use* of any chemical or the analysis of any sample. The employee must comply with all safety policies as presented in the TestAmerica - Nashville Division Safety Manual. Bottle labels also provide important information that must be noted. In the case of any questions or concerns with a particular sample or suspected waste, the Technical Director or EH&S Officer must be consulted.

2.2 Upon receipt, all samples are considered potentially hazardous or contaminated with foreign organisms and treated as such. Lab personnel are notified of any samples that have special handling precautions. Login designates special handling procedures on the login comment line, and the sample may also be tagged for special handling upon receipt.

2.3 In case of a spill of a quarantined soil, lab personnel are to clean soil into an empty glass soil container and mark as a "fire ant" soil waste for proper disposal.

2.4 Personnel performing disposal procedures may be working with flammables, poisons, toxics, carcinogens, teratogens, mutagens and/or biohazards. At minimum, appropriate gloves, safety glasses and lab coats are worn during disposal of samples or other waste. Samples are handled with as much care as any of the chemicals or solvents due to the unknown nature of their composition.

2.5 Because this procedure involves the heat-treating of soils at high temperature, caution and careful handling of hot glass or metal containers and soil is exercised. At a minimum, appropriate gloves and safety glasses are worn.

2.6 Appropriate personnel must review this document for knowledge and familiarity **annually**.

3.0 Definitions

3.1 **Soil** is a general term which includes: topsoil, forest litter, compost, humus, earthworm castings, and any of a variety of items composed of largely unidentifiable plant parts or mixtures of organic and inorganic ingredients which are capable of supporting biological activity and, therefore, capable of providing the means for carrying and introducing harmful pests or diseases.

- Outside of the scope of the regulations are pure sand, clay, talc, or other pure minerals, as well as rocks, gravel, and ore, which are not contaminated with soil or organic debris. Peat is also unregulated, provided it is pure. Cosmetic mud and other mud products may also be exempt from regulation, if processed to a smooth consistency and visibly free of contaminants or taken from 7 feet below the water surface.
- This document applies to untreated soil. Because of the nature of chemical analysis, the soil cannot be heat-treated at the port of entry and then be shipped to the lab. Laboratory analysis must be conducted prior to heat-treating.

3.2 **Foreign sources** include any non-domestic nations, specifically addressing certain locations as follows:

- Canadian soil regulated as foreign soil comes from Newfoundland and from that portion of the Municipality of Central Saanich in the Province of British Columbia east of the West Saanich Road. Soil from other parts of Canada may be imported subject to inspection and verification of its origin.
- Soil from Guam, Hawaii, Puerto Rico, and the U. S. Virgin Islands is handled as foreign soil.
- Domestic soil from quarantine areas in the continental U. S. and are collected from less than 3 feet are handled as "foreign soil." Quarantine areas are identified by USDA maps. See Figure 1.

3.3 **Approved Facility under a Valid Permit** is a facility in the United States with a USDA permit to receive foreign and quarantined soil. The permit is issued upon successful completion of a site visit and a signed compliance agreement stating that the facility will abide by the regulations.

3.4 **Soil Movement** must be from the port of entry directly to the approved facility under a valid permit by a bonded carrier or the mail and with a signed PPQ 550 label. An individual may only transport treated soil to the approved facility.

3.5 **PPQ Form 550 Black/White label:** a label attached to the exterior of each shipment being imported under a signed USDA permit. Movement within the continental U. S. does not require a PPQ 550. Additional labels may be requested by email at:

BlackWhiteGreenYellow.labelrequest@aphis.usda.gov

Specify the type of label, PPQ Form 550 Black/White label, and the number of labels needed.

3.6 **Bleach Solution:** Mix 100 mL bleach in 900 mL reagent water.

4.0 Procedure

4.1 When logging in samples to LIMS, Sample Receiving personnel must enter the site state. If a sample is a quarantined soil (see 4.3) Sample Receiving must change the Hazard Level in LIMS to 'foreign soil".and apply an orange sticker to the lid. An orange sticker is placed on each soil container requiring heat-treatment so that these containers may be quarantined (**stored separately from all other soil samples**) during sample storage.

4.2 Upon disposal, personnel generate a LIMS report of soil sample log numbers, heat-treating time, temperature, and approximate amount of soil remaining.

4.3 Affected Soils

- Since soil from all foreign locations must be heat-treated, Nashville **heat-treats all soils from outside the continental U. S.**
- **Heat-treat all soil samples shallower than three feet taken from the following U.S. states: New York, North Carolina, South Carolina, Georgia, Florida, Tennessee, Alabama, Mississippi, Louisiana, Arkansas, Texas, Oklahoma, New Mexico, Arizona, Virginia, California, Hawaii. See Figure 1.**
- **If the depth or the location (origin) of the soil sample is unknown, heat-treatment is required.**
- Aliquots or subsamples used for actual analysis are exempt from these requirements for heat treatment.
- If uncertain as to the proper procedure on any soil sample, consult with the Technical Director or EH&S Officer.

4.4 Heat-Treating: **Glass or metal soil containers and soil residues** are treated by heating to **250-309°F for 2.5 hours or 310-379°F for one hour** to allow for 30 minutes of heating after the materials have reached the appropriate temperature. **Record the temperature and times**. If the soil is not in a glass container, place the soil into a glass or metal pan for the heat-treatment process. The container must be solvent-rinsed or rinsed with bleach solution. Items in contact with soil, i e., spatulas, etc., must be cleaned with solvent or bleach solution by one of the following methods:

- **4.4.1** Material can be soaked in a fresh bleach solution of 10% (1:10) for at least 30 minutes.
- **4.4.2** Material can be soaked in 70% Ethanol.
- **4.4.3** Flamed with Ethanol.
- **4.4.4** Treated with quarternary ammonium compounds.
- **4.4.5** Autoclaved, incinerated, or dry heat sterilization.

Allow to cool to room temperature. Dispose of containers and soils as any other soil.

4.5 Using the LIMS report,

- Record beside the container size received the **approximate** amount of soil remaining in the container for those soils less than three feet or where the depth is unknown or where the soil is from a non-continental U.S. source. For example, if the container is ½ full, write ½ beside the container size received.

- Sign and date the report along with the phrase: "Heat-treated at ____°F from __:__ to __:__ in military time. Indicate to which samples this phrase applies with brackets.
- Retain this signed report for the disposal records.

5.0 Responsibilities and Documentation

5.1 Sample disposal personnel maintain the disposal record described above with the following **required** information: sample number, origin of sample, depth of sample, volume of sample received and remaining at disposal (approximate percentage full of __-oz. jar), date received, and date heat-treated, . The log is archived in a banker's box, file cabinet, or electronic file in the disposal area until the box is full at which time it is logged into the QA logbook archiving system.

5.2 If an analyst is uncertain as to how to assess the hazard of a sample or is uncertain of the disposal of a particular sample or chemical, the analyst must seek the guidance of the EH&S Officer or the Technical Director.

6.0 References/Cross References

6.1 **U. S. Department of Agriculture**, Animal and Plant Health Inspection Service, Plant Protection and Quarantine, Circular Q-330.300-1 Soil (6-93).

6.2 **RCRA** - Resource Conservation and Recovery Act, 1976.

6.3 **SOPs**: NV10-83 (Waste Disposal)

7.0 Attachments

7.1 Instructions for Heat-Treating Soil Samples to meet USDA Permit Conditions.

7.2 Imported Fire Ant Quarantine Map (December 2011)

7.3 Permit to Receive Soil (expiration 11/02/2013)

8.0 Revision History

- Revision 4, dated 30 September 2009
  - Integration of STL and TestAmerica operations.
- Revision 5, dated 30 April 2010
  - Updated quarantine map.
  - Section 4.3, first bullet, delete "the": Since soil from all foreign locations must be heat-treated, Nashville heat-treats all soils from outside the continental U.S.
  - Section 4.3, add new bullet at the end of the section:
  - If the sample origin is unknown, heat treatment is required.
- Revision 6, dated 30 November 2010
  - Addition of Permit to Receive Soil as an attachment.
  - Addition of date to the quarantine map.
  - Section 4.4, addition of "Record the temperature and times."
- Revision 7, dated 30 April 2012
  - Organizational changes.
  - Revised heat-treating temperature allowances and duration.
  - Updated the quarantine map, December 2011.
- Revision 8, dated 29 March 2013
  - Organizational changes.
  - Update for new LIMS.
- Revision 9, dated 12/31/2013
  - Organizational changes.
  - Addition of PPQ 550 label information and the use of bleach/solvent treatment of equipment.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Attachment 7.1

INSTRUCTIONS FOR HEAT-TREATING SOIL SAMPLES TO MEET USDA PERMIT CONDITIONS
Nashville, TN

I. **Store soils from all foreign locations and soils shallower than three feet deep from the states listed in II.B. below separately from all other soils. Sample Control will apply an orange sticker to these containers.**

II. At disposal time**, generate a report of soil sample log/bin numbers** in the LIMS. This report lists all soil samples from required U.S. states and foreign countries. When running the report, enter the dates for which disposal is planned, and print.

A. Since soil from all foreign locations must be heat-treated, the Nashville Division will **heat-treat all soils from outside the continental U. S.**
B. **Heat-treat all soil samples shallower than three feet taken from the following U. S. states: New York, North Carolina, South Carolina, Georgia, Florida, Tennessee, Alabama, Mississippi, Louisiana, Arkansas, Texas, Oklahoma, New Mexico, Arizona, California, Hawaii, Virginia.**
C. **If the depth or the location of the soil sample is unknown, heat-treatment is required.**
D. Aliquots used for actual analysis do not require heat treatment; a waiver has been granted for these small quantities.
E. If uncertain as to the proper procedure on any soil sample, consult with the Hazardous Waste Coordinator.

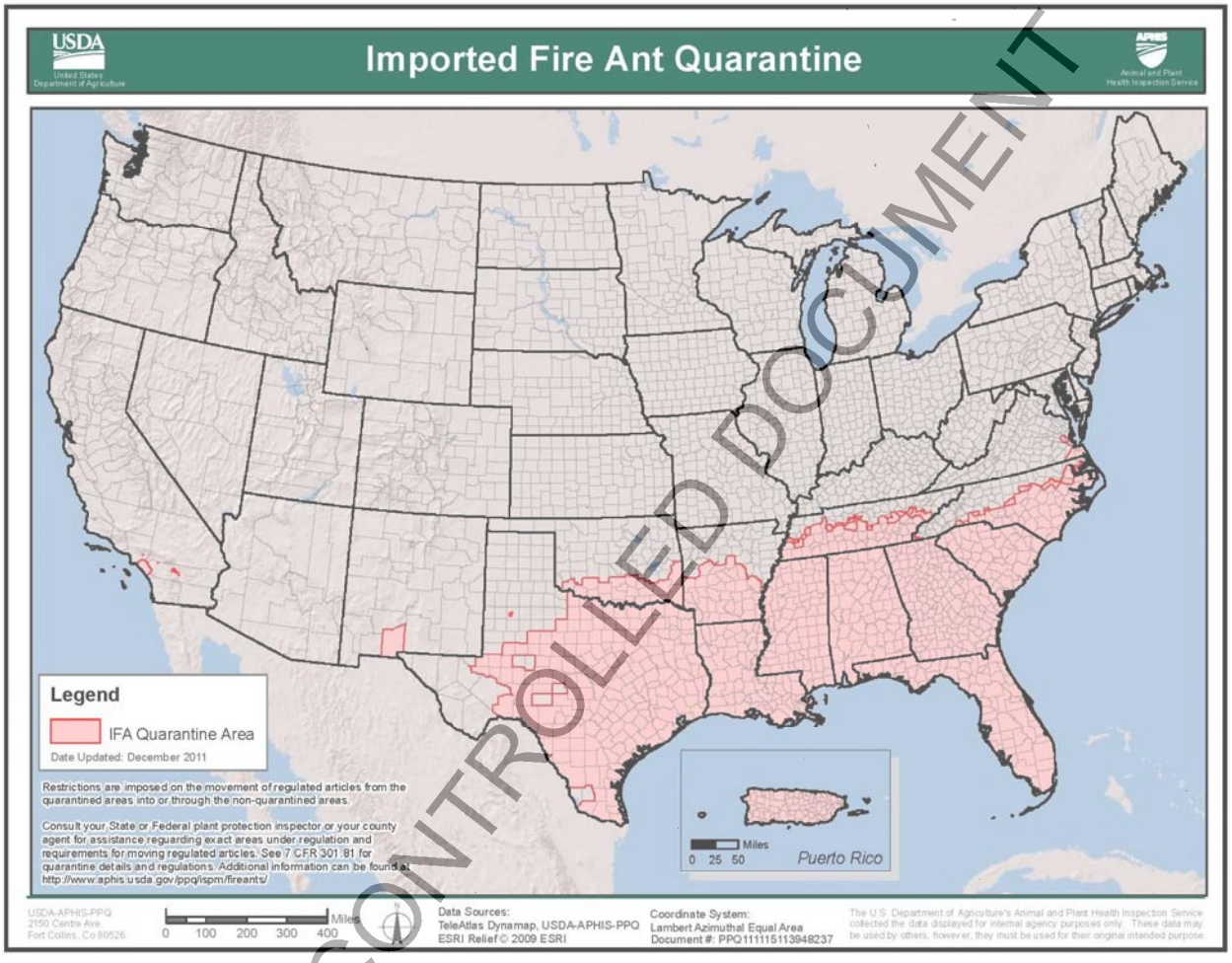
III. Heat-Treating: **Glass or metal soil containers and soil residues** must be treated by heating to **250-309°F for 2.5 hours or 310-379°F for one hour** to allow for 30 minutes of heating after the materials have reached the appropriate temperature. If the soil is not in a glass container, place the soil into a glass or metal pan for the heat-treatment process. Do not heat plastic or paper containers. Allow to cool to room temperature. Dispose of containers and soils in the non-hazardous soil bin.

IV. Documentation: Using the LIMS report,

A. Record beside the container size received the **approximate amount of soil remaining in the container** for those soils less than three feet or where the depth is unknown or where the soil is from a foreign source. For example, if the container is ½ full, write ½ beside the container size received.
B. **Sign and date** the report along with the phrase: **"Heat-treated at ___°F from __:__ to __:__ in military time. Indicate to which samples this phrase applies with brackets.**
C. Retain this signed report for the disposal records. The log will be archived in a banker's box in the disposal area until the box is full at which time it will be logged into the QA logbook archiving system.

Attachment 7.2

Figure 1. Imported Fire Ant Quarantine Map



Attachment 7.3

Figure 2. Permit to Receive Soil

APHIS Animal and Plant Health Inspection Service

Plant Protection & Quarantine

United States Department of Agriculture
Animal and Plant Health Inspection Service
4700 River Road
Riverdale, MD 20737

Permit to Receive Soil
Regulated by 7 CFR 330

This permit was generated electronically via the ePermits system.

PERMITTEE NAME:	Mr. Michael Dunn	**PERMIT NUMBER:**	P330-13-00306
COMPANY:	TestAmerica Laboratories, Inc.	**APPLICATION NUMBER:**	P525-130913-002
RECEIVING ADDRESS:	TestAmerica Laboratories, Inc. 2960 Foster Creighton Drive Nashville, TN 37204	**DATE ISSUED:**	11/03/2013
MAILING ADDRESS:	TestAmerica Laboratories, Inc. 2960 Foster Creighton Drive Nashville, TN 37204		
PHONE:	(615) 726-0177 Ext. 1143		
FAX:	(615) 726-3404	**EXPIRES:**	**10/30/2016**

PORTS OF ARRIVAL/PLANT INSPECTION STATIONS: AK, Anchorage; AL, Huntsville; AL, Mobile; AZ, Douglas; AZ, Lukeville; AZ, Naco; AZ, Nogales; AZ, Phoenix; AZ, San Luis; AZ, Tucson; CA, Calexico; CA, Fresno; CA, Hawthorne; CA, Long Beach; CA, Oakland; CA, Ontario; CA, Otay Mesa; CA, Port Hueneme; CA, Sacramento; CA, San Diego; CA, San Francisco; CA, San Jose; CA, San Ysidro; CA, Tecate; CO, Denver; CT, Hartford; CT, New Haven; DE, Dover; DE, Wilmington; FL, Ft. Lauderdale; FL, Ft. Myers; FL, Ft. Pierce; FL, Jacksonville; FL, Key West; FL, Miami; FL, Orlando; FL, Pensacola; FL, Port Canaveral; FL, Port Everglades; FL, Sanford; FL, Tampa; FL, West Palm Beach; GA, Atlanta; GA, Savannah; GU, Agana; HI, Hilo; HI, Honolulu; HI, Kahului; HI, Kailua-Kona; HI, Lihue; ID, Eastport; IL, Chicago; IN, Indianapolis; KY, Louisville; MA, South Boston; MD, Baltimore; MD, Beltsville; ME, Bangor; ME, Calais; ME, Houlton; ME, Portland; MI, Detroit; MI, Port Huron; MI, Romulus; MI, Sault Saint Marie; MN, Duluth; MN, Grand Portage; MN, International Falls; MN, Minneapolis; MO, Kansas City; MO, St. Louis; MP, Commonwealth of the Northern Mariana Islands; MS, Gulfport; MS, Port Bienville; MT, Raymond; MT, Roosville; MT, Sweetgrass; NC, Raleigh; NC, Wilmington; ND, Dunseith; ND, Pembina; ND, Portal; NJ, Linden; NJ, Newark; NM, Albuquerque; NM, Columbus; NM, SantaTeresa; NV, Las Vegas; NY, Albany; NY, Alexandria Bay; NY, Brooklyn; NY, Buffalo; NY, Champlain, Rouses Point; NY, Jamaica; NY, Jamaica; NY, Newburgh; OH, Ashtabula; OH, Cincinnati; OH, Cleveland; OH, Columbus; OH, Toledo; OH, Wilmington; OK, Oklahoma City; OR, Portland; PA, Allentown; PA, Harrisburg; PA, Philadelphia; PA, Pittsburgh; PA, Scranton; PR, Aguadilla; PR, Carolina; PR, Fajardo; PR, Mayaguez; PR, Ponce; RI, Warwick/Providence; SC, Charleston; TN, Memphis; TN, Nashville; TX, Austin; TX, Brownsville; TX, Corpus Christi; TX, Dallas; TX, Del Rio; TX, Eagle Pass; TX, El Paso; TX, Fabens; TX, Falcon; TX, Fort Hancock; TX, Galveston; TX, Hidalgo; TX, Humble; TX, Laredo; TX, Los Indios; TX, Pharr; TX, Port Arthur; TX, Presidio; TX, Progresso; TX, Rio Grande City; TX, Roma; TX, San Antonio; TX, Victoria; UT, Salt Lake City; VA, Dulles; VA, Norfolk; VI, St. Croix; VI, St. Thomas; VT, Berlin; Various Ports of Entry Staffed by CBP-Agriculture Inspection; WA, Blaine; WA, Oroville; WA, Port Angeles; WA, SeaTac; WA, Sumas; WI, Green Bay; WI, Milwaukee

HAND CARRY: No

Under the conditions specified, this permit authorizes the following:

Quantity of Soil per Shipment and Treatment

3 lbs or less: Sterilization will interfere with intended use - Your facility MUST be inspected and approved to receive this soil

SPECIAL INSTRUCTIONS TO INSPECTORS

See permit conditions below

Permit Number P330-13-00306

THIS PERMIT HAS BEEN APPROVED ELECTRONICALLY BY THE FOLLOWING PPQ HEADQUARTER OFFICIAL VIA EPERMITS.	DATE
Osmond Baron	10/30/2013

WARNING: Any alteration, forgery or unauthorized use of this Federal Form is subject to civil penalties of up to $250,000 (7 U.S.C.s 7734(b)) or punishable by a fine of not more than $10,000, or imprisonment of not more than 5 years, or both (18 U.S.C.s 1001)

Page 1 of 6

APHIS Animal and Plant Health Inspection Service

Plant Protection & Quarantine

INSTRUCTIONS TO DHS CBP INSPECTORS FOR IMPORTED SOIL SHIPMENTS ROUTED TO RECEIVING FACILITY:

For hand carry of soil, an official of CBP Agricultural Programs and Trade Liaison (APTL) would have been notified to document and facilitate the entry of the soil (See hand carry conditions below if stipulated). Otherwise:

1. Validate the permit in ePermits using the CBP search feature by logging on to: https://epermits.aphis.usda.gov/epermits
2. Confirm that the shipment is being routed directly to a USDA APHIS PPQ Inspected Facility authorized to receive soil by logging on to: https://web01.aphis.usda.gov/PPQ/AuthSoilLabs.nsf/web?openform
3. Confirm that the imported shipment has a valid USDA PPQ Form 550 Black/White label.
4. Confirm that the carrier of the shipment imported under this USDA PPQ 525 permit is commercially bonded.
5. For questions or concerns, contact the USDA APHIS PPQ Permit Unit in Riverdale, MD, at 866-524-5421 and ask to speak with a compliance officer.

PERMIT GUIDANCE

Receipt or use of foreign isolates or samples from countries under sanctions requires specific permission from the U.S. Department of Treasury (see http://www.treasury.gov/resource-center/sanctions/Programs/Pages/Programs.aspx for current country/regional listings) for current country listings.

This permit does not authorize importation, interstate movement, possession, and/or use of strains of genetically engineered regulated organisms (created by the use of recombinant DNA technology).

If an animal pathogen is identified in your shipment, to ensure appropriate safeguarding, please refer to http://www.aphis.usda.gov/import_export/animals/animal_import/animal_imports_anproducts.sh

tml.

If a human pathogen is identified, please see the CDC Etiologic Agent Import Permit Program at http://www.cdc.gov/od/eaipp/

This permit does not fulfill the requirements of other federal or state regulatory authorities. As appropriate, please contact the U.S. Environmental Protection Agency, the U.S. Fish and Wildlife Service, the U.S. Food and Drug Administration, the Centers for Disease Control and Prevention, the APHIS Veterinary Services unit, or your State's Department of Agriculture to ensure proper permitting.

If you are considering renewal of this permit, an application should be submitted at least 90 days prior to the expiration date of this permit to ensure continued coverage. Permits requiring containment facilities may take a longer period of time to process.

Approved Sterilization Methods:
All soil residues must be dry-heated, incinerated, hydroclaved or autoclaved.

DRY HEAT Treatment: use one of the following schedules:
110- 120.5 degrees C (230-249 F) for 16 hours
121-154 degrees C (250-309 F) for 2 hours
154.4 - 192.5 degrees C (310-379 F) for 30 minutes
193-220 degrees C (380-429 F) for 4 minutes
221-232 degrees C (430-450) for 2 minutes
Time starts when the entire sample reaches the required temperature, and a suitable temperature probe must be used for verification.

INCINERATION: With the exception of metal and glass containers, all regulated and associated material must be

Permit Number P330-13-00306

THIS PERMIT HAS BEEN APPROVED ELECTRONICALLY BY THE FOLLOWING PPQ HEADQUARTER OFFICIAL VIA EPERMITS.	DATE
Osmond Baron	10/30/2013

WARNING: Any alteration, forgery or unauthorized use of this Federal Form is subject to civil penalties of up to $250,000 (7 U.S.C.s 7734(b)) or punishable by a fine of not more than $10,000, or imprisonment of not more than 5 years, or both (18 U.S.C.s 1001)

Page 2 of 6

APHIS Animal and Plant Health Inspection Service

Plant Protection & Quarantine

reduced completely to ash at the end of the incineration cycle.

AUTOCLAVE soil and other material using the following conditions:
a. Soil must be autoclaved at 121 degrees Centigrade (250 degrees Fahrenheit) for a minimum of 30 minutes at 15 psi.
b. Autoclave tape or other indicators must be placed on each bag or sharps container prior to treatment. The autoclave tape or other indicator on each container must be checked to verify color change before disposal.
c. The autoclave log must be completed by each user for each autoclave cycle. All parameters must be noted as listed on the log for each autoclave load.
d. If the autoclave does not attain the minimum time and/or temperature or the autoclave tape does not change color, a notation must be made in the comment section of the autoclave log. The load must then be re-autoclaved after placing new tape on the material. If minimum time and temperature is not attained on the second cycle, users must contact the person responsible for maintaining the unit to initiate repairs. Waste must then be treated at an alternate autoclave facility that is approved by USDA.
e. Thermometers on the autoclave must be calibrated annually, and a written record must be maintained. This must be done by an authorized autoclave service company during routine servicing.
f. Every 6 months, you should use a commercially available test indicator kit that uses bacterial spores Bacillus stearothermophilus that are rendered unviable at 250 degrees F or 121 degrees C. For the test, ampules of B. stearothermophilus are autoclaved along with a load of waste. Upon completion of the cycle, the ampules are incubated for 48 hours and then observed for any sign of growth, which indicates insufficient sterilization.

HYDROCLAVE: Soil must be hydroclaved at 121oC/250oF for a minimum of 30 minutes or 1

PERMIT CONDITIONS

This permit authorizes the importation of soil from all foreign sources (except countries with sanctions or embargoes by U.S. State Department) only for chemical/ physical analysis in a controlled laboratory environment at the named facility on the permit.

1. This permit is issued only for the named permit holder at the address(s) identified on this permit. This permit cannot be transferred or assigned.

2. The permit holder verifies United States residency by initialing and accepting these permit conditions. If you are not a United States resident, it is unlawful for you to initial or accept these permit conditions because a USDA 525 soil Permit can only be issued to United States residents.

3. The permit holder is solely responsible for ensuring compliance with all statutory requirements and specifically listed permit conditions. Failure to comply with the terms and conditions of this permit is cause for the following: (a) cancellation of this permit, (b) cancellation of other permits issued to the permit holder, (c) seizure and/or destruction of regulated organisms, (d) denial of future permit applications by this permit holder, (e) liability for civil penalties, and (f) criminal prosecution under provisions in the Plant Protection Act.

4. Any alteration, forgery, unauthorized use of this permit and/or associated Federal Forms are subject to civil and criminal penalties including fines and imprisonment.

5. This permit must not be used for the movement or use of plant pathogens listed in the Public Health Security and Bioterrorism Preparedness and Response Act of 2002. If any organism listed as a Select Agent is identified from materials associated with this research, the permit holder is required to notify APHIS, Agricultural Select Agent Program (ASAP) within one business day by phone at 301-851-3300, and within seven (7) days submit APHIS/CDC Form 4 (Report of Identification of a Select Agent or Toxin in a Clinical or Diagnostic Laboratory) to APHIS, ASAP; 4700 River Rd, Unit 2, Riverdale, MD 20737 (see instructions at: http://www.aphis.usda.gov/programs/ag_selectagent/index.shtml). Failure to comply with this requirement is a violation of the Agricultural Bioterrorism Protection Act of 2002.

Permit Number P330-13-00306

THIS PERMIT HAS BEEN APPROVED ELECTRONICALLY BY THE FOLLOWING PPQ HEADQUARTER OFFICIAL VIA EPERMITS.	DATE
Osmond Baron	10/30/2013

WARNING: Any alteration, forgery or unauthorized use of this Federal Form is subject to civil penalties of up to $250,000 (7 U.S.C.s 7734(b)) or punishable by a fine of not more than $10,000, or imprisonment of not more than 5 years, or both (18 U.S.C.s 1001)

Page 3 of 6

APHIS Animal and Plant Health Inspection Service

Plant Protection & Quarantine

6. If a regulated organism is received in this shipment, the permit holder must take all prudent measures to contain the organism(s) and notify the permit unit within one business day by calling 866-524-5421 or by e-mail to pest.permits@aphis.usda.gov. The permit holder must immediately notify the permit unit of the destruction of regulated organisms received under this permit, as above. Similarly, the permit holder must immediately notify the permit unit if facilities are destroyed or decommissioned for any reason.

7. You as the permit holder are responsible for maintaining a valid permit for as long as the soil is in your possession. APHIS does not issue extensions or renewals of existing permits; the permit holder must submit a new permit application at least three months prior to the expiration of this permit, and obtain a new permit to continue uninterrupted authorization for the soil approved under this permit.

8. If an accidental release into the environment occurs, notification must be made within one business day to APHIS, PPQ, 4700 River Rd., unit 133; Riverdale, MD 20737; 866-524-5421. A written report of the incident must be submitted identifying: (a) the name of the permit holder (responsible person), (b) the permit number, (c) the country or State of origin of the soil, (d) the nature of the release, and (e) measures already taken to contain, reduce or limit the effects of the accidentally released soil. Any plans prepared to contain, reduce or limit the effects of the accidentally released soil may be submitted as developed.

9. Without prior notice and during reasonable hours, authorized PPQ and/or State regulatory officials shall be allowed to inspect the conditions associated with the regulated soil authorized under this permit.

10. The permit holder must maintain an official permanent work assignment at the address identified on this permit. If the permit holder ceases assignment/affiliation at the address identified on this permit, or personnel circumstances change in any way, then a compliance officer must be notified at the PPQ permit unit immediately (that is, within one business day) by either (a) email to pest.permits@aphis.usda.gov, (b) fax to 301-734-4300 or 8700/5392, or (c) conventional mail to USDA PPQ Permit Unit, 4700 River Road, Riverdale, MD 20737. Should the permit holder depart from the organization/facility, the permit holder must either (a) request cancellation of this permit and comply with all permit-specific termination conditions, (b) apply for and receive a permit to move the soil to a new facility, or (c) relinquish control of the regulated soil to a qualified individual who obtained a permit for the continued use of this regulated soil prior to this permit holder's departure.

11. A copy of this permit must accompany all shipments authorized under this permit.

12. CBP-AI and PPQ have the authority to order and approve treatment, re-exportation or destruction of a shipment, a portion of a shipment or any other material associated with the shipment (i.e. pallets, packaging, and means of conveyance). If an official of CBP-AI or PPQ determines that the shipment requires treatment as a condition of entry, is contaminated with a quarantine plant pest or pests, is commingled with prohibited plant material or the required documentation is incomplete or missing, then that official may order and approve treatment, re-exportation or destruction of a shipment, a portion of a shipment or any other material associated with the shipment (i.e. pallets, packaging, means of conveyance).

13. All solid wood packing material (SWPM) accompanying the shipment must be in compliance with ISPM 15 treatment regulations and IPPC stamp requirements and enforcement. Noncompliant shipments will be treated, re-exported or destroyed at the consignee's expense.

14. All costs and arrangements for safeguarding and transportation of the cargo are the responsibility of the importer, broker or other parties associated with the shipment.

15. All operations must be consistent with information submitted in association with the above listed APHIS-PPQ inspected facility and subject to the conditions below.

16. Soil must be shipped in a securely closed, watertight container (primary container, test tube, vial, etc.) which must be enclosed in a second, durable watertight container (secondary container).

17. The shipment must be free from foreign matter or debris, plants and plant parts including noxious weeds and infestations by other macroorganisms such as insects, Cyst nematodes, mollusks and acari. Authorized material found to be commingled with unauthorized material will be subject to the same action (i.e. re-export, destruction) as unauthorized material.

18. The imported article can be released without treatment at the port of entry to the permittee's address listed on the permit or label or to an authorized user only if the final destination is an approved facility listed at https://web01.aphis.usda.gov/PPQ/AuthSoilLabs.nsf/web?openform.

Permit Number P330-13-00306

THIS PERMIT HAS BEEN APPROVED ELECTRONICALLY BY THE FOLLOWING PPQ HEADQUARTER OFFICIAL VIA EPERMITS.	DATE
Osmond Baron	10/30/2013

WARNING: Any alteration, forgery or unauthorized use of this Federal Form is subject to civil penalties of up to $250,000 (7 U.S.C.s 7734(b)) or punishable by a fine of not more than $10,000, or imprisonment of not more than 5 years, or both (18 U.S.C.s 1001)

Page 4 of 6

APHIS Animal and Plant Health Inspection Service

Plant Protection & Quarantine

19. The soil must not be used in field research or release into the environment before sterilization.

The soil must not be used for isolation or culture of organisms, or for extracting and concentrating organisms from the soil.

The soil must not be used as a growing medium.

20. Further distribution of soil is not allowed without prior approval from Federal officials [State Plant Health Director or designee] (or from Federal officials with State concurrence): Access the website at http://www.aphis.usda.gov/ppq/sphd/ for a list of State Plant Health Offices. Access the website at http://nationalplantboard.org/member/index.html for a list of State Plant Regulatory Officials.

21. While in storage, all soil must be kept locked (e.g. in freezer, cabinet) in the approved lab with access limited to authorized personnel or they will be in a restricted access building that requires a key card entry and access is restricted to authorized personnel only; or it must be in locked room restricted to authorized personnel only.

22. The soil must be handled as quarantined material until sterilized. This will include keeping the soil enclosed in containers when not in use and labeling all containers and/or storage areas: "Quarantine Soil- Sterilize Before Disposal"

23. All packing material, media, substrate, and shipping containers must be sterilized or destroyed as approved and prescribed by the permit conditions after removing the soil.

24. All unconsumed soil, containers and effluent must be autoclaved, incinerated or properly sterilized by the permittee at the conclusion of the project as approved and prescribed by the permit conditions.

25. Any water residues (effluent) from the processing of soil samples must be treated by an approved sterilization procedure such as hydroclave or autoclave.

26. All soil residues must be dry-heated, incinerated, hydroclaved or autoclaved.

Dry Heat Treatment: use one of the following schedules:

110- 120.5 degrees C (230-249 F) for 16 hours
121-154 degrees C (250-309 F) for 2 hours
154.4 - 192.5 degrees C (310-379 F) for 30 minutes
193-220 degrees C (380-429 F) for 4 minutes
221-232 degrees C (430-450) for 2 minutes

Time starts when the entire sample reaches the required temperature, and a suitable temperature probe must be used for verification.

27. Autoclave soil and other material using the following conditions:

a. Soil must be autoclaved at 121 degrees Centigrade (250 degrees Fahrenheit) for a minimum of 30 minutes at 15 psi.

b. Autoclave tape or other indicators must be placed on each bag or sharps container prior to treatment. The autoclave tape or other indicator on each container must be checked to verify color change before disposal.

c. The autoclave log must be completed by each user for each autoclave cycle. All parameters must be noted as listed on the log for each autoclave load.

d. If the autoclave does not attain the minimum time and/or temperature or the autoclave tape does not change color, a notation must be made in the comment section of the autoclave log. The load must then be re-autoclaved after placing new tape on the material. If minimum time and temperature is not attained on the second cycle, users must contact the person responsible for maintaining the unit to initiate repairs. Waste must then be treated at an alternate autoclave facility that is approved by USDA.

e. Thermometers on the autoclave must be calibrated annually, and a written record must be maintained. This must be

Permit Number P330-13-00306

THIS PERMIT HAS BEEN APPROVED ELECTRONICALLY BY THE FOLLOWING PPQ HEADQUARTER OFFICIAL VIA EPERMITS.	DATE
Osmond Baron	10/30/2013

WARNING: Any alteration, forgery or unauthorized use of this Federal Form is subject to civil penalties of up to $250,000 (7 U.S.C.s 7734(b)) or punishable by a fine of not more than $10,000, or imprisonment of not more than 5 years, or both (18 U.S.C.s 1001)

APHIS Animal and Plant Health Inspection Service

Plant Protection & Quarantine

done by an authorized autoclave service company during routine servicing.

f. Every 6 months, you should use a commercially available test indicator kit that uses bacterial spores Bacillus stearothermophilus that are rendered unviable at 250 degrees F or 121 degrees C. For the test, ampules of B. stearothermophilus are autoclaved along with a load of waste. Upon completion of the cycle, the ampules are incubated for 48 hours and then observed for any sign of growth, which indicates insufficient sterilization. If any growth is observed, you must have the autoclave serviced and retested.

28. Equipment and supplies used to conduct operations or that have contacted the soil must be decontaminated using one of the following methods:

(a) Material can be soaked in a fresh bleach solution of 10 percent (1:10) for at least 30 minutes. (1:10 is a convention that means 1 in 10 or1 part 9 parts = 10 parts total, which is a 10 percent solution)
(b) Material can be soaked in 70 percent ethanol
(c) Flamed with ethanol
(d) Treated with quaternary ammonium compounds.
Note also that autoclaving, hydroclave, incineration, and dry heat sterilization are also acceptable sterilization/decontamination methods.

29. You must attach a PPQ Form 550 Black/White label to the exterior of each shipment being imported under this permit. If you are e-authenticated, you are instructed to request labels using the My shipment/my label option within ePermits at least 7 days in advance. Labels also may be requested by email at: BlackWhiteGreenYellow.labelrequest@aphis.usda.gov. All email requests must come from the permit holder or their authorized contact, if requested by an authorized contact the permit holder must be copied on all requests. You must specify PPQ Form 550 Black/White labels, the specific port(s) of entry and number of labels for each port when requesting labels. The requested labels will be sent to you through a bonded carrier.

30. Underlying packaging/wrapping must carry the address, billing, and any other information required to direct the shipment to its final destination (i.e., the permit holder's address). Please note: USDA APHIS does not defray any additional shipping costs incurred for transiting the shipment through an inspection station as the initial US destination).

END OF PERMIT CONDITIONS

Permit Number P330-13-00306

THIS PERMIT HAS BEEN APPROVED ELECTRONICALLY BY THE FOLLOWING PPQ HEADQUARTER OFFICIAL VIA EPERMITS.	DATE
Osmond Baron	10/30/2013

WARNING: Any alteration, forgery or unauthorized use of this Federal Form is subject to civil penalties of up to $250,000 (7 U.S.C.s 7734(b)) or punishable by a fine of not more than $10,000, or imprisonment of not more than 5 years, or both (18 U.S.C.s 1001)

Page 6 of 6

Title: WASTE DISPOSAL

Approvals (Signature/Date)

	11/14/12		11/20/12
Jared Knierim Disposal Department Manager	Date	Andy Johnson Client Services Manager	Date
	11/16/12		11/19/12
Michael H. Dunn Technical Director Quality Assurance Manager	Date	Johnny Davis Health & Safety Manager / Coordinator	Date
	11/26/12		
Amelia K. Kennedy Lab Director	Date		

1.0 Purpose and Scope

1.1 TestAmerica Nashville receives a variety of sample matrices for analysis and uses a variety of different chemicals and solvents in the testing procedures. This document provides guidance for proper disposal of samples, chemicals and solvents.

1.2 Regulations from the Environmental Protection Agency (EPA) Resource Conservation and Recovery Act (RCRA), Toxic Substance Control Act (TSCA), United States Department of Agriculture Soil Quarantine areas, and the Clean Water Act (CWA) apply to TestAmerica Nashville. All waste must be handled within the framework of these regulations. In addition, state and local regulations play a large part in determining disposal methods.

1.3 Aqueous samples are identified to determine those samples that can be discharged into the sanitary sewer and those samples that cannot and must be disposed of per EPA and RCRA regulations or returned to the client only on a case by case basis.

1.4 Soil samples are identified to determine those samples that can be disposed as a solid (non-hazardous) waste. Those samples that cannot be disposed as non-hazardous waste are disposed of per EPA and RCRA regulations or returned to the client on a case by case basis.

1.5 Non-aqueous liquid samples or miscellaneous solid samples are identified to determine those samples that can be disposed as solid, non-hazardous waste or disposed as hazardous waste.

1.6 The decision to return samples to clients is made on a case-by-case basis by the Laboratory Director.

1.7 Established wastestreams have been developed for the handling of laboratory chemicals and solvents. TestAmerica Nashville's Hazardous Waste Coordinator and Laboratory Director are responsible for notifying the licensed hazardous waste transporter when drum or lab packing disposal needs develop at the division.

1.8 All procedures in this document are in compliance with the requirements of the hazardous waste transporter or the local sanitary sewer department.

2.0 Safety

2.1 Every employee is directly responsible for complete awareness of all health hazards associated with every sample and chemical that he/she uses. The employee is aware of these hazards and all associated protective wear and spill clean-up procedures ***prior*** *to the use* of any chemical or the analysis of any sample. The employee must comply with all safety policies as presented in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention. Bottle labels also provide important information to be noted. In the case of any questions or concerns with a particular sample or suspected waste, both the applicable Material Safety Data Sheet (MSDS) and supervisor or Health & Safety Manager / Coordinator must be consulted.

2.2 Upon receipt, all samples are considered potentially hazardous and treated as such. Lab personnel should be notified of any samples that have special handling precautions or if the sample is known to be hazardous. Login will designate special handling procedures on the login comment line and the sample may also be tagged for special handling upon receipt.

2.3 Personnel performing disposal procedures may be working with flammables, poisons, toxics, carcinogens, teratogens, mutagens and/or biohazards. At a minimum, appropriate gloves, safety glasses and labcoats **must** be worn during disposal of samples or other waste, in addition to other measures prescribed by TestAmerica Nashville. Samples MUST be handled with as much care as any of the chemicals or solvents due to the unknown nature of their composition. When using the glass crusher, employees must wear hearing protection.

2.4 Yearly, appropriate personnel are given training on the regulations concerning the shipment of Hazardous Waste and Handling Waste. The Waste Disposal Coordinator is also required by RCRA to attend a yearly 2-day training course for recertification.

2.5 Annual training and audiogram are performed for personnel using the glass crusher.

2.6 Waste drums are grounded to prevent any electrical currents to the drums.

3.0 Definitions

3.1 Hazardous Waste is defined as any solid, liquid or contaminated gaseous material that is discarded by being disposed, incinerated or recycled. Hazardous waste can be the by-product of a manufacturing process or simply a commercial product that is used in testing procedures. There are two type of hazardous wastes:

3.1.1 *Listed Hazardous Waste* is considered hazardous if it appears on one of four published lists in the Code of Federal Regulations (40 CFR Part 261).

3.1.2 *Characteristic Waste* may be classified as hazardous if it demonstrates one or more of the following characteristics:

3.1.2.1 *Ignitable Waste* has a flashpoint of less than 140°F. Waste code is D001.

3.1.2.2 *Corrosive Waste* has a pH of less than 2.0 or greater than 12.5, or corrodes steel at a rate of greater than 6.35mm per year at 55°C. Waste code is D002.

3.1.2.3 *Reactive Waste* is unstable, reacts violently with water, is sufficiently cyanide or sulfide bearing to produce toxic gas, or is capable of detonation. Waste code is D003.

3.1.2.4 *Toxic waste* contains any of the regulated TCLP contaminants at or above the regulatory level. See Attachment I for the TCLP list and regulatory limits. Waste code is D004 - D043.

3.2 Samples as Hazardous Waste: If a sample of solid waste, water, air or soil is collected for the purpose of laboratory testing to determine its characteristics or composition, it is NOT SUBJECT to the requirements of RCRA when it is being stored or transported to and from the sample collector.

3.3 Small Quantity Generator (SQG)*:* Any business that generates between 100 and 1000 kg of hazardous waste in any one month. If the business generates more than 1 kg of P listed waste in a month or stores more than 1 kg at any time, it will be classified as a Large Quantity Generator.

3.4 Large Quantity Generator (LQG): Any business that generates greater than 1000 kg of hazardous waste in any one month, or 1 kg of any P listed waste in a month. It is necessary for both SQG and LQG business to obtain a 12 digit EPA state identification number. This allows the EPA and State to monitor hazardous waste activity. TestAmerica Nashville's active 12 digit EPA identification number is TNR000000638. This identification number **must** be on all waste manifests that are generated as a result of disposal activities.

3.5 Elementary Neutralization: The addition of an acid or a base to a wastewater to be discharged to the sanitary sewer in order to correct its pH to the acceptable limits in Metro Nashville's Sewer Use Ordinance.

3.6 See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for other laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Procedure

Waste added to drums for disposal must be recorded on the Waste Accumulation Logs.

4.1 **Accumulation** (unused sample is brought back to sample storage area).

4.1.1 Prep Lab

4.1.1.1 Solvents are collected in satellite containers under hoods within the prep area. When full these containers are emptied into a drum labeled "Hazardous Waste – Mixed Chlorinated Liquids". This drum is stored in the Waste Storage area. Captured Methylene chloride from reclamation is collected separately and recycled.

4.1.1.2 Water samples from the extraction procedure are elementary neutralized to a pH between 5 and 10 pH units for discharge into the sewer system.

4.1.1.3 Soils samples after the extraction procedure are placed in a box in the hood, so that the solvent can be evaporated off. When the soil is dry it is then disposed of in the trash, within prep lab.

4.1.1.4 Sodium sulfate that comes into contact with Methylene Chloride is stored under a vent hood overnight so the methylene chloride will evaporate off. Then the Sodium sulfate is disposed in the trash.

4.1.2 Volatiles / UST

4.1.2.1 Water samples after analysis are discharged into the sewer system by the Sample Disposal group after elementary neutralization, with the exception of any samples that appear to contain any amount of oil or other suspicious contamination. These samples are disposed into either the oil waste drum or the lab liquid waste, depending on the sample.

4.1.2.2 Soils samples after analysis are crushed and disposed of in the dumpster. These are the VOA vials with small amount of sample.

4.1.3 Extractables

4.1.3.1 Vials that contain sample extracts (NOT PCB vials) are stored together and disposed of as Hazardous waste.

4.1.3.2 When PCB samples are acid (Sulfuric acid) cleaned, the acid and the hexane extract are kept together in the 15 ml vial until they are ready for disposal. For disposal the acid and Hexane are separated or collected and disposed of as hazardous waste. The acid will be place with a mixed acid waste. The Hexane is disposed of with the PCB extract vials and PCB standards.

4.1.3.3 The neutral water waste from sulfur cleaning is discharged into the sewer system.

4.1.4 Inorganic / Metals

4.1.4.1 Acid waste: This somewhat concentrated acid is collected together, elementary neutralized, and discharged into the sanitary sewer by the Sample Disposal group.

4.1.4.2 Water and soil samples are disposed of as indicated in 4.1.2.1 and 4.1.2.2.

4.1.4.3 Metals digests are combined and taken to a pH range of 5 to 10 with Sodium hydroxide pellets. This solution is then disposed into the sewer system.

4.1.4.4 Mercury Corrosive waste: This waste is generated by the Lachat instruments in the Wet Chemistry department, collected together, and disposed of as hazardous waste.

4.1.5 Oils: Samples which are primarily oil (not PCB oil) are placed in the Waste Oil drum. Prior to shipment the drum is tested for Metals, Flashpoint and PCBs, if these are below "Hazardous Waste Limits", the drum is shipped as "Waste Oil - Non-Hazardous." If the tests are above the "Hazardous Waste Limit", then the drum is shipped as "Hazardous Waste Liquid."

4.1.6 Sample Disposal

Note: Samples that are shown to have high levels of PCBs are disposed of with the other PCB waste (Section 4.1.3.2).

4.1.6.1 Aqueous Samples

4.1.6.1.1 Groundwater, wastewater and drinking water samples are poured into the sample disposal tub to the fill line, well stirred, checked for pH, and elementary neutralized to a pH between 5 and 10 prior to discharge into the sewer system. When the sample disposal tub is empty, employees clean the bottom of the tub for any loose debris that may prevent proper drainage (i. e., lid liners). The bottles are crushed, and plastic bottle labels are defaced before disposal if the client name appears on the bottle. After the process is complete, the employee must complete the disposal checklist and scan the location to "Disposal."

4.1.6.1.2 Liquid samples that do not look like water are collected into a Lab Liquid Wastestream. This stream contains liquid from the disposal of samples and general liquid waste from analytical operation, which is not generally put into the drain. This waste is shipped as Hazardous Waste. If the client information appears on the container, **plastic container labels are destroyed with a grinder**

before disposal. Complete the disposal checklist and scan the location to "Disposal."

4.1.6.2 Solid Samples

4.1.6.2.1 See United States Department of Agriculture Quarantine Areas (SOP USDA Disposal / NV08-162) for the procedure of heat-treating quarantined domestic and foreign soils prior to disposal.

4.1.6.2.2 Soil samples are placed into a cubed box. When the container is full, a core sample is taken and tested for RCRA contaminants. The core sample is prepared by collecting small portions from randomly selected jars from multiple positions in the box. If the tests show that the drum is non-hazardous, then it is shipped as "Solid Waste - Non Hazardous." Otherwise, it is shipped under the prior shipping name and waste codes.

4.1.6.2.3 Fluorescent Bulbs: These bulbs may contain Mercury and are shipped in their Original Boxes if possible, as "Universal Waste, Mercury Lamps." This is not classified as Hazardous Waste.

4.2 **Lab Waste Disposal Procedures***:* TestAmerica Nashville has developed several wastestreams for the effective disposal of chemicals and solvents that are used in analytical testing procedures. These wastestreams are monitored by the Environmental Health & Safety Manager and the Environmental Health & Safety Director to ensure timely removal by a licensed waste transporter. TestAmerica Nashville is currently contracted with Clean Harbors, USEPA ID Number TNR000000638, for the disposal of these wastestreams. See Table 4 for a list of these wastestreams.

5.0 Responsibilities and Documentation

5.1 Waste added to drums for disposal must be recorded on the Waste Accumulation Logs.

5.2 All drums, pails and labpacks transported off site by a licensed waste transporter must be documented with an appropriate manifest and, if applicable, a land-ban form. Copies of the manifest are retained and filed in a dated folder specific to the date of the waste pickup. Manifests must be retained for at least 7 years.

5.3 If an analyst is uncertain as to how to assess the hazard of a sample or is uncertain of the disposal of a particular sample or chemical, the analyst must seek the guidance of the Waste Disposal Coordinator or the Technical Director.

5.4 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

5.5 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes must be stored, managed, and disposed of in accordance with all federal and state laws and regulations.

6.0 References/Cross References

6.1 **RCRA**: Resource Conservation and Recovery Act, 1976

6.2 **49 CFR Parts 171-177**, Safe Transportation of Hazardous Waste

6.3 **TSCA**: Toxic Substance Control Act

6.4 **USDA**: foreign and domestic soil quarantine criteria.

6.5 **MWS Metro Code of Laws**, Title §15.60.080, B.

6.6 **SOPs**: USDA Disposal / NV08-162.

6.7 **Controlled Documents**: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions, WD-3, Waste Accumulation Log-Mixed Chlorinated Liquids, WD-4, Waste Accumulation Log-Mixed Flammable Liquids, WD-6, Waste Accumulation Log-TKN Waste, WD-7, Waste Accumulation Log-Lab Vials, WD-8, Checklist for Sample Disposal.

7.0 Attachments

7.1 Table 1. RCI Characteristics

Characteristic	Regulatory Limit
Ignitability (D001)	Liquids with a flash point less then 140°F or non-liquids which cause fire and burn vigorously and persistently
Corrosivity (D002)	Aqueous solutions with a pH less than or equal to 2 or greater than or equal to 12.5 or liquids which corrode steel at a rate of greater than 6.35 mm (0.25 in.) per year at 55°C (130°F)
Reactivity (D003)	Reacts violently with water or cyanide or sulfide containing material which release toxic gases under a specified pH range

7.2 Table 2. TCLP List

Compound	CAS No.[1]	Regulatory Limit (mg/L)
Arsenic	7440–38–2	5.0
Barium	7440–39–3	100.0
Benzene	71–43–2	0.5
Cadmium	7440–43–9	1.0
Carbon tetrachloride	56–23–5	0.5
Chlordane	57–74–9	0.03
Chlorobenzene	108–90–7	100.0
Chloroform	67–66–3	6.0
Chromium	7440–47–3	5.0
o-Cresol	95–48–7	200.0[3]
m-Cresol	108–39–4	200.0[3]
p-Cresol	106–44–5	200.0[3]
Cresol		200.0[3]
2,4-D	94–75–7	10.0
1,4-Dichlorobenzene	106–46–7	7.5
1,2-Dichloroethane	107–06–2	0.5
1,1-Dichloroethylene	75–35–4	0.7
2,4-Dinitrotoluene	121–14–2	0.13[2]
Endrin	72–20–8	0.02
Heptachlor (and its epoxide)	76–44–8	0.008
Hexachlorobenzene	118–74–1	0.13[2]
Hexachlorobutadiene	87–68–3	0.5
Hexachloroethane	67–72–1	3.0
Lead	7439–92–1	5.0
Lindane	58–89–9	0.4
Mercury	7439–97–6	0.2
Methoxychlor	72–43–5	10.0
Methyl ethyl ketone	78–93–3	200.0
Nitrobenzene	98–95–3	2.0
Pentachlorophenol	87–86–5	100.0
Pyridine	110–86–1	5.0[2]

Compound	CAS No.[1]	Regulatory Limit (mg/L)
Selenium	7782–49–2	1.0
Silver	7440–22–4	5.0
Tetrachloroethylene	127–18–4	0.7
Toxaphene	8001–35–2	0.5
Trichloroethylene	79–01–6	0.5
2,4,5-Trichlorophenol	95–95–4	400.0
2,4, 6-Trichlorophenol	88–06–2	2.0
2,4, 5-TP (Silvex)	93–72–1	1.0
Vinyl chloride	75–01–4	0.2
1 Chemical abstracts service number.		
2 Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.		
3 If o-, m-, and p-Cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level of total cresol is 200 mg/l.		

7.3 Table 3. P Listed Waste

Chemical Name	EPA Waste Code
Acetaldehyde, chloro-	P023
Acetamide, N-(aminothioxomethyl)-	P002
Acetamide, 2-fluoro-	P057
Acetic acid, fluoro-, sodium salt	P058
Acetimidic acid, N-[(methylcarbamoyl)oxy]thio, methyl ester	P066
3-(alpha-acetonylbenzyl)-4-hydroxycoumarin and salts	P001
1-Acetyl-2-thiourea	P002
Acrolein	P003
Aldicarb	P070
Aldrin	P004
Allyl Alcohol	P005
Aluminum phosphide	P006
5(-Aminomehtyl)-3-isoxazolol	P007
4-aAminopyridine	P008
Ammonium picrate	P009
Ammonium vanadate	P119
Arsenic acid	P010
Arsenic (III) oxide	P012
Arsenic (V) oxide	P011
Arsenic pentoxide	P011
Arsenic trioxide	P012
Arsine, diethyl	P038
Aziridine	P054
Barium cyanide	P013
Benzenamine, 4-chloro	P024
Benzenamine, 4-nitro	P077
Benzene, (chloromethyl)	P028

Chemical Name	EPA Waste Code
1,2-Benzenediol, 4-[1-hydroxy-2-(methylamino)ethyl]-	P042
Benzenethiol	P014
Benzyl chloride	P028
Beryllium dust	P015
Bix(chloromethyl) ether	P016
Bromoacetone	P017
Brucine	P018
Calcium cyanide	P021
Camphene, octachloro	P123
Carbamimidoselenoic acid	P103
Carbon bisulfide	P022
Carbon disulfide	P022
Carbonyl chloride	P095
Chlorine cyanide	P033
Chloroacetaldehyde	P023
p-Chloroaniline	P024
1-(o-Chlorophenyl)thiourea	P026
3-Chloropropionitrile	P027
Copper cyanides	P029
Cyanides (soluble cyanide salts), not elsewhere specified	P030
Cyanogen	P031
Cyanogen chloride	P033
Dichlorphenylarsine	P036
Dieldrin	P037
Diethylarsine	P038
O,O-Diethyl S-[2-(ethylthio)ethyl] posphorodithioate	P039
Diehyl-p-nitrophenyl phosphate	P041
O,O-Diethyl P-pyrazinyl phosphorothioate	P040
Diisopropyl fluorophosphate	P043
Dimethoate	P044
3,3-Dimethyl-1-(methylthio)-2-butanone, O-[(methylamino)carbonyl]oxime	P045
O,O-Dimethyl O-p-nitrophenyl phosphorothioate	P071
Dimethylnitrosamine	P082
alpha, alpha-Dimethylphenethylamine	P046
4,6-Dinitro-o-cresol and salts	P047
4,6-Dinitro-o-cyclohexylphenol	P034
2,4-Dinitrophenol	P048
Dinoseb	P020
Diphosphoramide, octamethyl-	P085
Disulfoton	P039
2,4-Dithiobiuret	P049
Dithiopyrophosphoric acid, tetraethyl ester	P109
Endosulfan	P050

Chemical Name	EPA Waste Code
Endothall	P088
Endrin	P051
Epinephrine	P042
Ethanamine, 1,1-dimethyl-2-phenyl-	P046
Ethenamine, N-methyl-N-nitroso-	P084
Ethyl cyanide	P101
Ethylenimine	P054
Famphur	P097
Fluorine	P056
Fluoroacetamide	P057
Fluoroacetic acid, sodium salt	P058
Fulminic acid, mercury(II) salt (R,T)	P065
Heptachlor	P059
1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octoahydro-endo, endo-1,4:5,8-dimethanonaphthalene	P051
1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octoahydro-endo, exo-1,4:5,8-demethanonaphthalene	P037
1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-endo, endo-dimethanonaphthalene	P060
1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-endo, exo-dimethanonaphthalene	P004
Hexachlorohexahydro-exo-exo-dimethanonaphthalene	P060
Hexaethyl tetraphosphate	P062
Hydrazinecarbothioamide	P116
Hydrazine, methyl-	P068
Hydrocyanic acid	P063
Hydrogen cyanide	P063
Hydrogen phosphide	P096
Isocyanic acid, methyl ester	P064
3(2H)-Isoxazolone, 5-(aminomethyl)-	P007
Mercury, (acetato-O)phenyl-	P092
Mercury fulminate (R,T)	P065
Methane, oxybis(chloro-	P016
Methane, tetranitro-(R)	P112
Methanethiol, trichloro-	P118
4,7-Methano-1H-indene 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-	P059
Methomyl	P066
2-Methylazridine	P067
Methyl hydrazine	P068
Methyl isocyanate	P064
2-Methyllactonitrile	P069
Methyl parathion	P071
alpha-Naphthylthiourea	P072

Chemical Name	EPA Waste Code
Nickel carbonyl	P073
Nickel cyanide	P074
Nickel(II) cyanide	P074
Nickel tetracarbonyl	P073
Nicotine and salts	P075
Nitric oxide	P076
p-Nitroaniline	P077
Nitrogen dioxide	P078
Nitrogen(II) oxide	P076
Nitrogen(IV) oxide	P078
Nitroglycerine (R)	P081
N-Nitrosodimethylamine	P082
N-Nitrosomethylvinylamine	P084
5-Norbornene-2,3-dimethanol 1,4,5,6,7,7-hexachloro, cylic sulfite	P050
Octamethylpyrophosphoramide	P085
Osmium oxide	P087
Osmium tetroxide	P087
7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid	P088
Parathion	P089
Phenol, 2-cyclohexyl-4,6-dinitro-	P034
Phenol, 2,4-dinitro-	P048
Phenol, 2,4-dinitro-6-methyl-	P047
Phenol, 2,4-dinitro-6-(1-methylpropyl)-	P020
Phenol, 2,4,6-trinitro-, ammonium salt (R)	P009
Phenyl dichloroarsine	P036
Phenylmercuric acetate	P092
N-Phenylthiourea	P093
Phorate	P094
Phosgene	P095
Phosphine	P096
Phosphoric acid, diethyl p-nitropenyl ester	P041
Phosphorodithioic acid, O,O-dimethyl S-[2-(methylamino)-2-oxoethyl]ester	P044
Phosohorofluoric acid, bis(1-methylethyl)ester	P043
Phosphorothioic acid, O,O-diethyl S-(ethylthio)methyl ester	P094
Phosphorothioic acid, O,O-diethyl O-(p-nitrophenyl) ester	P089
Phosphorothioic acid, O,O-diethyl O-pyrazinyl ester	P040
Phosphorothioic acid, O,O-dimethyl O-[p-((dimethylamino)-sulfonyl)phenyl]ester	P097
Plumbane, tetraethyl-	P110
Potassium cyanide	P098
Potassium silver cyanide	P099
Propanal, 2-methyl-2-(methylthio)-,O-[(methylamino)carbonyl]oxime	P070
Propanenitrile	P101

Chemical Name	EPA Waste Code
Propanenitrile, 3-chloro-	P027
Propanenitrile, 2-hydroxy-2-methyl-	P069
1,2,3-Propanetriol, trinitrate-(R)	P081
2-Propanone, 1-bromo-	P017
Propargyl alcohol	P102
2-Propenal	P003
2-Propen-1-ol	P005
1,2-Propylenimine	P067
2-Propyn-1-ol	P102
4-Pyridinamine	P008
Pyridine, (S)-3-(methyl-2-pyrrolidinyl)-, and salts	P075
Pyrophosphoric acid, tetraethyl ester	P111
Selenourea	P103
Silver cyanide	P104
Sodium azide	P105
Sodium cyanide	P106
Strontium sulfide	P107
Strychnidin-10-one, and salts	P108
Strychnidin-10-one, 2,3-dimethoxy	P018
Strychnine and salts	P108
Sulfuric acid, thallium(II) salt	P115
Tetraethyldithiopyrophosphate	P109
Tetraethyl lead	P110
Tetraethylpyrophosphate	P111
Tetranitromethane (R)	P112
Tetraphosphoric acid, hexaethyl ester	P062
Thallic oxide	P113
Thallium (III) oxide	P113
Thallium (I) selenite	P114
Thallium (I) sulfate	P115
Thiofanox	P045
Thioimidodicarbonic diamide	P049
Thiophenol	P014
Thiosemicarbazide	P116
Thiourea, (2-chlorophenyl)-	P026
Thiourea, 1-naphthalenyl	P072
Thiourea, phenyl-	P093
Toxaphene	P123
Trichloromethanethiol	P118
Vanadic acid, ammonium salt	P119
Vanadium pentoxide	P120
Vanadium (V) oxide	P120
Warfarin	P001

Chemical Name	EPA Waste Code
Zinc cyanide	P121
Zinc phosphide (R,T)	P122

7.4 Table 4. Wastestreams Generated at TestAmerica Nashville

Waste ID	Waste Description	SSA Container	Main Collection Process or Container
TKN	Pyridine and mercury waste generated from Inorganics Department	5-gallon carboy, 2.5-gallon bottle, 5-liter bottle	55-gallon polyethylene, closed-top drum
MF	Mixed flammable Liquids: Acetone, Ethyl ether, Hexane, Pentane, Methanol	1 liter glass jars	55-gallon polyethylene, closed-top drum
MC	Mixed chlorinated liquids, Methylene chloride, Acetone, Chloroform	5-gallon carboy, 1-gallon jugs, 16-oz. glass jars	55-gallon, metal, closed-top drum
COD	COD waste	55-gallon, polyethylene, closed-top drum	55-gallon, polyethylene, closed-top drum
LV	Lab vial waste	2-mL vials	55-gallon, metal, open-top drum
PCB	PCB waste	16-oz. jar, 8-oz. jar, 4-oz. jar, 40-mL vials	Lab pack
AW	Acid waste from digestion of samples, PCB clean-up, and preserved samples ready for disposal	5-gallon carboy	Neutralized and discharged at the end of the day into the sanitary sewer system
MCR	Reclaimed Methylene chloride from KD process for recycling	55-gallon, metal, closed-top drum	55-gallon, metal, closed-top drum
X	Expired standard	Original containers	Lab pack
M	Mercury waste from broken thermometers	1-gallon plastic jug	Lab pack

8.0 Revision History

- Revision 7, dated 1 April 2010
  - Integration of STL and TestAmerica operations.
- Revision 8, dated 31 January 2011
  - Addition of Section 7.4, Table 4, Wastestreams Generated at TestAmerica Nashville. Reference to the new table in Section 4.2.
- Revision 9, dated 10 February 2012
  - Organizational changes.
  - Addition of disposal checklist and modification of wastewater neutralization for discharge to the sanitary sewer.
- Revision 10, dated 30 November 2012
  - Organizational changes,
  - Confirm procedures.
  - Add additional controlled document references.

Title: WISCONSIN METHOD OF DETERMINING DIESEL RANGE ORGANICS (DRO) METHOD WI DRO

Approvals (Signature/Date)			
Jessica Freeman	7/15/13		
Jessica Freeman Department Supervisor	Date		
Jacolby Robinson	6/26/13		7/15/13
Jacolby Robinson Department Supervisor	Date	Cory Spry Extractables Operations Manager	Date
Michael H. Dunn	6/11/13		6/27/13
Michael H. Dunn Technical Director Quality Assurance Manager	Date	Johnny Davis Health & Safety Manager / Coordinator Extractions Operations Manager	Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method measures the concentration of diesel range organics in water, soil, and wastes. This corresponds to a hydrocarbon range of C_{10} – C_{28}. As defined in the method, other organic compounds, including chlorinated hydrocarbons, phenols, phthalate esters, polynuclear aromatic hydrocarbons, kerosene, fuel oils and heavier oils are measurable.

1.2 Reporting Limits (RLs): The RL of this method is 0.1 mg/L for groundwater and 10 mg/kg for soils.

1.3 This method is based on a solvent extraction, gas chromatography (GC) procedure and involves the interpretation of gas chromatograms by skilled analysts. Each analyst demonstrates the ability to generate acceptable results with this method.

1.4 Any modification of this method, beyond those expressly permitted, is considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.5 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted on the worklist and in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

This method provides gas chromatographic conditions for the detection of semivolatile petroleum fractions, such as diesel, fuel oil #2, or kerosene. Samples are analyzed utilizing extraction to dissolve the organic constituents. The extract is dried, concentrated and injected into a capillary column gas chromatograph. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID). Quantitation is based on the FID detector response to a diesel component standard.

3.0 Definitions

3.1 Diesel Range Organics (DRO): All the chromatographic response falling between the onset of n-Decane (n-C_{10}) peak and the conclusion of n-Octacosane (n-C_{28}) peak. Quantitation is based on a direct comparison of the total area within this range to the total area of the Diesel Component Standard.

3.2 Diesel Component Standard: A 10-component blend of typical diesel compounds. This standard serves as a quantitation standard and is used to establish a retention time window for diesel range organics. It consists of Decane, Dodecane, Tetradecane, Hexadecane, Octadecane, Eicosane, Docosane, Tetracosane, Hexacosane, and Octacosane.

3.3 Laboratory Control Spike (LCS) - Water: Reagent water spiked with the Diesel Component Standard and run through the method with water samples as a quality control check.

3.4 Laboratory Control Spike (LCS) – Soil: Sodium sulfate spiked with the Diesel Component Standard and run through the method with soil samples as a quality control check.

3.5 Method Blank - Water: A reagent water sample extracted with the same volume of solvent used in samples, processed as a sample, and run as a quality control check. If contamination is found it is the lab's responsibility to determine its origin.

3.6 Method Blank - Soil: A reagent sand or clean soil extracted with the same volume of Methanol used in samples, processed as a sample, and run as a quality control check. If contamination is found it is the lab's responsibility to determine its origin.

3.7 Initial Calibration Verification (ICV): A mid-level, second-source standard analyzed to verify the calibration curve immediately after the calibration standards.

3.8 Continuing Calibration Verification (CCV): A mid-level calibration standard (using the primary standard) analyzed to verify the validity of the calibration curve on an ongoing basis.

3.9 See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for other laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 Other organic compounds; including chlorinated hydrocarbons, phenols, and phthalate esters are measurable. As defined in the method, the DRO results include these compounds.

4.2 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing it with tap water and Acetone or Methylene chloride. Method blanks must be analyzed with each batch or for every 20 samples to demonstrate that the analytical system is free of contamination.

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank to check for cross-contamination or the repeat analysis of the affected samples.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This method may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: None.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methylene chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Carbon disulfide	Flammable Irritant		Vapors cause irritation to the respiratory tract, affects nervous system. Contact may produce reddening, burning, cracking, peeling. Chronic exposure can cause kidney, liver, reproductive, nervous, cardiac, visual, psychosis effects.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Gas chromatograph
  - Gas Chromatograph (Hewlett Packard and Perkin Elmer): Analytical system complete with gas chromatograph and all required accessories, including a detector, column supplies, recorder, gases and syringes. A data system (CHROM) capable of determining peak areas and integrating DRO as defined in the method is used.
  - Column ZB1, 15 m x 0.53 mm with a film thickness of 0.5 ηm or equivalent, capable of resolving C_{10} from the solvent..
  - Detector: Flame ionization (FID).
  - **Operating Conditions:** Set the column temperature to 50°C for 1 minute, then 40°C/minute to 320°C and hold for 3 minutes. Set FID Detector to 320°C and injector to 290°C. Conditions may be altered to improve resolution of diesel range organics. Record the conditions and changes in the instrument maintenance log for individual instruments.
- Concentrator tube, Kuderna-Danish: 10-mL graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.
- Evaporative flask, Kuderna-Danish: Attach to concentrator tube with clamps, springs.
- Snyder column, Kuderna-Danish
- Nitrogen evaporator with high purity nitrogen gas source.
- Analytical balance capable of accurately weighing 0.0001 g (must be used for standards).
- Top-loading balance capable of weighing to the nearest 0.1 g (to be used for sample analysis).
- Ultrasonic bath.
- Water bath, heated, and capable of temperature control (± 50°C). The bath is used in a hood.
- Shaker table.

6.2 Supplies

- VOC Vials and Bottles, wide-mouth, 60-mL (2.0 oz.) or 120-mL (4.0 oz.) containers with Teflon™/silicone septa or Teflon™-lined caps for soils. Amber, 1 liter bottles with Teflon™-lined caps for waters.
- Microsyringes, 1 µL, 5 µL, 10 µL, 25 µL, 100 µL.
- Disposable pipets, Pasteur.

7.0 Reagents and Standards

7.1 Reagent water, analyte-free.

7.2 Solvents: Hexane, Methylene chloride, Carbon disulfide and Acetone, pesticide grade or equivalent.

7.3 DRO-free Sodium sulfate, (ASC) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray or pre-rinsed with the extraction solvent. A commercial product is acceptable.

7.4 Surrogate (C_{35}): C_{35} stock standard is prepared by weighing out 0.1 g of pure C_{35} material and diluting to 10.0 mL with CS_2 for a concentration of 10,000 µg/mL.

- Prepare the intermediate C_{35} standard by diluting 10 mL of the stock standard into 440 mL of Acetone, 440 mL Hexane, and 110 mL Carbon disulfide for a concentration of 100 µg/mL. Add 1 mL of the surrogate intermediate standard to all samples and quality control samples before extraction.
- The commercial C_{35} standard, Ultra TAM-502, or equivalent, at 10,000 µg/mL, is acceptable. Dilute by 100 for a 100 µg/mL standard.

7.5 Individual Component Stock Standards (Primary Standard): Volumetrically prepare stock standards for the diesel components in Hexane at approximately 2,000 µg/mL for each individual compound.

- Prepare a stock standard by weighing out 0.2 grams of each pure standard (C_8 – C_{40}) into about 30 mL of CS_2. Dilute to a final volume of 100 mL in Hexane. Exact amounts are recorded and concentration adjusted accordingly, concentrations are around 2,000 µg/mL for each compound with a total concentration of about 20,000 µg/mL for the C_{10} – C_{28} range. A commercial standard is acceptable (Restek Cat. No. 560727, or equivalent, 2,000 µg/mL each compound).

  Note: This standard is prepared with all even compounds from C_8 to C_{40}, because it is also used for other state TPH methods that have a wider range reported. Only the C_{10} - C_{28} range is used in this method. Add 50 mL of the stock standards to 200 mL mixture of 10% Methylene chloride, 15% Carbon disulfide, 75% Hexane for a 500 µg/mL each target working standard, 5000 µg/mL total.

- Transfer the stock standard solution into a Teflon™-sealed screw-cap/crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.
- Standards must be replaced after six months unless comparison with unexpired standards documents their accuracy.
- Standards used for MS/MSD and LCS must be prepared in Acetone or other water-soluble solution.

7.6 Diesel Component Stock Standard (Secondary Standard): Prepare the same as the primary standard, but use Ultra Cat. No. CUS-8083, or equivalent.

7.7 Also, see SOP Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214

8.0 Sample Collection, Preservation, Shipment and Storage

Analysis Method	Sample Storage	Holding Times from Date and Time of Collection			
		Solvent Addition	Shipping	Extraction	Analysis
Waters	Amber Bottle	NA	7 days	7 days	47 days
Soils	VOC vial	Within 10 days	10 days	47 days	47 days
	Brass Tube or Encore™	Within 10 days	10 days	47 days	47 days

The bottle and cap liner must be washed, rinsed with Acetone or Methylene chloride, and dried before use to minimize contamination. Certified clean bottles are acceptable.

8.1 Aqueous samples are collected in a one-liter amber bottle with a Teflon™-lined cap. The Teflon™ liner must contact the sample. Samples must be preserved with 5 mL of 50% HCl or other acid strength at the time of collection to obtain pH < 2, (acid must be added to the bottle

prior to adding the sample). Cool samples to 0-6°C immediately after collection. Water samples must be held at 0-6°C and extracted within 7 days of collection. Analysis must take place within 40 days of extraction. The pH of all water samples must be determined unless sample vials containing acid for field preservation were supplied by the lab. If sample pH is greater than two, sample results must be flagged.

8.2 **Soils** can be collected using a 30 mL plastic syringe with the end sliced off, a brass tube, an EnCore™ sampler or other appropriate devices. Samples cannot be analyzed if the amount of soil in the vial exceeds the weight maxima listed in Table 1. A sufficient number of vials (three recommended) should be collected to provide for backup analyses in the event of breakage. One vial must be collected for dry weight determination. Care must be taken to be sure the vial seals properly (no soil in the threads). This can be accomplished by using a clean toothbrush or other utensil to sweep particles off the threads of the vial. Collect and preserve soil samples by one of the following techniques.

8.2.1 Collect soil into tared containers following Table 1. Store samples on ice or at 0-6°C.

8.2.2 Pack soil with no headspace into a brass tube. Cap the tube using plastic endcaps with Teflon™ sheets placed between the endcaps and the sample. Store samples on ice or at 0-6°C. Immediately prior to solvent addition, subsample the soil from the brass tube into a VOC vial following Table 1. Subsampling involves removing one of the plastic endcaps, scraping away the surface soil, and then scooping out (with a spatula or other utensil), the appropriate weight of soil into the vial. Brass tubes must be cleaned appropriately prior to reuse.

8.2.3 Pack soil with no headspace into an EnCore™ sampler. Cap with the stainless steel "o-ring" cap. Store samples on ice or at 0-6°C. Soil stored in the EnCore™ sampler must be extruded from the device into a VOC vial immediately prior to solvent addition. The soil is extruded by using a pushrod supplied with the tool. Do not scoop soil out of the sampler using a spatula, etc. EnCore™ samplers must be cleaned appropriately (following the manufacturer's recommendations) prior to reuse.

8.3 Minimize shipping time. Samples must be received by the lab within 10 days.

8.4 Sample temperatures are determined upon receipt by the lab. Sample temperature may be recorded as "received on ice" only if solid ice is present in the cooler at the time the samples are received. "Received on ice" means sample containers are surrounded by an ice slurry, or crushed, cubed or chipped ice at the time of receipt in the laboratory. It is acceptable to place the sample containers in plastic bags to preserve sample and label integrity. The use of bubble wrap or other insulating material is not allowed. Samples cooled during shipping with ice packs or "blue ice" may not be recorded as "received on ice." If samples are not "received on ice," temperature is determined from the temperature of an actual sample using an IR gun. If the temperature is above 6.0ºC, contact the client and comment the temperature in LIMS.

9.0 Quality Control

Refer to the quality control section of TestAmerica Nashville's QA Manual for specific quality control (QC) policy. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 **Sample QC:** The following quality control samples are prepared with each batch of samples (not to exceed 20 samples).

QC Check	Frequency	Acceptance Criteria	Corrective Action
Method blank	One per prep batch	< ½ RL or MDL, whichever is greater.	Correct problem, then re-prep and analyze MB and all samples processed with the contaminated blank unless the sample concentration is >10X blank, then report and qualify.
LCS, 2nd Source	One per batch	75-115% for water, 70-120% for soil	Re-prep and analyze the LCS and all samples in the affected analytical batch. If LCS is high and samples are ND, OK to report.
LCS Duplicate,2nd Source	One per batch	75-115% for water, 70-120% for soil	Re-prep and analyze the LCS and all samples in the affected analytical batch. If LCS is high and samples are ND, OK to report.
Surrogate, C_{35}	Every sample, spike, standard, and method blank.	See LIMS	Check system, re-inject, re-extract. If high, check/qualify. If low, re-prep.

- Method Blank: Use reagent water for water batches or Sodium sulfate for soil batches.
- A **Laboratory Control Sample (LCS, or Blank Spike, BS, in Element)** is analyzed with each batch.
  - The LCS spiking solution is prepared by adding 10 mL of the 5000 µg/mL second-source standard to 200 mL of a 1:1 mixture of Hexane and Acetone, for a 250 µg/mL concentration.
  - For water batches, a liter of reagent water is spiked with 2 mL of the 250 µg/mL spiking solution and extracted in the same way as the other samples.
  - For soil batches, 25 grams of Sodium sulfate is spiked with 2 mL of the 250 µg/mL spiking solution and extracted in the same way as the other soil samples.
- A **LCS Duplicate** is analyzed with each batch of 20 or fewer samples. One LCS is run at the beginning of the batch and the duplicate LCS at the end.
- **Surrogate Standard**: 1 mL of the intermediate surrogate standard is added to all QC samples and client samples prior to extraction LIMS.

9.2 Instrument QC

QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration, minimum 5 points	When CCV fails or major changes to the instrument	$r^2 \geq 0.990$ ($r \geq 0.995$)	Correct problem, then repeat initial calibration
ICV, 2nd Source	Immediately after every calibration.	80-120% recovery	Correct problem, then repeat initial calibration. Make a fresh standard and rerun. If it fails, correct the problem and rerun.
CCV, primary source	Before and after each group of 10 samples.	80-120% recovery	Correct problem, then repeat initial CCV (re-calibrate if necessary) and re-analyze all samples since last successful CCV.
CCB	After each CCV	< ½ RL	Correct problem.

- See Section 10 for calibration.
- **Initial Calibration Verification (ICV):** This second-source, mid-level standard is run immediately after calibration.

- Prepare by adding 25 µL second-source standard to 500 mL Methylene chloride (250 µg/mL).

- **Continuing Calibration Verification (CCV):** Verify the working calibration curve at the beginning of each working day, every 10 samples, and at the end of the sequence, by the injection of a CCV,
  - Prepare by adding 25 µL of 5000 µg/mL primary standard to 500 µL Methylene chloride (250 µg/mL).
- **Continuing Calibration Blank (CCB)**: Run a blank after each CCV.

10.0 Procedure

10.1 Sample Preparation: See SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

Matrix	Sample Size
Water	1000 mL
Soil	25 grams

10.2 Extraction::

10.2.1 Water Extraction: Separatory Funnel: Refer to Method 3510 / NV03-24 for the procedure which is equivalent to WI DRO. Sample extracts should have a final volume of 1 mL in Methylene chloride.

Note: During initial solvent extraction, add 100 g NaCl to separatory funnel and shake for two minutes.

10.2.2 Solvent Extraction for Soil/Sediment: This method is based on extracting the sediment/soil with solvent. And aliquot of the extract is concentrated and injected on the GC.

- Upon receipt by the laboratory, weigh the tared sample vial to determine the actual weight. **Use Table 1 to determine the volume of solvent to add, or if the sample must be flagged or rejected**. If the laboratory analyzes soil samples exceeding the weight maxima in Table 1, the samples must not be reported as WI DRO.

Table 1. Weight Maxima

Vial Size	Target Sample Weight	Actual Sample Weight	Minimum Volume of Solvent	Action
60 mL	25 g	< 25 g	25 mL	Adjust RL
		25-35 g	≥ 25-35 mL	Add Solvent
		> 35 g	For any amount	Reject*
120 mL	25 g or 50 g	< 25 g	25 mL	Adjust RL
		25-70 g	≥ 25-70 mL	Add Solvent
		> 70 g	For any amount	Reject*

*With client approval, results can be reported as TPH-8015 DRO.

Note: The laboratory uses standard rounding rules to determine compliance with the maximum weight requirement. Sample weights are rounded to the nearest whole number. This means that a sample weighing between 34.5 – 35.4 g is rounded to

35.0 g, and a sample weighing between 69.5 – 70.4 g is rounded to 70.0 g. There must be NO allowances given past these tolerances for WI DRO.

- If tolerances in the above table are exceeded, contact the project manager who must contact the client to see if they want results reported as TPH-8015. Add a comment to the case narrative.
- Add Methylene chloride to the sample in a 1:1 ratio (or greater) of mL solvent to grams of sample. Solvent can be injected through the septa, or the vial may be quickly opened to allow the appropriate volume of solvent to be poured in. **Solvent (Methylene chloride) must be added to the sample within 10 days of sample collection.**
- It is not necessary for the lab to complete the extraction at the time of the injection of the solvent (addition of Sodium sulfate, sonication, etc.) The date of solvent addition must be reported in lieu of the extraction date. Completion of the extraction (addition of Sodium sulfate, sonication, etc.) need not be done until the time of analysis. Analysis must take place within 47 days of collection.
- Add 25 g of dried Na_2SO_4 to sample preserved in the above sections.
- Hand shake sample in its vial vigorously for 2 minutes, or place on the shaker table for 2 minutes. **Sonicate for 20 minutes. Record.** If the sample is not well mixed, then stir the mixture with a steel spatula, shake for 2 minutes and re-sonicate.
- Allow sediment to settle until a layer of solvent is apparent.
- Decant the solvent into a 150 mL beaker.
- **Repeat the extraction once more and combine the extracts.**
- Add to Kuderna-Danish (K-D) evaporative concentrator. Rinse the beaker with small amount of Methylene chloride. Add these rinses to the K-D.
- Add a boiling chip to the K-D and attach a Snyder to the top. Pre-wet the column by adding about 1 mL of solvent to the top.

  Note: The concentration step is critical; losses can occur if care is not taken.

- Place the K-D in a heated water bath set at a temperature appropriate for the chosen solvent (75-90°C) so that the receiver tube is immersed in hot water and the entire lower rounded surface is bathed in steam. When the appropriate volume (about 10 mL) has been reached, remove the K-D from the bath and allow it to cool completely.
- After the K-D has cooled, rinse the Snyder column and middle flask with a small amount of Methylene chloride.
- Carefully concentrate the extract to 1.0 mL under a gentle stream of nitrogen. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher. Transfer to a Class A volumetric flask for the final extract volume determination.
- Record the preparation information for the extraction and concentration steps. The sample extract is ready for analysis.

10.3 Calibration: Refer to SOP Selection of Calibration Points / CA-T-P-002 and Calibration Curves (General) / CA-Q-S-005. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

10.3.1 DRO Calibration: Quantitation of DRO is performed by the external standard method. The concentration of Diesel Range Organics in the sample is determined from a summation of the total response within the range of the elution of n-Decane and n-

octacosane using the calibration curve. **No area may be subtracted from the DRO retention time window in calculating DRO results.**

10.3.2 Calibration standards: Prepare the Calibration standards at five or more concentration levels in Methylene chloride from the Diesel Component Stock Standard. One of the concentration levels must be at the laboratory reporting limit. The remaining concentration levels must be evenly distributed to define the linear working range of the GC.

Calibration Levels (µg/mL) Each Individual Component	Equivalent µg/mL Total C_{10}-C_{28} range
5	50
7.5	75
10	100
25	250
50	500
75	750
150	1500

Note: All concentrations are approximate. See the standard prep log for actual concentrations.

10.3.3 Inject each calibration standard. A constant volume of extract (I µL) is injected for both samples and standards. Tabulate the entire area (baseline to baseline) for the ten components against the concentration injected. Instructions on baseline to baseline integration can be found in Section 10.5. The results are used to prepare a calibration curve by linear regression. The curve must have a correlation coefficient (r^2) of at least 0.990 ($r \geq 0.995$).

10.3.4 Run an **Initial Calibration Verification (ICV)** standard immediately after calibration. Evaluate acceptability with the QC criteria.

10.3.5 Each working day, every 10 samples, and at the end of the sequence, inject a **Continuing Calibration Verification Standard (CCV)** and CCB to evaluate acceptability.

10.4 Gas Chromatography: See SOP Acceptable Manual Integration Practices / CA-Q-S-002.

10.5.1 Because the petroleum products are complex mixtures, definition of a retention time window and automated quantitative analysis with a chromatographic data system may not be readily feasible.

10.5.2 **Retention Time Window and Quantitation**

- The retention time window is defined as beginning approximately 0.1 minutes before the onset of the n-Decane peak and ending 0.1 minutes after the conclusion of the n-octacosane peak in the calibration run.
- Diesel Range Organics (DRO): Quantitation is based on a direct comparison of the total area within the retention time window to the total area of the Diesel Component Standard.
- The laboratory verifies the placement of the retention time window at the beginning of each day and whenever a new GC column is installed or when significant retention time shifts occur. This can be accomplished as part of the calibration check.

- Integration must be "baseline to baseline," defined here as a flat baseline drawn parallel to the x-axis of chromatographic graph that includes all responses within the retention time window. See Attachment 1. **The correct baseline placement is a horizontal line drawn through the lowest point in the chromatogram (before the end of the window). The lowest point may be within the window, outside the window (on the early end of the window), or before the solvent front.** Baseline to baseline integration does not include the solvent peak. Placement of the baseline is determined for each sample. Each injection is verified for correct integration and RT windows.

  Note: Due to the integration requirements of this method, all of the procedures required in SOP CP01-03 (Manual Integration Procedures) need not be followed. The reason for the integration must be noted using the integration codes in CP01-03.

10.5.3 If the chromatographic response for the analyte exceeds the upper calibration standard, dilute the extract and reanalyze.

10.6 Recommended Analysis Batch Sequence:

1	Initial calibration, if needed
2	ICV, second source, immediately after calibration
	Method Blank
3	LCS
4	Sample 1
5	Samples 2-10
6	CCV
7	CCB
8	Sample 11
9	LCS Duplicate
10	Samples 12-20
11	CCV
12	CCB

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\text{LCS \% Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 Coefficient of Determination **Correlation Coefficient**

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2} \qquad r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Calibration factor
x = Concentration

11.3 % Difference, % Drift

$$\% \text{ Difference} = \frac{(CF_v) - (\text{Avg. CF}) \times 100}{\text{Avg. CF}}$$

CF_v = CF from verification standard
Avg. CF = Average CF from Initial Calibration.

$$\% \text{ Drift} = \frac{\text{Result} - \text{True Value} \times 100}{\text{True Value}}$$

11.4 Sample Concentrations

11.4.1 Determine the concentration of the analyte in the sample. Using the external standard method and linear regression of calibration standards GS responses (*R*) against their known concentration (*C* in µg/mL), derive the following linear equation.

$$C = mR + b$$

Using the slope (m) and the intercept (b) from this equation, the concentration of the sample can be calculated:

Water samples $C_s = [(C)(V_e)(d)] / V_s$

Soil Samples $C_s = [(C)(V_e)(d)] / W$

C_s = Concentration of sample in mg/L for waters and mg/kg on a dry weight basis for soils
C = concentration in µg/mL from the instrument
V_e = total volume of sample extract (after concentration) in mL
V_s = volume of water sample in milliliters
d = dilution factor if extract was diluted, default = 1, dimensionless
W = total dry weight of soil sample in g

11.4.2 **Peak areas measured from blanks must not be subtracted from sample peak areas**. All blank concentrations (above ½ the RL) must be reported. Section 9 gives acceptance criteria for blanks. Blank concentrations up to and including the acceptance criteria must be reported. Blank concentrations exceeding the acceptance criteria require reanalysis.

11.4.3 Report the presence of significant peaks outside the chromatographic window. Significant peaks are peaks, which can be distinguished above the noise in a chromatogram. Any peak 3 times the standard deviation of the signal to noise ratio is statistically significant. To accommodate heavier oils and to insure that peaks outside the DRO window are not missed, run the chromatogram out 5 minutes past the last component in the DRO component standard. All peaks (and baseline rises) outside the window are to be reported. If area outside the window is detected it must not be quantitated as part of the DRO result. Report that peaks or baseline rises were detected outside the C_{28} window as a comment in Element.

11.4.4 All area detected in the DRO window must be reported as "DRO." Reporting "non-pattern match," "non-applicable," "non-petroleum," etc. is not acceptable.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability

The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements

Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required for each matrix analyzed.

12.4 Proficiency Testing Studies

The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Vials are taken to the waste disposal area and placed in the halogenated waste drum.

15.0 References / Cross References

15.1 Wisconsin Method of Determining Diesel Range Organics (DRO), WI DNR, September 1995.

15.2 TestAmerica Nashville's Quality Assurance Manual.

15.3 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.4 SOPs: Acceptable Manual Integration Practices / CA-Q-S-002, Selection of Calibration Points / CA-T-P-002, Calibration Curves (General) / CA-Q-S-005, 3510 / NV03-24, Waste

Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, MDL / NV08-202, Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214, Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

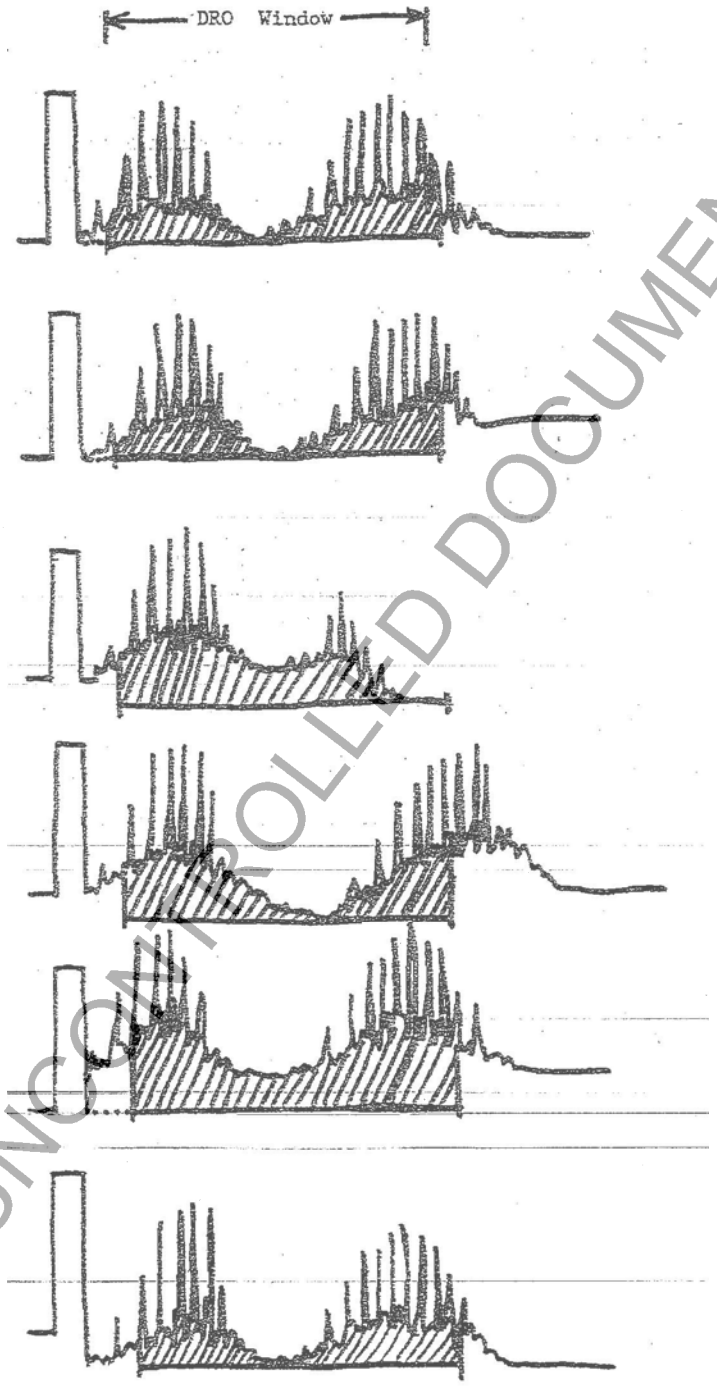
15.5 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

Item	Modification
1	Soil extraction extended to 10 days by WDNR

17.0 Attachments

Attachment 1. Integration Examples



18.0 Revision History

- Revision 5, dated 29 February 2008
  - Integration for TestAmerica and STL operations.
  - Change in concentrations of stock standard s and catalog numbers.
  - Change all references to solvent addition to soils within 72 hours to 10 days (Section 16).
- Revision 6, dated 31 July 2009
  - “ppm” changed to “µg/mL.”

  - Addition of corrective action details in Section 9.
  - Editorial improvements.
- Revision 7, dated 31 August 2011
  - Organizational changes.
  - Add instructions on reporting as WI DRO, rejecting the sample, or running/reporting as 8015.
  - Add QAF-45 and Section 14.2.
  - Allow the use of a shaker table in addition to hand shaking of the sample.
  - Insert reference to corporate SOPs Selection of Calibration Points / CA-T-P-002 and Calibration Curves (General) / CA-Q-S-005 and Nashville SOP Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214.
  - Emphasize the necessity of visual verification of each peak integration and RT window.
  - Change surrogate vendor catalog number and preparation.
- Revision 8, dated 31 July 2013
  - Organizational changes.
  - Specify that $r^2 \geq 0.990$.
  - Add Attachment 1.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure
(SOP) Change Form

SOP Number/Revision No.: **WI GRO / NV05-204.5a** Effective Date: **3/31/2014**

Last Mod. Date: **1/31/2014**

SOP Title: **Method WI GRO: Wisconsin DNR Modified GRO Method for Determining Gasoline Range Organics**

Affected SOP Section Number(s): Section 9.2, Instrument QC

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 05U

Revision Number with Mod ID: **5b**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

☐ Procedural Changes (Define Below) – Re-Training Required.

■ Other

2. Summary of Procedure Change: Add underlined text.

QC Check	Frequency	Acceptance Criteria	Corrective Action[1]
Continuing Calibration Blank	After each CCV	GRO < 50 µg/L for water, < 5.0 mg/kg for soil PVOC < 0.5 µg/L for water, < 0.025 mg/kg for soil	Correct problem, then re-prep and analyze blank and all samples processed with the contaminated blank.

3/21/14	Glen L. Norton 3/21/14
Department Supervisor Approval Date	Department Manager Approval Date
Steve Miller 3/25/14	Michael A. Brown 3/21/14
Quality Assurance Approval Date	Technical Director Approval Date

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure
(SOP) Change Form

SOP Number/Revision No.: **WI GRO / NV05-204.5** Effective Date: **1/31/2014**

Last Mod. Date: 7/31/2013

SOP Title: **Method WI GRO: Wisconsin DNR Modified GRO Method for Determining Gasoline Range Organics**

Affected SOP Section Number(s): Section 9.2, Instrument QC

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 05U

Revision Number with Mod ID: **5a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

☐ Procedural Changes (Define Below) – Re-Training Required.

■ Other

2. Summary of Procedure Change: Add underlined text; delete crossed-out text.

QC Check	Frequency	Acceptance Criteria	Corrective Action[1]
Initial calibration verification (ICV), must be from a 2nd source.	Once immediately following each initial calibration	GRO ≤ 20% of expected value, PVOC ≤ 15 ~~0.15~~%	When analyzed immediately after a calibration, correct problem then repeat initial calibration. When analyzed at the beginning of each working day, follow the corrective action criteria as outlined for the CCV.

1/20/14	1/20/14
Department Supervisor Approval Date	Department Manager Approval Date
1/30/14	1/17/14
Quality Assurance Approval Date	Technical Director Approval Date

Title: WISCONSIN DNR MODIFIED GRO METHOD FOR DETERMINING GASOLINE RANGE ORGANICS

Approvals (Signature/Date)			
	7/2/13		6/21/13
Daniel Otero Department Manager	Date	Glenn Norton Volatiles Operations Manager	Date
	7/2/13		6/27/13
Michael H. Dunn Technical Director Quality Assurance Manager	Date	Johnny Davis Health & Safety Manager / Coordinator	Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method is used to designed to measure the concentration of gasoline range organics in water, soil, and wastes. This corresponds to a hydrocarbon range of C_6 - C_{10}. As defined in the method, other organic compounds, including chlorinated solvents, ketones, ethers, mineral spirits, Stoddard solvents, and napthas are measurable.

1.2 Reporting Limits: The Limit of Quantitation (LOQ) of this method for gasoline range organics is nominally 10 mg/kg for soils and nominally 0.1 mg/L for water.

1.3 This method is based on a purge-and-trap, Gas Chromatography (GC) procedure. This method should be used by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use.

1.4 This method can be used to determine GRO and petroleum volatile organic compounds (PVOCs) concurrently.

1.5 PVOC is an acronym for petroleum volatile organic compounds. Analysis for PVOCs is required at some LUST sites in lieu of VOC analysis. The compounds included in the PVOC list are all of the compounds in the GRO component standard except naphthalene. GRO/PVOCs may be determined from a single analysis by placing a PID in series with the FID required for GRO analysis.

1.6 For PVOC compounds: For water samples, prepare per EPA SW-846 Methods 5030 / NV05-107 and 8021 / NV05-90. For soil samples, extract as prescribed and proceed with analysis procedures outlined in Methods 5035 / NV05-108 and 8021 / NV05-90.

1.7 Capillary columns are required.

1.8 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms. Each analyst demonstrates the ability to generate acceptable results with this method.

1.9 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 This method provides gas chromatographic conditions for the detection of volatile petroleum fractions such as gasoline, Stoddard solvent, or mineral spirits. Samples are analyzed utilizing purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID). Quantitation is based on FID detector response to a gasoline component standard.

2.2 This method is suitable for the analysis of waters, soils, or wastes. Water samples can be analyzed directly for gasoline range organics by purge-and-trap extraction and gas chromatography. Soil or waste samples are dispersed in Methanol to dissolve the volatile organic constituents. A portion of the Methanolic solution is then analyzed by purge-and-trap GC.

2.3 Soil core samples are collected in wide-mouth VOC vials and preserved with Methanol.

3.0 Definitions

3.1 Gasoline Range Organics (GRO): All the chromatographic response falling between the onset of the Methyl-tertiary-butyl ether peak and the conclusion of the Naphthalene peak. Quantitation is based on a direct comparison of the total area within this range to the total area of the Gasoline Component Standard.

3.2 Gasoline Component Standard: A 10-component blend of typical gasoline compounds (Table 4). This standard serves as a quantitation standard and is used to establish a retention time window for gasoline range organics.

3.3 Laboratory Control Spike - Water: A reagent water sample spiked with the Gasoline

Component Standard and run through the method with water samples.

3.4 Laboratory Control Spike - Soil: A reagent sand or clean soil sample spiked with the Gasoline Component Standard and run through the method with soil samples.

3.5 Method Blank - Water: A reagent water sample, processed as a sample, and run as a quality control check. If contamination is found it is the lab's responsibility to determine its origin.

3.6 Method Blank - Soil: A reagent sand extracted with the same volume of Methanol used in samples, processed as a sample, and run as a quality control check. If contamination is found it is the lab's responsibility to determine its origin.

3.7 Methanol Trip Blank: A reagent Methanol sample that accompanies samples in shipping and is transferred to a clean sample collection vial in the same manner as samples are preserved with Methanol. The transfer is made at some time during the sampling event and is used as a check on cross contamination of Methanol-preserved samples.

3.8 See TestAmerica Nashville's Quality Assurance Manual Appendix 5 for other laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 High levels of heavier petroleum products such as diesel fuel may contain some volatile components producing a response within the retention time range for GRO. Other organic compounds, including chlorinated solvents, ketones, and ethers are measurable. As defined in the method, the GRO results include these compounds. Spills of neat products should be quantified by specific analysis for the product in question. An example of a neat product would be a spill of (or storage tank containing) Benzene.

4.2 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage or by dissolution of volatiles into the Methanol for preservation. Trip blanks prepared from both reagent water and Methanol must be carried through sampling and subsequent storage and handling to serve as a check on such contamination.

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the purging device is rinsed between samples with reagent water. For volatile samples containing high concentrations of water-soluble materials, suspended solids, high boiling compounds or organohalides, it may be necessary to wash the purging device with a detergent solution, rinse with distilled water, and then dry in a oven at or above 105°C between analyses. The trap and other parts of the system are also subject to contamination, therefore, frequent bake-out and purging of the entire system is required. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank to check for cross-contamination. Contamination limits for blanks can be found in the QC section; if the blank is contaminated, re-run affected samples.

4.4 The retention time window definition (Methyl tertiary butyl ether to Naphthalene) introduces a negative bias of approximately 25%. This bias may be greater for weathered samples particularly, low level samples. Laboratories are required to report peaks detected outside the window so contamination outside the window is not missed. Use of a standardized window improves comparability between laboratory data. Note that gasoline blends often contain 10% ethanol which could be responsible for a portion of this negative bias.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This method may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health

practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- The gas chromatograph contains zones that have elevated temperatures. The injector and detector heating zones must be cooled to near room temperature prior to working on them.
- There are areas of high voltage in both the gas chromatograph Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.
- Kevlar gloves must be worn when handling VOA vials.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit[1]	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Instrumentation

- **Gas Chromatograph** – Analytical system (HP, Agilent, or equivalent) complete with gas chromatograph suitable for purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases and syringes. A data system (CHROM) capable of determining peak areas and integrating GRO as defined in the method is required.
  - Column: A 30 m x 0.53 mm DB-5, or equivalent, is used. The column must be capable of resolving typical gasoline components. It must also resolve Methyl tertiary butyl ether (MTBE) from the Methanol solvent front and Ethylbenzene from m/p-Xylene.
  - Detector: Flame ionization (FID), or FID in series with a Photoionization detector (PID) if GRO/PVOCs are being determined concurrently.
  - Purge-and-trap device (Tekmar, Encon, or equivalent) with autosampler (Arcon, Centurion, or equivalent). Several complete devices are commercially available.
    - The required purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. Purging volumes larger than 5 mL must not be used. The gaseous headspace between the water column and the top of the vessel should be at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column.
    - The recommended trap is the Carbopack C, 7 cm / Carbopack B, 7 cm (Supelco 20079-U). This trap is particularly good if problems are encountered with stability of

MTBE. Alternatively, a trap of 25 cm long with an inside diameter of at least 0.105 grade (Tenax GC or equivalent).

- Prior to initial use, the trap is conditioned per manufacturer's recommendations by backflushing with an inert gas flow of at least 20 mL/minute. The trap may be conditioned at temperatures above 180°C if it is recommended by the manufacturer. Prior to daily use, the trap is conditioned for 10 minutes at 180°C (or above) with backflushing. Traps other than the recommended should be desorbed according to the manufacturer's guidelines. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.
- The desorber should be capable of rapidly heating the trap to 180°C or greater for desorption.

Purge and Trap Operating Parameters

Purge gas	Nitrogen, 5-10 psig
Purge gas flow rate	40 ± 5 mL/minute
Purge time	11.0 + 0.01 minutes
Purge temperature	Ambient
Temperature program	40oC for 1 minute, then 12oC/minute to 100oC, then 40oC/minute to 240oC and hold for 5.0 minutes. Conditions may be altered to improve resolution of gasoline range organics.
Desorb temperature	180°C or manufacturer's recommendation
Backflush inert gas flow	20-60 mL/minute

- **Analytical balance:** A balance capable of accurately weighing 0.0001 g (must be used for standards). A top-loading balance capable of weighing to the nearest 0.1 g (should be used for sample analysis).
- **Ultrasonic bath.**

6.2 Supplies

- VOC Vials: Wide mouth 40 mL (1.4 oz.), 60 mL (2.0 oz.), or 120 mL (4.0 oz.) VOC vials with Teflon™/silicone septa or Teflon™ lined caps for soils and 40 mL (1.4 oz.) VOC vials with Teflon™/silicone septa for waters.
- Volumetric flasks: 10 mL, 50 mL, 100 mL, 500 mL, and 1,000 mL with a ground-glass stopper, Class A.
- Microsyringes, various.
- Disposable pipets: Pasteur.
- Spatula: Stainless steel.

7.0 Reagents and Standards

7.1 Reagent grade chemicals are used in all tests. Unless otherwise, indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 **Reagent water**, analyte-free.

7.3 **Methanol,** Purge-and-trap grade or equivalent. Store away from other solvents.

7.4 **GRO free sand**, Ottawa or sea sand or equivalent.

7.5 **Individual Component Stock Standards**: Volumetrically prepare stock standards for the gasoline components in Methanol at approximately 20 mg/mL (20,000 µg/mL).

1	Place about 8 mL of Methanol in a 10 mL tared, ground-glass, stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.
2	Using a 500 µL syringe, immediately add 200-300 µL of the gasoline component to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.
3	Dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in micrograms per microliter (µg/µL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.
4	Transfer the stock standard solution into a Teflon™-sealed screw-cap/crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.
5	Standards must be replaced after **six months** unless comparison with unexpired standards documents their accuracy

7.6 Gasoline Component Stock Standard: Commercially prepared gasoline component stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source. Gasoline Component Stock Standards can be prepared using individual component stock standard solutions. Prepare Gasoline Component Standard in Methanol, as needed: To a 100 mL volumetric flask containing 50 mL of Methanol, add 100 mg of each component for a 1000 µg/mL concentration of each target; bring to the final volume with Methanol.

Gasoline Component Standard and Concentrations

Component	Concentration, µg/mL
Methyl-t-butyl ether	1000
Benzene	1000
Toluene	1000
Ethylbenzene	1000
m-Xylene	1000
p-Xylene	1000
o-Xylene	1000
1,2,4-Trimethylbenzene	1000
1,3,5-Trimethylbenzene	1000
Naphthalene	1000
Total	10,000

Note: The concentration of the Gasoline Component Standard may be varied as long as the concentration of each component is the same. These standards must be stored with minimal headspace and must be checked frequently for signs of degradation or evaporation.

7.7 Also, see SOP Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214 for shelf-life and storage requirements for reagents and standards.

8.0 Sample Collection, Preservation, Shipment and Storage

Analysis Method	Sample Storage	Holding Times from Date and Time of Collection			
		MeOH Addition	Shipping	Extraction	Analysis
GRO/VOC/PVOC soils	VOC vial	Immediately	4 days	21 days	21 days
	Brass Tube	within 2 hours	4 days	21 days	21 days
	EnCoreTM	within 48 hours	40 hours	21 days	21 days
VOC/PVOC Confirmation soils	NA	NA	NA	NA	28 days
GRO/VOC/PVOC waters	VOC vial	NA	NA	14 days	14 days
GRO/VOC/PVOC carbonate aquifers	VOC vial	NA	2 days unless azide preserved	2 days unless azide preserved	14 days

Certified clean bottles are acceptable.

8.1 Aqueous samples are collected in triplicate (or the number of bottles directed by the laboratory) without agitation and without headspace in contaminant-free glass VOC vials with Teflon™-lined septa in the caps. The Teflon™ liner must contact the sample. Samples must be preserved with HCl at the time of collection, (acid must be added to the vial prior to adding the sample). Cool samples to 0-6°C immediately after collection. Samples from carbonate aquifers are extracted unpreserved within 48 hours of collection. Samples collected from carbonate aquifers must be flagged on the chain of custody. The pH of all water samples must be determined unless sample vials containing acid for field preservation were supplied by the lab. The pH measurement may be performed on left-over sample. If sample pH is greater than two, sample results must be flagged. Flagging is not required for carbonate aquifers samples extracted within 48 hours of collection.

8.2 Soil is collected using a 30 mL plastic syringe with the end sliced off, a brass tube, an EnCore™ sampler, VOA, or other appropriate devices. Samples cannot be analyzed if the amount of soil in the vial exceeds the weight maxima listed in the following table:

Weight Maxima Table

Vial Size	Target Sample Weight	Actual Sample Weight	Volume of Methanol	Action
40 mL (GRO only)	10 g	<8 g	10 mL	Flag
		8-11 g	10 mL	None
		>11 g<20 g	10 mL	Add Methanol
		>20 g	for any amount	Reject*
60 mL	10 g	<8 g	10 mL	Flag
		8-11 g	10 mL	None
		>11 g<35 g	10 mL	Add Methanol
	25 g	<20 g	25 mL	Flag
		20-26 g	25 mL	None
		>26 g<35 g	25 mL	Add Methanol
		>35 g	for any amount	Reject*
120 mL	10 g	<8 g	10 mL	Flag
		8-11 g	10 mL	None
		>11 g<70 g	10 mL	Add Methanol

Vial Size	Target Sample Weight	Actual Sample Weight	Volume of Methanol	Action
		<8 g	10 mL	Flag
	25 g	<20 g	25 mL	Flag
		20-26 g	25 mL	None
		>26 g<70 g	25 mL	Add Methanol
	50 g	<40 g	50 mL	Flag
		40-51 g	50 mL	None
		>51 g<70 g	50 mL	Add Methanol
		>70 g	for any amount	Reject*
Laboratories must use standard rounding rules to determine compliance with the maximum weight requirement. Sample weights are rounded to the nearest whole number. This means that a sample weighing between 34.5-35.4 is rounded to 35.0 g, and a sample weighing between 69.5-70.4 g is rounded to 70.0 g. There are NO allowances given past these tolerances.				

*With client approval, results can be reported as TPH-8015 GRO.

A sufficient number of vials (three recommended) should be collected to provide for backup analyses in the event of breakage and to allow for screening. One vial must be collected for dry weight determination (without Methanol). A Methanol trip blank must accompany each batch of samples (for each site and each day that samples are collected). See Sections 3.8 and 10.2 for further instructions on Methanol trip blanks. Ensure that the vial seals properly (no soil on the threads) which can be accomplished using a clean toothbrush or other utensil to sweep particles off the threads of the vial.

Methanol preservation is mandatory for the Modified GRO method and must be noted on the chain of custody. Sample collection time must be verifiable from the chain of custody. **Soil samples that arrive at the laboratory without Methanol and have not been stored properly must be rejected.** Flagging data for these samples is not acceptable. Results from soil samples not preserved in Methanol are rejected. If the laboratory analyzes soil samples not handled as indicated above, at the request of clients, the samples must not be reported as "WI GRO."

8.2.1 Collect and preserve soil samples by one of the following techniques. Methanol preservation techniques are found in Section 8.2.2.

8.2.1.1 Collect soil into tared VOC vials following the table above. Preserve immediately with Methanol. Store samples on ice or at 0-6°C. Note that any samples collected in this fashion which are not analyzed by a laboratory are considered hazardous waste. Vials should be shipped in an upright position. Vials can also be placed in separate "Ziplock" bags to avoid any problems that might occur if a vial leaks (such as the ink being removed from vial labels). Samplers should be aware that laboratories use a variety of vial taring methods so it is important to use only vials supplied by the laboratory performing the analysis.

8.2.1.2 Pack soil with no headspace into a brass tube. Cap the tube using plastic endcaps with Teflon™ sheets placed between the endcaps and the sample. Store samples on ice or at 0-6°C. **Preserve with Methanol within 2 hours of sample collection**. Immediately prior to Methanol preservation, the soil from the brass tube must be sub-sampled into a VOC vial following the above table. Sub-sampling involves removing one of the plastic endcaps, scrapping away the surface soil, and then scooping out, (with a spatula or other utensil), the appropriate weight of soil into the vial. Brass tubes must be cleaned appropriately prior to reuse.

8.2.1.3 Pack soil with no headspace into an EnCore™ sampler. Cap with the stainless

steel "o-ring" cap. Store samples on ice or at 0-6°C. **Preserve with Methanol within 48 hours of sample collection**. Note that this allows the possibility of having the laboratory preserve the sample. If you intend to have the laboratory preserve the sample, it must be received at the laboratory within 40 hours of sample collection. Soil stored in the EnCore™ sampler must be extruded from the device into a VOC vial immediately prior to Methanol preservation. The soil is extruded by using a pushrod supplied with the tool. Soil must not be scooped out of the sampler using a spatula, etc. EnCore™ samplers must be cleaned appropriately (following the manufacturer's recommendations) prior to reuse.

8.2.1.4 Alternate sample storage devices equivalent or superior in performance to the brass tube or the EnCore™ sampler may be used for sample storage prior to Methanol preservation. Alternate sample storage devices **must be approved** by the Department **prior to use**.

8.2.2 Methanol is added by one of the methods listed below. Vials must not be submitted to the laboratory for analysis of any volatile parameter (GRO, PVOC, VOC) if any of the Methanol has spilled in sampling. If the laboratory determines that a vial has leaked, by noting a visible reduction of volume, or an unusually low weight, this must be reported with analytical results. Only the vial that has leaked is in question, not the entire cooler or shipping package.

8.2.2.1 Samples collected directly into a VOC vial in the field can be placed into tared vials already containing the appropriate volume of Methanol (see Table 1). Samples stored in the brass tube, EnCore™ sampler, or an approved alternate storage device, can be added to tared vials already containing the appropriate volume of Methanol (see Table 1). Samples stored in the brass tube, EnCore™ sampler, or an approved alternate storage device, are preserved after screening of collected samples to determine which samples are laboratory-analyzed. Only those samples to be laboratory-analyzed should be Methanol-preserved. Store samples on ice or at 0-6°C.

8.2.2.2 Methanol can be added from pre-measured volumes provided by the laboratory or a commercial vendor. For samples collected directly into a VOC vial in the field or soils placed into a VOC vial after storage in an approved device, quickly open the soil vial and pour in the appropriate volume of Methanol, closing the sample vial immediately. Store samples on ice or at 0-6°C. Unused vials of Methanol may be used at other sites at the sampler's discretion. Professional judgment is used in determining how long vials with Methanol for preservation (or vials for trip blanks) can be stored. Labs may determine the shelf-life for these vials if they wish to offer an exact time period for storage to their clients.

8.2.2.3 Pre-measured volumes of Methanol can be added via syringe from a septa vial provided by the laboratory or a private vendor containing the appropriate volume or from bulk Methanol in the laboratory. For samples collected directly into a VOC vial in the field or soils placed into a VOC vial after storage in an approved device, draw the appropriate volume of Methanol into the syringe and add by puncturing the vial septa. Depending on the vial size and volume of Methanol added, venting of the vial may be necessary to facilitate adding the Methanol. If necessary, vent the vial by partially unscrewing the vial top. A fresh syringe needle is needed for each new vial to avoid cross contamination. Common laboratory glass syringes and non-coring type syringe needles are used. Store samples on ice or at 0-6°C.

8.2.2.4 Methanol can be added using a Teflon™ repeater pipet pump that attaches to a bottle of purge and trap grade Methanol and delivers the appropriate volume of Methanol. For samples collected directly into a VOC vial in the field or soils

placed into a VOC vial after storage in an approved device, quickly open the soil vial and depress the pipet pump to deliver the Methanol, closing the sample vial immediately. If this method is used it is important to make sure that purge-and-trap-grade Methanol be used. Store samples on ice or at 0-6°C. Note that the Methanol in the bottle can become contaminated if stored near any source of volatile fumes. Storage and use of this apparatus must be away from petroleum products and other volatile contaminants.

8.2.3 Shipping time must be minimized. Samples must be received by the lab within 4 days. Refer to Table 2 for soil sample holding times. Upon receipt by the laboratory weigh the tared sample vial to determine the actual weight. Use Table 1 to determine if the sample may be analyzed as is, requires addition of Methanol, flagging, or must be rejected. If the laboratory analyzes soil samples exceeding the weight maxima in Table 1, at the request of clients, the samples must not be reported as "WI GRO."

8.2.4 If tolerances in the above table are exceeded, contact the project manager who must contact the client to see if they want results reported as TPH-8015. Add a comment to the case narrative.

8.3 Sample temperature must be determined upon receipt to the lab. Sample temperature may be recorded as "received on ice" only if solid ice is present in the cooler at the time the samples are received. "Received on ice" means sample containers are surrounded by an ice slurry, or crushed, cubed or chipped ice at the time of receipt in the laboratory. It is acceptable to place the sample containers in plastic bags to preserve sample and label integrity. The use of bubble wrap or other insulating material is not allowed. Samples cooled during shipping with ice packs or "blue ice" may not be recorded as "received on ice." If samples are not "received on ice," temperature shall be determined from:

8.3.1 The temperature of an actual sample.

8.3.2 The temperature of a temperature blank shipped with samples.

8.3.3 The temperature of the melt water in the shipping container. When no ice is in the cooler, no temperature blank is provided, and there is not sufficient sample volume to sacrifice for a temperature measurement, the laboratory must flag the sample result and state the condition of sample upon receipt (i.e., not cooled during shipping, received at room temperature, etc.). **Note: If blue ice packs or similar methods are used, pre-cooling of samples to 0-6°C with ice or by refrigeration is required.**

9.0 Quality Control

Refer to the quality control section of TestAmerica Nashville's QA Manual for specific quality control (QC) procedures. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC: The following QC is run **every batch of no more than 20 samples:**

QC Check	Frequency	Acceptance Criteria	Corrective Action[1]
Method blank	Each batch	<50 µg/L for water, ≤ 5.0 mg/kg for soil	Re-prep and rerun all affected samples.
Duplicate LCS for all analytes must be from a 2nd source.	One at the beginning of the batch, one at the end of the batch.	80-120% recovery, RPD ≤20%.	Re-prep[2] and analyze the LCS and all samples in the affected analytical batch.
Surrogate	Every sample, spike, standard, and method blank	>80% recovery	Check system, re-inject, re-prep[2].

1 - All abnormalities must be noted in LIMS.
2 - If unable to re-prep the samples because of insufficient sample volume or holding time has expired, place a comment in LIMS.

- **To demonstrate the lack of laboratory contamination, run a**

- **Method Blank - Water**: Reagent water must be processed through the method in the same manner as water samples.
- **Method Blank - Soil**: Ottawa or sea sand must be processed through the method in the same manner as soil samples.

- **Duplicate Laboratory Control Spike - Water**: Two LCS-waters must be run with every batch of 20 water samples: one of the LCS-waters at the beginning of a batch of samples and the other at the end. One of the LCS - waters may qualify as a replacement for the CCS.
- **Duplicate Laboratory Control Spike - Soil**: Two LCS-soils must be run with every batch of 20 soil samples: one of the LCS-soils at the beginning of a batch of samples and the other at the end.

Note: Because it is not possible to perform the matrix spike/matrix spike duplicate required in Method 8021 for Methanol-preserved soil samples, laboratories should substitute in their place, the LCS-soil and LCS-soil-duplicate that are part of the required QC for the GRO method.

Note: If samples are reanalyzed in a subsequent "batch" because the original sample was not appropriately diluted, it is not necessary to rerun the LCS with the diluted sample. This allowance only applies if the LCS run with the sample initially was in control, and the same initial calibration curve is being used. All other QA requirements still apply.

- **Surrogates are mandatory for PVOC analysis.** The surrogate is chosen to avoid co-elution with sample contaminants. **A constant surrogate concentration, not to exceed 20 µg/L, must be maintained in all calibration standards, samples and blanks.** No more than one surrogate can be used to avoid co-elution interferences within the GRO window. Surrogates are added to samples and standards immediately prior to purging.

9.2 Instrument QC

QC Check	Frequency	Acceptance Criteria	Corrective Action[1]
Minimal five-point initial calibration for all target analytes	Initial calibration prior to sample analysis. Perform instrument re-calibration once per year minimum.	Linear regression correlation coefficient $r^2 \geq 0.990$, $r \geq 0.995$. RSD of CF ≤ 20%.	Correct problem then repeat initial calibration
Initial calibration verification (ICV), must be from a 2nd source.	Once immediately following each initial calibration	GRO ≤ 20% of expected value, PVOC ≤ 0.15%	When analyzed immediately after a calibration, correct problem then repeat initial calibration. When analyzed at the beginning of each working day, follow the corrective action criteria as outlined for the CCV.
Continuing Calibration Verification (CCV)	Before sample analysis, after every 10 samples, and at the end of the analysis sequence.	GRO ≤ 20% of expected value, PVOC ≤ 0.15% and within the RT Window.	Correct problem then repeat initial CCV (re-calibrate if necessary) and re-analyze all samples since last successful CCV.
Continuing Calibration Blank	After each CCV	<50 µg/L for water, ≤ 5.0 mg/kg for soil	Correct problem, then re-prep and analyze blank and all samples processed with the contaminated blank.
Retention time window calculated for each analyte.	System set-up, with each new column of major instrument maintenance. Update the mid-RTW at the start of the run or daily.	Each analyte of the LCS and CCV must be within the calculated RTW.	Correct the problem and re-process or re-analyze samples. If questions, see the supervisor of Technical Director.

1 – All abnormalities must be noted in LIMS.

- **Initial Calibration Verification (ICV and ICB):** For all determinations the laboratory analyzes the ICV and a calibration blank (ICB) immediately following initial calibration.
- **Continuing Calibration Verification (CCV and CCB), a**nalyzed at the beginning, middle, and end of the analytical sequence.
  - Analysis of the CCV solution must be within **± 20% for GRO, ± 15% for PVOC of calibration**. If the calibration cannot be verified within the specified limits, reanalyze either or both the CCV and the CCB. If the second analysis of the CCV or the CCB confirm calibration to be outside the limits, sample analysis must be discontinued, the cause determined, corrected and/or the instrument recalibrated. All samples following the last acceptable CCV must be reanalyzed. The analysis data of the CCB and CCV must be kept on file with the sample analyses data.
  - Prepare the ICV and CCV at a concentration near the mid-point of the calibration curve. Ensure that the ICV is from a different source than the calibration standards.
  - The CCB must not contain target analytes above the Method Blank. If not, repeat the analysis one more time. If the CCB is not less than the Method Blank, terminate the analysis, correct the problem, re-calibrate, and re-analyze the previous samples. If the CCB is less than 1/10 the concentration of the action level of interest, and no sample is within 10% of the action limit, analyses need not be rerun and recalibration need not be performed before continuation of the run.
- **Retention Time Window and Quantitation**
  - The retention time window is defined as beginning approximately 0.1 minutes before the onset of the Methyl tertiary butyl ether peak and ending 0.1 minutes after the conclusion of the Naphthalene peak in the calibration run.
  - Gasoline Range Organics (GRO): Quantitation is based on a direct comparison of the total area within the retention time window to the total area of the Gasoline Component Standard. Further instructions on quantitation can be found in Section 11. No area may be subtracted from the GRO retention time window in calculating GRO results.
  - The laboratory must verify the placement of the retention time window at the beginning of each day and whenever a new GC column is installed or when significant retention time shifts occur. This can be accomplished as part of the calibration check.
  - **Integration must be "baseline to baseline" as opposed to a "valley to valley."** Set integration/peak detect to: peak width 0.01 minute; detect=0, threshold=0. Baseline to baseline is defined here as a flat baseline drawn parallel to the x-axis of chromatographic graph that includes all responses, including “noise,” within the retention time window. The correct baseline placement would a horizontal line drawn through the lowest point in the chromatogram (before the end of the window). The lowest point may be within the window, outside the window (on the early end of the window), or before the solvent front. Baseline to baseline integration does not include the solvent peak. Chrom software is set up to perform the proper integration without analyst assistance. However, placement of the baseline is still to be evaluated for each sample in case manual integration of the baseline becomes necessary. Attachments 1 and 2 illustrate correct placement of the baseline for several chromatograms.

    Note: Due to the integration requirements of this method, all of the procedures required in SOP Acceptable Manual Integration Practices / CA-Q-S-002 need not be followed. The reason for the integration should be noted using the integration codes in the SOP.

10.0 Procedure

10.1 Sample Preparation: See SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

Matrix	Sample Size
Water	40 mL
Soil	8-70 grams

Volatile compounds are introduced into the gas chromatograph by purge-and-trap. Purge-and-trap is used directly on groundwater samples. Soils and solids are analyzed by Methanol extraction in the vial, followed by purge and trap. **Soil concentrations must be reported on a dry weight basis**.

10.2 Extraction of soil samples: This method is based on extracting the sediment/soil with Methanol. An aliquot of the extract is added to reagent water and purged at the conditions indicated in Section 6.1.

1	Hand shake sample in its vial vigorously for about 2 minutes. Sonicate for at least 20 minutes. Record the start and stop time.
2	Allow sediment to settle until a layer of Methanol is apparent.
3	Using a microliter syringe or pipet, withdraw an appropriate aliquot of the Methanol extract for sparging. A constant volume of Methanol must be purged for samples, standards and blanks. 1.0 mL of Methanol extract is diluted to a final volume of 50 mL with DI water. Enter in LIMS.
4	The Archon delivers a 5.0 mL aliquot to the sparge vessel for purging. Additional Methanol may be necessary to assure that a constant volume of Methanol is added to the reagent water for analysis. An appropriate dilution is one that keeps the response (both area and peak height) of major constituents in the upper half of the calibration range. If an initial dilution does not accomplish this then an intermediate dilution should be performed
5	If the responses exceed the calibration or linear range of the systems, use a smaller aliquot of Methanol extract or dilute aqueous sample.

10.3 Calibration: Refer to SOP Selection of Calibration Points / CA-T-P-002 and Calibration Curves (General) / CA-Q-S-005. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

1 Prepare the Gasoline Component Standard at a **minimum of five concentration levels**. One of the concentration levels must be at or below the LOQ. The remaining concentration levels must be evenly distributed to define the linear working range of the GC. NOTE: Additional low points may be necessary for the optional PID quantitation.

Working Standard Solution (100 µg/mL)		Concentration GRO (µg/mL)	PVOC (each) (µg/mL)
µL to 50 mL	µL to 100 mL		
0.25	0.5	0.005	0.0005
0.5	1.0	0.01	0.001
2.5	5.0	0.5	0.005
5.0	10	0.1	0.01
10	20	0.2	0.02
25	50	0.5	0.05
50	100	1.0	0.1
100	200	2.0	0.2

	200	400	4.0	0.4	
2	Transfer each standard to a VOA and place them in the autosampler.				
3	Transfer 5 mL of each calibration standard utilizing the purge-and-trap analysis. Tabulate the entire area (baseline to baseline) for the 10 components against the concentration injected. Instructions for performing baseline to baseline integration are found in Section 9.1. The results are used to prepare a calibration curve by linear regression. The curve must have a **correlation coefficient r^2 of at least 0.990 ($r \geq 0.995$)**.				
4	The MDL or Limit of Detection is confirmed by the running of the 0.0005 mg/L standard at the time of initial calibration. Targets must be detected.				
5	Run the Continuing Calibration Verification (CCV) in the beginning, middle, and end of the batch ± 15% for PVOC,± 20% for GRO..				
6	The Gasoline Component Standard is used to calibrate the PID for the optional concurrent determination of PVOCs. Remember, when calibrating, **a constant concentration of surrogate (not to exceed 20 µg/L) must be added to all samples and all calibration standards.** The response of the surrogate is included as part of the area used to generate the GRO calibration curve. Samples must be quantitated directly from the curve with no subtraction of surrogate response. **The inclusion of the surrogate within the calibration curve accounts for the surrogate added to the sample**. Surrogate recovery must be assessed from the PID.				
7	If performing PVOCs, additionally review SOP 8021 / NV05-90 for analysis procedures.				

10.4 **Sample Analysis:** See SOP Acceptable Manual Integration Practices / CA-Q-S-002.

1	Introduce the sample into the gas chromatograph using the purge-and-trap method (SOPs 5030 / NV05-107 for water, 5035 / NV05-108).
2	Adjust the purge gas flow rate (nitrogen) to 35-45 mL/minute.
3	Place the VOA in the autosampler and start the sequence.
4	If dilution is required, perform all steps without delay until the diluted sample is in a sealed VOA vial. Sample dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Dilutions may be made in Class A volumetric flasks (10 mL to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for highly concentrated samples.
5	Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this volume of reagent water to the flask.
6	Inject the proper aliquot of samples from the syringe as prepared in step 3 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask and invert three times. Repeat the above procedure for additional dilutions.
7	**Purge the sample for 11.0 ± 0.1 minutes.**
8	At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C and back-flushing the trap with inert gas between 15 and 20 mL/min for 4 minutes.
9	While the trap is desorbing into the gas chromatograph, empty the purging chamber. Wash the chamber with minimum of two 5 mL flushes of reagent water (or Methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.
10	After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. The trap temperature should be maintained at 180°C. Trap temperatures

	up to 220°C may be employed; however, the higher the temperature, the shorter the useful life of the trap. After approximately 7-10 minutes, turn off the trap heater and stop the gas flow through the trap. When cool, the trap is ready for the next sample.
11	If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has a saturated response from a compound, the laboratory must verify that carry-over did not occur. If carryover is found to have affected subsequent samples, the system must be decontaminated and the affected samples re-purged.

10.5 Recommended Analysis Batch Sequence*

1	Initial Calibration, if needed
2	ICV
3	Method Blank
4	LCS
5	Samples 1-10
6	CCV
7	CCB
8	Samples 11-20
9	LCSD

Methanol blanks should be run after soil samples suspected of being highly concentrated to prevent carryover.

10.6 Confirmation for Soil Samples

PVOC soil samples having concentrations for any compound between the LOD and the LOQ where the clean-up criteria are below the LOD must be qualitatively confirmed by an alternate method to avoid false positive results. Effectively, confirmation is required for soil PVOCs with a final reported concentration between 25 µg/kg and 60 µg/kg when the clean-up criteria is below the LOD or has not been established by Wisconsin (unless site specific criteria are available). See the examples of when confirmation is required:

Confirmation Example

Compound	WI Clean-up Criteria -NR 720 Table Values	Confirmation if results between:			
		Instrument raw value concentration		Equivalent calculated final report concentration	
Benzene	5.5 µg/kg	0.5 µg/L	1.2 µg/L	25 mg/kg	60 mg/kg
Ethylbenzene	2900 µg/kg	never	never	never	never
MTBE	ND	0.5 µg/L	1.2 µg/L	25 mg/kg	60 mg/kg
Toluene	1500 µg/kg	never	never	never	never
1,2,4-Trimethylbenzene	ND	0.5 µg/L	1.2 µg/L	25 mg/kg	60 mg/kg
1,3,5-Trimethylbenzene	ND	0.5 µg/L	1.2 µg/L	25 mg/kg	60 mg/kg
Xylenes, total	4100 µg/kg	never	never	never	never

Note that site specific clean-up criteria can be developed and would then supersede the table values. This table does not address compounds of interest other than the PVOCs.

Confirmation is defined as analysis of the sample by a second column of a different phase or

reanalysis using mass spectrometry (MS). Confirmation analyses must be performed with a methodology that has an LOD of 25 µg/kg or lower. Laboratories are not required to report compounds detected in the confirmation run that were not detected in the original run. Compounds that are not confirmed in the confirmation analysis will not result in additional clean-up at a site or hinder site closure.

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\% \text{ recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 Coefficient of Determination

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2}$$

Correlation Coefficient

$$r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response
x = Concentration

11.4 % Difference, % Drift

$$\% \text{ Difference} = \frac{(CF_v) - (\text{Avg. CF}) \times 100}{\text{Avg. CF}}$$

CF_v = CF from verification standard
Avg. CF = Average CF from Initial Calibration.

$$\% \text{ Drift} = \frac{\text{Result} - \text{True Value} \times 100}{\text{True Value}}$$

11.5 Final Concentration Calculation

From linear regression of calibration standard GC responses against their known concentrations (C in µg/L), derive the following linear equation:

$$C = mR + b$$

Using the slope (m) and the intercept (b) from this equation the concentration of the sample can be calculated from the following equations:

Water samples

$$C_s = (mR_s + b)(D)$$

Soil Samples

$C_s = [(mR_s + b)(D)(V_t)(K)]/[(V_p)(W)]$

C_s = Concentration of sample in µg/l for waters and mg/kg on a dry weight basis for soils
m = slope of the calibration curve
R_s = GC response of sample in the GRO retention time window
b = intercept of calibration curve
D = dilution factor if water sample or soil extract was diluted
V_p = volume of soil extract purged (units must be the same as those used for V_t)
V_t = total volume of soil extract
$K = 5 \times 10^{-6}$ l mg/µg (this constant adjusts for both conversion from µg/kg to mg/kg and for the dilution of the volume of extract purged up to the 5 mL used for purging)
W = total dry weight of soil sample in kg

- **Peak areas measured from blanks may not be subtracted from sample peak areas**. All blank concentrations (above the LOD) must be reported. Blank concentrations up to and including the acceptance criteria must be reported. Blank concentrations exceeding the acceptance criteria require reanalysis.
- **Report the presence of significant peaks outside the chromatographic window.** Significant peaks are peaks which can be distinguished above the noise in a chromatogram. Any peak 3 times the standard deviation of the signal to noise ratio is statistically significant. To insure that peaks outside the GRO window are not missed, run the chromatogram out 5 minutes past the last component in the GRO component standard. All peaks (and baseline rises) outside the window are to be reported. If area outside the window is detected it must not be quantitated as part of the GRO result. Laboratories may quantitate this area outside the window against the GRO standard and report a concentration detected outside the window or simply report that peaks or baseline rises were detected outside the window.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

Laboratories must achieve a **limit of detection (LOD) of 25 µg/kg or lower for soil PVOCs**. Lower detection limits are achievable for water samples. The Department uses 25 ug/kg as a reporting limit for soil PVOCs. A 25 µg/kg reporting limit means that laboratories need not report detection of PVOC compounds below 25 µg/kg (on a wet weight basis). The Department does not accept the use of reporting limits in lieu of actual LODs in other tests unless specified. The requirements for the LOD apply to all samples analyzed to meet the requirements of the NR 700 series. Sample results are not used to establish clean closure if the laboratory LOD for PVOCs is higher than 25 µg/kg for any reason.

If sample detection limits are elevated because of dilution (or other reasons) the Department considers the sample concentrations to be above levels acceptable for site closure. The LOD must not be adjusted for the dry weight of the sample; however, sample results must still be reported on a dry weight basis. The reported LOD must be adjusted if the volume of sample extract purged is less than the amount used to determine the LOD.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration. **For this method, a specific initial demonstration is required:**

- **The analyst must perform an initial DOC to generate acceptable accuracy and precision with the analytes in EPA Method 8021 with spike recoveries of 80-120% and a relative standard deviation <20%.**
- **Replicate Laboratory Control Spike - Water: Analysis of 5 replicates at a concentration of 100 µg/l. Recoveries must fall between 80%-120% of the known concentration and the RSD must be <20%.**
- **Replicate Laboratory Control Spike - Soil: Analysis of 5 replicates at a concentration of 10 mg/kg. Recoveries must fall between 75%-120% of the known concentration and the RSD must be <20%.**

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- VOA vials and instrument aqueous wastes are taken to the waste disposal area and neutralized prior to disposal.

15.0 References / Cross References

15.1 Modified GRO Method for Determining Gasoline Range Organics, Wisconsin, DNR, September 1995, PUBL-SW-140.

15.2 TestAmerica Nashville's Quality Assurance Manual.

15.3 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.4 SOPs: Acceptable Manual Integration Practices / CA-Q-S-002, Selection of Calibration Points / CA-T-P-002, Calibration Curves (General) / CA-Q-S-005, Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Determination of Method Detection Limits / NV08-202, Reagent and Standard Purchase / NV08-214, Sub-sampling & Compositing / NV08-229, 5030 / SA05-107, 5035 / SA05-108, 8021 / NV05-90.

15.5 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

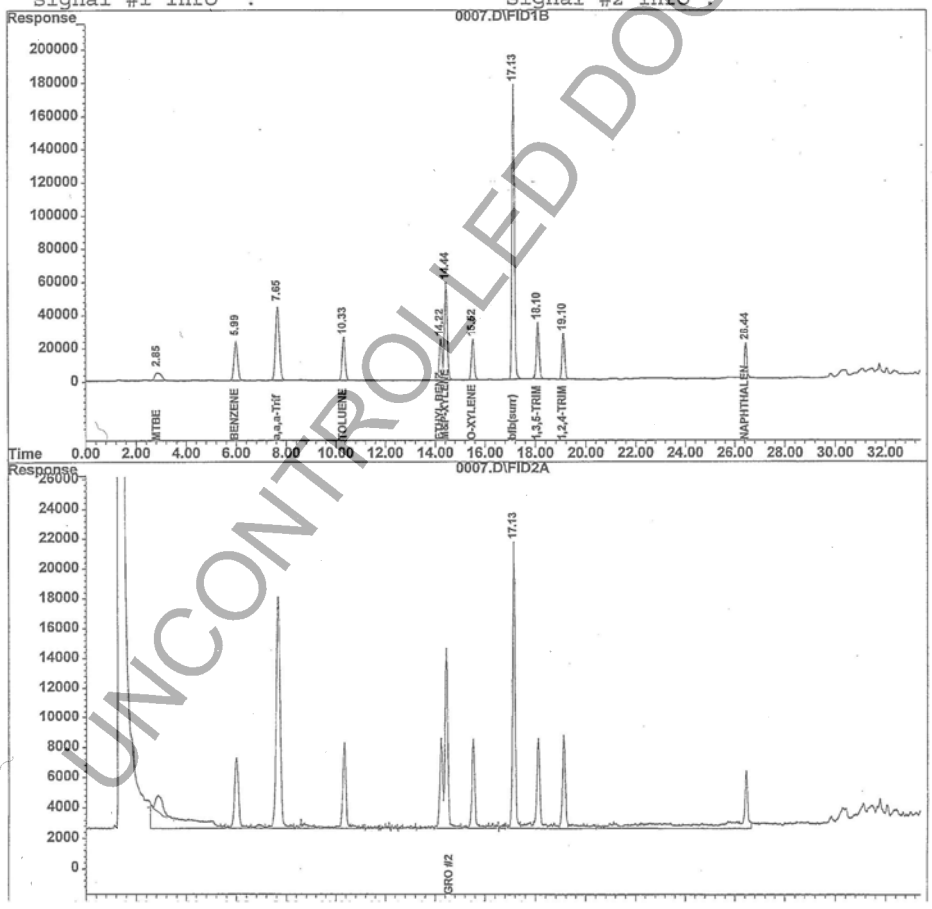
17.0 Attachments

Attachment 1. Quantitation Report Showing Integration Examples

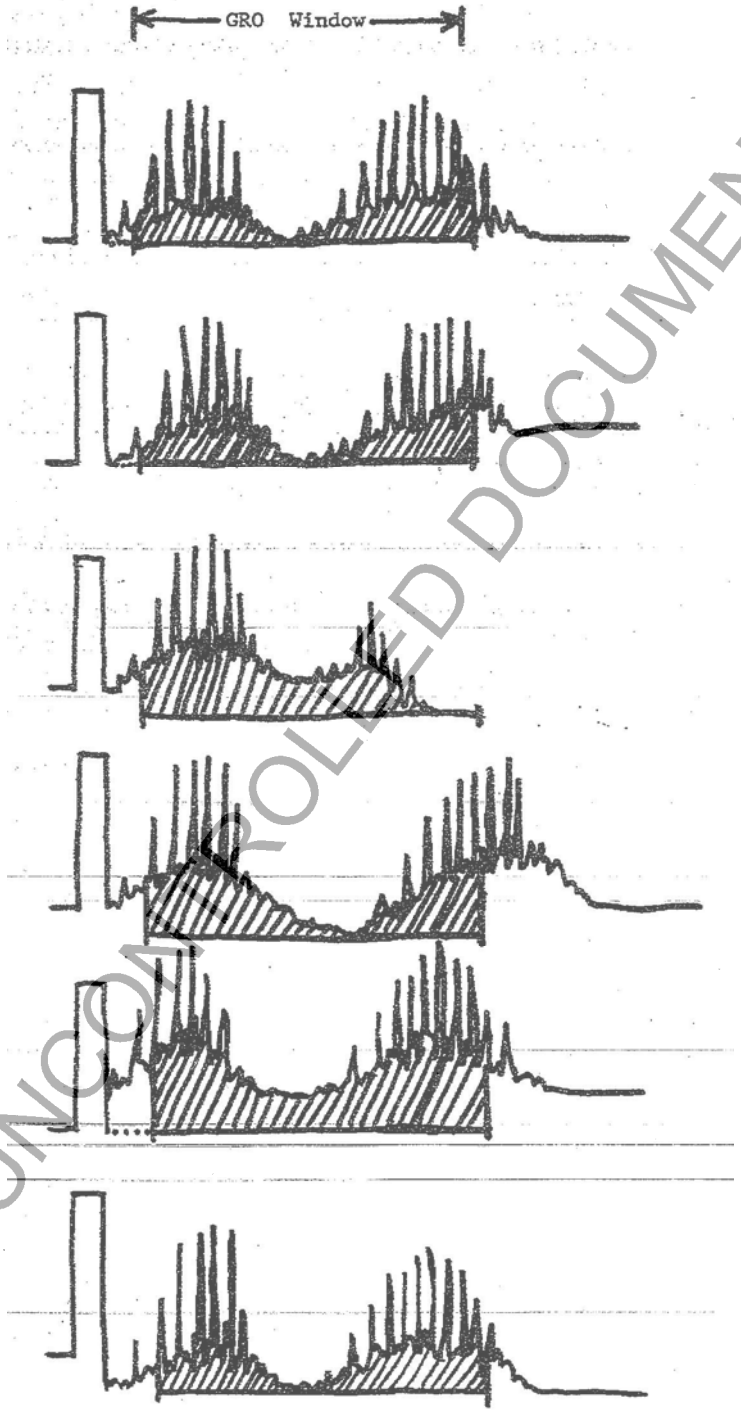
```
Signal #1 : C:\HPCHEM\1\DATA\012006\0007.D\FID1B.CH      Vial: 7
Signal #2 : C:\HPCHEM\1\DATA\012006\0007.D\FID2A.CH
Acq On    : 20 Jan 2006    5:16 pm                    Operator: EML
Sample    : 200/2.0                                   Inst    : HP2
Misc      :                                           Multiplr: 1.00
IntFile Signal #1: events.e      IntFile Signal #2: GRO.E
Quant Time: Jan 23  8:07 2006  Quant Results File: 121405MS.RES

Quant Method : C:\HPCHEM\1\DATA\METHODS\121405MS.M (Chemstation Integrato
Title        : PVOC-GRO hp2
Last Update  : Thu Dec 15 07:46:12 2005
Response via : Multiple Level Calibration
DataAcq Meth : PIDACQ.M

Volume Inj.     :
Signal #1 Phase :                    Signal #2 Phase:
Signal #1 Info  :                    Signal #2 Info :
```



Attachment 2: Integration Examples



18.0 Revision History

- Revision 2, dated 30 May 2008
  - Integration for TestAmerica and STL operations.
  - Addition of 0.4 mg/L PVOC standard (4.0 mg/L GRO standard).
- Revision 3, dated 30 December 2009

  - Addition of Minnesota RLV requirement.
  - Relocated Retention Time Window discussion to 9.1 from 9.2 and CCB to appear after CCV.
- Revision 4, dated 31 August 2011
  - Organizational changes.
  - Add QAF-45 and Section 14.2.
  - Add amendment 3a.
  - Insert reference to corporate SOP Calibration Curves (General) / CA-Q-S-005.
  - Emphasize the necessity of visual verification of each peak integration and RT window.
- Revision 5, dated 31 July 2013
  - Organizational changes.
  - Specify that $r^2 \geq 0.990$.
  - Update equipment section.
  - Remove the need for an internal standard and the reference to a MDLV. ICV does not need to be run daily at the beginning of the run.
  - Distinguish the difference in % recovery for QC parameters for GRO and PVOC and the frequency of the CCV.
  - Add Attachment 2.
  - Increase sample size for soil samples.

SOP Number/Revision No.: **8260 624 SM6200 B/ NV05-77.20** Effective Date: **8/31/2015**

Last Mod. Date: **6/30/15**

SOP Title: **Method 8260B, 624, SM6200 B: Volatile Organic compounds by Gas Chromatography / Mass Spectrometry (GC/MS)**

CONTROLLED DISTRIBUTION

ISSUED TO: \\TAFS\Lab\Nashville\Public\QA\SOPs, 05V

Revision Number with Mod ID: **20a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add highlighted text. Delete crossed-out text.

Section **9.2, Instrument QC**, CCV row:

QC Check	Frequency	Acceptance Criteria[1]	Corrective Action[2]
Continuing Calibration Verification (CCV)	Daily, before sample analysis and every 12 hours of analysis time.	8260B: CCCs: ≤20% difference (when using RFs) or drift (when using least squares regression). SPCCs: minimum RF. All other target compounds ≤ 50% ~~30%, except for specific compounds which may have a % difference ≤ 40%.~~ Surrogates ≤ 30%. *8260C: All targets of interest ≤ 20%. Up to 20% of targets may exceed this criterion. Common targets meet minimum RF.* 624: Use Q ranges in the 624 QC table. SM6200 B: 60-140% for gases; 70-130% for other analytes.	Correct problem then repeat CCV (re-calibrate if necessary) and re-analyze any samples processed with that CCV. If the CCV is high and the sample is ND, it is acceptable to report.[3]

Section **10.2, Initial Calibration**, step 2, add the following table after the Initial Calibration (5-point) table:

Soil (Methanol Extract) Initial Calibration Standards for High-concentration Soil				
µL Working Standard (100 µg/mL)	**Reagent Water (mL)**	**Methanol (µL)**	**Each 0.5 ug/L RL Target's Conc. (µg/L)**	**Each 0.1 mg/Kg RL Target's Conc. (mg/Kg)**
2	100	1998	2	0.1
5	100	1995	5	0.25
10	100	1990	10	0.5
50	100	1950	50	2.5
100	100	1900	100	5
200	100	1800	200	10
400	100	1600	400	20
µL C4-C12 Working Standard (5000 µg/mL)	**Reagent Water (mL)**	**Methanol (µL)**	**C4-C12 GRO Standard Conc. (µg/L)**	**C4-C12 GRO Conc. (mg/Kg)**
2	100	1998	100	5
4	100	1996	200	10
10	100	1990	500	25
20	100	1980	1000	50
40	100	1960	2000	100
80	100	1920	4000	200
160	100	1840	8000	400
µL C6-C10 Working Standard (5000 µg/mL)	**Reagent Water (mL)**	**Methanol (µL)**	**C6-C10 GRO Standard Conc. (µg/L)**	**C6-C10 GRO Conc. (mg/Kg)**
4	100	1996	400	20
10	100	1990	1000	50
20	100	1980	2000	100
50	100	1950	5000	250
100	100	1900	10000	500
150	100	1850	15000	750
200	100	1800	20000	1000

	8/31/15
	Organics Operations Approval Date
John Kelley 8/28/15	Michael A. Burns 8/28/15
Department Manager Approval Date	Technical Director Date

SOP Number/Revision No.: **8260 624 SM6200 B/ NV05-77.20a** Effective Date: 8/31/2015

Title: VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) SW-846 METHOD 8260B/C, EPA 624, and SM6200 B

Approvals (Signature/Date)			
Ryan Fitzwater	5/11/15 Date	Michael H. Dunn	5/10/15 Date
Health & Safety Manager / Coordinator		Technical Director	

TestAmerica Nashville is not certified to run 8260 SIM in South Carolina.

1.0 Scope and Application

1.1 Analyte, Matrices: This method is used to determine volatile organic compounds in a variety of matrices; it is applicable to nearly all types of samples, regardless of water content, i. e., ground and surface water, wastewater, leachates, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. In general, the methods are applicable as follows:

Method Reference	Appropriate Use
8260	GC/MS method for volatiles for groundwaters, leachates, and solids.
5030	Purge and trap technique for groundwaters, leachates and high concentration solids (RCRA). See 5030 602 624 / NV05-107
5035	Purge and trap technique for solids (RCRA). See 5035 / NV05-108.
624	Purge and trap technique and GC/MS for volatiles for wastewaters, surface waters (Clean Water Act). For this SOP, see 5030 602 624 / NV05-107 for the 624 purge and trap technique.
SM6200 B	Purge and trap technique and GC/MS for aqueous samples when requested by the client.

The following compounds can be determined by these methods:

CAS No. (a)	8260 Compounds	624 Compounds	SM6200 B Compounds
630-20-6	1,1,1,2-Tetrachloroethane[1, 2, 6, 7]	1,1,1,2-Tetrachloroethane[2]	1,1,1,2-Tetrachloroethane
71-55-6	1,1,1-Trichloroethane[1, 2, 5, 6]	1,1,1-Trichloroethane[1]	1,1,1-Trichloroethane
79-34-5	1,1,2,2-Tetrachloroethane[1, 2, 5, 6, 7]	1,1,2,2-Tetrachloroethane[1]	1,1,2,2-Tetrachloroethane
76-13-1	1,1,2-Trichloro-1,2,2-trifluoroethane[5,6,7]	1,1,2-Trichloro-1,2,2-trifluoroethane[2]	1,1,2-Trichloro-1,2,2-trifluoroethane
79-00-5	1,1,2-Trichloroethane[1, 2, 5, 6]	1,1,2-Trichloroethane[1]	1,1,2-Trichloroethane
75-34-3	1,1-Dichloroethane[1, 2, 5, 6, 7]	1,1-Dichloroethane[1]	1,1-Dichloroethane
75-35-4	1,1-Dichloroethene[1, 2, 5, 6, 7]	1,1-Dichloroethene[1]	1,1-Dichloroethene
563-58-6	1,1-Dichloropropene[1, 7]	1,1-Dichloropropene[2]	1,1-Dichloropropene
87-61-6	1,2,3-Trichlorobenzene[1]	1,2,3-Trichlorobenzene[2]	1,2,3-Trichlorobenzene
96-18-4	1,2,3-Trichloropropane[1, 2, 6, 7]	1,2,3-Trichloropropane[2]	1,2,3-Trichloropropane
526-73-8	1,2,3-Trimethylbenzene	1,2,3-Trimethylbenzene[2]	
120-82-1	1,2,4-Trichlorobenzene[1, 2, 5]	1,2,4-Trichlorobenzene[2]	1,2,4-Trichlorobenzene
95-63-6	1,2,4-Trimethylbenzene[1, 9]	1,2,4-Trimethylbenzene[2]	1,2,4-Trimethylbenzene
96-12-8	1,2-Dibromo-3-chloropropane[1, 2, 5, 7]	1,2-Dibromo-3-chloropropane[2]	1,2-Dibromo-3-chloropropane
95-50-1	1,2-Dichlorobenzene[1, 2, 5, 6, 7]	1,2-Dichlorobenzene[1]	1,2-Dichlorobenzene
107-06-2	1,2-Dichloroethane[1, 2, 5, 6, 7, 8]	1,2-Dichloroethane[1]	1,2-Dichloroethane
78-87-5	1,2-Dichloropropane[1, 2, 5, 6, 7]	1,2-Dichloropropane[1]	1,2-Dichloropropane
176-02-8	1,3,5-Trichlorobenzene[4]	1,3,5-Trichlorobenzene[2]	
108-67-8	1,3,5-Trimethylbenzene[1, 9]	1,3,5-Trimethylbenzene[2]	1,3,5-Trimethylbenzene

CAS No. (a)	8260 Compounds	624 Compounds	SM6200 B Compounds
541-73-1	1,3-Dichlorobenzene[1, 2, 5, 7]	1,3-Dichlorobenzene[1]	1,3-Dichlorobenzene
142-28-9	1,3-Dichloropropane[1, 7]	1,3-Dichloropropane[2]	1,3-Dichloropropane
106-46-7	1,4-Dichlorobenzene[1, 2, 5, 6, 7]	1,4-Dichlorobenzene[1]	1,4-Dichlorobenzene
123-91-1	1,4-Dioxane[2, 8]	1,4-Dioxane[2]	
590-20-7	2,2-Dichloropropane[1, 7]	2,2-Dichloropropane[2]	2,2-Dichloropropane
78-93-3	2-Butanone (MEK)[1, 2, 5, 6, 7, 8]	2-Butanone(Methyl ethyl ketone, MEK)[2]	
126-99-8	2-Chloro-1,3-butadiene (Chloroprene)[2, 7]	2-Chloro-1,3-butadiene (Chloroprene)[2]	
110-75-8	2-Chloroethyl vinylether[4]	2-Chloroethylvinyl ether[3]	
95-49-8	2-Chlorotoluene[1]	2-Chlorotoluene[2]	2-Chlorotoluene
591-78-6	2-Hexanone[1, 2, 5, 6, 7]	2-Hexanone[2]	
75-65-0	2-Methyl-2-propanol (tert-Butyl Alcohol)[3]	2-Methyl-2-propanol (tert-Butanol)[2]	
91-57-6	2-Methylnapthalene[4]	2-Methylnapthalene[2]	
79-46-9	2-Nitropropane[4]	2-Nitropropane[2]	
624-95-3	3,3-Dimethyl-1-butanol[3]		
107-05-1	3-Chloro-1-propene (Allyl chloride)[2,7]	3-Chloro-1-propene (Allyl chloride)[2]	
106-43-4	4-Chlorotoluene[1]	4-Chlorotoluene[2]	4-Chlorotoluene
99-87-6	4-Isopropyltoluene (p-Isopropyltoluene)[1, 9]	4-Isopropyltoluene (p-Isopropyltoluene)[2]	4-Isopropyltoluene (p-Isopropyltoluene)
108-10-1	4-Methyl-2-pentanone (MIBK)[1, 2, 5, 6, 7]	4-Methyl-2-pentanone (Methyl isobutyl ketone, MIBK)[2]	
67-64-1	Acetone[1, 2, 5, 6, 7]	Acetone[2]	
75-05-8	Acetonitrile[2, 7]	Acetonitrile[2]	
107-02-8	Acrolein (Propenal)[2, 7]	Acrolein (Propenal)[1, 4, 5]	
107-13-1	Acrylonitrile[2, 6, 7]	Acrylonitrile[1, 4]	
71-43-2	Benzene[1, 2, 5, 6, 7, 8, 9]	Benzene[1]	Benzene
100-44-7	Benzyl chloride[4]	Benzyl chloride[2]	
108-86-1	Bromobenzene[1]	Bromobenzene[2]	Bromobenzene
75-25-2	Bromoform[1, 2, 5, 6, 7]	Bromoform[1]	Bromoform
74-83-9	Bromomethane[1, 2, 5, 6, 7]	Bromomethane (Methyl bromide)[1]	Bromomethane (Methyl bromide)
106-99-0	Butadiene	Butadiene[2]	
STL00350	C4-C12		
80006-61-9	C6-C10		
75-15-0	Carbon disulfide[1, 2, 5, 6, 7, 8]	Carbon disulfide[2]	Carbon disulfide
56-23-5	Carbon tetrachloride[1, 2, 5, 6, 7]	Carbon tetrachloride[1]	Carbon tetrachloride
108-90-7	Chlorobenzene[1, 2, 5, 6, 7, 8]	Chlorobenzene[1]	Chlorobenzene
74-97-5	Chlorobromomethan[e1, 6, 7]	Chlorobromomethane[2]	Chlorobromomethane
124-48-1	Chlorodibromomethane[1, 2, 5, 6, 7]	Chlorodibromomethane[1]	Chlorodibromomethane

CAS No. (a)	8260 Compounds	624 Compounds	SM6200 B Compounds
75-00-3	Chloroethane[1, 2, 5, 6, 7]	Chloroethane[1]	Chloroethane
67-66-3	Chloroform[1, 2, 5, 6, 7, 8]	Chloroform[1]	Chloroform
74-87-3	Chloromethane[1, 2, 5, 6, 7]	Chloromethane (Methyl chloride)[1]	Chloromethane (Methyl chloride)
156-59-4	cis-1,2-Dichloroethene[1, 2, 5, 6, 7]	cis-1,2-Dichloroethene[1]	cis-1,2-Dichloroethen
10061-01-5	cis-1,3-Dichloropropene[1, 2, 5, 6, 7]	cis-1,3-Dichloropropene[1]	cis-1,3-Dichloropropene
110-82-7	Cyclohexane[4, 5]	Cyclohexane[2]	
108-94-1	Cyclohexanone[4]	Cyclohexanone[2]	
74-95-3	Dibromomethane[1, 2, 6, 7]	Dibromomethane[2]	Dibromomethane
75-27-4	Dichlorobromomethane[1,2, 6, 7]	Dichlorobromomethane[1]	Dichlorobromomethane
75-71-8	Dichlorodifluoromethane[1, 2, 5, 7]	Dichlorodifluoromethane[1]	Dichlorodifluoromethane
75-43-4	Dichlorofluoromethane[4]	Dichlorofluoromethane[2]	
64-17-5	Ethanol[3]	Ethanol[2]	Ethanol
141-78-6	Ethyl acetate[4]	Ethyl acetate[2]	
140-88-5	Ethyl acrylate	Ethyl acrylate[2]	
60-29-7	Ethyl ether (Diethyl ether)[4]	Ethyl ether (Diethyl ether)[2]	
97-63-2	Ethyl methacrylate[2, 7]	Ethyl methacrylate[2]	
100-41-4	Ethylbenzene[1, 2, 5, 6, 7, 8, 9]	Ethylbenzene[1]	Ethylbenzene
106-93-4	Ethylene dibromide (EDB, 1,2-Dibromoethane)[2]	Ethylene dibromide (EDB, 1,2-Dibromoethane)[2]	Ethylene dibromide (EDB, 1,2-Dibromoethane)
87-68-3	Hexachlorobutadiene[1, 2]	Hexachlorobutadiene[2]	Hexachlorobutadiene
110-54-3	Hexane[4]	Hexane[2]	Hexane
74-88-4	Iodomethane[2, 6, 7]	Iodomethane (Methyl iodide)[2]	
78-83-1	Isobutyl alcohol[2, 7]	Isobutyl alcohol (Isobutanol)[2]	
67-63-0	Isopropyl alcohol[4]	Isopropyl alcohol (Isopropanol)[2]	
180-20-3	Isopropyl ether (IPE, Di-isopropyl ether)[3]	Isopropyl ether (IPE, Di-isopropyl ether)[2]	Isopropyl ether (IPE, Di-isopropyl ether)
98-82-8	Isopropylbenzene (Cumene)[1, 5, 9]	Isopropybenzene (Cumene)[2]	Isopropybenzene (Cumene)
126-98-7	Methacrylonitrile[2, 7]	Methacrylonitrile[2]	
79-20-9	Methyl acetate[5]	Methyl acetate[2]	
80-62-6	Methyl methacrylate[2, 7]	Methyl methacrylate[2]	
1634-04-4	Methyl-t-butyl ether[1, 3, 4, 5, 9]	Methyl-tert-butyl ether (MTBE)[2]	Methyl-tert-butyl ether (MTBE)
108-87-2	Methylcyclohexane[5]	Methylcyclohexane	
75-09-2	Methylene chloride[1, 2, 5, 6, 7]	Methylene chloride[1]	Methylene chloride
108-38-3	m-Xylene[9]	m,p-Xylene[2]	m,p-Xylene
91-20-3	Naphthalene[1, 2, 9]	Naphthalene[2]	Naphthalene
71-36-3	n-Butanol (n-Butyl Alcohol)[4]	n-Butanol (n-Butyl alco-	

CAS No. (a)	8260 Compounds	624 Compounds	SM6200 B Compounds
		hol)[2]	
123-86-4	n-Butyl acetate[4]	n-Butyl acetate[2]	
104-51-8	n-Butylbenzene[1, 9]	n-Butylbenzene[2]	n-Butylbenzene
142-82-5	n-Heptane[4]	n-Heptane[2]	
103-65-1	n-Propylbenzene[1, 9]	n-Propylbenzene	n-Propylbenzene
95-47-6	o-Xylene [9]	o-Xylene[2]	o-Xylene
76-01-7	Pentachloroethane	Pentachloroethane[2]	
107-12-0	Propionitrile[2, 7]	Propionitrile[2]	
135-98-8	sec-Butylbenzene[1, 9]	sec-Butylbenzene[2]	Sec-Butylbenzene
100-42-5	Styrene[1, 2, 5, 6, 7]	Styrene[2]	Styrene
75-85-4	tert-Amyl-alcohol (TAA)[3]		
994-05-8	tert-Amyl-methyl-ether (TAME)[3]	tert-Amyl methyl ether (TAME)[2]	
637-92-3	tert-Butyl ethyl ether (Ethyl-tert-butyl-ether, ETBE)[3]	tert-Butyl ethyl ether (ETBE)[2]	
762-75-4	tert-Butyl formate (TBF)[3]		
98-06-6	tert-Butylbenzene[1, 9]	tert- Butylbenzene[2]	Tert-Butylbenzene
127-18-4	Tetrachloroethene[1, 2, 5, 6, 7]	Tetrachloroethene[1]	Tetrachloroethene
109-99-9	Tetrahydrofuran[4]	Tetrahydrofuran[2]	
108-88-3	Toluene[1, 2, 5, 6, 7, 8, 9]	Toluene[1]	Toluene
156-60-5	trans-1,2-Dichloroethene[1, 2, 5, 6, 7]	trans-1,2-Dichloroethene[1]	trans-1,2-Dichloroethene
10061-02-6	trans-1,3-Dichloropropene[1, 2, 5, 6, 7]	trans-1,3-Dichloropropene1	trans-1,3-Dichloropropene
110-57-6	trans-1,4-Dichloro-2-butene[2, 6, 7]	trans-1,4-Dichloro-2-butene[2]	
79-01-6	Trichloroethene[1, 2, 5, 6]	Trichloroethene[1]	Trichloroethene
75-69-4	Trichlorofluoromethane[1, 2, 5, 6, 7]	Trichlorofluoromethane[1]	Trichlorofluoromethane
108-05-4	Vinyl acetate[2, 6, 7]	Vinyl acetate[2]	
75-01-4	Vinyl chloride[1, 2, 5, 6, 7]	Vinyl chloride[1]	Vinyl chloride
1330-20-7	Xylene (total)[1, 2, .5, 6, 7, 8, 9]	Xylene (total)[1]	
[1] - Laboratory normal 8260 compound		[1] Normal laboratory 624 compounds, cis-1,2-Dichloroethene and trans-1,2-Dichloroethene, may be reported as total 1,2-Dichloroethene.	
[2] - Appendix IX compound		[2] Additional compounds by request only.	
[3] - Oxygenate		[3]Degrade in acid-preserved sample; re-quires a non-preserved vial.	
[4] - Additional compounds by request only		[4]Estimated unless pre-served at pH 4-5.	

CAS No. (a)	8260 Compounds	624 Compounds	SM6200 B Compounds
[5] TCL list (OLM 04.2 list)		[5]If unpreserved, analysis must occur in 3 days. See Section 8.	
[6] - Appendix I compound			
[7] -Appendix II compound			
[8] - Skinner list			
[9] - NY Stars List			
a = Chemical Abstract Service Registry Number			

1.2 Method 624 may be extended to screen samples for Acrolein and Acrylonitrile. All Arizona samples analyzed for these two analytes by 624 must be qualified with a T15 qualifier which states that the method used is for screening purposes only, and the result reported for the analyte is an estimate.

1.3 Reporting Limits (RLs): The RL for an individual compound is dependent on the choice of sample preparation/introduction method. The RL concentration is defined by the lowest non-zero standard in the calibration curve. Using standard quadrapole instrumentation and the purge-and-trap technique, RLs, (though highly matrix-dependent) are provided in the table below for guidance (and may not be achievable). RLs listed for soil are based on wet weight. When reported on a dry weight basis, RLs are generally higher, based on the percent dry weight in each sample. For the most current RL, refer to LIMS.

Nominal Reporting Limits

Compound	Water (µg/L)	Soil Wet Weight (µg/kg)
1,1,1,2-Tetrachloroethane	0.5 - 1	2
1,1,1-Trichloroethane	0.5 - 1	2
1,1,2,2-Tetrachloroethane	0.5 - 1	2
1,1,2-Trichloro-1,2,2-trifluoroethane	0.5 - 1	2
1,1,2-Trichloroethane	0.5 - 1	5
1,1-Dichloroethane	0.5 - 1	2
1,1-Dichloroethene	0.5 - 1	2
1,1-Dichloropropene	0.5 - 1	2
1,2,3-Trichlorobenzene	0.5 - 1	2
1,2,3-Trichloropropane	0.5 - 1	2
1,2,3-Trimethylbenzene	0.5 - 1	2
1,2,4-Trichlorobenzene	0.5 - 1	2
1,2,4-Trimethylbenzene	0.5 - 1	2
1,2-Dibromo-3-chloropropane	5 - 10	5
1,2-Dichlorobenzene	0.5 - 1	2
1,2-Dichloroethane	0.5 - 1	2
1,2-Dichloropropane	0.5 - 1	2
1,3,5-Trichlorobenzene	0.5 - 1	2

Compound	Water (µg/L)	Soil Wet Weight (µg/kg)
1,3,5-Trimethylbenzene	0.5 - 1	2
1,3-Dichlorobenzene	0.5 - 1	2
1,3-Dichloropropane	0.5 - 1	2
1,4-Dichlorobenzene	0.5 - 1	2
1,4-Dioxane	200	200
2,2-Dichloropropane	0.5 - 1	2
2-Butanone	50	50
2-Chloro-1,3-butadiene (Chloropropene)	5	5
2-Chloroethylvinyl ether	0.5 - 10	20
2-Chlorotoluene	0.5 - 1	2
2-Hexanone	5	50
2-Methyl-2-propanol	0.5 - 10	50
2-Methylnaphthalene	5 - 10	5
2-Nitropropane	5	10
3,3-Dimethyl-1-butanol	0.5 - 10	NA
4-Chlorotoluene	0.5 - 1	2
4-Isopropyltoluene (p-Isopropyltoluene)	0.5 - 1	2
4-Methyl-2-pentanone	5	50
Acetone	5	50
Acetonitrile	20	20
Acrolein	50	20
Acrylonitrile	0.5 - 10	10
Allyl chloride (3-Chloro-1-propene)	2	10
Benzene	0.5 - 1	2
Benzyl chloride	5 - 10	20
Bromobenzene	0.5 - 1	2
Bromoform	0.5 - 1	2
Bromomethane	0.5 - 1	2
Butadiene	0.5 - 1	2
Carbon disulfide	0.5 - 1	2
Carbon tetrachloride	0.5 - 1	2
Chlorobenzene	0.5 - 1	2
Chlorobromomethane	0.5 - 1	2
Chlorodibromomethane	0.5 - 1	2
Chloroethane	0.5 - 1	2
Chloroform	0.5 - 1	2
Chloromethane	0.5 - 1	2
cis-1,2-Dichloroethene	0.5 - 1	2
cis-1,3-Dichloropropene	0.5 - 1	2
Cyclohexane	1 - 5	10
Cyclohexanone	50	50

Compound	Water (µg/L)	Soil Wet Weight (µg/kg)
Dibromomethane	0.5 - 1	2
Dichlorobromomethane	0.5 - 1	2
Dichlorodifluoromethane	0.5 - 1	2
Dichlorofluoromethane	0.5 - 1	2
Ethanol	0.5 - 100	200
Ethyl acetate	5	50
Ethyl acrylate	5	10
Ethyl ether (Diethyl ether)	5	10
Ethyl methacrylate	0.5 - 10	10
Ethylbenzene	0.5 - 1	2
Ethylene dibromide (EDB, 1,2-Dibromoethane)	0.5 - 1	2
Hexachlorobutadiene	0.5 - 1	2
Hexane	0.5 - 2	10
Iodomethane	0.5 - 10	20
Isobutyl alcohol	50	100
Isopropyl alcohol	50	50
Isopropyl ether (IPE, Di-isopropyl ether)	0.5 - 2	2
Isopropylbenzene (Cumene)	0.5 - 1	2
m & p-Xylene	0.5 - 1	2
Methacrylonitrile	20	50
Methyl acetate	0.5 - 10	10
Methyl methacrylate	5	10
Methylcyclohexane	0.5 - 5	10
Methylene chloride	5	10
MTBE	0.5 - 1	2
Naphthalene	5	5
n-Butanol	20 - 100	100
n-Butyl acetate	0.5 - 10	40
n-Butylbenzene	0.5 - 1	2
n-Heptane	2	4
n-Propylbenzene	0.5 - 1	2
o-Xylene	0.5 - 1	2
Pentachloroethane	5	10
Propionitrile	0.5 - 10	50
sec-Butylbenzene	0.5 - 1	2
Styrene	0.5 - 1	2
tert-Amyl-alcohol (TAA)[3]	20	20
tert-Amyl-methyl-ether (TAME)	0.5 - 1	2
tert-Butyl ethyl ether (Ethyl-tert-butyl-ether, ETBE)	0.5 - 1	5
tert-Butylbenzene	0.5 - 1	2
tert-Butyl-formate (TBF)	20	20

Compound	Water (µg/L)	Soil Wet Weight (µg/kg)
Tetrachloroethene	0.5 - 1	2
Tetrahydrofuran	5	20
Toluene	0.5 - 1	2
trans-1,2-Dichloroethene	0.5 - 1	2
trans-1,3-Dichloropropene	0.5 - 1	2
trans-1,4-Dichloro-2-butene	5	10
Trichloroethene	0.5 - 1	2
Trichlorofluoromethane	0.5 - 1	2
Vinyl acetate	0.5 - 1	20
Vinyl chloride	0.5 - 1	2

1.4 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method. The analytes are introduced directly to a capillary column for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) directly interfaced to the gas chromatograph (GC).

2.2 Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major ion relative to an internal standard using at least a five-point calibration curve.

3.0 Definitions

3.1 **Q-value:** Tentatively Identified Compound (TIC) quality value of spectra match to library spectra expressed as a percent.

3.2 See TestAmerica Nashville's Quality Assurance Manual for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components are avoided, since such materials out-gas organic compounds which are concentrated in the trap during the purge operation. Analyses of blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, perform maintenance. **Subtracting blank values from sample results is not permitted**.

4.2 Contamination may occur when a sample or control containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. A technique to prevent this problem is to rinse the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. Common carryover targets are evaluated: 1,2,3-Trichlorobenzene, 1,2,4-Trichlorobenzene, 1-Methylnaphthalene, 2-Methylnaphthalene, and Hexachlorobutadiene.

Reanalyze any suspect samples. To reduce carryover, rinse the purging device and sample syringe with reagent water between samples. Follow the analysis of an unusually high concentration sample with a rinse blank to check for carryover contamination.

4.3 Special precautions are taken to analyze for Methylene chloride. The analytical and sample storage areas are isolated from all atmospheric sources of Methylene chloride. Otherwise, random background levels result. Since Methylene chloride permeates through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing is constructed from stainless steel or copper tubing.

4.4 Samples can be contaminated by diffusion of volatile organics (particularly Methylene chloride and Fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage. A trip blank, prepared from organic-free reagent water and carried through the sampling, handling, and storage, serve as a check on such contamination.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and should cool them to room temperature prior to working on them.
- The mass spectrometer is under vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.
- There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.
- Kevlar gloves **must be** worn when opening and closing VOA vials.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Sodium bi-sulfate	Irritant	None	Causes mild to severe irritation to the eyes. Prolonged exposure causes burn if not flushed with water. Causes mild irritation to skin. Prolonged exposure causes burn if not flushed with water.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Hydrochloric acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors causes coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and cause damage to the eyes. Contact causes severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Purge-and-trap device for aqueous samples or Methanol extract from bulk soil samples at ambient temperature, described in Method 5030 602 624 SM6200 B/ NV05-107.
- Purge-and-trap device for solid samples at 40°C, described in Method 5035 / NV05-108.
- The trap is VOCARB 3000 – 10.0-cm Carbopack™ B/6.0-cm Carboxin™ 1000/1.0-cm Carboxin 1001. The amount of thermal decomposition products formed must be routinely tracked by daily monitoring of the formation of Chloromethane and Bromomethane.
- Gas chromatography/mass spectrometer/data system
  - Gas chromatograph (HP): Analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection with appropriate interface for sample introduction device. The system includes all required accessories, including syringes, analytical columns, and gases.

Injector temperature:	250°C
MS interface temperature:	260°C
Carrier gas (He) flow rate:	Constant flow of 1.0 mL/minute.
Initial temperature:	45°C hold for 6 minutes.
Temperature program:	13°C/minute to 150°C; 18°C/minute to 220°C
Final temperature:	220°C, hold until all expected compounds have eluted (2 minutes)
Split ratio (min.)	1:10

May vary by instrument; see maintenance log for current program.

- The capillary column is directly coupled to the source.
- Gas chromatographic column: DB-624, 20 m x 0.18 mm with 1.0 µm film thickness, or equivalent.
- Mass spectrometer: Capable of scanning from 35 to 300 amu every 1 second or less using 70 volts (nominal) electron energy in the electron impact ionization mode. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.
- Data system (HP ChemStation with Enviroquant and CHROM): A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer has software that allows searching the GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software is used that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library is also available.

6.2 Supplies

- Microsyringes, 10, 25, 100, 250, 500, and 1,000 µL.
- Syringes, 5, 10, or 25 mL.
- Balance, analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.
- Glass scintillation vials, 20 mL, with PTFE-lined screw-caps or glass culture tubes with PTFE-lined screw-caps.
- Disposable pipets, Pasteur.
- Volumetric flasks, Class A, 10 mL, 50 mL and 100 mL, with ground-glass stoppers.
- Spatula, stainless steel, or wooden tongue depressor.
- Helium for carrier gas.
- Nitrogen for purge-and-trap gas.
- Narrow-range pH paper.
- Residual chlorine test strips.
- Sea or Ottawa sand for blank and LCS soil matrix.

7.0 Reagents and Standards

7.1 Reagent grade chemicals are generally used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. See the QA Manual and SOP Reagent and Standard Purchase / NV08-214 for more information on reagent chemicals, such as shelf-life and storage.

7.2 **Reagent water**, analyte-free.

7.3 **Methanol**, CH_3OH: Purge-and-trap grade or equivalent, demonstrated to be free of analytes at the MDL. Store apart from other solvents.

7.4 **Hydrochloric acid** (1:1 v/v), HCl: Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water. Commercially preserved sample containers are acceptable.

7.5 **Stock solutions:** Stock solutions are prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in Methanol, using assayed liquids. Any specific standards or procedure for making standards mentioned in this SOP may be substituted with equivalent standards or procedures. See LIMS for specific standard information.

7.5.1 **Primary Standards**

		For Working Standard		
Name of standard	**Vendor[2]/Conc (µg/mL)**	**Volume used (mL)**	**Final Volume (mL)**	**Conc. (µg/mL)**
Full List Non-gas Standard				
Custom 8260 VOC mega-mix[1] without gases	Restek 567641/2000, 4000, 10000,-20000, 40000	2.5	50	100 – 2000
Ketones	Restek 567642/10000	2.5	50	500
Acrolein	Restek 567644 /5000	2.5	50	250
Cyclohexanone	567648/20000	2.5	50	1000
Vinyl acetate	Restek 567646/4000	2.5	50	200
2-Chloroethyl vinyl ether	Restek 567643 /2000	2.5	50	100
List 2: Pentachloroethane, 2-Methylnaphthalene	Restek 567719 / 2000	2.5	50	100
1-Methylnaphthalene	Restek 31283/1000	0.1	2	50
2014 additions	Restek 568722 / 2000,4000,20000,50000	2.5	50	100
Polar additions	Restek 568723 /	2.5	50	100

		For Working Standard		
Name of standard	**Vendor[2]/Conc (µg/mL)**	**Volume used (mL)**	**Final Volume (mL)**	**Conc. (µg/mL)**
	2000,20000,100000			
Full List Gas Standard				
Gas Mix	Restek 567645/2000	1.0	20	100
Short List				
Short List Mix	Ultra CUS-7011/100-1000	5	10	50-500
3,3-Dimethyl-1-butanol	Restek 563892/20000	0.25	10	500
1 Custom 8260 VOC mix has variable concentrations. See the standard log for exact compound concentrations. 2 The vendors/catalog numbers are recommended; equivalent products are acceptable.				

7.5.1.1 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store, with minimal headspace and protected from light, at -10 to -20°C or less or as recommended by the standard manufacturer. Return standards to storage as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of target compounds.

7.5.1.2 **Frequency of Standard Preparation**

7.5.1.2.1 Monitor standards for the permanent gases frequently by comparison to the initial calibration curve. Prepare fresh standards if this check exceeds a 20% drift. **Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented**. Dichlorodifluoromethane and Chloromethane are usually the first compounds to evaporate from the standard and, therefore, are to be monitored very closely when standards are held beyond one week.

7.5.1.2.2 Monitor standards for the non-gases frequently by comparison to the initial calibration. Prepare fresh standards if this check exceeds a 20% drift. Undiluted standards for non-gases usually need to be replaced after **one month for working standards and three months for opened stock standard** or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-Chloroethyl vinyl ether and Styrene may need to be prepared more frequently.

7.5.1.3 **Secondary dilution standards:** Using stock standard solutions, prepare secondary dilution standards in Methanol containing the compounds of interest, either singly or mixed together. Secondary dilution standards are stored with minimal headspace and, except for gases, are good for 2-4 weeks unless acceptability is demonstrated. Replace secondary standards for gases after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. Handle and store standards as stated above and return them to the refrigerator or freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

7.5.1.3.1 The working calibration standard for the Non-Gas mixture is made by adding 2.5 mL of each of the first six standards in the Primary Standard table above in 50.0 mL Methanol in a Class A volumetric. The Gas

Standard is added right before use as described in the calibration section.

7.5.2 **Internal Standard/Surrogate Standard Mix (IS/SS)**

7.5.2.1 The internal standards are Fluorobenzene, Chlorobenzene-d_5, and 1,4-Dichlorobenzene-d_4. Prepare internal standard stock and secondary dilution standards in Methanol. Stock standard is 250 µg/mL, Restek 567649, or equivalent.

7.5.2.2 The surrogates are Toluene-d_8, 4-Bromofluorobenzene (the GC/MS Tuning Standard), 1, 2-Dichloroethane-d_4, and Dibromofluoromethane. Stock standard is 2500 µg/mL, Restek 567650, or equivalent.

7.5.2.3 Prepare a 250 µg/mL IS/SS standard by diluting 5.0 mL of stock internal standard (250 µg/mL) and 5.0 mL stock surrogate standard (2500 µg/mL) to a final volume of 50.0 mL of Methanol in a Class A volumetric.

7.5.3 **Bromoform Breakdown Check:** Purchase 50 g neat Bromoform from Sigma-Aldrich 241032-50G, or equivalent.

7.5.3.1 Prepare a 20 µg/L standard by adding 0.02 g of the neat Bromoform standard to 1000 mL reagent water.

7.5.4 **Second-Source Standards for Initial Calibration Standard (ICV):** The ICV is a **second-source** standard that contains all target compounds. Prepare as for the primary standard with the only difference being that the vendor numbers have a ".sec" on the end of the number.

7.6 Sodium bisulfate for soil sample preservation. See SOP 5035 / NV05-108. Commercially preserved sample containers are acceptable.

8.0 Sample Collection, Preservation, Shipment and Storage

See SOPs 5030 624 602 SM6200 B / NV05-107 and 5035 / NV05-108 for more detail.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time From Collection to Analysis	Reference
8260 Water[2]	3 x 40-mL VOAs (Optional: TSP)	40 mL	pH < 2 with Hydrochloric acid. Cool 0-6°C, No headspace. Keep in dark. If Chlorine residual present, add 0.008% $Na_2S_2O_3$.	14 days, 7 days if not acidified.	SW846 Chapters 2 and 4
8260 Low-concentration Solid	2 pre-weighed vials, stirring bar	5 g	0-6°C, 5 mL preservative[1]		
	2 EnCores™		0-6°C, Add 5 g sample and 5 mL preservative to pre-weighed vial with stirring bar within 48 hours of collection		
8260 High-concentration Solid	2-oz. glass[3] or 25 g Encore™	5g or 25 g	0-6°C, Add 1 mL Methanol/gram soil	Transfer to VOA within 48 hours, then 14 days	

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time From Collection to Analysis	Reference
624 Water, SM6200 B Water	3 x 40-mL VOAs	40 mL	pH < 2 with Hydrochloric acid. Cool 0-6°C, No headspace. Keep in dark.	14 days, 7 days if not acidified.	40 CFR 136, Standard Methods (on-line edition, 2011 editorial revisions)
624 Acrolein and Acrylonitrile	3 x 40-mL VOAs	40 mL	pH <4-5 with Hydrochloric acid. Cool 0-6°C, No headspace. 0.008% Na_2S2O3	14 days, 3 days if not acidified.	
624 Acrylonitrile	3 x 40-mL VOAs	40 mL	Cool 0-6°C, No headspace. 0.008% Na_2S2O_3	14 days	

[1] 0.2 gram Sodium bisulfate / mL reagent water. Missouri no longer requires Trisodium phosphate preservation, an optional sample preservative..

[2] 2-Chloroethyl vinyl ether degrades in acid-preserved samples; its analysis requires a non-preserved vial. If analyzing a sample for combined purgeable halocarbons, aromatics, Acrolein, and Acrylonitrile, analyze the sample within 7 days. Alternatively, collect at least 2 separate vials for analysis: one vial preserved to pH 4-5 with HCl for Acrolein and Acrylonitrile, and a second vial for the other analytes preserved to pH <2 with HCl.

[3] See SOPs 5030 602 624 SM6200 B / NV05-107 for waters and Methanol extracts and 5035 / NV05-108 for soils/solids.

Analysis Method	Sample Storage	Holding Times from Date and Time of Collection			
		MeOH Addition	Shipping	Extraction	Analysis
Wisconsin VOC Solids	VOC vial	Immediately	4 days	21 days	21 days
	Brass Tube	within 2 hours	4 days	21 days	21 days
	EnCore™	within 48 hours	40 hours	21 days	21 days

For 624 specifically:

- All samples must be iced or refrigerated from the time of collection until analysis. If the sample contains residual chlorine, add Sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 mg/L Cl_2) to the empty sample bottle just prior to shipping to the sampling site. Field test kits are available for this purpose. If chlorine is detected, add a qualifier.
- Grab samples must be collected in glass containers having a total volume of at least 40 mL. Fill the sample bottle just to overflowing in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. If preservative has been added, shake vigorously for 1 minute. Maintain the hermetic seal on the sample bottle until time of analysis.
- Experimental evidence indicates that some aromatic compounds, notably Benzene, Toluene, and Ethylbenzene, are susceptible to rapid biological degradation under certain environmental conditions. Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, TestAmerica Nashville supplies HCl-preserved containers for Method 624 analysis. All HCl-preserved 624 samples must be analyzed within 14 days of collection. Note: Acrolein and Acrylonitrile may be analyzed in pH 4.5-preserved samples within three days of collection.

9.0 Quality Control

The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

For 624 specifically:

QC Acceptance Criteria for Method 624[a]

Parameter	Range for Q (µg/L)	Range for P, P_s (%)
1,1,1-Trichloroethane	15.0-25.0	52-162
1,1,2,2-Tetrachloroethane	12.1-27.9	46-157
1,1,2-Trichloroethane	14.2-25.8	52-150
1,1-Dichloroethane	14.5-25.5	59-155
1,1-Dichloroethene	10.1-29.9	D-234
1,2-Dichlorobenzene	12.6-27.4	18-190
1,2-Dichloroethane	13.6-26.4	49-155
1,2-Dichloropropane	6.8-33.2	D-210
1,3-Dichlorobenzene	14.6-25.4	59-156
1,4-Dichlorobenzene	12.6-27.4	18-190
2-Chloroethylvinyl ether	D-44.8	D-305
Benzene	12.8-27.2	37-151
Bromoform	14.2-25.8	45-169
Bromomethane	2.8-37.2	D-242
Carbon tetrachloride	14.6-25.4	70-140
Chlorobenzene	13.2-26.8	37-160
Chlorodibromomethane	13.5-26.5	53-149
Chloroethane	7.6-32.4	14-230
Chloroform	13.5-26.5	51-138
Chloromethane	D-40.8	D-273
cis-1,3-Dichloropropene	4.8-35.2	D-227
Dichlorobromomethane	13.1-26.9	35-155
Ethylbenzene	11.8-28.2	37-162
Methylene chloride	12.1-27.9	D-221
Tetrachloroethene	14.7-25.3	64-148
Toluene	14.9-25.1	47-150
trans-1,2-Dichloroethene	13.9-26.1	54-156
trans1,3-Dichloropropene	10.0-30.0	17-183
Trichloroethene	13.3-26.7	71-157
Trichlorofluoromethane	9.6-30.4	17-181
Vinyl chloride	0.8-39.2	D-251

Q = Concentration measured In QC check sample, in µg/L (ICV, CCV)).
s = Standard deviation of four recovery measurements, in µg/L (Initial Demonstration of Capability).
X = Average recovery of four recovery measurements, in µg/L (Initial Demonstration of Capability).
P, P_s = Percent recovery measure (LCS, MS).
D = Detected result must be greater than zero.
[a] Criteria were calculated assuming a QC check sample concentration of 20 µg/L.
For non-624 targets, use the limits in LIMS.

9.1 Sample QC: The following QC is run **every batch of no more than 20 samples:**

QC Check	Frequency	Acceptance Criteria[1]	Corrective Action[2]
Method blank	One per analytical prep batch and after calibration (see Section 9.2)	No analytes detected ≥ ½ RL or MDL, whichever is greater	Correct problem then re-prep[3] and analyze method blank and all samples processed with the contaminated blank. If target > 10x blank, report but qualify.
LCS[4] for all analytes using the primary standard.	One[6] per prep batch	See LIMS[5]	Re-prep[3] and analyze the LCS and all samples in the affected analytical batch. If high and samples are ND, report. If low, re-prep. If the LCS exceeds the upper control limit AND a sample from that batch is greater than the RL, re-prep and re-analyze the batch. If the LCS exceeds the upper control limit AND the sample from that batch is less than the RL, the data is acceptable to report.
MS/MSD using the primary standard	One per batch per matrix, if insufficient sample for MS/MSD, then analyze a LCS/LCSD.	See LIMS	None (LCS is used to determine if data is acceptable).
Surrogate	Every sample, spike, standard, and blank.	See LIMS	Check system, re-analyze, re-prep[3], may qualify. If %recovery is high and the sample is ND, it is acceptable to report. If low, re-prep and rerun. If the surrogate % recovery exceeds the upper control limit AND a sample is greater than the RL, re-prepare and re-analyze the sample. If the surrogate % recovery exceeds the upper control limit AND the sample is less than the RL, data is acceptable to report. If the surrogate % recovery is lower than the lower control limit, re-prepare the sample. OH VAP requires all surrogates to be in control; otherwise, the samples must be re-prepared and re-analyzed
pH check	All water samples.	pH ≤2 or ≥ 11 For 624, pH ≤2 or, for Acrolein and Acrylonitrile, pH = 4-5	If the pH is > 2 but less than 11, comment the data and LIMS.
Residual chlorine check (NC samples only for 8260B, 8260C, and SM6200 B. NC and FL for 624)	Each sample.	Residual chlorine must be negative.	If the residual chlorine is positive, then comment the data, and LIMS.

[1]This is a summary of the acceptance criteria.
[2]All abnormalities must be noted in LIMS.
[3]If unable to re-prep the samples because of insufficient sample volume or holding time has expired, place a comment in LIMS.
[4] All AZ, MA, and TX samples require a LCS duplicate in each batch.
[5].See Section 16 for South Carolina LCS acceptance criteria and Minnesota Ethanol acceptance criteria.

- A **Method Blank** is run with each analytical batch. The blank is carried through all stages of the sample preparation and measurement using the appropriate blank matrix (reagent water or sand).
- A **Laboratory Control Sample (LCS)** is included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix (reagent water or sand) similar to the sample ma-

trix and of the same weight or volume. The LCS is spiked with the same analytes from the primary source.

Matrix	LCS Preparation	Final Concentration
8260 Water, SM6200 B	Add 50 µL of the primary source standard to 50.0 mL reagent water in a Class A volumetric flask.	50 – 5000 µg/L
624 Water	Add 20 µL of the primary source standard to 50.0 mL reagent water in a Class A volumetric flask.	20 – 2000 µg/L
8260 Low-concentration Soil	Add 5 µL of the primary source standard to a VOA vial containing 5.0 g sand and 5 mL preservative and a stirring bar.	50 - 5000 µg/kg
8260 High-concentration Soil (analyzed as waters)	Add 50 µL of the primary source standard to 50.0 mL reagent water in a Class A volumetric flask.	50 - 5000 µg/kg

- **Matrix Spike/Matrix Spike Duplicate:** Documenting the effect of the matrix includes the analysis of at least one matrix spike/matrix spike duplicate pair for each batch.

Matrix	MS/MSD Preparation	Final Concentration
8260 Water, SM6200 B	Add 43 µL of the primary source standard to the client's sample in VOA vials.	50 – 5000 µg/L
624 Water	Add 17 µL of the primary source standard to the client's sample in VOA vials.	20 – 2000 µg/L
8260 Low-concentration Soil	Add 5 µL of the primary source standard to a VOA vial containing 5 g preserved client sample (with stirring bars).	50 - 5000 µg/kg
8260 High-concentration Soil (analyzed as waters)	Add 1.0 mL of the Methanol-extract-of-client-sample and 50 µL of the primary source standard and dilute with reagent water in a 50-mL, Class A volumetric.	50 - 5000 µg/kg

- **Surrogate standards**: The analyst monitors both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, QA/QC standard, and blank with surrogate compounds which are not expected to be affected by method interferences. The surrogate and internal standards are prepared together as described in Section 7.
  - The 8260, SM6200 B IS/SS standard mix (250 µg/mL each) is added by the autosampler (nominally 1 µL) during all analyses with the exception of the calibration.

Purge Volume, mL	Concentration of IS/SS Standards in Sample, µg/L
5	50
10	25

  - The 624 working IS/SS standard mix (150 µg/mL each) is further diluted at a 1:5 ratio in Methanol. It is then added by the autosampler during all analyses. Its concentration is 30 µg/L in the sample.
- **pH Check:** The pH check with narrow-range pH paper is performed **after** sample analysis to avoid contamination and creation of a headspace (i. e., >6 mm diameter) in the sample vials.
  - For Methods 8260 and SM6200 B, the analyst must document that each sample has a pH ≤ 2 or ≥ 11.

- For Method 624, the analyst must document that each sample has a pH ≤ 2 except for the Acrolein/Acrylonitrile vial, pH = 4-5.
- Record as pH <2, >2, 4-5, or >11.

- **Residual Chlorine Check:** The analyst must document the presence/absence of residual chlorine as determined with residual chlorine test strips for the following:
  - in North Carolina samples (all methods)
  - In Florida Method 624 samples.

9.2 Instrument QC

Italicized information is unique to 8260C.

QC Check	Frequency	Acceptance Criteria[1]	Corrective Action[2]
a. Check of mass spectral ion intensities, i.e., BFB Tune	Prior to initial calibration or Continuing calibration verification, every 12 hours.	Refer to criteria for Tune criteria	Retune the instrument and verify (instrument maintenance may be needed).
b. Bromoform Break-down Check	At beginning of daily sequence.	≤ 0.5 µg/L Bromomethane; ≤ 0.5 µg/L Chloromethane	Re-condition or replace trap. Re-calibrate.
Minimal five-point initial calibration for all target analytes. Single-point surrogate calibration	Initial calibration prior to sample analysis. Perform instrument re-calibration once per year minimum.	8260B: SPCCs average RF ≥ 0.30 or 0.1 depending on the compound. % for CCCs ≤ 30% and all other target analytes %RSD < 15%. or correlation coefficient r^2 ≥ 0.990 or r ≥ 0.995. Re-calculate low point; must be within 30% true. *8260C: Minimum RF for initial and continuing calibration varies by analyte (see Calibration standards below). RSD ≤ 20% each target or correlation coefficient r^2 ≥ 0.990 r ≥ 0.995. Up to 10% of targets may exceed these criteria. If using linear regression, re-fit lowest calibration point. It must be within ≟ 30% of true.* 624: All target analytes %RSD for RF ≤ 35%. r^2 ≥ 0.990 or r≥ 0.995 SM6200 B: All target analytes %RSD for RF ≤ 20%. r^2 ≥ 0.988 or r ≥ 0.994	Correct problem then repeat initial calibration.
Initial calibration verification (ICV), **must be from a second source**	Immediately following each initial calibration.	All analytes within 30% of expected value. Problematic compounds may be within 40%. 624: Use Q ranges in the 624 QC table. SM6200 B: All analytes within 30% of expected value (gases within 40%).	Correct problem then repeat initial calibration. ICV must be run prior to reporting samples.
Continuing Calibration Verification (CCV)	Daily, before sample analysis and every 12 hours of analysis time.	8260B: CCCs: ≤20% difference (when using RFs) or drift (when using least squares regression). SPCCs: minimum RF. All other target compounds ≤ 30%, except for specific compounds which may have a % difference ≤ 40%. *8260C: All targets of interest ≤ 20%. Up to 20% of targets may exceed this criterion. Common targets meet minimum RF.* 624: Use Q ranges in the 624 QC table.	Correct problem then repeat CCV (re-calibrate if necessary) and re-analyze any samples processed with that CCV. If the CCV is high and the sample is ND, it is acceptable to report.[3]

QC Check	Frequency	Acceptance Criteria[1]	Corrective Action[2]
		SM6200 B: 60-140% for gases; 70-130% for other analytes.	
Continuing Calibration Blank	After each CCV.	< ½ RL or MDL, whichever is greater.	Correct problem, repeat.
Internal Standards[3]	Every sample, standard and blank.	Retention time ±30 seconds from retention time of the mid-point std. in the ICAL. EICP area within -50% to +100% of most recent ICAL mid-point std.	Inspect mass spectrometer and GC for malfunctions; mandatory re-analysis of samples analyzed while system was malfunctioning.
Retention time window calculated for each analyte	Each sample.	Relative retention time (RRT) of the analyte within 0.06 RRT units of the RRT of the internal standard.	Correct problem then re-analyze all samples analyzed since the last retention time check.

[1] This is a summary of the acceptance criteria.
[2] All abnormalities must be noted in LIMS.
[3]Target compounds associated with failed internal standards must be re-analyzed (undiluted if possible) if additional sample is available; if not available, qualify data in LIMS.

- **BFB Tuning and Breakdown Check**:
  - **BFB Tuning**: At the beginning of each 12-hour analytical shift and **prior** to the analysis of samples or calibration standards, inject 50 ng or less of the 4-Bromofluorobenzene standard into the GC/MS system (1 µL of 250 µg/mL standard /50 mL reagent water, purged at a 1:10 split for a 25 ng on the column). (BFB is one of the surrogate compounds.) The resultant mass spectra for the BFB **must** meet the tuning criteria below before sample analysis begins.

BFB (4-Bromofluorobenzene) Mass Intensity Criteria

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50%, but less than or equal to 120%, of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101 % of m/z 174
177	5 to 9% of m/z 176

  - Three options are available for acquiring the spectra for reference to meet the BFB tuning requirements:

Option 1 It is recommended that each initial tune verification utilize the "Autofind" function and be set up to look at the apex ± 1 scan and average the three scans. Background correction is required prior to the start of the peak but no more than 20 scans before. Background correction **cannot** include any part of the target peak. Sometimes the instrument does not always correctly identify the apex on some peaks when the peak is not perfectly shaped. It is acceptable to manually identify and average the apex peak ± 1 scan and background correct.

Option 2 The scan across the peak at one half peak height may be averaged and background-corrected.

Option 3 A single scan at the apex (only) may also be used for the evaluation of the tune. Background correction is still required.

Note: It is acceptable to adjust parameters within the specifications set by the manufacturer or the analytical method to properly tune the instrument. If the tune verification does not pass it may be necessary to clean the source or perform additional maintenance. Document any maintenance in the instrument log. **Excessive adjusting (more than two tries) without clear documentation is not allowed. No more than two consecutive tunes may be attempted. Perform necessary maintenance.**
Note: All subsequent standards, samples, controls, and blanks associated with a BFB tune **must** use identical mass spectrometer instrument conditions.

- **Bromoform Breakdown Check**: The daily BFB Tune/Breakdown Check containing surrogates, internal standards, BFB, and 20 µg/L Bromoform must be analyzed prior to the analysis of the Continuing Calibration Verification (CCV). If levels of Chloromethane or Bromomethane exceed 0.5 µg/L, then the trap may be too contaminated with salts or tightly bound contamination for analysis to continue. The trap must be replaced, and the system re-calibrated.

- **Calibration standards**: See Section 10.2.

SPCCs and CCCs are unique to 8260B. *Italicized text is unique to 8260C.*

- **Initial System Performance Check Compounds (SPCCs)**: A system performance check is made before the calibration curve is used. Five compounds (the System Performance Check Compounds) are checked for a minimum average response factor, compound instability, and degradation caused by contaminated lines or active sites in the system. These compounds are Chloromethane, 1,1-Dichloroethane, Bromoform, Chlorobenzene, and 1,1,2,2-Tetrachloroethane. The minimum mean response factors for the volatile SPCCs must be met and are as follows:

Chloromethane	0.10
Bromoform	0.10
1,1,2,2-Tetrachloroethane	0.30
1,1-Dichloroethane	0.10
Chlorobenzene	0.30

Example problems include:
  - Chloromethane is the most likely compound to be lost if the purge flow is too fast.
  - Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve Bromoform response.
  - Tetrachloroethane and 1,1-Dichloroethane are degraded by contaminated transfer lines or active sites in trapping materials.

- **Initial Calibration check compounds (CCCs):** The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites in the system. Meeting the CCC criteria is **not** a substitute for successful calibration of the target analytes. The CCCs are:

1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene
1,2-Dichloropropane	Vinyl chloride

- Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for **all** target analytes from the initial calibration with the equations in Section 11.
- The RSD must be less than or equal to **15% for each target analyte**; however, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%. If an RSD of greater than 30% is measured for any CCC, then corrective action to eliminate a system leak or contamination and/or column reactive sites is necessary before re-attempting calibration. The CCCs may not be in the project target list. If that is the case, each target must have a RSD < 15% or a correlation coefficient $r \geq 0.995$ ($r^2 \geq 0.990$) as calculated by the equations in Section 11. When using linear regression, re-calculate the low calibration point. It must be within 30% true.
- ***For 8260C**, the minimum RF for initial and continuing calibration is:*

RF	*For These Compounds*
0.05	*1,2-Dichloro-3-propane*
0.1	*Critical compounds*
0.2	*1,1-Dichloroethane, Chloroform, Trichlorethene, Bromodichloromethane, cis-1,3-Dichloropropene, Tetrachloroethane, and 1,2,4-Trichlorobenzene*
0.3	*o-Xylene, Styrene, 1,1,2,2-Trichloroethane*
0.4	*Toluene, 1,2-Dichlorobenzene*
0.5	*Benzene, Chlorobenzene, 1,4-Dichlorobenzene*
0.6	*1,3-Dichlorobenzene*

- **Initial Calibration Verification (ICV)** is verified immediately after calibration using the introduction technique used for samples. Analyze a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS.
  - Prepare as for the primary standard LCS with the only difference being that the vendor numbers have a ".sec" (second source) on the end of the number.
  - The ICV of each target must be within 30% of the expected value, with the exception of the following poor purge efficiency analytes that may be within 40% of the expected value. No more than 20% of analytes are allowed to fail this criterion.

1,4-Dioxane	1-Methylnaphthalene	2-Methylnaphthalene
Acrolein	Ethanol	t-Amyl alcohol (TAA)
t-Butyl alcohol (TBA)	t-Butyl formate (TBF)	Vinyl acetate

  - If ICV criterion is not met, correct the problem and re-calibrate.
- **Continuing Calibration Verification (CCV):** Run every 12 hours of sample analysis, CCVs are often made each day for several instruments in the following proportions, always from the **primary** calibration standards:
  - For 8260 and SM6200 B, add 25 µL of the working calibration Non-Gas Standard and 25 µL of the primary Gas Mix to a 50-mL, Class A volumetric and dilute to the mark with reagent water. The final concentration is 50-5000 µg/L. For SM6200 B, vary the concentration over time.
  - For 624, prepare the CCV with 40 µL of the calibration working standard per 100 mL reagent water for a final concentration of 20-2000 mg/L. Method 624 targets **must** be 20 µg/L or less.

- Area counts of the internal standards must be between 50 - 100% of the areas of the internal standards in the mid-point calibration standard. If not, inspect the GCMS for possible maintenance issues and then re-analyze. Contact the department supervisor for assistance in determining the appropriate course of action. **Do not report data from a failing internal standard associated with target compounds.**
- **For 8260B Only: Continuing System Performance Check Compounds (SPCCs)**
  - A System Performance Check **must** be made during every 12-hour analytical shift. Each SPCC compound in the calibration verification standard **must** meet its minimum response factor. This is the same check that is applied during the initial calibration.
  - If the minimum response factors are not met, the system **must** be evaluated, and corrective action **must** be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.
- **For 8260B Only: Continuing Calibration Check Compounds (CCCs)**
  - After the system performance check is met, the CCCs are used to check the validity of the initial calibration, if present in the target list. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. See Section 11 for equations.
  - If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i. e., greater than 20% difference or drift), for any one CCC, then corrective action **must** be taken prior to the analysis of samples. **If the CCCs are not included in the list of analytes for a project and therefore not processed in the calibration standards, then all analytes must meet the 20% difference or drift criterion.**
  - Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new five-point initial calibration must be generated. The CCC or target criteria **must** be met before sample analysis begins.
- **For 8260B Only: Continuing Evaluation of Non CCC/SPCC compounds** – The percent difference or drift for each of the non-CCC analytes is less than or equal to 30%. Recovery for some compounds with poor purge efficiency may exceed this 30% requirement and still be deemed acceptable provided all of the following criteria are met:
  - Poor performing analytes are one of the following: Acrolein, tert-Amyl alcohol (TAA), tert-Butyl alcohol (TBA), tert-Butyl formate (TBF), Ethanol, 2-Methylnaphthalene, Vinyl acetate.
  - The percent difference or drift is less than or equal to 40%.
- ***For 8260C**, the CCV % difference for each target must be ≤ 20% with only up to 20% of the targets of interest allowed to exceed 20% difference. The minimum RF must also be achieved..*
- **Continuing Calibration Blank (CCB):** The CCB is reagent water or sand.
- **Internal Standards** are used to evaluate the effect of the sample matrix. Any samples that do not meet the internal standard criteria must be evaluated for validity. If the change in sensitivity is a matrix effect, the sample is re-analyzed to confirm. If the change in sensitivity is due to instrumental problems, all affected samples must be re-analyzed after the problem is corrected.
  - The retention times of the internal standards in the calibration verification standard are evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made. When corrections are

made, reanalysis of samples analyzed while the system was malfunctioning is required. Note any maintenance in the logbook.

- Internal standards permit most of the components of interest in a chromatogram to have retention times of 0.80 - 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Attachment 1). If interferences are noted, use the next most intense ion as the quantitation ion.
- **Internal standard response** - If the EICP area for any of the internal standards in the calibration verification standard and samples changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required. Note any maintenance in the logbook.
- The laboratory re-analyzes any sample where the internal standard fails and there is no evidence of matrix interference. If there is no matrix interference, the sample must be reanalyzed at the original dilution.
  - If the internal standard is within criteria, report the second analysis.
  - If the internal standard is still outside of criteria, the sample must be analyzed at a second dilution.
  - If the internal standard still does not meet criteria, the sample must be diluted until the internal standard meets criteria. Multiple runs may be required.
- See Attachment 2 for the analytes corresponding to each internal standard.

- **Retention time windows**: Target analytes are identified on the basis of retention time windows.
  - Before establishing retention time windows, make sure that the chromatographic system is functioning reliably and that the operating parameters have been optimized for the target analytes and surrogates in the sample matrix to be analyzed.
  - Establish the retention time windows for target analytes.
  - The relative retention times of each target analyte in each calibration standard must agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

10.0 Procedure

10.1 Sample Preparation

Matrix	Sample Size
Water	VOA vial
Low-concentration Soil	5 grams
High-concentration Soil	1 mL Methanol extract of soil / 50 mL reagent water

- All samples and standard solutions are allowed to warm to ambient temperature before analysis.
- Refer to SOP 5030 602 624 SM6200 B / / NV05-107 for waters and 5035 / NV05-108 for soils/solids.
- For Wisconsin VOC soils, the following procedure must be performed for Methanol extraction of Soil/Sediment:

1	Hand-shake the sample in its vial containing Methanol vigorously for 2 minutes. Sonicate for 20 minutes.
2	Allow sediment to settle until a layer of Methanol is apparent.

3	Withdraw an appropriate aliquot of the Methanol extract for sparging and add to a VOA vial.
4	Analyze all reagent blanks and QC samples on the same instrument as that used for the samples.
5	If the responses exceed the calibration or linear range of the systems, use a smaller aliquot of Methanol extract or dilute the aqueous sample.

10.2 Initial Calibration: Refer to SOPs Acceptable Manual Integration Practices / CA-Q-S-002 and Calibration Curves and Selection of Calibration Points / CA-Q-P-003. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

1 Evaluate the **BFB tuning criteria.**

2 Prepare the **Initial calibration standards** at a minimum of five different concentrations from the secondary dilution of stock standards or from a premixed certified solution in organic-free reagent water. **At least one of the calibration standards corresponds to a concentration at or below the laboratory reporting limit.** This low standard must have valid ion abundances for all monitored ions. The remaining standards define the working range of the system. Initial calibration standards are mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

Initial Calibration (5-point)

Primary Working Standard	Final Volume (mL)	Concentraton (µg/L)
1	100	0.5-2.5
2	100	1 - 5
4	100	2 - 10
20	100	10 - 50
40	100	20 - 100
100	100	50 - 250
200	100	100 - 500

1 µL of IS/SS Standard at 250 µg/mL is added by the autosampler to 5 mL for a 50-µg/L concentration in the standards and samples with a 5-mL purge; 1 µL/10 mL for a 25 µg/L concentration. See Section 9.1 for make-up and final concentrations for other purge volumes. The surrogate calibration is a single-point.

- All target analytes for a particular analysis must be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes for which the method has been demonstrated. **However, the laboratory must not report a quantitative result for a target analyte that was not included in the calibration standard(s).**
- **Internal Standards:** The calibration standards must also contain the internal standards chosen for the analysis. Calibration standards for soils must also contain the preservative Na_2SO_4. See Method 5035 / NV05-108 for how to accomplish the preservation.
- **Surrogates**: Historically the surrogate compounds have been included in the multi-point initial calibration at variable concentrations in order to evaluate the linear response as with any target analyte. With improvements in instrumentation and more reliance on the autosampler, an option is available allowing the autosampler to spike the initial calibration standards with surrogates in the same manner as the samples are spiked. With this option, the surrogate standards in the initial calibration can be averaged to develop a response factor and an effective one-point calibration with the sole purpose to measure the surrogate recovery using the same concentration for each sample analysis. For this calibration option, the surrogate linear response is less important, since multiple

	concentrations of surrogates are not being measured. Instead, the surrogate concentration remains constant throughout, and the recovery of this known concentration can easily be attained without demonstrating if the response is linear. • **Technique:** To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a Class A, volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection and stopper. Mix by inverting the flask three times. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and are prepared daily, i. e., 24 hours. Transfer each standard to separate VOA vials. • **Water or Soil Samples:** A different calibration curve is necessary for Methods 5030 602 624 SM6200 B / NV05-107 and 5035 / NV05-108. Calibration **must** be performed using the same sample introduction technique that is used for samples. For Method 5030, the purging efficiency varies with purge volume; therefore, develop the standard curve with whichever volume of sample that is to be analyzed.
4	**Tabulate the area response of the characteristic ions** (see Attachment 1) against the concentration for each target analyte and each internal standard. Calculate response factors (RF) for each target analyte relative to one of the internal standards.

10.3 Daily GC/MS Calibration Verification

1	Evaluate the BFB tuning and Breakdown Check criteria.
2	For 8260B, evaluate the SPCC and CCC compounds for the continuing calibration criteria. For 8260C, SM6200 B, and 624: evaluate each target.
3	Evaluate the blank.

10.4 Example Analysis Queue / Sequence (based on 12 hours)

1	Tune/Breakdown Check
2	Initial Calibration, if needed.
3	ICV, if initial calibration run.
4	CCV, for daily and ongoing calibration check
5	LCS
6	Blank
7	Samples
8	Matrix Spike
9	Matrix Spike Duplicate
When 12 hours have passed, run a 2nd tune and CCV before running more samples, no more than 20 samples in a 12-hour batch.	

1	Analyze the samples using the same conditions used for calibration.
2	Allow the sample to come to ambient temperature. Place the VOA vial as received in autosampler and start the method.
3	Purge the sample for the prescribed time at ambient temperature.
4	After the purge, the sample is desorbed and begins the temperature program for the gas chromatograph. The trapped materials are transferred to the GC column by rapidly heating the trap to 250°C while back-flushing the trap with an inert gas at 20 mL/minute for 4 minutes.
5	After desorbing the sample for four minutes, recondition the trap by returning the purge and

	trap system to the purge mode. The trap temperature should be maintained at the manufacturer's recommendations. After approximately 7 minutes, turn off the trap heater. When the trap is cool, the next sample is started to purge and then analyzed.
6	If the response for any target exceeds the upper calibration standard, prepare a dilution of the sample with reagent water and reanalyze, as described below.
7	**Checking Sample pH**: After the sample has been analyzed, check the pH of the sample using narrow-range pH paper. Compare the test strip to the chart on the test strip container. **Record the pH on the runlog.** .
8	**Checking residual chlorine:** For North Carolina samples (all methods), check for and document residual chlorine. Also, for Florida Method 624 samples, check and document residual chlorine.
9	**High Molecular Weight (HMW) Compounds**: Some HMW compounds have demonstrated a tendency to carryover in subsequent analyses. When any of the following compounds are detected in a sample at greater than the specified carryover limit, any subsequent sample must be re-analyzed after either the analyses of two rinses have been or the instrument has been demonstrated to be free from carryover.

Compound	Carryover Limit	
	Water (mg/L)	Soil (mg/kg)
1,2,3-Trichlorobenzene	0.03	0.05
1,2,4-Trichlorobenzene	0.03	0.05
1,3,5-Trichlorobenzene	0.03	0.05
1,2-Dibromo-3-chloropropane	0.03	0.1
1,4-Dioxane	2	4
1-Methylnaphthalene	0.03	0.06
2-Methyl-2-propanol (tert-Butyl alcohol)	0.3	1
2-Methylnaphthalene	0.03	0.06
Ethanol	1	2
Hexachlorobutadiene	0.05	0.1
Isobutyl alcohol	1	2
Isopropyl alcohol	1	2
Naphthalene	0.1	0.1

To reduce carryover, rinse the purging device and sample syringe with reagent water between samples. Follow the analysis of an unusually high concentration sample with a rinse blank to check for carryover contamination.

10 **Dilutions**: If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the upper calibration standard, the sample must be reanalyzed at a higher dilution. **Secondary ion quantitation is allowed only when there are sample interferences with the primary ion**.

- When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of an organic-free, reagent water blank or the repeating of suspected samples. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences. Repeat all affected samples.
- Prepare dilutions such that the response of the major constituents (previously saturated peaks) is in the upper half of the linear range of the curve.

- The following procedure is used to dilute aqueous samples for analysis of volatiles. All steps must be performed without delays.

1	Dilutions are made in Class A, volumetric flasks (50 to 100 mL). Select the volumetric flask that allows for the necessary dilution. Intermediate dilution steps may be necessary for extremely large dilutions.
2	Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask, and add slightly less than this quantity of organic-free reagent water to the flask.
3	Inject the appropriate volume of the original sample from the syringe into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, three times. Repeat above procedure for additional dilutions.
4	Fill a VOA vial with the diluted sample and cap.

- For high concentration samples, see SOP 5035 / NV05-108.

10.5 Qualitative analysis

The qualitative identification of each compound determined by this method is based on relative retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be kept up to date and obtained through analysis of known standards on the instrument using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. See Attachment 1 for primary and secondary ions for each compound. Compounds are identified as present when the following criteria are met:

- The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time is accepted as meeting this criterion.
- The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.
- The relative intensities of the characteristic ions agree with 30% of the relative intensities of these ions in the reference spectrum. For example, an ion with an abundance of 50% in the reference spectrum must have a corresponding abundance in a sample spectrum between 20% and 80%. When two or more analytes that co-elute share secondary ions, and all the characteristic secondary ions for the target analyte are present but outside the ± 30 % relative intensity, report the compound as positive if there is no interference with the primary quantitation ion. If co-eluting peaks share the primary ion, the analyte may only be reported as a co-eluting pair.
- Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i. e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.
- Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes co-elute (i. e., only one chromatographic peak is apparent), the identification criteria may be met, but each

analyte spectrum might contain extraneous ions contributed by the co-eluting compound. If all of the ions associate with the reference spectrum for the target analyte are present and within the ± 30% criteria, a positive result must be assumed even in the presence of extraneous ion fragments without presumptive evidence for a negative identification. All ions associated with the target analyte are also present in the interfering peak. The analyst must carefully weigh the background spectrum and the spectrum of any co-eluting analytes whenever assessing a potential hit. Analyst experience in interpreting mass spectral data and the above specified guidelines are used together to interpret difficult matrices and to add appropriate qualifiers in the LIMS.

- Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.
- For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification is determined by the purpose of the analyses being conducted. Data system library search routines are not to use normalization routines that would misrepresent the library or unknown spectra when compared to each other. For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Use the following guidelines for tentative identifications:
  - Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification.
  - Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) must be present in the sample spectrum.
  - The relative intensities of the major ions must agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).
  - Molecular ions present in the reference spectrum must be present in the sample spectrum.
  - Review ions present in the sample spectrum but not in the reference spectrum for possible background contamination or presence of co-eluting compounds.
  - Review ions present in the reference spectrum but not in the sample spectrum for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.
  - If all the above conditions for a compound are met and if the Q value of the search is ≥ 85%, that compound will be reported as a tentatively identified compound (TIC). If the Q value is <85% or the mass spectral interpretation specialist indicates that no valid tentative identification can be made, the compound should be reported as unknown.
    - The mass spectral specialist may give additional classification of the unknown compound, if possible (i.e., unknown phthalate, unknown hydrocarbon, unknown acid, and unknown chlorinated compound). If probable molecular weights can be distinguished, include them on the TIC report.
    - Report only one type of unknown compound per retention time (RT).
  - If the library search produces more than one compound greater than or equal to 85%, report the compound with the highest percent match (report first compound if percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels that the highest match compound should not be reported or another compound with a lower match should be reported.
  - TIC concentrations are calculated using a RF of 1.0 and the nearest internal standard.

- TIC concentrations are estimated and should be "J" qualified.
- Assure that TICs are reported consistently for samples from the same site (i.e., TICs at the same RT and with the same spectrum should not be identified as different compounds when the samples were collected at the same site).
- Do not report carbon dioxide (CO2), reported target compounds, internal standards or surrogates as a TIC.
- Aldol condensation products are formed when acetone is used as an extraction solvent. Aldol condensation products, if present, should be reported as "Aldol Condensation Products". Aldol condensation reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.
- Siloxanes, if present, should be reported as "Column Bleed."

10.6 Quantitative analysis

- Once a compound has been identified, the quantitation of that compound is based on the integrated abundance from the EICP of the **primary** characteristic ion. The internal standard used is the one nearest the retention time of that of a given analyte. See Attachment 1.
- If the RSD of a compound's response factors is 15% or less (20% for SM6200 B), then the concentration is determined using the average response factor (*RF*) from initial calibration data.
- Where applicable, the concentration of any non-target analyte identified in the sample may be estimated. The same formulae are used with the following modifications: The areas A_x and A_{is} are from the total ion chromatograms, and the RF for the compound must be assumed to be 1.
- The resulting concentration is reported indicating:
  - that the value is an estimate, and
  - in Level 4 data packages, which internal standard was used to determine the concentration. Use the nearest internal standard free of interferences.

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\% \text{ Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 Response Factor

$$RF = \frac{A_s x C_{is}}{A_{is} x C_s}$$

A_s = Peak area of the analyte or surrogate.
A_{is} = Peak area of the internal standard.
C_s = Concentration of the analyte or surrogate.
C_{is} = Concentration of the internal standard

11.4 Standard Deviation, Relative Standard Deviation

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - RF_{mean})^2}{n-1}} \qquad RSD = \frac{SD \times 100}{RF_{mean}}$$

RF_i = RF for each of the calibration standards
RF_{mean} = mean RF for each compound from the initial calibration
n = Number of calibration standards, e. g., 5

11.5 % Difference, % Drift

$$\% \text{ Difference} = \frac{(RF_v) - (\text{Avg. RF}) \times 100}{(\text{Avg. RF})}$$

RF_v = RF from verification standard
Avg. RF = Average RF from Initial Calibration.

$$\% \text{ Drift} = \frac{\text{Result - True Value x 100}}{\text{True Value}}$$

11.6 Linear Calibration Using a Least Squares Regression: A linear calibration model based on a least squares regression may only be employed if RSD does not meet the acceptance criteria.

For calibration, x is the mass of the analyte in the sample aliquot introduced into the instrument and y is the area (or height) or the response, as in:

$x = C_s$ and $y = A_s$

A linear least squares regression attempts to construct a linear equation of the form:

$y = ax + b$

by minimizing the differences between the observed results (y_i, the instrument response) and the predicted results (y_i', the response calculated from the constructed equation). The regression equation is:

$y_i' = ax_i + b$

a = regression coefficient or the slope of the line.
b = the y-intercept.
y_i' = predicted (or calculated) response for the i^{th} calibration standard.
x_I = mass of analyte in the i^{th} calibration standard aliquot introduced into the instrument.

The sum of the squares of the differences is minimized to obtain a and b:

$$\sum_{i=1}^{n}(x_i - x_i')^2$$

n = total number of calibration points. The regression calculations attempt to minimize this sum of the squares, hence the name "least squares regression."

Weighting the sum of the square of the differences may significantly improve the ability of the least squares regression to fit the linear model to the data. The general form of the sum of the squares of the differences containing the weighting factor is:

$$\sum_{i=1}^{n} w_i(x_i - x_i')^2$$

w_i = weighting factor for the i^{th} calibration standard (w=1 for un-weighted least squares regression).
x_i – observed instrument response (area) for the i^{th} calibration standard.
x_i' = predicted (or calculated) response for the i^{th} calibration standard.
n = total number of calibration standards.

The mathematics used in least squares regression has a tendency to favor numbers of larger value over numbers of smaller value. Thus the regression curves that are generated tend to fit points that are at the upper calibration levels better than those points at the lower calibration levels. To compensate for this, a weighting factor which reduces this tendency can be used. Examples of allowed weighting factors which place more emphasis on numbers of smaller value are:

$w_i – 1/x_i$ or $w_i = 1/x_i^2$

Do not include the origin (0, 0) as an extra calibration point. The use of a linear regression may NOT be used as a rationale for reporting results below the calibration range demonstrated by the analysis of the standards. If it is necessary to report results at lower concentrations, then the analyst must run a calibration that reaches those lower concentrations.

The regression calculation generates a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.995 or $r^2 \geq 0.990$.

11.7 Coefficient of Determination **Correlation Coefficient**

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2} \qquad r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response ratio
x = Concentration

11.8 Concentration Calculation

Concentration = (µg/L from instrument) (dilution factor)

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Detection Limits / CA-Q-S-006. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

Specific to Method 624: The Demonstration of Capability requires running four aliquots of 20 µg/L each target and comparing the results to S and X in the table in Section 9.0. Prepare the 20 µg/L aliquots by adding 20 µL of the 100 µg/mL check concentration to 100 mL reagent water.

The large number of parameters presents a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed. If this happens, locate and correct the source of the problem and repeat the test for all parameters of interest. Further repeated failure confirms a general problem with the measurement system which must be corrected before proceeding.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes must be stored, managed, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Aqueous waste generated from analysis may have a pH of less than 2.0. Transfer to waste disposal for neutralization and then dump into the sanitary sewer.

- Solid waste generated from analysis is placed in the trash.

15.0 References / Cross References

15.1 EPA Method 8260B, SW-846 Update III, Revision 2, December 1999, **Method 8260C**, Update.IV, Rev. 3, August 2006.
15.2 Method 8000B, SW-846, Revision 2, December 1996, **Method 8000C**, Revision 3, March 2003.
15.3 Method TPH-GRO by Method 8260B, MRBCA (Missouri) Guidance Document, Final Draft, February 24, 2004.
15.4 California GRO, CA LUFT 8015.
15.5 SC UST Programmatic QAPP, Rev. 2.0, April 2013, Table E1.
15.6 EPA Method 624, Federal Register, 40 CFR Part 136, July 1, 1991.
15.7 SM6200 B - 1997, Standard Methods for the Examination of Water and Wastewater, on-line edition, 2011 editorial revision.
15.8 TestAmerica Nashville's Quality Assurance Manual.
15.9 Corporate Environmental Health and Safety Manual (CW-E-M-001).
15.10 SOPs: Acceptable Manual Integration Practices / CA-Q-S-002, Calibration Curves and Selection of Calibration Points / CA-Q-P-003, Waste Disposal / NV10-83, Training Procedures for Technical Staff / NV08-199, Detection Limits / CA-Q-S-006, Reagent and Standard Purchase / NV08-214, Sample Homogenization, Sub-sampling & Compositing / NV08-229, 5030 602 624 SM6200 B / NV05-107, 5035 / NV05-108.
15.11 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications for 8260

State	Modification
Ohio specific criteria	Only those compounds in EPA Method 8260B may be reported (superscript 1 in the table in Section 1.1). Some compounds in this SOP are not part of the original 8260B method. The method blank must be less than the RL for Ohio samples. See SOP 8260/NVOH05-77.
Missouri GRO	Prepare 1:1 mixture of unleaded gasoline and #2 diesel fuel in Methanol as GRO is defined by setting retention time window from 0.1 minutes before C_6 to 0.1 minutes after C_{10}. Verify RT window with the standard daily (every 24 hours).
California GRO	California LUFT GRO uses gasoline and the retention time window of C_4 (t-Butanol) to C_{12}.
Michigan GRO	See the Michigan GRO requirements below.
South Carolina	See the special LCS acceptance criteria and special state PQL requirements below.
Minnesota	See the special Ethanol analysis requirements below for water samples.

TPH-GRO by Method 8260B/C

Standards

- C4-C12 Standards
  - Primary: Restek 30096, 5000 µg/mL, or equivalent.
  - Secondary: O2SI 020246-S6, 10,000 µg/mL, or equivalent.
- C6-C10 Standards
  - Primary: Restek 31484, 20,000 µg/mL, or equivalent.
  - Secondary: Ultra CUS-8324, 10,000 µg/mL, or equivalent.

Sample Preservation

- Missouri no longer requires TSP preservation.

Sample Introduction

- Samples are purged onto the GC/MS system using all protocols specified in SW-846 Method 5030 and 5035.
- Surrogates and internal standards specified by Method 8260B are added to water and soil samples prior to purging.

Sample Analysis

- The GC/MS system is tuned to BFB tune criteria listed in Method 8260B at the frequency specified in Method 8260B.
- A 5-point standard curve is used to quantitate TPH-GRO by the internal standard technique.
- For **Missouri** GRO, the stock standard solution is unleaded gasoline.
- For **Californi**a GRO, the stock standard is unleaded gasoline.
- The lowest calibration standard should be at or below the reporting limit of the method.
- For **Missouri,** retention time windows are defined for TPH-GRO by analyzing a standard containing C_6 and C_{10}. The retention time window is defined as 0.1 minute before C_6 to 0.1 minute after C_{10}. The standard containing C_6 and C_{10} **must** be analyzed every day samples are analyzed in order to verify that the retention time windows are constant.
- For **California**, the retention time windows are defined as 0.1 minute before C_5 to 0.1 minute before C_{12}.
- For **Michigan**,
  - Use unleaded gasoline for calibration.
  - The retention time window is defined as C_6 (Hexane) to C_{10} (n-Decane).
  - The holding time for water and soil is 14 days.
  - For soil preparation, shake the Methanol and sample for 2 minutes, then sonicate in a water bath for 20 minutes.
  - For oil samples, add 2 g sample to 40 mL Methanol; wait 24 hours before analysis.
  - Use the internal calibration technique, summing the range.
  - Use only linear regression; $r \geq 0.990$, $r^2 \geq 0.981$.
  - ICV and CCV must be ± 20% true.
- Because the retention time window is several minutes wide for TPH-GRO, the GC/MS data system may not accurately or appropriately establish the proper baseline for calibration or quantitation. The analyst **must** visually examine the computer-generated baseline for every analytical run and manually adjust the baseline when needed. A properly drawn baseline must extend over the entire retention time window and include the area under the entire TPH-GRO series of peaks. It is not appropriate to draw the baseline “peak to peak.”
- The total ion chromatogram (TIC) **must** be used to calculate the area under the peak for TPH-GRO calibration and quantitation determinations over the entire retention time window.
- Area counts for the internal standards and surrogates added during sample preparation **must** be subtracted from the total area count for TPH-GRO. This is accomplished by subtracting the area count of the method blank from all subsequent calibration and analytical runs.
- The %RSD for the calibration curve for TPH-GRO must be less than or equal to 20%, so that linearity through the origin can be assumed and an average calibration factor used for calculations.

- A continuing calibration verification standard (CCV) must be analyzed at the beginning of each batch. The standard concentration should be at the mid-point of the calibration curve. If the %RSD exceeds 20%, a new curve must be generated.
- A method blank must be analyzed once per day to insure the analytical system is free of background contamination.

South Carolina LCS Acceptance Criteria and Special State PQL Requirements

- All routinely reported analytes require 70-130% LCS recovery except for 1,2-Dibromoethane (Ethylene dibromide. EDB), 60-140% recovery.
- Instrumentation used for South Carolina samples must be able to achieve and report the following South Carolina PQLs when those compounds are requested:
  - Acrolein 5 ug/L
  - Acrylonitrile 5 ug/L
  - 2-Chloroethyl vinyl ether 5 ug/L
  - Methylene chloride 2 ug/L

Minnesota Ethanol Analysis Requirements for Water Samples

- The calibration standard used for Ethanol must be a water-based standard and not a Methanol-based standard. Ethanol water-based standards must be stored at <4^{o}C.
- Initial calibration: The recovery (accuracy) for each point in the curve must be 70-130% except for the lowest point in the curve which must be 60-140%.
- Continuing calibration verification: Analyze one low-level Ethanol standard at the report level (RL) and one mid-level Ethanol calibration verification standard at approximately 500 µg/L prior to the samples. %R for Ethanol in the low-level standard must be 60-140% of the true value. %R for Ethanol in the mid-level standards must be 70-130% of the true value and a % difference of ≤ 30%.
- For samples, absolute areas of the quantitation ions for the internal standard and surrogate must not decrease by more than 50% from the initial calibration.
- %R for Ethanol for the MS/MSD must be 70-130% with a relative percent difference (RPD) of ≤30%. %R for the LCS/LCSD must be 70-130% with a RPD ≤ 30%.
- The quantitation ion for Ethanol is 45 atomic mass units (AMU). Confirmation ions are 46 and 47 AMU. Ethanol standards must be analyzed separately from the normal VOC list due to the interference from Ethyl ether.

17.0 Attachments

17.1 Attachment 1, Characteristic Masses (m/z) for Purgeable Organic Compounds.

17.2 Attachment 2, Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation.

Attachment 1, Characteristic Masses (m/z) for Purgeable Organic Compounds

Compound	Primary Characteristic Ion	Secondary Characteristic Ion
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,1-Trichloroethane	97	99, 61
1,1,2,2-Tetrachloroethane	83	131, 85
1,1,2-Trichloro-1,2,2-trifluoroethane	101	151, 103, 153
1,1,2-Trichloroethane	97	83, 85
1,1-Dichloroethane	63	65, 83
1,1-Dichloroethene	96	61, 63

Compound	Primary Characteristic Ion	Secondary Characteristic Ion
1,1-Dichloropropene	75	110, 77
1,2,3-Trichlorobenzene	180	182, 145
1,2,3-Trichloropropane	110	75, 77
1,2,3-Trimethylbenzene	105	120, 77
1,2,4-Trichlorobenzene	180	182, 145
1,2,4-Trimethylbenzene	105	120
1,2-Dibromo-3-chloropropane (DBCP)	157	155, 75
1,2-Dichlorobenzene	146	111,148
1,2-Dichloroethane	62	98
1,2-Dichloropropane	63	112
1,3,5-Trichlorobenzene	180	145, 182
1,3,5-Trimethylbenzene	105	120
1,3-Dichlorobenzene	146	111, 148
1,3-Dichloropropane	76	78
1,4-Dichlorobenzene	146	111, 148
1,4-Dioxane	88	58, 43, 57
2,2-Dichloropropane	77	97
2-Butanone (MEK)	72	43
2-Chloro-1,3-butadiene (Chloroprene)	53	88, 90, 51
2-Chloroethyl vinyl ether	63	65, 106
2-Chlorotoluene	91	126
2-Hexanone	58	43, 57, 100
2-Methyl-2-propanol (t-butyl alcohol)	59	41, 43
2-Methylnaphthalene	142	141, 115
2-Nitropropane	43	41, 39
3,3-Dimethyl-1-butanol	57	69, 41
3-Chloro-1-propene (Allyl chloride)	76	78
4-Chlorotoluene	91	126
4-Isopropyltoluene (p-Isopropyltoluene)	119	134, 91
4-Methyl-2-pentanone (MIBK)	58	43, 100, 85
Acetone	58	43
Acetonitrile	41	40, 39
Acrolein	56	55
Acrylonitrile	53	52, 51
Benzene	78	--
Benzyl chloride	91	126, 65, 128
Bromobenzene	77	156, 158
Bromoform	173	175, 254
Bromomethane	96	94
Butadiene	54	53, 39
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chlorobenzene	112	77, 114
Chlorobromomethane	130	49, 128
Chlorodibromomethane	127	129
Chloroethane	64	66 (51*)
Chloroform	83	85
Chloromethane	50	52 (51*)
cis-1,2-Dichloroethene	61	96, 98
cis-1,3-Dichloropropene	75	77, 39

Compound	Primary Characteristic Ion	Secondary Characteristic Ion
Cyclohexane	56	84, 41, 69
Cyclohexanone	55	42, 98
Dibromomethane	93	95, 174
Dichlorobromomethane	83	85, 127
Dichlorodifluoromethane	85	87
Dichlorofluoromethane	67	69
Ethanol	45	46
Ethyl acetate	43	45, 61, 88
Ethyl acrylate	55	56
Ethyl ether (Diethyl ether)	59	45, 74
Ethyl methacrylate	69	41, 99, 86
Ethylbenzene	91	106
Ethylene dibromide (EDB, 1,2-Dibromoethane)	107	109, 188
Hexachlorobutadiene	225	223, 227
Hexane	57	41, 43, 56
Iodomethane	142	127, 141
Isobutyl alcohol	43	41, 42, 74
Isopropyl alcohol	45	59
Isopropylbenzene	105	120
Isopropylether (IPE, Diisopropyl ether))	45	87, 59
m, p-Xylene	91	106
Methacrylonitrile	41	67, 39, 52
Methyl acetate	43	74, 59
Methyl methacrylate	41	69, 100, 39
Methylcyclohexane	83	55, 98, 41
Methylene chloride	84	86, 49
Methyl-t-butyl ether (MTBE)	73	57, 43
Naphthalene	128	-
n-Butanol (n-Butyl alcohol)	56	41, 43
n-Butyl acetate	43	56, 73, 61
n-Butylbenzene	91	92, 134
n-Propylbenzene	91	120
o-Xylene	91	106
Pentachloroethane	167	165, 169, 117, 83
Propionitrile (ethyl cyanide)	54	52, 55
sec-Butylbenzene	105	134
Styrene	104	78
tert-Amyl alcohol	59	55, 73, 43
tert-Amyl ethyl ether (TAME)	73	55, 87, 43
tert-Butyl ethyl ether (ETBE)	59	87, 41
tert-Butyl formate (TBF)	59	57, 41
tert-Butylbenzene	119	91, 134
Tetrachloroethene	166	129, 131, 164
Tetrahydrofuran	42	41, 71, 72
Toluene	91	92
trans-1,2-Dichloroethene	61	96, 98
trans-1,3-Dichloropropene	75	77, 39
trans-1,4-Dichloro-2-butene	53	88, 89
Trichloroethene	130	97, 95, 132
Trichlorofluoromethane	101	103, 105

Compound	Primary Characteristic Ion	Secondary Characteristic Ion
Vinyl acetate	43	86
Vinyl chloride	62	84
Internal Standards/Surrogates:		
Fluorobenzene	96	70
Chlorobenzene-d_5	117	82
1,4-Dichlorobenzene-d_4	152	115, 78
4-Bromofluorobenzene	95	174, 176
Dibromofluoromethane	111	113
1,2-Dichloroethane-d_4	65	67, 51
Toluene-d_8	98	100

Attachment 2, Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Fluorobenzene	Chlorobenzene-d_5	1,4-Dichlorobenzene-d_4
1,1,1-Trichloroethane	1,1,1,2-Tetrachloroethane	1,1,2,2-Tetrachloroethane
1,1,2-Trichloro-1,2,2-trifluoroethane	1,1,2-Trichloroethane	1,2,3-Trichlorobenzene
1,1-Dichloroethane	1,3-Dichloropropane	1,2,3-Trichloropropane
1,1-Dichloroethene	2-Chloroethylvinylether	1,2,3-Trimethylbenzene
1,1-Dichloropropene	2-Hexanone	1,2,4-Trichlorobenzene
1,2-Dichloroethane	3,3-Dimethyl-1-butanol	1,2,4-Trimethylbenzene
1,2-Dichloroethane-d_4 (s)	4-Methyl-2-pentanone (MIBK)	1,2-Dibromo-3-chloropropane (DBCP)
1,2-Dichloropropane	Benzyl chloride	1,2-Dichlorobenzene
1,4-Dioxane	Bromoform	1,3,5-Trichlorobenzene
2,2-Dichloropropane	Chlorobenzene	1,3,5-Trimethylbenzene
2-Butanone	Chlorodibromomethane	1,3-Dichlorobenzene
2-Chloro-1,3-butadiene (Chloro-prene)	cis-1,3-Dichloropropene	1,4-Dichlorobenzene
2-Methyl-2-propanol (tert-Butyl alcohol)	Ethyl methacrylate	2-Chlorotoluene
2-Nitropropane	Ethylbenzene	2-Methylnaphthalene
3-Chloro-1-propene (Allyl chloride)	Ethylene dibromide (1,2-Dibromoethane)	4-Chlorotoluene
Acetone	Isopropylbenzene	4-Isopropyltoluene (p-Isopropyltoluene)
Acetonitrile	m,p-Xylene	Bromobenzene
Acrolein	o-Xylene	Bromofluorobenzene (s)
Acrylonitrile	Styrene	Hexachlorobutadiene
Benzene	Tetrachoroethene	Naphthalene
Butadiene	Toluene	n-Butylbenzene
Chlorobromomethane	Toluene-d8 (s)	n-Propylbenzene
Bromomethane	trans-1,3-Dichloropropene	Pentachloroethane
Carbon disulfide		sec-Butylbenzene
Carbon tetrachloride		tert-Buylbenzene
Chloroethane		trans-1,4-Dichloro-2-butene

Fluorobenzene	Chlorobenzene-d_5	1,4-Dichlorobenzene-d_4
Chloroform		
Chloromethane		
cis-1,2-Dichloroethene		
Cyclohexane		
Cyclohexanone		
Dibromofluoromethane (s)		
Dibromomethane		
Dichlorobromomethane		
Dichlorodifluoromethane		
Dichlorofluoromethane		
Isopropyl ether (IPE, Diisopropyl ether)		
Ethanol		
Ethyl acetate		
Ethyl acrylate		
Ethyl ether (Diethyl ether)		
Hexane		
Iodomethane		
Isobutyl alcohol (Isobutanol)		
Isopropyl alcohol (Isopropanol)		
Methacrylonitrile		
Methyl acetate		
Methyl cyclohexane		
Methyl methacrylate		
Methylene chloride		
Methyl-tert-butyl ether (MTBE)		
n-Butanol (n-Butyl alcohol)		
n-Butyl acetate		
n-Heptane		
Propionitrile		
t-Amyl alcohol		
tert-Amyl methyl ether (TAME)		
tert-Butyl ethyl ether (ETBE)		
tert-Butyl formate		
Tetrahydrofuran		
trans-1,2-Dichloroethene		
Trichloroethene		
Trichlorofluoromethane		
Vinyl acetate		
Vinyl chloride		

18.0 Revision History

- Revision 12, 10 October 2008
  - Integration for TestAmerica and STL operations.
  - Insert corrective action procedures
- Revision 13, 25 September 2009
  - Move QC summary table and QC sample preparation instructions into Section 9.
  - Addition of new analytes: 3,3-Dimethyl-1-butanol (SC) and 1,3,5-Trichlorobenzene (NH).
  - Addition of Attachment 3 for South Carolina.

- Revision 14, 6 November 2009
  - Corporate review.
  - Addition of single-point surrogate calibration.
  - Incorporate Michigan GRO requirements.
- Revision 15, 30 October 2010
  - Addition of Amendments a (SC PQLs, Attachment 3), b (characteristic ions for 1,2,3-Trichloropropane), and c (WI soil extraction procedure).
  - Addition of new analytes: 1-Methylnaphthalene (New Mexico), Pentane, Octane, Nonane (Paraffin group).
  - Addition of QAF-45 and Section 14.2.
- Revision 16, 30 September 2011
  - Organizational changes.
  - Addition of requirement for non-preserved sample if 2-Chloroethyl vinyl ether is analyzed.
  - Addition of Minnesota Ethanol analysis requirements to Section 16.0.
  - Addition of reference to SOPs Calibration Curves (General) and Acceptable Manual Integration Practices / CA-Q-S-002.
  - Addition of 2-Chloroethyl vinyl ether, Acrolein, and Acrylonitrile preservation information.
- Revision 17, 29 February 2012
  - Organizational changes.
  - Addition of Bromoform Breakdown Check.
  - Remove paraffin standard reference.
  - TPH-GRO: change CCC frequency.
  - Corrected weighting equations.
- Revision 18, dated 30 August 2013
  - Organizational changes.
  - Specify that $r^2 \geq 0.990$.
  - OK no longer limits batch size to 10 samples.
  - Add Amendment a.
  - Add 8260C.
  - Add new standards and new analytes.
  - Change the LCS, MS, MSD to use the primary standard.
  - MA also requires LCSD.
  - Addition of GRO standards
- Revision 19, dated 29 August 2014
  - Organizational changes.
  - Amendment 18a: Section 1.2, Correct RLs for TAA, IPA, Allyl chloride, 3,3-Dimethyl-1-butanol; Section 9.2, Correct ICAP acceptance criteria (removed RF references); Section 9.2, Add 8260C minimum RF for 1,2-Dichloro-3-propane, Remove references to RF percentages; Section 9.2, Clarify 8260B criterion for allowing 20% of analytes failure; Section 9.2, Clarify 8260C CCV % difference and minimum RF requirements.
  - Amendment 18b, Section 9.2, BFB Tuning and Breakdown check: Add upper %recovery criterion for m/z 174.
  - Amendment 18c, Sections 3.0 and 10.5,Add Q-value definition and criteria.
  - Correct characteristic ions for 1,2,3-Trimethylbenzene, Butadiene, and Ethyl acrylate.
  - West Virginia no longer requires LCSDs.
  - Modification of SC requirements in Section 17.0, Attachments.
- Revision 20, dated 30 June 2015.
  - Organizational changes.

- Combination of 8260 / NV05-77.19a, 19b, 624 / NV05-66.9c, and SM6200 B / NV05-236.4a into one SOP and addition of:
  - 8260-19a: Addition of SIM.
  - 8260-19b: Add information for high-molecular-weight compounds and carryover.
  - 8260-19c: Add note about not being SC-certified for 8260 SIM and modify the HMW carryover criteria.
  - 624-9a: Clarify 174 m/z BFB mass intensity criterion.
  - 624-9b: Add Q-value definition and acceptance criterion.
  - 624-9c: Update primary standards vendor sources.
  - SM6200 B-4a: Updates added to 8260 and 624.
- Add 1,4-Dioxane to the list of analytes with poor purge efficiencies (ICV).
- Add more specific information about to Missouri GRO carbon range windows.
- Add new information for TIC evaluations.
- Specified pH and residual chlorine checks for methods and states.
- Replace SOP Determination of Method Detection Limits / NV08-202 with Detection Limits / CA-Q-S-006.

SOP Number/Revision No.: **8270 625 / NV04-22.17** Effective Date: **12/14/2015**

Last Mod. Date: **4/30/15**

SOP Title: **Method 8270C/D 625: Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS)**

CONTROLLED DISTRIBUTION

ISSUED TO: \\TAFS\Lab\Nashville\Public\QA\SOPs, 04B

Revision Number with Mod ID: **17a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Delete crossed-out text. Add highlighted text.

Section 1.1, Analyte, Matrices, add to list of analytes

CAS Number	8270 Analytes	625 Analytes
123-91-9	*1,4-Dioxane*[5]	*1,4-Dioxane*[3]
	[5] - Compounds that are available by GC/MS-SIM (by request only)	[3] - Compounds that are available by GC/MS-SIM (by request only)

Section 1.2, Reporting Limits (RLs) / Lower Limit of Quantitation (LLOQs, 8270D): The laboratory typical RL/LLOQ ~~report limit (RL)~~ is approximately 2 - 100 µg/L for water samples, 67 - 670 µg/kg (wet weight) for soil/sediment samples, 10 - 1000 mg/kg for wastes (dependent on matrix and method of preparation), and 100 µg/wipe or 100 µg/100 cm^2 surface area wiped for each compound. See the following table for typical RLs/LLOQs for each compound. For the most current analyte RLs/LLOQs, refer to LIMS.

Typical Reporting Limits/Lower Limits of Quantitation

Analyte	Water RL/LLOQ µg/L	Soil RL/LLOQ mg/kg	Analyte	Water RL/LLOQ µg/L	Soil RL/LLOQ mg/kg

Section 3.0, Definitions, add a new definition:

Lower Limit of Quantitation (LLOQ) for 8270D: The lowest point of Quantitation, or in most cases, the lowest point in the calibration curve, which is ideally less than or equal to the desired regulatory action level.

Section 9.1, Sample QC:

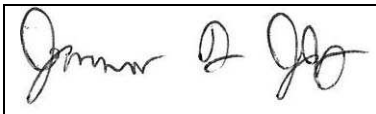
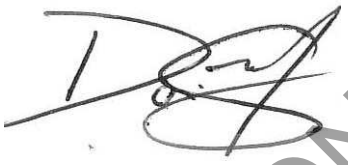
The following QC samples are run with <u>each batch of no more than 20 samples.</u>			
QC Check	Frequency	Acceptance Criteria[1]	**Corrective Action[2]**
Method blank	One per analytical prep batch	No analytes detected ≥ ½ RL (LLOQ for 8270D) or MDL, whichever is greater	Correct problem then re-prep[3] and analyze method blank and all samples processed with the contaminated blank.

Section 12.1, Method Detection Limit Study (MDL) for 8270C, 625 only:

Section 12.__, Lower Limit of Quantitation (LLOQ) for 8270D: The LLOQ is initially verified by the analysis of at least 7 replicate samples, spiked at the LLOQ and processed through all preparation and analysis steps of the method. The permitted mean recovery and RSD is within in-house limits (or within 80-120% initially). Annual verification uses a clean matrix sample spiked at 0.5 to 2 times the LLOQ and prepared and analyzed as a sample. All instruments must be LLOQ-verified on a three-year rotation. Reporting below the LLOQ is qualified as estimated.

Section 12.2, Demonstration of Capability for 8270C, 625, Initial Demonstration of Proficiency (IDP) for 8270D: Add to the paragraph: **For 8270D (2014)**, spike the clean matrix with the same standard as that used for calibration.

Section 15, References / Cross-References, add the new reference:
Method 8270D, SWS-846 Update V, Revision 5, July 2014.

 12/9/15	
Department Manager Approval Date	
 12/9/15	 12/8/15
Quality Assurance Approval Date	Technical Director Approval Date

Title: SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) EPA METHODS 8270C/D AND 625

Approvals (Signature/Date)

Steve Miller 4/17/15	Ryan Fitzwater 4/17/15
Steve Miller Date	Ryan Fitzwater Date
Quality Assurance Manager	Organic Operations Manager Health & Safety Manager / Coordinator
Michael H. Dunn 4/17/15	
Michael H. Dunn Date	
Technical Director	

Analyze and report by 8270D for **NJ, NC, OK, SC, and WV** samples.
TestAmerica Nashville is not SC-certified for 8270 SIM or LVI.

1.0 Scope and Application

1.1 Analyte, Matrices: This method is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of oily wastes, soils/sediments, concrete, wipes, wastewater, surface water, leachates, and groundwater samples. In general, the methods are applicable as follows:

Method Reference	Appropriate Use
8270	GC/MS method for semivolatiles for groundwaters and solids.
3510	Extraction technique for groundwaters (RCRA). See SOP 3510 608 608.2 610 625 /NV03-23.
3541 3546 3550	Extraction technique for solids (RCRA). See SOP 3541 / NV03-231. See SOP 3546 / NV03-247. See SOP 3550 / NV03-24.
3580	Extraction technique for oils and wipes (RCRA). See SOP 3580 / NV03-106.
625	Extraction technique and GC/MS for semivolatiles for wastewaters, surface waters (Clean Water Act). For this SOP, see SOP 3510 608 608.2 610 625 /NV04-24 for the 625 extraction technique.

The following compounds can be determined by this method:

CAS Number	8270 Analytes	625 Analytes
95-94-3	1,2,4,5-Tetrachlorobenzene[2]	1,2,4,5-Tetrachlorobenzene[2]
120-82-1	1,2,4-Trichlorobenzene[1, 2]	1,2,4-Trichlorobenzene[1, 2]
955-50-1	1,2-Dichlorobenzene[1, 2, 4]	1,2-Dichlorobenzene[1]
2199-69-1	1,2-Dichlorobenzene-d_4 (surr)	1,2-Dichlorobenzene-d_4 (surr)
122-66-7	1,2-Diphenylhydrazine[3]	1,2-Diphenylhydrazine[2]
99-35-4	1,3,5-Trinitrobenzene[2]	
541-73-1	1,3-Dichlorobenzene[1, 2, 4]	1,3-Dichlorobenzene[1]
99-65-0	1,3-Dinitrobenzene[2]	
106-46-7	1,4-Dichlorobenzene[1, 2, 4]	1,4-Dichlorobenzene[1]
3855-82-1	1,4-Dichlorobenzene-d_4 (IS)	1,4-Dichlorobenzene-d_4 (IS)
123-91-9	*1,4-Dioxane*[5]	
130-15-4	1,4-Naphthoquinone[2]	
106-50-3	1,4-Phenylenediamine[2]	
90-13-1	1-Chloronaphthalene[3]	
90-12-0	*1-Methylnaphthalene*[3, 4, 5]	1-Methylnaphthalene[2, 3]
134-32-7	1-Naphthylamine[2]	
58-90-2	2,3,4,6-Tetrachlorophenol[2]	
608-27-5	*2,3-Dichloroaniline*[3]	*2,3-Dichloroaniline*[2]
95-95-4	2,4,5-Trichlorophenol[1, 2]	2,4,5-Trichlorophenol[1]
118-79-6	2,4,6-Tribromophenol (surr)	2,4,6-Tribromophenol (surr)
88-06-2	2,4,6-Trichlorophenol[1, 2]	2,4,6-Trichlorophenol[1]
120-83-2	2,4-Dichlorophenol[1, 2]	2,4-Dichlorophenol[1]
105-67-9	2,4-Dimethylphenol[1, 2, 4]	2,4-Dimethylphenol[1]
51-28-5	2,4-Dinitrophenol[1, 2, 4]	
121-14-2	2,4-Dinitrotoluene[1, 2, 5]	2,4-Dinitrotoluene[1, 3]
87-65-0	2,6-Dichlorophenol[2]	
606-20-2	2,6-Dinitrotoluene[1, 2, 5]	2,6-Dinitrotoluene[1, 3]
53-96-3	2-Acetylaminofluorene[2]	
91-58-7	2-Chloronaphthalene[1, 2]	2-Chloronaphthalene[1]
95-57-8	2-Chlorophenol[1, 2]	2-Chlorophenol[1]

CAS Number	8270 Analytes	625 Analytes
93951-73-6	*2-Chlorophenol-d_4 (surr)*	*2-Chlorophenol-d_4 (surr)*
321-60-8	2-Fluorobiphenyl (surr)	2-Fluorobiphenyl(surr)
367-12-4	2-Fluorophenol (surr)	2-Fluorophenol (surr)
91-57-6	2-Methylnaphthalene[1, 2, 5]	2-Methylnaphthalene[2, 3]
95-48-7	2-Methylphenol[1, 2, 4]	2-Methylphenol[1]
91-59-8	2-Naphthylamine[2]	
88-74-4	2-Nitroaniline[1, 2]	
88-75-5	2-Nitrophenol[1]	2-Nitrophenol[1]
109-06-8	2-Picoline (2-Methylpyridine)[2]	
91-94-1	3,3'-Dichlorobenzidine[1, 2]	3,3'-Dichlorobenzidine[1]
119-93-7	3,3'-Dimethylbenzidine[2]	
95-77-2		*3,4-Dichlorophenol*[2]
56-49-5	3-Methylcholanthrene[2]	
108-39-4	3-Methylphenol[1, 2, 4]	3-Methylphenol[1]
99-09-2	3-Nitroaniline[1, 2]	
101-14-4	4,4'-Methylenebis(2-chloroaniline) (MOCA)[3]	
534-52-1	4,6-Dinitro-2-methylphenol[1, 2, 5]	2-Methyl-4,6-dinitrophenol[1, 3]
92-67-1	4-Aminobiphenyl[2]	
101-55-3	4-Bromophenyl phenylether[1, 2]	4-Bromophenyl phenylether[1]
59-50-7	4-Chloro-3-methylphenol[1, 2]	4-Chloro-3-methylphenol[1]
106-47-8	4-Chloroaniline[1, 2]	
7005-72-3	4-Chlorophenyl phenylether[2]	4-Chlorophenyl phenylether[1]
106-44-5	4-Methylphenol[1, 2, 4]	4-Methylphenol[1]
100-01-6	4-Nitroaniline[1, 2]	
100-02-7	4-Nitrophenol[1, 2]	4-Nitrophenol[1]
99-55-8	5-Nitro-o-toluidine[2]	
1705-85-7	*6-Methyl chrysene*[4]	
57-97-6	7,12-Dimethylbenz(a)anthracene[2, 4]	
122-09-8	a,a- Dimethylphenylethylamine[2]	
83-32-9	Acenaphthene[1, 2, 5]	Acenaphthene[1, 3]
15067-26-2	Acenaphthene-d_{10} (IS)	Acenaphthene-d_{10} (IS)
208-96-8	Acenaphthylene[1, 2, 5]	Acenaphthylene[1, 3]
98-86-2	Acetophenone[2]	Acetophenone[2]
7785-53-7	*Alpha-Terpineol*[3]	*Alpha-Terpineol*[2]
62-53-3	Aniline[2]	Aniline[2]
120-12-7	Anthracene[1, 2, 4, 5]	Anthracene[1, 3]
140-57-8	Aramite[2]	
1912-24-9	*Atrazine*	
103-33-3	*Azobenzene*[3]	
56-55-3	Benz(a)anthracene[1, 2, 4, 5]	Benz(a)anthracene[1, 3]
100-52-7	Benzaldehyde	
92-87-5	Benzidine[3]	Benzidine[2]
50-32-8	Benzo(a)pyrene[1, 2, 4, 5]	Benzo(a)pyrene[1, 3]
197-97-2	*Benzo(e)pyrene*[3,5]	
205-99-2	Benzo(b)fluoranthene[1, 2, 4, 5]	Benzo(b)fluoranthene[1, 3]
191-24-2	Benzo(g,h,i)perylene[1, 2, 5]	Benzo(g,h,i)perylene[1, 3]
205-85-3	*Benzo(j)fluoranthene*[4]	
207-08-9	Benzo(k)fluoranthene[1, 2, 4, 5]	Benzo(k)fluoranthene[1, 3]
65-85-0	Benzoic acid[3]	Benzoic acid[2]
100-51-6	Benzyl alcohol[2]	Benzyl alcohol[2]
92-54	Biphenyl (1,1'-Biphenyl)	
111-91-1	Bis(2-chloroethoxy)methane[1, 2]	Bis(2-chloroethoxy)methane[1]
111-44-4	Bis(2-chloroethyl)ether[1, 2, 5]	Bis(2-chloroethyl)ether[1, 3]
108-60-1	Bis(2-chloroisopropyl)ether[1, 2] (2,2'-oxybis[1-	Bis(2-chloroisopropyl)ether[1] (2,2'-

CAS Number	8270 Analytes	625 Analytes
	chloropropane])	oxybis[1-chloropropane])
103-23-1	*Bis(2-ethylhexyl)adipate*[3]	
117-81-7	Bis(2-ethylhexyl)phthalate[1, 2, 4, 5]	Bis(2-ethylhexyl)phthalate[1, 3]
80-05-7	*Bisphenol A*[3]	
85-68-7	Butyl benzyl phthalate[1, 2, 4]	Butyl benzyl phthalate[1]
105-60-2	*Caprolactam*	
86-74-8	*Carbazole*[1]	Carbazole[2]
510-15-6	Chlorobenzilate[2]	
218-01-9	Chrysene[1, 2, 4, 5]	Chrysene[1, 3]
1719-03-5	Chrysene-d_{12} (IS)	Chrysene-d_{12} (IS)
17627-76-8	*cis-Isosafrole*[2]	
2303-16-4	Diallate (cis and trans)[2]	2,4-Dinitrophenol[1]
226-36-8	*Dibenz(a,h)acridine*[4]	
53-70-3	Dibenz(a,h)anthracene[1, 2, 4, 5]	Dibenz(a,h)anthracene[1]
224-42-0	*Dibenz(a,j)acridine*[3]	
132-64-9	Dibenzofuran[1, 2, 5]	Dibenzofuran[2, 3]
84-66-2	Diethyl phthalate[1, 2, 4]	Diethyl phthalate[1]
60-51-5	Dimethoate[2]	
131-11-3	Dimethyl phthalate[1, 2, 4]	Dimethyl phthalate[1]
60-11-7	Dimethylaminoazobenzene[2]	
84-74-2	Di-n-butyl phthalate[1, 2, 4]	Di-n-butyl phthalate[1]
117-84-0	Di-n-octyl phthalate[1, 2, 4]	Di-n-octyl phthalate[1]
88-85-7	Dinoseb[2]	
298-04-4	Disulfoton[2]	
62-50-0	Ethyl methanesulfonate[2]	
52-85-7	Famphur[3]	
206-44-0	Fluoranthene[1, 2, 4, 5]	Fluoranthene[1, 3]
86-73-7	Fluorene[1, 2, 5]	Fluorene[1, 3]
118-74-1	Hexachlorobenzene[1, 2, 5]	Hexachlorobenzene[1, 3]
87-68-3	Hexachlorobutadiene[1, 5]	Hexachlorobutadiene[1, 3]
77-47-4	Hexachlorocyclopentadiene[1, 2, 5]	Hexachlorocyclopentadiene[1, 2, 3]
67-72-1	Hexachloroethane[1, 2]	Hexachloroethane[1, 2]
70-30-4	Hexachlorophene[2]	Hexachlorophene[2]
1888-71-7	Hexachloropropene[2]	
95-13-6	*Indene*[4]	
193-39-5	Indeno(1,2,3-cd)pyrene[1, 2, 5]	Indeno(1,2,3-cd)pyrene[1, 3]
465-73-6	Isodrin[2]	
78-59-1	Isophorone[1, 2]	Isophorone[1]
143-50-0	Kepone[2]	
91-80-5	Methapyrilene[2]	
66-27-3	Methyl methanesulfonate[2]	
298-00-0	Methyl parathion[2]	
91-20-3	Naphthalene[1, 2, 4, 5]	Naphthalene[1, 3]
1146-65-2	Naphthalene-d_8 (IS)	Naphthalene-d_8 (IS)
124-18-5	*n-Decane*[3]	n-Decane[2]
544-76-3	*n-Hexadecane*	
98-95-3	Nitrobenzene[1, 2]	Nitrobenzene[1]
4165-60-0	Nitrobenzene-d_5 (surr)	Nitrobenzene-d_5 (surr)
56-57-5	Nitroquinoline-1-oxide[2]	
55-18-5	n-Nitrosodiethylamine[2]	n-Nitrosodiethylamine[2]
62-75-9	n-Nitrosodimethylamine[2, 5]	n-Nitrosodimethylamine[2, 3]
924-16-3	n-Nitrosodi-n-butylamine[2]	n-Nitrosodi-n-butylamine[2]
621-64-7	n-Nitrosodi-n-propylamine[1, 2]	n-Nitrosodi-n-propylamine[1]

CAS Number	8270 Analytes	625 Analytes
86-30-6 122-39-4	n-Nitrosodiphenylamine[1, 2] Diphenylamine	n-Nitrosodiphenylamine[1] Diphenylamine
10595-95-6	n-Nitrosomethylethylamine[2]	
59-89-2	n-Nitrosomorpholine[2]	
100-75-4	n-Nitrosopiperidine[2]	
930-55-2	n-Nitrosopyrrolidine[2]	
593-45-3	*n-Octadecane*[3]	*n-Octadecane*[3]
126-68-1	o,o,o-Triethylphosphorothioate[2]	
95-53-4	o-Toluidine[2]	
56-38-2	Parathion[2]	
608-93-5	Pentachlorobenzene[2]	Pentachlorobenzene[2]
76-01-7	*Pentachloroethane*[2]	
82-68-8	Pentachloronitrobenzene[2]	
87-86-5	Pentachlorophenol[1, 2, 5]	Pentachlorophenol[1, 3]
1520-96-3	Perylene-d_{12} (IS)	Perylene-d_{12} (IS)
62-44-2	Phenacetin[2]	
85-01-8	Phenanthrene[1, 2, 4, 5]	Phenanthrene[1, 3]
1517-22-2	Phenanthrene-d_{10} (IS)	Phenanthrene-d_{10} (IS)
108-95-2	Phenol[1, 2, 4]	Phenol[1]
4165-62-2	Phenol-d_5 (surr)	Phenol-d_5 (surr)
298-02-2	Phorate[2]	
23950-58-5	Pronamide[2]	
129-00-0	Pyrene[1, 2, 4, 5]	Pyrene[1, 3]
110-86-1	Pyridine[2, 4]	Pyridine[2]
91-22-5	*Quinoline*[4]	
94-59-7	Safrole[2]	
1718-51-0	Terphenyl-d_{14} (surr)	Terphenyl-d_{14} (surr)
3689-24-5	*Tetraethyl dithiopyrophosphate (Sulfotepp)*[2]	
107-49-3	Tetraethylpyrophosphate[3]	
297-97-2	Thionazine[2]	
108-98-5	Thiophenol[4]	
4043-71-4	*trans-Isosafrole*[2]	
	Compounds in italics are not present in the EPA method.	[1] – Normal laboratory 625 compounds
	[1] – Normal laboratory 8270 compounds. ***For OH VAP projects, report only compounds designated by a 1 superscript; see Attachment 5.***	[2] - Additional compounds available by request only.
	[2] - Appendix IX compounds (by request only)	[3] - Compounds that are available by GC/MS-SIM (by request only)
	[3] - additional compounds available by this method (by request only)	
	[4] - Skinner List for Refinery Waste compounds (by request only)	
	[5] - Compounds that are available by GC/MS-SIM (by request only)	

IS = These compounds are used as internal standards.
surr = These compounds are used as surrogates.

This method is used to quantitate neutral, acidic, and basic organic compounds that are soluble in Methylene chloride and capable of being eluted, without derivatization, from a gas chromatographic fused-silica capillary column coated with a slightly polar methyl silicone phase. This method is not appropriate for the quantitation of multi-component analytes, e. g., Aroclors, Toxaphene, Chlordane, etc., because of limited sensitivity for those analyses. This method is

appropriate for confirmation of the presence of these analytes when concentration in the extract permits. However, it is appropriate for the multi-component analyte, Diesel Range Organics (DRO), as requested by Missouri and California; see Attachment 6.

1.2 Reporting Limits: The laboratory typical report limit (RL) is approximately 2 - 100 µg/L for water samples, 67 - 670 µg/kg (wet weight) for soil/sediment samples, 10 - 1000 mg/kg for wastes (dependent on matrix and method of preparation), and 100 µg/wipe or 100 µg/100 cm^2 surface area wiped for each compound. See the following table for typical RLs for each compound. For the most current analyte RLs, refer to LIMS.

Typical Reporting Limits

Analyte	Water RL µg/L	Soil RL mg/kg	Analyte	Water RL µg/L	Soil RL mg/kg
♦*Acenaphthene*	10	0.333	♣6-Methylchrysene	10	0.333
♦*Acenaphthylene*	10	0.333	♦Methyl methanesulfonate	10	0.333
♦*Acetophenone*	10	0.333	♣1-Methylnaphthalene	10	0.333
♦*2-Acetylaminofluorene*	10	0.333	♦2-Methylnaphthalene	10	0.333
♦*4-Aminobiphenyl*	10	0.333	♦Methyl parathion	10	1.67
♦*Aniline*	10	0.333	♦♣2-Methylphenol	10	0.333
♦♣*Anthracene*	10	0.333	♦♣3,4-Methylphenol	10	0.333
♦*Aramite*	50	1.67	♦♣Naphthalene	10	0.333
Atrazine	10	0.333	♦1,4-Naphthoquinone	10	1.67
Azobenzene	10	0.333	♦1-Naphthylamine	10	0.333
Benzaldehyde	10	1.67	♦2-Naphthylamine	10	0.333
Benzidine	100	1.67	♦2-Nitroaniline	25	0.833
Benzoic acid	50	1.67	♦3-Nitroaniline	25	0.833
♦♣*Benzo(a)anthracene*	10	0.333	♦4-Nitroaniline	25	0.833
♦♣*Benzo(a)pyrene*	10	0.333	♦Nitrobenzene	10	0.333
Benzo(e)pyrene	2	0.067	♦5-Nitro-o-toluidine	10	1.67
♦♣*Benzo(b)fluoranthene*	10	0.333	♦2-Nitrophenol	10	0.333
♦*Benzo(g,h,i)perylene*	10	0.333	♦♣4-Nitrophenol	25	0.833
♣*Benzo(j)fluoranthene*	10	0.333	♦Nitroquinoline-1-oxide	10	0.333
♦♣*Benzo(k)fluoranthene*	10	0.333	♦n-Nitrosodiethylamine	10	0.333
♦*Benzyl alcohol*	10	0.333	♦n-Nitroso-dimethylamine	10	0.333
Biphenyl	10	0.333	♦n-Nitrosodi-n-butylamine	10	1.67
♦*Bis(2-chloroethoxy) methane*	10	0.333	♦n-Nitroso-di-n-propyl-amine	10	0.333
♦*Bis(2-chloroethyl) ether*	10	0.333	♦n-Nitroso-diphenylamine and Diphenylamine	10	0.333
♦*Bis(2-chloroisopropyl) ether*	10	0.333	♦n-Nitrosomethylethylamine	10	0.333
♦♣*Bis(2-ethylhexyl) phthalate*	10	0.333	♦n-Nitrosomorpholine	10	1.67
♦*4-Bromophenylphenyl ether*	10	0.333	♦n-Nitrosopiperdine	10	1.67
♦♣*Butyl benzyl phthalate*	10	0.333	♦n-Nitrosopyrrolidine	10	1.67
Caprolactum	10	0.333	n-Octadecane	50	0.333
Carbazole	10	0.333	♦Parathion	10	1.67
♦*4-Chloro-3-methylphenol*	10	0.333	♦Pentachlorobenzene	10	1.67
♦*4-Chloroaniline*	10	0.333	♦Pentachloroethane	10	0.333
♦*Chlorobenzilate*	10	0.333	♦Pentachloronitrobenzene	10	1.67
1-Chloronaphthalene	10	0.333	♦Pentachlorophenol	25	0.833
♦*2-Chloronaphthalene*	10	0.333	♦Phenacetin	10	1.67
♦*2-Chlorophenol*	10	0.333	♦♣Phenanthrene	10	0.333
♦*4-Chlorophenylphenyl ether*	10	0.333	♦♣Phenol	10	0.333

Analyte	Water RL µg/L	Soil RL mg/kg	Analyte	Water RL µg/L	Soil RL mg/kg
♦♣*Chrysene*	10	0.333	♦1,4-Phenylenediamine	50	0.333
n-Decane			♦Phorate	10	0.333
♦*cis-Diallate*	10	0.333	♦2-Picoline	10	0.333
♦*trans-Diallate*	10	0.333	♦Pronamide	10	1.67
♦*Dibenzofuran*	10	0.333	♦♣Pyrene	10	0.333
♣*Dibenz(a,h)acridine*	10	0.333	♦♣Pyridine	10	0.67
Dibenz(a,j)acridine	10	0.333	♣Quinoline	10	0.333
♦♣*Dibenzo(a,h)anthracene*	10	0.333	♦Safrole	10	0.333
♦♣*1,2-Dichlorobenzene*	10	0.333	Terbufos	50	167
♦♣*1,3-Dichlorobenzene*	10	0.333	♦1,2,4,5-Tetrachlorobenzene	10	1.67
♦♣*1,4-Dichlorobenzene*	10	0.333	♦2,3,4,6-Tetrachlorophenol	10	0.333
♦*3,3'-Dichlorobenzidine*	10	0.333	♦Tetraethylpyrophosphate, Sulfotep	10	1.67
♦*2,4-Dichlorophenol*	10	0.333	♦Thionazine	10	1.67
♦*2,6-Dichlorophenol*	20	0.333	♣Thiophenol	50	1.67
3,4-Dichlorophenol	10	0.333	♦o-Toluidine	10	1.67
♦♣*Diethyl phthalate*	10	0.333	♦1,2,4-Trichlorobenzene	10	0.333
♦*Dimethoate*	10	1.67	♦2,4,5-Trichlorophenol	10	0..667
♦*p-Dimethylaminoazobenzene*	10	1.67	♦2,4,6-Trichlorophenol	10	0.333
♦*3,3'-Dimethylbenzidine*	50	0.333	♦o,o,o-Triethylphosphoro-thioate	10	1.67
♦♣*7,12-Dimethylbenz(a)an-thracene*	10	0.333	♦1,3,5-Trinitrobenzene	10	0.333
♦*a,a-Dimethylphenylethylamine*	50	1.67	1,4-Dioxane, SIM	3	
♦♣*2,4-Dimethylphenol*	10	0.333	4,6-Dinitro-2-methylphenol, SIM	1	
♦♣*Dimethyl phthalate*	10	0.333	Acenaphthene, SIM	0.1	0.00333
♦♣*Di-n-butyl phthalate*	10	0.333	Acenaphthylene, SIM	0.1	0.00333
♦*1,3-Dinitrobenzene*	10	1.67	Anthracene, SIM	0.1	0.00333
♦*4,6-Dinitro-2-methylphenol*	25	0.833	Benzo(a)anthracene, SIM	0.05	0.00333
♦♣*2,4-Dinitrophenol*	25	0.833	Benzo(a)pyrene, SIM	0.05	0.00333
♦*2,4-Dinitrotoluene*	10	0.333	Benzo(e)pyrene, SIM	0.1	0.00333
♦*2,6-Dinitrotoluene*	10	0.333	Benzo(b)fluoranthene, SIM	0.05	0.00333
♦♣*Di-n-octyl phthalate*	10	0.333	Benzo(g,h,i)perylene, SIM	0.1	0.00333
♦*Dinoseb*	10	0.333	Benzo(k)fluoranthene, SIM	0.1	0.00333
1,4-Dioxane	10	0.333	Bis(2-chloroethyl)ether, SIM	0.03	
1,2-Diphenylhydrazine	10	0.333	Bis(2-ethylhexyl)phthalate, SIM	2	
♦*Disulfoton*	10	1.67	Chrysene, SIM	0.1	0.00333
♦*Ethyl methanesulfonate*	10	0.333	Dibenzo(a,h)anthracene, SIM	0.05	0.00333
♦*Famphur*	10	0.333	Dibenzofuran, SIM	0.1	0.00333
♦♣*Fluoranthene*	10	0.333	2,4-Dinitrotoluene, SIM	0.05	0.0067
♦*Fluorene*	10	0.333	2,6-Dinitrotoluene, SIM	0.05	0.0067
♦*Hexachlorobenzene*	10	0.333	Fluoranthene, SIM	0.1	0.00333
♦*Hexachlorobutadiene*	10	0.333	Fluorene, SIM	0.1	0.00333
♦*Hexachlorocyclopentadiene*	10	0.333	Hexachlorobenzene, SIM	0.02	
♦*Hexachloroethane*	10	0.333	Hexachlorobutadiene, SIM	0.4	

Analyte	Water RL µg/L	Soil RL mg/kg	Analyte	Water RL µg/L	Soil RL mg/kg
♦*Hexachlorophene*	50	3.33	Hexachlorocyclopentadiene	0.5	
♦*Hexachloropropene*	50	3.33	Indeno(1,2,3-cd)pyrene, SIM	0.05	0.00333
n-Hexadecane	10		1-Methylnaphthalene, SIM	0.1	0.00333
♦*Indeno(1,2,3-c,d)pyrene*	10	0.333	2-Methylnaphthalene, SIM	0.1	0.00333
♣*Indene*	10	1.67	Naphthalene, SIM	0.1	0.00333
♦*Isodrin*	10	0.333	n-Nitrosodimethylamine, SIM	0.8	
♦*Isophorone*	10	0.333	Pentachlorophenol, SIM	0.3	
♦*Isosafrole*	50	1.67	Phenanthrene, SIM	0.1	0.00333
♦*Kepone*	10	0.333	Pyrene, SIM	0.1	0.00333
♦*Methapyrilene*	50	0.333	California / Missouri DRO	500	20
♦*3-Methylcholanthrene*	10	0.333	California / Missouri ORO	500	20

♦ indicates Appendix IX compound ♣Skinner List compound
Bold compounds are reported in a standard list.
Italicized compounds are only available upon special request by this method.
SIM = Selective Ion Monitoring

1.3 The following compounds may require special treatment when being determined by this method:

- Benzidine may be subject to oxidative losses during solvent concentration, and its chromatographic behavior is poor.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- n-Nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.
- n-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.
- Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
- Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. Use caution if modifying the injection port temperature as the performance of other analytes may be adversely affected.

1.4 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation. See SOPs 3510 610 625 / NV03-24 for waters, 3550 / NV03-23, 3546 / NV03-247, and 3541 / NV03-231 for soils and concrete, and 3580 / NV03-106 for oils and wipes, and, if necessary, sample cleanup procedures.

2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using at least a multi-point calibration curve.

3.0 Definitions

3.1 Reduced Volume Extraction / Large Volume Injection (RVE/LVI): The option to use a reduced sample volume for extraction combined with a larger volume extract injection on the instrument. Volumes for this option are shown in this document as RVE/LVI in brackets.

3.2 Q-value: Tentatively Identified Compound (TIC) quality value of spectra match to library spectra expressed as a percent.

3.3 See TestAmerica Nashville's Quality Assurance Manual for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe is rinsed with solvent between sample injections.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This method may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. Be aware of the locations of those zones, and cool them to room temperature prior to working on them.
- The mass spectrometer is under high vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.
- There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Causes coughing, dizziness, dullness, and headache.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Gas chromatography/mass spectrometer/data system
  - Gas chromatograph (HP or Agilent): Analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column is directly coupled to the source.
  - Column: 30 m x 0.25 mm ID with a 0.25 µm film thickness silicone-coated fused-silica capillary column (Phenomenex ZB-Semivolatiles 7HG-G027-11, or equivalent) [RVE/LVI: and a 5 m x 0.32 mm ID guard column (Phenomenex 7CG-G000-000-GZO, or equivalent].
  - Mass spectrometer capable of scanning from 35 to 500 amu every 1 second less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer is capable of producing a mass spectrum for Decafluorotriphenylphosphine (DFTPP) which meets the criteria in Table 2 when 1µL of the GC/MS tuning standard is injected (50 ηg or less of DFTPP).
  - Data system (Chemstation/Chrom): A computer system is interfaced to the mass spectrometer. The system allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer has software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software is also available that allows integrating the abundances in any EICP between specified time or scan-number limits. The EPA/NIST Mass Spectral Library is also available.
  - Suggested operating conditions (may vary by instrument; see maintenance log for current program):

Mass range:	35-500 amu
Scan time:	1 second/scan
Initial temperature:	40°C hold for 2 minutes
Temperature program:	Rate 1: 15°C/minute to 160°C
	Rate 2: 10°C/minute to 320°C
Final temperature:	320°C hold for at least 1.5 minute.
Injector temperature:	240-250°C

Transfer line temperature:	280°C
Source temperature:	According to manufacturer's specifications (nominally 250 – 275°C)
Injector:	Grob-type, split-less
Injection volume:	1 µL [RVE/LVI: 5 µL]
Carrier gas:	Helium at 1 mL/minute

6.2 Supplies

- Microsyringe, 10 µL.
- Balance, analytical, capable of weighing 0.0001 g
- Glass vials, glass with PTFE (polytetrafluoroethylene)-lined screw-caps or crimp tops.
- Volumetric flasks, Class A, appropriate sizes with ground-glass stoppers.
- Sterilized gauze or filter paper for blank wipe matrix.

7.0 Reagents and Standards

7.1 Reagent grade chemicals are used in all tests. Unless otherwise, indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water, analyte-free.

7.3 Stock Calibration Standards: Commercially prepared, certified stock standards are purchased:

- The primary standards for the typical 8270 compound list and the SIM list are the following, or equivalent, with the required targets at 200 µg/mL.

Analyte/Analyte Group	Vendor Catalog Number	Concentration (µg/mL)
Mega Mix	Restek 569729	500-2000
List 1 Std 5	Restek 567676	2000
List 1 Std 9	Restek 569730	2000
List 1 Std 10	Restek 569731	2000
List 1 Std 11	Restek 569732	2000
Surrogates	Restek 567685	5000
Internals	Restek 567684	2000

- For Appendix IX and miscellaneous compounds, the following primary source standards are purchased; equivalent substitutes are acceptable. A 200 µg/mL standard is made.

Analyte/Analyte Group	Vendor Catalog Number	Concentration (µg/mL)
List 2 Std 1	Restek 567678	1000
List 2 Std 2	Restek 569733	1000
List 2 Std 3	Restek 567680	2000
List 2 Std 4	Restek 567681	1000
List 2 Std 5	Restek 567682	2000
List 2 Std 6	Restek 567683	2000
List 2 Std 7	Restek 568726	2000
List 2 Std 8	Restek 568727	2000
Benzo(e)pyrene	Ultra Scientific RAH-081	Neat

7.4 Matrix Spike and Laboratory Control Standard contain all targets to be reported on the samples. The same compounds mentioned in Section 7.3 are designated as the SPCCs and CCCs for 8270C.

- For both a long semivolatile list and the SIM list, a secondary lot from Restek, or equivalent, is used. The standard is prepared at 100 µg/mL for target analytes.

Analyte/Analyte Group	Vendor Catalog Number	Concentration (µg/mL)
Mega Mix	Restek 569729.sec	500-2000
List 1 Std 5	Restek 567676.sec	2000
List 1 Std 9	Restek 569730.sec	2000
List 1 Std 10	Restek 569731.sec	2000
List 1 Std 11	Restek 569732.sec	2000
Surrogates	Ultra Scientific TAM-201	50
Internals	567684.sec	2000

- For Appendix IX and miscellaneous compounds, these second source standards are acceptable, as well as equivalents. Standard is prepared at 100 µg/L.

Analyte/Analyte Group	Vendor Catalog Number	Concentration (µg/mL)
List 2 Std 1	Restek 567678.sec	1000
List 2 Std 2	Restek 569733.sec	1000
List 2 Std 3	Restek 567680.sec	2000
List 2 Std 4	Restek 567681.sec	1000
List 2 Std 5	Restek 567682.sec	2000
List 2 Std 6	Restek 567683.sec	2000
List 2 Std 7	Restek 568726.sec	2000
List 2 Std 8	Restek 568727.sec	2000
Benzo(e)pyrene	Sigma Aldrich B-10102	Neat

7.5 Internal standard solutions: The internal standards are 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12}, and Perylene-d_{12}.

- Purchase certified, internal standard at 2000 µg/mL, as listed above, or equivalent.

7.6 GC/MS Tuning Standard: A Methylene chloride solution containing 50 µg/mL [RVE/LVI: 10 µg/mL] of Decafluorotriphenylphosphine (DFTPP) is prepared. The standard also contains 50 µg/mL each of 4, 4'-DDT, Pentachlorophenol, and Benzidine to verify injection port inertness and GC column performance.

- Purchase the tuning standard at 1000 µg/mL from Ultra Scientific, Catalog GCM-150, or equivalent.

7.7 Surrogate standards: The surrogates are Phenol-d_5, 2-Fluorophenol, 2,4,6-Tribromophenol, Nitrobenzene-d_5, 2-Fluorobiphenyl, and p-Terphenyl-d_{14}.

- Purchase the acid/base/neutral and SIM surrogates as listed above, or equivalent, at 50 µg/mL. [Dilute by five for RVE/LVI.]

7.8 Acetone, Hexane, Methylene chloride, Isooctane, Carbon disulfide, Toluene, and other appropriate solvents, commercial source.

7.9 Sodium sulfate for blank and LCS soil matrix.

7.10 Transfer the stock standard solutions into bottles with PTFE-lined screw-caps. Store, protected from light, at -10°C or less or as recommended by the standard manufacturer. Stock standard solutions must be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Replace after **one year or sooner** if

comparison with quality control check samples indicates a problem, or if the vendor specifies an expiration date sooner than one year.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	3 L or 3 250-mL, amber glass with Teflon™-lined cap	1 L* [RVE/LVI: 250 mL]*	Cool 0-6°C. Keep in dark.	7 days from collection until extraction, 40 days after extraction	SW-846 Chapter 2
Soil, Oil, Concrete	4 oz. glass jar with Teflon™-lined cap	30 g	Cool 0-6°C.	14 days from collection until extraction, 40 days after extraction	For 625: 40 CFR 136
Wipe	4-oz. glass jar with Teflon™ –lined cap	1 wipe	Cool 0-6°C.	14 days from collection until extraction, 40 days after extraction	

***For South Carolina water samples, 1 liter is the minimum volume required.**

9.0 Quality Control

The laboratory maintains a formal quality assurance program and records to document the quality of the data generated. Certain quality control and reporting criteria may vary depending on whether SW-846 8000B or 8000C criteria are required. In these cases, both sets of criteria have been noted in this SOP. 8000C criteria are required to be applied ONLY to Arizona, New York, and Washington samples. All other samples must be processed against referenced 8000B criteria. Exceptions may be required on a project-specific basis.

9.1 Sample QC:

The following QC samples are run with each batch of no more than 20 samples.			
QC Check	Frequency	Acceptance Criteria[1]	**Corrective Action[2]**
Method blank	One per analytical prep batch	No analytes detected ≥ ½ RL or MDL, whichever is greater	Correct problem then re-prep[3] and analyze method blank and all samples processed with the contaminated blank.
LCS[6] for all analytes (2nd source for 625)[6]	One[6] per prep batch	See LIMS and footnote 4 below. For 625, see LIMS and the table below.	Correct problem then re-prep[4] and analyze the LCS and all samples in the affected analytical batch.[4] If high and target is ND, OK to report.
MS/MSD (2nd source for 625)	One per batch per matrix, if insufficient sample for MS/MSD, qualify data[3]	See LIMS. For 625, see LIMS and the table below.	If both MS and MSD are similarly outside acceptable limits and the LCS is within acceptable limits, the batch is acceptable. If one analysis of the MS/MSD pair is within acceptable limits and the other is outside acceptable limits, repeat the analysis exhibiting unacceptable results.
Surrogate(s)	Every sample, spike, standard, and blank	See LIMS.[5]	Check system, re-analyze, re-prep[3, 5].

[1]This is a summary of the acceptance criteria. See special acceptance criteria for Method 625, Method 8270 for CT RCP, MA MCP, and NJ DKQP below.
[2]All abnormalities must be noted in LIMS.
[3]If unable to re-prep samples because of insufficient sample volume or the holding time has expired, then place a comment on the benchsheet and in LIMS.

[4]If the LCS exceeds the upper control limit AND a sample from that batch is greater than the RL, re-prep and re-analyze the batch. If the LCS exceeds the upper control limit AND the samples from that batch is less than the RL, the data is acceptable to report.
[5]If the surrogate % recovery exceeds the upper control limit AND a sample result is positive above the RL, re-prep and re-analyze the batch. If the surrogate % recovery exceeds the upper control limit AND the sample is less than the RL, data is acceptable to report. If the surrogate % recovery is lower than the lower control limit, re-prep the sample. OH VAP requires all surrogates to be in control; otherwise, the samples must be re-prepared and re-analyzed. See 8270 / NVOH-22 for OH VAP samples.
[6]LCSD is required for AZ, MA, TX.

QC Acceptance Criteria for Method 625

Parameter	Range for P,P(s) (Percent)	Parameter	Range for P,P(s) (Percent)
Acenaphthene	47-145	Hexachlorobutadiene	24-116
Acenaphthylene	33-145	Hexachloroethane	40-113
Anthracene	27-133	Indeno(1,2,3-cd) pyrene	D-171
Benzo(a)anthracene	33-143	Isophorone	21-196
Benzo(b)fluoranthene	24-159	Naphthalene	21-133
Benzo(k)fluoranthene	11-162	Nitrobenzene	35-180
Benzo(a)pyrene	17-163	n-Nitrosodi-n-propylamine	D-230
Benzo(ghi)perylene	D-219	Phenanthrene	54-120
Benzyl butyl phthalate	D-152	Pyrene	52-115
bis(2-Chloroethyl) ether	12-158	1,2,4-Trichlorobenzene	44-142
bis(2-Chloroethoxy) methane	33-184	4-Chloro-3-methylphenol	22-147
bis(2-Chloroisopropyl) ether	36.166	2-Chlorophenol	23-134
bis(2-Ethylhexyl) phthalate	8-158	2,4-Dichlorophenol	39-135
4-Bromophenyl phenyl ether	53-127	2,4-Dimethylphenol	32-119
2-Chloronaphthalene	60-118	2,4-Dinitrophenol	D-191
4-Chlorophenyl phenyl ether	25-158	2-Methyl-4,6-dinitrophenol	D-181
Chrysene	17-168	2-Nitrophenol	27-182
Dibenzo(a.h)anthracene	D-227	4-Nitrophenol	D-132
Di-n-butyl phthalate	1-118	Pentachlorophenol	14-176
1,2-Dichlorobenzene	32-129	Phenol	5-112
1,3-Dichlorobenzene	D-172	2,4,6-Trichlorophenol	37-144
1,4-Dichlorobenzene	20-124	Acetophenone	61-144
3,3'-Dichlorobenzidine	D-262	alpha-Terpineol	58-156
Diethyl phthalate	D-114	Aniline	46-134
Dimethyl phthalate	D-112	Carbazole	73-131
2,4-Dinitrotoulene	39-139	2-Methylphenol	55-126
2,6-Dinitrotoluene	50-158	4-Methylphenol	76-107
Di-n-octylphthalate	4-146	n-Decane	D-NS
Fluoranthene	26-137	2,3-Dichloroanaline	68-134
Fluorene	59-121	n-Octadecane	65-123
Hexachlorobenzene	D-152	Pyridine	33-158

QC Acceptance Criteria for Method 8270 for CT RCP, MA MCP, NJ DKQP

QC	CT RCP 8270C	MA MCP 8270D	NJ DKQP 8270D
Waters			
LCSREC %	40-140 30-130 for Phenols	40-140	70-130

QC	CT RCP 8270C	MA MCP 8270D	NJ DKQP 8270D
LCSRPD %	20	20	20
MDRPD %	30	NR	20
MSREC %	40-140 30-130 for Phenols	40-140	70-130*
MSRPD %	20	20	20
SUREC %	30-130 15-110 for Phenols	30-130 15-110 for Phenols	30-130 15-110 for Phenols
Solids			
LCSREC %	40-140 30-130 for Phenols	40-140	70-130
LCSRPD %	20	30	30
MDRPD %	50	NR	NR
MSREC %	40-140 30-130 for Phenols	40-140	70-130
MSRPD %	30	30	30
SUREC %	30-130	30-130	70-130

- A **Method blank** is extracted with every batch of samples.
- A **Laboratory Control Sample** (LCS) is included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume (reagent water for water batches, Sodium sulfate for soil batches). It is spiked with the same analytes at the same concentrations as the matrix spike. **All target analytes must meet the LCS QC criteria.** However, if the LCS is high, and a target is ND, it is acceptable to report the result.
  - The LCS spike is from the same source as **the calibration standards for 8270 and the second source for 625**. Using the 100 µg/mL LCS/MS/MSD standard:
    - **For Non-SIM batches:**
      - Water: add 500 µL [RVE/LVI: 100 µL] of the standard per liter reagent water before extraction by Method 3510C.
      - Soil: add 500 µL of the standard per 30 gram Sodium sulfate before extraction.
      - TCLP: add 1 mL [RVE/LVI: 200 µL] of the standard/500 mL TCLP extraction fluid before extraction by Method 3510C.
      - Waste, Wipe: to 1 gram of Sodium sulfate, add 2000 µL of the standard before dilution by 3580A.
      - The final concentration is 50 µg/mL on column for waters and solids, and 20 µg/mL for wastes/wipes.
    - **For SIM batches:**
      - Water: add 1 mL [RVE/LVI: 200 µL] of a 100 X dilution of the LCS/MS/MSD per liter reagent water.
      - Soil: add 1 mL of a 100 X dilution of the LCS/MS/MSD per 30 g Sodium sulfate.
      - The final concentration in the extracts is 1.0 µg/mL.
- **Matrix Spike / Matrix Spike Duplicate**: Documenting the effect of the matrix includes the analysis of at least one matrix spike/matrix spike duplicate pair.
  - The MS/MSD spike is from the same **source** as the calibration standards for 8270 and the second source for 625. Using the 100 µg/mL LCS/MS/MSD standard:
    - **For Non-SIM batches**:
      - Water: add 500 µL [RVE/LVI: 100 µL] of the standard per liter client sample.
      - Soil: add 500 µL of the standard to 30 g client sample.

- TCLP: add 1 mL [RVE/LVI: 200 µL] of the standard per 500 mL client TCLP extract.
- Waste, Wipe: to 1 gram of Sodium sulfate, add 2000 µL of the standard before dilution by 3580A.
- The final concentration is 50.0 µg/mL for waters and solids, and 20 µg/mL for wastes/wipes..

- **For SIM batches**:
  - Water: add 1 mL [RVE/LVI: 200 µL] of a 100 X dilution of the Restek standard per liter reagent water.
  - Soil: add 1 mL of 100 X dilution per 30 g client sample.
  - The final concentration is 1.0 µg/mL on column.

- **Surrogate recoveries:** The laboratory evaluates surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. The limits for surrogate recoveries are updated biannually. If any surrogate is outside QC limits, and there is no obvious matrix interference, then re-analyze and/or re-extract the sample. If surrogates are still outside limits, flag the data in LIMS. However, if high and all results are non-detect, results are reportable. If surrogate recoveries are low, re-prep the batch.
  - **For Non-SIM**, add 1000 µL [RVE/LVI: 200 µL] of the surrogate standard at a concentration of 50 µg/mL to each sample and batch QC samples prior to extraction for a 50 µg/mL concentration.
  - **For SIM,** prepare a 1 µg/mL standard (500 µL surrogate standard) to 500 mL in Methanol. Add 1.0 mL [RVE/LVI: 200 µL] to samples and QC (blanks, MS/MSD and LCS) prior to extraction. The concentration is 1.0 µg/mL.

9.2 Instrument QC

QC Check	Frequency	Acceptance Criteria[2]	Corrective Action[3]
GC/MS Tuning			
a. Check of mass spectral ion intensities[1], i.e., Tune	Prior to initial calibration or Continuing calibration verification, every 12 hours.	See below in this section for GC/MS Tuning criteria.	Retune the instrument and verify (instrument maintenance may be needed).
b. Column Breakdown	Prior to initial calibration or Continuing calibration verification, every 12 hours.	Breakdown ratio ≤ 20% (30% for 8270C). 625: no criterion specified	Injector or column maintenance and re-calibration.
c. Tailing Factor	Prior to initial calibration or Continuing calibration verification, every 12 hours.	8270C 8270D 625 Benzidine 3 2 Pentachlorophenol 5 2	Injector or column maintenance and re-calibration.

QC Check	Frequency	Acceptance Criteria[2]	Corrective Action[3]
Minimum five-point initial calibration for all target analytes	Initial calibration prior to sample analysis. Perform instrument re-calibration once per year minimum.	8270C: SPCCs average RF ≥ 0.050 and %RSD for RFs for CCCs ≤ 30% and all other target analytes %RSD for RF ≤ 15% If %RSD is > 15%, linear regression $r^2 \geq 0.990$, $r \geq 0.995$. 8270D: The minimum RF for all compounds in Attachment 5 must be met[5]. All targets RSD ≤ 20% or use linear regression. 625: If RSD is > 35%, linear regression $r^2 \geq 0.990$, $r \geq 0.995$.	Correct problem then repeat initial calibration.
Initial calibration verification (ICV) must be from a 2nd source.	Immediately following five-point initial calibration.	All analytes within 30% of expected value. Poor performing analytes may exceed 30% but have a maximum %D of 50%.[6] 625: All analytes within 20% of expected value.	Correct problem then repeat initial calibration.
Initial calibration blank	Immediately after ICV	All analytes < MDL	Correct problem, re-calibrate.
Continuing calibration verification (CCV)	Daily, before sample analysis and every 12 hours of analysis time.	8270C: SPCCs average RF ≥ 0.050 and CCCs: ≤30% difference (when using RFs) or drift (when using least squares regression). Non-CCC < 20% true, up to 5 may be < 40%. 8270D: The minimum RF for all compounds listed in Attachment 3 must be met and the percent difference or drift for each target compound ≤20%. Poor performing analytes may exceed the 20% criteria but the maximum %D is 50%. [6] 625: All analytes within 20% of the expected value.	Correct problem then repeat initial calibration and re-analyze all samples since last successful CCV.
Internal Standards	Every sample/standard and blank.	Retention time ±30 seconds from retention time of the mid-point std. in the ICAL for CCV. EICP area within -50% to +100% of ICAL mid-point std for the CCV and –50% to +100% of the prior CCV for the samples. See footnote 4 below.	Inspect mass spectrometer and GC for malfunctions; mandatory re-analysis of samples analyzed while system was malfunctioning (dilution of the sample may be required, see the supervisor or the technical manager for advice).
Relative Retention Time Window	Each sample.	Relative retention time (RRT) of the analyte within 0.06 RRT units of the RRT of the internal standard.	Correct problem then reprocess or re-analyze all samples analyzed since the last retention time check.
MDL verification (extracted)	Minimum yearly.	Detectible	Re-evaluate MDL standard used and MDL; see the technical manager.

[1]8270 requires DFTPP.
[2]This is a summary of the acceptance criteria.
[3]All abnormalities must be noted in LIMS.
[4]Target compounds associated with failed internal standards must be re-analyzed (undiluted if possible) if additional sample is available; if not available, qualify data in LIMS.
[5]LLCV: If RF is not met at the low-level standard, the criterion for a passing LLCV is detection only and must be run following the CCV.

[6]See ICV and CCV text below for the list of poor performers.

- **Tuning**

GC/MS Tuning (Full Scan)

- Prior to the analysis of samples or calibration standards, the GC/MS system is hardware-tuned using a 50 ηg or less injection of DFTPP (in the GC/MS Tuning Standard).
- The 50 µg/mL standard is prepared by adding 2.8 mL of 1000 µg/mL stock standard to 56 mL Methylene chloride. [RVE/LVI: Use a 5X dilution of this solution.]
- Analyses **must** not begin until the tuning criteria are met, and these criteria must be demonstrated at the beginning of each 12-hour period for 8270 or each 24-hour period for 625. Three options are available for acquiring the spectra for reference to meet the DFTPP tuning requirements:

Option 1 It is recommended that each initial tune verification utilize the "Autofind" function and be set up to look at the apex ±1 scan and average the three scans. Background correction is required prior to the start of the peak but no more than 20 scans before. Background correction **cannot** include any part of the target peak. Sometimes the instrument does not always correctly identify the apex on some peaks when the peak is not perfectly shaped. It is acceptable to manually identify and average the apex peak ± 1 scan and background correct

Option 2 The entire peak may be averaged and background-corrected. Average scans from 0.1 minute before to 0.1 minute after peak.

Option 3 A single scan at the apex (only) may also be used for the evaluation of the tune. Background correction is required.

Note: It is acceptable to adjust parameters within the specifications set by the manufacturer or the analytical method to properly tune the instrument. If the tune verification does not pass, it may be necessary to clean the source or perform additional maintenance. Document any maintenance in the instrument log. **Excessive adjusting (more than two tries) without clear documentation is not allowed. No more than two consecutive tunes may be attempted. Perform necessary maintenance**.

- All subsequent standards, samples, controls, and blanks associated with a DFTPP tune must use the identical mass spectrometer instrument conditions.
- Use the DFTPP mass intensity criteria as follows as tuning acceptance criteria.

DFTPP Key Ions and Ion Abundance Criteria

Mass	m/z Abundance criteria
51	30-60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	40-60 percent of mass 198.
197	Less than 1 percent of mass 198.
198	Base peak, 100 percent relative abundance.
199	5-9 percent of mass 198.
275	10-30 percent of mass 198.
365	Greater than 1 percent of mass 198.
441	Present but less than mass 443.
442	Greater than 40 percent of mass 198.
443	17-23 percent of mass 442.

- **Breakdown Standard**: The GC/MS Tuning Standard is also used to assess the injection port inertness by evaluating the degradation of DDT to DDE and DDD. This ratio must **not** exceed 20%; see Section 9.2 for **percent breakdown** calculation. Perform injector or column maintenance and recalibrate if the ratio maximum is exceeded for either compound. The breakdown of DDT is measured **before** verification standards and samples are analyzed and every 12 hours throughout the sequence.
- **Tailing Factor**: To evaluate the GC column, Benzidine and Pentachlorophenol (in the GC/MS Tuning Standard) must be present at their normal responses and evaluated for peak tailing. The Benzidine and Pentachlorophenol tailing factors are calculated by the following equation:

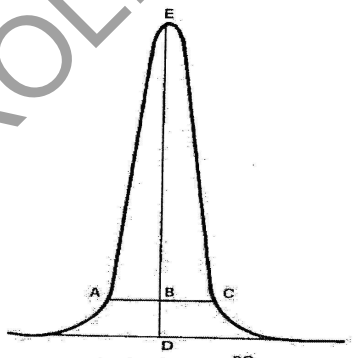
Tailing factor = BC/AB

Maximum Tailing Factor Ratios

Tailing Factor Compounds	8270C 625	8270D
Benzidine	3	2
Pentachlorophenol	5	2

where the peak is defined as follows: AC is the width at 10% height. DE is the height of peak and B is the height at 10% DE. This equation compares the width of the back half of the peak to the width of the front half of the peak at 10% of the height. (See Figure 1 for an example tailing factor calculation.)

FIGURE 1
TAILING FACTOR CALCULATION



TAILING FACTOR= $\frac{BC}{AB}$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm
Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

8270D - 72 Revision 4
February 2006

If all of the specified criteria are met, generate a hardcopy of the spectrum, the mass abundance data and the parameters under which the scans were acquired. This data is filed in the batch for documentation.

GC/MS Tuning (SIM)

- The objective of tuning for conventional full scan analysis is to produce a balanced mass spectrum over the range of interest. The DFTPP tune is, by necessity, done in the full scan mode. However, because the instrument is then immediately switched to the SIM mode, the DFTPP results have limited quality control value. In short, the DFTPP is not analyzed under the same conditions as the calibration, QC, and field samples. In the case of Selective Ion Monitoring (SIM) analysis, there are no comparisons between spectra; instead the instrument is optimized for the relative intensities of the pre-selected analyte ions of interest. For SIM analysis, the laboratory prints out a copy of the autotune (PFTBA) prior to analysis to demonstrate good mass assignment and peak width. No DFTPP tune is used while in SIM mode. A printout of the instrument autotune (PFTBA) is included with the data for each day that SIM analyses are run in order to demonstrate good mass assignment and peak width.

- **Calibration**: See Section 10.2.
- **Initial Calibration System Performance Check Compounds (SPCCs)**: A system performance check is performed to ensure that minimum average RFs are met before the calibration curve is used.
  - **For 8270C**: The SPCCs are

System Performance Check Standards (SPCCs)	
Base/Neutral Fraction	**Acid Fraction**
n-Nitrosodi-n-propylamine	2,4-Dinitrophenol
Hexachlorocyclopentadiene	4-Nitrophenol

The **minimum acceptable average RF for the SPCCs is 0.050.** They typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

  - **For 8270C SIM**, all compounds must meet ± 15%; RF is 0.05.
  - **For 8270D**, see Attachment 3 for required minimum response factor criteria for target analytes.
  - If the minimum response factors are not met, the system must be evaluated, and corrective action is taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. **This check must be met before sample analysis begins.** An option is to run a LLCCV to show sensitivity.
  - For 8270D SIM, all compounds must meet ± 20%; RF is 0.05.
- **Initial Calibration Check Compounds (CCCs) for 8270C only**: The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes. The CCCs are:

Calibration Check Compounds (CCC)	
Base/Neutral Fraction	**Acid Fraction**
Acenaphthene*	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
Diphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene*	2,4,6-Trichlorophenol
Benzo(a)pyrene*	

*For SIM

- Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte.

Initial Calibration RSD Differences	
8270C	**8270D**
The RSD must be less than or equal to **15%** for each target analyte; if not, see the section on linearity of target analytes in Section 10.2. However, the RSD for each individual CCC must be less than or equal to 30%. If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure.	The RSD must be less than or equal to **20%** for each target analyte; if not, see the section on linearity of target analytes in Section 10.2. If not, check errors in standard preparation, the possible presence of active sites in the GC system, poor chromatographic behaviors for analytes.

- The **Initial Calibration Verification (ICV)** is a second-source standard run immediately after the initial calibration. The acceptance limits are **70-130%** recovery for 8270C and 8270D, 80-120% for 625..
  - Add 250 µL of the second-source standard to 250 µL Methylene chloride in an amber vial to prepare an ICV standard at 50 µg/mL.
  - For SIM, use the second-source standard with the targets at 2000 µg/mL. A 10 µg/mL intermediate is made by taking 50 µL of the stock standard along with 20 µL of the base/neutral surrogates. The ICV at 1 µg/mL is made by taking 50 µL of intermediate into 450 µL of Methylene chloride in an amber vial.
  - If ICV acceptance criterion is not met, correct the problem and re-calibrate.
  - Poor performing compounds may exceed 30% but less than 50%. Poor performing compounds are as follows: Atrazine, Benzaldehyde, Benzidine, alpha,alpha-Dimethylphenylethylamine, 7,12-Dimethybenz(a)anthracene, Famphur, Hexachlorophene, Hexachloropropene, Kepone, Methylpyrilene, p-Phenylene diamine.
- **Initial Calibration Blank**: a reagent/solvent blank analyzed after the ICV to ensure the system is free of contaminants (< MDL). If not contaminant-free, re-run and/or perform system maintenance.
- The **Continuing Calibration Verification standard (CCV)** is evaluated each day (or every 12 hours) that analysis is performed to determine if the chromatographic system is operating properly.
  - Prepare a daily CCV at 50 µg/mL by adding 100uL of the primary stock solution to 300 µL Methylene chloride in an amber vial. [RVE/LVI: 20 µL to a final volume of 400 µL Methylene chloride].
  - For SIM, use the primary stock standard with the targets at 2000 µg/mL. A 10 µg/mL intermediate is made by taking 50 µL of the stock standard along with 20 µL of the

base/neutral surrogates. A daily CCV at 1 µg/mL is made by taking 50 µL of intermediate into 450 µL of Methylene chloride in an amber vial. [RVE/LVI: 5 µL to a final volume of 500 µL of Methylene chloride].

- The calibration verification standard is prepared at least weekly and stored at 4°C or less.
- **For 8270C**, each **SPCC** in the calibration verification (CCV) standard must meet a **minimum response factor of 0.050**. **For 8270D**, see Attachment 3 for required minimum response factor criteria for target analytes.
- After the system performance check is met, the **CCCs** are used for 8270C only to check the ongoing validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model.

CCC % Difference Evaluation Criteria	
8270C	**8270D**
CCCs ≤ 30% and all other target compounds require an RF ≤ 20%; however, up to 5 non-CCC target compounds may be ≤ 40%.	If the percent difference for each target compound is less than or equal to **20%**, then the initial calibration is assumed to be valid. If the criterion is not met (i. e., greater than 20% difference or drift) for any target, then corrective action is taken prior to the analysis of samples. All targets are considered as CCCs. Poor performing compounds may exceed 30% but less than 50%. Poor performing compounds are as follows: Atrazine, Benzaldehyde, Benzidine, alpha,alpha-Dimethylphenylethylamine, 7,12-Dimethybenz(a)anthracene, Famphur, Hexachlorophene, Hexachloropropene, Kepone, Methylpyrilene, p-Phenylene diamine.

  - If the CCV criteria cannot be met, a new initial calibration must be generated.
  - For 625, the CCV criterion is ± 20% for all targets.
- **Continuing Calibration Blank (CCB):** The CCB is run after each CCV. If the result is not ≤ MDL or ½ RL, correct the problem and re-run.
- **Internal standards** are added to every sample, standard, and QA/QC.
  - **Retention time** - The retention times of the internal standards in the continuing calibration verification (CCV) standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than **30 seconds** from that in the mid-point standard level of the **most recent initial calibration** sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.
  - **Response** - If the EICP area for any of the internal standards in the continuing calibration verification (CCV) standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the **most recent initial calibration sequence**, the mass spectrometer must be inspected for malfunctions and corrections must be made. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.
  - The laboratory re-analyzes any sample where the internal standard fails and there is no evidence of matrix interference. If there is no matrix interference, the sample must be reanalyzed at the original dilution.
    - If the internal standard is within criteria, report the second analysis.
    - If the internal standard is still outside of criteria, the sample must be analyzed at a second dilution.
    - If the internal standard still does not meet criteria, the sample must be diluted until the internal standard meets criteria. Multiple runs may be required.

- The target analytes are quantitated with specific internal standards as shown in this table:

Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation

1,4-Dichlorobenzene-d_4	**Naphthalene-d_8**	**Acenaphthene-d_{10}**
1,2-Dichlorobenzene	1,2,4,5-Tetrachlorobenzene	1,2-Diphenylhydrazine
1,2-Dichlorobenzene-d_4 (surr)	1,2,4-Trichlorobenzene	1,3,5-Trinitrobenzene
1,3-Dichlorobenzene	1,4-Naphthoquinone	1,3-Dinitrobenzene
1,4-Dichlorobenzene	1,4-Phenylenediamine	1-Naphthaleneamine
1,4-Dioxane	1-Chloronaphthalene	2,3,4,6-Tetrachlorophenol
2-Butoxyethanol	1-Methylnapthalene	2,4,5-Trichlorophenol
2-Chlorophenol	2,4-Dichlorophenol	2,4,6-Trichlorophenol
2-Chlorophenol-d_4 (surr)	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr)	2,6-Dichlorophenol	2,4-Dinitrotoluene
2-Methylphenol	2-Methylnaphthalene	2,6-Dinitrotoluene
2-Picoline	2-Nitrophenol	2-Chloronaphthalene
2-Toluidine	4-Chloro-3-methylphenol	2-Fluorobiphenyl (surr)
3,4-Methylphenol	4-Chloroaniline	2-Naphthaleneamine
Acetonphenone	6-Methylchrysene	2-Nitroaniline
Aniline	7,12-Dimethylbenz(a)anthra-cene	3-Nitroaniline
Benzaldehyde	a,a-Dimethylphenylethylamine	4-Aminobiphenyl
Benzyl alcohol	Benzoic acid	4-Chlorophenyl phenyl ether
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy) methane	4-Nitroaniline
Bis(2-chloroisopropyl) ether	**Caprolactam**	4-Nitrophenol
Ethylmethanesulfonate	Chrysene-d_{12}	5-Nitro-o-Toluidine
Hexachloroethane	cis-Isosafrole	Acenaphthene
Indene	Dibenz(a,h)acridine	Acenaphthylene
Methyl-methoanesulfonate	Hexachlorobutadiene	**Biphenyl**
n-Nitrosodiethylamine	Hexachloropropene	cis-Diallate
n-Nitrosodimethylamine	Isophorone	Dibenzofuran
n-Nitroso-di-n-propylamine	Naphthalene	Diethyl phthalate
N-Nitrosomethylethylamine	Nitrobenzene	Dimethyl phthalate
n-Nitrosomorpholine	Nitrobenzene-d_8 (surr)	Diphenylamine
n-Nitrosopiperidine	n-Nitrosodi-n-butylamine	Fluorene
n-Nitrosopyrrolidine	Quinoline	Hexachlorocyclopentadiene
Pentachloroethane	Safrole	**n-Hexadecane**
Phenol	trans-Isosafrole	Pentachlorobenzene
Phenol-d_5 (surr)		Phenacetin
Pyridine		trans-Diallate
Pyridine		
Thiophenol		

Phenanthrene-d_{10}	**Chrysene-d_{12}**	**Perylene-d_{12}**
2-Acetylaminofluorene	3-Methylcholanthrene	Benzo(a)pyrene
3,3'-Dimethylbenzidine	3,3'-Dichlorobenzidine	Benzo(b)fluoranthene
4-Dimethylaminozobenzene	4,4'-Methylenebis(2-chloro-aniline)	Benzo(e)pyrene
4-Nitroquinoline-N-oxide	Aramite	Benzo(g,h,i)perylene
Atrazine	Benzidine	Benzo(k)fluoranthene
Benzidine	Benzo(a)anthracene	Dibenz(a, h)anthracene
Bis (2-ethylhexyl)adipate	Bis(2-ethylhexyl) phthalate	Dibenz(a,j)acridine
Chlorobenzilate	Butyl benzyl phthalate	Di-n-octyl phthalate
Dimethoate	Chrysene	Indeno(1,2,3-cd)pyrene
Dinoseb	Pyrene	
Disulfoton	Terphenyl-d_{14} (surr)	
Hexachlorophene		

Isodrin
Kepone
Methapyrilene
Methyl Parathion
Parathion
Pentachloronitrobenzene
Carbazole
Pentachlorophenol
Phenanthrene
4,6-Dinitro-2-methylphenol
Anthracene
Di-n-butyl phthalate
4-Bromophenyl phenyl ether
Diphenylamine
n-Nitrosodiphenylamine
Fluoranthene
Hexachlorobenzene
Phorate
Pronamide
Sulfotepp
Thionazin
Tribromophenol (surr)

(surr)= surrogate

- The internal standards selected permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation. If interferences are noted, use the next most intense ion as the quantitation ion (i. e., for 1, 4-Dichlorobenzene-d_4, use 152 m/z for quantitation).
- Dilute the 4000 µg/mL internal standard by 2x with Methylene chloride. The resulting solution contains each internal standard mixture at a concentration of 2000 µg/mL. Each 0.5 mL sample extract undergoing analysis is spiked with 10 µL [RVE/LVI: 2µL] of the internal standard solution, resulting in a concentration of 40 µg/mL of each internal standard.
- For SIM**,** dilute the 2000 µg/mL internal standard mix by 10x with Methylene chloride for a 200 µg/mL standard. Each 0.5 mL of sample extract undergoing analysis is spiked with 10 µL [RVE/LVI: 5 µL] of internal standard solution, resulting in a concentration of 2 µg/mL of each internal standard.

- **Evaluation of target analyte retention time:** The relative retention time (RRT) of each target analyte in each calibration standard must agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement. This criterion is met with the use of a ± 0.25 minute retention time window. Representative retention times are shown in Attachments 1 and 2.
- **Method Detection Limit Verification (MDLV)**: Annually, verify that the MDL is detectible; if not, re-evaluate the MDL.

10.0 Procedure

10.1 Sample Preparation

Matrix	Sample Size
Water	**1000 mL [RVE/LVI: 250 mL]**
Soil, Concrete	**15-30 grams**
Oil	**1 gram**

Wipe	1 wipe

- Samples are nominally prepared by one of the following methods prior to GC/MS analysis:

Matrix	Methods	SOP #
Water	3510 608 608.2 610 625	NV03-24
Soil/sediment/Concrete	3541, 3546, 3550	NV03-231, NV03-25
Oily Waste	3580	NV03-106
Wipe	3580	NV03-106

- QC samples and client samples must be extracted by the same preparation method.
- All calibration standards, QC samples, and client samples are introduced into the GC/MS using the same injection volume, IS and SS concentrations, and instrument conditions.

10.2 Calibration and Daily Continuing Calibration Verification: Refer to SOP Calibration Curves and Selection of Calibration Points / CA-Q-P-003. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

- Initially and/or daily, evaluate the DFTPP tune criteria (Section 9.2).
- Evaluate the percent breakdown of DDT (Section 9.2).
- Evaluate the tailing factors for Benzidine and Pentachlorophenol (Section 9.2).

Initial calibration

1 Prepare calibration standards at five (minimum) different concentrations.

Traditional Concentration (µg/mL)	RVE/LVI Concentration (µg/mL)	µL 200 µg/mL standard/500 µL (1 µL injection)	RVE/LVI: µL 200 µg/mL standard/500 µL (5 µL injection)
1	--	2.5	--
2	0.4	5	1
5*	--	12.5	
10	2	25	5
20	4	50	10
50	10	125	25
80	16	200	40
100	20	250	50

*RL standard for NJ DKQP.

- At least one of the calibration standards corresponds to a sample concentration **at or below the laboratory reporting limit (RL)**. The remaining standards correspond to the working range of the GC/MS system.
- Each standard contains each analyte to be reported. These target analytes may not include the entire list of analytes for which the method has been demonstrated; however, the laboratory **must not** report a quantitative result for a target analyte that was not included in the calibration standard(s).
- Surrogates are included at the same concentrations.
- The internal standards are at a constant 40 µg/mL. Each 0.5 mL aliquot of calibration standard is spiked with 10 µL [RVE/LVI: 2 µL] of the internal standard solution prior to analysis.

<table>
<tr><td>2</td><td>For SIM, calibration standards are diluted from the intermediate standard solution to give the following concentrations:
<table>
<tr><th>Traditional Concentration (µg/mL)</th><th>RVE/LVI Concentration (µg/mL)</th><th>µL 10 µg/mL standard/500 µL (1 µL injection)</th><th>RVE/LVI: µL 2 µg/mL standard/500 µL(5 µL injection)</th></tr>
<tr><td>0.05*</td><td>0.01</td><td>2.5</td><td>2.5</td></tr>
<tr><td>0.1</td><td>0.02</td><td>5</td><td>5</td></tr>
<tr><td>0.5</td><td>0.1</td><td>25</td><td>25</td></tr>
<tr><td>1</td><td>0.2</td><td>50</td><td>50</td></tr>
<tr><td></td><td>0.4</td><td></td><td>100</td></tr>
<tr><td></td><td>0.8</td><td></td><td>200</td></tr>
<tr><td>5</td><td>1.0</td><td>250</td><td>250</td></tr>
<tr><td>10</td><td>2.0</td><td>500</td><td>500</td></tr>
</table>
*The lowest calibration standard must be used for low-level SIM analysis on samples from Wisconsin; i e., 0.02 µg/mL for Benzo(a)pyrene, Benzo(b)fluoranthene, and Chrysene. See the table in Section 1.2 for RL/low calibration standard required for NJ DKQP samples.

Surrogates are included at the same concentrations.
The internal standards are at a constant 2 µg/mL.
See Attachments 2 and 3 regarding SIM Mass groups.
</td></tr>
<tr><td>3</td><td>Analyze 1 µL [RVE/LVI: 5 µL] of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte. See Attachment 1. Two characteristic ions must be valid for the low standard to be used.</td></tr>
<tr><td>4</td><td>Calculate response factors (RFs) for each target analyte relative to one of the internal standards.</td></tr>
<tr><td>5</td><td>Evaluate the system performance check compounds (SPCCs): The minimum acceptable average RF for these compounds is 0.050 for 8270C. For 8270D, see Attachment 3. This check must be met before sample analysis begins.</td></tr>
<tr><td>6</td><td>Evaluate the calibration check compounds (CCCs): If the RSD of any CCC is greater than 8270C criteria, then correct the chromatographic system reactivity before analysis begins. For 8270D, all compounds are treated as CCCs and must be within ± 20%.</td></tr>
<tr><td>7</td><td>Evaluate the retention times.</td></tr>
<tr><td>8</td><td>Evaluate the linearity of target analytes: If the RSD (8270C ± 15%; 8270D ± 20%) of any target analytes is within acceptance limits , then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor is used for quantitation. If the RSD of any target analyte is greater than the acceptance criteria , linear regression is used for calibration. The correlation coefficient r^2 must be at least 0.990 ($r \leq 0.995$). If the calibration is not considered linear by either %RSD or linear regression, then correct the problem and re-calibrate. See Section 11 for equations and information on linear regression calibration.</td></tr>
<tr><td>9</td><td>Evaluate the intercept; it must be ≤ RL or re-calibrate.</td></tr>
</table>

Initial Calibration Sequence Summary

1	DFTPP Tuning Criteria/DDT Breakdown/Tailing Factors
2	Calibration Standards
3	ICV
4	ICB

Daily continuing calibration verification: Calibration verification is performed at the beginning of **each** 12-hour analytical shift.	
1	The initial calibration for each compound of interest is verified once every 12 hours and prior to sample analysis by analyzing a continuing calibration verification (CCV) standard.
2	Evaluate the **system performance check compounds (SPCCs):** Each SPCC in the calibration verification (CCV) standard must meet the **minimum response factor criteria** for 8270C or 8270D in the initial calibration.
3	Evaluate the **minimum response factors** of each of the most common target analytes in the calibration verification standard (same as SPCCs).
4	Evaluate the **calibration check compounds (CCCs)** for method criteria. For 8270D or for shortened compound lists, all target analytes must meet ± 20% criteria. Use the initial calibration criteria.
5	Evaluate the **internal standard retention times** in the CCV.
6	Evaluate the **internal standard responses**.
7	Analyze an extraction blank after the continuing calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants.

10.3 Sample Analysis: Refer to Acceptable Manual Integration Practices / CA-Q-S-002.

1	Allow the sample extract to warm to room temperature. Just prior to analysis, add 10 µL [RVE/LVI: 2 µL] of the internal standard solution to the 0.5 mL concentrated sample extract.
2	Inject a 1 µL [RVE/LVI: 5 µL] aliquot of the sample extract into the GC/MS system. The volume to be injected contains 50 ηg of base/neutral and 50 ηg of acid surrogates (assuming 100% recovery).
3	The recommended sequence for a 20-sample batch is as follows: 1 DFTPP Tuning Criteria /DDT Breakdown/Tailing Factors* 2 CCV 3 Method Blank 4 LCS 5 Matrix Spike 6 Matrix Spike 7 Samples 1-20 *Not used for SIM.
4	If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed in the upper half of the calibration range. Additional internal standard must be added to the diluted extract to maintain the same concentration as in the calibration standards (40 µg/mL, unless a more sensitive GC/MS system is being used, e. g., 2 µg/mL for SIM).
5	Evaluate the specific internal standard response. Dilutions may be required to meet this criterion. Notes: Specific analytes associated with an internal standard within -50 to +100% from the last calibration verification (CCV) may be reported with approval from the supervisor or manager even if other internal standards in that analysis are outside limits. Only analytes associated with the internal standard(s) within limits may be reported from that analysis.
6	The use of selected ion monitoring (SIM) is acceptable for applications requiring detection limits below the normal range of electron impact mass spectrometry. Multiple ions are used for compound identification; see Attachment 2. Secondary ions may drop below 30% relative intensity at concentrations less than 1 µg/mL.

10.4 Qualitative analysis

- The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be kept up to date and obtained through analysis of known standards on the instrument using the conditions of this method. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. Attachments 1 and 2 list the primary and secondary ions for each analyte. Compounds are identified when the following criteria are met.
- The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time is accepted as meeting this criterion.
- The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.
- The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. **Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.** When two or more analytes that co-elute share secondary ions, and all the characteristic secondary ions for the target analyte are present but outside the ±30% relative intensity, the compound is reported as positive if there is no interference with the primary quantitation ion. If co-eluting peaks share the primary ion, the analyte may only be reported as a co-eluting pair. (See Attachment 1.)
- Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i. e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.
- Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analyses co-elute (i. e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum contains extraneous ions contributed by the co-eluting compound. The analyst must carefully weigh the background spectrum and the spectrum of any co-eluting analytes whenever assessing a potential hit. Analyst experience in interpreting mass spectral data and the above specified guidelines are used together to interpret difficult matrices. If all of the ions associate with the reference spectrum for the target analyte are present and within the ±30% criteria, a positive result is assumed even in the presence of extraneous ion fragments without presumptive evidence (all ions associated with the target analyte are also present in the interfering peak) for a negative identification.
- Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights for 8270C and 50% of the average of the two peak heights for 8270D samples. Mathematically, the two equations used are equivalent. Verification is performed on a mid-level control each day of use. Otherwise, structural isomers are identified as isomeric pairs. (See Attachment 1.)
- For samples containing components not associated with the calibration standards or the requested target list, a library search may be made for the purpose of tentative identification.

The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines do not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

- For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Evaluate the "Q-value." If Q > 80, report. If Q< 80, evaluate by the following guidelines for tentative identification:
  1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) are present in the sample spectrum.
  2) The relative intensities of the major ions agree within ±20%. **Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.**
  3) Molecular ions present in the reference spectrum are present in the sample spectrum.
  4) Ions present in the sample spectrum but not in the reference spectrum are reviewed for possible background contamination or presence of co-eluting compounds.
  5) Ions present in the reference spectrum but not in the sample spectrum are reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

10.5 Quantitative analysis

- Once a compound has been identified, the quantitation of that compound is based on the integrated abundance of the primary characteristic ion from the EICP.
- If the RSD of a compound's response factor is 15% for 8270C and 20% for 8270D, or less, then the concentration in the extract is determined using the average response factor (RF) from initial calibration data. If greater than the criteria, use linear regression.
- Where applicable, the concentration of any non-target compounds identified in the sample is estimated. The same formulae are used with the following modifications: The areas A_x and A_t are from the total ion chromatograms, and the RF for the compound is assumed to be 1.
- The resulting concentration is reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

10.7 Instrument Maintenance

Careful examination of the standard chromatogram indicates whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. Re-calibration of the instrument must take place when the performance changes to the point that the calibration verification acceptance criteria cannot be achieved. In addition, significant maintenance activities or hardware changes may also require re-calibration. These significant maintenance activities include, changing, replacing, or reversing the column; cleaning the MS source; changing the electron multiplier; or injector port.

11.0 <u>Calculations / Data Reduction</u>

11.1 Accuracy

$$\% \text{ Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

RPD = Absolute value (orig. sample value – dup. sample value) x 100
(Orig. sample value + dup. sample value)/2

11.3 Breakdown Calculation:

% Breakdown of DDT = Sum of degradation peak areas (DDD + DDE) x 100
Sum of all peak areas (DDT + DDE + DDD)

11.4 Response Factor

$$RF = \frac{A_s x C_{is}}{A_{is} x C_s}$$

A_s = Peak area of the analyte or surrogate.
A_{is} = Peak area of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

11.5 Mean Response Factor, Standard Deviation, Relative Standard Deviation

$$RF_{mean} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

$$SD = \frac{\sum_{i=1}^{n} \left(RF_i - RF_{mean}\right)^2}{n-1}$$

RSD = SD x 100
RF_{mean}

11.6 % Difference, % Drift

% Difference = (RF_v) - (Avg. RF) x 100
(Avg. RF)

RF_v = RF from verification standard
Avg. RF = Average RF from Initial Calibration.

% Drift = Result – True Value x 100
True Value

11.7 Linear Calibration Using a Least Squares Regression: This approach is not used for analytes that meet the RSD limits. For calibration, x is the mass of the analyte in the sample aliquot introduced into the instrument and y is the area or the response, as in:

x = C_s and y = A_s

A linear least squares regression attempts to construct a linear equation of the form:

$y = ax + b$

by minimizing the differences between the observed results (y_i, the instrument response) and the predicted results (y_i', the response calculated from the constructed equation). The regression equation is:

$y_i' = ax_i + b$

a = regression coefficient or the slope of the line.
B = the y-intercept.
Y_i' = predicted (or calculated) response for the i^{th} calibration standard.
X_I = mass of analyte in the i^{th} calibration standard aliquot introduced into the instrument.

The sum of the squares of the differences is minimized to obtain a and b:

$$\sum_{i=1}^{n}(y_i - y_i')^2$$

n = total number of calibration points. The regression calculations attempt to minimize this sum of the squares, hence the name "least squares regression."

Weighting the sum of the square of the differences may significantly improve the ability of the least squares regression to fit the linear model to the data. The general form of the sum of the squares of the differences containing the weighting factor is:

$$\sum_{i=1}^{n} w_i(y_i - y_i')^2$$

w_i = weighting factor for the i^{th} calibration standard (w=1 for unweighted least squares regression).
Y_i – observed instrument response (area) for the i^{th} calibration standard.
Y_i' = predicted (or calculated) response for the i^{th} calibration standard.
N = total number of calibration standards.

The mathematics used in least squares regression has a tendency to favor numbers of larger value over numbers of smaller value. Thus the regression curves that are generated tend to fit points that are at the upper calibration levels better than those points at the lower calibration levels. To compensate for this, a weighting factor which reduces this tendency can be used. Examples of allowed weighting factors which can place more emphasis on numbers of smaller value are:

$w_i - 1/x_i$ or $w_i = 1/x_i^2$

Do not include the origin (0, 0) as an extra calibration point. Re-process each calibration standard as an unknown to determine the best fit model. Each calibration point above the RL must be ± 15% true (8000B) or ± 20% true (8000C); the RL-level standard must be ± 30% true.

The regression calculation generates a correlation coefficient I that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.995 or $r^2 \geq 0.990$.

11.8 Coefficient of Determination

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2}$$

Correlation Coefficient

$$r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response or Response ratio
x = Concentration

11.9 Calculation

- For **aqueous** samples:

Concentration (µg/L) = $\frac{A_x V_t D}{RF_{mean} V_s}$ or $\frac{(\mu g/mL \text{ from instrument})(D)(1000)}{mL \text{ extracted}}$

A_x = Area of the peak for the analyte in the sample.
V_t = Total volume of the concentrated extract (mL).
D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.
RF_{mean} = Mean response factor from the initial calibration (area/concentration).
V_s = Volume of the aqueous sample extracted in mL.

- For **non-aqueous** samples:

Concentration (µg/kg) = $\frac{A_x V_t D}{RF_{mean} W_s}$ or $\frac{(\mu g/mL \text{ from instrument})(D)(1000)}{g \text{ extracted}}$

A_x, V_t, D, RF_{mean} are the same as for aqueous samples, and
W_s = Weight of sample extracted (g). The wet weight or dry weight may be used, depending upon the specific application of the data.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average %

recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes must be stored, managed, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Dispose of waste extracts in the waste solvent drum.

15.0 References / Cross References

15.1 Method 8270C, SW-846 Update III Revision 3, December 1996 and **Method 8270D**, Update IV, Revision 4, February 2007.

15.2 Method 8000B, SW-846, Revision 2, December 1996, **Method 8000C**, Revision 3, March 2003.

15.3 Method 625, Federal Register, 40 CFR Part 136, July 1, 1991 and Attachment 1 to 625, Dec 22, 2000.

15.4 TestAmerica Nashville's Quality Assurance Manual.

15.5 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.6 SOPs: Acceptable Manual Integration Practices / CA-Q-S-002, Calibration Curves and Selection of Calibration Points / CA-Q-P-003, Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Determination of Method Detection Limits / NV08-202, Reagent and Standard Purchase / NV08-214, 3550 / NV03-23, and 3510 608 608.2 610 625 / NV03-24, 3541 / NV03-231, 3580 / NV03-106, 8270/NVOH04-22, 3546 / NV03-247, OA-2 / NV04-188.

15.7 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

15.8 Corporate Quality Memorandum No. CA-Q-QM-005, May 19, 2010.

16.0 Method Modifications

Item	Modification
1	See Attachment 5 for the State of Ohio specific criteria.
2	See Attachment 6 for the State of Missouri DRO, CA LUFT DRO by GC/MS.
3	Verify with state certifications the correct version of this method to report. **Analyze and report by 8270D for NJ, NC, OK, SC, and WV samples.**
4	Nashville is not certified in SC for SIM. SC has not approved RVE/LVI.
5	RVE/LVI.

17.0 Attachments

Attachment 1, Characteristic Ions for Semivolatile Compounds[a]

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
1,4-Dioxane	2.568	88	58
n-Nitrosodimethylamine	2.700	74	42, 44
Pyridine	2.714	79	52
2-Picoline	3.464	93	66, 92
n-Nitrosomethylethylamine	3.558	88	42, 43, 56
2-Fluorophenol (surr)	3.687	112	64
Methyl methanesulfonate	3.764	80	79, 65, 95
Benzaldehyde	3.785	105	77, 51
n-Nitrosodiethylamine	4.009	102	42, 57, 44, 56
Ethyl methanesulfonate	4.197	79	109, 97, 45, 65
Hexachloropropene	4.261	213	211,215,117,106,141
Phenol-d_5 (surr)	4.266	99	42, 71
Aniline	4.270	93	66, 65
Bis(2-chloroethyl) ether	4.294	93	63, 95
Phenol	4.275	94	65, 66
2-Chlorophenol	4.345	128	64, 130
1,3-Dichlorobenzene	4.425	146	148, 113
1,4-Dichlorobenzene-d_4 (IS)	4.444	152	150, 115
1,4-Dichlorobenzene	4.454	146	148, 113
Pentachloroethane	4.474	117	165, 167, 119
Benzyl alcohol	4.543	79	108, 77
n-Decane	4.550	57	
1,2-Dichlorobenzene	4.571	146	148, 113
2-Methylphenol	4.628	108	107, 77, 79, 90
Bis(2-chloroisopropyl) ether	4.632	45	77, 79
N-Nitrosodi-n-propylamine	4.717	130	42, 101, 70
3, 4-Methylphenol	4.717	107	108, 77, 79, 90
Hexachloroethane	4.764	117	201, 199
Nitrobenzene-d_5 (surr)	4.806	82	128, 54
Nitrobenzene	4.816	77	123, 65
n-Nitrosopyrrolidine	4.907	102	41, 42, 68, 69
Acetophenone	4.912	105	71, 51, 120
n-Nitrosomorpholine	4.916	56	116, 86
o-Toluidine	4.940	106	107, 77, 51, 79
Isophorone	4.957	82	95, 138
2-Nitrophenol	5.018	139	109, 65
2,4-Dimethylphenol	5.037	122	107, 121
Bis(2-chloroethoxy)methane	5.088	93	95, 123
Caprolactam	5.111	113	84, 55
n-Nitrosopiperidine	5.114	114	42, 55, 56, 41
Benzoic acid	5.116	105	122, 77
2,4-Dichlorophenol	5.168	162	164, 98
1,2,4-Trichlorobenzene	5.215	180	182, 145
Naphthalene-d_8 (IS)	5.248	136	68
Naphthalene	5.257	128	129, 127
o,o,o-Triethylphosphorthioate	5.302	198	121, 97
4-Chloroaniline	5.304	127	129, 65, 92
Hexachlorobutadiene	5.370	225	223, 227
a,a-Dimethylphenylethylamine	5.372	58	91, 65, 134, 42
2,6-Dichlorophenol	5.523	162	

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
Hexachloropropene	5.556	213	211, 215, 117, 106, 141
4-Chloro-3-methylphenol	5.615	142	107, 144
Biphenyl	5.661	154	153, 152
2-Methylnaphthalene	5.704	142	141
n-Nitrosodi-n-butylamine	5.729	84	57, 41, 116, 158
1,4-Phenylenediamine	5.734	108	80, 107
1-Methylnaphthalene	5.779	142	141, 115
Hexachlorocyclopentadiene	5.854	237	235, 272
Isosafrole (trans)	5.861	162	131, 104, 77
2,4,6-Trichlorophenol	5.911	196	198, 200
2,4,5-Trichlorophenol	5.944	196	198, 97, 132, 99
2-Fluorobiphenyl (surr)	5.953	172	171
2-Chloronaphthalene	6.033	162	127, 164
Isosafrole (cis)	6.054	162	131, 104, 77
1,2,4,5-Tetrachlorobenzene	6.063	216	214,179,108,143,218
2-Nitroaniline	6.118	138	92, 65
2,3-Dichloroaniline	6.134	161	90, 63
Safrole	6.204	162	104, 77, 103, 135
Dimethyl phthalate	6.245	163	194, 164
1-Chloronaphthalene	6.284	162	127, 164
2,6-Dinitrotoluene	6.296	165	63,89, 121
Acenaphthylene	6.320	152	151, 153
1,4-Naphthoquinone	6.374	158	104, 102, 76, 50, 130
3-Nitroaniline	6.404	138	108, 92
Acenaphthene	6.447	154	153, 152
2,4-Dinitrophenol	6.470	184	63, 154
1,3-Dinitrobenzene	6.486	168	76, 50, 75, 92, 122
4-Nitrophenol	6.527	65	109, 139
n-Hexadecane	6.559	57	71, 85
Dibenzofuran	6.560	168	139
2,4-Dinitrotoluene	6.574	165	63, 89, 182
Acenaphthene-d_{10} (IS)	6.656	164	162, 160
Diethyl phthalate	6.738	149	177, 150
4-Chlorophenyl phenyl ether	6.790	204	206, 141
Fluorene	6.799	166	165,167
Pentachlorobenzene	6.806	250	252,108,248,215,254
4-Nitroaniline	6.837	138	65, 108, 92, 80, 39
1-Naphthylamine	6.844	143	115, 89, 63
4,6-Dinitro-2-methylphenol	6.865	198	51, 105, 182, 77
n-Nitrosodiphenylamine	6.879	169	168, 167
2-Naphthylamine	6.895	143	115, 116
2,3,4,6-Tetrachlorophenol	6.900	232	131,230,166,234,168
1,2-Diphenylhydrazine	6.903	77	105, 182
2,4,6-Tribromophenol (surr)	6.987	330	332, 141
Thionazine	7.027	107	96, 97,143, 79, 68
5-Nitro-o-toluidine	7.051	152	77, 79, 106, 94
Diphenylamine	7.107	168	169, 167
4-Bromophenyl phenyl ether	7.138	248	250, 141
Hexachlorobenzene	7.255	284	142, 249
Sulfotepp	7.276	322	97, 202
Atrazine	7.312	200	215, 173
1,3,5-Trinitrobenzene	7.314	213	74, 120, 91, 63

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
Diallate (trans)	7.337	86	234, 43, 70
Phenacetin	7.337	108	180,179,109,137,80
Phorate	7.347	75	121, 97, 93, 260
Pentachlorophenol	7.387	266	264, 268
Diallate (cis)	7.403	86	234, 43, 70
Dimethoate	7.474	87	93, 125, 143, 229
Phenanthrene-d_{10} (IS)	7.476	188	94, 80
Phenanthrene	7.495	178	179, 176
Anthracene	7.528	178	176, 179
4-Aminobiphenyl	7.568	169	168, 170, 115
n-Octadecane	7.586	57	71
Pronamide	7.619	173	175, 145, 109, 147
Carbazole	7.641	167	139, 84
Pentachloronitrobenzene	7.676	237	142,214,249,295,265
Disulfoton	7.723	88	97, 89, 142, 186
Dinoseb	7.737	211	163, 147, 117, 240
Di-n-butyl phthalate	7.914	149	150, 104
Methyl parathion	8.000	109	125, 263, 79, 93
Parathion	8.292	109	97, 291, 139, 155
4-Nitroquinoline-1-oxide	8.310	190	101, 128, 75, 116
Methapyrilene	8.371	58	50, 191, 71
Fluoranthene	8.374	202	100, 101, 203
Benzidine	8.464	184	92, 185
Isodrin	8.522	193	66, 195, 263,265,147
Pyrene	8.543	202	100, 101, 200, 203
Terphenyl-d_4 (surr)	8.652	244	122, 212
Aramite	8.870	191	319, 334, 197, 321
Dimethylaminoazobenzene	9.001	120	77, 105, 148, 42
Butyl benzyl phthalate	9.028	149	91, 206
Chlorobenzilate	9.034	139	253, 111, 141
Hexachlorophene	9.070	196	198, 209
3,3'-Dimethylbenzidine	9.251	212	106, 196, 180
Bis (2-ethylhexyl) adipate	9.298	129	57, 112, 147
4,4'-Methylenebis (2-chloroaniline)	9.301	231	266, 140, 77
Kepone	9.316	272	274,237,178,143,270
3,3'-Dichlorobenzidine	9.423	252	254, 126
Benz(a)anthracene	9.446	228	229, 226
2-Acetylaminofluorene	9.453	181	180, 223, 152
Chrysene-d_{12} (IS)	9.456	240	120, 236
Chrysene	9.474	228	226, 229
Bis(2-ethylhexyl) phthalate	9.474	149	167, 279
Di-n-octyl phthalate	9.926	149	167, 43
Benzo(b)fluoranthene	10.292	252	253, 125
3-Methylcholanthrene	11.305	268	252,253,126,134,113
Benzo(k)fluoranthene	10.311	252	253, 125
Benzo(e)pyrene	10.55	252	253, 125
Benzo(a)pyrene	10.579	252	253, 125
7,12-Dimethylbenz_nthraxhracene	10.600	256	241, 239, 120
Perylene-d_{12} (IS)	10.631	264	260, 265
Indeno)1,2,3-c,d)pyrene	11.778	276	138, 277
Dibenz(a,h)anthracene	11.783	278	139, 279
Dibenz(a,j)acridine	11.987	279	280, 277, 250

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
Dibenz(a,j)acridine	11.987	279	280, 277, 250
Benzo(g,h,i)perylene	12.107	276	138, 277
IS = internal standard			
surr = surrogate			
[a]See Attachment 2 for Retention Times and Ions used with SIM.			

Attachment 2, Retention Times, Dwell Times, and Characteristic Ions for SIM

Compounds	RT	Dwell Time (minutes)	Primary	Secondary*
Compounds	RT	Dwell Time (minutes)	Primary	Secondary*
1,4-Dioxane	2.52	50	88	58
n-Nitrosodimethylamine	2.99	50	74	42
2-Fluorophenol	4.58	50	112	64
Phenol-d_5	5.35	15	99	71
Bis(2-chloroethyl)ether	5.43	15	93	63
1,4-Dichlorobenzene-d_4	5.63	50	150	152
Nitrobenzene-d_5	6.01	45	82	128
Naphthalene-d_8	6.52	20	136	68
Naphthalene	6.53	20	128	129
Hexachlorobutadiene	6.61	20	225	223
2-Methylnaphthalene	7.02	20	142	141
1-Methylnaphthalene	7.09	20	142	141
Hexachlorocyclopentadiene	7.12	20	237	235
2-Fluorobiphenyl	7.27	20	172	171
2,6-Dinitrotoluene	7.61	10	165	89
Acenaphthylene	7.67	10	152	151
Acenaphthene-d_{10}	7.78	10	164	163
Acenaphthene	7.80	10	153	154
2,4-Dinitrotoluene	7.91	10	165	89
Dibenzofuran	7.93	10	168	139
Fluorene	8.20	20	166	165
4,6-Dinitro-2-methylphenol	8.22	20	198	105
2,4,6-Tribromophenol	8.38	20	330	332
Hexachlorobenzene	8.63	10	284	249
Pentachlorophenol	8.78	10	266	268
Phenanthrene-d_{10}	8.94	10	188	80
Phenanthrene	8.96	10	178	176
Anthracene	9.00	10	178	176
Fluoranthene	9.92	15	202	200
Pyrene	10.11	15	202	200
Terphenyl-d_{14}	10.23	15	244	122
Benzo(a)anthracene	11.09	10	228	149
Chrysene-d_{12} (IS)	11.10	10	240	228
Bis(2-ethylhexyl)phthalate	11.10	10	149	167
Chrysene-d_{12}	11.10	10	240	278
Chrysene	11.12	10	228	226
Benzo(b)fluoranthene	11.97	10	252	253
Benzo(k)fluoranthene	12.00	10	252	253
Benzo(a)pyrene	12.28	10	252	250
Perylene-d_{12}	12.33	10	264	260
Indeno(1,2,3-cd)pyrene	13.47	50	276	277
Dibenzo(ah)anthracene	13.48	50	278	279

Compounds	RT	Dwell Time (minutes)	Primary	Secondary*
Compounds	RT	Dwell Time (minutes)	Primary	Secondary*
Benzo(ghi)perylene	13.81	50	276	277
Internal standards are in **bold.**				

Attachment 3, 8270D Minimum Response Factor Criteria for Initial and Continuing Calibration Verification Using the Suggested Ions from Attachments 1 and 2.

Compound	Minimum RF	Compound	Minimum RF
1,2,4,5-Tetrachlorobenzene	0.010	Butyl benzyl phthalate	0.010
1,1'-Biphenyl	0.010	Caprolactam	0.010
1,2,4-Trichlorobenzene	0.001	Carbazole	0.010
1,2-Dichlorobenzene	0.001	Chlorobenzilate	0.001
1,3,5-Trinitrobenzene	0.001	Chrysene	0.700
1,3-Dichlorobenzene	0.001	Di(2-ethylhexyl)adipate	0.001
1,3-Dinitrobenzene	0.001	Diallate	0.001
1,4-Dichlorobenzene	0.001	Diallate	0.001
1,4-Dinitrobenzene	0.001	Diallate Peak 1	0.001
1,4-Dioxane	0.05	Diallate Peak 2	0.001
1,4-Naphthoquinone	0.001	Dibenz(a,h)anthracene	0.400
1-Chloronaphthalene	0.001	Dibenz[a,h]acridine	0.001
1-Methylnaphthalene	0.001	Dibenz[a,j]acridine	0.001
1-Naphthylamine	0.001	Dibenzofuran	0.800
2,2'-oxybis[1-chloropropane]	0.010	Diethyl phthalate	0.010
2,3,4,6-Tetrachlorophenol	0.010	Dimethoate	0.001
2,3,5,6-Tetrachlorophenol	0.010	Dimethyl phthalate	0.010
2,3-Dichlorobenzenamine	0.001	Di-n-butyl phthalate	0.010
2,4,5-Trichlorophenol	0.200	Di-n-octyl phthalate	0.010
2,4,6-Tribromophenol	0.001	Dinoseb	0.001
2,4,6-Trichlorophenol	0.200	Diphenylamine	0.01
2,4-Dichlorophenol	0.200	Disulfoton	0.001
2,4-Dimethylphenol	0.200	Ethyl methanesulfonate	0.001
2,4-Dinitrophenol	0.010	Ethyl Parathion	0.001
2,4-Dinitrotoluene	0.200	Famphur	0.001
2,6-Dichlorophenol	0.001	Famphur Peak 1	0.001
2,6-Dinitrotoluene	0.200	Famphur Peak 2	0.001
2-Acetylaminofluorene	0.001	Fluoranthene	0.600
2-Chloronaphthalene	0.800	Fluorene	0.900
2-Chlorophenol	0.800	Hexachlorobenzene	0.100

Compound	Minimum RF	Compound	Minimum RF
2-Fluorobiphenyl (Surr)	0.001	Hexachlorobutadiene	0.010
2-Fluorophenol	0.001	Hexachlorocyclopentadiene	0.050
2-Methylnaphthalene	0.400	Hexachloroethane	0.300
2-Methylphenol	0.700	Hexachlorophene	0.001
2-Naphthylamine	0.001	Hexachloropropene	0.001
2-Nitroaniline	0.010	Hexadecane	0.001
2-Nitrophenol	0.100	Indene	0.001
2-Picoline	0.001	Indeno[1,2,3-cd]pyrene	0.500
2-Toluidine	0.001	Isodrin	0.001
3 & 4 Methylphenol	0.600	Isophorone	0.400
3,3'-Dichlorobenzidine	0.010	Isosafrole	0.001
3,3'-Dimethylbenzidine	0.001	Isosafrole Peak 1	0.001
3,4-Dichlorophenol	0.001	Isosafrole Peak 2	0.001
3-Methylcholanthrene	0.001	Kepone	0.001
3-Nitroaniline	0.010	Methapyrilene	0.001
4,4'-Methylene bis(2-chloroaniline)	0.001	Methyl methanesulfonate	0.001
4,6-Dinitro-2-methylphenol	0.010	Methyl parathion	0.001
4-Aminobiphenyl	0.001	Methyl Phenols,Total	0.001
4-Bromophenyl phenyl ether	0.100	Naphthalene	0.700
4-Chloro-3-methylphenol	0.200	n-Decane	0.001
4-Chloroaniline	0.010	Nitrobenzene	0.200
4-Chlorophenol	0.001	Nitrobenzene-d5	0.001
4-Chlorophenyl phenyl ether	0.400	N-Nitro-o-toluidine	0.001
4-Nitroaniline	0.010	N-Nitrosodiethylamine	0.001
4-Nitrophenol	0.010	N-Nitrosodimethylamine	0.001
4-Nitroquinoline-1-oxide	0.001	N-Nitrosodi-n-butylamine	0.001
6-Methylchrysene	0.001	N-Nitrosodi-n-propylamine	0.500
7,12-Dimethylbenz(a)anthracene	0.001	N-Nitrosodiphenylamine	0.010
Acenaphthene	0.900	N-Nitrosomethylethylamine	0.001
Acenaphthylene	0.900	N-Nitrosomorpholine	0.001
Acetophenone	0.010	N-Nitrosopiperidine	0.001
Acrylamide	0.001	N-Nitrosopyrrolidine	0.001
alpha,alpha-Dimethyl phenethylamine	0.001	n-Octadecane	0.001
Alpha-Terpineol	0.001	o,o',o'-Triethylphosphoro-thioate	0.001
Aniline	0.001	o-Terphenyl	0.001
Anthracene	0.700	p-Dimethylamino azoben-zene	0.001

Compound	Minimum RF	Compound	Minimum RF
Aramite Peak 1	0.001	Pentachlorobenzene	0.001
Aramite Peak 2	0.001	Pentachloroethane	0.001
Aramite, Total	0.001	Pentachloronitrobenzene	0.001
Aramite, Total	0.001	Pentachlorophenol	0.050
Atrazine	0.01	Phenacetin	0.001
Azobenzene	0.001	Phenanthrene	0.700
Benzaldehyde	0.010	Phenol	0.800
Benzidine	0.001	Phenol-d5	0.001
Benzo[a]anthracene	0.800	Phenylmercaptan	0.001
Benzo[a]pyrene	0.700	Phorate	0.001
Benzo[b]fluoranthene	0.700	p-Phenylene diamine	0.001
Benzo[e]pyrene	0.700	Pronamide	0.001
Benzo[g,h,i]perylene	0.500	Pyrene	0.600
Benzo[k]fluoranthene	0.700	Pyridine	0.001
Benzoic acid	0.001	Quinoline	0.001
Benzyl alcohol	0.001	Safrole, Total	0.001
Bis(2-chloroethoxy)methane	0.300	Sulfotepp	0.001
Bis(2-chloroethyl)ether	0.700	Terphenyl-d14	0.001
Bis(2-ethylhexyl) phthalate	0.010	Thionazin	0.001

Attachment 5, State of Ohio Specific Criteria.
Only those compounds in the original EPA Method 8270C may be reported. Any compounds in this SOP in italics in Section 1 are not part of the original 8270C method. Run Ohio VAP samples according to SOP 8270/NVOH04-22.

Attachment 6, Missouri Department of Natural Resources (and CA LUFT) require(s) that **DRO** be analyzed by GC/MS.

- Tuning and frequency requirements are the same as in 8270, omitting DDT, Pentachlorophenol, and Benzidine.
- Extract water samples per SOP 3510 608 608.2 610 625 / NV03-24 and solid samples per SOP 3550 / SA03-23.
- Only base/neutral surrogates are needed.
- Required GC/MS mass range is 35-550 amu.
- Use a five-point calibration curve with 1:1 unleaded gasoline and #2 diesel fuel at 1,000 µg/mL each in Methylene chloride.
- Retention time windows set using C_{10}, C_{21}, and C_{35}. For DRO, set RT 0.1 minutes after C10 to 0.1 minutes after C21. For ORO, set RT 0.1 minutes after C_{21} to 0.1 minutes after C_{35}. Verify RT daily (24 hours) by running component standard.
- Quantitative using baseline-to-baseline, not valley-to-valley. The Total Ion Chromatogram must be used to quantitate.
- The Response Factor determined for DRO (C_{10}-C_{21}) must be used for C_{21}-C_{35}.

- Subtract area from any Internal Standard and surrogates.
- % RSD ≤ 20.
- Run a CCV at the beginning and end of each batch; it must contain all targets reported, at mid-point of calibration, % D ≤ 20.
- Run a Method Blank every extraction batch, and LCS and MS/MSD per batch.
- May reprocess file to quantitate PAH if needed. For individual targets, % RSD ≤ 15.
- Quantitation of DRO must be by external standard.
- Required standards: #1 - #5 diesel, mineral spirits, kerosene, JP4, jet fuel, motor oil, and hydraulic fluid. See SOP OA-2 / NV04-188 for standards used.

18.0 Revision History

- Revision 12, 22 October 2008
  - Integration for TestAmerica and STL operations.
  - Insert corrective action procedures
  - To incorporate Update IV criteria.
- Revision 13, 9 October 2009
  - Consolidation of text, general editing.
  - Add Appendix IX and miscellaneous compound details.
  - Distinguish 8270C versus 8270D.
- Revision 14, 30 September 2011
  - Organizational changes.
  - Add amendments 13a and 13b.
  - Add reference to SOP 3541 for concrete and SOP Calibration Curves (General).
  - Add QAF-45 and Section 14.2.
  - Remove WY as a state requiring QC every 10 samples.
  - Change Attachment 5 to refer analysts to OH8270 SOP.
  - Add Attachment 7
  - Add option to run LLCCV to show sensitivity.
  - Add note about low-level calibration standard for SIM WI samples.
  - Lower several report limits.
  - Specify GC resolution between two isomer peaks for 8270C versus 8270D.
- Revision 15, 31 December 2012
  - Organizational changes.
  - Incorporation of amendments 14a, b, c.
  - OK no longer limits batch size to 10 samples.
  - Specify that $r^2 \geq 0.990$.
  - Substitute LIMS for the Control Limits Manual.
  - Distinguish between the RSD maximum for 8270C and 8270D. For 8270D, all targets are treated as CCCs.
  - Add re-fitting text to the linear calibration section.
  - Add Reduced Volume Extraction / Large Volume Injection (RVE / LVI).
- Revision 16, 31 March 2014
  - Organizational changes.
  - Add Change forms 15a, b, c.
  - Add reference to Method 3546, Microwave Extraction.
  - Addition of criterion for TIC evaluation.
  - Refer to “AutoSIM” function of the software instead of dwell times.
  - Update for new standards.
- Revision 17, dated 30 April 2015
  - Organizational changes.
  - Combine 8270 / NV04-22.16c and 625 / NV04-27=13c into one SOP. Move the purge

and trap portion of 625 to 3510 608 608.2 610 625 / NV03-107.

- 8270-16a: Addition of Benzo(e)pyrene.
- 8270-16b: Addition of wipes as a matrix, CT RCP 8270C, MA MCP 8270D, and NJ DKQP QC acceptance criteria.
- 8270-16c: Addition of Atrazine, Benzaldehyde, Biphenyl, Caprolactam, and n-Hexadecane to analyte list.
- 625-13a (and 8270-15c): In the SIM Mass Groups attachment, remove Dwell Time column and add that dwell times are in Chemstation AutoSIM.
- 625-13b: Addition of Q-value definition and an example of relative intensity acceptance.
- 625-13c: Addition of Chrysene-d_{12} (IS) RT and primary/secondary ions. Update standards used. Add note that SC requirese 1 Liter for water samples. Change the requirement that analysis must not begin until the tuning criteria are met and are demonstrated at the beginning of each 24-hour period, instead of each 12-hour shift.

- Addition of new Missouri RBCA guidelines
- The LCS/MS/MSD is now made from the primary source standards for 8270 only.
- Added details about wipes, LVI SIM, and DRO.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville Standard Operating Procedure (SOP) Change Form

SOP Number/Revision No.: **410.4 SM5220 D / NV07-08.7a** Effective Date: **11/28/2014**

Last Mod. Date: 10/31/14

SOP Title: **Method EPA 410.4 / SM5220 D: Chemical Oxygen Demand By Manual Colorimetry**

Affected SOP Section Number(s): Section 10.2, Calibration

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 07

Revision Number with Mod ID: **7b**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add underlined text; delete crossed-out text.

Section 10.2 Calibration
Prepare a calibration curve, using the primary stock standard.

Standard Curve Preparation:

Volume (mL) of 1000 mg/L Primary Standard	Final Volume (mL) in Reagent Water	Concentration (mg COD/L)
0.2	10	20
0.5	10	50
0.75	10	75
1.0	10	100
1.5	10	150
Use reagent water to zero instrument (420 nm).		

Approvals (Signature/Date)

Steve Miller	11/7/14	Michael H. Dunn	11/6/14
Steve Miller Quality Assurance Manager	Date	Michael H. Dunn Technical Director	Date

SOP Number/Revision No.: **410.4 SM5220 D / NV07-08.7** Effective Date: **10/31/2014**

Last Mod. Date: 2/28/14

SOP Title: **Method EPA 410.4 / SM5220 D: Chemical Oxygen Demand By Manual Colorimetry**

Affected SOP Section Number(s): Section 9.1

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 07

Revision Number with Mod ID: **7a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add underlined text; delete crossed-out text.

Section 9.1, Sample QC

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Method Blank	1 in 20 or fewer samples	< ½ RL or MDL, whichever is greater.	Reprep, rerun
Laboratory Control Sample (LCS)[1]	1[1] in 20 or fewer samples	410.4: 90-110% Recovery SM5220 D: 95-105%	Rerun
410.4: Matrix Spike (MS) ~~for EPA 410.4~~	1 in 10 or fewer samples	90-110% Recovery ~~for 410.4; see LIMS for SM5220 D~~.	None
SM5220 D: Matrix Spike / Matrix Spike Duplicate (MS/MSD) ~~for SM5220 D~~	1 in 20 or fewer samples	~~See LIMS~~ 95-105%	• If both MS and MSD are similarly outside acceptable limits and the LCS is within acceptable limits, the batch is acceptable. • If one analysis of the MS/MSD pair is within acceptable limits and the other is outside acceptable limits, repeat the analysis exhibiting unacceptable results.
SM5220 D: Sample Duplicate (~~SM5220 D only~~)	1 in 20 or fewer samples	≤ 20% RPD [1]	Report

1 All AZ, MA, and TX samples require a LCS duplicate in each batch.

SOP Number/Revision No.: **410.4 SM5220 D / NV07-08.7a** Effective Date: **11/28/2014**

Sessily Overton-Gray	10/31/14		
Sessily Overton-Gray Department Manager	Date		
Steve Miller	10/31/14	Michael H. Dunn	10/31/14
Steve Miller Quality Assurance Manager	Date	Michael H. Dunn Technical Director	Date

Title: CHEMICAL OXYGEN DEMAND BY MANUAL COLORIMETRY METHOD EPA 410.4 / SM5220 D

Approvals (Signature/Date)	
Sessily Overton-Gray 2/17/14	Johnny Davis 1/23/14
Sessily Overton-Gray Date Department Manager	Johnny Davis Date Health & Safety Manager / Coordinator
Steve Miller 1/25/14	Michael H. Dunn 2/27/14
Steve Miller Date Quality Assurance Manager	Michael H. Dunn Date Technical Director

1.0 Scope and Application

1.1 Analyte, Matrices: This method covers the determination of chemical oxygen demand (COD) in ground and surface waters, domestic and industrial wastes.

1.2 Reporting Limits: The reporting limit is nominally 20 mg/L.

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

Sample, blanks, and standards in sealed tubes are heated in a block digester in the presence of dichromate at 150°C. After two hours, the tubes are removed from the digester, cooled, and measured spectrophotometrically at 420 ηm

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion tubes to complex the chlorides.

4.2 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that bias analyte response.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: The disposable glass COD digestion tubes used in this analysis contain Mercuric sulfate, a compound composed of Mercuric Oxide Red which may affect the central nervous system, and Sulfuric acid. Wash spills with running water.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercuric oxide, Red	Oxidizer Corrosive Poison	0.1 mg/m^3 Ceiling (Mercury Com-pounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. **May affect the central nervous system.** Causes irritation and burns to the eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium dichromate	Oxidizer Corrosive Carcinogen	0.1 mg/m^3 TWA as CrO_3	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. May cause ulceration and perforation of the nasal septum. Symptoms of redness, pain, and sever burn can occur. Dusts and strong solutions may cause severe irritation. Contact can cause blurred vision, redness, pain, and severe tissue burns. May cause corneal injury or blindness.
Sulfuric acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and sever burn can occur. Contact can cause blurred vision, redness, pain, and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reaction.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- HACH COD Reactor, capable of maintaining 150 ± 2°C.
- HACH DR/6000 Spectrophotometer.
- Balance, analytical, capable of accurately weighing to the nearest 0.0001 gram.

6.2 Supplies

- Glassware, Class A volumetric flasks and pipets as required.
- Test tube rack.
- Chloride test strips, Hach 27513, or equivalent.

7.0 Reagents and Standards

7.1 Reagent water, analyte-free.

7.2 COD Digestion Reagent Vials

- Low-range, 0-150 mg COD/L, HACH 21258-25, or equivalent.

7.3 COD Stock Standard Solution, primary source, commercially available, 1000 µg/mL, HACH 22539-29.

7.4 COD Stock Standard Solution, secondary source, commercially available, 500 µg/mL, Accustandard WC-COD-5X-10ml.

7.5 Alternative to the commercially available standards, a stock potassium hydrogen phthalate standard can be made by dissolving 0.850 g KHP (dried overnight at 120°C) in 800 mL of reagent water and dilute to 1 liter for a 1000 mg/L standard. Add 3 drops of H_2SO_4 and store for up to 6 months. Two different vendors of KHP may be used to have two sources.

7.6 See SOP Reagent and Standard Purchase, Preparation, Control, and Documentation / NV08-214. Also, refer to benchsheets, logbooks, and LIMS.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	HDPE or Glass	125 mL	Cool 0-6°C, H_2SO_4 to pH , 2	28 days	40 CFR Part 136.3, SM Table 1060: I

9.0 Quality Control

Refer to the QA Manual for specific quality control policies. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC: The following quality control samples are prepared with each batch of no more than 20 samples. QC samples are prepared in the same manner as the samples.

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Method Blank	1 in 20 or fewer samples	< ½ RL or MDL, whichever is greater.	Reprep, rerun
Laboratory Control Sample (LCS)[1]	1[1] in 20 or fewer samples	90-110% Recovery	Rerun
Matrix Spike (MS) for EPA 410.4	1 in 10 or fewer samples	90-110% Recovery for 410.4; see LIMS for SM5220 D.	None
Matrix Spike / Matrix Spike Duplicate (MS/MSD) for SM5220 D	1 in 20 or fewer samples	See LIMS	- If both MS and MSD are similarly outside acceptable limits and the LCS is within acceptable limits, the batch is acceptable. - If one analysis of the MS/MSD pair is within acceptable limits and the other is outside acceptable limits, repeat the analysis exhibiting unacceptable results.
Sample Duplicate (SM5220 D only)	1 in 20 or fewer samples	≤ 20% RPD	Report

1 All AZ, MA, and TX samples require a LCS duplicate in each batch.

- The **Method Blank** is used to assess contamination from the laboratory environment. Use reagent water.
- **Laboratory Control Sample (LCS)**: To prepare the spiking solution for the **LCS**: Low-range: dilute 0.5 mL of secondary standard to 5.0 mL with reagent water for a 50 mg/L standard.
- **Matrix Spike (MS) / Matrix Spike Duplicate (MSD):** To prepare the spiking solution for the MS, add 0.20 mL of secondary standard to 2.0 mL client sample for a 50 mg/L standard. If the recovery falls outside the designated recovery range and the LCS is in control, the recovery problem encountered with the MS is judged to be either matrix or solution related, not system related. Qualify MS in LIMS.
- **Sample Duplicate:** A second, identical aliquot of one client sample per batch is required for SM5220 D.

9.2 Instrument QC

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Initial calibration, minimum 5-point and blank	Each new lot of COD Reagent Vials, every 6 months, or if CCV fails.	RSD ± 10% or use first-order linear regression with r ≥ 0.995 or r^2 > 0.990. All standards ± 10% of true (except RL standard at ± 25%) when re-fitted against initial calibration. .	Re-prepare standards and re-run.

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration Verification Sample (ICV), second source	Immediately after calibration	90-110% recovery	Recalibrate, rerun
Continuing Calibration Verification Sample (CCV)	Every 10 samples and at the end of the run	90-110%	If not verified, reanalyze. If still not verified, correct, re-calibrate (all samples since the last acceptable CCV must be reanalyzed.
Continuing Calibration Blank (CCB)	Following the CCV	< RL	Re-prep, rerun

- **Calibration:** See Section 10.
- **Initial Calibration Verification (ICV):** Prepare as for the LCS.
- **Initial Calibration Blank (ICB):** Use reagent water.
- **Continuing Calibration Verification (CCV):** To prepare the CCV**,** a mid-range check standard for the calibration, run every 10th sample and at the end of the run. The CCV is a 50 mg/L standard from the primary source (0.5 mL stock to 10 mL reagent water).
- **Continuing Calibration Blank (CCB):** Use reagent water.

10.0 Procedure

10.1 Sample Preparation

Matrix	Sample Size
Water	2 mL

1	Turn on the COD reactor, allowing to warm-up to Temperature (150 ± 2°C) before use.
2	Test each sample for chlorides using test strips. If > 1000 µg/mL, dilute the sample. Record.
3	Carefully remove the cap from a COD vial. Tilt the COD vial at a 45-degree angle away from the face and carefully add 2.0 mL of sample (or reagent water), or prepared QC solution.
4	Cap tubes tightly and inert gently several times to mix. CAUTION: Tubes are hot.
5	Place tubes into a preheated Reactor and heat for 2 hours ± 15 minutes. Record start/stop times and temperatures on the worklist. Turn off reactor and allow cooling to about 100°C before removing vials (about 20 minutes). • Samples that are above the upper calibration standard must be diluted and reanalyzed. Dilute sample in a flask or vial and add 2.0 mL of the diluted sample to an appropriate range COD reagent vial and analyze as before.
6	Remove vials from Reactor, invert to mix, and place in a test tube rack to cool to room temperature. Store in the dark until analysis.
7	Turn on DR/6000 Spectrophotometer and allow the instrument to warm up for about 15 minutes.

10.2 Calibration: Refer to SOPs Calibration Curves (General) / CA-Q-S-005 and Selection of Calibration Points / CA-T-P-002. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

1	The Linear Calibration Range (LCR) is determined at the time of a calibration. The verification of linearity must use a minimum of a blank and five standards. Each standard above the

	report limit must be within 10% of its known value (the low standard at the report limit, ± 25%), or linearity must be re-established.
2	Prepare a calibration curve, using the primary stock standard. **Standard Curve Preparation:** **Volume (mL) of 1000 mg/L Primary Standard** / **Final Volume (mL) in Reagent Water** / **Concentration (mg COD/L)** 0.2 / 10 / 20 0.5 / 10 / 50 0.75 / 10 / 75 1.0 / 10 / 100 1.5 / 10 / 150 Use undigested reagent blank for instrument reference.
3	Process the standards and blanks as described in Section 10.1.
4	After having read the standards for the calibration curve: • Right click on the data a pick save data to save the data onto the desktop in a text file. • Minimize all open programs and run the COD.exe program. • In the left hand pane, choose the data file that was just exported. • Click the appropriate calibration button depending on if you are calibrating the low range or the high range tubes. In this screen, enter the lot number of the tubes in the specified box. • From the first dropdown box, choose the number of standards in your curve. • Then, to the right, enter the concentrations of the standards in your calibration curve in the appropriate boxes. • In the second drop down box, choose at what position to look for the first calibration button point. (Example, if a blank is the first recorded data and the 10 mg/L calibration point is the second data point, choose 2 in the dropdown box.) • Click Calibrate. Look at the displayed calibration curve and verify that r^2 is greater than or equal to 0.990 (r≥0.995). Click Save. A first-order linear regression curve is used for both levels. See the QA Manual for calibration rules. • Choose the same data file and choose process. This will now recalculate the data points against the new curve so that linearity can be established.

10.3 Sample Analysis

1	From the Main Menu, touch the Custom Programs option. Choose program with the most recent calibration attach for low range COD tubes
2	Wipe each vial with a damp towel and dry with a dry towel before analysis.
3	Insert the water blank vial into the light path and close the lid.
4	Remove the blank vial and insert the CCV vial. Batch analysis can now begin.
5	Place the Method Blank vial into the light path. Touch “options” and “send data”. Repeat the process for the CCV, LCS, remaining QC and samples.
6	When data collection is complete, right click on the data in the HACHLink 2000 program and choose to save the data as a text file on the desktop. Minimize all open programs and run the COD.exe that contains the data in question and then click “go.”
7	The COD.exe program will calculate the concentration based on the absorbance data contained in the outputted text file against the previously stored linear calibration curve. The program will output the original data along with the calculated concentrations into a new file and open that in EXCEL so that it can be printed.

10.4 Example Analysis Sequence

1	Method Blank
2	ICV or CCV if using stored calibration curve
3	Method Blank
4	Samples 1-10
5	Matrix Spike
6	Matrix Spike Duplicate for SM5220 D
7	CCV
8	CCB
9	Samples 11-20*
10	Sample Duplicate for SM 5220 D
11	CCV
12	CCB

*May be up to 20 samples

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\% \text{ Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 Coefficient of Determination

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2}$$

Correlation Coefficient

$$r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response; x = Concentration

11.4 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard **must** be diluted and reanalyzed. Multiply answer by appropriate dilution factor. Report results in mg/L.

Concentration (mg/L) = (µg/mL from instrument) (Dilution)
If no dilution, the factor is 1.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses

performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an acceptable manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- COD vials are disposed of in the corrosive waste drum in the Inorganics Department. When full, the drum is taken to the waste disposal area for final disposal.

15.0 References / Cross References

15.1 Method SM5220 D - 1997, Standard Methods for the Examination of Water and Wastewater, on-line edition, 2011 editorial revisions.

15.2 EPA Method 410.4, Methods for Chemical Analysis of Water and Wastes, Approved for NPDES, issues 1993.

15.3 HACH Method 8000, "HACH Water Analysis Handbook," 3rd edition, 1997.

15.4 TestAmerica Nashville's Quality Assurance Manual.

15.5 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.6 SOPs: Calibration Curves (General) / CA-Q-S-005, Selection of Calibration Points / CA-P-T-002, Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213, Determination of Method Detection Limits / NV08-202, Reagent and Standard Purchase, Preparation, Control, and Documentation / NV08-214, Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

15.7 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachments

None.

18.0 Revision History

- Revision 3, dated 20 June 2008
  - Integration for TestAmerica and STL operations.
  - Update to MUR method references.
  - Edited for clarity.
- Revision 4, dated 30 September 2009
  - Addition of SC requirements.
- Revision 5, dated 30 April 2010
  - Distinguish between QC required for EPA 410.4 and SM5220 D in Section 9; separate Section 9 table into Sample QC and Instrument QC.
  - Addition of Section 14.2, QAF-45.
- Revision 6, dated 8 June 2012
  - Organizational changes. Update SM reference.
  - Addition of SOPs Calibration Curves (General) / CA-Q-S-005 and Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
  - Changes to Sections 9.1 and 9.2 to reflect blank criteria and different QC criteria for EPA 410.4 and SM5520 D. Added more blank information to Section 10.2.
- Revision 7, dated 28 February 2014
  - Organizational changes.
  - Raise RL to 20 mg/L and use only high range tubes.
  - Specify that $r^2 > 0.990$.
  - Add MA as one of the states requiring an LCSDs. OK no longer limits batch size to 10 samples.
  - Remove references to high range COD analysis.
  - Add the requirement to check for chlorides with the chloride test strips.

SOP Number/Revision No.: **6010 200.7 / NV06-44.16** Effective Date: **12/31/2015**

Last Mod. Date: 7/31/2015

SOP Title**: Methods 6010B/C, 200.7, Inductively Coupled Plasma-Atomic Emission Spectrometry**

CONTROLLED DISTRIBUTION

ISSUED TO: \\TAFS\Lab\Nashville\Public\QA\SOPs, 06

Revision Number with Mod ID: **16a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add highlighted information; delete crossed-out information.

Title Change: Methods 6010B/C/D, 200.7, Inductively Coupled Plasma-Atomic Emission Spectrometry

Section 1.1, Table 1

- Change the column headings: **Typical RL/LLOQ**
- Add footnote to the table: RL = Reporting Limit for 6010B/C, 200.7; LLOQ = Lower Limit of Quantitation for 6010D.

Section 1.2: Change as shown: **Reporting Limits (RLs)/Lower Limits of Quantitation (LLOQs):** Detection limits and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. Table 1 lists the analytical wavelengths and typical reporting limits (LLOQs) in clean matrices.

Section 3.0, Definitions, add a new definition:
Lower Limit of Quantitation (LLOQ) for 6010D: The lowest point of Quantitation, or in most cases, the lowest point in the calibration curve, which is ideally less than or equal to the desired regulatory action level.

Section 3.1, Instrument Detection Limits (IDLs), add new bullet:

- For 6010D, determine the IDLs by running 10 replicate reagent blanks, calculating the mean and standard deviation, and multiplying the standard deviation by 3. Negative values are zero. IDLs are needed for new instruments, after detector changes, for each preparatory method, annually at minimum.

Section 7.5, Standard Stock Solutions, add this sentence to the end of the paragraph:
The second-source standard is from a different vendor or a different lot from the same vendor as the

primary source.

Section 9.1, Sample QC

The following quality control samples must be prepared with each batch of no more than 20 samples:			
Quality Controls	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Method Blank	1 each batch	6010B/C: ≤ MDL or ½ RL whichever is greater. 6010D: ≤ ½ LLOQ 200.7: ≤ 2.2 x MDL or 10% target concentration, whichever is greater.	Re-analyze. If contamination persists, correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank. If target > 10X blank, acceptable to report.
Laboratory Control Sample (LCS)[1], second source	1 each batch	6010: 80-120% recovery 200.7: 85-115% recovery	Correct problem then re-prep and analyze the LCS and all affected targets in the affected analytical batch. If high and ND, OK to report. For 6010C, LCS may be re-analyzed once.
Matrix Spike	1 each batch	6010: 75-125%[2] recovery 200.7: 70-130% recovery	Perform post-digestion spike.
6010: Matrix Spike Duplicate	1 each batch	75-125%[2] recovery <20[2]% RPD	Perform post-digestion spike.
Post digestion spike addition	When MS/MSD fail.	Recovery within 25% for 6010B and within 20% for 6010C of the expected results.	Perform dilution test.
Dilution test	If MS/MSD fail.	1:4 fold dilution (5X) must agree within 10% of the original determination. 6010D: If the analyte concentration is within the linear range and ≥ 25 times the LLOQ, a 1:5 fold dilution must agree within 20% of the original determination.	Qualify results. 6010D: Failures are reported as estimated values.

Section 9.2, Instrument QC:

Quality Controls	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Inter-element Correction, single element standards	6 months	± RL	Alter wavelength or background correction.
6010B/C, 200.7 Spectral Interference Check Solutions, A and AB	Beginning of each day	6010: Target ± 2 times RL or ± 20% true. 200.7: Spiked targets ± 20% true. Non-spiked ± 2 x RL.	Terminate analysis; correct problem; re-analyze ICS; re-analyze all affected samples.
6010D ICAL Readback		Low-level 80-120% Other levels 90-110%	Recalibrate.
Instrument Detection Limits (IDL)	6010B/C, 200.7: Quarterly 6010D: Annually, at minimum	±3 standard deviations of the average response.	Re-run IDL. If > MDL, adjust MDL to equal IDL.
Independent Calibration Verification Sample (ICV), second source	Immediately after calibration	6010: 90-110 % recovery 200.7: 95-105%	Correct problem then repeat initial calibration.

6010D: Mid-level ICV		recovery RSD <3% from four integrations	
6010D Low-Level ICV (LLICV)		80-120% true	
Independent Calibration Blank (ICB)	Immediately after ICV	6010B/C: ≤ ½ RL 6010D: ≤ ½ LLOQ 200.7: No target analytes above IDL.	Correct problem, re-calibrate.
6010: Linear Range Standard	Daily	90-110% true	Repeat calibration (ICP2).
Continuing Calibration Verification Sample (CCV)	Every 10 samples and at the end of the run 6010D: If recalibration for drift needed during the analytical run, follow immediately with a CCV and CCB.	90-110% true	Re-analyze once. If fails again, then repeat calibration and re-analyze all samples since last successful CCV.
6010B/C: Undigested Low Level Continuing Calibration Verification (LLCCV)	Beginning and end of each batch. 6010D: Not needed	70-130% true	Re-calibrate.
Continuing Calibration Blank	Following the CCV	6010B/C: ≤ ½ RL 6010D: ≤ LLOQ 200.7: < 2-3 times MDL or RL, whichever is greater.	Correct problem then analyze calibration blank and previous 10 samples.
~~MDL Verification (digested)~~	~~Yearly~~	~~Detected~~	~~Re-evaluate MDL standard used and MDL; see Technical Director~~
Digested Lower Limit of Quantitation Check (LLQC), RLV/CRL 6010D: LLOQ determined by 7 replicates	6010: Quarterly 200.7: For **AZ, CA, HI, MN, NV**: 1 per batch, beginning of the batch	70-130% true 6010D: 65-135% true, RSD ≤ 20%.	Re-calibrate.
Internal Standards	All samples, standards, QC	60-140% true as compared to the calibration blank	Dilute and re-run. For blank and LCS, correct problem and re-run batch.

Spectral interference checking for all versions of the methods: Single element standards for all of the elements listed below are analyzed:

Al	As	Be	Cd	Cr	Cu	Pb	Mg	Mo	P	Se	Ag	Sr	Tl	Sn	Ur	Zn
Sb	Ba	B	Ca	Co	Fe	Li	Mn	Ni	K	Si	Na	S	Th	Ti	V	Zr

Observed interferences are mitigated by the use of appropriate off-peak background correction settings and interference correction equations or by changing to the use of a different wavelength. When setting interference correction equations, single element standards are analyzed at the upper concentration level established for the working range of the interfering element. The objective is to reduce interferences below the reporting limit.

For 6010B/C, 200.7, Spectral interference check solution (ICSA and ICSAB): The laboratory must periodically verify the inter-element correction routine by analyzing SIC solutions. The spectral interference check solution is run at the beginning and end of the day's sequence or every 8 hours, whichever is more frequent. If the SIC does not meet criteria, the SICs are re-analyzed. These solutions are used to periodically verify a partial list of the on-line (and possible off-line) inter-element spectral correction factors for the recommended wavelengths given in Table 1.

NOTE: The SIC solution must be analyzed more than once to confirm a change has occurred with adequate rinse time between solutions and before subsequent analysis of the calibration blank.

- To prepare the Spectral Interference Check Solutions, see Table 5:
  - The first solution is **ICSA solution.** Prepare as follows: Dilute 20 mL of ICSA Stock (SPEX INT-A1) + 10 mL HNO_3 to 200 mL with reagent water for final concentrations of 500 µg/mL each Al, Ca, Mg, and 200 µg/mL Fe.
  - The second solution is **ICSAB solution**. Prepare as follows: Dilute 20 mL of ICSA Stock (SPEX INT-A1) + 2 mL of ICSB Stock (SPEX INT-B1) + 2 mL of ICSB2 Stock (SPEX INT-B2) + 10 mL HNO_3 to 200 mL with reagent water. The final concentrations of the ICSAB are (original concentrations are shown for explanation)
- Ensure that the analytical results of ICS Solution A (ICSA) fall within the control limit of ± two times the RL of the analyte's true value or ± 20% of the analyte's true value, whichever is greater (the true value is zero unless otherwise stated) in the ICSA. For example, if the analysis result(s) for Arsenic (RL = 10 µg/L, ICSA true value = 0 µg/L) in the ICSA analysis during the run is 19 µg/L, then the analytical result for Arsenic falls within the ± two times the RL window for Arsenic in the ICSA. If the analytical results of the ICSA do not fall within the control limits, terminate the analysis, correct the problem, re-calibrate the instrument, and re-analyze the analytical samples analyzed since the last compliant ICSA was performed.
- Ensure that the results for the ICS Solution AB (ICSAB) during the analytical runs fall within the control limit of ± two times the RL of the true value or ± 20% of the true value, whichever is greater, for the analytes included in the ICSAB. If the analytical results of the ICSAB do not fall within the control limits, terminate the analysis, correct the problem, re-calibrate the instrument, and re-analyze the analytical samples analyzed since the last compliant ICSAB was performed.
- **For 6010D**, SIC solutions must be used regardless of whether or not interelement corrections are applied. They evaluate both potential spectral interferences and the accuracy of any correction equations.
  - Individual element SIC solutions are used to evaluate possible spectral interferences and to set interelement corrections if necessary. A solution of each element is prepared at the highest concentration in the linear range likely to be observed in samples. The acid strength should be equivalent to that of the calibration standards. SIC solutions are tested to verify that they are not contaminated with elements of interest. The verification of purity is done by analysis using an alternate technology, such as ICP/MS. For ICP/OES instruments with solid-state detectors, the verification might also be done by examining alternate wavelengths. If the SIC solutions are purchased ready-made, the vendor should provide details of any contaminants. In some cases it may not be possible to obtain solutions completely free of contaminants, in which case the known, verified concentration can be subtracted from the instrument result before assessing any interferences.

    At minimum, single element SIC checks must be run every six months for the following elements:
    Al 500 mg/L; B 50 mg/L; Ba 50 mg/L; Ca 500 mg/L; Cu 50 mg/L; Fe 200 mg/L; Mg 500 mg/L; Mn 50 mg/L; Mo 20 mg/L; Na 1,000 mg/L; Ni 20 mg/L; Se 20 mg/L; Si 200 mg/L; Sn 20 mg/L; V 20 mg/L; Zn 20 mg/L. The absolute value of the concentration observed for any unspiked analyte must be < 2* LLOQ.

  - A mixed element SIC solution is run as an ongoing daily check of freedom from spectral interferences immediately after the ICAL. The mixed element SIC solution contains the following elements and is made up in an acid solution equivalent to the calibration standards: Aluminum, 500 mg/L; Calcium, 500 mg/L; Iron, 200 mg/L; Magnesium, 500 mg/L. Documented contaminants are subtracted from the observed values in the mixed element SIC check. Results for unspiked elements (aside from known contaminants) must

be ≤ LLOQ (RL). If not, fix and re-analyze, or elevate the LLOQ to twice the concentration in the SIC check (aside from known contaminants).

- **Instrument Detection Limits (IDL):** Using the LIMS control chart for IDL 3010A 6010C, as representative for 6010B, 6010C, and 200.7, and 21 CCB data points (10 for 6010D), calculate the IDL for each element, each instrument. Determine IDLs at least every three months (annually for 6010D) and keep with the instrument logbook. Compare the calculated IDLs to the MDLs. MDLs are equal to or greater than three times the IDL or adjust the MDL to be equal to or greater than the IDL.

Section 10.3, Calibration, add to Step 1.

1	See Table 7 for calibration standard preparation. **For 6010B/C, 200.7** multi-point calibration, use first-order linear regression (**$r \geq 0.998$, $r^2 \geq 0.996$**). Higher order fits are not allowed. The lowest non-zero standard concentration is considered the lower limit of quantitation, i. e., RL. **For 6010D** multi-point calibration, **$r \geq 0.995$, $r^2 \geq 0.990$, RSD ≤ 20%**. Inversely weighted regressions are recommended (not allowed in SC). A second order fit is allowed for alkali and alkaline earth elements if r ≥ 0.995. The lowest non-zero standard concentration is considered the lower limit of quantitation, i. e., LLOQ. For the upper linear range, run single elements at the highest concentration likely to be observed in samples. If the vendor provides the concentrations of any contaminants, these verified concentrations can be subtracted from the instrument result before assessing any interferences. If a lab uses a linear range concentration greater than the highest calibration point, a daily linear range standard is required with an agreement of ±10% of the expected value. Otherwise, the highest standard analyzed for any specific element, the highest standard in the calibration becomes the linear range. **For 6010D**, if the ICV is prepared fresh daily and the results meet 90-110% recovery, calibration standards need only be prepared on an as-needed basis due to loss of stability.

Section 11.0, Calculations / Data Reduction. Add new section.

11.__ Unweighted Linear Least Squares Regression

$$r = \frac{n\sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{\left(\sqrt{n\sum_{i=1}^{n} x_i{}^2 - \left(\sum_{i=1}^{n} x_i\right)^2}\right)\left(\sqrt{n\sum_{i=1}^{n} y_i{}^2 - \left(\sum_{i=1}^{n} y_i\right)^2}\right)}$$

The value of r is such that $-1 \leq r \leq +1$.

Section 12.1, Method Detection Limit Study (MDL) for 6010B/C, 200.7 only:

Section 12.__, Lower Limit of Quantitation (LLOQ) for 6010D: The LLOQ is initially verified by the analysis of at least 7 replicate samples, spiked at ½ LLOQ or the LLOQ and processed through all preparation and analysis steps of the method. The permitted mean recovery is ± 35% of the true value and RSD ≤ 20%. Quarterly verification uses a clean matrix sample spiked at 0.5 to 2 times the LLOQ and prepared and analyzed as a sample. This may also be used to calculate MDL.

Section 12.2, Demonstration of Capability for 6010B/C/, 200.7, Initial Demonstration of

Proficiency (IDP) for 6010D: Add to the paragraph: For 6010D, spike the clean matrix with the same standard as that used for calibration.

Section 15, References / Cross-References, add the new reference:
Method 6010D, SWS-846 Update V, Revision 4, July 2014.

12/24/15	
Operations Manager Approval Date	
12/24/15	12/16/15
Quality Assurance Approval Date	Technical Director Approval Date

Title: INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY SW-846 METHOD 6010B/C, EPA METHOD 200.7

Approvals (Signature/Date)

Ryan Fitzwater 6/30/15 Health & Safety Manager / Coordinator	Date
Cliff Eaton 6/30/15 Department Manager	Date
Michael H. Dunn 7/21/15 Technical Director	Date

1.0 Scope and Application

1.1 Analyte, Matrices: The method is applicable to the elements listed below.

Table 1: Recommended Wavelengths and Typical Reporting Limits

Element	CAS #	Wavelength[a] (nm)	Typical RL (µg/L)	Typical RL (mg/kg)
Aluminum	7429-90-5	308.215	100	20
Antimony	7440-36-0	206.833	10	10
Arsenic	7440-38-2	189.0	10	2.0
Barium	7440-39-3	233.5	10	2.0
Beryllium	7440-41-7	313.042	4	1.0
Boron	7440-42-8	249.678x2	50	10
Cadmium	7440-43-9	226.502	1	1.0
Calcium	7440-70-2	373.6 317.933	1000	200
Chromium	7440-47-3	267.716	5	1.0
Cobalt	7440-48-4	228.616	10	2.0
Copper	7440-50-8	324.754	10	2.0
Iron	7439-89-6	271.4 259.9	100	40
Lead	7439-92-1	220.353	5	1.0
Lithium	7439-93-2	670.784	50	10
Magnesium	7439-95-4	279.079	1000	200
Manganese	7439-96-5	257.610	15	3.0
Molybdenum	7439-98-7	202.030	50	10
Nickel	7440-02-0	231.604x2	10	2.0
Phosphorus	7723-14-0	177.495	100	20
Potassium	7440-09-7	766.491	1000	200
Selenium	7782-49-2	196.026	10	2.0
Silver	7440-22-4	328.068	5	1.0
Sodium	7440-23-5	589.5 330.2	1000	200
Strontium	7440-24-6	421.5	50	10
Sulfur	7704-34-9	182.0	250	50
Thallium	7440-28-0	190.864	10	2.0
Tin	7440-31-5	189.980	50	10
Titanium	7440-32-6	334.941	50	10
Vanadium	7440-62-2	292.402	20	10
Zinc	7440-66-6	213.856	50	10
Yttrium	7440-65-5	224.3 , 360.0	IS	IS
Indium	7440-74-6	230.6	IS	

All matrices, excluding filtered groundwater samples but including ground water, aqueous samples, TCLP and SPLP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. Groundwater samples that have been pre-filtered and acidified do not need acid digestion. For 6010, refer to SOPs 3005 / NV06-103, 3010 / NV06-18, 3050 / NV06-93, and 3051 / NV06-94 for the appropriate digestion procedures.

Method Reference	Appropriate Use
6010	ICP method for groundwaters and solids.
3005	Digestion procedure for dissolved elements in groundwaters (RCRA): See SOP 3005 / NV06-103.
3010	Digestion procedure for total elements in groundwaters (RCRA): See SOP 3010 / NV06-18.
3050 3051	Digestion procedure for solids (RCRA). Wipes and Filters: See SOP 3050 / NV06-93. Solids: See SOP 3051 / NV06-94.
200.7	Digestion and ICP method for wastewaters, surface waters (Clean Water Act).

1.2 Reporting Limits: Detection limits and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. Table 1 lists the analytical wavelengths and typical reporting limits in clean matrices.

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 Prior to analysis, samples are solubilized or digested using appropriate Sample Preparation Methods. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This method describes multi-elemental determinations by ICP-AES using simultaneous and sequential systems. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background is measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, is determined by the complexity of the spectrum adjacent to the analyte line. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

3.0 Definitions

3.1 Field Reagent Blank: An aliquot of reagent water that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose is to determine if method analytes or other interferences are present in the field environment.

3.2 Instrument Detection Limits (IDLs) are useful means to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with the lower limit of quantitation, nor should they be used in establishing this limit.

3.3 Internal Standard: Pure analyte added to a sample, in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.4 Linear Range (LR): The concentration range over which the instrument response to an analyte is linear, established by multi-point calibration, i. e., highest standard or a linear range

standard.

3.5 Interference Check Solution (ICS): Used to prepare ICSA (IC Solution A) and ICSAB (IC Solution AB). A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known inter-element spectral interferences with respect to a defined set of method criteria. See Thermo Jarrell Ash method 136972-00 revision 0 (7/28/95) for procedure.

3.6 Inter-element Correction (IEC): Single element solutions are used to determine the appropriate location for background correction and to establish the inter-element correction routine.

3.7 200.7 Total Recoverable Analyte: The concentration of analyte determined by analysis of the solution or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method.

3.8 200.7 Report Limit Verification / Certified Reporting Limit (RLV/CRL): A low standard used to verify the report limit.

3.9 Toxicity Characteristic Leaching Procedure (TCLP): An extraction process which attempts to simulate the leaching of samples into the ground/soil at a municipal landfill.

3.10 TCLP Blank Matrix: An aliquot of TCLP fluid that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. This blank is used to determine if method analytes or other interferences are present in the TCLP extraction fluid used in the preparation of TCLP samples.

3.11 Synthetic Precipitation Leaching Procedure (SPLP): An extraction process which attempts to simulate the leaching of samples in to the soil from a rain event.

3.12 SPLP Blank Matrix: An aliquot of SPLP fluid that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. This blank is used to determine if method analytes or other interferences are present in the SPLP extraction fluid used in the preparation of SPLP samples.

3.13 Dissolved Analyte: The concentration of analyte in an aqueous sample that passes through a 0.45 µm membrane filter assembly prior to sample acidification.

3.14 See TestAmerica Nashville's QA Manual for other laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

4.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. The locations selected for the measurement of background intensity are determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (inter-element or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.

4.1.2 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for inter-element contributions. Instruments that use equations for inter-element correction require the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences produce false positive determinations and are reported as analyte concentrations. Analysts may apply inter-element correction equations determined on their instruments with tested concentration ranges to compensate for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in the Thermo software.

4.1.3 When using inter-element correction equations, the interference may be expressed as analyte concentration equivalents (i. e., false analyte concentrations) arising from the linear range of the interference element. The interference effects **must** be evaluated for each individual instrument since the intensities vary. This evaluation is filed in the method of the instrument's computer.

4.1.4 Inter-element correction accuracy must be verified daily by analyzing spectral interference check solutions. Inter-element correction factors must be verified according to the requirements in Section 9.2 of this SOP.

4.2 Physical interferences are effects associated with the sample nebulization and transport processes. Physical interferences are reduced by diluting the sample and by using an internal standard.

4.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by matrix matching. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.4 Memory interferences result when analyses in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. This method requires a rinse period of at least 45 seconds between samples and standards.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.
- The inductively coupled plasma should only be viewed with proper eye protection from the ultraviolet emissions.
- The ICP uses high voltage.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydro-chloric acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors causes coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Causes redness, pain, and severe skin burns. Vapors are irritating and cause damage to the eyes. Contact causes severe burns and permanent eye damage.
Nitric acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors causes breathing difficulties and leads to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Causes redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and cause damage to the eyes. Contact causes severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Inductively coupled plasma emission spectrometer, Thermo Scientific ICAP 6500 Series, or equivalent.
  - Computer-controlled emission spectrometer with background- correction capability. The spectrometer must be capable of meeting and complying with the requirements described and referenced in Section 4.0.
  - Radio-frequency generator compliant with FCC regulations.
  - Argon gas supply - High purity grade (99.99%).
  - A peristaltic pump is required to deliver both internal standard and sample solutions to the nebulizer.
  - Mass flow controller to regulate the argon flow rate, especially the aerosol transport gas.
  - See Table 2 for instrument operating conditions selected as being optimal to provide the lowest reliable instrument detection limits and method detection limits.

Table 2: Inductively Coupled Plasma Instrument Operating Conditions

Incident rf power	1150 watts
Reflected rf power	--
Viewing height above work coil	--
Injector tube orifice i.d.	2 mm center tube
Argon supply	liquid Argon
Argon pressure	80+ psi
Coolant argon flow rate	12 L/min
Aerosol carrier argon flow rate	0.5 L/min
Auxiliary (plasma) argon flow rate	0.5 L/min
Sample uptake rate controlled to	50 rpm

rf: radiofrequency
i.d.: inner diameter

- Specific wavelengths are listed in Table 1.
- **Optimization of the plasma operating conditions:** The routine runs automatically when

the plasma is ignited. See the Thermo instrument manual for further information.

- Analytical balance, with capability to measure to 1 mg.

6.2 Supplies

For determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, (2) depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) must be sufficiently clean for the task objectives.

- Volumetric flasks, 25 mL, 100 mL, 200 mL, Class A.
- Adjustable Eppendorf pipettors, 10 µL - 100 µL, 100 µL - 1000 µL, with disposable plastic tips.
- Graduated Cylinders, 50 mL, 250 mL, 500 mL, Class A.
- Beakers, 150 mL, with ribbed watch glass.
- Digestion tubes, plastic, 50 mL, certified, graduated, with screw caps.
- Digestion tubes, certified, Environmental Express, or equivalent.
- Watch glass, plastic, ribbed
- Plastic digestion tube racks.
- Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125 L to 1-L capacities.
- One-piece stem FEP wash bottle with screw closure, 125 L capacity.
- pH test strips.
- Teflon™ boiling chips for solid matrix blank (Chemware P/N D1069103, or equivalent).
- Syringe, free of leachable target analytes.
- Syringe filters, 25 mm with 0.45 µm, PTFE membrane, VWR International 28145-497, or equivalent. Each lot must be pre-tested prior to use as evidence that the target analytes are not present greater than ½ RL or MDL, whichever is greater. Results are recorded in the maintenance log.

7.0 Reagents and Standards

7.1 **Reagent water**, analyte-free.

7.2 Reagents may contain elemental impurities, which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society specifications are used. If the purity of a reagent is in question, analyze for contamination. All acids used for this method **must be** of ultra high-purity grade or equivalent.

7.3 **Hydrochloric acid**, concentrated (sp.gr. 1.19), HCl. To prepare a 5% solution, add 10 mL concentrated HCl to 190 mL reagent water.

7.4 **Nitric acid**, concentrated (sp.gr. 1.41), HNO_3. To prepare a 5% solution, add 10 mL concentrated HNO_3 to 190 mL reagent water.

7.5 **Standard Stock Solutions**: Stock standards are purchased as certified commercial solutions at 100, 500 or 1000 µg/mL (recommended). Stock solutions are stored in FEP bottles. Replace stock standards yearly when succeeding dilutions for preparation of calibration standards cannot be verified. Store standards containing silver in the dark.

7.6 **Spectral Interference Check (SIC) Solutions** are prepared in the same acid mixture as the calibration standards and stored in FEP bottles. See Table 5 for SIC Preparation (ICSA and ICSAB).

7.7 **Internal Standards**: Yttrium and Indium. Purchase Ultra Scientific, or equivalent, commercial standards at 1000 µg/mL in 2% HNO_3: IAA-249-5 for Indium; IAA-239-5 for Yttrium. Dilute 5 mL Yttrium and 30 mL Indium to 1 liter with 5% HNO_3.

7.8 Inter-element Correction (IEC) Single-element Standards: Purchase the following Guide 34 single-element standards at 1000 µg/mL from Environmental Express High Purity (HP) and Inorganic Ventures (IV) for Phosphorus, or equivalent:

Element	Catalog #	Element	Catalog #	Element	Catalog #
Aluminum	HP10001	Iron	HP100026	Silicon	HP100050
Antimony	HP10002	Lead	HP100028	Silver	HP100051
Arsenic	HP10003	Lithium	HP100029	Sodium	HP10M52
Barium	HP10004	Magnesium	HP10M31	Strontium	HP100053
Beryllium	HP10005	Manganese	HP100032	Sulfur	HP100054
Boron	HP10007	Molybdenum	HP100034	Thallium	HP100058
Cadmium	HP10008	Nickel	HP100036	Tin	HP10061
Calcium	HP10M9	Phosphorus	IV CGP1-5	Titanium	HP100062
Chromium	HP100012	Potassium	HP10M41	Vanadium	HP100065
Cobalt	HP100013	Selenium	HP100049	Zinc	HP100068
Copper	HP100014				

7.9 Analytical results from newly acquired lots of standard materials are compared to results from previous lots at the time of receipt. Concentrations of analytes in calibration standards must be ±10% and concentrations of QC standards (e.g., LCS) must be ±20% of the standards currently in use. Otherwise, the newly acquired lots of standard material cannot be used. Raw data (initialed and dated by the Department Manager or Supervisor) is stored in LIMS with the certificate of analysis.

7.10 See SOP Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214 for shelf-life and storage requirements for reagents and standards.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water, Leachates	HDPE or Glass	125 mL	HNO_3 to pH ≤ 2[1]	6 months	SW-846 Chapter 2 40 CFR Part 136
Solid, Wipe, Filter	HDPE or Glass	50 grams	No requirement	6 months	SW-846 Chapter 2

[1]If water samples are preserved in the lab, they should be held for at least 24 hours before analysis; record acidification start/stop time and pH. Temperature preservation is not required.

8.1 Prior to the collection of an aqueous sample, consideration should be given to the type of data required (i. e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples is tested using pH test strips immediately prior to taking an aliquot for processing to ensure the sample has been properly preserved. The sample pH is recorded on the benchsheet. If properly acid preserved, the sample can be held up to 6 months before analysis.

8.2 For the determination of the dissolved elements, the sample **must** be filtered prior to acid preservation through a 0.45-µm pore diameter, PTFE membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical.) Use a portion of the filtered sample to rinse the filter flask; discard this portion and collect the required volume of filtrate. Acidify the filtrate with concentrated Nitric acid

immediately following filtration to pH < 2. Return to the original container. Hold for 24 hours prior to digestion.

8.3 For the EPA 200.7 determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1+1) Nitric acid to pH< 2. Preservation may be done at the time of collection; however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, it is recommended (except for cases where Boron is to be analyzed and reported) that the sample be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, **held for 24 hours**, and then verified to be pH < 2 using pH test strips just prior to withdrawing an aliquot for processing. The sample pH is then recorded on the benchsheet. If for some reason, such as high alkalinity, the sample pH is verified to be > 2, more acid must be added and the sample held for at least 24 hours until verified to be pH < 2. Record the acidification start-date, start-time, stop-date, stop-time, the amount and LIMS ID of acid used. Samples requiring the analysis and reporting of Boron must be acidified in the field at the tine of collection.

9.0 Quality Control

Refer to TestAmerica-Nashville's QA Manual for specific quality control (QC) policies. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC

The following quality control samples must be prepared with each batch of no more than 20 samples:			
Quality Controls	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Method Blank	1 each batch	6010: ≤ ½ RL or MDL whichever is greater. 200.7: <2.2 x MDL or 10% target concentration, whichever is greater.	Re-analyze. If contamination persists, correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank. If target > 10X blank, acceptable to report.
Laboratory Control Sample (LCS)[1], second source	1 each batch	6010: 80-120% recovery 200.7: 85-115% recovery	Correct problem then re-prep and analyze the LCS and all affected targets in the affected analytical batch. If high and ND, OK to report. For 6010C, LCS may be re-analyzed once.
Matrix Spike	1 each batch	6010: 75-125%[2] recovery 200.7: 70-130% recovery	Perform post-digestion spike.
6010: Matrix Spike Duplicate	1 each batch	75-125%[2] recovery <20[2]% RPD	Perform post-digestion spike.
Post digestion spike addition	When MS/MSD fail.	Recovery within 25% for 6010B and within 20% for 6010C of the expected results.	Perform dilution test.
Dilution test	If MS/MSD fail.	1:4 fold dilution (5X) must agree within 10% of the original determination.	Qualify results.

[1]AZ, MA, and TX require an LCS duplicate in each batch.
[2]If historical limits are calculated, they cannot exceed these limits.

- **Method Blank:** The laboratory prepares and analyzes one blank (reagent water or Teflon™ boiling chips) with each batch of up to 20 samples of the same matrix.
- A **Laboratory Control Sample (LCS)** must be analyzed with every batch. See Table 3 for

LCS preparation using 50 mL reagent water for water batches and 0.5 gram Teflon™ chips for soil batches.

- **Matrix Spike / Matrix Spike Duplicate:** Analyze a matrix spike and matrix spike duplicate at a frequency of one per matrix batch up to 20 samples. In each case the MS aliquot must be a duplicate of the aliquot used for sample analysis and for total recoverable determinations added prior to sample preparation. See SOP Sample Homogenization, Subsampling, and Compositing / NV08-229. The added analyte concentration and standard source must be the same as that used in the LCS (Table 3).
  - For each batch, check for matrix effects as follows:
    - If MS/MSD is outside the QC limits, the same sample from which the MS/MSD aliquots were prepared is also spiked with a **post-digestion spike** (i. e., nominally add 250 µL of the LCS/MS/MSD solution to 25 mL digested aliquot). Otherwise, another sample from the same preparation is used as an alternative. An analyte spike is added to a portion of a prepared sample, or its dilution, and is recovered as described in the above table. The spike addition produces a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. If this spike fails, then the dilution test is run on this sample. If both the MS/MSD and the post-digestion spike fail, then matrix effects are confirmed.
    - **Dilution test**: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution (5X) should agree within 10% of the original determination. If not, a chemical or physical interference effect is suspected.

9.2 Instrument QC

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Inter-element Correction, single element standards	6 months	± RL	Alter wavelength or background correction.
Spectral Interference Check Solutions, A and AB	Beginning of each day	6010: Target ± 2 times RL or ± 20% true. 200.7: Spiked targets ± 20% true. Non-spiked ± 2 x RL.	Terminate analysis; correct problem; re-analyze ICS; re-analyze all affected samples.
Instrument Detection Limits (IDL)	Quarterly	±3 standard deviations of the average response.	Re-run IDL. If > MDL, adjust MDL to equal IDL.
Independent Calibration Verification Sample (ICV), second source	Immediately after calibration	6010: 90-110 % recovery 200.7: 95-105% recovery RSD <3% from four integrations	Correct problem then repeat initial calibration.
Independent Calibration Blank (ICB)	Immediately after ICV	6010: < ½ RL 200.7: No target analytes above IDL.	Correct problem, re-calibrate.
6010: Linear Range Standard	Daily	90-110%	Repeat calibration (ICP2).
Continuing Calibration Verification Sample (CCV)	Every 10 samples and at the end of the run	90-110% true	Re-analyze once. If fails again, then repeat calibration and re-analyze all samples since last successful CCV.

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
6010: Undigested Low Level Continuing Calibration Verification (LLCCV)	Beginning and end of each batch.	70-130% true	Re-calibrate.
Continuing Calibration Blank	Following the CCV	6010: < ½ RL 200.7: < 2-3 times MDL or RL, whichever is greater.	Correct problem then analyze calibration blank and previous 10 samples.
MDL Verification (digested)	Yearly	Detected	Re-evaluate MDL standard used and MDL; see Technical Director
Digested Lower Limit of Quantitation Check (LLQC), RLV/CRL	6010: Quarterly 200.7: For **AZ, CA, HI, MN, NV**: 1 per batch, beginning of the batch	70-130% true	Re-calibrate.
Internal Standards	All samples, standards, QC	60-140% true as compared to the calibration blank	Dilute and re-run. For blank and LCS, correct problem and re-run batch.

- **Inter-element Correction (IEC):** When correction is appropriate, the concentration of all targets must be within ± the RL, i. e., RL = 0.01, acceptance is -0.01 to +0.01. Once established, the entire routine must be initially and periodically verified when one of the following occurs – whichever comes first:
  - every six months, or
  - whenever there is major instrument maintenance, or
  - when ICSA or ICSAB fail criteria

  Single element standard concentrations that must be analyzed every six months are shown as follows:

Element	Required Final Concentration (mg/L)	Stock Standard Solution (µg/mL)	Volume of Stock Standard Solution (mL)	Final Volume (mL)
Aluminum	50	1000	25	50
Antimony	10	1000	0.5	50
Arsenic	50	1000	2.5	50
Barium	50	1000	2.5	50
Beryllium	10	1000	0.5	50
Boron	50	1000	2.5	50
Cadmium	10	1000	0.5	50
Calcium	100	1000	5.0	50
Chromium	50	1000	2.5	50
Cobalt	50	1000	2.5	50
Copper	50	1000	2.5	50
Iron	100	1000	5.0	50
Lead	50	1000	2.5	50
Lithium	25	1000	1.25	50
Magnesium	100	1000	5.0	50
Manganese	10	1000	0.5	50
Molybdenum	10	1000	0.5	50

Element	Required Final Concentration (mg/L)	Stock Standard Solution (µg/mL)	Volume of Stock Standard Solution (mL)	Final Volume (mL)
Nickel	50	1000	2.5	50
Phosphorus	50	1000	2.5	50
Potassium	100	1000	5.0	50
Selenium	20	1000	1.0	50
Silicon	50	1000	2.5	50
Silver	10	1000	0.5	50
Sodium	100	1000	5.0	50
Strontium	50	1000	2.5	50
Sulfur	100	1000	5	50
Thallium	20	1000	1.0	50
Tin	50	1000	2.5	50
Titanium	50	1000	2.5	50
Vanadium	50	1000	2.5	50
Zinc	10	1000	0.5	50
Zirconium	50	1000	2.5	50

If interferences are observed, they must be mitigated by the use of interference correction equations or by changing to a different wavelength. The objective is to reduce interferences.

Required ICSA and ICSB solutions are described in Table 5 for daily verification. Initial and periodic verification data of the routine are filed in the maintenance of the instrument's computer.

- **Spectral interference check solution (ICSA and ICSAB):** The laboratory must periodically verify the inter-element correction routine by analyzing SIC solutions. The spectral interference check solution is run at the beginning and end of the day's sequence or every 8 hours, whichever is more frequent. If the SIC does not meet criteria, then the SICs are re-analyzed. These solutions are used to periodically verify a partial list of the on-line (and possible off-line) inter-element spectral correction factors for the recommended wavelengths given in Table 1.

  NOTE: The SIC solution must be analyzed more than once to confirm a change has occurred with adequate rinse time between solutions and before subsequent analysis of the calibration blank.

  - To prepare the Spectral Interference Check Solutions, see Table 5:
    - The first solution is **ICSA solution.** Prepare as follows: Dilute 20 mL of ICSA Stock (SPEX INT-A1) + 10 mL HNO_3 to 200 mL with reagent water for final concentrations of 500 µg/mL each Al, Ca, Mg, and 200 µg/mL Fe.
    - The second solution is **ICSAB solution**. Prepare as follows: Dilute 20 mL of ICSA Stock (SPEX INT-A1) + 2 mL of ICSB Stock (SPEX INT-B1) + 2 mL of ICSB2 Stock (SPEX INT-B2) + 10 mL HNO_3 to 200 mL with reagent water. The final concentrations of the ICSAB are (original concentrations are shown for explanation)
  - Ensure that the analytical results of ICS Solution A (ICSA) fall within the control limit of ± two times the RL of the analyte's true value or ± 20% of the analyte's true value, whichever is greater (the true value is zero unless otherwise stated) in the ICSA. For example, if the analysis result(s) for Arsenic (RL = 10 µg/L, ICSA true value = 0 µg/L) in

the ICSA analysis during the run is 19 µg/L, then the analytical result for Arsenic falls within the ± two times the RL window for Arsenic in the ICSA. If the analytical results of the ICSA do not fall within the control limits, terminate the analysis, correct the problem, re-calibrate the instrument, and re-analyze the analytical samples analyzed since the last compliant ICSA was performed.

- Ensure that the results for the ICS Solution AB (ICSAB) during the analytical runs fall within the control limit of ± two times the RL of the true value or ± 20% of the true value, whichever is greater, for the analytes included in the ICSAB. If the analytical results of the ICSAB do not fall within the control limits, terminate the analysis, correct the problem, re-calibrate the instrument, and re-analyze the analytical samples analyzed since the last compliant ICSAB was performed.

- **Instrument Detection Limits (IDL):** Using the LIMS control chart for IDL 3010A 6010C, as representative for 6010B, 6010C, and 200.7, and 21 CCB data points, calculate the IDL for each element, each instrument. Determine IDLs at least every three months and keep with the instrument logbook. Compare the calculated IDLs to the MDLs. MDLs are equal to or greater than three times the IDL or adjust the MDL to be equal to or greater than the IDL.
- **Independent Calibration Verification (ICV and ICB):** The laboratory analyzes the ICV and a calibration blank (ICB) immediately following daily calibration. See Table 6 for ICV preparation using a second-source standard. The ICB must not contain target analytes above the lower limit of quantitation.
- **6010: Linear Range Standard (LRS):** For single-point calibration, run at the beginning of the analytical sequence. Run the highest standard level, to show linearity to that concentration. All samples exceeding **90%** this concentration are diluted. The LRS concentrations are Al, Fe, Ca and Mg at 200 µg/mL, Na, K, at 100 µg/mL, Ba at 50 µg/mL, Ag at 5 µg/mL, and all other elements at 10 µg/mL. The standard must be within 10% of the true values to continue.
- **Undigested Low-Level Continuing Calibration Verification (LLCCV):** Analyze an undigested LLCCV at the beginning and end of each batch. Prepare it from the primary calibration standard at the RL.
- **Continuing Calibration Verification and Blank (CCV and CCB):** Analyze after every 10th sample and at the end of the analytical sequence.
  - See Table 4 for CCV preparation using the primary source standard at the mid-point of the calibration curve. All samples **must be bracketed** by acceptable CCVs and CCBs.
  - 6010: The CCB (prepared by adding 25 mL concentrated HNO_3 to 500 mL reagent water) must not contain target analytes above the MDL or ½ the RL, whichever is greater. If the criterion is not met, terminate the analysis, correct the problem, and re-analyze the previous 10 samples.
  - 200.7: The CCB must not contain target analytes above 2-3 times MDL or RL. If the CCB is less than 1/10 the concentration of the action level of interest, and no sample is within 10% of the action limit, analyses need not be rerun and recalibration need not be performed before continuation of the run.
- **6010: MDL Verification:** A solution containing all target analytes at 2-3 times the MDL must be **digested** and analyzed after the completion of the MDL study and on an annual basis. Detection limits are verified when all analytes in the MDL check solution are detected.
- **6010: Lower Limit of Quantitation Check Sample (LLQC**): The lower limit of quantitation check (LLQC) sample is analyzed once daily. This check sample and the low-level calibration verification standard are prepared at the same concentrations (Table 7) with the only difference being the LLQC sample is carried through the digestion procedure.
- **200.7: RLV/CRL:** The RLV/CRL applies to **Arizona, California, Hawaii, Minnesota, and Nevada** samples only. Analyze a RLV/CRL at the beginning of each analytical sequence for

samples from these states. See Table 7 for RLV preparation.

- **Internal Standards:** Use the internal standard technique by adding one or more elements (not in the samples and verified not to cause an uncorrected inter-element spectral interference) at the same concentration (which is sufficient for optimum precision) to the prepared samples (blanks and standards) that are affected the same as the analytes by the sample matrix. Use the ratio of analyte signal to the internal standard signal for calibration and quantitation. Internal standards (Yttrium and Indium) are automatically added to all calibration standards, samples, and QC, by the instrument.

10.0 Procedure

10.1 Sample Preparation: Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater samples which have been pre-filtered and acidified do not need acid digestion. Samples which are not digested must use an internal standard. See Section 1.1 for digestion SOPs.

Matrix	Sample Size	Digestion SOP
6010 Water	50 mL of sample	3005, 3010
200.7 Water	50 mL of sample	6010 200.7 Section 10.1
6010 Leachate	10 mL of extract	3010
6010 Solid, Oil	0.5 gram of sample	3051
6010 Filter or Wipe	1 filter or 1 wipe	3050

- 200.7 Digestion

1	Transfer a 50 - 51 mL aliquot from a well mixed, acid-preserved or filtered sample to a certified, 50-mL digestion tube. When necessary, smaller sample aliquot volumes may be used.
2	Add 1.0 mL 1:1 Nitric acid and 0.5 mL of 1:1 Hydrochloric acid to the vessel containing the measured volume of sample. Place the container in the block digester for solution evaporation. The block digester should be located in a fume hood and previously adjusted to provide evaporation at a temperature of approximately but no higher than 85°C. (See the following note.) The vessel should be covered with an **elevated** plastic watch glass. Note: When a digestion tube is covered, the temperature of the water should be about 95°C.
3	Reduce the volume of the sample aliquot to about 20 mL by gentle heating at 85-95°C. DO NOT BOIL. This step takes about 1 to 2 hours for a 50-mL aliquot.
4	Cover the digestion vessel with a loose cap to reduce additional evaporation and gently reflux the sample for 30 minutes. (Slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the HCl-H_2O) azeotrope.)
5	Allow the digestion vessel to cool. Dilute to 50.0 mL volume with reagent water; cap and mix.
6	Allow any undissolved material to settle overnight, filter using a PTFE membrane, or centrifuge a portion of the prepared sample until clear. Record the filter ID and lot number. The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted sample cannot be characterized, all analyses should be performed as soon as possible after the completed preparation. If any sample is filtered, the Method Blank and LCS must also be filtered.

10.2 Instrument Setup

1	Inspect the sample introduction system including the nebulizer, torch, center tube, and uptake tubing for salt deposits, dirt and debris that would restrict solution flow and affect instrument performance. Clean the system when needed or on a daily basis.

2	Power up all accessories and the unit. Allow the instrument to become thermally stable before beginning (usually requiring about 30 minutes of operation prior to calibration).
3	Click on the plasma icon in the lower right of the Analyst screen. Then click the instrument status button. Make sure all interlocks have a green light. Then push the plasma on button. Confirm flow to the plasma.
4	To shutdown, click the plasma icon and push the plasma off button.
5	Instrument is automatically optimized when the program is opened.
6	Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. The analyst must follow the instructions provided by the instrument manufacturer and this SOP. For the 6500 series, the conditions usually vary from 750-1350 watts power, 10-20 liters/minute coolant gas flow, 0.25-1.5 liters/minute nebulizer gas flow, 0.25-2 liters/minute auxiliary gas flow, 20-125 rpm pump rate with a 40 second flush time and 30 seconds maximum integration time. Perform two replicate integrations; report the average. The relative standard deviation for replicate integrations must be <5% for the ICV and CCV and ≤10% for samples with concentrations more than two times the reporting limit.
7	Establish sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.
8	All samples that exceed the upper calibration standard must be diluted and re-analyzed or a linear range standard must be run with 10% of the true value.

10.3 Calibration: Refer to SOP Calibration Curves and Selection of Calibration Points / CA-Q-P-003. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

1	See Table 7 for calibration standard preparation. For multi-point calibration, use first-order linear regression (**$r \geq 0.998$, $r^2 \geq 0.996$**). The lowest non-zero standard concentration is considered the lower limit of quantitation, i. e., RL. Higher order fits are not allowed.
2	The absolute value of the results of the calibration blank is less than the value of the MDL.
3	After initial calibration, the calibration curve must be verified by use of an initial calibration verification (ICV) standard. The calibration curve must be verified at the end of each analysis batch and after every 10 samples by use of a continuing calibration verification (CCV) standard and a continuing calibration blank (CCB).
4	The calibration curve must also be verified prior to the analysis of any samples and at the end of the batch by use of a low-level continuing calibration verification (LLCCV) standard.
5	Run LRS standards and evaluate by the criteria in Section 9.
6	Verify the inter-element correction factors at the beginning of the daily sequence.

10.4 Sample Analysis

1	After completion of the initial startup and calibration requirements of this method, samples are analyzed in the same operational manner used in the calibration routine with the rinse blank also being used between all sample solutions, LCSs, MS, and other QC samples. Follow the analysis sequence in Table 8.
2	Sample analyte concentrations that are 90% or more of the upper calibration standard **must** be diluted with reagent water that has been acidified in the same manner as calibration blank and reanalyzed. Also, for the inter-element spectral interference correction routines to remain

	valid during sample analysis, the interferent concentration must not exceed the concentration used for the SIC. If the interferent concentration is exceeded, sample dilution with acidified reagent water and reanalysis is required. In these circumstances analyte detection limits are raised.

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\textbf{\% Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\textbf{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 Calibration Factor

$$\textbf{CF} = \frac{\text{Total Area}}{\text{Total Concentration Injected (µg/mL)}}$$

Note: The internal standard is used to evaluate the matrix only.

11.4 % Drift

$$\textbf{\% Drift} = \frac{(\text{Result - True Value}) \times 100}{\text{True Value}}$$

11.5 Linear Calibration Using a Least Squares Regression: This is most easily achieved by performing a linear regression of the instrument response versus the concentration of the standards. Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). This is a statistical requirement and is not simply a graphical convention.

The regression produces the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

y = instrument response (peak area)
a = slope of the line
x = concentration of the calibration standard
b = the intercept

The regression calculation generates a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit.

11.6 Coefficient of Determination Correlation Coefficient

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2} \qquad r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response ratio
x = Concentration

11.7 Concentration: Sample data are reported in units of mg/L for aqueous samples, mg/kg for solid samples. LIMS calculates the concentration from the raw data provided by the analyst.

Concentration (mg/L or mg/kg) = $\frac{\text{(µg/mL* from instrument)(digest volume, mL)(Dilution factor)}}{\text{Sample Volume (mL) or Mass (g)}}$

µg/mL from instrument = y = mx + b

***average of two replicates**

11.8 For dissolved aqueous analytes, report the data generated directly from the instrument with allowance for sample dilution. Do not report analyte concentrations below the MDL.
11.9 Account for any additional dilution of the prepared sample solution needed to complete the determination of analytes exceeding 90% or more of the LRS upper limit. Do not report data below the determined analyte MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Detection Limits / CA-Q-S-006. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.
12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.
12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.
12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.
12.5 Control Charts: Laboratory method performance can be shown with the use of control charts, available from LIMS or the QA department.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Acidic aqueous wastes are taken to the waste disposal area, neutralized, and discharged to the sanitary sewer.

15.0 References / Cross-References

15.1 Method 6010B, SW-846 Update III, Revision 2, December 1996, and **Method 6010C**, SW-846 Update IV, Revision 3, February 2007.

15.2 EPA Method 200.7. Supplement I, Revision 4.4, May 1994.

15.3 TestAmerica Nashville's Quality Assurance Manual.

15.4 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.5 SOPs: Calibration Curves and Selection of Calibration Points / CA-Q-P-003, 3005 / NV06-103; 3010 / NV3010; 3050 / NV06-93; 3051 / NV06-94; Waste Disposal / NV10-83, Training Procedures for Technical Staff / NV08-199, Balance Calibration / NV08-213, Detection Limits / CA-Q-S-006, Sample Homogenization, Sub-sampling, and Compositing / NV08-229, Reagent and Standard Purchase / NV08-214.

15.6 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

Item	Modification
1	For OK, NV, SC, and WY samples, reference 6010C. For all other states, reference 6010B.
2	Corporate Quality Memorandum CA-Q-QM-004, Technical Guidance on Checking for Spectral Interferences in Optical ICP Analysis, September 24, 2009.

17.0 Attachments

Table 3: LCS and MS/MSD Spiking Solution
High-Purity Standards HP6099
Use 0.5 mL as received/50 mL

Analyte	Stock Std Concentration (µg/mL)	Final Concentration of Digestate (µg/mL)
Aluminum	200	2.0
Antimony	10	0.1
Arsenic	5	0.05
Barium	200	2.0
Beryllium	5	0.05

Analyte	Stock Std Concentration (µg/mL)	Final Concentration of Digestate (µg/mL)
Boron	100	1.0
Cadmium	5	0.05
Calcium	500	5.0
Chromium	20	0.2
Cobalt	50	0.5
Copper	25	0.25
Iron	100	1.0
Lead	5	0.05
Lithium	100	1.0
Magnesium	500	5.0
Manganese	50	0.5
Molybdenum	50	0.5
Nickel	50	0.5
Phosphorus	100	5
Potassium	500	5.0
Silver	5	0.05
Sodium	500	5.0
Sulfur	100	1.0
Thallium	5	0.05
Titanium	100	1.0
Vanadium	50	0.5
Zinc	50	0.5

Table 4: Calibration Solutions

Element	Calibration Blank Reagent Water CALSTD 0	1:100 Dilution of HP4381-250 CRI Stock Standard CAL STD 1	1:50 Dilution of HP6103-1L CCV Stock Standard CALSTD 2	1:10 Dilution of HP6103-1L CCV Stock Standard CALSTD 3	Made from Single Element Stock Standards CALSTD 4	HP4526-1L (500 µg/mL) LRS Standard CALSTD 5
As	0	RL	2	10		
Ba	0	RL	10	50		
Cd	0	RL	2	10		
Cr	0	RL	2	10		
Pb	0	RL	2	10		
Se	0	RL	2	10		
Ag	0	RL	1	5		
Cu	0	RL	2	10		
Ni	0	RL	2	10**		
Al	0	RL	10	50		
Sb	0	RL	2	10		
Be	0	RL	2	10		
Ca	0	RL	20	100	250	500
Co	0	RL	2	10		
Fe	0	RL	6	30**	250	

Element	Calibration Blank Reagent Water CALSTD 0	1:100 Dilution of HP4381-250 CRI Stock Standard CAL STD 1	1:50 Dilution of HP6103-1L CCV Stock Standard CALSTD 2	1:10 Dilution of HP6103-1L CCV Stock Standard CALSTD 3	Made from Single Element Stock Standards CALSTD 4	HP4526-1L (500 µg/mL) LRS Standard CALSTD 5
Mg	0	RL	20	100	250	500
Mn	0	RL	2	10**		
K	0	RL	20	100		
Na	0	RL	20	100**	250	500
Tl	0	RL	2	10		
V	0	RL	2	10		
Zn	0	RL	2	10**		
B	0	RL	2	10		
Mo	0	RL	2	10		
Sn	0	RL	2	10		
Sr	0	RL	2	10		
Ti	0	RL	2	10		
Li	0	RL	2	10		
S	0	RL	2	10		
P	0	RL	2	10	50	

*Ca (HP10M9-1), Fe (HP100M26-1), Mg (HP10M31-1), Na (HP10M52-1), P (HP100039-1)
**Remove point to fine-tune for 200.7 (ICV), if needed.

CCV and RLV Sources and Concentrations

Analyte	CCV HP4529 (µg/mL)	RLV HP6100(µg /mL)
Aluminum	10.0	0.1
Antimony	1.0	0.01
Arsenic	1.0	0.01
Barium	2.0	0.01
Beryllium	1.0	0.004
Boron	1.0	0.05
Cadmium	1.0	0.001
Calcium	10.0	1.0
Chromium	1.0	0.005
Cobalt	1.0	0.02
Copper	1.0	0.01
Iron	10.0	0.05
Lead	1.0	0.005
Lithium	1.0	0.05
Magnesium	10.0	1.0
Manganese	1.0	0.015
Molybdenum	1.0	0.05
Nickel	1.0	0.01
Phosphorus	10	0.05
Potassium	10.0	1.0

Analyte	CCV HP4529 (µg/mL)	RLV HP6100(µg /mL)
Selenium	1.0	0.01
Silver	1.0	0.005
Sodium	10.0	1.0
Strontium	1.0	0.05
Sulfur	1.0	0.5
Thallium	1.0	0.01
Tin	1.0	0.05
Titanium	1.0	0.05
Vanadium	1.0	0.02
Zinc	1.0	0.05

Table 5: Spectral Interference Check Solutions

ICSA Standard

ICSA Stock, SPEX # INT-A1
ICSA Solution: Dilute 25 mL of ICSA Stock + 12.5 mL HNO_3 to 250 mL with reagent water.

Analyte	ICSA Stock Conc. (µg/mL)	ICSA Conc. (µg/mL)
Aluminum	5000	500
Calcium	5000	500
Magnesium	5000	500
Iron	2000	200

ICSAB Standard

ICSA Stock, SPEX # INT-A1
ICSB Stock, SPEX # INT-B1
ICSB2 Stock, SPEX # INT-B2

ICSAB Solution*: Dilute 25 mL of ICSA Stock + 2.5 mL of ICSB Stock + 2.5 mL of ICSB2* Stock + 12.5 mL HNO_3 to 250 mL with reagent water.

Analyte	ICSA Stock Conc. (µg/mL)	ICSB Stock Conc. (µg/mL)	ICSB2 Stock Conc. (µg/mL)	ICSAB Conc. (µg/mL)
Aluminum	5000		100	501
Calcium	5000		10	500.1
Magnesium	5000		10	500.1
Iron	2000		10	200.1
Barium		50		0.5
Beryllium		50		0.5
Cadmium		100		1.0
Chromium		50		0.5
Cobalt		50		0.5
Copper		50		0.5
Lead		100		1.0
Manganese		50		0.5

Analyte	ICSA Stock Conc. (µg/mL)	ICSB Stock Conc. (µg/mL)	ICSB2 Stock Conc. (µg/mL)	ICSAB Conc. (µg/mL)
Nickel		100		1.0
Silver		100		1.0
Vanadium		50		0.5
Zinc		100		1.0
Antimony			100	1.0
Arsenic			100	1.0
Boron			100	1.0
Molybdenum			100	1.0
Selenium			100	1.0
Silica			10	0.1
Sodium			100	1.0
Thallium			100	1.0

Table 6: ICV Standard
Source: *For all Elements except Sn, S, P*: Inorganic Ventures STLTN-CAL-3
***For Sn, Inorganic Ventures CGSN1-5*, 1000 µg/mL**
ICV Preparation: 0.05 mL Tin standard to 50 mL STLTN-CAL-3

***For S, Inorganic Ventures CGS1-5*, 1000 µg/mL**
ICV Preparation: 0.05 mL Sulfur standard to 50 mL STLTN-CAL-3

***For P, Inorganic Ventures CGP1-5*, 1000 µg/mL**
***ICV Preparation: 0.05 mL Phosphorus standard to 50 mL* STLTN-CAL-3**

Analyte	STLTN-CAL-3 (µg/mL)	Inorganic Ventures CGSN1-5 Sn (µg/mL)	Inorganic Ventures CGS1-5 (µg/mL)	Inorganic Ventures CGP1-5 (µg/mL)	ICV Conc. (µg/mL)
Aluminum	10				10
Antimony	1				1
Arsenic	1				1
Barium	2				2
Beryllium	1				1
Boron	1				1
Cadmium	1				1
Calcium	10				10
Chromium	1				1
Cobalt	1				1
Copper	1				1
Iron	10				10
Lead	1				1
Lithium	1				1
Magnesium	10				1
Manganese	1				1
Molybdenum	1				1

Analyte	STLTN-CAL-3 (µg/mL)	Inorganic Ventures CGSN1-5 Sn (µg/mL)	Inorganic Ventures CGS1-5 (µg/mL)	Inorganic Ventures CGP1-5 (µg/mL)	ICV Conc. (µg/mL)
Nickel	1				1
Phosphorus				10	
Potassium	10				10
Selenium	1				1
Silver	1				1
Sodium	10				10
Strontium	1				1
Sulfur		1000			1
Thallium	1				1
Tin			1000		1
Titanium	1				1
Vanadium	1				1
Zinc	1				1

Table 7: Linear Range Standard/High Calibration Standards

Analyte	HP4526 Conc. (µg/mL)	Environmental Express HP6101 Conc. µg/mL)
Al, Ca, Mg, Na	500	
Fe	200	
K	100	
P		10

Table 8: Typical Analytical Sequence

	Definitions
0.0 mg/L standard(or blank)	Calibration Standard
0.5 mg/L	Calibration Standard
1.0 mg/L	Calibration Standard
2.0 mg/L	Calibration Standard
10.0 mg/L	Calibration Standard
LRS	High Range Calibration Verification
100 mg/L	Calibration Standard
300 mg/L	Calibration Standard
50 mg/L	Calibration Standard
ICV	Independent (initial) Calibration Verification
ICB	Initial Calibration Blank
RLV	Report Limit Verification
ICSA	Initial Spectral Interference Check
ICSAB	Initial Spectral Interference Check
Up to 10 samples	
MS	Matrix Spike
MSD	Matrix Spike Duplicate
CCV	Continuing Calibration Verification
CCB	Continuing Calibration Blank

Up to 10 samples	
MS	Matrix Spike
MSD	Matrix Spike Duplicate
LCS	Laboratory Control Sample
RLV (as needed)	Report Limit Verification
CCV	Continuing Calibration Verification
CCB	Continuing Calibration Blank
ICSA	Spectral Interference Check
ICSAB	Spectral Interference Check
Up to 10 samples	
MS	Matrix Spike
MSD	Matrix Spike Duplicate
CCV	Continuing Calibration Verification
CCB	Continuing Calibration Blank
Up to 10 samples	
MS	Matrix Spike
MSD	Matrix Spike Duplicate
CCV	Final Continuing Calibration Verification
CCB	Final Continuing Calibration Blank
RLV	Final Report Limit Verification
ICSA	Final Spectral Interference Check
ICSAB	Final Spectral Interference Check

18.0 Revision History

- Revision 10, dated 29 February 2008
  - Integration for TestAmerica and STL operations.
  - Addition of control limits for ICSA and ICSAB.
  - Addition of text on Spectral Interference Check Solutions
  - Change from CRDL/CRQL to CRL, current terminology
  - Addition of current catalog numbers for Table 6 individual elements.
  - Correction of order of Table 8
- Revision 11, dated 17 October 2008
  - Updated to SW-846 Update IV
- Revision 12, dated 30 October 2009
  - Inserted information on new ICV standard, new standards for ICP4.
  - Modified analytical sequence and added ICP4 sequence.
  - Reformatting and condensing.
  - Addition of requirements of Corporate Quality Memorandum CA-Q-QM-004, Technical Guidance on Checking for Spectral Interferences in Optical ICP Analysis, September 24, 2009.
  - Corporate review.
- Revision 13, dated 21 February 2011
  - Addition of QAF-45 and Section 14.2
  - Addition of Sulfur information, updated wavelengths in Table 1.
  - Addition of operating conditions optimization for ICP4 and 5.
  - New vendor IDs for elements.
  - Delete ICP1, taken out of service.
  - ICP2 new calibration standard preparation; changed SIC solution preparation.
- Revision 14, dated 14 September 2012
  - Organizational changes.
  - Amendments 13a,b,c.

- Iron RL change from 50 to 100 µg/L; from 10 mg/kg to 20 mg/kg.
- Removal of ICP2.
- Addition of Sulfur throughout.
- Remove the requirement for 10-sample batches if samples are from OK or WY.
- Addition of SOPs Calibration Curves (General) / CA-Q-S-005, and Selection of Calibration Points / CA-T-P-002. Remove 3015 / NV06-19 (archived).

- Revision 15, dated 30 September 2014
  - Organizational changes.
  - Add phosphorus and new standards
  - Add references to spectral interferences found in the instrument software and the plasma operating conditions in the instrument manual.
  - Remove ICP2; add ICP6.
  - Change acceptance criterion for ICB and CCB to < ½ RL.
  - Change frequency of digested LLQC/RLV to quarterly.
  - Add criteria for RSD of replicate integrations for ICV, CCV, and samples.
  - Revision 16, dated 31 July 2015Combine SOPs 6010 / NV06-44-15c and 200.7 / NV06-17.11c
    - 6010-15a, 200.7-11b: frequency of inter-element correction.
    - 6010-15b: improved abbreviation and acronym clarification; add MA to the states requiring a LCSD; remove WV; update Table 4
    - 6010-15c and 200.7-11c: add syringe filter and standard material testing.
    - 200.7-11a: specify final digestate volume as 50 mL instead of 50.0 mL.
  - WV no longer requires a LCSD; however, MA does.
  - Update SOP references. Clarify acronyms. Add TALS IDL procedure.
  - Remove reference to digestion 3030C. Add information for dissolved analytes.

SOP Number/Revision No.: **6020 200.8 / NV06-215.8b** Effective Date: **12/31/2015**

Last Mod. Date: 11/1/2015

SOP Title**: Methods 6020/6020A and 200.8: Metals Analysis by Inductively Coupled Plasma – Mass Spectrometry**

CONTROLLED DISTRIBUTION

ISSUED TO: \\TAFS\Lab\Nashville\Public\QA\SOPs, 06

Revision Number with Mod ID: **6020 200.8 / NV06-215.8c**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add highlighted information; delete crossed-out information.

Title Change: Methods 6020/6020A/6020B and 200.8: Metals Analysis by Inductively Coupled Plasma – Mass Spectrometry

Section 1.1

- Change the column headings: **Reporting Limit/LLOQ**
- Add footnote to the table: RL = Reporting Limit for 6020/6020A, 200.8; LLOQ = Lower Limit of Quantitation for 6020B.

1.1 Section 1.2: Change as shown: **Reporting Limits (RLs)/Lower Limits of Quantitation (LLOQs):** Typical RLs (LLOQs) are shown in the table above.

Section 3.0, Definitions, add a new definition:
Lower Limit of Quantitation (LLOQ) for 6020B: The lowest point of Quantitation, or in most cases, the lowest point in the calibration curve, which is ideally less than or equal to the desired regulatory action level.

Section 3.1, Instrument Detection Limits (IDLs), add new bullet:

- For 6020B, determine the IDLs by running 10 replicate reagent blanks, calculating the mean and standard deviation, and multiplying the standard deviation by 3. Negative values are zero. IDLs are needed for new instruments and after detector changes.

Section 3.4, Spectral Interference Check (SIC) Solution and 9.2, Instrument QC: Used to prepare ICSA and ICSAB. 6020B does not require ICSAB.

Section 9.1, Sample QC

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Method Blank	1 per 20 samples	6020/6020A/6020B: < ½ RL or MDL, whichever is greater. 200.8: <MDL	Correct problem then re-prep and analyze method blank and all samples processed with the contaminated blank.
Laboratory Control Sample (LCS)[1]	1 per 20 samples	6020: 80-120[2]% recovery 200.8: 85-115%recovery	Correct problem then re-prep and analyze the LCS and all affected targets in the affected analytical batch. If high and ND, OK to report.
Matrix Spike	1 per 20 samples	6020: 75-125[2]% recovery 200.8: 70-130% recovery	Run post-digestion spike.
Matrix Spike Duplicate	1 per 20 samples	<20[2]% RPD	Run post-digestion spike.
6020 Only: Dilution test	If MS/MSD fail.	6020/6020A: If concentration is high enough, at least 10 times RL, run 1:4 fold dilution, must agree within 10% of the original determination. 6020B: If concentration is ≥ 25 times the LLOQ, run 1:5 fold dilution, must agree within 20% of the original determination.	Report and qualify
6020 Only: Post digestion spike addition	When dilution test fails	6020/6020A: Recovery within 20% of the expected results 6020B: Recovery within 25% of the expected results.	Re-run, report, and qualify.

- **6020B Dilution test**: If the analyte concentration is within the linear range of the instrument and sufficiently high (minimally, a factor of 25 times the LLOQ), an analysis of a 1:5 dilution should agree within 20% of the original determination. If not, a chemical or physical interference effect is suspected. Report and qualify.

Section 9.2, Instrument QC:

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Tune	Daily, prior to analysis of samples.	Adjust sensitivity with a stability ≤5% RSD.	Adjust instrument setting and re-run.
Pulse/Analog Check Standard	Immediately after Tune	0.05 or greater for targets	Adjust concentration, re-run.
Tune Check Standard	Each day	± 0.1 amu and RSD of 5 replicates ≤ 5%	Adjust and re-run
Calibration Standards	Each day	6020/6020A/200.8: Linear regression: $r \geq 0.998$, $r^2 \geq 0.996$. Mid and Upper ± 10% true; low ± 30% true. 6020B: $r \geq 0.995$, $r^2 \geq 0.990$, RSD ≤ 20%. Inversely weighted regressions are recommended.	Clean, adjust, and re-calibrate.
Calibration Blank	Each day	≤ MDL or ½ RL, whichever is greater.	Re-run calibration.
6020/6020A/200.8: Spectral Interference Check Solutions, A and AB	Beginning of analytical run or once every 12 hours, whichever is more frequent	Target ± 2 times RL or ± 20% true.	Terminate analysis; correct problem; re-analyze ICS; re-analyze all affected samples.

Instrument Detection Limits (IDL)	Quarterly	±3 standard deviations of the average response.	Adjust MDL.
Independent Calibration Verification Sample (ICV), second source	Immediately after calibration	90-110 % recovery	Correct problem then repeat initial calibration.
Independent Calibration Blank (ICB)	Immediately after ICV	6020/6020A/200.8: No target analytes above RL. 6020B: ≤ ½ RL	
Continuing Calibration Verification Sample (CCV)	Every 10 samples and at the end of the run	90-110% recovery	Repeat calibration and re-analyze all samples since last successful calibration.
6020/6020A: Undigested Low Level Continuing Calibration Verification (LLCCV)	After the ICB, Method Blank, and end of each batch.	70-130% true	Re-calibrate.
Continuing Calibration Blank (CCB)	Following the CCV	≤ RL	Correct problem then analyze calibration blank and previous 10 samples.
Digested Lower Limit of Quantitation Check (LLQC/LLOQ) or Report Limit Verification (RLV)	Quarterly (7 replicate study, see Section 12)	70-130% recovery 6020B: ± 35%, ≤ 20% RSD	Re-calibrate.
Internal Standards	All samples, standards, QC	6020: 70-130% recovery 200.8: 60-125% recovery	Dilute and re-run. For blank and LCS, correct problem and re-run batch.
~~MDL Verification (digested)~~	~~Yearly~~	~~Detected~~	~~Re-evaluate MDL standard used and MDL; see Technical Director.~~

- **6020, 6020A, 200.8 Spectral Interference Check Solution (ICS A and ICS AB):** The laboratory periodically verifies the inter-element correction (IEC) routine by analyzing SIC solutions. The spectral interference check solution is run at the beginning of the analytical sequence or every **12 hours**, whichever is more frequent. If the SIC does not meet criteria, then the SICs are re-analyzed.
  - Ensure that the analytical results of ICS A fall within the control limit of ± 2 times the RL of the analyte's true value or ± 20% of the analyte's true value, whichever is greater (the true value is zero unless otherwise stated) in the ICSA. For example, if the analysis result(s) for Arsenic (RL = 10 µg/L, ICSA true value = 0 µg/L) in the ICSA analysis during the run is 19 µg/L, then the analytical result for Arsenic falls within the ± 2 times the RL window for Arsenic in the ICSA. If the analytical results of the ICS A do not fall within the control limits, terminate the analysis, correct the problem, re-calibrate the instrument, and re-analyze the analytical samples analyzed since the last compliant ICS A was performed.
  - Ensure that the results for the ICS AB during the analytical runs fall within the control limit of ± 2 times the RL of the true value or ± 20% of the true value, whichever is greater, for the analytes included in the ICS AB. If the analytical results of the ICS AB do not fall within the control limits, terminate the analysis, correct the problem, re-calibrate the instrument, and re-analyze the analytical samples analyzed since the last compliant ICS AB was performed.
- **EPA 6020B** does not require the ICS AB. Also, the concentrations of unspiked elements can be subtracted if
  - the vendor of the ICS A solution provides the documented concentrations of unspiked elements or
  - if their concentrations are determined using multiple isotopes of the element in the correct ratios.

Section 10.2, Calibration:

- If a linear range concentration greater than the highest calibration point is used, a daily linear range standard is required.
- If the ICV is prepared fresh daily and the results meet 90-110% recovery, calibration standards need only be prepared on an as-needed basis due to loss of stability.
- For step 7 of the table:

7	Prepare a standard curve by calculating the counts per second (cps) of standards versus the corresponding target concentrations using first-order linear regression. **For 6020/6020A/200.8**: The correlation coefficient r must be greater than or equal to 0.998 ($r^2 \geq 0.996$), or re-calibrate. **NOTE:** The multi-point calibration establishes the linear dynamic range (LDR) provided the low standard is within 30% of the true value and the upper standard, representing the linear range standard (LRS), is within 10% of the true value. **For 6020B**: The correlation coefficient r must be greater than or equal to 0.995 ($r^2 \geq 0.990$), or re-calibrate. **NOTE:** The multi-point calibration establishes the linear dynamic range (LDR) provided the low standard is within 20% of the true value and the upper standard, representing the linear range standard (LRS), is within 10% of the true value.

Section 11.0, Calculations / Data Reduction. Add new sections.

11.__ Unweighted Linear Least Squares Regression

$$r = \frac{n\sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{\left(\sqrt{n\sum_{i=1}^{n} x_i{}^2 - \left(\sum_{i=1}^{n} x_i\right)^2}\right)\left(\sqrt{n\sum_{i=1}^{n} y_i{}^2 - \left(\sum_{i=1}^{n} y_i\right)^2}\right)}$$

The value of r is such that $-1 \leq r \leq +1$.

Section 12.1, Method Detection Limit Study (MDL) for 6020/6020A, 200.8 only:

Section 12.__, Lower Limit of Quantitation (LLOQ) for 6010D: The LLOQ is initially verified by the analysis of at least 7 replicate samples, spiked at the LLOQ and processed through all preparation and analysis steps of the method. The permitted mean recovery is ± 35% of the true value and RSD ≤ 20%. Quarterly verification uses a clean matrix sample spiked at 0.5 to 2 times the LLOQ and prepared and analyzed as a sample.

Section 12.2, Demonstration of Capability for 6020/6020A/, 200.8, Initial Demonstration of Proficiency (IDP) for 6020B Add to the paragraph**: For 6020B, spike** the clean matrix with the same standard as that used for calibration.

Section 15, References / Cross-References, add the new reference:
Method 6020B, SWS-846 Update V, Revision 2, July 2014.

12/17/15	
Operations Manager Approval Date	
12/17/15	12/9/15
Quality Assurance Approval Date	Technical Director Approval Date

SOP Number/Revision No.: **6020 200.8 / NV06-215.8a** Effective Date: **11/11/15**

Last Mod. Date: 3/31/2015

SOP Title**: Methods 6020/6020A and 200.8: Metals Analysis by Inductively Coupled Plasma – Mass Spectrometry**

CONTROLLED DISTRIBUTION

ISSUED TO: \\TAFS\Lab\Nashville\Public\QA\SOPs, 06

Revision Number with Mod ID: **6020 200.8 / NV06-215.8b**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add highlighted information; delete crossed-out information.

Section 1.1, Analyte, Matrices: To the element listing table, add

Element	CAS #	Reporting Limit (mg/L)	Reporting Limit (mg/kg)
Boron	7440-42-8	0.05	10
Lithium	7439-93-2	0.05	10
Strontium	7440-24-6	0.002	10

Section 7.3 Stock Standard Solutions: Each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Take care when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon or polyethylene bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging.

- **Primary Calibration Stock Standard:** Purchase: Inorganic Ventures TA-40 Custom Solution, or equivalent: All element concentrations are 100.0 µg/mL.
- Environmental Express HP10M31-1, or equivalent, containing 10,000 µg/mL Na.
- Environmental Express HP10M41-1, or equivalent, containing 10,000 µg/mL Mg.
- Environmental Express HP10M52-1, or equivalent, containing 10,000 µg/mL K.
- Environmental Express HP10M9-1, or equivalent, containing 10,000 µg/mL Ca.
- Ultra Scientific IAA-213-5, or equivalent, containing 1,000 µg/mL Al.
- Ultra Scientific IAA-256-5, or equivalent, containing 1,000 µg/mL Ba.
- Environmental Express HP100026-1, or equivalent, containing 1,000 µg/mL Fe.
- Ultra Scientific IAA-225-5, or equivalent, containing 1,000 µg/mL Mn.
- Ultra Scientific IAA-230-5, or equivalent, containing 1,000 µg/mL Zn.
- Ultra Scientific IAA-205, or equivalent, containing 1,000 µg/mL B.

- Ultra Scientific IAA-203, or equivalent, containing 1,000 µg/mL Li.
- Ultra Scientific IAA-238, or equivalent, containing 1,000 µg/mL Sr.

- **Secondary Spiking Stock Standard for Initial Calibration Verification:** Purchase the following:
  - High Purity Standards HP6547-500
    - 10 µg/mL Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn
    - 100 µg/mL Al, Fe
    - 1000 µg/mL Ca, K, Mg, Na
  - ~~Inorganic Ventures TA-41 Custom Solution, or equivalent, containing~~
    - ~~10 µg/mL As, Cr^{+3}, Co, Cu, Pb, Mn, Ni, V, Zn, Se, Ba, Be, Cd, Tl~~
    - ~~100 µg/mL Al, Fe~~
    - ~~1000 µg/mL Ca, Mg, K, Na~~
  - ~~Inorganic Ventures TA-42 Custom Solution, or equivalent, containing~~
    - ~~10 µg/mL Ag, Mo, Sn, Ti, Sb~~

Section 7.5 The **interference check solution (ICS)** is prepared to contain known concentrations of interfering elements that demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate chemical corrections for chloride-related interferences such as $^{35}Cl^{16}O^{+}$ on $^{51}V^{+}$ and $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system or collision cell within quality control limits.

NOTE: The ICS solutions in the table below are intended to evaluate corrections for known interferences on only the analytes in Section 1.1. If this method is used to determine an element not listed in the table below, it is the responsibility of the analyst to modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of correction of interferences on the unlisted element (see Section 8.4).

These solutions are prepared from ultra-pure reagents, obtained commercially (Inorganic Ventures, or equivalent).

- **Working ICS Solution A** (6020ICS-A) is prepared by adding 5.0 mL of Inorganic Ventures 6020ICS-0A, or equivalent, plus 45 mL mixed acid diluent. ICS solution A must be prepared fresh weekly. 6020ICS-0A contains 10,000 µg/mL chloride, 2,000 µg/mL carbon, 1,000 µg/mL each aluminum, calcium, iron, potassium, magnesium, phosphorus, sodium, and sulfur, and 20 µg/mL each molybdenum and titanium.
- **Working ICS Solution B** (6020ICS-B) is prepared by adding
  - 0.5 mL of Inorganic Ventures TA-STD-1 (contains all targets), or equivalent. TA-STD-1 contains 2.0 µg/mL each Arsenic, Barium, Beryllium, Cadmium, Cobalt, Chromium, Copper, Lead, Manganese, Nickel, Selenium, Silver, Tin, Thallium, Vanadium, and Zinc.
  - 50 µL of a 20 µg/mL solution of Ultra Scientific IAA-251, or equivalent, containing 1,000 µg/mL Sb.
  - Plus 49.5 mL mixed acid diluent.
  - ICS solution B must be prepared fresh weekly.
- **ICS AB:** Add 5 mL of 6020ICS-0A to ICS B (50 mL).

Recommended Interference Check Sample Components and Concentrations			
Solution Component (mg/L)	**ICS A Concentration 1:10 (mg/L)**	**ICS B Concentration 1:100 (mg/L)**	**ICS AB Concentration (mg/L)**
Al	100		100.0
Ca	100		100.0
Fe	100		100.0
Mg	100		100.0
Na	100		100.0
P	100		100.0
K	100		100.0
S	100		100.0
C	200		200.0
Cl	1000		1000
Mo	2.0		2.0
Ti	2.0		2.0
As	0	0.02	0.02
Cd	0	0.02	0.02
Cr	0	0.02	0.02
Co	0	0.02	0.02
Cu	0	0.02	0.02
Mn	0	0.02	0.02
Ni	0	0.02	0.02
Ag	0	0.02	0.02
Zn	0	0.02	0.02
Ba	0	0.02	0.02
Sb	0	0.02	0.02
Be	0	0.02	0.02
Pb	0	0.02	0.02
Se	0	0.02	0.02
Tl	0	0.02	0.02
Sn	0	0.02	0.02
V	0	0.02	0.02
B	0	1.0	1.0
Li	0	0.50	0.50
Sr	0	0.02	0.02

7.6 Internal Standards: Purchase Inorganic Ventures 6020ISS, or equivalent; it contains 10 µg/mL ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, ^{209}Bi. Purchase Environmental Express HP100020-1, or equivalent; it contains 1000 µg/mL ^{72}Ge.

- Prepare a 1 µg/mL solution by diluting 50 mL 6020ISS and 0.5 mL HP100020-1 to 500 mL mixed acid diluent. When added to the sample or standard by the instrument at 1:20, the resulting concentration is 50 ug/L. Generally, an internal standard is no more than 50 amu removed from the analyte.

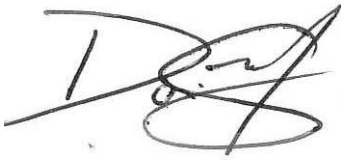
Isotopes, Internal Standards, and Reaction Gas for Selected Elements			
Element of Interest	**Mass**	**IS**	**Reaction Gas**
Aluminum	27	45	Helium
Antimony	121	103	No gas
Arsenic	75	72	Helium
Barium	137	159	No gas

Beryllium	9	45	Helium
Bismuth (IS)	209		No gas, Helium
Cadmium	111	103	Helium
Calcium	40	45	Helium
Chromium	52	45	Helium
Cobalt	59	72	Helium
Copper	65	72	Helium
Germanium (IS)	72		No gas, Helium
Holmium (IS)	165		No gas, Helium
Indium (IS)	115		No gas, Helium
Iron	56	72	Helium
Lead	(206) (207) 208	209	No gas
Lithium (IS)	6[a]		No gas, Helium
Magnesium	24	45	Helium
Manganese	55	72	Helium
Molybdenum	95	103	Helium
Nickel	60	72	Helium
Potassium	39	45	Helium
Rhodium (IS)	103		No gas, Helium
Scandium (IS)	45		No gas, Helium
Selenium	78	72	Helium
Silver	107	103	Helium
Sodium	23	45	Helium
Terbium (IS)	159		No gas, Helium
Thallium	205	209	No gas
Tin	118	103	No gas
Titanium	47	72	Helium
Vanadium	51	72	Helium
Zinc	66	72	Helium
Boron	11	6	No gas
Lithium	7	6	No gas
Strontium	88	103	No gas

[a]Internal standard must be enriched in the ^{6}Li isotope. This minimizes interference from indigenous Lithium.

Section 9.2, Instrument QC, Report Limit Verification (RLV):

- Prepare a 2 µg/L LLCCV (however, Al is 20 µg/L; Fe is 25 µg/L; Zn is 25 µg/L, Minerals are 1000 µg/L):
  - Add 10 mL of 10 µg/L primary standard solution.
  - Add 0.9 mL of 1 µg/mL Al primary standard ~~(Ultra Scientific IAA-213-5, or equivalent, 1000 µg/mL)~~.
  - Add 1.2 mL of 1 µg/mL Fe primary standard ~~(Ultra Scientific IAA-226-5, or equivalent, 1000 µg/mL)~~.
  - Add 1.2 mL of 1 µg/mL Zn primary standard ~~(Ultra Scientific IAA-230-5, or equivalent, 1000 µg/mL)~~.
  - Add 49.9 µL of the 1000 µg/mL Cation ~~Minerals~~ spiking solution (25 mL of each of the Ca, K, Mg, Na primary standards diluted to 250 mL reagent water) ~~(5 µL TA-9/50 mL reagent water)~~.
  - Add 0.25 mL of 10 mg/L B primary standard.
  - Add 0.25 mL of 10 mg/L Li primary standard.
  - Add 0.10 mL of 1 mg/L Sr primary standard.

11/11/15	
Operations Manager Approval Date	
 11/11/15	 11/11/15
Quality Assurance Approval Date	Technical Director Approval Date

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP)
Change Form

SOP Number/Revision No.: **200.7 / NV06-17.11b**
6010 / NV06-44.15b
6020 200.8 / NV06-215.8

Effective Date: **3/31/2015**

Last Mod. Date: 1/21/2015

SOP Title**: EPA Method 200.7, Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry; Method 6010B/C: Inductively Coupled Plasma-Atomic Emission Spectrometry; Methods 6020/6020A and 200.8: Metals Analysis by Inductively Coupled Plasma – Mass Spectrometry**

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 06

Revision Number with Mod ID: **200.7 / NV06-17.11c, 6010 / NV06-44.15c, 6020 200.8 / NV06-215.8a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add highlighted information.

To each SOP, Section 6.2, Supplies, add to the syringe filter description: Each lot must be pre-tested prior to use as evidence that the target analytes are not present greater than ½ RL or MDL, whichever is greater. Results are recorded in the maintenance log.

To 6010, add Section 7.11; to 200.7 and 6020 200.8, add 7.10:

Analytical results from newly acquired lots of standard materials are compared to results from previous lots at the time of receipt. Concentrations of analytes in calibration standards must be ±10% and concentrations of QC standards (e.g., LCS) must be ±20% of the standards currently in use. Otherwise, the newly acquired lots of standard material cannot be used.

Raw data (initialed and dated by the Department Manager or Supervisor) is stored in LIMS with the certificate of analysis.

3/9/15	
Operations Manager Approval Date	
3/9/15	3/9/15
Quality Assurance Approval Date	Technical Director Approval Date

Title: METALS ANALYSIS BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY SW-846 METHOD 6020/6020A EPA 200.8

Approvals (Signature/Date)			
	10/20/14		11/26/14
Cliff Eaton	Date	Ryan Fitzwater	
Metals Operations Manager		Health & Safety Manager / Coordinator	
	11/10/14		10/21/14
Steve Miller	Date	Michael H. Dunn	Date
Quality Assurance Manager		Technical Director	

1.0 Scope and Application

1.1 Analyte, Matrices: Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of concentrations of a large number of elements in water and soil samples and in waste extracts or digests. When dissolved constituents are required, samples are filtered and acid-preserved prior to analysis. In general, the regulatory methods are applicable as follows:

Method Reference	Appropriate Use
6020 ICP/MS Analysis	Aqueous samples and solids (RCRA)
3005 Preparation	Dissolved metals in aqueous samples
3010 Preparation	Total acid-leachable elements in aqueous samples
3050 Preparation	Total acid-leachable elements in wipes and filters
3051 Preparation	Total acid-leachable elements in solid samples
200.8 Preparation and ICP/MS Analysis	Wastewaters (Clean Water Act)
200.8 Preparation and ICP/MS Analysis	Drinking water (Safe Drinking Water Act

No digestion is required prior to analysis for dissolved elements in water samples (SOP 3005 / NV06-103). Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, wipes, filters, and other solid wastes for which total acid-leachable elements are required (SOPs 3010 / NV06-18, 3050 / NV06-93, 3051 / NV06-3051). The elements are:

Element	CAS #*	Reporting Limit (ug/L)	Reporting Limit (mg/kg)
Aluminum	7429-90-5	20	5.0
Antimony	7440-36-0	2	0.50
Arsenic	7440-38-2	2	0.50
Barium	7440-39-3	2	0.50
Beryllium	7440-41-7	2	0.50
Cadmium	7440-43-9	1	0.50
Calcium	7440-70-2	1000	50
Chromium	7440-47-3	2	0.50
Cobalt	7440-48-4	2	0.50
Copper	7440-50-8	2	0.50
Iron	7439-89-6	25	5.0
Lead	7439-92-1	2	0.5
Magnesium	7439-95-4	1000	50
Manganese	7439-96-5	2	0.50
Molybdenum	7439-98-7	2	0.50
Nickel	7440-02-0	2	0.50
Potassium	7440-09-7	1000	50
Selenium	7782-49-2	2	0.50
Silver	7440-22-4	2	0.50
Sodium	7440-23-5	1000	50
Thallium	7440-28-0	2	0.50
Tin	7440-31-5	2	0.50
Titanium	7440-32-6	2	0.50
Vanadium	7440-62-2	2	0.50

Element	CAS #*	Reporting Limit (ug/L)	Reporting Limit (mg/kg)
Zinc	7440-66-6	25	5.0

*Chemical Abstract Service

1.2 Reporting Limits: Typical RLs are shown in the table above.

1.3 If this method is used to determine any analyte not listed above, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the matrix to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the same manner as the listed elements and matrices.

1.4 Use of this method is relegated to spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS.

1.5 An appropriate internal standard is used for each analyte determined by ICP-MS. The internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{72}Ge, ^{159}Tb, ^{165}Ho, ^{209}Bi. The Lithium internal standard has an enriched abundance of ^{6}Li, so that interference from lithium native to the sample is minimized.

1.6 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 This method describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences are assessed and valid corrections applied or the data is flagged to indicate problems. Interference correction includes compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

2.2 When analyzing groundwater or other aqueous samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid-preserved prior to analysis.

3.0 Definitions

3.1 Instrument Detection Limits (IDLs) are the concentrations equivalent to the analytes' signal which is equal to three times the standard deviation of a series of seven (7) replicate measurements of the calibration blank signal at the same wavelength. IDLs are useful tool to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with MDLs or report limits. It may be helpful to compare the calculated IDL to the MDL and RL; however, it should be understood that the RL must be verified. Each measurement must be performed as though it were a separate analytical sample (i. e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analyses of separate samples).

- IDLs should be determined at least every three months. Analyze seven consecutive reagent blank solutions on three non-consecutive days; calculate the average of the standard deviation of each element.

3.2 Internal Standard: Pure analyte added to a sample, in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.3 Linear Dynamic Range (LDR): The concentration range over which the instrument response to an analyte is linear.

3.4 Spectral Interference Check (SIC) Solution: Used to prepare ICSA and ICSAB. A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting inter-element spectral interferences with respect to a defined set of method criteria.

3.5 Report Limit Verification (RLV): The RLV is a report limit concentration primary standard used to verify the RL.

3.6 See TestAmerica Nashville's QA Manual for other laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). The data system and collision cell are used to correct for these interferences. This involves reaction with Helium and/or determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal.

Isobaric molecular and doubly charged ion interferences are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature. The Agilent 7500ce/cx addresses these interferences by using He as the reactive gas within a collision cell.

Possible Polyatomic Interferences in Typical Environmental Samples and the ORS Mode Used to Eliminate Them

Analyte Isotope	Principal Interferences	Corrective ORS Mode
^{24}Mg	$^{12}C^{12}C$	He
^{27}Al	$^{12}C^{14}N^{1}H$	He
^{51}V	$^{35}Cl^{16}O$	He
^{52}Cr	$^{40}Ar^{12}C$, $^{35}Cl^{16}O^{1}H$, $^{36}Ar^{16}$)	He
^{55}Mn	$^{40}Ar^{16}O$, $^{40}Ca^{16}$)	He
^{56}Fe	$^{40}Ar^{16}O$, $^{23}Na^{37}Cl$, $^{43}Ca^{16}O^{1}H$, ArS	He
(63,65)Cu	$^{40}Ar^{23}Na$, SO_2	He
(64,66,68)Zn	SO_2, ArS	He
^{75}As	$^{40}Ar^{35}Cl$, $^{40}Ca^{35}Cl$	He
$^{(78,80)}Se$	$^{40}Ar^{38}Ar$, SO_3	He

4.2 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total dissolved solid levels below 0.1% (1,000 mg/L) have been currently recommended to minimize solid deposition. Internal standards are used to correct for physical interferences. When intolerable physical interferences are present in a sample, a significant suppression of the internal standard signals (to less than 70% of the signals in the calibrations standard) is observed. Dilution of the sample usually eliminates the

problem.

4.3 Memory interferences can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples is long enough to reduce significant memory interference.

4.4 If there is poor relative standard deviation (precision) on standards and sample:

4.4.1 Check that the interface cones are in good condition and that the orifices of both cones are round and of the proper size.

4.4.2 Evaluate the nebulizer to see if it is operating properly by checking the aerosol with the plasma off and the spray chamber removed. If the aerosol is not forming properly clean or replace the gem tips.

4.4.3 Check that the peristaltic pump tubing is in good condition. Follow air bubbles through the tubing to insure that the flow is smooth and not pulsating.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This method may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.
- The inductively coupled plasma should only be viewed with proper eye protection from the ultraviolet emissions.
- The ICP-MS uses high voltage.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table below contains a summary of the primary hazards listed in the SDS for each of the materials listed.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydro-chloric acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors causes coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Causes redness, pain, and severe skin burns. Vapors are irritating and cause damage to the eyes. Contact causes severe burns and permanent eye damage.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors causes breathing difficulties and leads to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Causes redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and cause damage to the eyes. Contact causes severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- **Inductively coupled plasma mass spectrometer:** Agilent 7500ce/cx is capable of providing resolution, better than or equal to 0.9 amu at 10% peak height. The system has a mass range from 6 to 240 amu and a collision cell and data system that allows corrections for interferences and the application of the internal standard technique. A mass-flow controller for the nebulizer Argon and Helium and peristaltic pumps for the sample solution are used.

Tune Adjustment Variables		
Instrument Parameter	**Normal Mode**	**Helium Mode**
RF Power	1500	1500
Carrier gas	~1.1 L/min	Same as Normal
Makeup gas	0.0	Same as Normal
Sample Depth	7-10mm	Same as Normal
Persitaltic Pump Speed	0.1 rps	Same as Normal
Spray Chamber	2°C	Same as Normal
Extract 1	0 V	Same as Normal
Extract 2	-120 to -150 V	Same as Normal
Omega bias	-15 to -40 V	Same as Normal
Omega lens	5 to -5 V	Same as Normal
Cell entrance	-30 to -10 V	-25 V
QP focus	3 V	-10 V
Cell exit	-30 to -8 V	-45 V
OctP RF	160 to 200 V	Same as Normal
OctP bias	-10 to -3 V	-18 V
QP bias	-7 to -0.5 V	-15 V

- Set up the Instrument with the proper operating parameters according to the instrument manufacturer's instructions. Load tunes: normal.U and He.U (see examples in Section 17). Load "60202008" method and calibration.
- Operating conditions. Follow the instructions provided by the instrument manufacturer. Allow at least 30 minute for the instrument to equilibrate before analyzing any samples. Verify by analyzing a tuning solution at least **five integrations** with relative standard deviations of ≤ 5% for the analytes contained in the tuning solution.

6.2 Supplies

6.2.1 Supplies for ICP/MS Analysis

- Helium: High-purity grade (99.99%)
- Argon gas supply: high purity grade (99.99%).
- Macropipettes and micropipettes with disposable tips.
- Autosampler tubes.
- Disposable Centrifuge Tubes: 50 mL with caps.
- Teflon™ boiling chips for solid matrix blank (Chemware P/N D1069103, or equivalent).
- Syringe filter, 25 mm with 0.45 µm PTFE membrane, VWR International 28145-497, or equivalent.

6.2.2 Equipment and Supplies for 200.8 Digestion

- Analytical balance, with capability to measure to 0.01 g.
- A temperature adjustable hot plate or block digester capable of maintaining a temperature of 95 ± 2°C.
- Volumetric flasks, 25 mL, 100 mL, 200 mL, Class A.
- Adjustable Eppendorf pipettors, 10 µL - 100 µL, 100 µL - 1000 µL, with disposable plastic tips.
- Graduated Cylinders, 50 mL, 250 mL, 500 mL, Class A.
- Centrifuge tubes, plastic, 50 mL, graduated, with screw caps.
- Digestion tubes, Environmental Express, or equivalent.
- Watch glass, plastic, ribbed (for use with the digestion tubes).
- Plastic centrifuge tube racks.
- Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125 L to 1-L capacities.
- One-piece stem FEP wash bottle with screw closure, 125 L capacity.
- pH test strips.

Labware: For determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, (2) depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Several procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for four hours or more in 20% (v/v) nitric acid or a mixture of HNO_3 and HCl (1+2+9), rinsing with reagent water and storing. Chromic acid cleaning solutions **must be avoided** because chromium is an analyte.

7.0 <u>Reagents and Standards</u>

7.1 Reagent water, analyte-free.

7.2 Acids used in the preparation of standards and for sample processing are of ultra high purity. Concentrations of antimony and silver between 50-500 µg/L require 0.5% (v/v) HCl for stability. For concentrations above 500 µg/L Ag, additional HCl may be needed.

7.2.1 **For 200.8 Digestion**: **Hydrochloric acid**, concentrated (sp.gr. 1.19), HCl. To prepare a 1:1 ratio, add 500 mL acid and 500 mL reagent water.

7.2.2 **For 200.8 Digestion**: **Nitric acid**, concentrated (sp.gr. 1.41), HNO_3: To prepare a 1:1 ratio, add 500 mL acid and 500 mL reagent water.

7.3 Stock Standard Solutions: Each stock solution must be analyzed separately to

determine possible spectral interferences or the presence of impurities. Take care when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon or polyethylene bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging.

- **Primary Calibration Stock Standard:** Purchase: Inorganic Ventures TA-40 Custom Solution, or equivalent: All element concentrations are 100.0µg/mL.
- Environmental Express HP10M31-1, or equivalent, containing 10,000 µg/mL Na.
- Environmental Express HP10M41-1, or equivalent, containing 10,000 µg/mL Mg.
- Environmental Express HP10M52-1, or equivalent, containing 10,000 µg/mL K.
- Environmental Express HP10M9-1, or equivalent, containing 10,000 µg/mL Ca.
- Ultra Scientific IAA-213-5, or equivalent, containing 1,000 µg/mL Al.
- Ultra Scientific IAA-256-5, or equivalent, containing 1,000 µg/mL Ba.
- Environmental Express HP100026-1, or equivalent, containing 1,000 µg/mL Fe.
- Ultra Scientific IAA-225-5, or equivalent, containing 1,000 µg/mL Mn.
- Ultra Scientific IAA-230-5, or equivalent, containing 1,000 µg/mL Zn.

- **Secondary Spiking Stock Standard for Initial Calibration Verification:** Purchase the following:
  - Inorganic Ventures TA-41 Custom Solution, or equivalent, containing
    - 10 µg/mL As, Cr^{+3}, Co, Cu, Pb, Mn, Ni, V, Zn, Se, Ba, Be, Cd, Tl
    - 100 µg/mL Al, Fe
    - 1000 µg/mL Ca, Mg, K, Na
  - Inorganic Ventures TA-42 Custom Solution, or equivalent, containing
    - 10 µg/mL Ag, Mo, Sn, Ti, Sb

7.4 Mass Spectrometer Tuning Standards. A solution containing elements representing all of the mass regions of interest is analyzed to verify that the resolution and mass calibration of the instrument are within the required specifications. This solution is also used to verify that the instrument has reached thermal stability.

- **Instrument Tuning Standard:** Purchase the following:
  - Agilent Tuning Solution 5184-3566, or equivalent, containing 10 µg/L Li, Co, Y, Ce, Tl.
- **Tune Check Standard:** Prepare solution of 100 µg/L Be, Mg, Co, Y, In, and Pb by adding the following to 250 mL mixed acid diluent
  - 25 µL Ultra Scientific IAA-204-5, or equivalent, containing 1,000 µg/mL Be
  - 2.5 µL Environmental Express HP10M31-1, or equivalent, containing 10,000 µg/mL Mg
  - 25 µL Ultra Scientific IAA-227-5, or equipment, containing 1,000 µg/mL Co
  - 25 µL Environmental Express, or equivalent, containing 1,000 µg/mL Y
  - 25 µL Environmental Express, or equivalent, containing 1,000 µg/mL In
  - 25 µL Ultra Scientific IAA-282-5, or equivalent, containing 1,000 µg/mL Pb

7.5 The **interference check solution (ICS)** is prepared to contain known concentrations of interfering elements that demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate chemical corrections for chloride-related interferences such as $^{35}Cl^{16}O^{+}$ on $^{51}V^{+}$ and $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system or collision cell within quality control limits.

NOTE: The ICS solutions in the table below are intended to evaluate corrections for known

interferences on only the analytes in Section 1.1. If this method is used to determine an element not listed in the table below, it is the responsibility of the analyst to modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of correction of interferences on the unlisted element (see Section 8.4).

These solutions are prepared from ultra-pure reagents, obtained commercially (Inorganic Ventures, or equivalent).

- **Working ICS Solution A** (6020ICS-A) is prepared by adding 5.0 mL of Inorganic Ventures 6020ICS-0A, or equivalent, plus 45 mL mixed acid diluent. ICS solution A must be prepared fresh weekly. 6020ICS-0A contains 10,000 µg/mL chloride, 2,000 µg/mL carbon, 1,000 µg/mL each aluminum, calcium, iron, potassium, magnesium, phosphorus, sodium, and sulfur, and 20 µg/mL each molybdenum and titanium.
- **Working ICS Solution B** (6020ICS-B) is prepared by adding
  - 0.5 mL of Inorganic Ventures TA-STD-1 (contains all targets), or equivalent. TA-STD-1 contains 2.0 µg/mL each Arsenic, Barium, Beryllium, Cadmium, Cobalt, Chromium, Copper, Lead, Manganese, Nickel, Selenium, Silver, Tin, Thallium, Vanadium, and Zinc.
  - 50 µL of a 20 µg/mL solution of Ultra Scientific IAA-251, or equivalent, containing 1,000 µg/mL Sb.
  - Plus 49.5 mL mixed acid diluent.
  - ICS solution B must be prepared fresh weekly.
- **ICS AB:** Add 5 mL of 6020ICS-0A to ICS B (50 mL).

Recommended Interference Check Sample Components and Concentrations

Solution Component (mg/L)	ICS A Concentration 1:10 (mg/L)	ICS B Concentration 1:100 (mg/L)	ICS AB Concentration (mg/L)
Al	100		100.0
Ca	100		100.0
Fe	100		100.0
Mg	100		100.0
Na	100		100.0
P	100		100.0
K	100		100.0
S	100		100.0
C	200		200.0
Cl	1000		1000
Mo	2.0		2.0
Ti	2.0		2.0
As	0	0.02	0.02
Cd	0	0.02	0.02
Cr	0	0.02	0.02
Co	0	0.02	0.02
Cu	0	0.02	0.02
Mn	0	0.02	0.02
Ni	0	0.02	0.02
Ag	0	0.02	0.02
Zn	0	0.02	0.02
Ba	0	0.02	0.02

Recommended Interference Check Sample Components and Concentrations			
Solution Component (mg/L)	**ICS A Concentration 1:10 (mg/L)**	**ICS B Concentration 1:100 (mg/L)**	**ICS AB Concentration (mg/L)**
Sb	0	0.02	0.02
Be	0	0.02	0.02
Pb	0	0.02	0.02
Se	0	0.02	0.02
Tl	0	0.02	0.02
Sn	0	0.02	0.02
V	0	0.02	0.02

7.6 Internal Standards: Purchase Inorganic Ventures 6020ISS, or equivalent; it contains 10 µg/mL ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, ^{209}Bi. Purchase Environmental Express HP100020-1, or equivalent; it contains 1000 µg/mL ^{72}Ge.

- Prepare a 1 µg/mL solution by diluting 50 mL 6020ISS and 0.5 mL HP100020-1 to 500 mL mixed acid diluent. When added to the sample or standard by the instrument at 1:20, the resulting concentration is 50 ug/L. Generally, an internal standard is no more than 50 amu removed from the analyte.

Isotopes, Internal Standards, and Reaction Gas for Selected Elements			
Element of Interest	**Mass**	**IS**	**Reaction Gas**
Aluminum	27	45	Helium
Antimony	121	103	No gas
Arsenic	75	72	Helium
Barium	137	159	No gas
Beryllium	9	45	Helium
Bismuth (IS)	209		No gas, Helium
Cadmium	111	103	Helium
Calcium	40	45	Helium
Chromium	52	45	Helium
Cobalt	59	72	Helium
Copper	65	72	Helium
Germanium (IS)	72		No gas, Helium
Holmium (IS)	165		No gas, Helium
Indium (IS)	115		No gas, Helium
Iron	56	72	Helium
Lead	(206) (207) 208	209	No gas
Lithium (IS)	6[a]		No gas, Helium
Magnesium	24	45	Helium
Manganese	55	72	Helium
Molybdenum	95	103	Helium
Nickel	60	72	Helium
Potassium	39	45	Helium
Rhodium (IS)	103		No gas, Helium
Scandium (IS)	45		No gas, Helium
Selenium	78	72	Helium

Isotopes, Internal Standards, and Reaction Gas for Selected Elements			
Element of Interest	**Mass**	**IS**	**Reaction Gas**
Silver	107	103	Helium
Sodium	23	45	Helium
Terbium (IS)	159		No gas, Helium
Thallium	205	209	No gas
Tin	118	103	No gas
Titanium	47	72	Helium
Vanadium	51	72	Helium
Zinc	66	72	Helium

[a]Internal standard must be enriched in the ^{6}Li isotope. This minimizes interference from indigenous Lithium.

7.7 Hydrochloric acid (HCl), concentrated. To prepare a 5% solution, add 10 mL concentrated HCl to 200 mL reagent water.
7.8 Nitric acid (HNO_3), concentrated. To prepare a 5% solution, add 10 mL concentrated HNO_3 to 200 mL reagent water.
7.9 Mixed Acid Diluent: A mixture of 1% HNO_3 and 0.5% HCl (volume/volume) in reagent water is used to prepare standards and blanks.

- Add 2 mL HNO_3 and 1 mL HCl to 200 mL reagent water.

7.10 See SOP Reagent and Standard Purchase, Preparation, Control, Documentation / NV08-214 for additional shelf-life and storage requirements for reagents and standards.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water, TCLP Extract	HDPE or Glass	125 mL	HNO_3 to pH ≤ 2[1]	6 months	SW-846 Chapter 3; 40 CFR 136
Soil	HDPE or Glass	50 grams	No requirement	6 months	SW-846 Chapter 3

[1]If water samples are preserved in the lab, they should be held for at least 24 hours before analysis; record acidification start/stop time and pH. Temperature preservation is not required.

For the determination of dissolved elements, the sample **must** be filtered prior to acid preservation through a 0.45-µm pore diameter, PTFE membrane filter at the time of collection or as soon thereafter as practically possible.

9.0 Quality Control

Refer to TestAmerica-Nashville's QA Manual for specific quality control (QC) policies. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC: The following quality control samples must be prepared with each batch:

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Method Blank	1 per 20 samples	6020: < ½ RL or MDL, whichever is greater.	Correct problem then re-prep and analyze method blank and all samples processed with the

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
		200.8: <MDL	contaminated blank.
Laboratory Control Sample (LCS)[1]	1 per 20 samples	6020: 80-120[2]% recovery 200.8: 85-115%recovery	Correct problem then re-prep and analyze the LCS and all affected targets in the affected analytical batch. If high and ND, OK to report.
Matrix Spike	1 per 20 samples	6020: 75-125[2]% recovery 200.8: 70-130% recovery	Run post-digestion spike.
Matrix Spike Duplicate	1 per 20 samples	<20[2]% RPD	Run post-digestion spike.
6020 Only: Dilution test	If MS/MSD fail.	If concentration is high enough, at least 10 times RL, run 1:4 fold dilution, must agree within 10% of the original determination.	Report and qualify
6020 Only: Post digestion spike addition	When dilution test fails	Recovery within 20% of the expected results	Re-run, report, and qualify.

[1]AZ, MA, TX require an LCS duplicate in each batch.
[2]If historical limits are calculated, they cannot exceed these limits.

- **Method blank:** For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation, including pre-filtering, digestion, dilution, filtering, and analytical process.
  - Use the same volume of reagent water or weight of Teflon™ boiling chips as the samples.
- **Laboratory Control Sample (LCS):** For each batch of samples processed, at least one LCS must be carried throughout the **entire sample preparation and analytical process**. Spike equivalent aliquots of reagent water for water batches or Teflon™ boiling chips for soil batches with each analyte of interest at the approximate mid-point of the linear dynamic range.
  - Prepare the LCS by diluting 500 µL of each of the standards to 50 mL mixed acid diluent.
- **Matrix Spike / Matrix Spike Duplicate:** Take separate, identical aliquots from a sample for replicate and spiked analyses to assess the effect and document the bias and precision of a method in a given sample matrix. See SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
  - The added analyte concentration and standard source must be the same as that used in the LCS.
  - Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unspiked sample, and compare these values to the designated MS recovery range
  - If less than acceptable accuracy and precision are obtained, additional tests are required:
    - If MS/MSD is outside the QC limits, the same sample from which the MS/MSD aliquots were prepared is also spiked with a **post-digestion spike**. Otherwise, another sample from the same preparation is used as an alternative. The spike addition produces a minimum level of 10 times the RL. If this spike fails, an interference effect is suspected, and the dilution test is run on this sample. If both the MS/MSD and the post-digestion spike fail, then matrix effects are confirmed. Report and qualify.
  - **6020 Dilution test**: If the analyte concentration is sufficiently high (minimally, a factor of 10 times the report limit), an analysis of a 1:4 (5X) dilution should agree within 10% of the original determination. If not, a chemical or physical interference effect is suspected. Report and qualify.

9.2 Instrument QC

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Tune	Daily, prior to analysis of samples.	Adjust sensitivity with a stability ≤5% RSD.	Adjust instrument setting and re-run.
Pulse/Analog Check Standard	Immediately after Tune	0.05 or greater for targets	Adjust concentration, re-run.
Tune Check Standard	Each day	± 0.1 amu and RSD of 5 replicates ≤ 5%	Adjust and re-run
Calibration Standards	Each day	Linear regression: r 0.998, r^2 ≥ 0.996. Mid and Upper ± 10% true; low ± 30% true.	Clean, adjust, and re-calibrate.
Calibration Blank	Each day	≤ MDL or ½ RL, whichever is greater.	Re-run calibration.
Spectral Interference Check Solutions, A and AB	Beginning of analytical run or once every 12 hours, whichever is more frequent	Target ± 2 times RL or ± 20% true.	Terminate analysis; correct problem; re-analyze ICS; re-analyze all affected samples.
Instrument Detection Limits (IDL)	Quarterly	±3 standard deviations of the average response.	Adjust MDL.
Independent Calibration Verification Sample (ICV), second source	Immediately after calibration	90-110 % recovery	Correct problem then repeat initial calibration.
Independent Calibration Blank (ICB)	Immediately after ICV	No target analytes above RL.	
Continuing Calibration Verification Sample (CCV)	Every 10 samples and at the end of the run	90-110% recovery	Repeat calibration and re-analyze all samples since last successful calibration.
6020: Undigested Low Level Continuing Calibration Verification (LLCCV)	After the ICB, Method Blank, and end of each batch.	70-130% true	Re-calibrate.
Continuing Calibration Blank (CCB)	Following the CCV	≤ RL	Correct problem then analyze calibration blank and previous 10 samples.
Digested Lower Limit of Quantitation Check (LLQC) or Report Limit Verification (RLV)	Quarterly	70-130% recovery	Re-calibrate.
Internal Standards	All samples, standards, QC	6020: 70-130% recovery 200.8: 60-125% recovery	Dilute and re-run. For blank and LCS, correct problem and re-run batch.
MDL Verification (digested)	Yearly	Detected	Re-evaluate MDL standard used and MDL; see Technical Director.

- **Tune**: See Section 6.1, primary mass check and collision cell optimization.
- **Pulse/Analog Check Standard**: This standard contains 100 µg/L of all targets.
  - Prepare by taking about 0.25 mL of 100 µg/mL primary calibration standard and 12.5 mL of 1 µg/mL internal standard solution to 250 mL mixed acid diluent. Establish the detector

choice, i. e., pulse/analog, for each element.

- **Tune Check Standard:** Verify that the instrument has reached thermal stability, is aligned correctly, and is properly tuned. Use the Tune Check Standard to perform this check. Target analytes must have <5% RSD, <0.1 amu true resolution, and <0.9 amu at 10% peak height.
- **Calibration**: See Section 10.
- **Calibration Blank:** This blank is used in establishing the calibration curve. It consists of the mixed acid diluent (1% HNO_3 and 0.5% HCl (volume/volume) in reagent water) and the selected concentrations (50 µg/mL, added on-line) of internal standards such that there is an appropriate internal standard element for each of the analytes.
- **Rinse Blank Solution**: After calibration, flush the system with the rinse blank solution until the signal levels return to the method's levels of quantitation (usually about 75 seconds) before the analysis of each sample.
  - The rinse blank consists of 4% HNO_3 and 4% HCl (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.
- **Spectral Interference Check Solution (ICS A and ICS AB):** The laboratory periodically verifies the inter-element correction (IEC) routine by analyzing SIC solutions. The spectral interference check solution is run at the beginning of the analytical sequence or every **12 hours**, whichever is more frequent. If the SIC does not meet criteria, then the SICs are re-analyzed.
  - Ensure that the analytical results of ICS A fall within the control limit of ± 2 times the RL of the analyte's true value or ± 20% of the analyte's true value, whichever is greater (the true value is zero unless otherwise stated) in the ICSA. For example, if the analysis result(s) for Arsenic (RL = 10 µg/L, ICSA true value = 0 µg/L) in the ICSA analysis during the run is 19 µg/L, then the analytical result for Arsenic falls within the ± 2 times the RL window for Arsenic in the ICSA. If the analytical results of the ICS A do not fall within the control limits, terminate the analysis, correct the problem, re-calibrate the instrument, and re-analyze the analytical samples analyzed since the last compliant ICS A was performed.
  - Ensure that the results for the ICS AB during the analytical runs fall within the control limit of ± 2 times the RL of the true value or ± 20% of the true value, whichever is greater, for the analytes included in the ICS AB. If the analytical results of the ICS AB do not fall within the control limits, terminate the analysis, correct the problem, re-calibrate the instrument, and re-analyze the analytical samples analyzed since the last compliant ICS AB was performed.
- **Instrument Detection Limits (IDL):** On a quarterly basis, analyze seven consecutive reagent blanks per day on three non-consecutive days; calculate the average of the standard deviations.
- **Independent Calibration Verification (ICV and ICB):** The laboratory analyzes a mid-level and an ICB immediately following daily calibration
  - Weekly, prepare the 100 µg/mL ICV by diluting 500 µL of each of the 100 µg/mL **second-source** standards to 50 mL 1% HNO_3:0.5% HCl (mixed acid diluent).
- **Continuing Calibration Verification (CCV and CCB):** Analyze after every 10th sample and at the end of the analytical sequence.
  - For the CCV, add 500 µL of the primary calibration stock standard and 500 µL of the 100 µg/mL of the Al, Fe cation spike to 50 mL mixed acid diluent.
  - If the calibration cannot be verified within the specified limits, reanalyze either or both the CCV and the CCB. If the second analysis of the CCV or the CCB confirm calibration to be outside the limits, sample analysis must be discontinued, the cause determined, corrected and/or the instrument recalibrated. All samples following the last acceptable CCV must be reanalyzed. All samples **must be bracketed** by acceptable CCVs and CCBs.
  - The CCB (prepared by acidifying reagent water to the same concentrations of the acids as

used for the standards) must not contain target analytes above the RL. If it does, repeat the analysis one more time. If the CCB is still not less than the RL, terminate the analysis, correct the problem, re-calibrate, and re-analyze the previous 10 samples.

- **Report Limit Verification (RLV):** %D must be ± 30%. Run at the beginning and end of each batch.
  - Prepare a 2 µg/L LLCCV (however, Al is 20 µg/L; Fe is 25 µg/L; Zn is 25 µg/L, Minerals are 1000 µg/L):
  - Add 10 mL of 10 µg/L primary standard solution.
  - Add 0.9 mL of 1 µg/mL Al primary standard (Ultra Scientific IAA-213-5, or equivalent, 1000 µg/mL).
  - Add 1.2 mL of 1 µg/mL Fe primary standard (Ultra Scientific IAA-226-5, or equivalent, 1000 µg/mL).
  - Add 1.2 mL of 1 µg/mL Zn primary standard (Ultra Scientific IAA-230-5, or equivalent, 1000 µg/mL).
  - Add 49.9 µL of the 1000 µg/mL Minerals spiking solution (5 µL TA-9/50 mL reagent water).
- **Lower Limit of Quantitation Check Sample (LLQC):** Ideally, this check sample and the low-level calibration verification standard are prepared at the same concentrations with the only difference being the LLQC sample is carried through the **entire preparation and analytical procedure including digestion**. See Section 10 for preparation.
- **Internal Standards:** Use the internal standard technique by adding one or more elements (not in the samples and verified not to cause an uncorrected inter-element spectral interference) at the same concentration (which is sufficient for optimum precision) to the prepared samples (blanks and standards) that are affected the same as the analytes by the sample matrix. Use the ratio of analyte signal to the internal standard signal for calibration and quantitation. Internal standards are automatically added to all calibration standards, samples, and QC, by the instrument.

  The intensities of all internal standards must be monitored for every analysis. If the intensity of any internal standard in a sample falls below **70%** of the intensity of that internal standard in the initial calibration standard, a significant matrix effect must be suspected. Use the following procedure:

1	Make sure the instrument has not drifted by observing the internal standard intensities in the nearest clean matrix (calibration blank).
2	If the low internal standard intensities are also seen in the nearest calibration blank, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.
3	If drift has not occurred, matrix effects need to be removed by dilution of the affected sample. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards.
4	If the first dilution does not eliminate the problem, this procedure must be repeated until the internal-standard intensities rise to the minimum **70%** limit. Correct all reported results for all dilutions.

- **MDL Verification:** A solution containing all target analytes at 2-3 times the MDL must be **digested** and analyzed after the completion of the MDL study and on an annual basis. Detection limits are verified when all analytes in the MDL check solution are detected.

10.0 Procedure

10.1 Sample Preparation: See SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

Matrix	Sample Size	Matrix	Sample Size
Water	50 mL of sample	Soil	0.5 gram of sample

10.1.1 **6020 Digestions:** Use metal digestion SOPs 3005 / NV06-103, 3010 / NV06-18, or 3051 / NV06-94.

10.1.2 **200.8 Digestions**

10.1.2.1 **Aqueous Sample Preparation, Dissolved Analytes:** For the determination of dissolved analytes, transfer an aliquot (≥ ~50 mL) of the filtered, acid preserved sample to a 50 mL polypropylene centrifuge tube. Add an approximate value of (1+1) nitric acid to adjust the acid concentration of the aliquot to approximate 1% (v/v) nitric acid sample (e.g., add 0.4 mL (1+1) HNO_3 to a 20 mL aliquot of sample). The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations.

Note: If a precipitate forms during acidification, transport, or storage, the sample aliquot must be treated using the procedure described in Section 10.2 prior to analysis.

10.1.2.2 **Sample Preparation, Total Recoverable Analytes**

1	For the determination of total recoverable analytes, transfer a 50 mL (± 0.5 mL) aliquot from a well mixed, acid preserved sample to a digestion vessel. (When necessary, smaller sample aliquot volumes may be used.) Note: If the sample contains undissolved solids >1%, a well mixed, acid preserved aliquot containing no more than 1 g particulate material should be cautiously evaporated to near 10 mL and extracted using the acid mixture procedure described in the following sections.
2	Add 1.0 mL (1+1) nitric acid and 0.5 mL of (1+1) hydrochloric acid to the container containing the measured volume of sample. Place the container on the hot block for solution evaporation. The hot block should be located in a fume hood and previously adjusted to provide evaporation at a temperature of approximately but no higher than 85° C. The digestion tube should be covered with an elevated watch glass or other necessary steps should be taken to prevent sample contamination from the fume hood environment. **Note**: For proper heating, adjust the temperature control of the block digester such that a 50-mL centrifuge tube containing 50 mL of water placed in the center of the block digester can be maintained at a temperature approximately but no higher than 85°C. When the centrifuge tube is covered with a watch glass, the temperature of the water will rise to approximately 95°C.)
3	Reduce the volume of the sample aliquot to about 20 mL by gentle heating at about 85℃. DO NOT BOIL. This step takes about 1 hour for a 50-mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. (A spare digestion tube containing 20 mL of water can be used as a gauge.)
4	Cover the lip of the digester vessel with a loose cap to reduce additional evaporation and gently reflux the sample for 30 minutes. (Slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the HCl-H_2O) azeotrope.)
5	Allow the digestion tube to cool and fill with reagent water to 50 mL mark. Tubes are certified to measure 50 mL by Environmental Express.
6	Allow any undissolved material to settle overnight, filter using a PTFE membrane, or centrifuge a

	portion of the prepared sample until clear. The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted sample cannot be characterized, all analyses should be performed as soon as possible after the completed preparation. If any sample is filtered, the Method Blank and LCS must also be filtered.
7	The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted sample cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

10.2 Instrument Setup

1	Initiate appropriate operating configuration of the instrument's computer, according to the instrument manufacturer's instructions. Click "Instrument Control" and turn plasma "ON,"
2	Load tunes "normal.U" and "He.U." Load "60202008" method and calibration.

10.2 Calibration: Refer to SOP Selection of Calibration Points / CA-T-P-002 and Calibration Curves (General) / CA-Q-S-005. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

1	Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. Verify by analyzing the Tuning solution at least **five integrations** with relative standard deviations of ≤ 5% for the analytes contained in the tuning solution.
2	Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution is verified to be less than 0.9 amu full width at 10 percent peak height. The tune limits are:

Tune	m/z	Criteria	Tune	m/z	Criteria
Normal	7	<5% RSD	He	59	<5% RSD
	89	<5% RSD		51	low counts
	205	<5% RSD		52	low counts
	156/140	m/z ratio <3%		75	low counts
	70/140	m/z ratio <3%			

At least four integrations are required.

3	Run P/A (Pulse/Analog) check standard daily using the P/A standard.
4	Run the Tune Check daily using the Tuning solution.
5	Calibrate the instrument for the analytes of interest (recommended isotopes for the analytes in Section 1 are provided in Section 4), using the calibration blank and at least three calibration standards.

For the calibration standards, serially dilute the 100 µg/mL calibration standard as follows:

mL of 100 µg/mL Calibration Standard	Final Volume (mL) of 1% HNO_3: 0.5% HCl.	Calibration Standard Concentration (µg/L)
0	50	0
0.5	50	1
5.0	50	10
0.050	50	100

	PREPARE FRESH WEEKLY. To prepare the 1000 µg/L calibration standard for Al, Ca, Fe, K, Mg, Na dilute 50 µL Al, and Fe primary standards (1,000 µg/mL) and 50 µL Cation Spike (1,000 µg/mL) to 50 mL reagent water. To prepare the 10000 µg/L standard for Al, Ca, Fe, K, Mg, Na, dilute 0.5 mL each of the Al and Fe primary standards (1,000 µg/mL) and 0.5 mL Cation Spike (1,000 µg/mL) to 50 mL reagent water. To prepare the Linear Range Standard, dilute 500 µL of TA-40 primary standard (100 µg/mL) and 1000 µL TA-13 (5,000 µg/mL) to 50 mL reagent water. NOTE: Improved performance in calibration stability may be obtained if the instrument is exposed to the interference check solution after cleaning sampler and skimmer cones. Improved performance is also realized if the instrument is allowed to rinse for 5 or 10 minutes before the calibration blank is run.
6	**Use the average of at least three integrations for both calibration and sample analyses. The relative standard deviation for instrument QC must be <5%. The RSD for samples with concentrations greater than two times the reporting limit is < 20%.**
7	Prepare a standard curve by calculating the counts per second (cps) of standards versus the corresponding target concentrations using first-order linear regression. The correlation coefficient r must be greater than or equal to 0.998 ($r^2 \geq 0.996$), or re-calibrate. **NOTE:** The multi-point calibration establishes the linear dynamic range (LDR) provided the low standard is within 30% of the true value and the upper standard, representing the linear range standard (LRS), is within 10% of the true value.
8	Monitor all masses which could affect data quality to determine potential effects from matrix components on the analyte peaks.
9	After initial calibration, the calibration curve must be immediately verified by use of an initial calibration verification (ICV) standard.
10	For samples from Arizona, California, Hawaii, Minnesota, and Nevada, the calibration curve must also be verified prior to the analysis by use of a Report Limit Verification (RLV) standard, ± 30% true.
11	Verify that the inter-element spectral interference correction routine is still valid by analyzing the ICSA and ICSAB.
12	The calibration curve must be verified at the end of each analysis batch and after every 10 samples by use of a continuing calibration verification (CCV) standard and a continuing calibration blank (CCB).
13	The calibration curve must also be verified prior to the analysis of any samples by use of a low-level continuing calibration verification (LLCCV) standard.
14	Verify the inter-element correction factors at the beginning of the daily sequence or every 12 hours, whichever is more frequent.
15	Flush the system with the rinse blank solution until the signal returns to ≤ RL.

10.3 Sample Analysis

1	Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Use at least three integrations.
2	Dilute and re-analyze samples that are more concentrated than the upper calibration standard for an analyte (or species needed for a correction) or measure an alternative less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration.

10.4 Example Analysis Queue / Sequence*

1	Tune
2	P/A Standard
3	Tune Check Standard
4	ICAL
5	ICV
6	ICB
7	LLCCV (undigested)
9	ICS A
10	ICS AB
11	Rinse x 2-4
12	CCV
13	CCB
14	LLCCV (undigested)
15	Method Blank
16	LCS*
17	Samples 1-10
18	CCV
19	CCB
20	Samples 11-20
21	Matrix Spike
22	Matrix Spike Duplicate
23	CCV
24	CCB
25	LLCCV (undigested)

*AZ, MA, TX require an LCS duplicate in each batch.

11.0 Calculations / Data Reduction

11.1 Relative Standard Deviation (RSD)

RSD = (SD / $\overline{x_i}$) x 100

$$SD = \sqrt{\sum_{i=1}^{n} \frac{\left(x_i - \overline{x_i}\right)^2}{n-1}}$$

11.2 Accuracy

% Recovery = $\frac{\text{Measured concentration x 100}}{\text{Known concentration}}$

11.3 Precision (RPD)

RPD = $\frac{\text{Absolute value (orig. sample value - dup. sample value) x 100}}{\text{(Orig. sample value + dup. sample value)/2}}$

11.4 Response Factor

$$RF = \frac{\text{Intensity}}{\text{Concentration}}$$

11.5 % Drift

$$\% \text{ Drift} = \frac{(\text{Result - True Value}) \times 100}{\text{True Value}}$$

11.6 Linear Calibration Using a Least Squares Regression: This is most easily achieved by performing a first-order linear regression of the instrument response versus the concentration of the standards. Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). This is a statistical requirement and is not simply a graphical convention.

The regression produces the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

y = instrument response (peak area)
a = slope of the line
x = concentration of the calibration standard
b = the intercept

The acceptance criteria for the calibration standard recovery should be ± 10% of its true value for all standards except the lowest concentration. A recovery of ± 30% of its true value should be achieved for the lowest concentration standard.

11.7 Coefficient of Determination Correlation Coefficient

$$\mathbf{r}^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2} \qquad \mathbf{r} = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response ratio; x = Concentration

11.8 Concentration Calculation: Sample data are reported in units of µg/L for aqueous samples, µg/kg for solid samples. LIMS calculates the concentration from the raw data provided by the analyst. Include appropriate interference corrections, internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundance of these isotopes between samples and standards.) All results are reported with up to **three significant figures**.

$$\text{Concentration (µg/L or µg/kg)} = \frac{(\text{µg/mL}^{*} \text{ from instrument})(\text{digest volume, mL})(\text{Dilution factor})}{\text{Sample Volume, mL, or Mass, g}}$$

µg/mL from instrument = Intensity/RF

***average of at least three integrations**

11.9 For dissolved analytes, report the data generated directly from the instrument with allowance for sample dilution. Do not report analyte concentrations below the MDL.
11.10 If solid results are needed on a dry weight basis, calculate as follows: Perform a separate determination of % solids. The concentrations determined in the digest are reported on the basis of the dry weight of the sample:

$$\text{Conc. (µg/kg dry weight basis)} = \frac{\text{(µg/mL from instrument)(digest volume, mL)(Dilution factor)}}{\text{(Wet Sample Mass, g)(\% Solids/100)}}$$

11.11 Account for any additional dilution of the prepared sample solution needed to complete the determination of analytes exceeding 90% or more of the upper calibration standard. Do not report data below the determined analyte MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency. Compare the MDL to the IDL. The MDL must be ≥ the IDL or adjust.
12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.
12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.
12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.
12.5 Control Charts: Laboratory method performance can be shown with the use of control charts, available from LIMS or the QA department.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are managed, stored, and disposed of in accordance with all federal and state laws and regulations. Waste description rules

and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Acidic aqueous wastes are taken to the waste disposal area, neutralized, and discharge to the sanitary sewer.

15.0 References / Cross-References

15.1 Method 6020, SW-846 Update II, Revision 0, September 1994 and **Method 6020A**, SW-846 Update IV, Revision 1, February 2007.

15.2 EPA Method 200.8, Methods for Chemical Analysis of Water and Wastes, Revision 5.4 (1994), Collision Cell Technique approved March 12, 2007.

15.3 TestAmerica Nashville's Quality Assurance Manual.

15.4 Corporate Environmental Health and Safety Manual (CW-E-M-001).

15.5 SOPs: Selection of Calibration Points / CA-T-P-002, Calibration Curves (General) / CA-Q-S-005, Method 3005 / NV06-103; Method 3010 / NV3010, Method 3050 / NV06-93; Method 3051 / NV06-94; Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213, Determination of Method Detection Limits / NV08-202, Sample Homogenization, Subsampling, and Compositing / NV08-229.

15.6 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

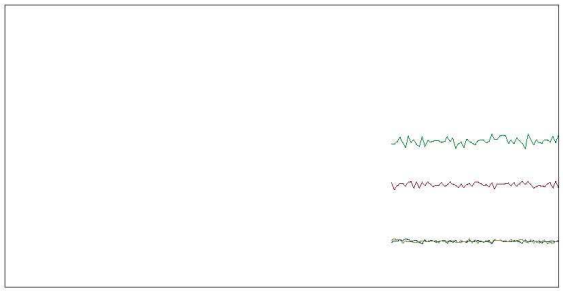
Item	Modification
1	If 3030C digestion is specified, see the attachment in SOP 3005 / NV06-103 for that procedure.

17.0 Attachments

Example Tune File for Normal.U

Sensitivity

Tune File : NORMAL.U



Integration Time: 0.1000 sec
Sampling Period: 0.7200 sec
n: 61

m/z	Range	Count	Mean	RSD%
7	100,000	15994.0	16213.0	2.20
89	100,000	53785.0	51687.8	2.39
205	100,000	16676.0	16220.7	2.48
59	100,000	35117.0	36280.9	2.08
156/140	2	1.235%	1.217%	6.32
70/140	5	1.839%	1.711%	4.89

Tuning Parameters

===Plasma Condition===			===Ion Lenses===			===Q-Pole Parameters===		
RF Power	:	1550 W	Extract 1	:	0 V	AMU Gain	:	125
RF Matching	:	1.76 V	Extract 2	:	-145 V	AMU Offset	:	126
Smpl Depth	:	8 mm	Omega Bias-Ce	:	-20 V	Axis Gain	:	0.9989
Torch-H	:	-0.1 mm	Omega Lens-Ce	:	-1.4 V	Axis Offset	:	-0.03
Torch-V	:	0.1 mm	Cell Entrance	:	-30 V	QP Bias	:	-3 V
Carrier Gas	:	0.8 L/min	QP Focus	:	3 V			
Makeup Gas	:	0.1 L/min	Cell Exit	:	-30 V	===Detector Parameters===		
Optional Gas	:	--- %				Discriminator	:	8 mV
Nebulizer Pump	:	0.1 rps	===Octopole Parameters===			Analog HV	:	2100 V
Sample Pump	:	--- rps	OctP RF	:	150 V	Pulse HV	:	1360 V
S/C Temp	:	2 degC	OctP Bias	:	-6 V			

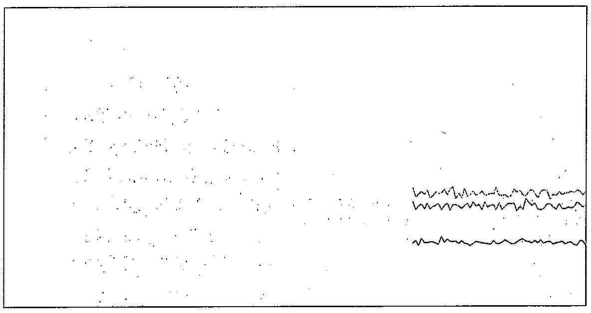
===Reaction Cell===								
Reaction Mode	:	QPF						
H2 Gas	:	--- mL/min	He Gas	:	0 mL/min	Optional Gas	:	--- %

Generated : Jul 15, 2013 13:06:03
Printed : Jul 15, 2013 13:06:08

Example Tune File for He.U

Sensitivity

Tune File : HE.U



Integration Time: 0.1000 sec
Sampling Period: 0.7200 sec
n: 60

m/z	Range	Count	Mean	RSD%
89	20,000	3993.0	4250.3	2.89
205	20,000	6693.0	6657.7	2.75
59	20,000	7657.0	7513.1	2.61
51	20	2.0	5.0	46.98
52	200	164.0	173.1	8.27
75	20	17.0	14.2	28.67
78	20	0.0	1.2	104.94

Tuning Parameters

===Plasma Condition===			===Ion Lenses===			===Q-Pole Parameters===		
RF Power	:	1550 W	Extract 1	:	0 V	AMU Gain	:	125
RF Matching	:	1.76 V	Extract 2	:	-145 V	AMU Offset	:	126
Smpl Depth	:	8 mm	Omega Bias-ce	:	-30 V	Axis Gain	:	0.9989
Torch-H	:	-0.1 mm	Omega Lens-ce	:	-1.4 V	Axis Offset	:	-0.03
Torch-V	:	0.1 mm	Cell Entrance	:	-30 V	QP Bias	:	-16 V
Carrier Gas	:	0.8 L/min	QP Focus	:	-10 V			
Makeup Gas	:	0.1 L/min	Cell Exit	:	-40 V	===Detector Parameters===		
Optional Gas	:	--- %				Discriminator	:	8 mV
Nebulizer Pump	:	0.1 rps	===Octopole Parameters===			Analog HV	:	2100 V
Sample Pump	:	--- rps	OctP RF	:	150 V	Pulse HV	:	1360 V
S/C Temp	:	2 degC	OctP Bias	:	-18 V			

===Reaction Cell===								
Reaction Mode	:	ON						
H2 Gas	:	--- mL/min	He Gas	:	5.6 mL/min	Optional Gas	:	--- %

Generated : Jul 15, 2013 13:14:12
Printed : Jul 15, 2013 13:14:17

18.0 Revision History

- Revision 3, dated 30 December 2009
  - Integration for TestAmerica and STL operations.
  - Updated to 6020A.
- Revision 4, dated 31 August 2011
  - Organizational changes.
  - Addition of QAF-45 and Section 14.2.
  - Addition of corporate SOPs Selection of Calibration Points / CA-T-P-002 and Calibration Curves (General) / CA-Q-S-005.
  - Update ICS A and ICS B concentrations and vendor, with concentration changes to ICS AB. Remove 20 mg/L mineral standard.
  - Addition of Tune Check to Section 9.
  - Addition of a 1 µg/L calibration standard.
  - Deletion of repetitive language.
  - Remove requirement to run batches of 10 for WY samples.
- Revision 5, dated 30 November 2011
  - Add minerals to list of analytes, changing primary, secondary standard, Working ICS Solution B, LCS, ICV, LLCCV, and calibration standard preparations; Isotopes, Internal Standards, and Reaction Gases for Selected Elements.
  - Add preparation of mixed acid diluent.
  - Change some tune criteria.
  - Remove system flushing between each standard solution in the calibration instructions.
  - Modify the analytical sequence with the mention of a rinse instead of a memory check.
- Revision 6, dated 30 August 2013
  - Organizational changes
  - Addition of filter information.
  - Update standard identification, source, related preparations.
  - Update Reporting Limits (RLs).
  - Addition of Agilent 7500cx.
  - Remove use of Hydrogen (H_2) as reaction gas from literature, tables, attachments, etc.
  - Update Isotopes, Internal Standards, and Reaction Gas for Selected Elements.
  - Change frequency of Matrix Spike / Matrix Spike Duplicate.
  - Change some tune criteria.
  - Modify the analytical sequence with the mention of Digested RLV before analysis of ICS A and ICS AB and Undigested RLV after analysis of CCB at beginning and end of batch.
  - Remove the requirement to run batches of 10 for OK samples.
- Revision 7, dated 30 September 2014
  - Organizational changes.
  - Incorporate amendment 6a, the requirements for the RSD for instrument setup QC.
  - WV no longer requires LCSD.
  - Change the acceptance criteria for the Tune Check Standard. Require the LLQC to be run quarterly. Require the LLCCV to be run after the ICB, Method Blank, and at the end of the batch.
- Revision 8, dated 28 November 2014
  - Combine SOPs 6020 / N06-215.7 and 200.8 / NV06-216.4.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP) Change Form

SOP Number/Revision No.: **7470 245.1 SM3112 B / NV06-41.18a** Effective Date: **1/31/2016**

Last Mod. Date: 12**/31/15**

SOP Title: **Method 7470A, 245.1, 245.2 (SC), SM3112 B: Mercury in Liquid Waste (Manual Cold Vapor Technique)**

CONTROLLED DISTRIBUTION

ISSUED TO: \\TAFS\Lab\Nashville\Public\QA\SOPs, 06

Revision Number with Mod ID: **18b**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other: Audit recommendation.

2. Summary of Procedure Change: Add highlighted text; delete crossed-out text.

Section 6.1, Instrumentation

- Hot water bath or digestion block. - Adjustable and capable of maintaining a temperature of 95 ~~90~~ ± 5 °C.

Section 10.1, Sample Preparation, step 5

5	Add 2.4 mL of Potassium persulfate to each bottle, mark liquid level, and cap. Heat for 120 ± 10 minutes in a water bath maintained at 95 ± 5 ~~2~~°C. Record start and stop time and temperature.

Section 10.2, Calibration, step 6

6	Add 2.4 mL of Potassium persulfate to each bottle, mark liquid level, and cap. Heat for 120 ± 10 minutes in a water bath maintained at 95 ± 5 ~~2~~°C. Record start and stop time and temperature.

1/27/16	
Department Manager Approval Date	
1/27/16	1/27/16
Quality Manager Approval Date	Technical Director Approval Date

SOP Number/Revision No.: **7470 245.1 SM3112 B / NV06-41.18** Effective Date: **12/31/2015**

Last Mod. Date: **7/31/15**

SOP Title: **Method 7470A, 245.1, 245.2 (SC), SM3112 B: Mercury in Liquid Waste (Manual Cold Vapor Technique)**

CONTROLLED DISTRIBUTION

ISSUED TO: \\TAFS\Lab\Nashville\Public\QA\SOPs, 06

Revision Number with Mod ID: **18a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other: Audit recommendation.

2. Summary of Procedure Change: Add highlighted text; delete crossed-out text.

Section 1.1, Analyte, Matrices, add a last sentence: For solids, wastes, and oils, see SOP 7471 / NV06-100.

Section 6.1, Instrumentation

- Hot water bath or digestion block. - Adjustable and capable of maintaining a temperature of 90 ± 5 ~~90-95~~°C.

Section 8.0, Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	HDPE or Glass	30.0 mL	HNO_3 to pH ≤ 2*	28 days from collection	SW-846 Chapter 3, 40 CFR Part 136.3; SM Table 1060:I ~~2,~~
TCLP Leachate		3.0 mL		28 days from leachate preparation	SW-846 Method 1311

Section 9.1, Sample QC [Only the changed controls are shown.]

The following quality control samples are prepared with **each batch of no more than 20 samples.**			
Quality Controls	**Frequency**	**Acceptance Limits**	**Corrective Action**
Laboratory	1[1] per batch	7470: 80-120%	Correct problem, then re-prep and

Control Sample[1] (LCS)~~, second source~~		recovery 245.1 & SM3112 B: 85-115% recovery, < 20 ~~25~~% RPD[2]	analyze the LCS, all samples, and QC in the affected analytical batch. If high and sample is ND, it is OK to report.
Matrix Spike Duplicate	7470 & SM3112 B: 1 per batch; 245.1: 1 per 10 samples.	7470: 75-125% recovery, < 20% RPD 245.1 & SM3112 B: 70-130% recovery, < 20 ~~25~~% RPD[2]	
7470 only: Post-digestion Spike	If results of dilution test or MS/MSD do not agree.	80-120%	Dilute and reanalyze

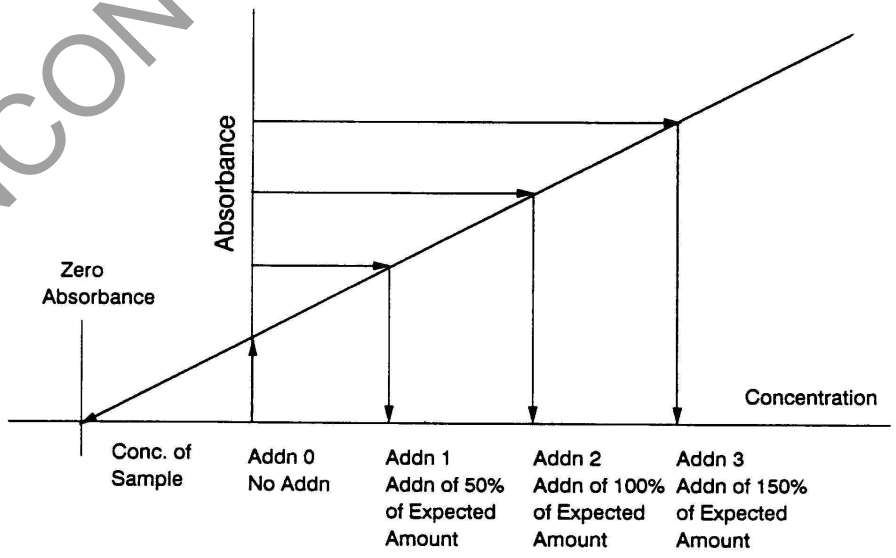
1 All AZ, MA, and TX samples require a LCS duplicate in each batch.
~~2 VELAP Guidance Document, 6/22/15.~~

- **Matrix Spike/Matrix Spike Duplicate (MS/MSD)**

Prepare the spike solution by adding 30 µL of 1.0 µg/mL standard to 30.0 mL sample ~~reagent water~~ for the MS/MSD in a certified, centrifuge tube for a final concentration of 1.0 µg/L.

- **Method of Standard Addition (MSA)**: If the MS/MSD < 50% recovery, the concentration is less than 0.2 mg/L, and the TCLP result is within 20% of the TCLP limit (0.2 mg/L), perform MSA which involves adding a known amount of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal. Improved results are obtained by employing a series of standard additions.

To equal volumes of the sample add a series of standard solution containing different known quantities of the analyte and dilute all solutions to the same final volume. The absorbance of each solution is determined and plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in the figure. A linear regression program is used to obtain the intercept concentration. For validity, the apparent concentrations from the calibration curve must be linear over the concentration range of concern and the effect of the interference does not vary as the ratio of analyte concentration to sample matrix changes. For additional information, see EPA 7000B.



Section 9.2, Instrument QC [Only the changed controls are shown.]

Quality Controls	Frequency	Control Limit	Corrective Action
Initial Calibration Verification Sample (ICV), second source	Immediately after calibration	7470 & SM3112 B: 90-110% recovery. 245.1 ~~&~~ ~~SM3112 B~~: 95-105% recovery Replicates >RL: <10% RPD. Replicates < RL: <30% RPD.	Correct problem, then repeat initial calibration. If the RPD fails for a concentration level, run two new replicates.
SM3112 B: Report Limit Verification (RLV)	Beginning of each batch	± 50% true	Correct problem, re-run, re-calibrate.

Section 10.1, Sample Preparation

Matrix	Sample Size
Water	30 mL
TCLP Leachate	3.0 mL

1	Transfer 30.0 mL of aqueous sample into a 50-mL, certified, digestion tube. For a TCLP leachate, add 3.0 mL and dilute to 30.0 mL with reagent water. ~~Record the digestion tube lot number.~~ For the LCS, add 30.0 mL reagent water to a 50-mL, certified, digestion tube. For a TCLP leachate batch, the LCS is 3.0 mL TCLP blank fluid diluted to 30.0 mL with reagent water. Record the digestion tube lot number.

Section 10.3, Calibration, Step 6, and add Step 12

6	Add 2.4 mL of Potassium persulfate to each bottle, mark liquid level, and cap. Heat for 120 ± 10 minutes in a water bath or block digester maintained at 95 ± 5 ~~2~~ ^{o}C. Record start and stop time and temperature.
12	• See Section 9.1 for MSA for TCLP extracts.

Section 15.7, SOPs, add the following: 7471 / NV06-100.

12/8/15	
Department Manager Approval Date	
12/8/15	12/7/15
Quality Manager Approval Date	Technical Director Approval Date

Title: MERCURY IN LIQUID WASTE (MANUAL COLD VAPOR TECHNIQUE) METHOD 7470A, 245.1, 245.2 (SC), SM3112 B

Approvals (Signature/Date)

Cliff Eaton Department Manager	7/30/15 Date
Ryan Fitzwater Health & Safety Manager / Coordinator Laboratory Director	7/31/15 Date
Michael H. Dunn Technical Director, Interim QA Manager	7/30/15 Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method uses cold-vapor atomic absorption for determining the concentration of mercury in groundwaters and leachates (EPA 7470A) and drinking water, surface water, groundwater, sea or brackish water, and wastewater (EPA 245.1, 245.2 (SC), and SM3112 B).

1.2 Reporting Limits: The typical detection limit for this method is 0.0002 mg/L.

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

This method is a cold-vapor atomic absorption technique and is based on the absorption of radiation at 253.7-nm, by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual for laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 Potassium permanganate is added to eliminate possible interference from sulfide.

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

4.3 Samples high in chlorides may require additional permanganate because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the Mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent, allowing the sample to sit approximately one hour before reduction, or by dilution of the sample.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This method may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: Perform the digestion in an operational fume hood.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury	Oxidizer Corrosive Poison	0.1 mg/m^3 Ceiling (Mercury Com-pounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. Can cause burns. Can cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. Can affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; can cause serious and permanent eye damage.
Nitric acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which can be fatal. Other symptoms can include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and can cause damage to the eyes. Contact can cause severe burns and permanent eye damage.
Hydro-chloric acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and can cause damage to the eyes. Contact can cause severe burns and permanent eye damage.
Potassium perman-ganate	Oxidizer	5 mg/m^3 for Mn Com-pounds	Causes irritation to the respiratory tract. Symptoms can include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Sulfuric acid	Corrosive Oxidizer Dehydra-tor Poison Carcino-gen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Potassium persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Leeman Mercury Cold Vapor Analyzer Hydra II, or equivalent: Instrument settings recommended by the particular manufacturer are followed.
- Recorder: Data acquisition by PC running Leeman software.
- Air pump: Any peristaltic pump capable of delivering 1 liter air/minute is used.
- Flowmeter: Capable of measuring an air flow of 1 liter/minute.

- Hot water bath or digestion block. - Adjustable and capable of maintaining a temperature of 90-95°C.

6.2 Supplies

- Volumetric flasks and pipettes of suitable precision and accuracy (Class A).
- Certified, digestion tubes, 50-mL, Environmental Express, or equivalent.

7.0 Reagents and Standards

7.1 Reagent water, analyte-free.

7.2 Hydrochloric acid, HCl, concentrated, commercial.

7.3 Nitric acid (HNO_3), concentrated: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to change lots of the Nitric acid.

7.4 Sulfuric acid, concentrated, commercial, reagent grade.

7.5 Stannous chloride: Add 100 g Stannous chloride to 100 mL HCl, dilute to 1000 mL with reagent water in a 1-L container.

7.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 120 g of Sodium chloride and 120 g of Hydroxylamine sulfate in reagent water and dilute to 1000 mL with reagent water in a 1-L container. (Hydroxylamine hydrochloride may be used in place of Hydroxylamine sulfate.)

7.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 50 g of Potassium permanganate in 1000 mL of reagent water in a 1-L container.

7.8 Potassium persulfate, 5% solution (w/v): Dissolve 50 g of Potassium persulfate in 1000 mL of reagent water in a 1-L container.

7.9 Stock mercury solution: Stock solutions are purchased at 1000 µg/mL from CPI and Ultra Scientific. Use caution in handling mercury solutions.

7.10 Mercury intermediate working standard: Make dilution of the stock mercury solution to obtain a working standard containing 1.0 µg/mL. Dilute 0.05 mL 1000 µg/mL stock to 50.0 mL with 1% HNO_3 in a Class A, volumetric flask. Prepare monthly.

7.11 Initial Calibration Verification (ICV): Prepare from a **different** source than the calibration standards.

7.12 See SOP Reagent and Standard Purchase, Preparation, Control, and Documentation / NV08-214 for shelf-life and storage requirements for reagents and standards.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	HDPE or Glass	30.0 mL	HNO_3 to pH ≤ 2*	28 days from collection	SW-846 Chapter40 CFR Part 136.3; SM Table 1060:I 2,

*If the lab adds the preservative, hold the samples for 16 hours before digestion.
Temperature preservation is not required. Certified cleaned containers are supplied by TestAmerica Nashville.

9.0 Quality Control

Refer to the QA Manual for quality control (QC) policies. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC

The following quality control samples are prepared with **each batch of no more than 20 samples.**			
Quality Controls	**Frequency**	**Acceptance Limits**	**Corrective Action**
Method Blank	1 per batch	< MDL	Correct problem, then re-prep and analyze method blank, all samples, and QC processed with the contaminated blank.
Laboratory Control Sample[1] (LCS), second source	1[1] per batch	7470: 80-120% recovery 245.1 & SM3112 B: 85-115% recovery, <25% RPD[2]	Correct problem, then re-prep and analyze the LCS, all samples, and QC in the affected analytical batch. If high and sample is ND, it is OK to report.
Matrix Spike	7470 & SM3112 B: 1 per batch; 245.1: 1 per 10 samples.	7470: 75-125% recovery 245.1 & SM3112 B: 70-130% recovery	If both MS and MSD are similarly outside acceptable limits and the LCS is within acceptable limits, the batch is acceptable.
Matrix Spike Duplicate	7470 & SM3112 B: 1 per batch; 245.1: 1 per 10 samples.	7470: 75-125% recovery, < 20% RPD 245.1 & SM3112 B: 70-130% recovery, <25% RPD[2]	If one analysis of the MS/MSD pair is within acceptable limits and the other is outside acceptable limits, repeat the analysis exhibiting unacceptable results.
Dilution Test	1 per batch	5X dilution sample result must be within 10% RPD of the undiluted sample result.	Perform post-digestion spike.
Post-digestion Spike	If results of dilution test or MS/MSD do not agree.	80-120%	Dilute and reanalyze

1 All AZ, MA, and TX samples require a LCS duplicate in each batch.
2 VELAP Guidance Document, 6/22/15.

- **Method blank:** The laboratory prepares and analyzes at least one blank (30 mL reagent water) with each batch.
- A **Laboratory Control Sample (LCS):** To evaluate the ability of analyzing a clean matrix of known concentration, prepare one LCS per batch exactly as client samples, and compare the % recovery to the control limits.
  - Add 30 µL of 1.0 µg/mL standard to 30.0 mL reagent water for the LCS in a certified, centrifuge tube for a final concentration of 1.0 µg/L.
- A **Matrix Spike/Matrix Spike Duplicate (MS/MSD)** are analyzed every batch. If the recovery for the MS/MSD cannot be determined, due to the high concentration (4 times greater than the spike level) of the sample used for spiking, then run a dilution test.
  - Prepare the spike solution by adding 30 µL of 1.0 µg/mL standard to 30.0 mL reagent water for the MS/MSD in a certified, centrifuge tube for a final concentration of 1.0 µg/L.
- **Dilution Test:** Dilute the sample by a minimum of five fold and re-analyze. Agreement within 10% between the concentration for the undiluted sample and five times the concentration for the diluted sample indicates the absence of interferences. If the results do not agree, run a post-digestion spike.

- **Post-Digestion Spike:** If the post-digestion spike or the MS/MSD is not within 80-120%, dilute the original sample and re-run.

9.2 Instrument QC

Quality Controls	Frequency	Control Limit	Corrective Action
Initial Calibration Verification Sample (ICV), second source	Immediately after calibration	7470: 90-110% recovery. 245.1 & SM3112 B: 95-105% recovery Replicates >RL: <10% RPD. Replicates < RL: <30% RPD.	Correct problem, then repeat initial calibration. If the RPD fails for a concentration level, run two new replicates.
Initial Calibration Blank	Beginning of each batch	< MDL	Correct problem, then re-digest and re-analyze calibration and entire digestion batch.
Continuing Calibration Verification Sample (CCV)	Every 10 samples and end of batch	90-110%	If CCV falls outside of range low rerun once and if still out of range, correct problem, recalibrate and rerun all affected samples. If high and sample is ND, OK to report.
Continuing Calibration Blank	Following the CCV	< ½ RL	Rerun affected samples.
7470: Report Limit Verification (RLV)	Beginning of each batch	0.14-0.26 µg/L, ± 30% true	Correct problem, re-run, re-calibrate.
245,1: Report Limit Verification (RLV)	For **AZ, CA, HI, MN, NC, NV**: 1 per batch, at the beginning of the batch.	**NC**: 70-130% recovery **AZ, CA, HI, NV**: 65-135% recovery **MN**: 60-140% recovery	Re-run, re-prep. If it fails again, perform instrument maintenance and repeat initial calibration, re-run all samples.

- **Initial Calibration Verification (ICV)** and **Initial Calibration Blank (ICB):** A verification standard made from a **different** source than the calibration standards is run immediately after calibration.
  - Prepare ICV by adding 75 µL of the 1.0 µg/mL second-source standard to 30.0 mL acidified reagent water in a certified, centrifuge tube for a final concentration of 2.5 µg/L.
  - The ICB contains the same acid and reagent water as the calibration standards.
  - The ICV and ICB are digested per the procedure given in Section 10.1.
- **Continuing Calibration Verification** (CCV) and **Continuing Calibration Blank (CCB)**: Every 10 samples and at the end of the sequence, a mid-level standard (2.0 µg/L) is analyzed. If the CCV is outside of range, rerun once and, if still out of range, correct problem, recalibrate and rerun all affected samples.
  - Prepare CCV by adding 60 µL of the 1.0 µg/mL primary source standard to 30.0 mL acidified reagent water in a certified, centrifuge tube for a final concentration of 2.0 µg/L.
  - The CCB contains the same acid and reagent water as the calibration standards.
  - The CCV and CCB are digested per the sample preparation procedure in Section 10.

- **Report Limit Verification (RLV):** Daily, analyze a low calibration verification at 0.2 µg/L at the beginning of the analytical sequence. If the percent recovery falls outside the limits, the CRA/RLV must be re-analyzed immediately. If it fails again, correct the problem, re-calibrate. The CRA/RLV is also used as the MDL verification and establishes the report limit.
  - Prepare by diluting the 2.0 µg/L CCV standard by 10x (3.0 mL to 30.0 mL). The acceptance range is 0.14 µg/L to 0.26 µg/L.

10.0 Procedure

10.1 Sample Preparation: Refer to SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

Matrix	Sample Size
Water	30 mL

1	Transfer 30.0 mL of sample into a 50-mL, certified, digestion tube. Record the digestion tube lot number. For the LCS, add 30.0 mL reagent water to a 50-mL, certified, digestion tube.
2	Prepare the spiked QC samples as described in Section 9.1.
3	Add 1.5 mL of H_2SO_4 and 0.75 mL of concentrated HNO_3, mixing after each addition.
4	Add 4.5 mL of 5% Potassium permanganate solution to each sample bottle. Mix. Continue adding 5% Potassium permanganate until the purple color persists. Ensure that equal amounts of permanganate are added to standards and blanks.
5	Add 2.4 mL of Potassium persulfate to each bottle, mark liquid level, and cap. Heat for 120 ± 10 minutes in a water bath maintained at 95 ± 2°C. Record start and stop time and temperature.
6	If Potassium permanganate is reduced during sample preparation, remove the sample from the batch, and re-prepare as a dilution that allows permanganate to persist throughout all of the sample preparation.
7	Cool, if needed, bring to mark with reagent water, and add 1.8 mL of Sodium chloride hydroxylamine sulfate to reduce the excess permanganate. Additional hydroxylamine solution may be needed to complete de-colorization. Allow to sit open for approximately one hour. Place in autosampler and start analysis.

10.2 Calibration: Refer to SOP Calibration Curves and Selection of Calibration Points / CA-Q-P-003. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

1	Start-up the instrument computer, using "WinHg runner," the software: Go to the control tab and turn the pump on at 5 mL/minute. Turn lamp and gas on. The instrument turns on and goes through a warm-up period. Because of instrument variation refer to the manufacturer's recommended operating conditions when using this method. Allow the instrument to proceed through a warm-up period before beginning the calibration sequence.
2	Standard preparation: **Daily**, prepare calibration standards from 1.0 µg/mL working standard in 30.0 mL of 1% HNO_3.

mL Standard/30.0 mL final volume	Final Concentration, µg/L
0.0	0.0
0.006	0.2
0.015	0.5
0.030	1.0
0.060	2.0
0.075	2.5

	0.150 | 5.0
3	Transfer into a 50-mL**,** certified, digestion tube. Record the tube lot number.
4	Mix thoroughly and add 1.5 mL of concentrated H_2SO_4 and 0.75 mL of concentrated HNO_3 to each bottle.
5	Add 4.5 mL of $KMnO_4$ solution to each bottle.
6	Add 2.4 mL of Potassium persulfate to each bottle, mark liquid level, and cap. Heat for 120 ± 10 minutes in a water bath or block digester maintained at 95 ± 2°C. Record start and stop time and temperature.
7	Cool, if needed, bring to mark with reagent water, and add 1.8 mL of Sodium chloride hydroxylamine sulfate to reduce the excess permanganate. Additional hydroxylamine solution may be needed to complete de-colorization. Allow to sit open for approximately **one** hour. Place in autosampler and start analysis.
8	After computer start-up (see Sample Analysis below), put the appropriate standards for the method selected in the standard rack. Click on standard tab.
9	Depress standard buttons for standards 1, 2, 3, 4, 5, and 6.
10	Depress Rep 1 and Rep 2 buttons, then click standard Auto. The instrument begins calibration, using a linear calibration curve model. Only linear models are allowed.
10	To view first order linear regression curve, click data base button and the cal curve tab. The new curve is displayed. If its correlation coefficient $r \geq 0.995$ (or $r^2 \geq 0.990$), then check the accepted box and the new curve is stored. Verify that the upper calibration point is within 10% true.
11	Ensure the control limits in Section 9.2 for initial calibration are achieved.

10.3 Sample Analysis

1	Replenish the stannous chloride reservoir for automated addition of reagent.
2	Running samples: • Click rack editor button to open appropriate rack file (1 or 2), then enter sample ID into appropriate cup position. • Save information before returning to WinHg runner. • Return to runner and click sample tab. • Choose rack number to be run, start cup number and end cup number. • To begin, click run auto button; the instrument begins the sequence. Spiked samples and check standards are analyzed.
3	Shut-down procedure: • Return to control tab. Turn gas and pump off, and loosen tubes. • Turn off the power to the lamp if the instrument is not used for 24 hours or longer.

10.4 Example Analysis Queue / Sequence*

	7470	**245.1**	**SM3112 B**
1	Initial Calibration (daily)	ICAL	ICAL
2	ICV (daily)	ICV	ICV
3	ICB (daily)	ICB	ICB
4	RLV (daily)	MDLV/ RLV	MDLV/ RLV
5	Method Blank	Method Blank	Method Blank
6	LCS	LCS	LCS
7	Matrix Spike	Sample 1	Sample 1

8	Matrix Spike Duplicate	Matrix Spike	Matrix Spike
9	Samples 1-10	Samples 2-10	Matrix Spike Duplicate
10	CCV	CCV	Samples 2-20
11	CCB	CCB	CCV
12	Samples 11-20	Sample 11	CCB
13	CCV	Matrix Spike	
14	CCB	Samples 12-20	
15		CCV	
16		CCB	

*May be up to 20 samples.

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\text{LCS \% Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 % Drift

$$\text{\% Drift} = \frac{(\text{Result - True Value}) \times 100}{\text{True Value}}$$

11.4 Linear calibration using a least squares regression

Perform a linear regression of the instrument response versus the concentration of the standards. Non-linear equations are not allowed for this analysis. Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). This is a statistical requirement and is not simply a graphical convention.

The regression produces the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

y = instrument response (peak area)
a = slope of the line
x = concentration of the calibration standard
b = the intercept

Do not force the line through the origin, but have the intercept calculated from the data points. The use of a linear regression is not used as a rationale for reporting results below the lowest calibration standard. The regression calculation generates a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.995 or $r^2 \geq 0.990$.

11.4 Coefficient of Determination **Correlation Coefficient**

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2} \qquad r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response or Response ratio
x = Concentration

11.5 Sample Concentrations: Record metal concentrations directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account.

Concentration (µg/L) = (µg/L from instrument) (dilution factor)

Dilution factor = 1 if there is no dilution.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Detection Limits / CA-Q-S-006. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required for each matrix.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are managed, stored, and disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Acid waste: transfer to the waste disposal area for neutralization.
- Mercury waste: dispose in Mercury waste drum.

15.0 References / Cross-References

15.1 EPA Method 7470A, SW-846 Revision 1, September 1994.
15.2 EPA Method 7000B, SW-846 Revision 2, February 2007.
15.3 EPA Method 245.1, Methods for Chemical Analysis of Water and Wastes, 1974 and Supplement I, Revision 3.0, May 1994.
15.4 SM3112 B - 2009, Standard Methods for the Examination of Water and Wastewater, on-line edition, 2011 editorial revisions.
15.5 TestAmerica Nashville's Quality Assurance Manual.
15.6 Corporate Environmental Health and Safety Manual (CW-E-M-001).
15.7 SOPs: Calibration Curves and Selection of Calibration Points / CA-Q-P-003, Waste Disposal / NV10-83, Training Procedures for Technical Staff / NV08-199, Detection Limits / CA-Q-S-006, Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
15.8 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

Item	Modification
1	For South Carolina samples, reference Method 245.2 as opposed to 245.1.

17.0 Attachments

None.

18.0 Revision History

- Revision 10, 15 May 2009
  - Integration of STL and TestAmerica formats.
  - Correction of acid addition volumes to samples based on 50-mL final volume.
- Revision 11, 25 September 2009
  - Incorporation of OH VAP requirements.
  - Revision of preparation of LCS, MS/MSD, ICV, CCV, and standards due to change of pipettors.
- Revision 12, dated 31 October 2011
  - Organizational changes.
  - Incorporation of amendments 11a and 11b.
  - Addition of QAF-45 and Section 14.2.
  - Addition of reference to the corporate SOPs Selection of Calibration Points / CA-T-P-002 and Calibration Curves (General) / CA-Q-S-005.
  - OK is now the only state requiring batches of no more than 10 samples.
  - Add % drift equation.
  - Change volume additions of Sulfuric acid, Nitric acid, Potassium permanganate, Potassium persulfate, and Hydroxylamine.
- Revision 13, dated 30 November 2011
  - Modification of Sample Preparation steps 4 and 5, Calibration steps 6 and 7.
- Revision 14, dated 29 February 2012
  - Correction of reagent additions in Section 10.

- Revised instruction on reduction of Potassium permanganate.

- Revision 15, dated 31 July 2012
  - OK no longer limits batch size to 10 samples.
  - ICV and CCV are digested.
  - Clarification of sample preparation and calibration sections.
- Revision 16, dated 31 January 2014
  - Organizational change.
  - Addition of Changes 15a, b, c. Return CCV limits to 90-110%.
  - WV no longer requires a LCSD.
  - Specify that $r^2 \geq 0.990$.
- Revision 17, dated 31 July 2014
  - Combine SOPs for Methods 7470, 245.1, SM3112 B.
  - Organizational changes.
  - Add instruction to allow the samples to sit approximately one hour before placement in the autosampler.
- Revision 18, dated 31 July 2015
  - Organizational changes.
  - Annual review (drinking water).
  - If the lab preserves an unpreserved sample, hold for 16 hours before digestion.
  - Update SOP references.
  - Method blank changed to < MDL. Add MS/MSD failure to be the same as the post-digestion spike acceptance criteria.

Title: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS AND SOLID SAMPLES BY COLD VAPOR ATOMIC FLUORESCENCE

[Method: 1631E]

Approvals (Signature/Date):

Technology Specialist	01/07/15 Date	Health & Safety Coordinator	11/04/14 Date
Quality Assurance Manager	11/05/14 Date	Technical Director	11/17/14 Date

This SOP was previously identified as SOP No. NC-MT-001, Rev 6, dated 9/26/13

Facility Distribution No. _____ Distributed To:_____

The controlled copies of this SOP are the PDF copy of the SOP that is posted to the laboratory's SOP Directory and, where applicable, the SOP that is printed and placed in the General Chemistry SOP binder. Printed or electronic copies of this SOP distributed outside of the facility are considered uncontrolled.

TABLE OF CONTENTS

LIST OF APPENDICES

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS) using Method 1631E.

1.2. CVAFS analysis provides for the determination of total mercury (organic and inorganic). The oxidant, bromine monochloride, has been found to give quantitative recovery with both types of analytes. Detection limits, sensitivity, and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation, and volume of sample used.

1.3. Method 1631E (hereafter abbreviated to Method 1631 in this SOP) is applicable to the preparation and analysis of mercury in ground water, surface water, effluents, and other aqueous samples. Appendix A to Method 1631 is applicable to the preparation and analysis of mercury in sediments, soils, biological media and other solid samples. All matrices require sample preparation prior to analysis.

1.4. The laboratory instrumentation uses the flow injection process. Any method criteria applying to the bubbler method is not applicable to 1631E prep or analysis as performed according to this SOP.

1.5. The TestAmerica Canton reporting limit for mercury in aqueous matrices is 0.5 ng/L by Method 1631. The reporting limit for mercury by Method 1631 in solid matrices is 1.0 ug/kg.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solids, biological, and aqueous solutions. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor and fluorescence at 253.7 nm. For aqueous samples, a representative portion of the sample is digested and oxidized in bromine monochloride. For solid or biological samples, 1 gram of sample is digested with cold aqua regia (HCL/HNO_3), diluted, and further oxidized with bromine monochloride. Excess free halogens in the digestate are then reduced with hydroxylamine hydrochloride. The mercury (Hg^{+2}) is reduced to its elemental state with stannous chloride and purged from solution with argon in a gas / liquid separator. For Method 1631, the mercury vapor is collected on a gold trap and then thermally desorbed to the detector. The mercury vapor passes through a cell positioned in the light path of an atomic fluorescence spectrometer. Fluorescence is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample fluorescence to the calibration curve (fluorescence vs. concentration).

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM),

current version.

4. INTERFERENCES

4.1. Chemical and physical interferences may be encountered when analyzing samples using this method.

4.2. Gold, silver, and iodide are known interferences. At a mercury concentration of 2.5 ng/L and at increasing iodide concentrations from 30 to 100 mg/L, test data have shown that mercury recovery will be reduced dramatically.

4.3. The use of a brominating digestion coupled with atomic fluorescence detection overcomes many of the interferences. No interferences have been noted for sulfide concentrations below 24 mg/L.

4.4. Water vapor may collect in the gold traps (Method 1631), and subsequently condense in the fluorescence cell upon desorption, giving a false peak due to scattering of the excitation radiation. Condensation can be avoided by pre-drying the gold trap and by discarding those traps that tend to absorb large quantities of water.

4.5. The fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause *quenching* of the excited atoms.

4.6. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. All glassware is cleaned per SOP NC-QA-014. Be aware of potential sources of contamination, and take appropriate measures to minimize or avoid them. The analytical instrument and sample / standards preparation area should be protected from mercury vapor or particulates in the laboratory air. Samples, standards, and blanks should only be opened in a clean area. Gloves must be powder free, and should be checked for mercury contamination. Do not use powdered nitrile gloves as they have been shown to contribute both low-level mercury contamination and interferences. Only clean gloves should touch the instrument and all other equipment used to process blanks, standards, and samples.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or

when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Bromine Monochloride	Corrosive Poison Oxidizer	0.1 (Br) ppm TWA	May be fatal if inhaled. Causes severe eye and skin burns. Causes damage to the following organs: Lungs, mucous membranes, respiratory tract, skin, central nervous system, eyes, lens or cornea.
Potassium Bromate	Oxidizer	0.1 mg/m^3 TWA	Irritates respiratory tract. May cause coughing and shortness of breath. Causes irritation to the skin. May cause redness, itching, and pain. In the presence of liquids, it is slowly absorbed in toxic amounts. Prolonged exposure may cause burns. Causes irritation to eyes with redness, pain. May cause eye damage.
1 – Always add acid to water to prevent violent reactions.			

2 – Exposure limit refers to the OSHA regulatory exposure limit.

5.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and cleanup techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion, or absorption through skin. All lines should be checked for leakage, and the mercury vapor must be vented into a hood or passed through a mercury–absorbing media such as a carbon filter.

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. Exposure to hazardous chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

5.7. Do not look directly into the beam of the Hg lamp. The UV light these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution in accordance with local regulations. It is recommended that, wherever possible, cylinders are located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAFS apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Atomic Fluorescence Spectrophotometer equipped with:

6.1.1. Fluorescence Cell with quartz ends. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.1.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL)

6.1.3. Peristaltic pump

6.1.4. Flowmeter

6.1.5. Recorder or printer

6.1.6. Gas /Liquid separator

6.1.7. Drying devices: Nafion Dryer soda lime trap

6.1.1 Gold traps (2): Quartz tube containing gold-coated sand

6.1.2 Hotblock maintaining a temperature of 50-110°C

6.2. Sample bottles, 40 mL borosilicate glass VOC vials, QEC or equivalent, < 0.5 ng/L contamination when used for Method 1631 samples. In actual practice, should contribute less than 0.1 ng/L to facilitate meeting method blank criteria. Unless tested by the manufacturer for cleanliness and accuracy, four vials from each lot must be gravimetrically tested in triplicate at the 40 mL point. Cleanliness is assessed by adding 0.2 mL BrCl (Section 7.15). Store the test vials at room temperature for at least 12 hours and analyze as samples. All vial results must be less than the reporting limit.

6.3. Argon gas supply, high purity, or equivalent: A gold trap may be used in-line to further purify the argon.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a US Filter PureLab Plus deionized water system or equivalent. Reagent water must be free of mercury and interferences as demonstrated through the analysis of reagent and method blanks.

7.2. Stock (10 mg/L) mercury standards (in 5-10% HNO_3) are purchased. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year, and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 ug/L): Fill a 100 mL volumetric flask about half full with reagent water. Add 0.5 mL of BrCl solution (Section 7.15). Add 0.10 mL of the stock mercury standard (Section 7.2) and dilute to 100 mL with reagent water. The intermediate mercury standard should be replaced every nine months.

7.4. Working mercury standard (1 ug/L): Fill a 40 mL vial about half full with reagent water. Add 0.2 mL of BrCl solution (Section 7.15). Add 4.0 mL of the intermediate mercury standard (Section 7.3) and dilute to 40 mL with reagent water. The working

mercury standard should be replaced every three months. Additional information can be found in SOP NC-QA-017.

7.5. The calibration standards listed in Table I must be prepared fresh from the working standard (Section 7.4) by adding 0, 0.02, 0.04, 0.08, 0.2, 0.4,1.0, and 4.0 mL of a mercury standard to 40 mL vials and diluting to volume with reagent water. For Method 1631, use the working standard (Section 7.4). BrCl (Section 7.15) and $NH_2OH•HCl$ (Section 7.12) reagent solutions are also added.

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

7.6. The initial calibration verification standard (QCS or ICV) must be made from a different manufacturer or lot than that of the calibration standards.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification, and spiking solutions. All standards must be processed with all reagents that are used for sample preparation.

7.8. Hydrochloric acid (HCl), concentrated, trace metal grade.

Note: Ultra trace mercury HCl should be used to prepare the bromine monochloride solution Trace metal grade HCl may be used to prepare the stannous chloride and 2% HCl rinse solutions provided that these solutions are purged with argon prior to use.

7.9. Autosampler rinse solution (2%): 400 mL trace metal grade HCl diluted to 20 L reagent water. Add 1 mL of stannous chloride working solution and purge with argon (0.5 L/min) for at least 24 hours.

7.10. Stannous Chloride Solution Concentrate: Add 500 g of $SnCl_2•2H_2O$ to 2.4 L trace metals concentrated HCl. Allow the $SnCl_2•2H_2O$ to completely dissolve. (ACS Reagent grade suitable for mercury determination (< 1 ppb) is recommended.)

7.11. Stannous Chloride Working Solution: Fill a 2.5 L glass bottle (HCl leached) with 2.25 L of reagent water. Add sufficient stannous chloride concentrate (Section 7.10) to bring the total volume to 2.5 L. This produces a reductant solution that is 10% HCl and 2% $SnCl_2•2H_2O$. Purge with argon (0.5 L/min) for at least 1 hour. Analyze a reagent blank with this solution prior to analysis of samples (Section 9.7).

7.12. Hydroxylamine Hydrochloride Solution: Purchased

7.13. Bromine monochloride, intermediate solution: Purchased 10 mL tubes

7.14. Bromine monochloride, working solution: Place 10 mL of Bromine monochloride intermediate solution (1 tube) into 90 mL of concentrated Hydrochloric acid. Invert to

mix.

Note: Prior to placing a new lot of BrCl into production, spike 1 mL into a blank and LCS and analyze. If recovery is < 80%, re-prep the BrCl reagent. If it fails again, the reagent lot is not approved for use.

7.15. Nitric acid, concentrated, trace metal grade

7.16. Sulfuric Acid, concentrated, trace metal grade

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Preservation and Holding Time

8.1.1. Holding time from time of collection is extended to 28 days when the sample is preserved with HCl or the oxidation step is performed in the sample bottle used for collection. Preservation/oxidation is verified by the persistence of the yellow color of the BrCl. Up to 1 mL additional BrCl may be added if the preservative/oxidizer is consumed. If more than 1 mL BrCl is required, a 10 x dilution on the original sample vial is required and the digestion process is repeated. Record any additional BrCl used (see Section 11.2.5). Samples to be analyzed for dissolved Hg must be transferred to the filtering apparatus within 48 hours of collection then preserved as above. Once preserved, holding time is 90 days from sample collection to analysis.

8.1.2. Solid and biological sample holding time for Hg is one year from collection to digestion and preservation. The holding time for digested and preserved solid samples is 90 days from sample preparation.

8.2. Collection and Storage

8.2.1. The clean hands/dirty hands procedure should be followed for collection. Standard sampling kits include environmental sample kit (2 x 40mL vials), MS/MSD kit (4 x 40mL vials), field blank kit (2 empty + 2 DI-filled 40mL vials), and trip blank kit (2 DI-filled 40mL vials). Alternative client-specified configurations of sample kits may be provided. Samples are stored in a mercury-clean area in the laboratory.

8.2.2. Solid samples may be stored in fluoropolymer or borosilicate glass or polyethylene bags.

8.2.3. Tissue samples may be shipped to the laboratory frozen or chilled at 0-4 degrees C, and may be processed and stored in one of the following ways:

8.2.3.1. Tissue that arrives frozen, should be keep frozen until time for homogenization. Thaw, homogenize, and then refreeze the tissue in a glass container. Subsampling can occur immediately after

homogenization before the refreeze or at a later date with another thaw/refreeze cycle. Tissue which is frozen will maintain integrity for 1 year from sample collection.

8.2.3.2. Tissue that arrives cold (0-4 ºC) but not frozen can be homogenized within 24 hours and frozen in a glass jar. Subsampling can occur immediately after homogenization before the freeze or at a later date with another thaw/refreeze cycle.

8.2.3.3. Tissues that arrive cold (0-4 ºC) but not frozen can be frozen upon receipt and kept frozen until time for homogenization. Thaw, homogenize, and refreeze the tissue in a glass container. Subsampling could occur immediately after homogenization before the refreeze or at a later date with another thaw/refreeze cycle

9. QUALITY CONTROL

9.1. Preparation Batch

9.1.1. A group of up to 20 samples of the same matrix processed together using the same procedures and reagents. The preparation batch must contain a method blank (MB), LCS, and matrix spike/matrix spike duplicate pair (2 MS/MSD pairs if the batch has more than ten samples). In some cases, at client request, it may be appropriate to process a MS and un-spiked sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB should not contain any mercury at, or above, the reporting limit. If a sample result is less than a minimum of 10 times the MB contamination level, the sample must be re-prepared in a new batch and re-analyzed.

9.2.2. If concentrations of mercury are not greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.2.3. Re-preparation and re-analysis of all samples associated with an unacceptable MB is required when reportable concentrations are determined in the samples (see exceptions noted above).

9.2.4. If the above criteria are not met and re-analysis is not possible due to limited sample quantity, then the sample data must be qualified. This anomaly must be addressed in the project narrative and the client must be notified.

9.2.5. Preparation blanks must be prepared for 0.2, 0.4, 0.6, 0.8, and 1 mL volumes of BrCl on each day samples are prepped using these volumes of BrCl. If there is a positive detection in any of these blank samples, this information must be included in the case narrative of any job containing samples that were spiked with a corresponding level of BrCl. This prep blank does not have any method-specific acceptance criteria. Acceptance is based on the experience and judgment of the analyst

9.2.6. For Wisconsin project work, see Work Instruction WI-NC-0125.

9.3. System / Subtraction Blank

9.3.1. The system (calibration) blank consisting of all reagents used to prepare samples and standards will be used for background subtraction and system cleanliness monitoring. Three system blanks are prepared and analyzed with the initial calibration curve (ICal). Apply the average calibration factor from the ICal to the average raw response from these three system blanks. The calculated mercury concentration must be less than the reporting limit. The standard deviation of the three blanks must be < 0.10 ng/L. Subsequent system blanks are analyzed as ICB and CCB in conjunction with the ICV (identified in Method 1631E as the QCS) and CCV (identified in Method 1631E as the OPR). These IC and CC blanks are used to monitor the cleanliness of the instrument, are calculated in the same manner as samples, and are not used for background subtraction purposes. The absolute value of the calculated mercury concentration in the ICB and CCB must be less than the reporting limit.

9.4. Reagent Blank

9.4.1. Reagent blanks are used to demonstrate that the reagents used to prepare samples for Hg analyses are free from contamination. The Hg concentration in reagent blanks is determined by analyzing the reagent solutions.

9.4.2. Reagent blanks are required whenever a new batch of reagents (bromine monochloride, hydroxylamine hydrochloride, and stannous chloride) is prepared. The amount of Hg in a reagent blank containing BrCl solution, stannous chloride solution, and hydroxylamine hydrochloride solution must be < the RL.

9.5. Laboratory Control Sample (LCS).

9.5.1. One aqueous LCS must be processed with each preparation batch. The LCS is a second source standard used to monitor the accuracy of the analytical

process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure and must be spiked with a second source standard. The method specific acceptance criterion is 77-123% (for Wisconsin work, the LCS low limit is 70%; other analytical programs have other specific limits that must be used). If the LCS is outside established control limits the system is out of control and corrective action must be performed.

9.5.2. In the instance where the LCS recovery is greater than the maximum and the sample results are < RL, the data may be reported with qualifiers**. Such action must be addressed in the case narrative.**

9.5.3. Corrective action will be re-preparation and re-analysis of the batch unless other corrective action is agreed upon with the client.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1. One MS/MSD pair must be processed for each 10 samples in a preparation batch. An MS is a field sample to which a known concentration of mercury has been added. An MSD is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and MS. Some client-specific data quality objectives (DQOs) may require the use of un-spiked sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Method 1631 requires that each matrix be spiked at a 10% frequency. Some regulatory agencies interpret each discharge or sampling point as a separate matrix. It is the client's responsibility to determine which sample(s) is to be matrix spiked each time samples are submitted for analysis. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

9.6.2. If mercury recovery or RPD falls outside the acceptance range, corrective action will include:

9.6.2.1. If the MS/MSD fails due to the high background concentration of mercury in the parent sample, spike concentration will be adjusted accordingly, and the parent sample, MS, and MSD will be reanalyzed. Alternately, the parent sample and MS/MSD pair may be diluted and re-analyzed.

9.6.3. MS/MSD results which again fall outside the control limits must be addressed in the case narrative.

9.7. Additional information on QC samples can be found in QA Policy QA-003.

9.8. Control Limits

9.8.1. Control limits are prescribed in method 1631E. Control limits are easily accessible via LIMS.

9.9. Method Detection Limits (MDLs) and MDL Checks (MDL Verifications or MDLVs)

9.9.1. MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.9.2. MDLs are easily accessible via LIMS

9.10. Nonconformance and Corrective Action

9.10.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Carry-Over Determination.

10.1.1. The carry-over determination is to be analyzed once on every instrument. The results from the determination must be kept on file.

10.1.2. Analyze system blanks immediately after calibration solutions containing successively higher concentrations of Hg – from this test determine the amount of Hg that will carry >0.5 ng/L of Hg into a succeeding system blank. When a sample with one half or more of this determined amount is analyzed, then a system blank or sample must be demonstrated to be below the reporting limit before a subsequent sample can be reported. Samples with detectable Hg analyzed after the high sample, but before system cleanliness is demonstrated, must be re-analyzed.

10.2. Calibration standards must be processed through the preparation procedure as described in Section 11.2, except they do not need ta minimum of 12 hours of oxidation time and can be used immediately since the mercury is already in an oxidized state in the standard.

10.3. Calibration may be performed daily (every 24 hours), but is required only when indicated by instrument and preparation QC problems. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer (Table II). Allow the instrument to become thermally stable before

beginning calibration (approximately 1-2 hours of warm-up is required if the lamp has been turned off). The most stable results are obtained if the lamp is left on full time. Refer to the CVAFS instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of six standards and three calibration blanks. One standard must be at the TestAmerica North Canton reporting limit. Analyze standards in ascending order of concentration, beginning with the blanks. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration factors across the calibration range must have less than 15% RSD or the instrument shall be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable RSD. Also, the low standard must calculate back against the curve within ±25% of the true value.

10.7. Initial Calibration Verification/Initial Calibration Blank (ICV/ICB)

10.7.1. Calibration accuracy is verified by analyzing a second source standard (ICV) immediately following an Initial Calibration. The ICV result must fall within 20% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within ? the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected, and the instrument recalibrated (see Section 11.5.5 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related, the corrective action will include repreparation of the ICV, ICB, CCV, and CCB with the calibration curve.

10.8. Continuing Calibration Verification/Continuing Calibration Blank (CCV/CCB)

10.8.1. Calibration accuracy is monitored in the analytical sequence through the analysis of a known standard at the end of the analytical sequence or every 12 hours. Additional CCVs may be analyzed as necessary. The CCV concentration must be at 5 ng/L for 1631. The CCV result must fall within 77-123% of the true value for that solution for 1631. A CCB is analyzed immediately following each CCV. (See Section 11.5.5 for required run sequence). The CCB (system blank) must fall within ± the reporting limit (RL) from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs.

10.8.2. In the instance where the CCV or CCB is greater than the maximum acceptance criteria and the sample results are < RL, the data may be reported. Such action must be addressed in the case narrative.

11. PROCEDURE

11.1. Aqueous Sample Preparation

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, and CCB) and laboratory QC samples (LCS, MB, MS, and MSD) are processed with the same digestion reagents used for the field samples.

11.1.2. Remove about 2.7 mL from each sample vial. This will leave 40 mL in the bottle. Confirm by checking the meniscus and the 40mL calibration point as determined by verifying vials from each new lot. Set the cap back on the original vial. Repeat this process for all 40 mL vial aliquots of the sample.

11.1.3. Temporarily lift the cap and add 0.20 mL of BrCl (Section 7.15) to the 40 mL sample vial, reseal and mix. Store the sample vials at room temperature for at least 12 hours.

11.1.4. For aqueous MS/MSDs, two vials will be digested. Equal amounts from each vial will be aliquoted into a 40 mL vial to make the final analytical sample. Three 12.8 mL aliquots will be removed from this vial to create the parent sample and the MS/MSD pair. The MS and MSD aliquots will be spiked with 0.2 mL of the MS/MSD spike solution prior to analysis.

11.1.5. Starch/iodide paper may be used to detect excess halogens (i.e., BrCl) in colored samples where the yellow color of the BrCl cannot be seen. If the yellow tint from the BrCl disappears and starch/iodide paper does not detect halogens, add additional BrCl to the 40 mL sample vial, reseal, mix and allow to digest for another 12 hours.

11.1.6. If starch/iodide paper still does not detect halogens, make a 10x dilution on the aliquot generated from section 11.1.5 and resume the digestion process. . Store the sample vials at room temperature for at least 12 hours. Record the lot number of the starch/iodide paper **and the total amount of BrCl added to the sample** in the LIMS prep batch comments.

11.1.7. If the 1 mL maximum was reached and the yellow BrCl color still does not persist, perform a 10x dilution on the same aliquot and resume the bromination process with iterations of BrCl as described above in sections 11.2.5-11.2.7.

11.1.8. Preparation blanks must be prepared for 0.2, 0.4, 0.6, 0.8, and 1 mL volumes of BrCl on each day samples are prepped using these BrCl volumes. If there is a positive detection in any of these blank samples, this information must be included in the case narrative of any job containing samples that were spiked with a corresponding level of BrCl.

Note: To meet IL EPA requirements the vials must be heated at

approximately 50°C for six hours. If the oxidizer has been consumed, add additional BrCl and heat for an additional six hours.

11.2. Biological Sample Preparation

11.2.1. This procedure is intended for tissue and other primarily organic matrices (excluding coal). It does, however, give quantitative recovery for Hg on finely divided geological matrices such as sediments and soils.

11.2.2. Accurately weigh 1.0 gram of sample directly into a tared digestion vessel.

Note: The use of too much organic material will consume all of the acid **i**n the digestion, resulting in low recovery.

11.2.3. To each sample, add 3 mLs of H_2SO_4 and 7 mLs of HNO_3. Place the digestion vessel in an acid fume hood and loosely cap with a clean marble or equivalent. For wood, paper or other dry carbohydrates that can react violently with the HNO_3/H2SO_4 solution, allow the sample to sit in the acid at room temperature for at least 4 hours before heating.

11.2.4. After digesting at room temperature, place the digestion vessel in a hotblock in the hood and slowly bring to a gentle boil by incrementally increasing the plate temperature over a 1-hour period to 85-95°C. If excessive sample foaming occurs, bring to temperature more slowly. Reflux for 2-3 hours to fully oxidize remaining organic matter. The mineral portion of soil and sediment samples will not dissolve, but will be effectively leached by this digestion.

11.2.5. After the digestion is complete, allow the sample to cool. Add 1mL of BrCl and bring to the calibration mark on the digestion vessel with water. Shake the sample/BrCl solution to homogenize, and allow to sit at least 4 hours prior to analysis to oxidize remaining dissolved methyl Hg.

11.2.5.1. For the MB, add approximately 1 g of Teflon boiling chips.

11.2.5.2. For the LCS, add 1.0 mL of the 10 ug/L intermediate mercury standard (Section 7.3) to1g of Teflon boiling chips.

11.2.5.3. For the MS/MSD, add 1.0 mL of the 10 ug/L intermediate mercury standard (Section 7.3) in addition to the 1g of solid sample.

11.2.6. Proceed to Section 11.4.

11.3. Solid Sample Preparation

11.3.1. Solid sample homogenization:

11.3.1.1. The selection of a portion of solid sample for analysis of low level mercury is problematic due to the very small sample size used for the actual preparation and analysis. The application of the method to soil analysis presupposes that the sample will be relatively uniform and composed of fine particles. This is not always the case.

11.3.1.2. When large stones or pieces of material are included in the sample vial, but the bulk of the sample is fine-grained material, the fine-grained material will be selected as the sample aliquot for analysis.

11.3.1.3. If the sample is almost entirely comprised of one particular kind of material, then that material is the representative sample and a portion of this will be selected. The analyst, with consultation with the client and/or PM, will make the decision of what comprises the most representative aliquot for any given sample and will narrate what portion of the sample was selected when these issues occur.

11.3.2. Following the above guidelines, homogenize the sample then weigh 1 g into a 40 mL VOA vial. The VOA vials used for this method must come from a lot that has been pre-screened for Hg contamination and approved for use (Section 6.2).

11.3.2.1. For the MB, add approximately 1g of Teflon boiling chips.

11.3.2.2. For the LCS, add 1.0 mL of the 10 ug/L intermediate mercury standard (Section 7.3) to1g of boiling chips.

11.3.2.3. For the MS/MSD, add 1.0 mL of the 10 ug/L intermediate mercury standard (Section 7.3) to the 1g of solid sample.

11.3.3. In a fume hood, add 8 ml of concentrated HCl, swirl, and add 2 mL concentrated HNO_3 to the sample in the 40 mL vial. Cap and allow the sample to digest for at least 4 hours.

11.3.4. Add 1.0 ml of BrCl (Section 7.15) to the digestate, then dilute with reagent water (Section 7.1) to the 40 mL calibration point. Shake, then allow to settle until supernatant is clear. Store the sample vials at room temperature for at least 12 hours. Centrifuge or filter, if necessary to remove particulates.

11.3.5. For screening, transfer 50 uL of the supernatant into a “10X dilution” 10 ml culture tube and dilute to 10 mL with reagent water. For analysis, transfer 2 mL of the supernatant into a pre-screened VOA vial and dilute to the 40 mL calibration point with reagent water, add 200 uL of BrCl, then cap and shake. The “10X dilution” aliquot may be analyzed as specified in Section 11.3. The 40 mL VOA vial sample is ready for analysis and may be analyzed as specified in Section 11.4. Based on sample matrix and/or historical results, a greater dilution may be required.

11.4. Sample Screening

11.4.1. Transfer 1 mL of a preserved sample to a "10X dilution" labeled tube and add 9 mL of reagent water. Reseal the original sample vial caps if it will be greater than three minutes before the next step is performed.

11.4.2. Add 0.05 mL of hydroxylamine solution (Section 7.12) and analyze the 10X screening aliquot of the sample using a single-point calibration (10 ng/L)

11.4.3. If the sample response (note that this is a 10X dilution) exceeds that of the (FORMATTING?)5 ng/L standard, then the sample concentration is beyond the normal calibration range of Method 1631. Prepare the appropriate dilution.

11.4.4. If the 10X dilution screen response is non-detect at 5 ng/L, then the sample may be analyzed without dilution, depending on the reporting limit needed by the client, unless matrix interferences warrant dilution.

11.5. Sample Analysis

11.5.1. When ready to begin analysis, add 0.10 mL of hydroxylamine hydrochloride solution (Section 7.12) to the samples to reduce the excess BrCl (the BrCl has been reduced when no yellow color remains). Cap and shake. Add the hydroxylamine solution in 0.10 mL increments until the BrCl is completely reduced. Record the total volume used on the benchsheet.

Note: Spiking of QC samples is done before the addition of the hydroxylamine hydrochloride reagent.

11.5.2. With instrument control parameters set to appropriate values (see Table II), load samples into autosampler.

11.5.3. Start autosampler sequence.

11.5.4. All measurements must fall within the defined calibration range to be valid. Dilute and re-analyze all samples for analytes that exceed the highest calibration standard.

11.5.5. The following analytical sequence must be used:

Instrument Calibration
ICV (QCS)
ICB
CCV (OPR)
CCB
Maximum 12 hours
CCV
CCB

Repeat sequence every 12 hours between CCV/CCB pairs as required to complete run
CCV
CCB

11.5.6. Refer to Quality Control Section 9 for the appropriate quality control criteria.

Notes: Samples include the MB, LCS, MS, MSD, duplicate, field samples, and sample dilutions.

11.5.7. Instrument calibration need not be performed if the QC parameters for the run indicate that the system is in control.

11.5.8. To facilitate the early identification of QC failures and samples requiring rerun, it is strongly recommended that sample data is reviewed periodically throughout the run.

11.5.9. Five scenarios that will require an automatic re-analysis.

11.5.9.1. Laboratory sample duplicates showing poor RPD.

11.5.9.2. Field duplicates showing poor RPD (when these are identified by the client)

11.5.9.3. MS, MSD, and un-spiked samples that don't make sense (sample is higher in concentration than the spiked MS and/or MSD, MS and/or MSD is off by an order of magnitude, etc.)

11.5.9.4. Field-generated blanks with concentrations of mercury above the reporting limit.

11.5.9.5. Serial dilutions that show poor agreement with the initial run.

11.5.10. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance, and troubleshooting.

11.5.11. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

11.5.12. Any unauthorized deviations from this procedure must also be documented as a non-conformance with a cause and corrective action described.

11.6. Analytical Documentation

11.6.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.6.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.6.3. Record all sample results and associated QC in LIMS. Level I and Level II reviews are performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calibration Factors are calculated according to the equation:

$$CF(x) = \left(\frac{Area(x) - Area(b)}{Conc(x)} \right)$$

Where:
CF(x) = calibration factor of standard (x)
area(x) = area of standard (x)
conc(x) = concentration of standard (x)
area(b) = average area of 3 calibration blanks

12.2. ICV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{Found(ICV)}{True(ICV)} \right)$$

12.3. CCV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{Found(CCV)}{True(CCV)} \right)$$

12.4. Matrix spike recoveries are calculated according to the following equation:

$$\%R = 100 \left(\frac{SSR - SR}{SA} \right)$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.5. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.6. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD-MS|}{\left(\frac{MSD+MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.7 The final concentration for an aqueous sample is calculated as follows:

$$ng/L = C \times D$$

Where:
C = Concentration (ng/L) from instrument readout
D = Instrument dilution factor

12.8 The final concentration for a solid sample is calculated as follows:

$$ug/kg = C \times D \times W \times P$$

Where:

C = Concentration (ng/L) from instrument readout
D = Instrument dilution factor
W = Weight/volume factor = 0.040, when 1 g of sample is digested and diluted to 40 mL
P = Preparation factor = 20, when 2 mL of digestate is diluted to 40 mL

12.9 Appropriate factors must be applied to sample values if dilutions are performed.

13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of performance capability data on file. Initial Demonstrations of Capability (IDOCs) and Continuing Demonstrations of Capability (CDOCs) are filed and tracked in the analyst's technical training file.

13.2. Method performance is determined by the analysis of method blanks and laboratory control samples. The method blanks must meet the criteria in Section 9.2.

13.3. Training Qualification

The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Acid waste-aqueous waste generated by the analysis. Samples vials are collected and taken to the waste storage building. The vials are

crushed and the liquid waste and glass are separated. The liquid waste is neutralized and released to the POTW. The glass is disposed of in the trash.

16. REFERENCES

16.1. References

16.1.1. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, U.S. EPA, August 2002

16.1.2. Appendix to Method 1631, Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation, U.S. EPA, January 2001

16.1.3. Corporate Quality Management Plan (CQMP), current version

16.1.4. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.5. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.6. Revision History

Historical File:		Revision 1: 04/05/01		Revision 5.2: 03/11/09
		Revision 2: 08/14/01		Revision 5.3: 08/17/10
		Revision 3: 09/18/02		Revision 5.4: 12/09/11
		Revision 4: 12/16/02		Revision 5.5: 02/20/12
		Revision 5.0: 01/17/05		Revision 6: 09/26/13
		Revision 5.1: 07/28/07		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.5. Standards and Reagents, NC-QA-017

16.2.6. Subsampling, NC-IP-001

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from Reference Method

17.1.1. Section 9.1.7 of the reference method requires three method blanks per analytical batch. The section also describes an analytical sequence that includes a CCV (OPR) only at the beginning and end of the sequence, and that includes no CCBs (system blanks) after calibration. This SOP requires only one method blank per preparation batch, but requires additional stability and cleanliness checks through the analysis of a CCV/CCB pair at the beginning, end and after every 12 hours during an analytical run.

17.1.2. Section 9.2.1 of the method recommends that an MDL be determined whenever a new operator begins work. At this laboratory, a new operator receives proper, documented training and must prove competence through an initial demonstration of performance that includes the successful analysis of four LCSs (see Section 9.3.2 of this SOP).

17.1.3. Section 9.4.5.1 of the method recommends that field blank analysis immediately before analyzing samples from the batch. Field blanks are analyzed as normal samples in this laboratory with no particular run order requirement.

17.1.4. Section 9.4.7 of this method recommends that 5% of the bottles in a lot be monitored. Bottle cleanliness in this laboratory is verified by the initial analysis of 5% of the bottles from three boxes of a lot of 40 mL sample vials.

17.1.5. The volume descriptions for the equation in Section 12.3.2 of the method includes subtraction of the volume of reagent used in the standards and the samples. Since the volume of reagents used in samples and standards is typically the same (or differs insignificantly in rare cases), this subtraction is not included in the determination of Hg concentration in this laboratory.

17.1.6. Interpretations and Differences from Method 1631 Appendix A

17.1.7. In the method, after digestion with aqua regia is complete, the digestate is diluted with 0.07 N BrCl for elemental carbon-containing samples. In this SOP, all samples are diluted reagent water to which 1 mL of 0.2 N BrCl has been added. This presents a BrCl concentration in the diluted digestate comparable to the concentration achieved using the method technique. Also, since it is added to all digestates (not only those known to contain elemental carbon), the analyzed digestate will always contain some BrCl, and thereby be more comparable to the calibration standards.

APPENDIX A

TABLE I

MERCURY REPORTING LIMITS, CALIBRATION STANDARD, QC STANDARD, AND SPIKING LEVELS (ng/L)

	1631E			
	Conc ng/L	**µL Std (Sec.7.4)**	**Conc ug/kg Solid**	**µL Std (Sec.7.3) Solid**
Standard Water RL	0.5			
Standard Solid RL			1.0	
Std 1 (in triplicate)	0	0		
Std 2	0.5	20		
Std 3	1	40		
Std 4	2	80		
Std 5	5	200		
Std 6	10	400		
Std 7	25	1000		
Std 8	100	4000		
ICV (QCS)	5	200 (Sec 7.6)		
CCV (OPR)	5	200		
LCS	5	200	10	1000
MS/MSD	5	200	10	1000

TABLE II

RECOMMENDED INSTRUMENT PARAMETERS
(LEEMAN LABS HYDRA AF GOLD PLUS)

Instrument Parameter	1631
Argon flow (L/min)	0.5
Pump flow (mL/min)	10
Rinse (sec)	60
Uptake (sec)	240
Sample volume (mL)	40
Integration (sec)	0.70 (70 sec total)
Method	CVAFS with trap
Furnace 1 temp (? C)	600
Furnace 2 temp (? C)	600
Dry Time (sec)	5
Desorption time (sec)	70
Stabilize time (sec)	10

APPENDIX B

TROUBLESHOOTING GUIDE

Problem	Possible Cause
Poor or No Fluorescence or Sensitivity Check Failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on “Continuous”
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won’t Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards Reading Twice or Half Normal Fluorescence or Concentration	Incorrect standard used Incorrect dilution performed Dirty cell

APPENDIX C

CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 hydrochloric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered Gloves must not be used in the mercury laboratory since the powder contains mercury, as well as other metallic analytes. Only powder free gloves should be used in the Metals Laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and discard.

APPENDIX D

PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman Labs Hydra AF Gold Plus) [1]

Daily	Semi-annually	As Needed
Check argon flow	Check Hg lamp intensity	Change Hg lamp
Check pump tubing		Change liquid/gas separator
Check drain		Change Nafion dryer
Check soda lime drying tube		

APPENDIX E

INSTRUMENT SETUP FOR ANALYSIS

Hg Analysis (Leeman Labs Hydra AA Gold Plus)

SCREENING ANALYSIS

There are 3 separate screens to use **WinHgRunner**, **WinHgDatabase**, and **Rack Editor**

1. To Set Your Protocol and Dataset

   Find a previous protocol under the **WinHgDatabase** screen on the right hand side Dataset/Proto

   Use the arrow down to find a 245.7 protocol

   Save a new protocol File-**Save Protocol**- type in file name (245.7 (date) ex. 24570101) Then select the **(RN) key** (this will take you to the **WinHgRunner** screen)

   WinHgRunner – **File**-**New**- type in dataset name ((date)(letter) for ex. 0101A) type in batch name (ex. Screen)

   Need to find new protocol created in **WinHgDatabase**

2. Activate Gas and Pump

   WinHgRunner – under **Control tab** turn on Gas and pump

3. To Calibrate Curve (standards are loaded in the far left tray)

   WinHgRunner – under the **Standard tab** turn on **S1 S2 Rep1** load the 2 standards (blank and 10ppt) to begin analyzing **Stnd Auto tab**

4. To Check Calibration Curve

   WinHgDatabase – under **Cal Curve tab** (blank recommended to be below 50 counts and 10 ppt recommended to be above 600 counts) then **Accept** curve

5. Typing Labels

   Rack Editor - **File**-**New** (pick 44 rack)- type in labels under sample ID and **Save As** ((date)(letter) ex. 0101A)

   The first sample will be a 10ppt standard (using the remaining 10ppt calibration standard) and proceeding with samples

6. To Begin Analyzing Sample

WinHgRunner – under **Sample tab** - type in rack name, start cup, end cup, cups per rack (44 for screen) then to analyze select **Run Auto tab**

7. Checking Results

WinHgRunner – under **Report tab** results are shown

Each sample is analyzed at a 10x dilution.

Therefore if a result reads 2.5ppt multiply by 10 for a result of 25ppt (which would need diluted at a 2x). Any sample that reads over 25ppt should be diluted since 25ppt is your high standard.

SAMPLE ANALYSIS

There are three separate screens to use: **WinHgRunner**, **WinHgDatabase**, and **Rack Editor**

1. To Set Your Protocol and Dataset

Find a previous protocol under the **WinHgDatabase** screen on the right hand side Dataset/Proto

Use the arrow down to find a 1631 protocol

Save a new protocol File-**Save Protocol**- type in file name (1631(date) ex. 16310101) Then select the **(RN) key** (this will take you to the **WinHgRunner** screen)

WinHgRunner – **File**-**New**- type in dataset name ((date)(letter) for ex. 0101A) type in batch name (ex. Screen)

Select a new protocol created in **WinHgDatabase**

2. Activate Gas and Pump

WinHgRunner – under **Control tab** turn on Gas and Pump

3. To Calibrate Curve (standards are loaded in the far left tray; all blanks are analyzed in cup 1)

WinHgRunner – under **Standard tab** (in this step you need to run 2 blanks then the calibration curve)

First blank - Select **S1 Rep3** then analyze **Stnd Auto tab** when completed

Second blank - Select **S1 Rep2** then analyze **Stnd Auto tab** when completed

Calibration curve - Select **S1 S2 S3 S4 S5 S6 S7 Rep1** then analyze **Stnd Auto tab**

4. To Check Calibration Curve

WinHgDatabase – under **Cal Curve tab** – the following criteria should be met %RSD CF <15%, Avg. BB <0.5 and %Recovery 75-125%. If curve passes criteria – Select **Accept**

5. Check Verification Standards

Rack Editor – **File**-**New** (pick 14 rack) – type in labels under sample ID (ICV, ICB, CCV, CCB) and **Save As** ((date)(letter) ex. 0101A)

6. Analyze Verification Standards

WinHgRunner – under **Sample tab** type in rack name, start cup, end cup, cups per rack (14) then to analyze select **Run Auto**

7. Check Verification Results

WinHgRunner - under **Report tab** the results should be ICV (80-120%), CCV (77-123%) and ICB/CCV (>0.5ppt)

8. Typing Labels

Rack Editor - **File**-**New** (pick 14 rack)- type in labels under sample ID and select **Save AS** ((date)(letter) ex. 0101A)

9. Analyzing Additional Samples

WinHgRunner – under **Sample tab** type in rack name, start cup, end cup, cups per rack (14) then to analyze select **Run Auto**

10. Checking Results

WinHgRunner – **Select** Report tab

Sequence of Run:
Instrument Calibration (Step #3 and #4)
ICV (Step #5, #6, #7)
ICB
CCV
CCB
Maximum 12 hours (Step #8, #9)
CCV
CCB
Repeat sequence

PRINTING REPORTS

To print Cal curve:

WinHgDatabase – under **Cal Curve tab** select **Print Cal** to print curve

To print Report:

WinHgDatabase – under **Report tab** under format turn on report select **Generate** to print

To transfer run:

Select PRN fomat and select Generate to transfer the file to the N drive using a unique file name.

Locate the file on the N drive. Right click and send to TALS Import.

Title: TOTAL PHOSPHORUS BY COLORIMETRIC, AUTOMATED, BLOCK DIGESTER AA II EPA METHOD 365.4 AND SM4500-P B, H

Approvals (Signature/Date)

Sessily Overton-Gray	1/28/16	Ryan Fitzwater	12/29/15
Sessily Overton-Gray Department Manager	Date	Ryan Fitzwater Health & Safety Manager / Coordinator Laboratory Director	Date
	12/17/15	Michael H. Dunn	12/17/15
Donovin Mulvaney Quality Assurance Manager	Date	Michael H. Dunn Technical Director	Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method covers the determination of total phosphorus in drinking and surface water, leachates, domestic and industrial wastes. EPA 365.4 has been modified for use on soils; this method is equivalent to SM4500-P B, H.

1.2 Reporting Limits: The nominal RL is 0.1 mg P/L for waters and 10 mg P/kg for soils.

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

The sample is heated in the presence of sulfuric acid, K_2SO4 and $HgSO_4$, for two and one half hours. The residue is cooled, diluted to 20.0 mL and placed on the Lachat Flow Injection Analysis (FIA) instrument for determination.

3.0 Definitions

See TestAmerica Nashville's Quality Assurance Manual for laboratory definitions. Also, refer to Controlled Document TestAmerica Nashville Acronyms, Keywords, and Definitions (QAF-45).

4.0 Interferences

- Background color of a sample can interfere.
- High levels of phosphorus may deplete digestion solution.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This method may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: Mercury and strong acid.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Sulfuric acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Mercuric oxide	Oxidizer Poison Allergen Flammable	0.1 mg/m^3 TWA skin	May be fatal if swallowed. Harmful if inhaled or absorbed through skin. Causes severe irritation to eyes, skin and respiratory tract. May cause burns, allergic skin reaction. May affect kidneys and central nervous system. Contact with other material may cause fire.
1 – Exposure limit refers to the OSHA regulatory exposure limit. TWA = Time-weighted average			

6.0 Equipment and Supplies

6.1 Instrumentation

- Lachat Block Digestor BD-40, or equivalent.
- Lachat Model 8000 or 8500 FIA with Omnion software, or equivalent.

6.2 Supplies

- Acid-washed glassware: Test tubes and cuvettes/reaction vessels used for the determination of phosphorus are disposed of after a single use.
- Teflon™ boiling chips for blank soil matrix.

7.0 Reagents and Standards

7.1 Reagent water, analyte-free.

7.2 Mercuric Sulfate: Dissolve 8 g red Mercuric oxide (HgO) in 50 mL of 1:4 Sulfuric acid (10 mL conc. H_2SO_4: 40 mL reagent water at low heat and dilute to 100 mL with reagent water). Replace after two months.

7.3 Digestion Solution (Sulfuric acid-mercuric sulfate-potassium sulfate solution): Dissolve 133 g of K_2SO_4 in 500 mL of reagent water and 200 mL of concentrated H_2SO_4. Add 25 mL of Mercuric sulfate solution and dilute to 1 liter with reagent water. Replace after one month.

7.4 Molybdate Stock Solution: Dissolve 40 g of Ammonium molybdate tetrahydrate in about 800 mL of reagent water. Dilute to 1 liter with reagent water and mix with a magnetic stirrer for at least four hours. Store up to two months in plastic and refrigerate.

7.5 Stock Antimony Potassium Tartrate Solution: In a 1 liter volumetric flask, dissolve 3.0 g Antimony potassium tartrate in approximately 800 mL reagent water. Dilute to the mark and mix with a magnetic stirrer until dissolved. Store up to two months in a dark bottle and refrigerate.

7.6 Molybdate Color Reagent: To a 1 liter volumetric flask, add about 500 mL reagent water and then add 213 mL Ammonium molybdate Solution and 72 mL Antimony potassium tartrate Solution. Dilute to the mark with reagent water and invert to mix. Degas with Helium. Prepare weekly.

7.7 Ascorbic Acid Reducing Solution: Dissolve 60 g of Ascorbic acid in 600 mL of reagent water; dilute to 1 liter with reagent water and degas with Helium. Add 1 g sodium dodecyl sulfate. Replace after 2 days.

7.8 Diluent Water: Add 240 mL of digestion solution to 600 mL reagent water; mix and dilute to 1 liter with reagent water.

7.9 Carrier: Add 50 mL of concentrated Sulfuric acid and 31.7 g of K_2SO_4 to 800 mL of ammonia-free, reagent water; cool and dilute to 1 liter with reagent water.

7.10 Primary Standard, Stock Phosphorus Standard (for CCV and Calibration): Commercial source, 1000 µg/mL as P, Environmental Resource Associates 061, or equivalent.

- Dilute 1.0 mL of stock standard (1000 µg/mL) to 10 mL with reagent water for a 100 µg/mL working standard.

7.11 Secondary Standard, Stock Phosphorus Standard (for ICV, LCS and MS/MSD Spiking): Commercial source, 50 µg/mL as phosphate, LabChem LC 18600-1, or equivalent.

Note: Primary and Secondary standards are subsequently digested.

7.12 Also, see SOP Reagent and Standard Purchase, Preparation, Control, and Documentation / NV08-214 for shelf-lives and storage requirements.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water and Lea-chates	HDPE or Glass	125 mL	Cool 0-6°C; 2 mL conc. H_2SO_4/L to pH < 2.	28 days	40 CFR Part 136.3 SM Table 1006:I (on-line edition)
Soil		10 g	Cool 0-6°C		

9.0 Quality Control: See Total Phosphorus Data Review Checklist (IF-117).

Refer to TestAmerica Nashville's QA Manual for specific quality control (QC) policies. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC

- .The **Method Blank** is reagent water for water batches or Teflon™ boiling chips for soil batches.
- The **LCS** consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. It is spiked with the same solution at the same concentration as the matrix spike, but a solution **different** from the calibration and CCV standard.
  - Prepare by diluting 0.8 mL 50 µg P/mL standard to 20.0 mL reagent water (2.0 µg/mL concentration) for water batches or 0.2 g Teflon™ boiling chips + 20.0 mL reagent water for soil batches. The LCS is digested.
- A **MS/MSD** pair is run with each batch, at a concentration of 2.0 mg/L, using the same standard solution as the LCS (second-source). Prepare as for the LCS but use identical aliquots of a client sample.

9.2 Instrument QC

- **Initial Calibration Verification (ICV)** is a digested 2.0 µg/mL second-source standard run immediately after calibration. Prepare as for the LCS.
- **Initial Calibration Blank (ICB): reagent water, following ICV.**
- **Continuing Calibration Verifications (CCV):** Digest the CCV.
  - Make a 2.5 µg/mL concentration from the same standard as the calibration standards: 0.125 mL of 1000 µg/mL stock to 50.0 mL reagent water.
  - Prepare a 1.25 mg/L concentration from the calibration standard: 2.5 mL of 2.5 µg/mL stock to 5.0 mL reagent water. Digest this CCV and run once after the LCS.
- A **Continuing Calibration Blank (CCB)** follows each CCV.

10.0 Procedure

10.1 Sample Preparation

Matrix	Sample Size
Water, Leachate	20 mL
Soil	0.2 g

1	Water Samples: To 20.0 mL of sample, add 5 mL of digestion solution and mix. Soil Samples: To 0.2 grams of sample, add 20.0 mL reagent water, then 5 mL digestion solution; mix. Use a vortex mixer.

	See SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
2	Add 4-8 boiling chips. Too many boiling chips may cause samples to boil over.
3	With block digester in manual mode, set low and high temperature at 160°C and preheat unit to 160°C. Place tubes in digester and switch to automatic mode. Set low temperature timer for 1 hour. Reset high temperature to 380°C and set times for 1½ hours. For a total of 2½ hours.
4	Cool sample and dilute to 20.0 mL with reagent water. If TKN is to be determined, the sample should be diluted with ammonia-free water.

10.2 Calibration: Refer to SOPs Calibration Curves and Selection of Calibration Points / QA-Q-P-003. See Section 11 for equations. Calculations are performed by vendor software and LIMS.

1	**Standard phosphorus solution**: Digest the high standard using the primary 100 µg/mL working standard and serially dilute it for the following concentrations of calibration standards and CCV. At least five calibration standards are required.

mL of 100 µg/mL Standard	Final Volume (mL)	Concentration, mg P/L
0.01	10	0.1
0.05	10	0.5
0.1	10	1.0
0.25	10	2.5
0.5	10	5.0

2	Process the standards and blank exactly as the samples, i. e., digested. If the standards do not agree within ± 10% of the true value (± 30% for 0.1 µg/mL standard), re-run standards.
3	Prepare a standard curve by calculating the peak area of standards versus the corresponding phosphorus concentration values. Evaluate for linearity success; if the correlation coefficient is too low ($r \geq 0.995$. $r^2 \geq 0.990$), re-calibrate. **The use of weighting factors is acceptable except for South Carolina samples.**

10.3 Sample Analysis

1	Refer to SOP Lachat / NV07-39.
2	Check the level of all reagent containers to ensure an adequate supply.
3	Place all reagent lines in their respective containers, connect the sample probe to the sampler and start the proportioning pump.
4	After a stable baseline has been obtained, start the sampler.

10.4 Example Analysis Queue / Sequence*

1	Initial calibration, if needed.
2	ICV (second source)
3	ICB
4	CCV (daily)
5	CCB
6	Method Blank
7	LCS, digested
8	Samples 1-10
9	Matrix Spike

10	Matrix Spike Duplicate
11	CCV, digested
12	CCB
13	Samples 11-20
14	Sample duplicate
15	CCV digested
16	CCB

*May be up to 20 samples
If the batch contains samples from AZ, MA, or TX, run a LCSD.

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\% \text{ Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 Linear Calibration Using a Least Squares Regression: A linear calibration model based on a least squares regression is employed for this method. For external standard calibration, x is the mass of the analyte in the sample aliquot introduced into the instrument and y is the area (or height) or the response, as in:

$x = C_s$ and $y = A_s$

A linear least squares regression attempts to construct a linear equation of the form:

$y = ax + b$

The mathematics used in least squares regression has a tendency to favor numbers of larger value over numbers of smaller value. Thus the regression curves generated tend to fit points at the upper calibration levels better than points at the lower calibration levels. To compensate for this, a weighting factor which reduces this tendency is used. Examples of acceptable weighting factors which place more emphasis on numbers of smaller value are:

$w = 1/x$ or $w = 1/x^2$

Do not include the origin (0, 0) as an extra calibration point. Re-process each calibration standard as an unknown to determine the best-fit model. Each calibration point above the RL must be ± 10% true; the RL-level standard must be ± 30% true.

The regression calculation generates a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.995 or $r^2 \geq 0.990$.

11.4 Coefficient of Determination **Correlation Coefficient**

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2} \qquad r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response
x = Concentration

11.5 Obtain the concentration value of each sample directly from the prepared standard curve. Report results as P, mg/L.

Concentration (µg/mL or µg/g) = $\frac{\text{(µg/mL instrument)(dilution factor)(final volume*)}}{\text{mL or g of sample}}$

*final volume, nominally 20 mL

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Detection Limits / CA-Q-S-006. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are managed, stored, and disposed of in accordance with state and federal laws and regulations. Waste description rules

and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Wastes are transferred to the TKN waste drum in the waste disposal area.

15.0 References / Cross-References

15.1 EPA Method 365.4, Methods for Chemical Analysis of Water and Wastes, approved for NPDES, CWA, issued 1974.

15.2 SM4500-P B(4) -- 1999 and SM4500-P H -- 1999, Standard Methods for the Examination of Water and Wastewater, on-line edition, 2011 editorial revisions.

15.3 TestAmerica Nashville's Quality Assurance Manual.

15.4 Corporate Environmental Health and Safety Manual (CW-E-M-001.

15.5 SOPs: Calibration Curves and Selection of Calibration Points / CA-Q-P-003, Waste Disposal / NV10-83, Training Procedures for Technical Staff / NV08-199, Balance Calibration / NV08-213, Detection Limits / CA-Q-S-006, Reagent and Standard Purchase, Preparation, Control, and Documentation / NV08-214, Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

15.6 Controlled Documents: TestAmerica Nashville – Acronyms, Keywords, and Definitions (QAF-45), Total Phosphorus Data Review Checklist (IF-117).

16.0 Method Modifications

None,

17.0 Attachment

None.

18.0 Revision History

- Revision 5, dated 30 April 2008
  - Integration for TestAmerica and STL operations.
- Revision 6, dated 10 September 2008
  - Change Step 4 in Section 10.1 to omit additional addition of digestion solution.
- Revision 7, 31 October 2009
  - Addition of second CCV concentration.
  - Clarification of soil preparation, adding reagent water before digestion solution.
- Revision 8, 30 November 2011
  - Organizational changes.
  - Addition of QAF-45, Section 14.2, and reference to SOP Calibration Curves (General) / CA-Q-S-005.
  - Remove requirement for undigested QC samples. All are digested. Calibration standards start with a digested high standard and are serially diluted after the digestion process.
  - Addition of reference to SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
- Revision 9, dated 31 January 2014
  - Organizational changes.
  - OK no longer limits batch size to 10 samples. Add MA to list of states requiring LCSD. WV no longer requires an LCSD.
  - Change of control limit for ICB and CCB. Change to example sequence.
- Revision 10, dated 31 January 2016
  - Organizational changes.
  - Addition of change form 9a (3/31/15), adding the SM method for solids.

- Update SOP references.
- Add leachate matrix.
- Replace the QC tables in Section 9.0 with reference to the Total Phosphorus Data Review Checklist (IF-117).

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP) Change Form

SOP Number/Revision No.: **1664 9070 / NV03-112.11** Effective Date: **11/9/2015**

Last Mod. Date: 5/31/15

SOP Title: **n-Hexane Extractable Material and Silica Gel Treated n-Hexane Extractable Material by Extraction and Gravimetry, Method 1664/9070A**

CONTROLLED DISTRIBUTION

ISSUED TO: \\TAFS\Lab\Nashville\Public\QA\SOPs, 03P

Revision Number with Mod ID: **11a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add highlighted text; delete crossed-out text.

Section 9.1, Sample QC, Precision and Recovery (PAR) / Laboratory Control Sample (LCS)

1	Fill a clean sample bottle with approximately 800 mL of reagent water. Note the volume.
2	Acidify the water to pH 2.0 with concentrated HCl or H_2SO_4. DO NOT over-acidify the water as this could cause the disk packing to break down. Bring the volume to 1 L with reagent water. Cap the bottle and shake well.
3	Using a calibrated 5.0- ~~10.0~~-mL syringe, transfer 4.0 ~~10~~ mL of the HEM standard. Verify that there are no air bubbles in the syringe.
4	Touching the tip of the syringe to the inside of the neck of the bottle, allow the standard to slowly and gently flow down the side of the bottle and to settle on the water layer. A cloudy precipitate will form on the water. *Avoid shooting the standard into the water or introducing it too quickly. Use of automatic pipettes will pose a problem because they shoot the standard into the water and the rate of introduction cannot be controlled. If the standard is not properly floated, it can cause flow problems during the sample-processing step.*
5	DO NOT SHAKE THE BOTTLE. Attach a closed water inlet valve to the bottle with the correct bottle adapter.

11/9/15	
Department Manager Date	
11/9/15	11/9/15
Quality Manager Approval Date	Technical Approval Date

Title: n-HEXANE EXTRACTABLE MATERIAL (HEM; OIL AND GREASE) AND SILICA GEL TREATED n-HEXANE EXTRACTABLE MATERIAL (SGT-HEM; NON-POLAR MATERIAL) BY EXTRACTION AND GRAVIMETRY
METHODS EPA 1664A/B AND SW-846 9070A

Approvals (Signature/Date)	
Steve Miller Quality Assurance Manager	5/15/15 Date
Ryan Fitzwater Organics Operations Manager Health & Safety Coordinator/Manager	5/7/15 Date
Michael H. Dunn Technical Director	5/5/15 Date

1.0 Scope and Application

1.1 Analyte, Matrices: This method is used for determination of n-Hexane extractable material (HEM; oil and grease) and n-Hexane extractable material that is not adsorbed by silica gel (SGT-HEM; non-polar material) in surface and saline waters and in industrial domestic and industrial aqueous wastes. It is based on prior EPA methods for determination of "oil and grease" and "total petroleum hydrocarbons".

1.2 Reporting Limits: The required method detection limit is 1.4 mg/L and the minimum level of quantitation (ML) is 4.0 mg/L.

1.3 This method is for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act; the Resource Conservation and Recovery Act; the Comprehensive Environmental Response, Compensation, and Liability Act; and other EPA regulatory programs.

1.4 This method is not applicable to measurement of materials that volatilize at temperatures below approximately 85 ℃. Petroleum fuels from gasoline through #2 fuel oil may be partially lost in the solvent removal operation.

1.5 Some crude oils and heavy fuel oils contain a significant percentage of materials that are not soluble in n-Hexane. Accordingly, recoveries of these materials may be low.

1.6 The laboratory is permitted to modify the method to overcome interferences or lower the cost of measurements, provided that all performance criteria in this method are met.

1.7 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

2.1 A one liter sample (or less if the concentration is > 1000 mg/L) is acidified to pH <2 with HCl or H_2SO_4 and extracted by automated solid phase extraction. Sub-sampling is generally not allowed. The solvent is evaporated and the residue weighed and reported as HEM.

2.2 If the HEM is to be used for determination of SGT-HEM, the HEM is re-dissolved in n-Hexane. An amount of silica gel proportionate to the amount of HEM is added to the solution containing the re-dissolved HEM to remove polar materials. The solution is filtered to remove the silica gel, the solvent is evaporated, and the SGT-HEM is weighed.

3.0 Definitions

3.1 HEM and SGT-HEM are method-defined analytes; i.e., the definitions of both HEM and SGT-HEM are dependent on the procedure used. The nature of the oils and/or greases, and the presence of extractable non-oily matter in the sample will influence the material measured and interpretation of results.

3.2 Silica Gel Treated N-Hexane Extractable Material (SGT-HEM): components of n-Hexane extractable material (HEM) that are not absorbed by silica gel; i. e., non-polar material (NPM).

3.3 Oil and grease is a conventional pollutant under the Clean Water Act and codified at 40 CFR 401.16. The term "n-Hexane extractable material" reflects that this method can be used to determine materials other than oils and greases. Similarly, the term "silica gel treated n-Hexane extractable material" reflects that this method can be used to determine material that is not adsorbed by silica gel (non-polar material).

3.4 See TestAmerica Nashville's Quality Assurance Manual for other laboratory definitions. Also, refer to Controlled Document QAF-45, TestAmerica Nashville Acronyms, Keywords, and Definitions.

4.0 Interferences

4.1 All materials used in the analysis shall be demonstrated to be free from interferences by running laboratory blanks.

4.2 Sodium sulfate and silica gel fines have the potential to inflate results for HEM and SGT-HEM by passing through the filter paper. Use Whatman 41 filter paper or finer to ensure that no fines pass through to the weighing receptacle.

4.3 Interferences extracted from samples will vary considerably from source to source, depending upon the diversity of the site being sampled. For those instances in which samples are thought to consist of complex matrices containing substances (such as particulates or detergents) that may interfere with the extraction procedure, a smaller sample may need to be collected for analysis.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements:

- n-Hexane has been shown to have increased neuro-toxic effects over other Hexanes and some other solvents. Inhalation of n-Hexane should be minimized by performing all operations with n-Hexane in an explosion-proof hood or well-ventilated area.
- n-Hexane has a flash point of -23℃ (-9℉), has exp losive limits in air in the range of 1 – 7 percent, and poses a serious fire risk when heated or exposed to flame. n-Hexane can react vigorously with oxidizing materials.
- Unknown samples may contain high concentrations of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure.

5.2 Primary Materials Used: There are no materials used in this method that have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-Ceiling	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Hydro-chloric acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; Symptoms may parallel inhalation exposure. Irritant to the eyes.
Sulfuric acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Horizon SPE-DEX ® 1000XL or 3000 XL Automated Extractor System.
- Horizon Speed Vap™Solvent evaporation System.

6.2 Supplies

- SPE Disks: 90 mm (Pacific O & G Disks, JT Baker Speedisk™ 50 mm, CPI Nu-Phase ™ SPE Disks, Whatman® SPE Oil % Grease, or 3m Empore™ Oil and Grease Extraction Disks.)
- Fast-flow pre-filters, 90 mm, Pacific Par# FFP-90HT, or equivalent.
- 1-L Boston Round bottles 33 X 400-mm, 89 X 400, 53 X 400, 48 X 400, 58 X 400, 63 X 400, 83 X 400 mm, and I-Chem 33 X 430 mm bottles.
- Bottle cap adapters for wide-mouth sample containers. The Water Inlet Valves for the SPE-DEX® 3000 XL and 1000 XL are designed to fit a 33 X 400-mm Boston Round bottle.
- 40-mL collection vessels (VOA vials) for 47 mm disks or 125-mL Erlenmeyer flasks for 90 mm disks.
- 19/22 adapter for 40-mL VOA vessel (cat # 160-0001).
- 5-Gal safety-coated water waste recovery bottle (P/N 180-0005-01).
- 2.5-L safety-coated solvent bottles (P/N 27-0042), 2 for 1000XL unit, 4 for 3000XL.
- Aluminum weighing pans: 70-mm if using 47-mm disks (P/N 40-002-HT), 105-mm if using 900-mm disks (P/N 50-005-02-HT).
- pH indicator strips, non-bleeding pH 0.0-14.0 range.
- Boiling chips: Silicon carbide.
- Volumetric flasks, Class A, various sizes.
- Oven, drying.
- Balance, analytical.
- Pipettes, Class A, glass.
- Ruler.
- Graduated cylinder, 500 ± 5 mL.

7.0 Reagents and Standards

7.1 Reagent water, analyte-free.

7.2 Gas (dry N_2) source or any inert gas source. Air suppressors are not recommended.

7.3 **Methanol**, ACS Reagent grade.
7.4 **Hydrochloric Acid (HCl) and Sulfuric Acid (H_2SO_4)**, concentrated, reagent, ACS-grade.
7.5 **Hexane**, 85% minimum purity, 99% minimum saturated C6 isomers, residue < 1 mg/L.
7.6 **Acetone**, ACS-grade, residue less than 1 mg/L
7.7 **Sodium Sulfate**, ACS-grade, granular anhydrous. Dry at 400℃ for 4 hours minimum or buy a commercially certified-clean product. Store in a sealed glass container. It is acceptable to use solvent-phase separation paper.
7.8 **Silica Gel,** anhydrous, 75 - 150 micrometers, Davisil Grade 923 (Supelco 21447-7A, or equivalent). Dry at 150℃ for 24 hours minimum and store in a desiccator or tightly sealed container. Silica gel can also be kept in the oven until use. Determine the n-Hexane soluble material content of the silica gel by extracting 30 g of silica gel with n-Hexane and distilling the n-Hexane to dryness. The silica gel must contain less than 5 mg of n-Hexane soluble material per 30 g (< 0.17 mg/g). (The method blank checks for this criterion.)
7.9 **HEM Standard:**

7.9.1 **Hexadecane**, 98% minimum purity, commercial source.
7.9.2 **Stearic Acid**, 98% minimum purity, commercial source.
7.9.3 **Hexadecane/ Stearic Acid (1:1) spiking solution:** Prepare in Acetone at a concentration of 4,000 µg/mL each. Commercial, certified standards are acceptable. If using a certified standard, a second-source standard is required. It must be analyzed monthly.

- Place 2000 ± 5 mg (2 g) Stearic acid and 2000 ± 5 mg (2 g) hexadecane in a 1000-mL volumetric flask and fill to the mark with Acetone. The solution may require warming for complete dissolution of Stearic acid. (5000 ± 5 (5 g) portions are also acceptable.
- After the Hexadecane and Stearic acid have dissolved, transfer the solution to a 1L glass container with fluoropolymer-lined cap. **Mark the solution level on the vial and store in the dark at room temperature**.
- Each HEM standard vial contains 2000 µg/mL of Hexadecane and 2000 µg/mL of Stearic acid, yielding a combined weight of 4000 µg/mL. A concentration of 40 mg/L can be achieved by spiking 10.0 mL of the solution into a 1-L sample.

7.9.4 Immediately prior to use, verify the level on the vial and bring to volume with Acetone, if required. Warm to re-dissolve all visible precipitate. If in doubt of the concentration, verify the concentration by removing 10.0 ± 0.1 mL in a volumetric pipet and place in a tared weighing pan, and evaporate to dryness in a fume hood. The weight must be 40 ± 1 mg. If not, prepare a fresh solution. The spiking solutions should be checked frequently for signs of degradation or evaporation. Replace after six months or sooner if degradation has occurred.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	Glass, Teflon™-lined cap	1 L	Cool 0-6℃, HCl or H_2SO_4 to pH < 2.	28 days	40 CFR Part 136, Table II

- Collect approximately one liter of representative sample in a glass bottle following conventional sampling practices, except that the bottle must not be pre-rinsed with sample before collection. To allow for potential QC failures, it is recommended that additional sample aliquots be collected.

- Adjust the sample pH to less than 2 with HCl or H_2SO_4 solution at the time of collection, and refrigerate at 0–6℃ (40 CFR 136, Table II). To establish the volume of HCl or H_2SO_4 required, collect a **separate aliquot**, adjust the pH of this aliquot to less than 2 with acid, and add the volume of acid determined to each sample bottle prior to collection.
- If a sample is known or suspected to contain greater than 1000 mg/L of extractable material, **collect** a proportionately smaller volume of sample (the volume required will depend upon the estimated amount of extractable material) in a glass bottle. Add a proportionately smaller amount of HCl or H_2SO_4 solution to the smaller sample if preservation is necessary.
- Collect an additional two aliquots of a sample for each set of 20 samples or less for the matrix spike. For those circumstances requiring the collection of multiple aliquots of one sample, each aliquot is to be collected in either of the following ways: 1) collect simultaneously in parallel, if possible, or 2) collect as grab samples in rapid succession.
- The high probability that extractable matter may adhere to sampling equipment and result in measurements that are biased low precludes the collection of composite samples for determination of oil and grease. Therefore, samples must be collected as grab samples. If a composite measurement is required, individual grab samples collected at prescribed time intervals must be analyzed separately and the concentrations averaged.
- If visual observation indicates solids, then determine whether the sample contains >20% solids. Using a ruler, measure total sample height. Next, measure solids layer. Calculate using the following equation: height soil (100) / height sample = % solids. If the sample contains greater than about 20% solids, notify the client to obtain instruction on how to proceed (i. e., approval to use Method 9071B).

9.0 Quality Control

Refer to TestAmerica-Nashville's QA Manual for specific quality control (QC) procedures. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC: The following quality control samples are prepared with **each batch of no more than 20 samples.**

Quality Controls	Control Limit	Corrective Action
Method Blank (MB)	< RL	Re-prep batch, rerun
Laboratory Control Sample[1] (LCS), ongoing PAR	HEM 78-114% recovery SGT-HEM 64-132% recovery	Rerun batch
Matrix Spike (MS Duplicate for MN)	HEM 78-114% recovery SGT-HEM 64-132% recovery; See LIMS for MN MS RPD.	Qualify. Obtain less sample volume and re-prep.

1 All AZ, MA, and TX samples require a LCS duplicate in each batch.

- QC samples are prepared in the same manner as the samples.
- **Laboratory blanks:** Extract and concentrate a laboratory reagent water blank with each analytical batch or each day.
- **Calibration verification:** Verify calibration of the balance per Section 10.4 before and after each analytical batch. If calibration is not verified after measurement of the analytical batch, recalibrate the balance and reweigh the batch. Record the two balance checks.
- **Precision and Recovery (PAR) / Laboratory Control Sample (LCS):** To demonstrate that the analysis system is in control, and acceptable accuracy is being maintained with each analytical batch, the laboratory extracts and concentrates a LCS with each analytical batch. Compare the recovery with the limits for ongoing recovery in the above table.
  - If the recovery is in the range specified, the extraction, evaporation, and weighing processes are in control and analysis of blanks and samples may proceed.

- If, however, the recovery is not in the specified range, the analytical process is not in control. In this event, correct the problem, re-extract the analytical batch, and repeat the LCS.
- The laboratory monitors performance using PAR/LCS % recovery and prepares control charts to calculate average and standard deviation periodically. Calculated control limits are compared against the method-defined on-going precision and accuracy.

1	Fill a clean sample bottle with approximately 800 mL of reagent water. Note the volume.
2	Acidify the water to pH 2.0 with concentrated HCl or H_2SO_4. DO NOT over-acidify the water as this could cause the disk packing to break down. Bring the volume to 1 L with reagent water. Cap the bottle and shake well.
3	Using a calibrated 10.0-mL syringe, transfer 10 mL of the HEM standard. Verify that there are no air bubbles in the syringe.
4	Touching the tip of the syringe to the inside of the neck of the bottle, allow the standard to slowly and gently flow down the side of the bottle and to settle on the water layer. A cloudy precipitate will form on the water. *Avoid shooting the standard into the water or introducing it too quickly. Use of automatic pipettes will pose a problem because they shoot the standard into the water and the rate of introduction cannot be controlled. If the standard is not properly floated, it can cause flow problems during the sample-processing step.*
5	DO NOT SHAKE THE BOTTLE. Attach a closed water inlet valve to the bottle with the correct bottle adapter.

- **Quality Control Sample (QCS):** Obtain a QCS from a certified proficiency provider (a **source different** from the source for the hexadecane and Stearic acid used routinely in this method), and that the QCS be used for verification of the concentrations of HEM and SGT-HEM. The QCS should be analyzed approximately quarterly by the laboratory. Use of previous PT concentrates is acceptable so long as the spiked concentration is known.
- **Matrix spikes:** The laboratory must spike a minimum of 1 in 20 samples from a **given sampling site** or, if for compliance monitoring, from a given discharge/waste stream (matrix spike) with an aliquot of the Hexadecane/Stearic acid spiking solution (same as the LCS). Calculate the percent recovery of HEM or SGT-HEM in each aliquot and compare with the limits in the table in Section 9.1.
  - If the results of the spike fail the acceptance criteria, and the recovery of the LCS for the analytical batch is within the acceptance criteria, an interference is present and the failed recovery will be flagged on the report. In this case, the result may not be reported or used for regulatory compliance purposes and the laboratory must assess the potential cause for the interference. The laboratory will notify the client of the potential interference, and proceed as requested by the client. If the interference is attributable to sampling, the site or discharge/waste stream should be re-sampled. If the interference is attributable to a matrix problem and if sufficient sample is provided, the laboratory must modify the method, i.e., reduce the sample volume and repeat the analysis of the sample and the MS. Most matrix interference problems are attributable to the formation of emulsions in the extraction. The extraction section provides suggestions for overcoming emulsion problems.
  - If the results of both the spike and the LCS fail the acceptance criteria, the analytical system is judged to be out of control, and the problem shall be identified and corrected, and the sample batch reanalyzed. **All samples must be associated with a valid MS and LCS.**
  - As part of the QC program for the laboratory, the method accuracy for samples is assessed and records maintained. After the analysis of five or more spiked samples in

which the recovery passes the QC criteria, compute the average percent recovery (P_a) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $P_a - 2s_p$ to $P_a + 2s_p$. For example, if P_a = 90% and s_p = 10% for five or more analyses of HEM or SGT-HEM, the accuracy interval is expressed as 70–110%. Although this exercise is performed, the method initial control limits are those used for client samples.

- **If a sample from Minnesota is in the batch, a matrix spike duplicate must be performed.**

9.2 Instrument QC: Not applicable.

10.0 Procedure

10.1 Balance Calibration: The analytical balance is calibrated at 2 mg and 1000 mg using class "S" weights. Calibration must be within ± 10% (i.e., ± 0.2 mg) at 2 mg and ± 0.5% (i. e., ±5 mg) at 1000 mg. If values are not within these limits, the balance is adjusted / repaired, or use another balance. This calibration is performed before and after residue weighing or before and after each day; record these balance checks on the benchsheet. See SOP Balance Calibration / NV03-213.

10.2 Sample Preparation

Matrix	Sample Size
Water	Nominally 1 L of sample

- Refer to SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229. Sub-sampling is not allowed.

1	Bring the analytical batch of samples (containing less than 20% solids as determined in Section 8.0), including the sample aliquot for the MS, to room temperature
2	Verify that the pH of the sample is less than 2: • Adjust the pH if needed. Record the ID of the acid. If the acid volume is greater than 1% of the sample volume, correct for dilution. DO NOT over acidify the samples, as this will cause the disk material to break down and result in low recoveries. Cap and invert the sample bottle several times to mix. • Insert and withdraw the glass rod, or equivalent, and allow a drop of the sample to fall on or touch the pH paper. Record the pH. Do NOT dip the pH paper into the bottle or touch it to the sample on the lid. • Rinse the glass rod with a small portion of n-Hexane that will be used for extraction (to ensure that no extractable material is lost on the glass rod). Collect the rinsate back into the client container to be used for sample extraction.
3	Measure the volume by comparing the meniscus to a calibrated bottle of the same size and shape. (See Section 17 of SOP 3510 608 608.2 610 625 / NV03-24 for how to calibrate bottles.)
4	Add the appropriate amount of HCl or H_2SO_4 solution to the blank, LCS, and MS to adjust the pH of these solutions to <2. Add the spike to the LCS and the sample for MS. Mix.
5	Attach a closed Water Sample Inlet Valve to the bottle. Use an adapter if necessary.
6	The standard, samples, and blank are now ready for processing.

10.3 System Performance Checks, Startup Procedure

1	Verify that all connections are properly in place.
2	Empty all waste recovery bottles (water and solvent) if necessary.

3	Fill the solvent bottles with appropriate solvents as follows: Pre-wet 1: Hexane connected to Pre-wet Fitting #1 on Extractor Pre-wet 2: Methanol connected to Pre-wet Fitting #2 on Extractor Rinse: Hexane connected to Rinse Fitting #2 on Extractor Secure the caps on the solvent bottles. Loss of pressure in the bottles occurs if the caps are loose.
4	Turn on the main power switch on the back of the Controller and allow the Liquid Level Sensor(s) to stabilize for 3 to 5 minutes.
5	Turn on the gas source and slowly increase the main gas source pressure while checking for liquid and gas leak. Adjust the main gas source pressure in increments, checking for leaks as the pressure is increased to minimum of 60 psi and a maximum of 80 psi.
6	Turn on the vacuum pump and check for vacuum leaks. The main vacuum source gauge should read between -25” Hg and -30” Hg.
7	Verify that there are no crimped lines that may impede the flow of liquids, gas, and vacuum.
8	Free the Elute Check valve(s) using the Check Valve Release Tool (P/N 02-0725). In the center of the platform, below the drain hole, is the Sample Collect Check Valve. Gently insert the needle straight down into the opening and tap the head several times to free the check valve. This will move the Check Valve Ball off of the seat assembly. An internal spring will gently push the ball back into the sealing position.
9	Lift and move the Liquid Sensor / Pre-wet Arm into the Disk Holder Base.
10	If using a VOA vial as a collection vessel, attach a glass adapter to the vessel by screwing it on using the turquoise cap. Do not screw on the adapter by using the glass part; this may not produce a good seal. Place the collection vessel in position on the Taper of the unit by lifting and twisting to ensure a vacuum tight seal. An adapter is not required for an Erlenmeyer flask with 19/22 taper.
11	Lower the Water Sample Bottle Arm.
12	Attach an empty sample bottle to the Water Sample Inlet Valve and place the valve into position on the Water Sample Bottle Arm.
13	A Purge sequence is run to remove any air from the solvent lines and to wash the parts of the extractor. This is also a good way to verify that the system is installed correctly and operating properly. The Purge sequence performs much like an actual extraction method by introducing the selected pre-wet and rinse solvents. Press the STATUS key to display the status for all three stations.
14	Select Station #1 by pressing the A-key. Press the DRAIN function key (E-key). Then press the PURGE key (D-key). Press the A-key for YES to begin the purge on Station #1. Follow the same procedure for Stations #2 & 3 if using the 3000XL extractor system. Run the purge sequence three times to ensure all air has been removed from the lines when first installed or when refilling the solvent bottles.
15	Use the following conditions: Methanol Pre-wet: 5 sec Dispense 1 sec Saturate 10 Sec Saturate 0 sec Drain Air Dry 10 sec 3 sec Dispense

10.4 Extraction Procedure

1	Attach the Water Sample Inlet Valve(s) to the sample bottle(s). Use an adapter if required.

2	Place the screen in the Disk Holder Base. Place the SPE disk on the screen. Use a 90-mm pre-filter and disk if processing dirty samples. SPE filters must be of the same manufacturer, diameter, and lot number for all samples in the batch.
3	Insert the Riser into the Disk Holder Base over the disk. The Riser holds the disk in place. Screw on the aluminum Locking Ring, load the Disk Holder assembly onto the Extractor platform and place the Liquid Sensor / Pre-wet Arm in the Disk Holder Assembly. Load the Disk Holder Assembly on each station being used.
4	Place a collection vessel with adapter in position by lifting and twisting to ensure a vacuum tight seal. Use 40-mL VOA vials if using 47-mm disks and 125-mL flasks if using 90-mm disks for dirty samples.
5	Lower the Sample Holder Arm on the extractor unit for each station used.
6	Load the sample bottles onto the unit. Minimize the agitation of the standard (refer to Section 10.1 Sample Preparation). With the Water Sample Inlet Valve aluminum shaft facing you, place your finger over the solvent rod on the right-hand side. This will prevent the sample from leaking out. Gently invert the bottle and place it onto the Holder Arm of the unit. Help guide the Water Sample Inlet Valve shaft onto the actuator key. Firmly press the valve in place.
7	Select the appropriate method for the extraction process according to the disk size and type. EPA Method 1664A Method 2 - Programmed into the SPE-DEX® 3000XL Controller (90mm Pacific Premium SPE disk)

Method 2	Time		Time
Pre-wet Hexane		Pre-wet Methanol	
Dispense	6 seconds	Dispense	6 seconds
Saturate	1 second	Saturate	1 second
Soak	30 seconds	Soak	30 seconds
Drain	1 minute	Drain	3 seconds
	Air dry	3.00 minutes	
Rinse	Dispense	Soak	Elute
1. Hexane	4 seconds	45 seconds	0 seconds
2. Hexane	4 seconds	45 seconds	45 seconds
3. Hexane	4 seconds	45 seconds	0 seconds
4. Hexane	4 seconds	45 seconds	45 seconds

	From STATUS mode, select the station with the sample loaded for processing by pressing the appropriate key. Press A-key to increase the method number or the B-key to decrease the method number to the one desired.
8	Return to the STATUS mode and proceed as in step 7 of this section to load the method to each station being used.
9	Return to the STATUS screen and confirm that the stations are set to the desired method.
10	Press the E-key to run all stations. If running only one station, select the station by pressing the appropriate key and then press the A-key to start the extraction. Confirm the start of the extraction by pressing the A-key again.

10.5 Gravimetric Determination

1	Turn on the Speed-Vap™ using the switch located on the back of the unit. Set the temperature to 40℃. Record in the logbook or in L IMS.

2	Pre-weigh disposable, clean, dessicated, aluminum pans using a calibrated analytical balance and record the initial weighs.
3	After the extraction has been completed, remove the collection vessel(s) from the unit. Remove the adapted, if applicable.
4	Transfer the Hexane extract by opening the separatory funnel's Teflon™ stopcock. Once the Hexane has been transferred, RINSE THE SIDES OF THE COLLECTION VESSEL THREE TIMES using small volumes of clean Hexane. Transfer each rinse to the pre-weighed pan. Repeat for each sample extracted. Then carefully pour the Hexane extract into the weighed aluminum pan. Use tweezers or gloves when handling the aluminum pan to avoid adding moisture or oil from the fingers.
5	Place the pans containing the Hexane extracts in the Speed-Vap™ until all visible liquid is evaporated. Place in the desiccator for at least 30 minutes.
6	Weight the pan with the residue once evaporation is complete. Record this as "Weight Check" on the benchsheet.
7	Place the pan back in the desiccator for about 30 minutes.
8	Weigh the pan with residue again. Record this as "Final Weight" on the benchsheet. If there is a difference greater than 4% (0.0005 g) between the "Weight Check" and the "Final Weight," place the pan back in desiccator for about another 30 minutes. Continue until a constant weight has been achieved. Record each weighing.
9	Proceed to calculations.

10.6 SGT-HEM Determination: Use the HEM residue for the SGT-HEM determination.

1	To ensure that the capacity of the silica gel is not exceeded, the amount of HEM must be less than 100 mg or, if above 100 mg, must be known. It is presumed that 3 g will normally adsorb 100 mg of all absorbable materials. Use a proportionate amount of silica for HEM above 100 mg up to a maximum of 30 g for 1000 mg HEM.
2	Add a small aliquot of n-Hexane to the pan to re-dissolve the HEM. Warm the solution if necessary.
3	Transfer the extract to a clean collection vessel (VOA vial or 125-mL flask, depending on volume of Hexane used) containing 3.0 ± 0.3 g of anhydrous silica gel for every 100 mg of HEM. Record.
4	Repeat steps 10.6.2 and 10.6.3 several times to ensure that all residue has been re-dissolved. Add each Hexane rinse to the collection vessel containing the silica gel.
5	Gently shake the collection vessel for about 5 minutes. Let the collection vessel sit for a few minutes and allow the silica gel to settle.
6	Transfer the Hexane by preparing a filter cone with Whatman 41 filter paper, or equivalent, and 3 to 10 g sodium sulfate. Pour the silica gel-treated Hexane into the filter cone to drain into a clean, weighed, aluminum pan. If silica gel gets into the pan, results will be overstated.
7	Rinse the collection vessel at least three times with aliquots of Hexane, transferring with each rinse to the evaporation pans.
8	Evaporate the Hexane and determine the weight of SGT-HEM by subtracting the tare weight from the total weight. Refer to Section 10.5 for how to accomplish the constant weight check. Refer to Section11.3 for calculation of the result.
9	Place the pans containing the Hexane extracts in the Speed-Vap™ until all visible liquid is evaporated. Place in the desiccator for at least 30 minutes.
10	Weigh the pan with the residue once evaporation is complete. Record this as "Weight Check" on the benchsheet.
11	Place the pan back in the desiccator for about 30 minutes.
12	Weigh the pan with residue again. Record this as "Final Weight" on the benchsheet. If there

	is a difference greater than 4% (0.0005 g) between the "Weight Check" and the "Final Weight," place the pan back in desiccator for about another 30 minutes. Continue until a constant weight has been achieved. Record each weighing.
13	Proceed to calculations.

10.7 Shut-down Procedure for Extractors

1	Remove the Disk Holder Assembly(s) from the extractor unit and discard the used disks.
2	Pour water in the platform cavity of the station(s). Select the station from the STATUS mode. Press the DRAIN (E-key) function and then the ELUTE (C-key). Repeat for each station. This procedure will remove any residual solvent from the check valve.
3	Turn off the vacuum pump and vent by removing the line attached to the waste bottle.
4	Turn off the gas supply.
5	Turn off the controller power.
6	Flush the Water Sample Inlet Valves by manually turning them open and closed while flushing under warm running water. Non-surfactant soap may be used to clean the valves. Make sure to thoroughly rinse them out. Do not scrub using a cleaning brush.
7	Leave the Water Sample Inlet Valves in a half-open position to allow the water to drain.

10.8 Example Analysis Queue / Sequence*

1	Method Blank
2	PAR/LCS
3	Samples 1
4	Matrix Spike
5	Matrix Spike Duplicate (optional)**
	Samples 2-20

*May be up to 20 samples for a 12-hour shift.
**MN requires a Matrix Spike Duplicate.

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\text{LCS \% Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value} - \text{dup. sample value)} \times 100}{[(\text{Orig. sample value} + \text{dup. sample value})/2]}$$

11.3 Concentration Calculations

1	Weigh the pan with the standard residue once evaporation is complete and calculate the recovery as follows: $[(W_2 - W_1) / 40\ mg] \times 100\% = \%\ Rec.$ W_1 = *Weight of empty aluminum pan (mg)* W_2 = *Weight of aluminum pan with sample (mg)*
2	Calculate the concentration of HEM content from the samples as follows: $(W_2 - W_1) / V_s = mg/L$

	V_s = Volume of original sample (L)
3	Calculate the concentration of SGT-HEM (non-polar material) content as follows: $(W_2 - W_1) / V_s = mg/L$ *V_s = Volume of original sample (L)*
4	Calculate the concentration of the polar material as follows: $C_P = C_T - C_{NP}$ *C_P = Concentration of the polar material* *C_T = Total oil and grease (HEM-oil and grease)* *C_{NP} = Concentration of non-polar material (SGT-HEM)*

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

- **A MDL less than or equal to the required MDL of 1.4 mg/L or less than 1/3 the regulatory compliance limit must be achieved prior to the use of this method.**

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

- **Initial precision and recovery (IPR):** To accomplish the ability to generate acceptable precision and accuracy, the laboratory must determine the concentration of HEM and/or SGT-HEM in four samples of the PAR/LCS standard and compute the average percent recovery (X) and the standard deviation of the percent recovery (s) for HEM and for SGT-HEM (if determined). When determining SGT-HEM, the true concentration (T) must be divided by 2 to reflect the concentration of hexadecane that remains after removal of Stearic acid. Calculate the standard deviation of the percent recovery and compare with the corresponding limits. If the acceptance criteria are met, system performance is acceptable and analysis of samples may begin. If not, correct the problem and repeat the test.

$$s = \sqrt{\frac{\sum x^2 - \frac{(\sum x)^2}{n}}{n-1}}$$

N= Number of Samples

X=% Recovery in each sample

- The same criteria are used on an ongoing basis as for this initial evaluation.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an acceptable manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Unused samples are neutralized and discharged to the sanitary sewer.
- Solid residues are disposed to a trash receptacle.
- Solvent waste is placed in mixed flammable waste drums for disposal off-site.

15.0 References / Cross-References

15.1 Method 1664A, U.S. EPA Office of Water, EPA-821-R-98-002, February 1999, and **1664B**, February 2010, promulgated May 18, 2012.
15.2 SW-846 Method 9070A, Update IIIB, November 2004
15.3 Horizon Technology User's Guide, SPE-DEX® 1000XL Series Extractor
15.4 Horizon Technology User's Guide, SPE-DEX® 3000XL Series Extractor
15.5 Horizon Technology User's Guide, SPEED-VAP™ II 9000
15.6 Horizon Technology User's Guide, Solvent Trap™.
15.7 Horizon Technology Standard Operating Procedure for the Gravimetric Determination of Oil and Grease in Water Using Automated Solid Phase Extraction, SPE-DEX® 1000/3000XL Extractors, 12/9/02.
15.8 TestAmerica Nashville's Quality Assurance Manual.
15.9 Corporate Environmental Health and Safety Manual (CW-E-M-001)
15.10 SOPs: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213, Determination of Method Detection Limits / NV08-202, Method Start-up / NV08-203, Sample Homogenization, Sub-sampling, and Compositing / NV08-229, 3510 608 608.2 610 625 / NV03-24.
15.11 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

Item	Modification
1	For Minnesota samples, add a Matrix Spike Duplicate to each batch.

17.0 Attachment

None.

18.0 Revision History

- Revision 6, dated 20 June 2008
  - Integration for TestAmerica and STL operations.
  - Make Horizon automated solid phase extraction system the primary extraction process.
- Revision 7, dated 25 September 2009
  - Replace 37% HCl with concentrated HCl.
  - Add option of using 90 mm fast flow pre-filters.
  - Add Minnesota requirement for MSD.
- Revision 8, dated 30 October 2010
  - Added Sulfuric Acid to section 5.2 and section 7; Added additional supplies to section 6.2
  - Added "Note" to section 10.1 regarding what to do when solids are present.
  - Clarified language on SPE disk and pre-filter use in section 10.3.
  - Addition of QAF-45 and Section 14.2.
- Revision 9, dated 28 September 2012
  - Organizational changes.
  - Addition of Amendments 8a (2/18/11) and 8b (10/31/11)
  - Addition of EPA 1664B.
  - Requirement for a second-source standard if using a certified standard.
  - OK and WY now allow 20-sample batches.
  - pH lower limit for preservation depending on which acid is used.
  - Use a glass rod instead of a pipette to verify sample pH with pH paper (Sample Preparation section).
  - Clarify the use of desiccators in the procedure.
  - Modify Example Analysis Queue/Sequence.
  - Clarification that unused samples are neutralized before discharge to the sanitary sewer.
- Revision 10, dated 30 April 2013
  - Add amendment 9a.
  - Correct volume of spike added to 4.0 mL.
  - Add solvent waste disposal.
  - Added AZ and TX to the states that require LCSD.
- Revision 11, dated 31 May 2015
  - Organizational changes.
  - Addition of change form 10a (modification of gravimetric procedure and the SGT-HEM determination for clarity.)
  - Add reference to SOP 3510 608 608.2 610 625 / NV03-24 for how to calibrate bottles for volume measurement.

SOP Number/Revision No.: **SM5210 B/ NV07-05.17b** Effective Date: 11/30/2015

Last Mod. Date: **4/30/15**

SOP Title: **Method SM5210 B: Biochemical Oxygen Demand and Carbonaceous Biochemical Oxygen Demand**

CONTROLLED DISTRIBUTION

ISSUED TO: \\TAFS\Lab\Nashville\Public\QA\SOPs, 07

Revision Number with Mod ID: **17c**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add highlighted text; delete crossed-out text.

9.1 Sample QC

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Unseeded Blank (Dilution water), may be used for Drift check.	1 in 20 or fewer samples	Should not deplete more than 0.20 mg/L DO.	If > 0.20 mg/L, note in LIMS. See trouble-shooting (Section 17.2).
~~Method Blank~~	~~1 in 20 or fewer samples~~	~~BOD < 2.0 mg/L.~~	~~Qualify in LIMS~~
Glucose-Glutamic acid (GGA) (LCS), three test bottles	1 set per 20 samples.	Average GGA should be 167.5-228.5 mg/L.	The amount of seed added may have to be adjusted to achieve results within this range. If this criterion is not met, note in LIMS.
Seed Controls	1 in 20 or fewer samples	Average: 0.6-1.0 mg/L	Adjust the ratio of the seed to water or amount of seed added to BOD bottles.
Sample Duplicate	1 in 20 or fewer samples	≤ 20% RPD	Qualify in LIMS, report

~~The **method blank:** Prepare by adding nominally 2.5 mL Polyseed to 300 mL nutrient water.~~

10.0 Example Analysis Queue / Sequence*

Manual Analysis	
1	Unseeded Blank
2	GGA , i. e., LCS (in triplicate)
3	~~Seeded Blank~~
4	Seed Control (in triplicate)
5	Samples 1-10
6	Duplicate
7	Samples 11-20
8	Duplicate

PC BOD Analyzer	
1	Calibration (probe)
2	Unseeded blank
3	GGA (in triplicate)
4	~~Seeded Blank~~
5	Seed Control (in triplicate)
6	Samples 1-5
7	Calibration Check
8	Samples 6-10
9	Calibration Check
10	Samples 11-15
11	Calibration Check

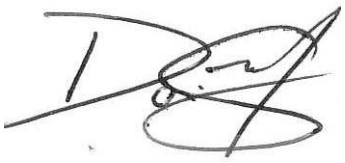
*May be up to 20 samples

11.3 BOD or cBOD, mg/L = (DO_1-DO_2) - (seed correction factor) (dilution) / P

DO_1 = initial DO, mg/L
DO_2 = DO after 5 day incubation, mg/L
P = mL of sample used / 300

Qualify results when any of the following apply:

- The unseeded or dilution water blank > 0.20 mg/L.

	Jessily Overton-May 11/16/15
	Department Manager Approval Date
 11/23/15	Michael A. Brown 11/4/15
Quality Assurance Manager Date	Technical Director Approval Date

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure
(SOP) Change Form

SOP Number/Revision No.: **SM5210 B/ NV07-05.17a** Effective Date: 4/30/2015

Last Mod. Date: **/27/2015**

SOP Title: **Method SM5210 B: Biochemical Oxygen Demand and Carbonaceous Biochemical Oxygen Demand**

CONTROLLED DISTRIBUTION

ISSUED TO: \\TAFS\Lab\Nashville\Public\QA\SOPs, 07

Revision Number with Mod ID: **17b**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add highlighted text; delete crossed-out text.

Section 7.11, pH Buffers: Commercial source. Use ~~two~~ buffers at pHs of 4.0, ~~and~~ 7.0, and 10.0.

Section 10.1, Sample Preparation, step 6. Add
Note: West Virginia requires that the nutrient water be added before the seed is added.

	Sessily Overton-May 4/27/15
	Department Manager Approval Date
Steve Shilley 4/27/15	Michael A. Brown 4/27/15
Quality Assurance Manager Date	Technical Director Approval Date

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Nashville
Standard Operating Procedure (SOP)
Change Form

SOP Number/Revision No.: **SM5210 B/ NV07-05.17** Effective Date: **2/27/2015**

Last Mod. Date: 12/31/14

SOP Title: **Method SM5210 B: Biochemical Oxygen Demand and Carbonaceous Biochemical Oxygen Demand**

CONTROLLED DISTRIBUTION

ISSUED TO: QA Server, 07

Revision Number with Mod ID: **17a**

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Reason for SOP Change:

☐ Typographical Corrections (Non-Technical) – Re-Training Not Required.

☐ Typographical Corrections (Technical – Define) – Analyst acknowledgement of corrections is required.

■ Procedural Changes (Define Below) – Re-Training Required.

☐ Other

2. Summary of Procedure Change: Add highlighted text; delete crossed-out text.

Section 10.1, Step 3

3	**COD Screen**: Screen by running a COD on each sample to determine the approximate initial sample dilution required. If sample quickly turns green in the COD determination, indicating high organic content, dilute such that no green color is observed. Use that dilution for BOD analysis; **however, all samples are run undiluted, also, unless the client provides specific dilutions.**. See SOP 410.4 & SM5220 D / NV07-08. **Samples that require a dilution greater than 1:100 (i. e., when 3 ~~2~~ mL or less sample volume is used) require that a pre-dilution step be performed before making the final dilution. For example, instead of using 3 ~~2~~ mL of sample and diluting it to 300 mL, perform a pre-dilution by using 50 mL of sample and diluting it to 500 mL. Then take 20 mL of the diluted sample (from the 500 mL volumetric) and dilute that to 300 mL. Both of these dilution techniques result in an effective final dilution factor of 150 and the latter method provides a more representative sample dilution. Pre-dilution information must be documented in LIMS. The smallest sample volume that can be used without requiring a pre-dilution step is 3 mL. Note: When using wide-bore pipettes for smaller volume dilutions, always deliver into a Class A, glass, graduated cylinder. Quantitatively transfer to the filter or beaker.

Section 10.3.1, Manual Analysis, Step 1

1	Fill the bottle to the neck. Tap to remove visible air bubbles. Measure the initial DO. Record the initial DO and sample temperature from the probe. Stopper, cap and incubate. The initial DO **must** be between 70-105% saturation ~~7.0 and 8.9 (at 21°C), 8.7 mg/L (at 22°C), or 8.6 mg/L (at 23°C) mg/L for samples and QA/QC~~. If low, oxygenate; if high, reduce by helium sparging or shaking/stirring in an open container. Add the dilution water to the bottle lip.

	Sessily Overton-May 2/4/15
	Department Manager Approval Date
Steve Shilley 2/4/15	Michael A. Burns 2/4/15
Quality Assurance Manager Date	Technical Director Approval Date

Title: BIOCHEMICAL OXYGEN DEMAND AND CARBONACEOUS BIOCHEMICAL OXYGEN DEMAND METHOD SM5210 B

Approvals (Signature/Date)

Sessily Overton-Gray	12/31/14	Ryan Fitzwater	11/26/14
Sessily Overton-Gray Department Manager	Date	Ryan Fitzwater Health & Safety Manager / Coordinator	Date
Steve Miller	11/8/14	Michael H. Dunn	11/6/14
Steve Miller Quality Assurance Manager	Date	Michael H. Dunn Technical Director	Date

1.0 Scope and Application

1.1 Analyte, Matrices: The biochemical oxygen demand (BOD) and carbonaceous BOD (cBOD) method is used for determining the relative oxygen requirements of municipal and industrial wastewaters. It is an empirical bioassay-type procedure which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present.

1.2 Reporting Limits: The report limit is nominally 2.0 mg/L.

1.3 If for any reason a part of this method cannot be followed, seek the guidance of the Department Supervisor, Department Manager, or the Technical Director. All abnormalities must be noted in the Laboratory Information Management System (LIMS).

2.0 Summary of Method

The sample of waste is incubated for 5 days at 20^{o}C in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand. When a nitrification inhibitor is used, carbonaceous BOD (cBOD) is determined.

3.0 Definitions

Definitions are available in the Quality Assurance Manual. Also, refer to Controlled Document, QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

4.0 Interferences

Strong oxidizers and reducers as well as high organics can interfere.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: When screening for COD, tilt the sample away from you; remember it is hot and contains strong mineral acids.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sodium hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.
Sulfuric acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Sodium sulfite	Irritant	NA	May be harmful if swallowed or inhaled. May cause irritation to skin, eyes, and respiratory tract.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium dichromate	Oxidizer Corrosive Carcinogen	0.1 mg/m^3 TWA as CrO3	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. May cause ulceration and perforation of the nasal septum. Symptoms of redness, pain, and severe burn can occur. Dusts and strong solutions may cause severe irritation. Contact can cause blurred vision, redness, pain and severe tissue burns. May cause corneal injury or blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- PC-BOD Analyzer, Mantech, or equivalent.
- Incubator, commercial, capable of 20 ± 1°C.
- DO Meter, YSI 5100, or equivalent.
- DO Probe, YSI 5010, or equivalent.
- pH Meter, Orion model 300, or equivalent.
- pH combination electrode.

6.2 Supplies

- Bottles, 300-mL having a ground-glass, stopper and a flared mouth, glass or plastic, disposable, BOD bottles.
- Filter, Whatman qualitative, No. 1, Fisher 1001 110 or equivalent.
- Wide-bore pipettes, various volumes.

7.0 Reagents and Standards

7.1 Reagent water, analyte-free.

7.2 Phosphate Buffer: Dissolve 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $Na_2HPO_4 \cdot 7H_2O$ and 1.7 g NH_4Cl in about 500 mL reagent water. When solution is complete, dilute to 1 liter. The pH of this buffer should be 7.2 ± 0.1 without further adjustment. Commercial source is acceptable. Store in refrigerator.

7.3 Magnesium sulfate Solution: Dissolve 22.5 g Magnesium sulfate ($MgSO_4 \cdot 7H_2O$) in reagent water and dilute to 1 liter. Commercial source acceptable. Store in refrigerator.

7.4 Calcium chloride solution: Dissolve 27.5 g Calcium chloride in reagent water and dilute to 1 liter. Commercial source acceptable. Store in refrigerator.

7.5 Ferric chloride Solution: Dissolve 0.25 g of Ferric chloride*$6H_2O$ in reagent water and dilute to 1 liter. Commercial source acceptable. Store in the refrigerator.

Note - Discard any of these nutrient solutions into the sanitary sewer if there is any evidence of bacterial growth in the stock bottles or if the volume is less than 2/3 full.

7.6 Acid and Alkali Solutions: 1.0 N H_2SO_4 and 1.0 N NaOH.

7.7 BOD Standard (Glucose-Glutamic acid solution (GGA)), used for the LCS: Dissolve 0.15 g each of reagent grade Glucose (1-dextrose) and Glutamic acid, which has been dried at approximately 105°C for an hour, in reagent water and dilute to 1 liter. Prepare fresh monthly. A commercial source is acceptable. Store in a refrigerator.

7.8 Seeding Material: Acclimated bacteria, Polyseed from Polypac Corporation, or equivalent. Use as required to meet method criteria.

7.9 Sodium Sulfite Solution: Dissolve 0.158 g anhydrous Na_2SO_3 in 100 mL reagent water for a 0.025 N solution; prepare fresh daily Alternatively, a commercial source is acceptable.

7.10 Nitrification Inhibitor: 2-Chloro-6-(trichloromethyl) pyridine (Hach or equivalent) for cBOD determination.
7.11 pH Buffers: Commercial source. Use two buffers at pHs of 4.0 and 7.0.
7.12 COD vials: Commercial source. HACH low level COD vials (0-150 mg/L), used for screening.
7.13 Nutrient dilution water: Collect a quantity of reagent water, sufficient for all samples, at least 24 hours (preferably 2-3 days) prior to use. Store at approximately 20°C in an incubator. Aerate to obtain a DO of 7.5 to 9 mg/L prior to adding nutrients. Prepare nutrient dilution water by adding 1.0 mL each of phosphate buffer, Magnesium sulfate solution, Calcium chloride, and Ferric chloride solutions to each liter of reagent water being prepared. Check the pH; it should be 6.5 to 7.5 pH units. If not, discard and re-make. Do not keep more than 24 hours.
7.14 Dissolved Oxygen Probe Electrolyte: Prepare by diluting 4.57 g Sodium sulfate and 1.85 g Potassium chloride into 35 mL reagent water. A commercial product is also acceptable.
7.15 See SOP Reagent and Standard Purchase, Preparation, Control, Documentation for information on shelf-life and storage requirements.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	HDPE or Glass	1000 mL	Cool 0-6°C	As soon as possible but no more than 48 hours	40 CFR Part 136.3, SM Table 1006: I (20th)

9.0 Quality Control

Refer to TestAmerica Nashville's QA Manual for specific quality control (QC) policies. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC

Quality Controls	Frequency	Acceptance Criteria	Corrective Action
Unseeded Blank (Dilution water), may be used for Drift check.	1 in 20 or fewer samples	Should not deplete more than 0.20 mg/L DO.	If > 0.20 mg/L, note in LIMS. See trouble-shooting (Section 17.2).
Method Blank	1 in 20 or fewer samples	BOD < 2.0 mg/L.	Qualify in LIMS
Glucose-Glutamic acid (GGA) (LCS), three test bottles	1 set per 20 samples.	Average GGA should be 167.5-228.5 mg/L.	The amount of seed added may have to be adjusted to achieve results within this range. If this criterion is not met, note in LIMS.
Seed Controls	1 in 20 or fewer samples	Average: 0.6-1.0 mg/L	Adjust the ratio of the seed to water or amount of seed added to BOD bottles.
Sample Duplicate	1 in 20 or fewer samples	≤ 20% RPD	Qualify in LIMS, report

- The **method blank:** Prepare by adding nominally 2.5 mL Polyseed to 300 mL nutrient water.
- **Unseeded blank (also Drift check):** Add 300 mL nutrient water (DO 7–9 mg/L) to BOD bottle, i. e., dilution water.
- **Seed Control:** Prepare "seed" by adding about 0.25 to 0.5 g of "Polyseed" to about 500 mL

nutrient water. Aerate and stir for at least **one** hour. Allow to settle for about 15 minutes; decant the seed to another clean container leaving bran behind. Seed must be used within 6 hours of hydration. The seed may be heated to 30°C during its preparation. The amount of nutrient water may vary; note the exact amount in LIMS. Place 10, 15, 20 mL seed in separate BOD bottles, and add nutrient water. If running cBOD, add the nitrification inhibitor (Section 10). Results of the "**good**" seed controls are averaged together, and the average should be 0.6 – 1.0 mg/L.

- Prepare 2% **Glucose-Glutamic check standard** in triplicate by adding 6.0 mL of Glucose-Glutamic acid standard to a BOD bottle. Add some nutrient dilution water, about 2.5 mL Polyseed, fill to volume with nutrient dilution water. If running cBOD, add nitrification inhibitor to one pair of GGA standards. The average GGA results **must** be within the range of 198 ± 30.5 mg/L for BOD and cBOD.
- **Sample Duplicate:** Prepare at least one duplicate per batch by analyzing an identical aliquot of one client sample. The RPD should be < 20%. If not, note in LIMS.

9.2 Instrument QC: See Section 10.2

10.0 Procedure

10.1 Sample Preparation: Refer to SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.

Matrix	Sample Size
Water	300 mL

1	Allow samples and reagents to reach room temperature (20 ± 3°C). Shake prior to use.
2	For soluble BOD, filter a sufficient volume for the test with qualitative filter paper. A filtered blank and control are also required.
3	**COD Screen**: Screen by running a COD on each sample to determine the approximate initial sample dilution required. If sample quickly turns green in the COD determination, indicating high organic content, dilute such that no green color is observed. Use that dilution for BOD analysis; **however, all samples are run undiluted, also, unless the client provides specific dilutions.**. See SOP 410.4 & SM5220 D / NV07-08. **Samples that require a dilution greater than 1:100 (i. e., when 2 mL or less sample volume is used) require that a pre-dilution step be performed before making the final dilution. For example, instead of using 2 mL of sample and diluting it to 300 mL, perform a pre-dilution by using 50 mL of sample and diluting it to 500 mL. Then take 20 mL of the diluted sample (from the 500 mL volumetric) and dilute that to 300 mL. Both of these dilution techniques result in an effective final dilution factor of 150 and the latter method provides a more representative sample dilution. Pre-dilution information must be documented in LIMS. The smallest sample volume that can be used without requiring a pre-dilution step is 3 mL.
4	Calibrate the pH meter using pH buffers 4 and 7 or 4, 7, and 10 being sure to bracket the pHs of the samples. Record buffer and LIMS ID. Slope must be ≥ 95 or each within 0.05 pH units of known. Check the pH of a volume, i. e., approximately 500 mL, of the sample. If the sample pH is outside of 6.0 to 8.0, adjust the pH to 7.0 to 7.2, using 1.0 N Sulfuric acid or 1.0 N Sodium hydroxide, as required. Note - If excessive volume (more than 0.5 mL per 100 mL sample) of 1.0 N Sulfuric acid solution is required, use a more concentrated solution. Record.

5	**BOD Oxidizing Agents Test**. The presence of residual chlorine is checked using indicator strips. If positive, remove by addition of Na_2SO_3 solution until the sample tests ND for residual chlorine. Take a 100-mL aliquot and slowly add Na_2SO_3. Cap and shake then retest. Continue until the test strip is ND. Record the amount of Na_2SO_3/100 mL of sample. Do not add excess Na_2SO_3. Add that amount per 100 mL of sample. Allow to sit for about 20 minutes.
6	Using either the new disposable or acid-washed (1N H_2SO_4) glass bottles, **prepare samples** as follows, in the order specified; dilute if indicated by the COD screen: • 300 mL sample + nominal 2.5 mL seed, 0.3 mL buffer, 0.3 mL $MgSO_4$, 0.3 mL $CaCl_2$, 0.3 mL $FeCl_2$. **All samples must be run undiluted even if the COD screen indicates a dilution unless the dilutions are specified by the client.** • 10 mL sample + nominal 2.5 mL seed, fill with nutrient dilution water. • 30 mL sample + nominal 2.5 mL seed, fill with nutrient dilution water. • 100 mL sample + nominal 2.5 mL seed, fill with nutrient dilution water. • 300 mL sample + nominal 2.5 mL seed, 0.3 mL buffer, 0.3 mL $MgSO_4$, 0.3 mL $CaCl_2$, 0.3 mL $FeCl_2$. Measure the initial DO within 30 minutes of the addition of the dilution water. The sample temperature must be 20 ± 3°C or adjust it. Record the initial DO and temperature. Note: The amount of seed added may vary with each lot of seed. Record the exact volume used in LIMS.

10.2 Calibration: See SOP SM4500-O G / NV07-20, Oxygen, Dissolved.

10.3 Sample Analysis

10.3.1 Manual Analysis

1	Fill the bottle to the neck. Tap to remove visible air bubbles. Measure the initial DO. Record the initial DO and sample temperature. Stopper, cap and incubate. DO **must** be between 7.0 and 8.9 (at 21°C), 8.7 mg/L (at 22°C), or 8.6 mg/L (at 23°C) mg/L for samples and QA/QC. If low, oxygenate; if high, reduce by helium sparging or shaking/stirring in an open container. Add the dilution water to the bottle lip.
2	Read the weaker to highest sample ratio. Rinse the electrode between samples with reagent water. Note: If nitrification inhibition is desired, add amount of sample to bottle, add 3 mg or one dispersal cap volume of 2-Chloro-6-(trichloromethyl) pyridine (TCMP) to each bottle, stir to mix and dissolve, and add dilution water, if needed, before capping. Add to one set of GGA controls (GGA and a blank). **Note: Pure TCMP may dissolve slowly and can float on top of the sample.** Note the use of nitrogen inhibition in reporting results by reporting cBOD.
3	After every few samples or any unusual-appearing sample, read the drift check bottle. If the drift ≥ 0.20 mg/L, re-calibrate and re-read all affected samples. This bottle contains dilution water.
4	Place a plastic seal cap over each bottle.
5	Place all bottles in the dark incubator at 20 ± 1°C for 5 days ± 6 hours. Record date and time placed in the incubator.

6	After incubation, record the date and time removed from incubator and determine the final DO on each bottle. Record on the BOD benchsheet.

10.3.2 PC-BOD Analyzer

1	Place the rack in position on the autosampler by placing hooks into the holes designated for rack positioning.
2	Open the BOD program.
3	Click on "BOD," and select "BOD Run."
4	Load the template: For BOD samples only, load "BOD Daily." For CBOD samples only, load "CBOD Daily." For BOD and CBOD samples, load "BOD—CBOD Daily."
5	Click "Edit." Add x rows for the number of additional rows needed in the template.
6	Type in the sample volume, seed volume, and GGA volume for all samples.
7	Type in pre-dilutions to samples.
8	Prime all reagent pumps and check for pump operation and leaks.
9	Click "Start" and follow the software instructions.
10	Follow normal SOP procedures.
11	After the daily runs, rinse out the seed and dilution water containers and fill them with reagent water to rinse the pump lines.
To re-analyze samples after DO adjustment:	
1	Click "Stop."
2	Select the tab "Run Information/Template Controls." Select "Edit."
3	Reset desired DO reading sby removing the DO value using the delete key or space bar. To re-run the entire rack, click "Erase Rack DOs." Enter the rack number. Press "OK."
4	Click "Done Edit."
5	Click "Start." Enter the rack number. Click "OK."
6	If the rack is the first rack with the probe calibration, the autoanalyzer prompts "Do you want to re-calibrate?" Click "No" if not; click "Yes" if re-calibration is desired. Run begins at the designated sample or rack.
To add samples during the run:	
1	Click "Stop."
2	Select the tab "Run Information/Template Controls." Select "Edit."
3	To add additional rows, select "Add x rows."
4	Once finished, click "Done Edit."
5	Press "Start;" enter the rack number; press "OK." The run starts at the beginning of the new bottles.

10.4 Example Analysis Queue / Sequence*

Manual Analysis			**PC BOD Analyzer**	
1	Unseeded Blank		1	Calibration (probe)
2	GGA , i. e., LCS (in triplicate)		2	Unseeded blank
3	Seeded Blank		3	GGA (in triplicate)
4	Seed Control (in triplicate)		4	Seeded Blank
5	Samples 1-10		5	Seed Control (in triplicate)
6	Duplicate		6	Samples 1-5
7	Samples 11-20		7	Calibration Check
8	Duplicate		8	Samples 6-10

	9	Calibration Check
	10	Samples 11-15
	11	Calibration Check

*May be up to 20 samples

11.0 Calculations / Data Reduction

11.1 Accuracy

$$\% \text{ Recovery} = \frac{\text{Measured concentration} \times 100}{\text{Known concentration}}$$

11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)} \times 100}{\text{(Orig. sample value + dup. sample value)/2}}$$

11.3 BOD or cBOD, mg/L = $(DO_1\text{-}DO_2)$ - (seed correction factor) (dilution) / P

DO_1 = initial DO, mg/L
DO_2 = DO after 5 day incubation, mg/L
P = mL of sample used / 300

Seed Correction Factor = (initial DO - final DO) (mL of seed in sample) / mL of seed used.

Report results as cBOD if nitrification inhibitor was added.

Enter the variables in LIMS for the calculations.

Report the average of the acceptable results. Procedure for determining which results are acceptable:

- The change in DO should be ≥ 2 mg/L.
- The residual DO ≥ 1.0 mg/L.
- The average of the results that meet criteria is reported. If unseeded dilution water has a demand > 0.2 mg/L, do not use it if the 300-mL whole volume sample is acceptable.

Qualify results when any of the following apply:

- The dilution water blank > 0.20 mg/L.
- The GGA average is outside the acceptance limits.
- The test replicates, including seed controls, show more than 30% difference between high and low results.
- The minimum dissolved oxygen is less than 1.0 mg/L.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL): The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses

performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability: The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements: Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

12.4 Proficiency Testing Studies: The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are managed, stored, and disposed of in accordance with all state and federal regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

14.2 Wastestreams Produced by the Method:

- Samples are discharged to the sanitary sewer.
- COD tubes are placed in the corrosive drum in the Inorganics Department.

15.0 References / Cross-References

15.1 Method SM5210 B - 2001 and SM5220 D - 1997, Standard Methods for the Examination of Water and Wastewater, on-line edition, 2011 editorial revisions.

15.2 EPA Method 410.4, Methods for Chemical Analysis of Water and Wastes, Approved for NPDES, issues 1993.

15.3 HACH Method 8000, "HACH Water Analysis Handbook," 3rd edition, 1997.

15.4 TestAmerica Nashville's Quality Assurance Manual.

15.5 Corporate Environmental Health and Safety Manual (CW-E-M-001)

15.6 SOPs: Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213, Determination of Method Detection Limits / NV08-202, Sample Homogenization, Sub-sampling, and Compositing / NV08-229, 410.4 & SM5220 D / NV07-08, SM4500-O G / NV07-20.

15.7 Controlled Document: QAF-45, TestAmerica Nashville – Acronyms, Keywords, and Definitions.

16.0 Method Modifications

None.

17.0 Attachments

17.1 Attachment 1: Winkler Titration

1	Fill four BOD bottles with reagent water. Place the DO probe in one of the bottles being careful to exclude all air bubbles. To the other bottles, add 2 mL Manganous sulfate solution followed by 2 mL alkaline Iodide-azide solution. Add reagents below the surface of the water. Stopper the bottle carefully excluding any air bubbles and mix well by inverting the bottle several times. When the precipitate settles, leaving a clear supernatant above the Manganese hydroxide floc, shake again. When settling has produced at least 200 mL of clear supernatant, carefully remove the stopper and immediately add 2 mL concentrated Sulfuric acid by allowing the acid to run down the neck of the bottle. Re-stopper and mix by gentle inversion until the iodine is uniformly distributed throughout the bottle.
2	Transfer the bottle contents into a 500 mL Erlenmeyer flask and titrate with 0.025 N Sodium thiosulfate to a pale straw color. Add 1-2 mL starch solution and continue to titrate to the first disappearance of the blue color. Repeat titration on all three bottles and average results.
3	Volume of titrant used, in mL, is equal to mg/L DO. The DO should be between 9.06 and 8.26 or re-titrate.

17.2 Attachment 2: Troubleshooting

1	Clean delivery tubes weekly by rinsing with 25 mL bleach / 1 L water. Rinse well with water. Test for residual chlorine.
2	Use latex tubing when possible. Replace frequently.
3	Clean storage containers (preferably glass) weekly using 25 mL bleach / 1 L water. Rinse well with water. Test for residual chlorine.
4	Use non-phosphate glass cleaner.
5	Do not use “air stone” for aeration.
6	Avoid tubing contact with water. Use glass tips.
7	Allow at least two hours (preferably overnight) for DO meter membrane to stabilize after change.
8	Observe DO meter drift over several minutes: a) drift down: let warm up longer. b) drift jumping around: check probe connections/membrane.
9	Replace DO probe membrane and solution weekly.
10	Be certain GGA is at room temperature prior to use.
11	Do not leave dilution water open to the air.
12	Filter the air used to aerate using an in-line filter.
13	Pre-filter the dilution water through an 0.2-micron pore size filter (bacterial).

18.0 Revision History

- Revision 6, dated 31 May 2009
  - Integration for TestAmerica and STL operations.
  - Update to MUR method references
  - Edited for clarity and changes in NC rules.
- Revision 7, dated 30 October 2009
  - Modifications for South Carolina.
- Revision 8, dated 30 April 2010
  - Retirement of EPA method reference 405.1.
  - Seed control average is 0.6 - 1.0 mg/L.
  - Modified Attachments 1 and 2.
  - Addition of 14.2.
- Revision 9, dated 29 June 2010
  - Add Winkler titration and edit probe calibration.

- Use one unseeded blank.
- Revision 10, dated 31 May 2011
  - Incorporate Amendment 9a, holding time for AZ samples.
  - Addition of corporate information on seed blank flagging (email 040711, Verl Preston).
  - Addition of Sodium thiosulfate to Section 5.2 and change from Sodium sulfite in Section 7.0. Commercial source is acceptable.
  - Expand on Step 4 in Section 10.1 about BOD Oxidizing Agents Test.
  - Remove reference to EPA 405.1. Add reference to the COD SOP.410.4 & SM5220 D / NV07-08.
  - Organizational changes in signature block.
- Revision 11, dated 31 August 2011
  - Incorporate Amendments 10a (Section 10.1 clarify dilution water) and 10b (change Sodium thiosulfate to Sodium sulfite), correct Attachment reference.
  - Specify auto versus manual DO probe calibration.
- Revision 12, dated 30 November 2011
  - Organizational changes.
  - Remove instructions to average duplicate GGA results.
  - Revise sample QC, sample preparation, and analysis instructions.
- Revision 13, dated 31 May 2012
  - Emphasize that the nitrification inhibitor for cBOD must be added to seed control bottles.
  - Oklahoma no longer limits batch size limit to 10 samples.
  - Remove the instruction to avoid dilutions less than 10X.
  - Add the requirement to run an undiluted sample for every sample, regardless of COD screen results.
- Revision 14, dated 28 September 2012
  - Organizational changes.
  - Incorporate change form 13a (remove the AZ requirement for a 24-hour holding time).
  - Update SM references.
  - Remove the use and reference to BOD EXCEL spreadsheets for calculations. Use LIMS.
  - Add troubleshooting attachment.
  - Modify the order of steps in preparing the nutrient dilution water.
  - Add the possibility of 3 pH buffers needed for calibration of the pH meter.
  - Add a table of recommended sample volumes to the sample preparation section.
  - Add SOP SM4500-O G / NV07-20.
- Revision 15, dated 31 May 2013
  - Add amendment 14a.
  - Add SOP Sample Homogenization, Sub-sampling, and Compositing / NV08-229.
  - Emphasize that the GGA is run in triplicate and the results averaged.
- Revision 16, dated 4 October 2013
  - Organizational changes.
  - Addition of Change Form 15a, instruction for qualifying results.
  - Addition of PC-BOD Analyzer.
- Revision 17, dated 31 December 2014
  - Organizational changes.
  - Addition of Change Form 16a, oxygen depletion cannot be ≥ 0.20 mg/L; add temperature-related DO information to the manual analysis procedure.
  - Addition of Change Form 16b, Sodium sulfite solution must be prepared fresh daily or use a commercial source.
  - Addition of Change form 16c, oxygen depletion cannot be ≥ 0.20 mg/L.
  - Add wide-bore pipettes, various volumes, in the supplies section.
  - Add direction for dilutions greater than 1:100.

- Add the requirement for measuring and recording the initial DO at a temperature of 20 ± 3°C.

Appendix G

Health and Safety Plan for Phase 2 Wet Dredge

Report

Health and Safety Plan for Phase 2 Wet Dredge

Ashland/NSP Lakefront Site

Project I.D.: 16X002

NSPW

Eau Claire, Wisconsin

December 2016

Foth | Envirocon

Joint Venture

Foth | Envirocon
Joint Venture

101 International Drive, P.O. Box 16655
Missoula, MT 59808

December 22, 2016

Mr. Eric Ealy
Project Coordinator
Xcel Energy, Inc., on behalf of NSPW
414 Nicollet Mall-2
Minneapolis, MN 55401

Dear Mr. Ealy:

RE: *Health and Safety Plan for Phase 2 Wet Dredge*
Ashland/NSP Lakefront Site

On behalf of Foth Infrastructure & Environment/Envirocon Joint Venture (FE JV), this *Health and Safety Plan for Phase 2 Wet Dredge* (*HASP*) for the Ashland/NSP Lakefront Site is enclosed.

This *HASP* provides safety-related information and requirements specific to the task and work location(s) for the Wet Dredge Project Area.

If you have any questions concerning this report, please contact either of the undersigned at (920) 497-2500.

Sincerely,

Foth Infrastructure & Environment/Envirocon Joint Venture

Steve J. Laszewski, Ph.D.
Management Committee Member

Denis M. Roznowski, P.E.
Project Manager

Health and Safety Plan for Phase 2 Wet Dredge

Distribution

No. of Copies	Sent To
1	Eric Ealy Project Coordinator Xcel Energy, Inc., on behalf of NSPW 414 Nicollet Mall-2 Minneapolis MN 55401
1	Jamie Dunn Project Manager Wisconsin Dept. of Natural Resources 810 W. Maple St. Spooner WI 54801
1	Denis Roznowski Project Manager Foth Infrastructure & Environment/ Envirocon Joint Venture 2121 Innovation Ct., Suite 300 De Pere WI 54115
1	Chris Seider Project Health and Safety Officer Foth Infrastructure & Environment/ Envirocon Joint Venture 2121 Innovation Ct., Suite 300 De Pere WI 54115
1	Dan Allen Project Health and Safety Supervisor Foth Infrastructure & Environment/ Envirocon Joint Venture 7878 Wadsworth Blvd, Suite 340 Arvada CO 80003
1	Scott Hansen Remedial Project Manager U.S. Environmental Protection Agency 77 W. Jackson Blvd. (SR-6J) Chicago IL 60604-3590
1	Steve Laszewski Management Committee Member Foth Infrastructure & Environment/ Envirocon Joint Venture 2121 Innovation Ct., Suite 300 De Pere WI 54115
1	Alan Buell Deputy Project Manager Foth Infrastructure & Environment/ Envirocon Joint Venture 7878 Wadsworth Blvd, Suite 340 Arvada CO 80003
1	David Hardy Project Health and Safety Manager Foth Infrastructure & Environment/ Envirocon Joint Venture 7878 Wadsworth Blvd, Suite 340 Arvada CO 80003
1	Master Project Files Foth Infrastructure & Environment/Envirocon Joint Venture

Health and Safety Plan for Phase 2 Wet Dredge

Project ID: 16X002

Prepared for

NSPW

Eau Claire, Wisconsin

Prepared by

Foth Infrastructure & Environment/
Envirocon Joint Venture

December 2016

101 International Drive, P.O. Box 16655 • Missoula, MT 59808

Health and Safety Plan for Phase 2 Wet Dredge

Contents

Contents (continued)

Contents (continued)

Contents (continued)

Contents (continued)

Contents (continued)

Contents (continued)

Tables

Appendices

List of Abbreviations, Acronyms, and Symbols

°	degree
ACGIH	American Conference of Governmental Industrial Hygienists
AGA	American Gas Association
AIHA	American Industrial Hygiene Association
ANSI	American National Standards Institute
AOC	Administrative Order by Consent {or Area of Concern}
APR	Air-Purifying Respirator
ARAR	Applicable or Relevant and Appropriate Requirements
ASSE	American Society of Safety Engineers
ASTM	American Society for Testing Materials
ATW	Authorization to Work
BBS	Behavior Based Safety
BMP	Best Management Practices
bpm	beats per minute
CAS	Chemical Abstracts Service (Number)
CAMU	Corrective Action Management Unit
CBI	BBS Critical Behavior Inventory
CDL	Commercial Driver's License
CERCLA	Comprehensive Environment Response, Compensation and Liability Act
cfm	cubic feet per minute
CFR	Code of Federal Regulations
CGA	Compressed Gas Association
CKD	Cement Kiln Dust
COC	Contaminants of Concern
CWA	Clean Water Act
dB	decibels
dB(A)	Decibels A-Scale
DNAPL	Dense Non-Aqueous Phase Liquids
DOL	Department of Labor
DOT	Department of Transportation
EMT	Emergency Medical Technician
Envirocon	Envirocon, Inc.
EPA	Environmental Protection Agency
FE JV	Foth Infrastructure & Environment/Envirocon Joint Venture
FID	Flame Ionization Detector
Foth	Foth Infrastructure & Environment, LLC
FR	Federal Register
GC	gas chromatography
GFCI	Ground Fault Circuit Interrupter
GFI	see GFCI (Ground Fault Circuit Interrupter)
gpm	gallons per minute
HAZ COMM	Hazardous Communication Standard
HEPA	High-Efficiency Particulate Air (filtration)
Hg	Mercury

HPAH	High density Poly Aromatic Hydrocarbons
HSO	Health and Safety Officer
HSS	Health and Safety Supervisor
HSM	Health and Safety Manager
IARC	International Agency for Research on Cancer
IDLH	Immediately Dangerous to Life and Health
ISCO	in-situ chemical oxidation
JSA	Job Safety Analysis
LEL	Lower Explosive Limit
LNAPL	Light Non-Aqueous Phase Liquid
LPAH	Low density Poly Aromatic Hydrocarbons
lpm	liters per minute
LUST	Leaking Underground Storage Tank
mg/m^3	milligrams per meter cubed
MGP	manufactured gas plant
mil	one mil equals 1/1000 of a unit
MOC	Management of Change
mppcf	million particles per cubic foot
MTTD	Medium Temperature Thermal Desorption
MUTCD	Manual for Uniform Traffic Control Devices
NEMA	National Electrical Manufacturer's Association
NEPA	National Environmental Policy Act
NFC	National Fire Code
NFRAP	EPA designated "No Further Remedial Action Planned" site
NFPA	National Fire Protection Association
NHTSA	National Highway Traffic Safety Administration
NIOSH	National Institute of Occupational Safety and Health
NPDES	National Pollutant Discharge Elimination System
NRR	Noise Reduction Rating
NSP	Northern States Power Company
NSPW	Northern States Power Company, a Wisconsin Corporation
NTP	National Toxicology Program OR Normal Temperature and Pressure
OSHA	Occupational Safety and Health Administration
OU	Operable Unit
OV	Organic Vapor (e.g., respirator cartridges)
OVA	Organic Vapor Analyzer
PAH	Poly Aromatic Hydrocarbons (see also PNA, HPAH and LPAH)
PAPR	Powered Air-Purifying Respirator
PCB	polychlorinated biphenyls
PEL	Permissible Exposure Limit (OSHA exposure standard)
PFD	personal flotation device
PID	Photo Ionization Detector
PLHCP	physician or other licensed health care professional
PM	Project Manager

PNA	Poly Nuclear Aromatic (see also PAH, HPAH, LPAH)
POTW	publically owned treatment works
ppb	parts per billion, 1 x 10-9
PPE	Personal Protective Equipment
ppm	parts per million, 1 x 10-6
psi	pounds per square inch
psig	pounds per square inch gauge
PVA	Polyvinyl Alcohol
PVC	Polyvinyl Chloride
QLFT	Qualitative Fit Testing
QNFT	Quantitative Fit Testing
RA	Remedial Action
HASP	*Health and Safety Plan for Phase 2 Wet Dredge*
RAO	Remedial Action Objectives
RCRA	Resource Conservation and Recovery Act
REL	Recommended Exposure Limit (NIOSH equivalent of the OSHA PEL)
RQ	Reportable quantity
ROD	*Record of Decision*
SAP	*Sampling and Analytical Plan*
SARA	Superfund Amendment and Reauthorization Act
S-B	Soil-Bentonite
SCBA	Self-Contained Breathing Apparatus
SCP	Safety Competent Person
SDS	Safety Data Sheet
SOW	Statement of Work
SPCC	Spill Prevention, Control and Countermeasures
SSE	Short Service Employee (refer to SSE Addendum to EI Procedure 1403.004)
STEL	Short-Term Exposure Limit (typically 15 minutes)
SVOC	Semi Volatile Organic Compounds
SWMU	Solid Waste Management Unit
TCLP	Toxicity Characteristic Leachate Procedure
TLV	Threshold Limit Value (ACGIH equivalent of the OSHA PEL)
TSCA	Toxic Substance Control Act
TWA	Time Weighted Average (typically 8 hours)
UEL	Upper Explosive Limit
UFC	Uniform Fire Code
UL	Underwriters Laboratory
USEPA	U.S. Environmental Protection Agency
VOC	Volatile Organic Compounds
WDNR	Wisconsin Department of Natural Resources
WWTP	Wastewater Treatment Plant

HEALTH AND SAFETY PLAN ACKNOWLEDGMENT SHEET

I acknowledge having received a briefing on this Health and Safety Plan and that I understand the requirements of this plan, including the potential for random or for-cause drug and alcohol testing. I further acknowledge that failure to follow the requirements of this plan may result in removal from this Site.

Printed Name	Company	Signature	Date

A. Site Introduction

This *Health and Safety Plan for Phase 2 Wet Dredge* (*HASP*) provides safety-related information and requirements specific to the task and work location(s) for the full-scale dredge operations. General requirements contained in the Envirocon, Inc. (Envirocon) *Health and Safety Program Manual* (Envirocon, 2013), along with this site-specific *HASP*, will be implemented except where noted. A hard copy of the Envirocon Health and Safety Program Manual will be available at the site for reference.

A.1. Scope

This *HASP* applies to the Ashland/Northern States Power Company, a Wisconsin Corporation (NSP/NSPW), Lakefront Site Remedial Action (RA); will be implemented by Foth Infrastructure & Environment/Envirocon Joint Venture (FE JV); and applies to the FE JV team members, subcontractors, and visitors to the Site. FE JV is responsible for control of the Site along with NSPW. The Site Superintendent is a direct employee of Envirocon, a FE JV team member, and is responsible for implementing the safety program. They are responsible for enforcing its compliance with the program with personnel performing duties on the Site and visitors.

While the Envirocon *Health and Safety Program Manual* serves as the reference program guidance, FE JV team members may implement additional requirements covering their personnel or activities under their direct control provided that the additional requirements are at least as protective of site personnel, the environment, and the community as described in the Envirocon *Health and Safety Program Manual*. Appendix A includes JF Brennan Co.'s Health and Safety Plan.

A.2. Site Description

The Site is located in Ashland, Wisconsin along the southern shore of Chequamegon Bay (Bay), which is part of southwestern Lake Superior. Approximately 40 acres of the National Priority List (NPL) Site includes 24 acres upland (onshore) and 16 acres offshore. This RA is strictly limited to the near shore and offshore sediments and debris of the Site and is bounded to the north by the recently constructed Breakwater, to the south by the shoreline/sheet pile wall, to the east by the East Peninsula boat launch and west by the West Peninsula located near the Ashland Marina.

A former manufactured gas plant (MGP) operated from 1885 until 1947 in the area of the Former NSPW Service Center above the lakefront on the Upper Bluff, where other contemporaneous industrial facilities operate; including a series of lakefront saw mills and wood treatment operations, as well as an active railroad corridor. The Schroeder Lumber Company operated in the location currently occupied by Kreher Park, and the city of Ashland and the county of Ashland each owned (and the City still owns) portions of Kreher Park. The Soo Line Rail owned and operated rail lines in Kreher Park for 116 years from 1871 to 1987, and that property is now owned by Canadian National Rail Line.

Kreher Park was formed from man-made land containing 4 to 5 feet of soil overlying wood debris deposited in the late 1800s by various sawmill operations.

A.3. History of Previous Investigations, Record of Decision and Remedies

The Site was added to the NPL in 2002. The U.S. Environmental Protection Agency (USEPA) and NSPW completed a *Remedial Investigation Report (RI Report)* (URS, 2007) */Feasibility Study* (*FS*) (URS, 2008) under an Administrative Order of Consent (AOC) for the entire Site. The USEPA issued the *Record of Decision (ROD)* (USEPA, 2010) in September 2010 and a Notice of Completion of the *RI Report/FS* AOC in December 2010.

NSPW installed a recovery system on the Former NSPW Service Center property in 2000 to collect non-aqueous phase liquids (NAPL) discovered in the Copper Falls Aquifer. In 2002, NSPW excavated the contaminated soil in a seep area in Kreher Park, installed a low permeability cap over the area, and installed a groundwater extraction well at the base of the Filled Ravine. NSPW excavated contaminated soil beneath St. Claire Street in 2003 where access and repair of utilities was required.

A.4. Project Scope of Work

The *ROD, as amended by the EPA's issuance of the "Explanation of Significant Differences" (ESD), anticipated to be signed and lodged in January 2017* describes the selected remedy for several areas associated with Phase 2 RA activities.

Task 1 – Mobilization of Equipment and Personnel, Site Preparation and General Construction Activities

Description of Activity

The FE JV will mobilize all personnel, materials, tools, and equipment necessary to complete containment system installation, sediment and debris removal from wet dredge activities in the Bay and along the shoreline, stabilization and loading of material for offsite transport, and restorative layer placement. The FE JV will require an area for lay down, parking and staging materials and equipment for the duration of the project.

Task 2 – Woody Debris Removal

Description of Activity

Woody debris will be removed from the lake bottom using excavators staged both on the shore and on a floating barge. Larger pieces of debris to be removed will require the excavators equipped with a grapple, debris rake, or conventional bucket with a thumb. Finer material such as wood chips or sawdust will be removed with a standard dredge bucket or environmental bucket. For the offshore removal operations, the removed debris will be transported to shore via a material barge. Once on shore, the woody debris will be transported (following sizing, if required to the sediment processing tent).

Task 3 – Security and Erosion Controls

Description of Activity

Site security will involve the daily monitoring of all perimeter fences at the site. Additionally when fences need to be removed, temporary construction fences will be placed. Temporary construction fences will be removed during daily remediation operations and replaced every night.

Throughout the project soil erosion control measures will be installed to control erosion of soils that are being excavated from the site. Approved control measures will be used such as the use of silt fence and covering of soils with polyethylene sheeting (Visqueen) to stop the flow of rain of water on the soil allowing soil to erode and wash off site. Determination for the installation of silt fence or the use of Visqueen will be made at the time of project activities.

The silt fence will be installed and maintained throughout the project. The determination for the use of these control measures will be based on the project activities performed in a day which may leave the site in a position that covering of soils may not be needed. Covering of storm drains will also be done to prevent any possibility of materials getting into them.

Task 4 – Barrier System Installation

Description of Activity

A barrier system will be placed in the Bay around the entire perimeter of the Wet Dredge area to control turbidity and sheens from drifting out of the project area. Posts will hold the curtain in place and will be clearly marked.

Task 5 – Sediment Dredging

Description of Activity

The FE JV will utilize a barge mounted excavator to mechanically remove sediment and debris from the Wet Dredge area. Dredged sediment will be loaded into material barges for transport to the offloading area.

Task 6 – Restorative Layer Placement

Description of Activity

Following dredging operations, restorative, granular backfill will be placed throughout the entire Phase 2 Wet Dredge Area. This procedure will be completed using the land excavator, barge mounted excavator used for dredging operations, and spreading equipment.

Task 7 – Sediment Processing

Description of Activity

An excavator will be utilized to offload sediment and load restorative layer material. The excavator may utilize various attachments based on the different type of material and job task. New processing equipment will be added for the Full Scale project. This includes, but is not limited to the following: vibrating grizzly/finer deck grid, two pocket conveyors with one belt scale, blade mill, pebble lime silo with PLC controlled auger feed, two jump conveyors, and radial stacking conveyor. The safe operation of this equipment will be addressed in specific task JSAs established and reviewed by site personnel prior to operation.

Task 8 – Crane Operations

Description of Activity

Crane operations will be utilized for launching segmental barges, hydraulic dredge, marine excavators, and other ancillary equipment used for the project. The tasks will include but are not limited to the lifting of equipment described above from shore to the water where they will be transported to the project site.

Task 9 – Site Restoration

Description of Activity

Once all necessary RA activities are completed, FE JV will restore the project site to the specifications shown on the project drawings. Following completion of restorative layer installation, FE JV will complete general housekeeping activities to bring the site to a neat and orderly appearance. An FE JV representative will tour the site with the client representative to ensure all tasks are completed to the site specifications and established punch list items have been addressed.

A.5. Tasks

The scope of work associated with this project includes supervision, labor, equipment and expertise to perform the following:

- Site mobilization tasks;
- Erosion controls;
- Water quality monitoring and sampling;
- Perimeter air quality and noise monitoring;
- Grubbing, site clearing;
- Site security fencing modifications for access;
- Installation of temporary building structures for material handling;
- Construct and/or maintain haul roads;
- Barrier system installation, integrity evaluation and maintenance;
- Mechanical and hydraulic sediment dredging;

- Post-mechanical and hydraulic interim and final confirmation sampling to confirm dredge completion
- Loader/excavator material handling;
- Crane operations;
- Surveying;
- Equipment fueling/spill containment;
- Sheet pile wall installation and protection measures (as applicable);
- Dewatering and impacted water management/treatment;
- Restorative layer placement;
- Processing of sediment (removal of oversize and debris);
- Sediment stabilization;
- Loading and hauling materials;
- Transport of stabilized material to a Subtitle D landfill facility;
- Site restoration;
- Maintaining and operating ancillary features; and
- Site demobilization tasks.

B. Basis

This section will discuss the basis in regulations, standards, and policies for the project. It includes Occupational Safety and Health Administration (OSHA) regulations, the NSPW Contractor Safety System, and Envirocon's *Health and Safety Program Manual*.

B.1. Preparation and Approval

This plan is based upon existing available information regarding the site and upon past experience at other sites. This document is also based on OSHA regulations, contractual specifications applicable to the scope of work, the client's health and safety plans and procedures. FE JV team members and lower tier subcontractors are required to adhere to all of these documents during the course of this project.

B.1.a. Prepared For

This plan was prepared for:

Northern States Power Company (NSPW)
414 Nicollet Mall-2
Minneapolis, MN 55401

B.1.b. Prepared By

This plan was prepared by and under the direction of:

David Hardy, CHST
Project Health and Safety Manager
Envirocon, Inc.
7878 Wadsworth Blvd, Suite 340
Arvada, CO 80003

B.1.c. Approvals and Modifications

This plan and future changes must be approved as follows:

1) The designated Project Manager, Denis Roznowski, is responsible for the final approval of this *HASP*.

2) After preparation and approval by the Project Manager and FE JV, this *HASP* will be submitted to the client in accordance with the applicable contract and specifications.

3) David Hardy, the Envirocon Health and Safety Manager, is responsible for implementation of this *HASP* and for any future modifications after preparation.

Note: Certified Safety and Health Professionals (CIH, CSP or CHST) working directly on the execution of this RA are hereby approved to make changes to this plan on an as needed basis during the execution of the work adapting to Site and work conditions.

B.2. Incident-Free Performance of Work

Incident-free performance means error-free project execution: no injuries, illnesses, property damage, community or environmental impacts, or incidents that could have resulted in these occurrences under different conditions. Incident-free performance does not happen by chance. It is achievable through the integration of safety into all management systems, the project process, and individual efforts. The FE JV believes that all incidents are preventable. In order to respond to employee emergencies, employees are asked to complete a Voluntary Employee's Emergency Information Data Sheet. This form is located in Appendix B.

B.3. Policies and Regulatory Basis

Key applicable regulations and standards are listed in Table B.3.

Table B.3. Some Important Applicable Regulations and Standards

Latest Revision	Contract Specifications Applicable to the Scope of Work
29 CFR 1910.20	Access to employee exposure and medical records
29 CFR 1910.38	Employee emergency plans
29 CFR 1910.95	Occupational noise exposure
29 CFR 1910.134	Respiratory protection
29 CFR 1910.120	Hazardous waste operations
29 CFR 1910.151	Medical services and first aid kit
29 CFR 1910.157	Portable fire extinguisher
29 CFR 1910.1000	Air contaminants
29 CFR 1910.1200	Hazard communication
29 CFR 1926	Construction Industry Standards

CFR = Code of Federal Regulations

B.4. Changing Conditions and Management of Change

B.4.a. Management of Change

The plan presents a realistic approach to the anticipated hazards at the site. It is expected that site conditions may vary throughout the duration of the project.

B.4.b. Changing Conditions

Changes in conditions and identification of previously unrecognized hazards are identified by the following processes:

- Site inspections by supervisory and site safety personnel;
- Observations and suggestions by all personnel;
- Proper planning for each new phase of operations;
- Authorization to Work (ATW) process and its required walk down;

- Job Safety Analysis Job Safety Analysis (JSA) for each new phase of operations;
- Communicating plans and controls to all affected employees;
- Accident investigations and lessons learned from this and other projects; and
- Contract modifications.

B.4.c. Response to Changes in Conditions

1) A risk assessment will be conducted in response to changing conditions.

2) An ATW form (Appendix C) will be completed by the work crew.

3) This plan, JSAs, and/or other plans shall be changed, as necessary, to reflect the risk assessment.

4) Changes in plans will be authorized by responsible individuals.

B.4.d. HASP and JSA Familiarization

The information presented in this plan will be reviewed with the employees during site-specific training to be completed before working on site. These site entry briefings will focus on the specific tasks of those being briefed. A copy of this plan will be available at all times on the site for anyone to review thoroughly and the crews for those tasks will be briefed on the appropriate JSA(s) to review (Appendix D). JSAs will highlight applicable controls from this plan. All assigned personnel, visitors, and regulatory personnel are therefore expected to be familiar with and comply with all aspects of this plan. If the safety requirements are unclear, each individual is responsible for getting clarification from their supervisor. The qualifications required for various tasks on this project are summarized in the training and qualifications section below.

B.5. Compliance

Failure to follow the rules and procedures prescribed in this document potentially jeopardizes the working environment of other employees. For this reason, the FE JV is prepared to enforce the progressive disciplinary procedures described in Section D.5.d, Discipline, for those who fail to follow the established policies and procedures for this project.

C. Site Organization and Key Personnel

29 CFR 1910.120 requires an effective site organization to be responsible for supervision of all work at hazardous waste sites. The purpose of this section is to describe this site's organization as it applies to this project.

C.1. Quality Assurance Project Manager: Peter Joy

The Quality Assurance (QA) Project Manager is responsible for oversight and management of all aspects of the project including health and safety, QA, construction, RD, equipment, and personnel.

- The Project Manager is responsible for project health and safety performance in accordance with incident-free performance goals;
- Conducting periodic site inspections;
- Participating in incident investigations; and
- Provides safety leadership through example and by holding all personnel assigned to this project accountable for their safety responsibilities.

C.2. Construction Manager: Brad Hay

The Construction Manager serves as the site's general supervisor in accordance with the requirements of 29 CFR 1910.120(b)(2)(i)(A). The Construction Manager is responsible for coordinating activities with the Project Manager and the Site Safety Officer (SSO). This includes:

- Enforcing the provisions of this *HASP*;
- Preparing for new tasks in advance of field operations in accordance with the Envirocon Field Operations Manual;
- Ensuring that a JSA has been completed before any new work commences;
- Ensuring an ATW has been completed by the crew;
- Briefing crew members before assigning them to the new task;
- Ensuring that employee safety suggestions are fairly and respectfully evaluated and that employees are informed of the outcome of the evaluations;
- Monitoring the conduct of operations in the field to ensure safe delivery of a quality product for the client;
- Supervising subcontractors in accordance with this plan; and
- Ensuring that injured personnel (with or without life threatening injuries) are escorted to medical treatment by the SSO or other supervisory personnel.

C.3. FE JV Director of Health and Safety: Frank Sullivan, CIH, CSP, PMP

The FE JV Director of Health and Safety is responsible for the development and implementation of the FE JV Health and Safety Program. The program contains accident prevention plans and procedures and other related plans, policies and procedures required by OSHA standards. The FE JV Director is responsible for:

- Ensuring that all health and safety issues on site are resolved;
- Ensuring that employee complaints are addressed in accordance with FE JV safety policies and procedures; and applicable laws;
- Ensuring that all employee complaints received by the director are kept confidential;
- Ensuring appropriate investigation of all incident reports;
- Ensuring that audit findings are corrected in accordance with FE JV safety policies and procedures; and applicable laws; and
- Providing professional support for the Project Manager's Health and Safety Program.

C.4. Project Health & Safety Coordinator: Chris Seider

The Project Health & Safety Coordinator provides overall coordination between the different elements of the overall project, specifically between the professional service-related activities such as pre-design investigations work, post mechanical/hydraulic interim sampling, final confirmation sampling, air/water quality monitoring and sampling, and vibration monitoring; and construction activities.

The Project Health & Safety Coordinator is responsible for the following:

- Coordinating health and safety program implementation between the Program and Project Manager; and
- Verifying that any health and safety issues that are identified by the Project Health & Safety Manager or other personnel during periodic inspections and audits of the project site are addressed.

C.5. Project Health & Safety Manager: David Hardy, CHST

The Project Health & Safety Manager is the senior health and safety professional assigned to the construction elements of the project and provides technical assistance to the Project Manager and on-site health and safety personnel. The Project Health & Safety Manager reports to the Corporate Director of Health and Safety with regard to project health and safety issues.

The Project Health & Safety Manager is responsible for the following:

- Developing and implementing the Project Manager's site-specific health and safety program and procedures;
- Providing professional technical support for the Project Manager with regard to all matters of health and safety associated with the project;
- Technical supervision of the Health and Safety Officers (HSO) and technicians assigned to the project;
- Assisting HSOs in developing and reviewing project health and safety procedures, hazard analysis and other supporting documents;
- Implementing and administers this *HASP*;
- Designating Site Competent Person;
- Conducting periodic inspections and audits of the project site for the Corporate Director of Health and Safety;
- Coordinating the activities of other health and safety department personnel supporting the project with the senior health and safety official on site and the Project Manager;
- Coordinating all health and safety activities with the Project Manager; and
- In the event that personnel fail to adhere to established safety guidelines, recommending disciplinary and/or corrective actions to the Project Manager.

C.6. Project Health & Safety Supervisor: Dan Allen

The Project Health & Safety Supervisor is the senior designated HSO assigned to the project and is responsible for the following:

- Developing and implementing the Project Manager's site-specific health and safety program and procedures;
- Providing professional technical support for the Project Manager with regard to all matters of health and safety associated with the project;
- Technical supervision of the HSOs and technicians assigned to the project;
- Assisting HSOs in developing and reviewing project health and safety procedures, hazard analysis and other supporting documents;
- Implementing and administers this *HASP*;
- Conducting periodic inspections and audits of the project site for the Corporate Director of Health and Safety;
- Coordinating all health and safety activities with the Project Manager; and

- In the event that personnel fail to adhere to established safety guidelines, recommending disciplinary and/or corrective actions to the Project Manager.

C.7. Site Health & Safety Officer(s): Dan Allen

The HSO(s) are the employees designated as the health and safety competent persons for this project.

The HSO(s):

- Serves as the OSHA "Site Safety and Health Supervisor" as defined in the HAZWOPER Standard 29 CFR 1910.120/1926.65(b) (Note: This includes authorization to administer the requirements of this plan, the Envirocon Health and Safety Program, and applicable OSHA regulations on site);
- Implements the provisions of this *HASP*;
- Serves as a safety and health competent person (SCP);
- Conducts and documents daily site safety inspections;
- Maintains the site health and safety logs;
- Maintains health and safety records on site;
- Reports and documents incidents and issues related to site safety;
- Assists the Project Manager with incident investigations related to health and safety;
- Supervises decontamination of personnel and equipment;
- Conducts monitoring tasks on site;
- Monitors the use of personal protective equipment (PPE) to ensure proper usage;
- Inventories and inspects PPE;
- Selects PPE within the guidelines of this plan;
- Ensures all personnel are qualified and "Fit for Duty;"
- Inspects first aid kits/fire extinguishers and emergency response equipment;
- Accompanies employees, as needed, to clinics or other health care providers to ensure proper care and evaluation of injured or ill employees; and
- Reports and coordinates return-to-work issues with the Corporate Director of Health and Safety.

C.8. Site Competent Persons

OSHA's general safety and health provisions from the construction industry standards (29 CFR 1926.20(b) and 29 CFR 1910.120(b)(2)(i)(B)) include accident prevention responsibilities. Such programs shall provide for frequent and regular inspections of the job sites, materials, and equipment to be made by competent persons designated by the employers. OSHA's regulations regarding scaffolding, excavation and hazardous waste operations have similar requirements. The construction safety competent person is defined in 29 CFR 1926.32 to mean "one who is capable of identifying existing and predictable hazards in the surroundings or working conditions which are unsanitary, hazardous, or dangerous to employees, and who has authorization to take prompt corrective measures to eliminate them."

Competent persons are designated on the form that follows this section. Each competent person is given responsibility and authority for certain aspects of safety on site. It is important for each competent person to recognize the limits of their own knowledge, training, experience and capability. It is the responsibility of each competent person to act within the limits of their own knowledge, training, experience, and capabilities.

C.8.a. Site Safety Competent Persons

The HSO(s) serve as the general site competent person (SCP) responsible for accident prevention in accordance with 29 CFR 1926.20 and 29 CFR 1910.120(b)(2)(i)(B). The competent person is responsible for, and authorized to act to ensure that personnel are not working under conditions which are unsanitary, hazardous, or dangerous to their health or safety.

1) The competent person's accident prevention responsibilities includes:

    a. Frequent and regular inspections of the job site;

    b. Inspections of materials on site; and

    c. Inspection of equipment on site.

2) The Project Manager may designate additional competent persons.

3) Designated persons, in accordance with 29 CFR 1926.32, must be capable of identifying existing and predictable hazards in the surroundings or working conditions which are unsanitary, hazardous, or dangerous to employees.

4) Once designated, these competent persons share the Site Safety Officer's authority to take prompt corrective measures to eliminate these hazards.

C.8.b. Excavation Competent Person

This individual will have direct supervisory control over all excavation activities involving entry into excavations or trenches. All competent persons shall be authorized and acknowledge authorization in the Competent Person Designation form located in Section C.10.

1) Compliance standards

The excavation competent person ensures compliance with 29 CFR 1926, Subpart P (1926.650 thru 652). The scope of these regulations includes all excavations (e.g., hand digging, equipment excavation, with or without personnel entry). Additional competent persons may be designated by the Project Manager in consultation with the Corporate Director of Health and Safety. Designation will be based on experience and knowledge of these standards.

2) Specific duties include:

   a. Assists Project Safety Supervisor with planning excavations;

   b. Ensures that utilities are located and marked (underground or overhead hazards) prior to excavating. Hand dig to locate when excavating within six feet of utilities;

   c. Where personnel entries are involved, classifies soils in accordance with OSHA soil classification in 29 CFR 1926 Subpart P;

   d. Ensures the use of protective systems in accordance with Subpart P where personnel entries are required;

   e. Monitors all excavation activities for associated hazards;

   f. The competent person is authorized by the Project Safety Coordinator to take corrective action to eliminate hazardous or dangerous situations. This includes halting excavation operations and/or removing personnel from excavations; and

   g. Performs inspections of excavations prior to the start of work, as needed throughout the shift and after every rainstorm.

C.8.c. Scaffold Competent Person

This individual(s) will have direct supervisory control over all scaffold activities. All competent persons shall be authorized and acknowledge authorization in the Competent Person Designation form located in Section C.10.

1) Compliance standards

   The scaffold competent person ensures compliance with 29 CFR 1926, Subpart L (1926.451 thru 453). Additional competent persons may be designated by the Project Manager in consultation with the Corporate Director of Health and Safety. Designation will be based on experience and knowledge of these standards.

2) Specific duties include:

   a. Supervises scaffold erections:

   b. Inspects scaffold repairs:

   c. Inspects scaffolds daily: and

d. The competent person is authorized by the Project Safety Coordinator to take corrective action to eliminate hazardous or dangerous situations. This includes halting operations and/or removing personnel from scaffolds.

C.9. Lower Tier Subcontractors

Lower tier subcontractors are responsible for supervising their work and personnel in accordance with this plan and applicable site policies and procedures. Regardless of other requirements, lower tier subcontractors shall adhere to all federal, state, and local laws and regulations. In particular this includes the requirements of 29 CFR 1910.120/1926.65 HAZWOPER Standards. Lower tier subcontractors' personnel will be supervised in accordance with the same requirements and standards as FE JV and subcontractor personnel. Where their programs, policies, and procedures exceed the requirements of this document and the applicable site policies and procedures, the lower tier subcontractor may use their own policies and procedures to implement these requirements. Regardless, they must at a minimum meet the requirement established in this *HASP*.

C.9.a. Site Access Control

FE JV is in part responsible for controlling access to this site along with our client. FE JV reserves the right to deny access to personnel who in their opinion pose a hazard to operations through serious, willful, or repeated violation of safety requirements; and those personnel who are not otherwise qualified to work on site.

This *HASP* does not necessarily address all of the hazards specific to lower tier subcontractors' work. Lower tier subcontractors shall submit either a Site-Specific HASP (Appendix A) for their particular operation(s) or prepare and submit appropriate JSA(s) to append to this plan.

C.10. Competent Person Designation Form

COMPETENT PERSON DESIGNATION		
The following individual(s) has been designated as the "Competent Person," meaning one who is capable of identifying existing and predictable hazards in the surroundings or working conditions which are unsanitary, hazardous, or dangerous to employees, and who is hereby authorized by Envirocon to take prompt corrective measures to eliminate them. The person(s) named below has knowledge of the systems, equipment, conditions and procedures in relationship to the proper use, inspection, manufacturers' recommendations and instructions, and maintenance as designated below. This person(s) has been delegated the responsibility to coordinate all activities and operations as defined by the designation(s). In carrying out these responsibilities, it shall be the duty of the competent to act within the limits of their knowledge and training.		
Competent persons added to the list must be approved by the Project Manager and HSO.		
NAME/DESIGNATION(S)	**COMPANY**	**COMPETENT PERSON**
Dan Allen	Envirocon	☒Excavation, ☒Site Safety, ☒Scaffolds
Project Manager's approval: _____; HSM/HSO Approval: _____ Acknowledged: _____ Date _____ Competent Person's Signature		
Dave Gehring	Envirocon	☒Excavation, ☒Site Safety, ☒Scaffolds
Project Manager's approval: _____; HSM/HSO Approval: _____ Acknowledged: _____ Date _____ Competent Person's Signature		
Brad Hay	Envirocon	☐Excavation, ☒Site Safety, ☐Scaffolds
Project Manager's approval: _____; HSM/HSO Approval: _____ Acknowledged: _____ Date _____ Competent Person's Signature		
	Envirocon	☐Excavation, ☐Site Safety, ☐Scaffolds
Project Manager's approval: _____; HSM/HSO Approval: _____ Acknowledged: _____ Date _____ Competent Person's Signature		

C.11. Authorization to Work

C.11.a. Discussion

1) The RA activities for the Site will require several contractors and subcontractors to be working in close proximity and using paths for access to tasks that pass through, or are co-located in the work zones of an unaffiliated work group. It is essential that a procedure be established that mandates a disciplined and regular communication method to protect personnel from an unexpected hazard not inherent in their own task as they move and work around the Site.

C.11.b. Basis

1) OSHA Directives CPL 02-00-124 and CPL 2-0.124−Multi-Employer Citation Policy (Dec. 10, 1999) describe the requirement for multi-employer worksites to perform hazard analysis identify how each employer may be in one or several categories: Controlling, Exposing, Creating and/or correcting a recognized hazard.

C.11.c. Planning Requirements

1) Every employer on the Site will be required to have each employee or subcontractor under their supervision perform the following:

    a. Review specifically the task;

    b. Review the hazards associated with performing the task;

    c. Walk down the work area at some point in the planning process;

    d. Review that controls for each hazard that will protect:

        i. workers,

        ii. other personnel entering their work zone,

        iii. the environment, and

        iv. the public;

    e. Ensure the tools, personal protective equipment, monitoring, and work zone controls are available and ready for implementation;

    f. Identify any paths of travel through another contractor's work zone; and

    g. Determine whether another contractor is likely to also work in the proximity of their task.

2) The Construction Manager shall be responsible for ensuring that adequate planning is performed. Employees are expected to participate in all above elements of the planning process.

3) Planning shall occur if a task or work location changes, but at a minimum shall be pre-shift before the commencement of any activity. The required crew walk down of the work area may occur at the end of a shift in anticipation of the following calendar day's activities if weather or other changes have not occurred during the interim.

C.11.d. Documentation

1) The document that establishes that the above elements have been performed is the ATW. Appendix C provides examples of these. Standardization of a common-use form is not the objective. The forms may be customized, and a short form for a short task is acceptable.

2) All personnel who participate in the task must sign the ATW. The Construction Manager, or HSO, must also sign the ATW.

3) A copy of the ATW must be immediately available to the work crew, and in the trailer used by the Construction Manager or HSO.

4) The ATW is not a substitute for a JSA. It is a way to make sure a JSA has been prepared and is correct in identifying hazards and setting controls.

C.11.e. Multi-Employer Sites

1) If a work area is such that a crew may be exposing another work group to hazards, at a minimum, they must do the following:

    a. Review and sign each other's ATWs: and

    b. Document on each ATW how hazard communication will be conducted.

        Examples are:

        i. Channel 2 of radio to let crew know when water truck will pass.

        ii. Flagger at gate entrance to monitor haul truck and cross-traffic.

2) The employer who is responsible for creating or controlling a hazard has final say over the means by which they will control the hazard including setting controls and conditions in their ATW that other work crews entering their work zone must follow.

3) Contractors or their employees responsible for preventing the exposure to site hazard, but willfully deficient in doing so, or deficient in correcting a recognized hazard will be subject to disciplinary or contractual processes. Examples of deficiencies would include;

    a. No barricades, warnings, monitors, preventing exposure to an open vertical wall trench in a common use area

    b. Personnel using a route through a materials handling area where loaders/excavators running without identifying the route on an ATW, and checking with that work area supervisor on ATW controls.

C.11.f. Safety Time-Out

1) Any employee may call a safety time-out if an individual who has not signed an ATW enters a work area with an identified hazard.

2) Safety time out may also be called as described in Section G.3.e.

C.11.g. Best Management Practices

The following are suggestions demonstrating implementation Best Management Practices (BMP).

1) Safety meetings or Plan-of-the-Day sessions that include subcontractors and as many other FE JV team member's subcontractors as possible. Safety meetings may actually benefit from being held at the end of shift for the next day's activity.

2) Large sign at every site entrance instructing every entrant to sign in and get site briefing from SSO/Superintendent. The visitor/vendor/new hire can then be guided through the ATW process.

3) Site map or bulletin board that posts all active shift ATWs to facilitate a quick check on activities and hazards.

4) Regular spot checks by Superintendents and SSOs in the field for work groups to ensure they have participated in the ATW process.

5) The required crew walk down of the work area may occur at the end of a shift in anticipation of the following calendar day's activities, if weather or other changes have not occurred during the interim.

D. Site Security

D.1. Site Security and Controls

This section deals with site access and general project rules, physical security of the project work areas, and the controls related to waste management and access to impacted areas to ensure qualifications of personnel.

The work areas associated with this project are within the confines of the Site. Site security will be maintained to prevent access and vandalism to the Site.

D.2. NSPW Screening of Personnel Needing Reoccurring Site Access

NSPW requires direct compliance with their in-house security process prior to being granted site access. Access to the site may be denied if it is determined that a threshold of unacceptable security risk is in evidence. This process is comprised of two parts:

1) Personal questionnaire (residences, criminal history, etc.) and

2) Security screening that will look at:
    a. Criminal records
    b. Driving records
    c. Social security number trace

D.3. FE JV Security Responsibilities

D.3.a. Security Officer

The FE JV Project Manager is responsible for the overall security of the project site.

1) The Project Manager will be assisted in these duties by the Project Health & Safety Supervisor who will serve as security officer.

2) The security officer's responsibilities include:

    a. Ensuring that all personnel entering the site are in compliance with NSPW's security procedures.

    b. Ensuring that authorized personnel conduct themselves in accordance with the established security and safety requirements.

    c. Ensuring that personnel sign in and sign out at the beginning and end of each shift, and visitors are directed to the main office.

    d. Establishing and maintaining appropriate exclusion zone boundaries around contaminated areas.

    e. Work areas and zones shall be adequately marked and posted along access routes to give warning of restrictions to visitors.

f. Ensuring that adequate barriers and warnings are used to prevent site access by the general public or unqualified personnel.

g. Providing adequate surveillance and lock-up for:

   i. Trailers and storage facilities;

   ii. Fuel and hazardous materials storage;

   iii. Materials of potential homeland security concern;

   iv. Heavy equipment, vehicles, and related equipment; and

   v. Small equipment and pilferable items.

h. Ensuring that heavy equipment is adequately secured after working hours to prevent theft or mischief.

D.4. Public Safety

The Site perimeter must be secured to prevent access to ensure safety for neighborhood children, associated with a nearby school, or other vulnerable people that may be attracted to the work area.

The work area shall be suitably delineated (i.e., as appropriate for a construction site with recognized chemical contamination) in order to prevent unauthorized entry. Typical signage language may read as follows:

> "Warning." Materials on-site may pose a risk to public health through direct contact. Entry is restricted. Authorized personnel must sign in at Main Office or call (insert phone number) for further information."

Visitors shall be directed to the Project Manager's designated representative to seek authorization when appropriate. Visitors shall be logged onto the site. Visitors that are not qualified for work in the Exclusion Zone shall be escorted or otherwise prevented from accidentally entering the Exclusion Zone.

All unattended equipment will be secured physically and mechanically during periods of nonuse. Keys shall be removed from equipment and stored in a secure location.

D.5. Project Rules

The project rules have been developed by FE JV and NSPW to create a problem-free and rewarding work environment; one in which the employee understands what is expected of them on the project site. An employee who fails to maintain at all times the proper standards of conduct or who violates any of the following rules and regulations may be subject to disciplinary action, including but not limited to, termination of employment or denial of access.

D.5.a. Unacceptable Conduct

Unacceptable employee conduct and/or violation of a project rule or requirement may be reason for disciplinary action up to and including suspension without pay, termination of employment, or denial of access to the work area or client facilities. Examples of unacceptable employee (including contractor and subcontractor) conduct and/or rule violation are as follows:

- Being mentally or physically unfit for duty at any time while on the job, such as reporting to work under the influence of drugs or alcohol, or when ill, fatigued, or under mental stress to a degree that could affect job performance or safety.
- Possessing, when not authorized, project's or other person's property or services or theft of the same;
- Altering, damaging, or mutilating project's or other person's property;
- Violating the security rules;
- Reporting or badging for other employees or other identification misrepresentation;
- Making or stating false claims or falsifying reports or records;
- Refusing to submit to a search;
- Refusing to submit to drug and alcohol screening or testing or other similar inspections;
- Possessing or using alcoholic beverages, controlled substances, or weapons on the project;
- Using or possessing keys or other devices used for lock opening without specific permission;
- Sleeping on the project;
- Improperly using, or failure to use, toilet facilities;
- Failure or refusal to perform assigned work as directed;
- Fighting;
- Negligence resulting in an infraction of health and safety or project rules or requirements;
- Taking unauthorized work breaks;
- Engaging in horseplay of any kind;
- Engaging in gambling or the sponsoring of raffles;
- Not using trash receptacles or otherwise creating unsanitary conditions;

- Smoking, using tobacco, or eating in prohibited areas;
- Unauthorized cooking on the project;
- Selling food, beverages, or other items on the project;
- Failure to display identification badge or area access credentials in the proper manner and in a conspicuous place;
- Violating health and safety or project rules or requirements;
- Sexual harassment;
- Abusing equipment, vehicles, or other FE JV member's property or rentals;
- Operating equipment or vehicles without authorization and proper qualification;
- Failure to operate equipment or vehicles in the manner specified by the manufacturer (including proper maintenance and repairs);
- Not reporting use of prescription drugs;
- Not reporting equipment or material damage;
- Not reporting an accident or incident; and
- Displaying pornographic, sexually explicit or otherwise offensive photographs, calendars, or other materials that may be objectionable to other individuals or groups.

The above is not an all-inclusive list. If you are unsure what may constitute unacceptable behavior, ask your Construction Supervisor.

D.5.b. Prohibited Articles, Materials, Substances

The use, possession, concealment, transportation, promotion, or sale of the following items or substances is prohibited on site premises. Employees who violate this policy will be subject to disciplinary action up to and including removal from site and/or termination. Project management reserves the right to conduct drug and/or alcohol search and screening consistent with NSPW's facility policy.

- Illegal, look-alike, designer drugs and drug paraphernalia;
- Controlled substances, such as medications, when usage is abused;
- Valid medications, when not kept in marked prescription bottles;
- Alcoholic beverages;
- Firearms, weapons, and ammunition;
- Unauthorized explosives;
- Stolen property or contraband;
- Unauthorized cameras or photographic equipment; and
- Unauthorized recording devices

D.5.c. Substance Abuse

It is the policy of FE JV and NSPW (Policy 9.3 Alcohol and Drug-free Workplace) to run a drug-free workplace.

1) Substance abuse policy and program description are contained in Procedure 1403.006. The detailed procedures for performing substance abuse tests are contained in the medical surveillance procedures (Procedure 1403.005M.f).

2) On-site personnel are subject to the following substance abuse testing in accordance with procedures described above:

    a. Pre-employment and pre-project
    b. Post-accident
    c. Random
    d. Reasonable suspicion

3) It is not anticipated that for the purpose of the FE JV random substance abuse testing that a common pool be established, but it is the requirement of this *HASP* that the FE JV shall separately and faithfully comply independently with their own random selection method from their designated pool.

D.5.d. Discipline

FE JV reserves the right to take disciplinary action, at its discretion, up to and including suspension or termination of employment or denial of access to the site work areas, depending on the severity of the violation.

1) At the discretion of management, suspension with/without pay may be given in lieu of discharge.

2) FE JV members should refer to their primary employer's Employee Information Manual for policies and procedures related to employee conduct and disciplinary action.

3) Verbal warnings and written reprimands are forms of discipline used to document and intended to correct, undesirable actions.

4) Unacceptable conduct or failure to adhere to established policies and procedures willfully or repeatedly may be subject to removal from this project and/or termination.

D.5.e. Subcontractors

Subcontractors shall also adhere to established policies and procedures applicable to this project site.

1) Subcontractors are responsible for disciplinary actions regarding their own employees and their lower tier subcontractors.

2) Failure of subcontractor employees to adhere to policies and procedures as described in this document will result in verbal or written warnings to the responsible subcontractor.

3) FE JV reserves the right to permanently or temporarily remove and bar subcontractor employees from the project site. Unacceptable conduct or failure to adhere to established policies and procedures willfully or repeatedly may result in such removal from the project site.

D.6. Communications

Personnel in the Exclusion Zone will remain in constant communication or within sight of the Project Manager, or his\her representative. Two-way radio is the primary method of communication.

1) If radio communication and hand signals are not feasible:

    a. The Project Manager will identify the site activities that can continue without communication, if any; and

    b. If necessary, one long air horn signal will be used to evacuate the site until communications have been restored.

2) Emergencies

    a. One long or continuous horn blast.

    b. Unless otherwise directed, all personnel will leave the Exclusion Zone.

    c. The audible signals in Table D.6, using an air horn, will be used as appropriate:

Table D.6. Emergency Signals

One long or continuous blast	Emergency, including fire/explosion Evacuate unless otherwise directed
One short blast	Attention-getter; stop work and assemble at Contamination Reduction Zone
Two short blasts	All is clear

D.7. Site Access

Access to the site shall be limited to those personnel that are qualified and have an acceptable (in the judgment of the client facility's designated representatives and the Security Manager) reason for being on site. Continuing access is further conditioned on adherence to the established site policies and procedures.

D.7.a. Motor Vehicles

Privately owned vehicles are subject to site rules and regulations when operated on site. Seat belts are required for all vehicle drivers and passengers when the vehicle is in motion.

D.7.b. Parking

Parking areas are provided for employee vehicles as designated by the client's project manager. Privately owned vehicles are prohibited from entering the work areas. Employees who illegally park in fire lanes, areas posted with no parking signs, handicapped parking spaces, or visitor parking spaces are subject to disciplinary action and removal of the vehicle at the workers expense.

D.7.c. Inspection

All employees are subject to search upon entering or leaving the job site.

D.7.d. Cameras/VCRs

No photos or recordings are permitted without prior authorization from site management.

D.8. Contamination Control Boundaries

The HSO is responsible for establishing and maintaining contamination control boundaries and supervising decontamination.

D.8.a. Postings

All work areas and zones shall be posted and demarcated adequately in order to communicate the following:

1) The nature of the boundary.
2) The hazards associated with the area.
3) Applicable controls, work rules or restrictions associated with the area.

D.8.b. Work Areas

The work area, for purposes of this project, is that area defined by hazardous waste and supporting operations. The work area is that area that is regulated by 29 CFR 1910.120 and/or 1926.65.

D.8.c. Exclusion Zone

The Exclusion Zone is that part of the work area where, at a given time, workers may potentially come in contact with contaminated materials. This contact is generally defined as inhalation of airborne levels exceeding site-specific action limits or 50% of established exposure limits (OSHA or American Conference of Industrial Hygienists [ACGIH]). Contact also includes any ingestion, skin contact, injection, or other contact route of exposure to materials exceeding USEPA or other established levels of contamination for the site.

D.8.d. Regulated Areas

Regulated areas are those areas managed in compliance with certain vertical standards contained in the following OSHA Subparts:

- 29 CFR 1910, Subpart Z - Toxic and Hazardous Substances

- 29 CFR 1926, Subpart D - Occupational Health and Environmental Controls
- 29 CFR 1926, Subpart Z - Toxic and Hazardous Substances

Regulated areas will be established as a form of Exclusion Zone, as described in the applicable standard.

1) Typically, these areas will require special training and medical qualifications as described in the applicable standards.

2) In establishing these areas the HSO shall rely on the guidance of a qualified person, familiar with the applicable regulations.

D.8.e. Contamination Reduction Zone

The Contamination Reduction Zone is that part of the work area between the Exclusion Zone and support areas where contamination from the Exclusion Zone is controlled in such a way as to remove the potential for contaminating support areas.

D.8.f. Support Area

The support area is that part of the work area where supporting tasks are conducted, and where the potential for exposure to contaminants has been fully controlled (i.e., personnel are not exposed to potential contact with contaminants).

D.8.g. Boundaries

Boundaries are established by the HSO based on the definitions above as compared to actual site conditions as monitored. Boundaries are flexible and should reflect current site conditions.

1) Boundaries are to be marked with suitable barriers such as yellow banner guards, brightly colored ropes, barricades, or orange snow fence to clearly establish the specified areas and the applicable regulations for that area.

2) If rope is used, pennants should be tied to the rope to help increase the visibility to foot and vehicle traffic and to provide a suitable warning.

D.9. Decontamination

The HSO is responsible for establishing and supervising decontamination on site. The following procedures are intended to establish guidelines for this purpose. As work progresses, control zones may be altered. It is essential that the HSO adjust this process as necessary to ensure that:

- Personnel and equipment leave the site free of contamination; and
- Contamination is not spread to other areas on site.

D.9.a. Contamination Reduction Zone

Contamination Reduction Zone(s) are those areas established for the purpose of transition between an Exclusion Zone and adjoining areas. Contamination Reduction Zone(s) should be

established for personnel and/or equipment to decontaminate during exit from an Exclusion Zone into:

1) Clean support areas; and/or
2) An adjoining Exclusion Zone with different or lesser contamination.

D.9.b. Frequency

1) All equipment will be inspected and be adequately decontaminated to avoid cross-contamination when moving out of an Exclusion Zone.

2) All equipment will be decontaminated before leaving the site.

3) All personnel will be decontaminated before leaving a designated Exclusion Zone.

4) Decontamination of equipment shall be documented using the Equipment Decontamination Log Form located in Appendix E.

D.9.c. Personnel Decontamination Procedures

1) Entering contaminated area through Support Zone:

    a. Pick up clean PPE and boots.

    b. All donning of clothing and equipment, taping, etc. is done here.

    c. Equipment contaminated from the preceding day is to be picked up in the contamination control area when exiting the decontamination area.

    d. Proceed to contamination control area.

2) Entering Contamination Reduction Zone:

    a. Prior to entering this area, be sure that all PPE is in good working condition.

    b. Conduct final inspection of tape and PPE.

    c. In Exclusion Zone.

3) Exiting Exclusion Zone:

    a. Personnel and equipment leaving the Exclusion Zone shall be thoroughly decontaminated.

    b. The following protocols shall be used for the decontamination stations according to the level of protection as follows. Where a step involves an article that is not prescribed, skip the step.

Table D.9.c. Decontamination Procedures

	Level C	Level D
1	equipment drop	equipment drop
2	outer boot rinse	outer boot rinse
3	outer boot removal	outer boot removal
4	outer glove removal	outer glove removal
5	remove hard-hat	remove hard-hat
6	remove respirator	NA
7	wash respirator	NA
8	rinse respirator	NA
9	Tyvek® removal	Tyvek® removal
10	remove inner gloves	NA
11	wash hands and face	wash hands and face
12	change to street clothing	change to street clothing

D.9.d. Contingency Plan – Emergency Decontamination – Evacuation to Support Areas for Mobile and Immobile Victims

This procedure applies to circumstances requiring exit decontamination. Emergency decontamination procedures are intended to be a guideline. Depending on the nature of the actual emergency, response personnel and evacuees will ultimately be responsible for weighing the risks of the emergency against the risk of incomplete decontamination.

1) Exclusion Zone evacuation to Support Zone areas.

    a. The main objective in this case is to shed contaminated materials quickly (with the idea that discarded articles can be decontaminated later when the emergency is over).

2) Mobile victims will be expeditiously evacuated from the area for medical treatment in support areas.

    a. Victims will be decontaminated (to the degree this can be safely and expeditiously accomplished).

    b. Emergency Medical Technicians and medical facilities must be advised that the employee may still have some contamination.

D.9.e. Equipment Decontamination

1) Equipment decontamination for release from the site will be performed on the facility decontamination pad.

2) Decontamination of equipment will be documented using the Equipment Decontamination Log form located in Appendix E.

3) Prior to exiting an Exclusion Zone, the equipment operator will ensure that the equipment is inspected for visible gross contamination. Visible gross contamination will be removed using shovels and hand equipment as necessary to prevent cross-contamination of the site. If necessary, a low pressure water hose will be used to remove materials.

4) Before release from the site, all equipment will be thoroughly decontaminated at the decontamination pad using water hoses, low pressure mechanical washers as necessary to remove visible contamination.

    a. Initially, equipment will be brushed free of contaminated materials with brooms. Equipment coming from exclusion zone tasks will be washed, if necessary, with high-pressure hoses. Special attention must be given to mud flaps, wheel wells, tracks, undercarriage and foot surfaces (cab floor, control pedals, or walking boards).

    b. If water is used, the vehicles will be held in the area for a short time to allow for collection of drippings.

    c. Excavators/loaders moved from one area to another will have wheels/tracks frisked and cleaned and buckets wrapped in plastic.

    d. Following decontamination and prior to release the Project Manager or a designated alternate, shall be responsible for insuring that each piece of equipment (i.e., monitoring instruments, tools, generators, etc.) has been sufficiently decontaminated.

    e. The final inspection for release will be logged and the log entry documented to the Project Manager.

5) If material is judged as un-cleanable, it will not be used outside the Contamination Zone and will be disposed of at the end of its usefulness.

D.9.f. Small Equipment Procedure

Surface debris and dirt will be removed from small equipment and tools with vigorous brushing.

D.9.g. Disposition of Decontamination Wastes

All equipment and solvents used for decontamination shall be decontaminated or disposed of with the established waste streams.

D.10. Waste Management and RCRA Compliance

The purpose of this procedure is to establish site-specific practices for compliance with environmental requirements of Resource Conservation and Recovery Act of 1976 (RCRA). The scope of this procedure includes all work conducted under the project heading.

D.10.a. Training

All personnel responsible for any aspect of waste handling on site shall receive a briefing on this procedure. Training will be documented and submitted as a safety meeting record. Personnel files regarding qualifications on site will be updated accordingly and maintained by the HSO.

D.10.b. Hazardous Waste Manager

1) The Hazardous Waste Manager for this site will be designated by the Project Manager.

2) The Hazardous Waste Manager is responsible for compliance with RCRA and associated environmental compliance standards.

3) Envirocon's Construction Manager or the Project Manager's designated representative shall serve as the QA/Quality Control (QC) Engineer responsible for hazardous waste coordination for Envirocon's activities regarding waste materials. The QA/QC Engineer shall ensure that:

    a. The instructions of the client's Hazardous Waste Manager are strictly followed by Envirocon personnel; or

    b. In the event of disputed procedures, the QA/QC Engineer shall immediately notify the Project Manager of the concern for resolution before proceeding.

D.10.c. Reporting Incidents

1) All incidents must be reported in accordance with the project *HASP*.

2) The Construction Supervisor is responsible for ensuring that the Hazardous Waste Manager is informed of any spills.

3) This includes, but is not limited to, the following:

    a. Accidents (with or without damages);

    b. Finding unusual material conditions (e.g., previously disturbed soils, materials with unusual odors, materials with unusual coloration, etc.);

    c. Spills of remediation waste; or

    d. Spills of lubricants, coolants, fuels, or any other hazardous materials.

D.10.d. Waste Stream Management

1) All waste must be segregated into the established waste streams. It is very important not to mix waste streams unless directed by the Hazardous Waste Manager.

2) The QA/QC Engineer will be responsible for field identification and sorting in accordance with the directions of the Hazardous Waste Manager.

3) If you are unclear which type of waste is which, ask your Supervisor.

4) Anticipated waste streams generated by the FE JV include:

    a. Simple trash.

    b. Recyclable oils (including lubricants, greases and related products that the recycler will accept).

    c. Non-recyclable oils (e.g., oils contaminated with heavy metals).

D.10.e. Categorization

1) Waste streams will be categorized in accordance with the directions of the Hazardous Waste Manager.

2) Employees SHALL NOT determine if a waste stream is a "hazardous waste." Only the Hazardous Waste Manager shall make this determination.

3) Waste streams will be placed in the appropriate containers designated by the Hazardous Waste Manager.

4) Waste streams will be labeled in accordance with the Hazardous Waste Manager's instruction.

5) Waste streams SHALL NOT be labeled as "hazardous waste" unless expressly authorized by the Hazardous Waste Manager.

D.10.f. Tracking Records

1) All regulated waste streams (i.e., those identified in the *ROD* for the site) shall be identified and logged immediately after being contained for storage or disposal.

2) FE JV will track and document the movement and disposition of all regulated wastes in the waste handling log until the materials are removed from site or otherwise transferred to the responsibilities of other entities.

3) The disposition of waste streams and the tracking records shall be maintained in accordance with the site QA/QC Engineer's instructions.

4) The transfer of regulated wastes shall be performed in accordance with the directions of the Hazardous Waste Manager for the site.

D.10.g. Air Quality Controls

1) TVOC

    a. *HASP* monitoring requirements for protection of personnel. Recognized limits for this monitoring include the Department of Labor (OSHA) Permissible Exposure Limits (PEL) and/or the ACGIH Threshold Limit Values (TLV).

b. Perimeter TVOC levels will be monitored as described in the *Monitoring Plan* (Appendix C of the *95% Design for Phase 2 Wet Dredge* [*95% Design*] [FE JV, 2016a]) to avoid public nuisance.

c. Exceedance of a Breathing Zone Action Level in an Exclusion Zone (Section F) shall be controlled by a combination of the following:

   i. Changing control zone boundaries;

   ii. Upgrading respiratory protection controls;

   iii. Slowing or suspending intrusive work;

   iv. Application of material barriers;

   v. Application of a foam barrier; and

d. Exceedance of a perimeter Action Level (Table 7-4 of the *Monitoring Plan* [(Appendix C of the *95% Design*]) at a Site perimeter monitoring station shall be controlled by a combination of the following:

   i. Take all possible steps to minimize vapors;

   ii. Cover stockpiles with tarp or foam;

   iii. Halt non-essential material management operations; and

   iv. Halt operations if necessary to re-assess situation.

2) PM_{10}

a. *HASP* monitoring requirements for protection of personnel. Recognized limits for this monitoring include the Department of Labor (OSHA) PEL, and/or the ACGIH TLV.

b. Perimeter PM_{10} levels will be monitored as described in the *Monitoring Plan*, (Appendix C of the *95% Design*), to avoid public nuisance.

c. Exceedance of a Breathing Zone Action Level in an Exclusion Zone (Section F) shall be controlled by a combination of the following:

   i. Changing control zone boundaries;

   ii. Upgrading respiratory protection controls;

   iii. Slowing or suspending intrusive work;

   iv. Application of material barriers;

   v. Application of a foam barrier; and/or

d. Exceedance of a perimeter Action Level (Table 7-4 of the *Monitoring Plan* [(Appendix C of the *95% Design*])) at a Site perimeter monitoring station shall be controlled by a combination of the following:

i. Take all possible steps to minimize fugitive dust;

ii. Cover and/or spray stockpiles;

iii. Use water and/or dust suppressants (foam) on traffic routes; and

iv. Reduce trucking rate

D.10.h. Spill Response and Prevention

Spill prevention controls and response procedures are documented in the emergency response procedures of this *HASP*.

D.10.i. Waste Management

1) All hazardous waste streams will be managed in accordance with the established waste management procedures. Each waste stream is to be segregated in the field in accordance with these procedures.

2) Segregated materials will be temporarily stored and protected until they can be replaced or remediated.

D.10.j. Waste Minimization

1) Waste generated on site will be minimized by proper sampling and categorization of waste streams.

2) Waste generated on site will be minimized by protecting segregated wastes from wind, weather and runoff.

3) Waste generated on site will be minimized through the proper selection of PPE, use of launderable materials where prudent, and reuse of decontaminated materials.

D.11. Qualifications and Access Requirements

Personnel access to project site is conditioned upon approval of NSPW security, maintaining FE JV qualifications with regard to training, medical monitoring, drug and alcohol testing, adherence to required procedures, and related requirements. Failure to maintain these qualifications may result in removal from site and/or termination of employment.

D.11.a. Training Qualifications Summary

Table D.11.a summarizes the training qualifications for this project.

Table D.11.a. Training Summary

	HAZWOPER & OSHA Training[a]				Site Specific[b]		
	40 hr with respirator training	8 hr annual refresher	8 Hr Super-visor	Site *HASP* Briefing	Site orienta-tion	Applicable JSAs	Daily safety briefings 20 min[Φ]
Supervisors	X	X	X	X	X	A	X
Level C (i.e., with potential use of respirators)	X	X		X	X	A	X
Modified D in Exclusion Zone	X	X		X	X	X	X
Level D work only surveyors, engineers, mechanics	X	X		X	X	A	X
Work outside of Exclusion Zone				X	X	A	X
Personnel doing truck driving, perimeter fencing, or asphalt paving①				X	X	A	X
Trailer staff				X	X		
Delivery personnel				E	A	A	
Site Visitors	X	X		X	X		

Notes: **X** = required. **A** = those that are applicable. **E** = escorted

① Personnel doing truck driving, perimeter fencing, or asphalt paving are not anticipated to have contact with contaminated soil. For example, truck must not leave the vehicle while on site within the Exclusion Zone or Contamination Reduction Zone and not perform any decontamination procedures.

[a] Applies to areas identified as Exclusion Zones

[b] Applies to area outside Exclusion Zones

1) All personnel performing work at the project site will receive a briefing on the *HASP*. This training must be acknowledged on the sign-up sheet at the front of this plan. Personnel will also undergo briefings on task specific JSA(s).

2) Personnel entering the Exclusion Zone shall have a minimum of 40 hours of HAZWOPER training in accordance with 29 CFR 1910.120 or 1926.65, also known as 40 Hour RCRA Remediation Training (Project Specifications, Schedule A, Scope Of Work & Technical Specifications, Section 01010).

3) Personnel required to wear respiratory protection will have a minimum of 40 hours of HAZWOPER training, to include respiratory protection training.

4) Supervisors will have an additional 8 hours of supervisory training for work in the Exclusion Zone.

5) Personnel required to have HAZWOPER training must be up to date on annual 8 hour refresher training.

6) Personnel performing support functions (i.e., work outside of the Exclusion Zone) are not required to have HAZWOPER training but shall be briefed on this *HASP* and applicable JSA(s).

7) Daily Safety Meetings. In order to maintain qualifications, it is necessary to have regular meetings in order to enhance planning efforts and to pass information from lessons learned or changes in procedures.

    a. A "toolbox" or "tailgate" safety meeting will be held at least daily before starting work. Safety meetings will also be held when site conditions change, before starting new activities, and after accidents.

    b. These daily meeting shall be used to keep personnel up to date on changes in plans and procedures since their initial training and also to ensure coordinated work assignments by outlining the day's activities and job assignments.

    c. These meetings may also serve a coordinating function for multi-employer ATW reviews (refer to Section C.11).

    d. Attendance is mandatory for all site personnel including lower tier subcontractors.

    e. Meetings will also be used to discuss:

        i. Topics of interest or concern of the crew;

        ii. Suspected hazards for that day's work and what precautions are necessary to deal with these hazards as documented on the ATW;

        iii. Necessary training requirements and site work rules;

        iv. Changes in work practices or environmental conditions;

        v. Precautions or safe work practices related to the day's site activities;

        vi. New or modified site-wide procedures or requirements; and

        vii. Incident alerts provided by the client.

    f. Documentation of daily safety meetings shall be maintained on site.

    g. Daily safety meetings shall be used as a time for personnel to make safety suggestions. Suggestions shall be noted in the minutes and evaluated by supervisory and safety personnel. Actions taken on suggestions should be noted on the daily safety meeting form.

    h. The daily safety meeting shall function as the project's Environmental Health and Safety Committee. At the option of the Project Manager, a separate committee may be established. Members shall be determined from nominations of the wage earning employees.

D.11.b. Medical Qualifications Summary

The following medical qualifications are required to perform work in certain areas.

Table D.11.b. Medical Qualifications Summary

TEST COMPONENT[1]	Level D Exclusion Zone[1]	Level C Exclusion Zone[1]	Support Zone Workers[1]	New Hires[1] [5]	Post-Accident/ Exposure[1]	End of Project [1][2]
Occupational History/update	X	X	(5)	X		(6)
Audiometric Exam	X	X		X		
Manual lifting protocol	X	X		X		
Drug testing[1]				(5)	(4)X	
DOT Breathalyzer Alcohol Testing					(4)X	
Fitness to return to work (after work/non-work related injuries or illness).					X	
Fitness for Hazardous Waste Work (29 CFR 1910.120) including liver functions		X			(1)	(6)
Fitness to wear respirators (29 CFR 1910.134)		(3)		(3)		
Basic Fitness For Duty (Level D, Construction, or non-HAZWOPER)	X	X	(5)	(5)		X

NOTES:
(1) WorkCare provides medical monitoring for all Envirocon employees through local health care facilities. The appropriate protocol will be scheduled by an authorized FE JV representative and should never be scheduled by the employee (except in the case of a medical emergency). Lower tier subcontractors and guest are required to produce their own protocols equivalent to those indicated and/or in accordance with the referenced regulatory requirements. Employee may be required at any scheduled exam, examinations conducted after accidents, randomly, or as part of facility procedures to donate specimens for drug and alcohol testing. Failure to conform to medical monitoring requirements, drug & alcohol, or other related requirements may be grounds for removal from site and termination of employment.
(2) This column refers to certain site-specific protocols. It IS NOT A TERMINATION OF EMPLOYMENT EXAM requirement. All Envirocon employees should be notified of potential eligibility for termination exams when they are terminated from employment. If they request such an exam, the Director of Health and Safety will review the request and determine eligibility under the Envirocon Medical Monitoring Program in accordance with 29 CFR 1910.120.
(3) Must be completed prior to wearing respiratory protection
(4) As determined by Envirocon policy and the Director of Health and Safety accidents, incidents, injuries, or illnesses involving medical evaluations, potential OSHA recordability, potential property damages in excess of $500, involving damages or injuries to parties not affiliated with Envirocon shall be evaluated.
(5) New employees are hired provisionally based on their ability to pass the fitness for duty examination. WorkCare makes the final determination regarding fitness for duty for Envirocon employees (this includes all aspects of fitness for duty and drug testing results). New hires may begin Level-D work (i.e., this evaluation does not authorize work where exposures may exceed the action levels for chemical exposures) with the basic fitness for duty evaluation provided by the attending or examining physician. The examining or attending physician's evaluation is considered temporary (not to exceed 30 days) until final evaluation by WorkCare's final evaluation.
(6) Employees that will be terminated at the end of the project and have not had a HAZWOPER physical within the last six months shall be offered a termination examination.

E. Hazards

An effective safety and health program includes a variety of processes for recognizing and evaluating hazards in order to plan controls. Hazard identification and evaluation must be a continuing process although the focal point is the planning phases of tasks.

E.1. Accident Prevention Program

Envirocon's Health and Safety Program Manual serves as the primary accident prevention program document in accordance with the requirements of 29 CFR 1926.20. This *HASP* further develops the site-specific procedures to prevent accidents at the site. Beyond these documents, the accident prevention program is an ongoing process which involves the participation of all personnel through hazard identification, hazard analysis and hazard control. Refer to Envirocon's Health and Safety Program Procedure 1403.014 "Correcting Unsafe Conditions and Work Practices."

E.1.a. Elements of the Accident Prevention Program

The accident prevention process at this site includes a number of ways to identify hazards and develop appropriate controls. They include the following programs and procedures.

1) Proper planning: There are a number of planning processes that take place prior to execution of a given task. Based on many other plans and programs, FE JV has developed a *HASP* for the site. The Envirocon Field Operations Manual Procedure 1401.030 documents the project procedures for developing individual task plans.

2) Job Safety Analysis: (refer to Appendix D).

    a. The planning and hazard assessment process continues into the individual job task through the use of JSAs.

    b. The HSO contributes to the task planning process required by Envirocon's Field Operations Manual 1401.030 by preparing JSAs with the assistance of the activity participants.

        In order to better manage change, duplication should be avoided. Example: There should not be two JSAs for excavation activities or a JSA duplicating a *HASP* section on excavations.

    c. JSAs shall be developed for all significant work tasks associated with this project. New tasks, or previously unrecognized hazards, require a new JSA or redraft existing ones. As needed, this *HASP* may be modified in order to accommodate control requirements identified through the JSA process. JSAs are developed in accordance with Envirocon's Health and Safety Program Procedure 1403.013.

3) Authorization to Work: The planning and hazard analysis processes come together in their final details at the employee/daily level with the ATW.

    a. ATW(s) should be newly prepared each shift because it is intended to be changed and redrafted as necessary to meet changes in the tasks or site conditions.

    b. ATWs are prepared by each work crew and approved by their foreman/team leader. To encourage employee participation, groups must be kept as small as possible.

    c. Every front line supervisor (foreman/team leader) with the assistance of the HSO must prepare their own ATW(s) with their crew.

    d. Employee participation is critical to the ATW process. Everyone on the team must sign their ATW. If task assignments change during the day, personnel should review the new team's ATW and sign it.

4) Workplace Inspections: All supervisory personnel, safety officers, and competent persons shall conduct site inspections. Site inspections are intended to ensure that established plans and procedures are followed, changes in conditions are identified, effectiveness of controls are assessed, and new hazards identified.

5) Employee Involvement: The active involvement of every employee is encouraged through the ATW process, site incentives program, "time out for safety" authority, safety observer program, and daily safety briefings. Employee involvement is the cornerstone of the incident-free performance goal. This goal will not be met (and has no real meaning) without every employee's complete focus at all times on every task. Additionally, every employee is required to look out for their coworkers when their focus falters.

6) Incident Investigations: Employees are required to immediately report all incidents in order to ensure a timely investigation. Incident investigation is aggressive at site in order to capture lessons learned from minor incidents and correct controls before significant accidents occur.

E.1.b. Responsibilities

1) Responsibilities for planning, safety and quality shall be specifically assigned and acknowledged. The primary means for accomplishing this is as follows:

    a. Project Plans (e.g., *Tech Memo* and *HASP*) are assigned to the Project Manager, Health & Safety Supervisor, QA/QC Engineer, etc. and shall be signed by the individuals' assigned responsibility for the document.

    b. 1401.030 Task Plans and JSAs are assigned to and signed by the appropriate Superintendent (or other operations supervisor); HSO; QA/QC Engineer; and any other technical supervisors required for proper planning associated with the task. For example, tasks involving crane operations should have a lift supervisor assigned to the task plan.

c. Daily ATWs are assigned to every front line supervisor and shall be signed by the responsible supervisor and every member of the work team.

2) Supervisors, assisted by safety and health personnel are responsible for implementing effective accident prevention processes. This includes:

   a. Conducting required planning;

   b. Conducting required inspections;

   c. Aggressively investigating all incidents;

   d. Encouraging employee participation; and

   e. Taking a leadership role in achieving Incident-free performance.

3) Employees are responsible for:

   a. Following established procedures;

   b. Actively participating in training processes;

   c. Reporting all incidents immediately to their supervisors;

   d. Participating in behavior observation, and assisting in the preparation of JSAs and ATW;

   e. Positively assisting in investigations of incidents; and

   f. Looking out for their coworkers (i.e., "buddies").

E.2. Risk Assessment

For purposes of this *HASP*, risk will be described by a ranking methodology. This purpose of this ranking is to focus attention on significant hazards for purposes of better utilizing limited resources. The purpose of this assessment is not to determine precise probabilistic measures (it is actually intended that high potentials will go unrealized by focused attention). Two cases define the issue of risk versus hazard in the accident prevention context. Severe hazards that are infrequently encountered, and low severity hazards that are frequently encountered both represent cases where controls may not receive the attention they merit. This ranking system will consider three factors that contribute to overall risk potential. They include severity of outcome, frequency of exposure, and potential for occurrence when exposed.

E.2.a. Severity

Severity describes the significance of consequences if the potential is realized.

1) High severity means the following:
   a. There is a distinct possibility of fatal injury or illness.
   b. A factor of 4 will be used to score risk potential.

2) Moderate severity means the following:
    a. There is a distinct possibility of permanent disabling injury or illness.
    b. There may be a residual possibility of fatal injury or illness.
    c. A factor of 2 or 3 will be used to score risk potential.

3) Low severity means the following:
    a. It is unlikely to result in fatality.
    b. There may be a residual possibility of permanent disabling injury/illness.
    c. There is a distinct possibility of medical treatment.
    d. A factor of 1 will be used to score risk potential.

E.2.b. Frequency of Exposure

For this analysis, frequency represents the amount of exposure to the hazard, or how often risk is experienced.

1) Frequent exposure means the following:
    a. Regular or daily exposure to the hazard.
    b. A factor of 4 will be used to score risk potential.

2) Moderate frequency of exposure means the following:
    a. Weekly or biweekly exposure to hazard, or
    b. Seasonally, it becomes a frequent exposure to hazard.
    c. A factor of 2 or 3 will be used to score risk potential.

3) Infrequent exposure means the following:
    a. Exposures occur several times a year or less.
    b. A factor of 1 will be used to score risk potential.

E.2.c. Probability of Occurrence

Probability reflects the likelihood of injury or illness when exposed to the hazard. For purposes of this analysis, probability includes consideration of efficiency of identifying hazards in order to implement controls and effectiveness of controls.

1) Probable means the following.
    a. Difficult to recognize.
    b. Controls tend to have limited effectiveness.
    c. A factor of 4 will be used to score risk potential.

2) Somewhat probable means the following.
    a. Either the hazard is difficult to recognize or controls tend to have limited effectiveness.
    b. A factor of 2 or 3 will be used to score risk potential.

3) Generally improbable means the following.
    a. The hazard is readily recognized and reliably controlled.

b. A factor of 1 will be used to score the risk potential.

E.2.d. Number of Employees and/or Third Party Personnel Exposed

This reflects the population of employees exposed to this particular risk. Heat stress for example generally affects ground laborers wearing PPE. Equipment operators or supervisory personnel in enclosed air-conditioned cabs are not exposed to the stress.

1) Score of 4 = more than 50.
2) Score of 3 = 10 to 50.
3) Score of 2 = 3 to 10.
4) Score of 1 = 1 to 3.

E.2.e. Risk Assessment

Table E.2.e. Hazard Descriptions

Type of Hazard	Severity Score	Frequency Score	Probability Score	Number of Employees	RISK Potential	Description of Potential Hazards
Safety	4	3	1	3	36	Heavy equipment
	1	4	2	3	24	Slips/trips/falls and walking and working surfaces
	4	2	2	2	32	Working on or near water.
	3	2	2	2	24	Falls from heights > 6 feet
	4	3	1	2	24	Vehicle traffic
	2	3	2	2	24	Manual lifting
	3	2	1	2	12	Excavations collapse
	2	2	1	2	8	Structural and equipment fires
	4	1	2	1	8	Utility strikes during intrusive activities
	4	1	1	1	4	Utility strikes of overhead line, guyline
Toxic	1	3	1	1	3	PAH sediment excavation and transport
Biological/ Mental	1	4	2	3	24	Noise from equipment
	2	1	1	4	8	Heat or cold stresses
	2	2	1	2	8	Poisonous plants and insects

PAH = Polyaromatic Hydrocarbons

E.3. Potential Chemical Waste Hazards

The waste contaminants of concerns (COC) are described along with their hazards and properties in Appendix F.

F. Industrial Hygiene Program Controls

OSHA mandates programmatic controls for many hazards. This section describes the programs in place to control safety and health hazards on site.

F.1. Site Monitoring

Table F.1. Air Monitoring Requirements[1]

Chemical Hazard	PEL/TLV	Instrument	Method[1]	Action Level	Action[3]
Oxygen (O_2)	19.5% to 23.5%	O_2 meter (w/ Combustible Gas)	Direct read area sample prior to confined space entry.	<19.5%, or >23.5%	Ventilate until readings can be brought to 21% +/- 1% or do not enter. Ventilate until readings can be brought to 21% +/- 1% or do not enter.
Combustible Gas/Vapors (CG)	NA	Combustible Gas/ O_2 meter	Direct reading area sample prior to entering confined space	>10% LEL	Clean, secure source of vapors, ventilate until readings can be brought to +/- 1% LEL or do not enter.
			• Prior to hot work near flammables • Suspect gas leak	Any detection above background drift or fluctuation.	Clean, secure source of vapors, ventilate until readings indicate source has been controlled.
Benzene Ethyl Benzene Toluene Xylene	1 ppm/5ppm STEL	PID in Breathing zone of worker.	Breathing Zone[2] for 5 minutes	1 ppm above background	Determine benzene concentration with Drager tube method or other direct reading instrument
	100ppm/100ppm			>50% < 10x PEL or TLV	Apply engineering controls (vapor suppression methods as necessary) Upgrade PPE to level C[3].
	200ppm/50ppm			>50X PEL or TLV	Apply engineering controls(foaming, vapor suppression misting) Upgrade PPE to level B[3].
	100ppm/100ppm			>1000 PPM or > IDLH	Stop work, determine source of hazard and apply an engineering control.

Chemical Hazard	PEL/TLV	Instrument	Method[1]	Action Level	Action[3]
Benzene	1 ppm/5ppm STEL	Drager pump and benzene tube or equivalent	Breathing Zone[2]	>50% < 10x PEL or TLV	Apply engineering controls (vapor suppression reagents) Sample with media by method below. Upgrade PPE to level C[3].
				>50X PEL or TLV	Apply engineering controls(foaming, vapor suppression misting) Upgrade PPE to level B[3].
				>1000 PPM or > IDLH	Stop work, determine source of hazard and apply an engineering control.
Benzene Ethyl Benzene Toluene Xylene	1 ppm/5ppm STEL 100ppm 100 ppm 200ppm/50 ppm 100ppm/100ppm	Air Sampling Pump <0.2 L/min or personal air monitoring badge	Breathing Zone[2] NIOSH 1501	>50% < 10x PEL or TLV	Apply engineering controls(vapor suppression reagents) Upgrade PPE to level C[3].
				>50X PEL or TLV	Apply engineering controls(foaming, vapor suppression misting) Upgrade PPE to level B[3].
				>1000 PPM or > IDLH	Stop work, determine source of hazard and apply an engineering control.
Naphthalene and PAHs	Naphthalene 10 PPM PAHs 0.2 mg/m3	(4)	Breathing Zone[2] [4]	>50% < 10x PEL or TLV	Apply engineering controls Upgrade PPE to level C[3].
				>50X PEL or TLV	Apply engineering controls(foaming, vapor suppression misting) Upgrade PPE to level B[3].
				>1000 PPM or > IDLH	Stop work, determine source of hazard and apply an engineering control.
Respirable PNOC (Particulates Not Otherwise Classified)	5mg/m3	Personal sampling pumps, pre-weighted PVC filter cassette in breathing zone of worker	NIOSH 0600 when suspect or monthly	>50% < 10x PEL or TLV	Apply engineering controls Upgrade PPE to level C[3].

Comments or special instructions:

1) Methodology determines the analytical method used by the laboratory
2) Breathing zone is the location of the sampling media. It would be attached to the workers shoulder at approximately the same height of the workers nose and mouth.
3) For PPE upgrades refer to Table **F.2.c** for respiratory protection selection guidelines and Table **F.2.a** for other PPE items.
4) Concentrations of PAHs will be characterized using a modified version of National Institute for Occupational Safety and Health (NIOSH) Method 5515 – "Polycyclic Aromatic Hydrocarbons in Air by Gas Chromatography." Samples will be collected at a flow rate of 2 L/min using sorbent tubes containing XAD-2 resin. Collected samples will be returned to the laboratory where they will be extracted and analyzed for naphthalene and other PAHs as provided in the analytical method. The required detection limit for this method is approximately 0.001 mg/m3.

F.1.a. Monitoring

1) All monitoring will be conducted in accordance with the equipment manufacturer's operating instructions.

2) Readings will generally be taken where indications exceed normal background and drift of the equipment.

3) Readings other than peak readings will generally be taken as sustained readings lasting for several seconds.

F.1.b. TWA Sampling

TWA (time weighted average) sampling may include time weighted average sampling of personal exposures as well as specific areas (e.g., Exclusion Zone boundaries or worst case locations).

1) All TWA sampling will be conducted in accordance with NIOSH or OSHA standard methods for purposes of documenting exposure compliance. In some cases TWA sampling may be used for other purposes such as detecting exposure potential, but these samples shall not be documented as compliance samples.

2) Routine TWA sampling includes worst case breathing zone sampling. If three consecutive samples are below action levels, no further testing is required unless/until conditions changes.

3) Where worst case samples indicate exposures above action levels, conduct area TWA sampling of Exclusion Zone boundaries and discrete job tasks. Where three consecutive samples indicate exposures below the action levels, no further testing is required unless/until there is a change in conditions.

F.1.c. Characterization and Confirmation

1) Characterize means:

    a. Collect three worst case TWA personal exposure samples.

        i. These samples shall be taken at different times.

        ii. Each sample shall reflect a full shift of activities and exposures.

        iii. These samples shall be matched against applicable direct reading monitoring results.

        iv. More samples may be taken to evaluate effectiveness of control modifications.

    b. At such time as the three latest TWA samples indicate a consistent result the work process may be considered to be characterized if the HSO determines that there

are no other indications that these samples should not be considered representative. Consistent results include:

i. Three (3) consecutive samples below the action level;

ii. Three (3) consecutive samples at or below Level C half mask requirements; and

iii. Three (3) consecutive samples at or below Level C full face requirements.

c. Must be repeated or confirmed whenever a change in conditions is identified. Indications of a change in condition include the following:

i. New materials are encountered that have been determined to contain significant changes in contaminant concentrations.

ii. Odors have changed significantly.

iii. Operational methods have changed in a way that could produce different exposures.

iv. Direct reading instrument results are no longer consistent with the results taken during characterization.

- For example, the direct reading instrument results associated with a TWA characterization that was half of the action level are now getting close to doubling.

- A confirmatory TWA sample should be taken to ensure that the current direct readings are still indicative of TWA exposures less than the action level.

- A change in condition must be assumed and therefore controls must be upgraded (e.g., upgrade respiratory protection).

2) Confirmation means:

a. A direct reading monitoring result or a TWA exposure sample that is consistent with the latest characterization is a confirmation sample or monitoring result.

b. One (1) UP confirmation sample to upgrade/Three DOWN confirmation samples to downgrade.

i. At any time that a confirmatory TWA sample produces a new result which is inconsistent with the latest characterization, a change in condition must be assumed and therefore controls must be upgraded (e.g., upgrade respiratory protection).

ii. While any single direct reading or TWA result inconsistent with a lower level of controls must indicate upgrading controls; a full set of three consecutive TWA results indicate a consistent characterization appropriate for downgrading controls.

iii. Similarly, three consecutive direct reading results must be produced to downgrade (provided the direct reading results have been previously confirmed against applicable TWA levels).

c. Routine confirmation by TWA sampling and direct reading monitoring should be performed.

i. Routine confirmation monitoring or sampling means to perform the evaluation even if there is no other indication of a change in conditions.

ii. Unless otherwise specified, routine confirmation sampling is conducted daily for direct reading instrument monitoring and monthly for TWA sampling.

d. Confirmation wipe samples mean to collect a sample from the same location and over the same amount of surface area as a previously characterized location.

3) Downgrading of respiratory protection shall be approved by Certified Industrial Hygienist.

F.1.d. Documentation

See the recordkeeping section below.

1) All calibration, sampling information and results will be documented using a log or Envirocon standard forms.

2) Results collected for specific individuals will be passed directly to the applicable employee. Result briefings will be documented.

3) Results will be generically passed (without mention of specific employee names) to all personnel during morning safety meetings.

F.2. Personal Protective Equipment

F.2.a. Summary of PPE Requirements

Table F.2.a. Summary of Standard PPE

Activity	Head/Face	Foot	Hands	Respirator	Clothing
General site labor, non-intrusive support zone tasks	• Hard hat(2) • Safety glasses(2)	Steel toed boots	Leather gloves as needed.	None(1)	• Shirt w/sleeves • Long pants • High visibility vest(5)
Supervision of support zone work	• Hard hat(2) • Safety glasses(2)	Steel toed boots		None(1)	• Shirt w/sleeves • Long pants • High visibility vest(5)
Dry equipment decontamination	• Hard hat(2) • Safety glasses(2) • Face shields or goggles	Steel toed PVC/rubber outer boots	Leather or PVC coated outer gloves	None(1)	• Tyvek(3) • High visibility vest(5)
General site labor tasks in dry contaminated areas	• Hard hat • Safety glasses(2)	PVC/rubber outer boots w/steel toes, or steel toed boots w/ boot covers(4)	Leather or PVC coated cotton as needed	None(1)	• Tyvek(3) • High visibility vest(5)
General site labor tasks in wet contaminated areas	• Hard hat • Safety glasses(2)	Steel toed boots with water resistant outer boot covers(6) (8)	Nitrile or Leather or PVC coated cotton as needed	None(1)	• Water resistant outer coveralls (3)(6) • High visibility vest(5)
General site labor tasks working on/near water	• Hard hat • Safety Glasses	Steel toed boots	Leather gloves as needed	None(1)	• Shirt w/sleeves • Long pants • High visibility vest(5) • USCG type III PFD
Wet Decontamination	• Hard hat • Safety glasses(2) • Face shield	Steel toed boots with water resistant outer boot covers(6) (8)	Nitrile gloves in combination with Leather or PVC coated cotton gloves	None(1)	• Water resistant outer coveralls(3) (6) (7) • High visibility vest(5)
Drivers	• (9)	• (9)	• (9)	• None(1)	• long pants • shirts with sleeves(9)

(1) Refer to Table F.2.b. for initial respiratory protection requirement options.
Voluntary use of respirators is authorized for nuisance dusts and exposures known to be below PEL levels. For nuisance dust use disposable N, R or P 95 or better (dispose of N or R types daily and P type weekly) For odors use half mask with OV or OV/P95 or better (change at start of week)

(2) Hard hats and safety glasses are not required inside of enclosed cabs with windshields; or when working outside of the contaminated areas performing non-labor tasks such as walking to and from buildings/trailers, typing, or making notes.

(3) Dust resistant outer coveralls such as Tyvek. These are not allowed for use when contact with hazardous materials is likely. The safety officer will evaluate this requirement for tasks that involve minimal risk of contact with contaminants on personal clothing or skin.

(4) Boot covers are any suitable covering capable of resisting dust penetration which would contaminate steel toed boots, and with durability appropriate for the task.

(5) High visibility vests are for use in work areas within 25 feet of vehicular or equipment traffic. For heat stress considerations, an orange/high-visibility T-Shirt, or an orange/high-visibility hard hat may be substituted for the vest.

(6) When working with wet contaminated materials, PVC or other equivalent water resistant outer boot covering will be used to prevent contamination of steel toed boots.
(7) For purposes of preventing heat or cold stress, decontamination personnel may use water proof outer coverings with holes in the backs or aprons to allow for perspiration to escape (provided inner garments do not get wet as a result.
(8) Wet work and decontamination may use a PVC steel-toed boot in place of a leather boot with cover.
(9) Drivers entering contaminated areas shall be prepared to put on the applicable personal protective clothing worn in that area in the event of an emergency exit.

F.2.b. Respiratory Protection Selection; Initial Assignment

Initial assignment of personnel to wear respiratory protection shall be based on the assumption that COCs have not been characterized with assurance and until they have been so characterized some tasks shall be undertaken in Level C. When a characterization and confirmation as described in Section F.1.d. has been completed, a downgrade in respiratory protection may be made.

Table F.2.b. shall be used as guidance for the decision for the PPE ensemble. Table F.2.b. shall be used for initial assignment of respiratory protection, but at the discretion of the HSO may be upgraded. Personnel may make a voluntary selection of the next highest level of respiratory protection up to Full-Face Negative Pressure.

Table F.2.b. Initial Assignment of Respiratory Protection

Task	Required Respiratory Protection
Site mobilization tasks	None
Grubbing, site clearing	Disposable filtering facepiece
Surveying	Determine at time of assignment – use work area prior characterizations.
Erosion controls	None
Installation, operation and maintenance of perimeter air monitoring stations	None
Protection of sheet pile wall	None
Dredging, dewatering and contaminated water management	Determine at time of assignment. PID measurements for characterization and decision.
Staging and processing of sediment (removal of oversize and debris).	Determine at time of assignment. PID measurements for characterization and decision.
Sediment processing	Determine at time of assignment. PID measurements for characterization and decision.
Loading and hauling materials	Determine at time of assignment. PID measurements at well-head employed for characterization and decision.
Restorative Layer Placement	None
Maintaining and operating ancillary features	None
Demobilization tasks	None

F.2.c. Respirator Selection Based on Monitoring/Sampling

Table F.2.c. Respirator Selection[1]

It is anticipated that during the Wet Dredge portion of this project personnel might be exposed to contaminants at or above action levels or established PELs. Should the exposure become apparent, below summarizes the required respirator selection.

Hazard	Levels		Respirator Type[2]	Cartridge Type	Cartridge Change Schedule	Notes
	lower	upper				
PNOC (dust)		5 mg/m^3 total dust		P100 or P99 N100 or N99 R100 or R99	WEEK for P100 or P99 SHIFT for N100 or N99 R100 or R99	Optional: Provide for voluntary use.
	5 mg/m^3 total dust or 2.5 mg/m3 respirable	25 mg/m^3 total dust or 12.5 mg/m3 respirable	HM APR	P100 or P99 N100 or N99 R100 or R99	WEEK for P100 or P99 SHIFT for N100 or N99 R100 or R99	
	25 mg/m^3 total dust or 12.5 mg/m^3 respirable	250 mg/m^3 total dust or 125 mg/m^3 respirable	FF APR	P100 or P99 N100 or N99 R100 or R99	SHIFT	
	250 mg/m^3 total dust or 125 mg/m^3 respirable		FF PP SA	Airline or SCBA	n/a	
Respirable Combined	25 ug/m^3	50 mg/m^3	FF, HM, APR	P100	Week for P100	(4) (5)
benzene	0.5 ppm	10 ppm	HM APR	OV	each SHIFT	(4) (5)
	10 ppm	50 ppm	FF APR	OV	each SHIFT	(4) (5)
	50 ppm	500 ppm	FF PP SA	n/a	n/a	(4) (5)
	500 ppm		JSA[3]			(4)(5)

Hazard	Levels		Respirator Type(2)	Cartridge Type	Cartridge Change Schedule	Notes
	lower	upper				
TEX (toluene, xylene, ethylbenzene or mixed organic vapors other than benzene)	10 ppm	50 ppm	HM APR	OV	each WEEK	
	50 ppm	200 ppm	FF APR	OV	each SHIFT	
	200 ppm	500 ppm	FF PP SA	n/a	n/a	
	500 ppm		FF PP SA w/EE	n/a	n/a	
PAHs		0.2 mg/m^3	Voluntary use dust mask.	P100 or P99 N100 or N99 R100 or R99	WEEK for P100 or P99 SHIFT for N100 or N99 R100 or R99	Optional: Provide for voluntary use.
	0.2 mg/m^3	10 mg/m^3	HM APR	P100 or P99 N100 or N99 R100 or R99	WEEK for P100 or P99 SHIFT for N100 or N99 R100 or R99	
	10 mg/m^3	100 mg/m^3	FF APR	P100 or P99 N100 or N99 R100 or R99	SHIFT	
	100 mg/m^3		FF PP SA	Airline or SCBA	N/A	

Abbreviations:

acid = acid gas
APR = Air Purifying Respirator
combo = combination cartridges
DFF = disposable filtering face piece
EE = Emergency Egress SCBA (escape only)
EEO = emergency escape only
FF = full face
(H) = hood
HM = half mask N100 R100 P100 = NIOSH approval types (for dust filtering cartridges)
OV = organic vapor
PP = positive pressure/pressure demand mode
SA = supplied air (airlines or SCBA)
SCBA = self-contained breathing apparatus
SHIFT = start each shift with a new cartridge(5)
WEEK = start each week with a new cartridge(5)

Notes:

(1) This table sets the initial respiratory protection selection options. The Project Health and Safety Manager, the Corporate Director of Health and Safety, or an Envirocon CIH may approve additions or changes to this table based on a written hazard analysis. An Envirocon CIH must approve respiratory protection downgrades.

(2) This represents the minimum respiratory protection allowed. Respirators with a higher protection factor assigned by NIOSH may also be used.

(3) Job Safety Analysis (JSA) must be approved by the Project Health and Safety Manager, the Corporate Director of Health and Safety, or an Envirocon CIH.

(4) Ensure compliance with OSHA 29 CFR 1910.1028 benzene regulated areas, medical surveillance and training, etc.

(5) Regardless of the change schedule, chemical cartridges should always be changed if warning properties are detected.

F.2.d. PPE Rules

1) Downgrading respiratory protection must be approved by the FE JV CIH.

2) All personnel are required to use the PPE specified for their work. This may include, but is not limited to, cartridge respirator, protective suit, gloves, boots, hard hat, hearing protection, and safety glasses.

3) All respirator use to be done in accordance with FE JV Respiratory Protection Program and/or site-specific procedures. Refer to Section F.3 for the site-specific respiratory protection program and procedures.

4) Safety Boots/Shoes:

    a. Safety steel-toed boots/shoes that meet the requirements and specifications of American National Standards Institute (ANSI) Z41.1 shall be worn while working in field locations.

    b. Boots/shoes must be in good repair and laced or fastened. Sandals and tennis-style shoes of any type shall not be worn while working.

5) Safety/Hard Hats:

    a. Approved safety hats that meet requirements and specifications established in ANSI Z89.1 shall be worn at all times in the field or construction zone/yard removal locations.

    b. Safety hats are not required to be worn in vehicles (passenger cars or trucks) or offices. Safety hats are not required in construction equipment with enclosed cabs. Safety hats must be worn in all construction equipment (loaders, bobcats, excavators, dump trucks, backhoe, etc.) that do not have enclosed cabs.

6) Eye Protection:

    a. As a minimum, ANSI-approved safety glasses with side shields will be worn at all times when working on this site.

    b. ANSI-approved safety glasses must be worn by equipment operators while in cabs unless eye hazards are adequately controlled by other methods listed in the most recent eye hazards analysis for this project.

    c. Proper eye protection (goggles, safety glasses, etc.) must be worn when performing work with a recognized hazard to the eyes such as wire brushing, hammering, buffing, chipping, grinding, welding, cutting wire rope, working on rust, dirty chains, cables, or handling chemicals. If the job might result in eye injury, then eye protection is required.

    d. Special goggles must be worn while helping or working within close range of welders.

e. Goggles or transparent full-face shields must always be worn when grinding.

f. FE JV will not provide prescription safety glasses; FE JV will provide safety glasses capable of fitting over prescription glasses.

7) Hearing Protection:

a. Approved earplugs or earmuffs must be worn in areas of high noise levels.

b. High noise level is defined as areas where noise levels exceed, or may exceed, 90 decibels A-scale (dBA).

8) Safety Vests:

a. Reflective high visibility safety vests are required anytime personnel are working around operating equipment.

b. This requirement applies to equipment operators whose duties involve them leaving the cab of their equipment and working in general area.

9) Clothing:

a. Sleeved shirts must be worn on the job.

b. Tank tops will not be allowed.

c. Long pants shall be worn. Pants shall cover the work boot top.

d. Loose or ragged clothing shall not be worn.

10) All personnel are responsible to clean and maintain the protective equipment issued to them. Any noted defects in the equipment shall immediately be reported to the FE JV Project Manager or the site superintendent, as appropriate.

F.3. Site-Specific Respiratory Protection

F.3.a. Documents

Envirocon's written Respiratory Protection Program is contained in Procedure 1403.016. This health and safety plan procedure serves as the site-specific procedure for the use of respirators on this project.

F.3.b. Administration

1) The Respiratory Protection Program Administrator is Frank Sullivan.

2) The designated Site Safety Officer for this project will serve as Assistant Program Administrator.

3) Medical qualification procedures are evaluated and implemented by WorkCare.

F.3.c. Continuing Respirator Effectiveness

1) The Assistant Administrator (Site Health & Safety Officer) is responsible for conducting daily site inspections, including special inspections described in the inspections section of this procedure.

2) Daily site inspections shall include surveillance of work place conditions. In particular the following conditions shall be assessed.

    a. Potential changes in contaminant concentration;

    b. Changes in employee exposure or stress; and

    c. Respirator effectiveness.

F.3.d. Training

1) Envirocon Respiratory Protection Training Procedure:

    a. Employees may be trained using the Envirocon Respiratory Protection Program lesson plan.

2) 40 hr HAZWOPER Training. Employees may be trained in a recent 40 hour or Emergency Response training courses (within the last year), or a recent 8 hour refresher training course which covers the use of respiratory protection (within the last year).

3) Respirator wearers may also be trained by certified training using a lesson plan covering the 1998 revised respiratory protection program standard.

F.3.e. Voluntary Use of Respirators

1) The voluntary use of respirators by employees (e.g., for control of odors or dusts) must be qualified.

2) Voluntary use of respirators is only allowed in areas characterized as not requiring respiratory protection.

3) The specific type of respirator and conditions of use must be approved by the Director of Health and Safety.

4) Voluntary use of respirators must otherwise be in accordance with this procedure.

5) Employees voluntarily using respirators must be trained in the information provided in Appendix D to CFR Sec. 1910.134 “Information for Employees Using Respirators When Not Required under the Standard.”

6) Voluntary use of disposable dust masks does not require medical evaluation. Voluntary use of these masks does not require a fit test.

F.3.f. Medical Qualifications

1) Envirocon (physician or other licensed health care professional [PLHCP]):

    a. Respirator wearer's shall be medically evaluated by a company designated PLHCP.

    b. Envirocon's PLHCP are the physicians of WorkCare.

    c. The physicians of WorkCare will be assisted in these duties by a local PLHCP. Local PLHCPs will also be licensed physicians. Fitness to wear respiratory protection will be determined by the local PLHCP and reviewed by the physicians of WorkCare.

F.3.g. Fit Testing

1) General requirements:

    a. Before an employee uses any respirator with a negative or positive pressure tight-fitting face piece, the employee must be fit tested with the same make, model, style, and size of respirator that will be used.

    b. Positive pressure (i.e., pressure-demand mode) supplied air respirators (SAR) or SCBA with tight-fitting face pieces are included in this requirement.

    c. Unless noted otherwise, fit test shall be administered using an OSHA-accepted Quantitative Fit Testing (QNFT) protocol.

    d. A Qualitative Fit Testing (QLFT) protocol may be used to fit test negative pressure air-purifying respirators that must achieve a fit factor of 100 or less (i.e., half mask air purifying respirators).

    e. Fit testing of tight-fitting atmosphere-supplying respirators and tight-fitting powered air-purifying respirators shall be accomplished by QNFT or QLFT.

2) Tight-fitting atmosphere-supply and powered air-purifying respirators:

    a. Fit testing of tight-fitting atmosphere-supplying respirators and tight-fitting powered air-purifying respirators shall be accomplished by performing QNFT or QLFT in the negative pressure mode, regardless of the mode of operation (negative or positive pressure) that is used for respiratory protection.

    b. QLFT of these respirators shall be accomplished by temporarily converting the respirator user's actual face piece into a negative pressure respirator with appropriate filters, or by using an identical negative pressure air-purifying respirator face piece with the same sealing surfaces as a surrogate for the atmosphere-supplying or powered air-purifying respirator face piece.

    c. QNFT of these respirators shall be accomplished by modifying the face piece to allow sampling inside the face piece in the breathing zone of the user, midway

between the nose and mouth. This requirement shall be accomplished by installing a permanent sampling probe onto a surrogate face piece, or by using a sampling adapter designed to temporarily provide a means of sampling air from inside the face piece.

d. Any modifications to the respirator face piece for fit testing shall be completely removed, and the face piece restored to NIOSH-approved configuration, before that face piece can be used in the workplace.

e. Voluntary use respirators:

i. Voluntary use of disposable paper masks for dusts does not require a fit test.

ii. Voluntary use of disposable paper masks for dusts does not require medical evaluation.

iii. Voluntary use of any other respiratory protection requires normal fit testing and medical evaluations.

3) Loose-fitting respirators:

a. Loose-fitting respirators include respirators such as hood or helmet-type continuous flow (type C or CE) respirators.

b. Loose-fitting respirators do not require fit testing.

4) Envirocon fit testing will be done in accordance with the OSHA-accepted QLFT and QNFT protocols and procedures are contained in Appendix A, 29 CFR 1910.134.

F.3.h. Fit Testing Period

1) Fit test results are good for a period of one year.

2) If an employee using a tight-fitting face piece respirator will be assigned a different respirator face piece (size, style, model or make) the fit testing must be repeated.

3) Fit test results are voided whenever the employee, a supervisor, a safety officer, the PLHCP, or program administrator makes visual observations of, changes in the employee's physical condition that could affect respirator fit. Such conditions include, but are not limited to:

a. Facial scarring;

b. Dental changes;

c. Cosmetic surgery; or

d. An obvious change in body weight.

F.3.i. Use of Respirators

1) Employees are not allowed to use respirators with tight-fitting face pieces with:

    a. Facial hair that comes between the sealing surface of the face piece and the face or that interferes with valve function; or

    b. Any condition that interferes with the face-to-face piece seal or valve function.

2) If an employee wears corrective glasses, Envirocon will obtain the appropriate spectacle kit and have it fitted with prescription lenses.

3) Employees are required to perform a fit check when donning all tight-fitting respirators.

F.3.j. General Inspection and Repairs

1) Inspection requirements:

    a. All respirators used in routine situations shall be inspected before each use and during cleaning.

2) Repairs:

    a. Respirators that fail an inspection or are otherwise found to be defective are removed from service, and are discarded or repaired or adjusted in accordance with these procedures.

    b. Repairs or adjustments to respirators are to be made only by persons appropriately trained to perform such operations.

    c. Repairs shall be made using only the respirator manufacturer's NIOSH-approved parts designed for the respirator.

    d. Repairs shall be made according to the manufacturer's recommendations and specifications for the type and extent of repairs to be performed.

    e. Reducing and admission valves, regulators, and alarms shall be adjusted or repaired only by the manufacturer or a technician trained by the manufacturer.

3) Employees shall inspect their respirator carefully and paying particular attention to:

    a. Exhalation valve(s);

    b. Inhalation valve(s);

    c. Tightness of components;

    d. Elasticity of components;

    e. Look for missing components;

f. Look for cracked components;

g. Look for missing cartridge gaskets;

h. Look for damage to cartridges (in particular the seat that seals with the cartridge gasket); and

i. Ensure that all filters, cartridges and canisters used are labeled and color coded with the NIOSH approval label and that the label is not removed and remains legible.

4) For supplied air systems also inspect for:

a. Proper functioning of regulators;

b. Final regulator pressures not exceeding 125 psi;

c. Air lines (low pressure) not exceeding 300 feet in length; and

d. Grade D certification of breathing air.

F.3.k. Respirator Cartridges Changes

1) Respirator cartridges shall be changed:

a. In accordance with manufacturer's recommendations; and

b. As prescribed by this *HASP* or JSA.

2) Cartridges shall also be changed:

a. If the wearer detects vapor or gas breakthrough;

b. If the wearer detects changes in breathing resistance; or

c. If the wearer detects leakage of the face piece.

F.3.l. Cleaning and Disinfecting

1) Cleaning:

a. Whenever respirators are doffed, employees shall wash their faces and respirator face pieces in order to prevent eye or skin irritation.

b. Cleaning shall be accomplished by using soap and water or equivalent cleaning solutions.

2) Disinfecting requirements:

a. Respirators issued to more than one employee shall be cleaned and disinfected before being worn by different individuals.

b. Respirators maintained for emergency use shall be cleaned and disinfected after each use.

c. Respirators used in fit testing and training shall be cleaned and disinfected after each use.

d. Respirators used by a single individual shall be disinfected at least weekly.

3) Disinfecting procedures:

a. Respirator components should be immersed for two minutes in one of the following:

i. Disinfecting agent recommended for respirator sanitizing; or

ii. Hypochlorite solution (50 parts per million [ppm] of chlorine) made by adding approximately one milliliter of laundry bleach to one liter of water at 43°C (110°F); or

iii. Aqueous solution of iodine (50 ppm iodine) made by adding approximately 0.8 milliliters of tincture of iodine (6-8 grams ammonium and/or potassium iodide/100 cc of 45% alcohol) to one liter of water at 43°C (110°F).

b. Rinse components thoroughly in clean, warm (43°C [110°F] maximum), preferably running water.

c. Drain. (The importance of thorough rinsing cannot be overemphasized. Detergents or disinfectants that dry on face pieces may result in dermatitis. In addition, some disinfectants may cause deterioration of rubber or corrosion of metal parts if not completely removed.)

d. Use a mild solution of baking soda to remove chlorine or disinfectant residues.

e. Components should be hand-dried with a clean lint-free cloth or air-dried.

f. Reassemble face piece, replacing filters, cartridges, and canisters where necessary.

g. Test and inspect the respirator to ensure that all components work properly.

F.3.m. Storage

1) All respirators shall be stored to protect them from damage, contamination, dust, sunlight, extreme temperatures, excessive moisture, and damaging chemicals.

2) All respirators shall be packed or stored to prevent deformation of the facepiece and exhalation valve.

3) Emergency respirators shall be:

    a. Kept accessible to the work area;

    b. Stored in compartments or in covers that are clearly marked as containing emergency respirators; and

    c. Stored in accordance with any applicable manufacturer instructions.

F.3.n. IDLH Atmospheres

1) Use of respirators in Immediately Dangerous to Life and Health (IDLH) atmospheres must be approved by the Respiratory Protection Program Administrator The administrator will approve the entry by reviewing and signing off on the JSA for the entry.

2) A specific JSA shall be written for each IDLH entry. The JSA will include:

    a. The type of respirators to be used;

    b. Area monitoring requirements;

    c. Escape provisions; and

    d. Rescue provisions.

3) At least one employee will serve as an attendant.

    a. Attendants will remain outside the IDLH atmosphere.

    b. The attendant shall maintain visual, voice, or signal line communication with the employee(s) in the IDLH atmosphere.

    c. Attendants and rescue personnel will be trained in the approved JSA/JHA for the entry.

    d. Attendants shall not attempt a rescue until provisions have been made for someone else to assume responsibilities as attendant.

F.3.o. Site Inspections

1) The Assistant Administrator (Site Health & Safety Officer) is responsible for conducting certain site inspections on a routine basis.

2) Program inspections:

    a. Site inspections will be conducted daily.

b. The HSO is responsible for these inspections, including special inspections described in the inspections section of this procedure.

c. Daily site inspections shall include surveillance of work place conditions. In particular the following conditions shall be assessed:

   i. Potential changes in contaminant concentration;

   ii. Changes in employee exposure or stress; and

   iii. Respirator effectiveness.

F.4. Heat Stress

The site heat stress program shall be enforced prior during periods when the ambient temperature of 80°F. Training shall be accomplished prior to implementation.

F.4.a. Training

All site personnel shall be trained in the hazards and controls of heat stress prior to the onset of hot weather.

F.4.b. Acclimatization

Personnel become acclimatized in about 7 to 10 days (and loose acclimatization in about the same period of time). Extra attention should be given during transitional weather and to new employees that are not used to heat stressful conditions.

F.4.c. Fluids

Workers shall be encouraged to increase consumption of water. Cool or cold water shall be used to enhance palatability and consumption. Electrolyte-containing beverages may also be used to encourage consumption.

F.4.d. Shelter

Shelter from radiant heat (i.e., shade) shall be available for ground laborers exposed to direct sunlight (i.e., radiant heat loading) during conditions of heat stress. Shelter does not necessarily require air conditioning, and air conditioning may actually be uncomfortable for employees working in heat stressful conditions.

F.4.e. Clothing

Clean dry undergarments help prevent some heat stress related problems. Provisions should be made for changing PPE garments that may become sweaty and dirty. Showering also helps to rehab personnel that show signs of high stress. Every effort should be made to minimize PPE requirements which may increase the heat stress of personnel without a commensurate gain in personal protection.

F.4.f. Monitoring

1) One of the most important aspects of monitoring for heat stress is the buddy system. Employees, through their training must be sensitive to early warning signs. Self/buddy checks of pulse are a simple method of extending this principle.

2) The HSO will implement a program of personal stress monitoring as appropriate for personnel wearing PPE (e.g., level Mod D/C workers) and for most other situations.

F.4.g. Personal Monitoring Programs

A program of personal stress monitoring should be used for most situations where whole body chemical protective clothing PPE is in use. It may also be used for other situations as well. The HSO shall use pulse as the primary method for monitoring but may use any combination of the following which includes pulse.

F.4.h. Pulse

1) Pulse is the primary means of personal monitoring for heat stress. Pulse should be less than 110 beats per minute (bpm). (The radial or carotid pulse should be taken seated or standing if necessary.)

2) Finger or wrist cuffs are a simple and objective measuring device which can be used by employees to monitor their own crews. If employees are used as part of a monitoring program these devices should be available to ensure objective observations. Training in such case should include: signs and symptoms, this procedure, and thorough reading of the instructions provided for the monitoring device(s) that will be used.

3) Take reading before or at the beginning of a break whenever heat stress conditions exist. Workers should be rehabbed until the pulse returns below 100 bpm.

4) The HSO is responsible for establishing a schedule for monitoring and should include the following minimum requirements (additional monitoring may be required on certain days or for more sensitive individuals).

Table F.4.h. Pulse Monitoring Schedule

Conditions	8 a.m. to 11 a.m.	11 a.m. to 3 p.m.	3 p.m. to shift end
Personnel do not show any signs or symptoms and monitoring is negative.	• Monitor for signs and symptoms	• 2 hr. interval	• 1 hr. interval
Personnel show any signs or symptoms and monitoring is negative.	• Monitor for signs and symptoms	• 1 hr. interval	• 1 hr. interval
Monitoring shows employee stress.	• 2 hr. interval	• 1 hr. interval	• half hour interval

For ANY employee that has already removed for stress and is being returned.	• Interval should be cut in half for any individual that has been removed from work for rehab earlier in the shift and is now returning to work. Additional monitoring should also be performed on the following days until employee becomes acclimatized and is no longer showing symptoms or positive monitoring results.

F.4.i. Rehab

Rehabilitation should include at a minimum: seated rest in a shady location; removal of some/all outer garments; fluids; observation; reduction in the ratio of work/rest periods; and increased monitoring after return to work.

F.4.j. Action Level for Personal Monitoring

An action level for personal heat stress monitoring has been established at 85°F ambient temperature when site personnel are wearing chemical protective clothing during the performance of field activities.

At temperatures exceeding 100°F ambient temperature, all ground laborers, regardless of PPE, should be monitored.

F.4.k. Work/Rest Regimen

The following work/rest schedule may be used to help control heat stress when monitoring removals dictate the need. Ground labor and PPE labor should also be scheduled for early morning or evening if possible.

Table F.4.k. Work/Rest Regimen

Ambient Temperature (°F)	Work Period (minutes)	Rest Period (minutes)
72-80	120	15
80-85	90	15
85-90	60	15
90-95	30	15
95-100	15	15

F.4.l. Cold Stress

To minimize cold related illnesses, site supervisors are to be aware of the symptoms and environmental conditions that lead to cold-related illnesses. Appropriate steps shall be taken to take to prevent their occurrence of these illnesses. This procedure describes the causes, symptoms, treatment and/or prevention of cold-related illness.

F.4.m. Thermal Balance

When the temperature of the surrounding air or water is cooler than the worker, the body's physical processes must increase to maintain thermal balance.

Shivering is the body's attempt to generate increased heat.

F.4.n. Cold Stress Symptoms

1) Common (but unreliable) symptoms:

    a. Shivering, pain, and numbness, although commonly associated with cold stress, are not trustworthy indicators to cold exposures.

    b. The reason you should not trust these is because prolonged cold exposure numbs all body sensations.

    c. If these symptoms are detected, cold stress should be suspected.

    d. The lack of these symptoms DOES NOT rule out the possibility of cold stress.

2) Wind-chill temperature is a better means of evaluation as it takes into account the wind's ability to strip heat from the body through convection.

3) Water conducts heat away from the body much faster than air. Personnel are especially exposed to a cold stress hazard when performing spill cleanup in boats or around open water in cold weather situations. Falling into cold water can rob body heat very quickly.

4) Clothing that is wet with perspiration (as well as from water contact) will cause heat loss through conduction.

F.4.o. Cold Injury

1) Trench Foot:

    a. Cause: Occurs as a result of extended exposure of the feet to cold and moisture.

    b. Injury: Capillary walls of the feet are injured, resulting in tingling, itching and pain.

    c. Recognition: Blisters may form followed by ulceration of the skin.

2) Frost-Nip:

    a. Cause: Is a localized superficial freezing of extremities such as ears, nose, toes, and fingers.

    b. Injury: Worker experiencing frost nip are susceptible to future injury and should avoid chilling.

c. Recognition: Initially there is a dark bluish color due to bleeding under the skin which at times can become gangrenous.

3) Frostbite:

a. Cause: Frostbite occurs when the moisture in the skin actually freezes, forming ice crystals, resulting in the damage of skin cells. The ears, nose, toes and fingers are most susceptible because of poorer circulation in these areas. The body may shut down flow to the extremities in order to maintain warmth in body core areas.

b. Injury: Tissues are destroyed when bodily fluids turn to ice. Damaged area can become gangrenous resulting in the loss of tissue, finger tips and toes.

c. Recognition:

i. A burning pain is noted initially, then pain decreases and numbness sets in.

ii. The injured area becomes red, then blue/red.

iii. The skin becomes waxy pale in appearance because of lack of oxygen.

4) Hypothermia:

a. Cause: Occurs when heat production of the body is not sufficient to replace heat lost to the environment.

b. Injury: The core body temperature is lowered and the pulse rate slows. Metabolic processes in the body are finely tuned to perform at normal body temperature. As the temperature is lowered, muscular weakness occurs, mental abilities dull and the worker becomes uncoordinated. Cardiac arrest follows if core temperature continues to fall.

c. Recognition:

i. Signs of hypothermia are evident at 95°F body core temperature.

ii. Consciousness is lost between 89.6° - 86.0°F.

iii. At lower core temperatures, cardiac arrest is possible.

iv. Exposure to cold water decreases the body core temperature rapidly and consciousness is quickly lost.

v. Workers on or over water should be acutely aware of the danger of immersion during cold weather.

vi. Hypothermia results in dulling of senses and could result in poor decision making.

F.4.p. Prevention

1) Training and recognition:

    a. Prevention of cold stress is, in many ways, similar to preventing heat stress. Training and recognition of the hazard is especially important.

    b. All personnel will receive training on the cause, symptoms, and most importantly, methods of prevention of cold stress injuries.

2) Clothing:

    a. Prevention of hypothermia and other cold injuries is best accomplished by protecting workers from cold and moisture.

    b. Clothing is the most important factor in prevention of injury.

    c. Personnel working on land should layer clothing with outer layer being wind and water resistant.

    d. The layers should be capable of being vented at wrist, neck and waist to reduce wetting by perspiration.

    e. Protect extremities that have poor circulation.

    f. Keep head and face covered.

    g. Wear insulated footwear, keep socks dry (bring extra socks as needed).

    h. Gloves are extremely important.

    i. Never allow bare skin to contact metal surfaces at sub-zero temperatures.

3) Acclimatization:

    a. Do not count on acclimatization.

    b. A limited degree of acclimatization can occur from exposure and working in cold environments.

    c. Some physiological changes do occur but people also learn how to more effectively protect themselves from temperature extremes.

4) Fluid Replacement:

    a. As with heat stress, blood circulation and heat transfer is critical to dealing with cold temperature extremes.

    b. Cold weather causes significant water loss as a result of the dryness of the air.

c. Fluid intake should be increased to prevent dehydration which directly affects blood volumes and flow to the extremities.

d. Warm, sweet, caffeine-free, nonalcoholic drinks and soup offer the best fluid replacement and provide caloric energy.

5) Work-Rest Regimens:

a. When temperatures are less than 20° F (actual or wind-chill) heated warming shelters should be made available.

b. Workers should use these on regular basis. See Table F.4.k. for guidelines for scheduling breaks.

6) Diet:

a. As with any work in extreme temperatures, personnel will be instructed to eat a well-balanced diet to replace calories burned and provide necessary vitamins and nutrients.

7) Environmental Monitoring:

a. Regular monitoring of the environment by recording wind speed and actual thermometer readings for comparison to the wind-chill chart should occur at regular intervals depending on conditions.

8) Prohibited Activities:

a. Alcohol should not be consumed since it increases blood circulation to the skin and interferes with internal thermostatic control. Alcohol also interferes with mental acuity which can lead to risk taking.

b. Cigarette smoking should be prohibited since the nicotine restricts flow of blood to the extremities.

9) ACGIH TLV Guidelines:

a. The current edition of the American Council of Governmental Industrial Hygienists' Threshold Limit Values (TLV) provides a reference on cold stress prevention. Some of the TLV information is summarized in Appendix G.

F.4.q. Treatment of Injuries

1) Trench Foot, Frosting and Frost Bite:

a. These injuries require immediate response, including removal of the individual from a cold environment, the gradual warming of the affected areas, having the victim not use the affected limbs, (drive victim or carry, do not allow the victim to walk).

b. Obtain immediate medical attention as these types of injuries become more severe as exposure progresses.

c. AVOID RAPID WARMING OF EXTREMITIES.

2) Hypothermia:

a. Hypothermia is a life threatening condition that requires immediate response. Remove victim to a warm area. The individual may be disorientated and unable to talk clearly or understand you.

b. Help the individual to a warm place and wrap them in warm blankets or bathe them (if possible) in warm (not hot) water.

c. If they are conscious give hot (non-caffeine) liquids to drink.

d. Summon immediate medical attention. UNTREATED HYPOTHERMIA CAN LEAD TO VENTRICULAR FIBRILLATION (HEART ATTACK) AND DEATH.

F.5. Hazard Communication Program

The Envirocon Program, in its entirety, is located in a separate labeled notebook in the Envirocon project trailer and in the Envirocon online data base. The notebook is available for review by employees at any time during normal work shift. Envirocon will be responsible for maintaining a copy of their Hazardous Communication Program and Safety Data Sheets (SDS) on site. The online data base is available MSDS Online:

https://msdsmanagement.msdsonline.com/61fa7928-2936-4d21-806b-300a7e5d1da2/ebinder/?nas=True.

Posters are also located at the site with online web address and hard copies (e.g. books) will be kept in crew trailers and LTWTS building.

F.5.a. Subcontractors

Subcontractors will be responsible for keeping an individual copy of their respective programs.

F.5.b. Safety Data Sheets

SDSs will be located in a separate labeled notebook in the Envirocon project trailer and in the Envirocon online data base. SDSs will be available to all employees for review during the work shift. Copies of all SDSs for materials on site will be provided to Bureau of Reclamation prior to material delivery on the site.

F.5.c. Container Labeling

All containers received on site will be inspected to ensure the following:

1) All containers clearly labeled;

2) Appropriate hazard warning; and
3) Name and address of the manufacturer.

F.5.d. Employee Training and Information

Prior to starting work, each employee will attend a health and safety orientation and will receive information and training on the following: An overview of the requirements contained in the Hazardous Communication Program. This training shall include at a minimum the following:

1) Hazardous chemicals brought to the site for the project;
2) The location and availability of the written Hazardous Communication Program;
3) Physical and health effects of the hazardous chemicals;
4) Methods of preventing or eliminating exposure;
5) Emergency procedures to follow if exposed;
6) How to read labels and review SDSs to obtain information; and
7) Location of SDS file and location of hazardous chemical list.

G. Site Safety Procedures

This section addresses safe work practices and site-specific safety procedures that will be used to control hazards on site.

G.1. Code of Safe Work Practices

Every employee has a responsibility to ensure that the program proceeds efficiently and safely. The following procedures constitute the basic safe work practices expected of every employee.

G.1.a. Conducting Yourself in a Responsible Manner

Safety programs are not only for your safety, but the safety of everyone on site. Your conduct potentially impacts your coworkers.

1) Perform all tasks in a safe and approved manner.

2) Do not direct an air hose at another person. Do not use compressed air to remove debris from clothes, hair, or any part of the body.

3) Honor the barricades erected by other contractors on the job site.

4) Do not stand in front of a door that opens toward you.

5) Do not work while your ability or alertness is so impaired by fatigue, illness, or other causes that they might unnecessarily expose yourself or others to injury.

6) Do not bring, keep, or use alcoholic beverages, controlled substances, or weapons on site.

7) Anyone known to be under the influence of drugs or intoxicating substance, which impair the employees ability to safely perform the assigned duties, shall not be allowed on the job while in that condition.

8) Workers shall not handle or tamper with any electric equipment in a manner not within the scope of their duties, unless they have received instructions from a qualified, licensed electrician.

9) Do not use any form of solvent, gasoline or kerosene for cleaning hands or clothing. Use soap and water or other cleansers intended for the purpose.

10) Keep hands and other part of your body out of pinch points, for example:

- DO NOT use your hands to dislodge rocks or jams in tailgates (instead raise and lower the bed to use the gate's weight to clear materials and jams);
- DO NOT get between counterweights on excavators or cranes and tracks, walls, excavation cuts etc.; and
- DO NOT reach into belts with running machinery.

11) Use handrails when climbing or descending stairs and walkways.

12) Do not run, except as necessary in an emergency.

13) Horseplay, scuffling, and other acts which tend to have an adverse influence on the safety or the well-being of other employees is prohibited.

14) Do not jump from one level to another or one place to another. For example:

- Get on and off equipment using three points of contact;
- Walk down stairs without jumping or skipping steps;
- Use ladders or ramps provided to descend into trenches;
- Do not jump out of pickup beds; and
- Do not jump across trenches.

15) Always stand on an approved ladder to remove articles that may out of reach from floor level. Do not stand on chairs, boxes, or other makeshift devices.

16) Loose or frayed clothing, hanging long hair, dangling ties, finger rings, etc., shall not be worn around moving machinery or other areas where they may become entangled.

17) Get help lifting heavy objects from heavy equipment, lifting devices, or help from another employee, and do not lift objects greater than 50 lbs. unaided.

18) Do not improperly use, mishandle, or tamper with health and safety equipment and sampling devices.

19) Personnel shall not drop or throw any articles or materials of any kind unless a specific procedure has been developed to do so safely.

20) Do not harass, feed, or photograph wildlife. If you find an injured or dead animal, contact the nearest gate attendant or the U.S. Fish and Wildlife Service.

G.1.b. Participate in Your Safety Programs

There are a number of ways for you to influence the safety on site. Don't just complain about problems; participate in your own safety.

1) Attend each day's work briefing as scheduled.

2) Attend all required safety meetings, training, or briefings.

3) Participate in ATW discussions.

4) Complete safety observer reports when you want to make a suggestion, observe a commendable act of safety or quality, take a "time out for safety" to correct an unsafe act or condition.

5) Approach every task with incident-free performance in mind.

6) Ask questions when you are uncertain about a procedure or equipment use.

7) Participate in the evaluation or investigation of any accident or incident when you are requested to do so.

8) If you fear reprisal, use the Envirocon safety Hotline **800-224-7389**.

G.1.c. Practice Good Housekeeping

Housekeeping is the hallmark of:

1) Keep your work area clean and orderly.

2) Good housekeeping practices shall be maintained continually.

3) Keep work, storage, and access areas clean of tools, equipment, and debris.

4) All means of egress shall be kept unblocked, kept clear of debris and slip or trip hazards, kept well lighted, and kept unlocked at times.

5) Immediately remove spilled liquids from the floor.

6) Clean up or otherwise remove slip/trip/fall hazards immediately.

7) Do not leave boards with protruding nails or other loose material on the floor where they may be stepped on.

8) Keep aisles and walkways clear of electrical and telephone cords.

9) Do not overload electrical outlets.

10) Electric cords shall not be exposed to potential damage from vehicles.

11) Mark or barricade slip/trip/fall hazards that cannot be removed.

12) Any time work is performed overhead, barricades shall be erected.

13) Barricades shall consist of caution (yellow) or danger (red) barricade colors and appropriately worded tape or signs.

14) All barricades shall be removed when not in use.

G.1.d. Follow Standard Procedures

Hazardous waste operations involve a number of standard procedures which are particularly important. Make these procedures a habit.

1) Use the Buddy System when performing operations in hazardous areas; when working with hazardous contaminants; when physical capabilities may become stressed (heat stress); or working in proximity of operating machinery or equipment.

2) Practice contamination-avoidance techniques.

3) Enter and exit the Exclusion Zone and the Contamination Reduction Zone through designated areas.

4) Complete sign-in/out logs when required.

5) Do not eat, drink, chew tobacco or gum, smoke, or engage in any other activity that may increase the possibility of hand-to mouth contact in the Exclusion Zone or the Contamination Reduction Zone. (Exceptions may be permitted by the Project Health and Safety Manager for other reasons, such as to allow fluid intake during heat stress conditions.)

6) Do not use lighters or matches in the Exclusion Zone and Contamination Reduction Zone.

7) Employees under a physician's care and/or taking prescribed narcotics must notify the designated site safety supervisor.

8) Lift material in a safe manner and avoid strains. Bend your knees, keep your back straight, and push upwards with your legs when lifting. The lifting of heavy and bulky objects will normally be done by or more shop personnel. Lifting heavy/bulky objects improperly can result in needless injury.

9) Get help (mechanical help or more people) when lifting heavy or awkward materials.

10) Wear the PPE specified in the *HASP*, including hard hats, steel toed boots, and safety glasses that must be worn at all times in active work areas.

11) If you are required to wear a respirator, remove facial hair (beards, long sideburns, or mustaches) that may interfere with the satisfactory fit of the respirator mask.

12) Use safety devices provided for your protection (e.g., handrails, guards, pressure relief valves, and seat belts). Do not remove these devices while the equipment is being operated.

13) Never approach within 25 feet of the operating area of a piece of equipment without first making eye contact with the operator, signaling your intention, and receiving an acknowledgement from the operator. If you wish to approach the equipment (e.g., to

speak with the operator, the operator must first lower all buckets, blades, etc. and idle the engine before you approach).

14) When ground personnel support heavy equipment, pay particular attention to pinch points (e.g., the counterweight swing radius and the tracks of an excavator). Keep out from under suspended loads.

G.1.e. Follow Safety Procedures

In addition to standard procedures, there will be many site specific procedures to learn and follow. You need to learn these from your site-specific training and follow the procedures. If you feel the procedures are incorrect or inadequate it is improper to take it upon yourself to modify procedures. Ask your supervisor, make suggestions, or raise questions during planning and training.

1) Attend, pay attention, and ask questions during procedure training and briefings.

2) Implement, adhere to, and follow established rules, guidelines, procedures, plans, etc., as specified.

3) Follow proper decontamination procedures.

4) Make sure fall prevention, fall protection or fall arrest systems are in place when working at elevations greater than 4 feet above the surrounding work area.

5) Follow the work-rest regimens and other practices required by the heat stress program.

6) Where appropriate, lockout procedures shall be used.

7) Employees shall not work under vehicles supported by jacks or chain hoists without protective blocking that will prevent injury if jacks or hoists should fail.

8) Obey all authorized safety signs and demarcations. Do not place or remove these items except as authorized by the Site Health and Safety Supervisor (HSS).

9) Become familiar with the on-site hazards, work zones, PPE requirements, and decontamination methods.

G.1.f. Permit Required Procedures

Many of the most important procedures dealing with the most dangerous hazards involve permit requirements to ensure that necessary precautions are taken before work begins. Pay particular attention to these procedures.

1) Do not enter a permit-required Confined Space without a permit, and follow all requirements of permits as issued.

2) Don’t rely on postings to warn you of confined space hazards. When in doubt ask for a permit and testing. Manholes, underground vaults, chambers, certain confining excavations, tanks, silos or other similar spaces may have a confined space hazard.

3) Check with your Supervisor prior to starting any hot work operation (welding or cutting operations) and, if you are working in an area that requires a hot work permit, follow the permit as issued.

4) Depending on the fire hazards at your facility, hot work permits may be required for use of cigarette lighters, electrical equipment that is not intrinsically safe, flash photography, motors, engines, or spark producing metal tools.

5) The combination of hot work and confined spaces is particularly dangerous even if you don't plan to enter the space. No burning, welding, or other source of ignition shall be applied to, or near any enclosed tank or vessel, even if there are some openings, until it has first been determined that no possibility of explosion exists and authority for the work is obtained from the foreman or superintendent. This includes small voids too. A sealed can, double space, storage compartments or similar small spaces can contain flammable debris or explosive vapors.

6) Do not dig or drive objects into the ground without first:

    a. Ensuring that necessary permits have been obtained;

    b. A competent person has been assigned;

    c. A competent person has inspected the site;

    d. Utilities have been located prior to beginning excavation activities;

    e. Checking that excavations slopes are checked daily for stability and air quality; and

    f. Do not enter an excavation greater than 5 feet deep unless authorized by the HSS and then only after the excavation has been sloped or shored properly. Maintain safe means access and egress from all excavations.

7) Follow lockout/tagout procedures when working on equipment involving moving parts or hazardous energy sources. Install and remove locks and tags only in accordance with procedure and only when authorized.

G.1.g. Use Tools Properly

Tools, especially hand tools, are used frequently with minimal supervision. It can be all too easy to use tools improperly and create serious safety hazards.

1) Use all tools in the manner intended and/or prescribed. The operating instructions for all tools and equipment ARE MANDATORY.

2) Modification of use or design must be in accordance with the written instructions or permission of the manufacturer.

3) Do not suspend tools or any other items using electrical cords.

4) In locations where the use of a portable power tool is difficult, the tool shall be supported by means of a rope or similar support of adequate strength.

5) Air hoses shall not be disconnected at compressors until the hose line has been bled.

6) Inspect safety devices before every use, including but not limited to:

    a. Respirators;

    b. Personal protective equipment;

    c. Body harnesses;

    d. Lanyards;

    e. Monitors;

    f. Fire extinguishers;

    g. Confined space retrieval systems (not the same as fall protection harnesses); and

    h. Man baskets.

7) Inspect other tools and equipment before use.

    a. A competent person must inspect scaffolds and man lifts before each day's use.

    b. Ladders must be in good service, placed at the proper angle, secured, and extents to the proper length (for access to heights the ladder must be 3 feet above the landing).

    c. Inspect power tools, looking especially for damaged insulation or missing ground plugs on electrical cords.

    d. Inspect cutting devices looking especially for properly sharpened and guarded edges.

    e. Inspect hand tools look especially for chisels, hammers and punches with mushroomed heads; files without handles, and hammers with broken handles.

8) Do not use defective equipment.

    a. Don't leave defective equipment in service for others to use. Remove it from service and report the problem to your supervisor.

    b. At a minimum, defective equipment must be tagged out of service.

        i. Use a red tag placed near starting switches or levers.

        ii. Describe the reason the equipment is tagged out.

iii. Write your name and the date on the tag.

c. Alternatively, defective equipment can be taken out of service by destruction and disposal.

9) Use ground fault circuit interrupters (GFCI) for cord and plug equipment used outdoors, in damp locations, or when equipment is not plugged directly into permanent wiring.

10) Use only extension cords rated for hard service or junior hard service (e.g., SO, JSO, SOW, JSOW). An Underwriters Laboratory (UL) label on a local hardware store flat cord is probably NOT rated for this service.

11) Keep electrical cords out of walkways and accumulations of water unless protected and rated for such service.

G.1.h. Operate Equipment Safely

1) All equipment is to be operated in accordance with manufacturer's written instructions and/or manuals.

2) Equipment shall not be modified or operated out of specified limits without written permission from the manufacturer and the HSM for the project.

3) Only trained and authorized persons shall operate machinery or equipment.

4) Do not operate equipment unless you are properly trained and authorized to do so in a manner consistent with the owner/operators manual.

5) DO NOT use a piece of equipment, which has been tagged out of service. Do not remove red tags without authorization from the person placing the tag or the person responsible for the repairs.

6) Inspect equipment before using it.

   a. Heavy equipment inspections shall be documented. Note all discrepancies and tag out equipment that may be dangerous to operate.

   b. Red tags must have a description of the reason for the tag, the name of the person placing the tag, and the date the tag was applied.

7) Machinery shall not be serviced, repaired, or adjusted while in operation, nor shall oiling of moving parts be attempted, except on equipment that is designed or fitted with safeguards to protect the person performing the work.

8) Use vehicle or equipment seat belts any time the vehicle or equipment is in motion.

9) Excavating equipment shall not be operated near tops of 'cuts, banks, or cliffs if employees are working below.

10) Do not maneuver equipment into the working area of other equipment without first making eye contact with the operator working in the area and signaling your intentions to maneuver into that area.

11) Always acknowledge that you understand that other equipment or ground personnel may enter your working area.

12) Do not allow people on foot to approach without lowering hydraulically lifted or suspended components (e.g., buckets, blades, bellies) and reducing engine speed to idle.

13) Tractors, bulldozers, scrapers, and carryalls shall not operate where there is a possibility of overturning in dangerous areas such as the edges of deep fills, cut banks, and steep slopes.

14) Do not allow supporting ground personnel to work within pinch points of the equipment (e.g., the swing radius of a counterweight and the tracks on an excavator) or under suspended loads.

G.1.i. Prepare Yourself for Incidents

1) Become familiar with the emergency response plan so that you can respond properly in an emergency.

2) Become familiar with the locations and types of emergency equipment, such as fire extinguishers, emergency showers, or air horns.

3) Report all incidents to your supervisor immediately.

4) Participate fully and truthfully in incident investigations.

G.1.j. Supervisors Play a Leadership Role in Safety

As with all aspects of conducting operations, the supervisor is ultimately responsible for carrying out work in accordance with company policies and procedures, and in accordance with the specifications and applicable regulations.

1) Take a leadership role in establishing safety a safety culture on site.

2) Give employees frequent accident prevention instruction and encouragement.

3) First through encouragement and incentives, ensure that employees observe and obey all applicable company, state or federal regulation and order as is necessary to the safe conduct of the work. When necessary, compliance must be compelled using progressive disciplinary measures described in this document.

4) Ensure that employees are qualified for the work they are assigned.

5) No one shall knowingly be permitted or required to work while the employee's ability or alertness is so impaired by fatigue, illness, or other causes that they might unnecessarily expose the employee or others to injury.

6) Do not allow anyone to remain on site when under the influence of drugs or intoxicating substance, which impair their ability to safely perform assigned duties.

7) Daily "tailgate" safety meetings shall be held to discuss safety concerns, instruct on new procedures, and discuss lessons learned from investigations and other related safety topics.

8) Encourage and listen to the suggestions of all employees.

9) All work shall be thoroughly planned and supervised to prevent injuries in the handling of materials and in working together with equipment.

10) Inspect the site daily.

11) Investigate all incidents.

12) Ensure thorough documentation of all aspects of the safety program.

G.2. Site Contingency Plan Summary

The contingency plan for the Site is embedded by reference in various sections. For clarity, they are summarized as follows:

G.2.a. Emergency Contacts

Reference Section I.8, Emergency Contacts.

G.2.b. Planning Dates for Community/Emergency Response Providers

To be determined.

G.2.c. First Aid Medical Information

Reference Section I, Incident and Emergency Procedures.

G.2.d. Air Monitoring Plan

Reference *Monitoring Plan* (Appendix C of the *Final Design*).

G.2.e. Spill Prevention, Control and Countermeasures Plan

Reference Section I, Incident and Emergency Procedures.

G.3. Employee Participation

This project has established a variety of procedures to encourage the participation of employee in their own safety. Employee participation includes all FE JV, and lower tier subcontract personnel.

G.3.a. Training

Training is required for each employee before starting any new task or working in a new area. Training is considered an employee participation process. Employees are encouraged to ask questions and utilize training sessions to familiarize themselves with procedures.

G.3.b. Daily Safety Briefing

Each day's work begins with a safety briefing. These briefings shall be conducted in a manner to encourage employee participation.

1) Supervisors shall report the plan of the day for all employees. This should include other work that may occur near the project site or impact on project work. Special tasks expected for the day. Waste loads expected that will require special procedures.

2) Discuss lessons learned from incidents on this site or others.

3) Report and discuss safety observations made by employees.

4) Report and discuss times out for safety.

5) Participate in ATW discussions.

6) Discuss employee suggestions.

7) Recognize safety performance (good and unsatisfactory).

G.3.c. Safety Observer

This site has an established, behavior-based safety observer program. A minimum of two safety observer reports will be discussed each week. Employees will be instructed in the concept of unsafe conditions and behaviors. The primary interest is to draw attention to correcting unsafe conditions and adopting safe behaviors. Safety observations shall be documented and provided to the HSS.

1) To encourage everyone to participate in this program, employees will take turns making the mandatory weekly reports.

2) Voluntary observations are encouraged at any time and shall be handled as a safety suggestion.

3) Positive reports are encouraged to point out laudable behaviors for recognition.

4) All lower tier subcontractors shall be included in the safety observer program.

G.3.d. "Buddy System" Plus

Envirocon's incident-free performance objective is very demanding. This objective can only be met if every employee performs all work without incident. Since none of us is perfect, it is further necessary for each person to take responsibility not only for themselves, but the others

working with you. This concept is what Envirocon refers to as an expanded buddy system concept.

1) The HAZWOPER standard requires that employees remain in contact with at least one other "buddy" in the event of an emergency or accident.

2) The "buddy system" plus challenges each employee on site to not wait for an accident to happen to our buddies. Instead, correct unsafe conditions or challenge unsafe behaviors around us.

    a. Don't let it pass. If you see that someone else is about to make a mistake or hasn't recognized a hazard, take responsibility to challenge the situation.

    b. It's not enough to not be at fault. Stop looking on accidents as someone's fault. Instead, look on an accident as everyone's failure to prevent the accident.

G.3.e. Stopping Work

Each employee has the right to call for work to stop when they observe a serious potential for injury. The SSO in particular is responsible for stopping work if there is a hazardous condition. Short of stopping work, FE JV encourages employees to get involved before things escalate to a threat of injury. Employee "time-outs" and "challenges" help to identify changes in conditions or to challenge improper procedures.

1) "Time-Out" for Safety Authority:

    Changes in conditions, deviations from plans, unexpected or surprise events that have not yet caused an accident, threaten the safety of an operation or job task. These are hazardous conditions that must be recognized and controlled.

    The "time-out" authority is intended to challenge each employee to control these hazards by giving each member of the crew the authority to take a "time out" when they recognize such potential problems. Take a "time-out" when:

    a. Conditions change. Examples might include:
        i. Changes in weather;
        ii. Changes in soil types;
        iii. Changes in the equipment you are using;
        iv. Changes in other work performed nearby;
        v. Changes in materials being used to do the work;
        vi. Changes in the toxicity of wastes;

    b. Unexpected conditions are found.

    c. Personnel who have not signed the ATW move into an area where they could be exposed to hazard created by your work group.

d. Work deviates from plans.

e. An unplanned event occurs that might lead to an accident.

f. You don't understand what the plan for work is.

g. The work plan no longer seems safe.

2) Taking a "Time-Out" Means:

a. Identifying one of the conditions above exists;

b. Communicating a concern to your supervisor or safety officer;

c. Updating or preparing an ATW;

d. The supervisor or safety officer evaluate the concern;

e. An appropriate response is determined. This might include:

i. The plan is not being followed and the team must be regrouped to get back to the planned way of doing the work;

ii. The crew must regroup and revise plans/procedures;

iii. The crew must regroup and change PPE;

iv. The employee must be trained in the appropriate procedures;

v. The employee must be requalified for new equipment being used;

vi. The employee needs to be informed of the reason for the current plans/procedures and why they are best for the task.

f. Regroup the work team (when needed to revise plans, procedures, training, etc.).

g. Communicate revised plans to all concerned.

3) Employee Challenges:

The site safety and health program is the responsibility of all employees. Each employee is required to challenge unsafe conditions or behaviors in their work areas.

The "employee challenge" system is intended to encourage employees to take initiative in correcting unsafe conditions or behaviors. Where an unsafe condition or behavior poses an imminent threat that can be readily addresses without a change in procedure or policy, each employee is encouraged to challenge those responsible.

a. Challenge another employee that is driving in the wrong direction.

b. Challenge a visitor to the work area that might not have signed in or is not accompanied by a qualified worker.

c. Grab a roll of barrier tape to mark a broken step on a stairway and report it to your supervisor.

d. Flag traffic around a spill until a response crew arrives.

4) When an operation is stopped due to a safety hazard challenge, notify the site supervisor immediately. The Supervisor shall report the challenge to the Project Manager and Site HSO.

G.4. Clearing and Grubbing

G.4.a. Chain Saws, Tree Trimming/Removal

1) Chain Saw:

a. All chain saws must have an automatic chain brake or kickback device.

b. The idle speed shall be adjusted so that the chain does not move when the engine is idling.

c. Operators will wear the following PPE:

i. Steel toe leather boots;

ii. Safety glasses;

iii. Hardhat;

iv. Chainsaw chaps;

v. Hardhat visor;

vi. Hearing protection; and

vii. Leather gloves.

d. Chain saws will not be fueled while running, hot, or near open flame.

e. The operator will hold the saw with both hands during all cutting operations.

f. The chain saw must never be used to cut above the operator's shoulder height.

2) Tree Removal:

a. Prior to removal operations, the employee shall consider:

i. The tree and surrounding area for anything that may be potentially damaged during tree removal;

ii. The shape of the tree, the lean of the tree, and decayed or weak spots;

iii. Wind force and direction;

iv. Location of other people;

v. Above-ground utility lines and electrical hazards; and

vi. Steps shall be taken during the removal of all trees to ensure that property improvements which are not planned to be removed as part of the remediation activities are not damaged.

b. Prior to felling operations, the work area shall be cleared to permit safe working conditions and an escape route shall be planned.

c. Tree cutting teams will work in pairs.

d. Each worker shall be instructed as to exactly what he is to do.

e. All workers not involved in the operations shall be kept clear of the work area.

f. Before starting to cut, the operator shall be sure of his footing and must clear away brush, fallen trees, limbs and other materials that might interfere with cutting operations.

g. The employee shall work from the uphill side whenever possible.

h. Just before the tree or limb is ready to fall, an audible warning shall be given to all those in the area; all persons shall be safely out of range when the tree falls.

i. If there is danger that the trees being felled may fall in the wrong direction or damage property, wedges block and tackle, rope, or wire cable shall be used to lower limbs to the ground.

j. All limbs shall be removed from trees to a height and width sufficient to allow the tree to fall clear of any wires and other objects in the vicinity.

k. Special precautions shall be taken when roping rotten or split trees due to the potential for falling in an unexpected direction even though the cut is made on the proper side.

l. Persons shall be kept back from the butt of a tree that is starting to fall.

m. In general, trees are to be taken down and removed in sections or parts. Free falling of trees will not be allowed without prior approval from the Project Manager.

n. Working From Branches/Fall Protection.

o. All cutting involving personnel working at heights greater than 4 feet above the base of the trunk will utilize fall prevention or fall protection systems.

p. Options:

i. Hydraulic manlift; and

ii. Personnel secured to trunk of tree.

G.4.b. Debris Removal

1) Use approved paths only, clear existing walkways of debris, vegetation, and excavated material.

2) Use face shields and chaps when using hand held power equipment for cutting vegetation.

3) Wear cut resistant work gloves, when the possibility of lacerations or other injury may be caused by sharp edges or objects, watch where you are stepping.

4) Wear the proper PPE for the task that you are performing (i.e., rubber gloves, boots, poly coated Tyvek®).

5) Review hazardous properties of site contaminants before starting work.

6) Observe proper lifting techniques, obey sensible lifting limits (50 lb max. per person manual lifting).

7) Use mechanical lifting equipment (hand carts, trucks or machinery) to move large awkward loads.

8) Keep eye contact with operator, wear high visibility safety vests, and isolate equipment swing areas.

9) Stay out from under the dead side of the excavator or crane boom, and don't stand beneath suspended loads.

10) Secure loads tightly before you attempt to move it to the decontamination pad or off site.

G.5. Excavations, Trenching, and Other Intrusive Work

The OSHA standards for excavation safety (29 CFR 1926, Subpart P) shall be followed at all times during excavation activities. Excavations include "any man-made cut, cavity, trench, or depression in an earth surface, formed by earth removal." This includes trenches. This standard applies regardless of the depth of the excavation although NSPW confined space requirements do apply when personnel enter a depth exceeding 4 feet. Utility locates should be done at any depth for example.

The Envirocon Excavation and Trenching Plan is found in Appendix G.

G.5.a. NSPW Requirements

1) A competent person shall be designated and supervise all intrusive work.

G.5.b. Excavations that Personnel Will Be Entering

In excavations 4 feet deep or deeper, a competent person shall ensure that the following requirements are met.

1) An evaluation of excavation or trench as a confined space is made. Reference the Confined Space Plan, Appendix H.

2) Provide safe access and egress. This includes ladders or ramps. In trenches, a point of egress must be within 25 feet at all times while in the trench. Ramps shall be sloped so as not to require the use of hands to walk out of the excavation.

3) Employees must be protected from cave-ins.

    a. In trench excavations the competent person must have all sides sloped in accordance with OSHA requirements on either side of the trench where personnel are working.

    b. In excavations, at a minimum, employees within a distance equal to the depth of a cut face shall be protected. Where employees are in excavating equipment, at a minimum, the equipment shall not undercut a face in such a way that the cab is closer than the height above the cab.

4) Alternative protections, specified by OSHA include trench boxes or shoring.

5) In excavations where employees may be required to enter, excavated or other materials shall be effectively stored and retained at least 2 feet or more from the edge of the trench.

G.5.c. Water

Whenever, groundwater may be encountered; a specific classification and slope adjustment will be made on site by the competent person. At a minimum, an additional 1/2 to 1 slope will be added if flowing conditions are encountered at the toe of the slope where personnel are working.

G.5.d. General Excavation Practices

1) In excavations with potential airborne vapor hazards, where employees may be required to enter shall have the atmosphere tested before each entry and as conditions change.

2) Employees exposed to vehicular traffic shall be provided with and instructed to wear warning vests made of reflective or high visibility materials.

3) All employees in trenches shall wear the appropriate PPE, e.g., hard hats, safety glasses, hard-toed boots, etc.

4) No employees will be permitted under loads.

5) Dust conditions shall be kept to a minimum in accordance with the project dust control plan.

6) Where employees or equipment are allowed to cross over excavations, all walkways and/or bridges will have guardrails.

7) Adequate barrier protection will be provided at remotely located excavations (e.g., reflective cones or sawhorse barriers).

8) Each excavation must be inspected daily. If evidence of cave-ins or slides is apparent, all work in the excavation must cease until necessary precautions have been taken to safeguard employees.

9) Where vehicles or equipment operate near excavations or trenches, the sides of the excavation must be shored or braced as required to withstand the forces exerted by the superimposed load.

G.5.e. Utility Lines

Utility lines, both above and below ground, must be addressed in any excavation activity regardless of depth.

1) Be aware and always suspect the existence of underground utilities such as electrical power, gas, petroleum, telephone, sewer and water. Underground utilities are a concern at any depth. Then Superintendent shall call and document contact with Diggers Hotline: Wisconsin's One-Call Center CALL 811 or (800) 242-8511.

2) Utility markings must be clear, visible. Utility locates tickets must be maintained every 10 day if work isn't completed and/or markings are not maintained.

3) Refer to Envirocon Utility Location and Identification safety guidance documentation. Address above and below ground utilities in site planning COW - 1401.030 and 1403.011 form as well as JSA and crew CAP

4) Overhead and buried utilities should be located, noted and emphasized on all excavation and work plans (regardless of depth of excavation). Post warning barricades on the ground along the line of excavation in order to alert excavating equipment approaching overhead utilities.

5) When excavating within 6 feet of buried utilities, first locate and mark the expected location. Ideally, the utility should be shut off and excavating should be done with a spotter and extra care. Due to the inaccuracies of locating, if the utility cannot be shut off, hand digging (i.e., potholing) will be used to visually confirm the utility location before using heavy equipment.

6) When excavating within 6 feet of underground utilities, a spotter shall be used to assist mechanical excavating equipment in locating utilities.

7) When excavating within 6 feet of underground electrical, phone, flammable gas/liquid lines make every effort to de-energize lines.

8) The requirements above should be taken as a minimum. High volume or high pressure mains should be given a wider margin. Fiber-optical lines should be given additional margin. High pressure or high volume water lines should be approached in the same manner as "more dangerous" utilities.

9) Overhead Utilities:

   When overhead electrical power lines exist at or near an excavation site, consider all wires to be alive and dangerous. Support overhead utility lines as necessary. Overhead electrical lines may induce a current without actually touching the lines. Be sure to maintain clearances from electrical lines of 50 kilovolt (kV) or greater in accordance with 29 CFR 1926.550(a)(15). Place ground markers to indicate overhead hazards as well as those below ground.

G.5.f. Competent Person

The excavation competent persons are assigned in the organization and key personnel section earlier in this document. The excavation competent person is authorized to, and shall take prompt action to correct unsanitary, hazardous, or dangerous working conditions. Other responsibilities include (but are not limited to):

1) The competent person will supervise each intrusive work permit and its attendant ATW.

2) The competent person will directly oversee all operations and be present on site at all times while employees are in the excavation.

3) The competent person will make a daily inspection of the excavation area before each shift begins, after any changes in the excavation area or after a rainstorm.

4) The competent person will ensure that personnel in excavations will not work under suspended loads.

5) The competent person will ensure that work activities on the surface of the excavated area will be restricted to prevent working above personnel.

6) The competent person will ensure that banner guard and barriers will be placed across public access to the excavation areas at night to protect and warn personnel as necessary.

7) The competent person will ensure that personnel exposed to high traffic areas will wear high visibility vests; orange for daytime and reflective for night operations.

G.6. Falling and Tripping Hazards

G.6.a. Falls – Housekeeping and Materials Storage

1) All material shall be stored in a manner that will ensure that the material is safe from unexpected movement, falling, rolling, blowing, or any other uncontrolled motion.

2) Materials and supplies shall be kept away from edges of floors, stairways and access/egress routes (36 inches minimum).

3) Forms and scrap lumber with protruding nails and all other debris shall be cleared from work areas, passageways, stairs, and in and around buildings or other structures.

4) Tripping hazards, protruding nails, oil slicks, scrap materials and other hazardous conditions occurring during the course of the job shall be eliminated as work progresses.

5) Tools and equipment shall not be strewn about where they might cause tripping or falling hazards and shall, at the end of each workday, be collected and stored or disposed of as appropriate.

6) All food waste and oily/greasy rag containers shall be equipped with tight closing lids.

7) Protruding reinforcing steel (rebar) shall be properly capped or otherwise protected to prevent a hazardous condition.

8) All non-hazardous trash, oily wastes, PPE, debris and trash of any kind shall be segregated according to the applicable waste segregation scheme; and shall be labeled accordingly.

9) Covers on all roll-offs, drums, and containers of any type shall be securely covered at the end of the day.

G.6.b. Falls – Slippery Surfaces, Unstable Surfaces, Uneven Terrain

1) Wet conditions on the site caused by rain and/or work activities are likely to be encountered during the project.

2) Employees will be informed of the hazards associated with walking on slippery and or uneven surfaces.

3) Mark or remove trip hazards.

4) Proper foot wear will be provided to all employees involved with work activities during these conditions.

5) When possible, pedestrian traffic will be redirected around potentially dangerous areas.

6) Everyone should keep the work area and other areas where people may walk clean and orderly.

7) Tools, debris, and other objects should not be left on the floor, decking, or other areas where they present hazards during a job or after a job is completed.

8) Oil spills and slippery spots shall be cleaned up immediately.

9) Extra precautions should be taken when walking on steel decking during wet/icy weather and/or oily conditions.

10) Never walk on piping, never take dangerous shortcuts, and avoid jumping from elevated places.

G.6.c. Falls – Ladders

1) Personnel must visually inspect each ladder for defects before use; defective ladders shall not be used.

2) When working from a ladder, wear fall protection if work requires your body to extend past the margins of the ladder sides.

3) While ascending or descending a ladder, carry nothing which will prevent holding onto the ladder with both hands.

4) Metal ladders will not be used if there are any existing or potential electrical hazards in the work area.

5) All ladders must be securely tied off or secured by an attendant while the ladder is in use.

6) When working from ladders, work facing the ladder with both feet on the rungs.

7) Workers shall not stand with their waist above the top step of a ladder without wearing a safety belt that is securely tied off to a local structure.

8) Short ladders shall not be spliced together to make a longer ladder.

9) The base of the ladder must be set back a safe distance from the vertical; approximately one-fourth the working length of the ladder.

G.6.d. Falls – Fall Protection Working From Elevated Surfaces

No worker shall willfully be exposed to fall hazards. When a worker observes a fall hazard, he or she will notify his or her supervisor of the hazard. Measures will be taken to immediately correct the hazard. One hundred percent continuous fall protection or prevention shall be required for fall hazards greater than 4 feet.

Personal fall arrest systems, when stopping a fall, shall be rigged such that an employee can neither free fall more than 6 feet, nor contact any lower level or obstruction.

For duties involving heights greater than 4 feet above the ground:

1) Utilize fall protection or restraint system as described in the Envirocon Fall Protection Program.

2) Append a task specific JSA to this plan to specify type and design of fall prevention or protection system on a case by case basis.

G.6.e. Scaffolds

1) The following requirements shall apply to all scaffold use:

a. Scaffolds shall be erected, moved, dismantled, or altered only under the supervision and direction of a competent person qualified in scaffold erection, moving, dismantling or alteration.

b. Scaffold components shall be inspected for damage or defect prior to use. Defective components shall be immediately removed from service.

c. The Contractor's employees shall be prohibited from working on scaffolds covered with ice, snow or other slippery materials, except as necessary for removal of such materials.

d. Debris shall not be allowed to accumulate on scaffold platforms.

e. A competent person shall be on-site anytime a scaffold is in use and shall inspect each scaffold prior to the start of each shift.

2) Scaffolds shall be clearly marked and identified using a three-tag system, such as:

a. Green tag-shall indicate the scaffold is properly erected with no deficiencies, hazards or missing components.

b. Yellow tag-shall indicate the presence of an identified hazard, which indicates special precaution usage.

c. Red tag-shall indicate the scaffold is in the process of erection or dismantlement and shall not be accessed except by those performing either the erection or dismantlement.

G.6.f. Illumination

Light plants or other sources of light shall be used as necessary to maintain the requirements described in Table D 65.1 of 29 CFR 1926.65.

Table D-65.1 Illumination of Work Areas

Foot Candles	Area of Operations
5	General Site Areas
3	Excavation and waste areas, access ways, active storage areas, loading platforms, refueling, and field maintenance areas.
5	Indoors: Warehouses, corridors, hallways, and exit ways.
5	Tunnels, shafts, and general underground work areas. (Exception: minimum of 10 foot-candles is required at tunnel and shaft heading during drilling, mucking, and scaling. Mine Safety and Health Administration approved cap lights shall be acceptable for use in the tunnel heading.

10	General shops (e.g., mechanical and electrical equipment rooms, active storerooms, barracks or living quarters, locker or dressing rooms, dining areas, and indoor toilets and workrooms.
30	First aid stations, infirmaries, and offices.

G.7. Portable Tools

G.7.a. Deadman Switches

Portable electrical power tools will be equipped with constant pressure switches or controls that will shut off power when the pressure is released.

G.7.b. Guards

All tools will be equipped with appropriate guards, the guards will be properly adjusted, and the guards will be replaced if they are damaged.

G.7.c. Field Modifications

Hand/powered tools may be used only for their intended purpose. The design or guard capacity shall not be exceeded or circumvented by unauthorized attachments or modifications.

G.7.d. Electrical

1) All portable electrical powered tools shall be double insulated or grounded.
2) Ground Fault Interrupters (GFCI) will be used with all outdoor temporary wiring.
3) Power tools shall be hoisted or lowered by a hand line; never by the cord or hose.

G.8. Fire Prevention

G.8.a. Use of Gasoline in Vehicles and Small Containers

The use of gasoline is very common on and off the job. The familiarity of its use may lead to complacency regarding the properties of this highly dangerous fuel. Thousands of people are treated each year for burn injuries related to the misuse of gasoline. It is important to remember that gasoline has only ONE proper use - to power vehicles or machinery. Remember that gasoline is highly volatile. Just one gallon of gasoline is equivalent to 14 sticks of dynamite in explosive force.

Vapors from gasoline are also dangerous. Gasoline vapors are heavier than air; they flow invisibly along the ground and can ignite from a flame, spark, hot surface or static electricity causing a shattering explosion.

1) Before Refueling

    a. Turn off your vehicle engine while refueling.

    b. Put your vehicle in park and/or set the emergency brake.

c. Disable or turn off any auxiliary sources of ignition such as a camper or trailer heater, cooking units, or pilot lights.

2) Ignition Sources

a. Do not smoke, light matches or lighters while refueling at the pump or when using gasoline anywhere else.

b. Turn off your cell phone or any other electrical devices that are not explosion proof or intrinsically safe.

3) Refueling

a. Use only the refueling latch provided on the gasoline dispenser nozzle - never jam the refueling latch on the nozzle open.

b. Do not re-enter your vehicle during refueling.

c. In the unlikely event a static-caused fire occurs when refueling, leave the nozzle in the fill pipe and back away from the vehicle. Notify the station attendant immediately.

d. Do not over-fill or top-off your vehicle tank, which can cause gasoline spillage.

e. Avoid prolonged breathing of gasoline vapors.

f. Do not "top off" tank (i.e., adding additional fuel after the automatic shutoff has tripped) in order to allow for expansion.

g. Place cap tightly on the fuel tank - do not use caps that do not seal properly.

h. If gasoline spills, make sure that it has been cleaned up before starting the vehicle or equipment.

i. Report spills to your supervisor and the station attendant if refueling at a commercial gasoline filling station.

4) Store gasoline and other fuels in approved containers such as:

a. OSHA fire safety containers of 5 gallons size or less.

b. Manufacturer's installed or approved equipment fuel tanks.

c. Fuel depot tanks in accordance with fuel depot procedures.

5) Use gasoline in accordance with refueling procedures and flammable materials handling procedures.

a. Use gasoline only in open areas that get plenty of fresh air.

b. Keep your face away from the nozzle or container opening.

c. When dispensing gasoline into a container, use only an approved portable container and place it on the ground when refueling to avoid a possible static electricity ignition of fuel vapors.

d. Containers should never be filled while inside a vehicle or its trunk, the bed of a pickup truck or the floor of a trailer.

e. When filling a portable container, manually control the nozzle valve throughout the filling process.

f. Fill a portable container slowly to decrease the chance of static electricity buildup and minimize spilling or splattering.

g. Fill container no more than 95% full to allow for expansion.

h. Place cap tightly on the container after filling - do not use containers that do not seal properly.

i. If gasoline spills on the container, make sure that it has evaporated before you place the container in your vehicle.

j. Report spills to your supervisor and the station attendant if refueling at a commercial gasoline filling station.

k. When transporting gasoline in a portable container make sure it is secured against tipping and sliding, and never leave it in direct sunlight or in the trunk of a car.

l. Never siphon gasoline by mouth nor put gasoline in your mouth for any reason. Gasoline can be harmful or fatal if swallowed. If someone swallows gasoline, do not induce vomiting. Contact a doctor immediately.

m. Keep gasoline away from your eyes and skin; it may cause irritation. Remove gasoline-soaked clothing immediately.

n. Use gasoline as a motor fuel only. Never use gasoline to wash your hands or as a cleaning solvent.

6) Filling Containers Inside Vehicles or Pickup Beds

a. The National Highway Traffic Safety Administration (NHTSA) has urged motorists to avoid risk of fire by placing portable gasoline containers on the ground while filling them because filling them while they are located in beds of pickup trucks or in trunks or passenger car compartments can be hazardous.

b. Take the portable gas container out of your vehicle and set it on the ground while filling it with gasoline.

c. Static electricity could cause fire to erupt while fueling when it is in your car or pickup bed, NHTSA Administrator says:

   i. Adding to the danger is the location where these fires could occur -- at a gas station while getting fuel for your snow blower or emergency generator.

   ii. Cold, dry days in winter increase the chance of ignition, so preventive measures are important.

   iii. Pickups with bed liners require special concern. A bed liner is a plastic, protective lining that acts as an electrical insulator, allowing static electricity to build up on the gasoline container while it is being filled. The flow of gasoline through the pump nozzle can produce static electricity.

   iv. During fueling, this can create a spark between the container and the fuel nozzle, igniting gasoline vapors and causing a fire or explosion. This danger also applies to other nonmetallic containers capable of building up a static charge.

   v. Reports also describe fires that resulted while portable gasoline containers were being filled in trunks and passenger compartments of vehicles, when carpeting acted as an insulator.

d. NHTSA recommends the following safe procedures for filling portable gasoline containers:

   i. Dispense gasoline only into approved containers.

   ii. Do not fill a container while it is inside a vehicle, a vehicle s trunk, pickup bed or on any surface other than the ground.

   iii. Bring the fill nozzle in contact with the inside of the fill opening before operating the nozzle.

   iv. Contact should be maintained until the filling operation is complete.

G.8.b. Extinguishers

1) Extinguishers will be readily available on site. At a minimum, extinguishers will be placed as follows. (Extinguishers of greater size or inclusive types may be substituted.)

2) Heavy equipment will be equipped with a 5# ABC fire extinguisher rated at 2-A:10-B:C.

3) Fuel depots and flammable liquid storage/handling areas.

   a. 20# ABC fire extinguishers with a rating of 2-A:40-B:C will be provided within 75 feet of, but no closer than 25 feet to, all refueling depots and flammable storage areas.

b. 10# ABC fire extinguishers with a rating of 2-A:40-B:C will be provided within 75 feet of, but no closer than 25 feet to, all mobile fueling stations, flammable liquid transfer areas, and generators.

4) Trailers, buildings and work areas

a. All trailers and work areas will have at least a 5 # ABC fire extinguisher rated at 2-A:10-B:C.

b. Extinguishers in trailers will be mounted near a clear evacuation egress point (door).

c. Extinguishers on site will be located at the primary entrance to the work area.

5) Access routes to fire extinguisher shall be kept clear at all times.

6) All fire extinguishers shall be inspected monthly and serviced annually.

G.8.c. Fighting Fires

1) Personnel are authorized to fight fires in the beginning stages of development and only to the extent that they judge this can be done safely. Personnel are not required to fight fires.

2) When a fire is detected, first ensure that the area is safely evacuated and the supervisor is being notified so that the fire department can be summoned.

3) Ensure your own evacuation route before attempting to extinguish a fire.

4) If more people or more extinguishers are needed, the effort should be abandoned.

5) Contact the fire department if applicable.

G.8.d. Facility Systems

1) A site-specific procedure will be developed where project work (such as demolition) potentially jeopardizes facility systems.

2) Site managers will generally be notified when any work is done above facility systems such as fixed fire suppression systems for buildings, or where excavations encroach on facility systems such as fire hydrants or related piping.

3) When excavating or performing demolition near facility systems, the facility systems should be uniquely marked to avoid damaging these systems.

G.8.e. Flammable Liquids, Fuels, and Fueling

1) Protection of depots:

a. Depots will be located in such a manner as to provide clear access for fire trucks.

b. Depots will be protected from damage from vehicle or equipment damage using bollards, bails, curbs or similar devices.

2) Portable containers:

a. All portable fuel cans shall be free of deformities which threaten the integrity of the container.

b. All flammable storage cans of 1 gallon capacity or greater shall have self-closing lids and flame arresters (i.e., safety cans).

c. All flammable storage containers shall be labeled as to their contents, and shall include a warning regarding flammable contents.

d. Gasoline engines shall not be fueled while the engine is running.

G.8.f. Containments

1) All equipment shall be fueled through funnels or spouts that prevent spillage. All spouts and funnels must be of metal construction.

2) National Fire Protection Association (NFPA) flammables (e.g., gasoline) will not be stored in the same containment as NFPA combustibles (diesel fuels).

3) Containers and depot tanks in excess of 5 gallons will be held or stored in containments designed to collect spillage.

4) Covered containments must be capable of containing a volume equal to:

a. The capacity of the largest tank; plus

b. The combined displaced volumes of all tanks and containers stored in the containment.

5) Uncovered containments must be capable of containing a volume equal to:

a. The capacity of the largest tank; plus

b. The combined displaced volumes of all tanks and containers stored in the containment; plus

c. 25% excess capacity for rain collection.

d. Uncovered containments will be kept free of standing water.

i. Water in excess of 5% containment capacity will be pumped off within a 48-hour period.

ii. Water will not be discharged onto the ground unless free of visible residues or films.

6) Bonding and grounding:

    a. Any transfer of a flammable liquid from one container to another requires bonding from one container to the other.

    b. All flammable fuel depot tanks set up on site will be grounded.

G.8.g. Smoking, Fire, and Hot Work

1) Hot work permits shall be issued for all applicable hot work according to site requirements.

2) Smoking and hot work will not be allowed within 50 feet of fuel depots or other flammable liquid storage and/or transfer areas.

3) Fuel depots or other flammable liquid storage and/or transfer areas will be posted against smoking, open flames, or hot work.

4) Oily rags:

    a. Oily rags, trash and other combustible scrap materials shall be placed in closed receptacles separate from other trash.

    b. Oily rags shall be stored in containers approved for this purpose.

G.8.h. Welding, Cutting, and Hot Work

1) General:

    a. All welding and hot work will be done in accordance with Envirocon's Health and Safety Procedures 1403.011 and 1403.012;

    b. All welding and hot work will be done in accordance with facility requirements.

2) Equipment Operation:

    a. Welding equipment shall be used only for operations for which it is approved, and as recommended by the manufacturer.

    b. Workers assigned to operate or maintain oxygen/fuel gas supply equipment and resistance welding equipment shall be thoroughly instructed in the safe use of such equipment.

3) Personal Protective Equipment:

    a. Eye and Face Protection:

        i. Welding helmets and hand shields shall be used during all arc welding/cutting operations, excluding submerged arc welding.

ii. Safety goggles or glasses (with side shields) are also worn during arc welding/cutting operations. The goggles or glasses may be either of clear or colored glass, depending upon the type of exposure in welding operations. Helpers or attendants wear proper eye protection.

iii. Safety goggles or glasses with side shields and suitable filter lenses shall be permitted for use during gas welding operations on light work, torch brazing, or inspection.

iv. All operators and attendants on resistance welding or brazing equipment will use face shields or goggles, depending on the particular job.

b. Protective Clothing:

i. All welders/cutters shall wear flameproof gauntlet gloves.

ii. Flameproof aprons made of leather, or other suitable material, must be used as protection against radiated heat and sparks.

iii. Leather jackets will be utilized if personnel are performing hot cutting/welding work above their shoulders.

iv. Nylon clothing is not permitted for welding/cutting operations.

v. All outer clothing, such as jumpers or overalls, should be free from oil or grease.

c. Respiratory Protective Equipment:

i. When respiratory protective equipment is required, the Respiratory Protection Program shall be adhered to.

ii. Respiratory protection will be required depending on job duration and contaminant specific personal time weighted average air sample results.

iii. Supplied air respiratory protection is required for cutting on lead paint until personal exposure sampling indicates exposure requiring lower levels of protection.

4) Gas Welding and Cutting Safety:

a. Fuel gas hose and oxygen hose are easily distinguishable from each other.

i. The contrast is made by different colors or by surface characteristics readily distinguishable by touch.

ii. Oxygen and fuel gas hoses shall not be interchangeable.

iii. A single hose having more than one gas passage shall not be used.

b. When parallel sections of oxygen and fuel gas hose are taped together, not more than 4 inches out of 12 inches shall be covered by tape.

c. All hose in use shall be inspected at the beginning of each working shift. Defective hose shall be removed from service.

d. Hoses, cables, and other equipment shall be kept clear of walkways, ladders, and stairs.

e. Clogged torch tip openings shall be cleaned with approved cleaning wires, drills, or other devices designed for this purpose.

f. Torches to be used shall be inspected at the beginning of each working shift for leaking shutoff valves, damaged hose couplings, and clogged tip connections. Defective torches will not be used.

g. Torches shall be ignited by friction lighters or other approved devices only. Matches, flame lighters, or hot work will not be used to ignite torches.

h. Oxygen and fuel gas pressure regulators, including related gauges, shall be in proper working order.

i. All oxygen cylinders and fittings shall be kept away from oil or grease. Cylinders, cylinder caps and valves, couplings, regulators, hose, and apparatus shall be kept free from oil or greasy substances and shall not be handled with oily hands or gloves. Oxygen shall not be directed at oily surfaces or greasy clothes, or used within a fuel oil or other storage tank or vessel.

j. Flash back arresters shall be installed on all oxygen and fuel gas setups, at a minimum at the gauges.

k. Torches and hoses shall be completely depressurized (bled) prior to storage, or at the end of each shift.

l. Torches and hoses shall not be stored in enclosed areas (e.g., gang boxes, lockers) while connected to cylinders.

m. Do not hang torches from the regulators attached to the cylinder.

n. Release the hose pressure and close the cylinder valves when work is interrupted for an extended period (breaks, lunch).

o. Don’t leave a pilot flame burning at the tip of the torch during interruption of operations.

p. When working in an elevated position:

    i. Provide a screen to keep hot metal, electrode stubs, hot metal slag, etc. from falling below;

ii. Provide toe boards when working from scaffolding under which workers may be passing or working; and

iii. Restrict access to the area below the work site.

5) Arc Welding and Cutting Safety:

a. Electrode holders shall be designed for arc welding/cutting and are capable of safely handling the maximum rated current required.

b. Exposed current-carrying parts of electrode holders shall be insulated in a manner which provides full protection against electrical shock for operators of arc welders/cutters.

c. All arc welding/cutting cables must be completely insulated and flexible, capable of handling the maximum current requirements of the work.

d. Only cable free from repair or splices for a minimum distance of 10 feet from the electrode holder is used. Cables with standard insulated connectors or splices with insulating quality that is equal to that of the cable may be permitted.

e. If it is necessary to splice lengths of cable, insulated connectors equivalent to that of the cable are used. If connections are made by cable lugs, they are securely fastened together and provide a good electrical contact. Exposed metal parts of the lugs must be completely insulated.

f. If electrode holders are left unattended, the electrodes shall be removed and the holders placed so that they cannot make electrical contact with employees or conducting objects.

g. Electrode holders shall not be dipped in water.

h. The power supply to the equipment shall be turned off whenever the arc welder or cutter leaves work or stops work for any appreciable length of time, or when the arc welding/cutting machine is to be moved.

i. Any faulty or defective equipment shall be reported to the supervisor and tagged out of service until repaired.

j. All arc welding/cutting operations shall be shielded by noncombustible or flameproof screens which will protect employees and other persons working in the vicinity from the direct rays of the arc or from arc flash.

k. The frames of all arc welding and cutting machines shall be grounded.

l. Never weld on any line or equipment until it has been connected to the ground connection of the welding machine.

m. Never pull or disconnect a ground line while the arc is in use.

n. Never let the live metal parts of the welding circuit touch damp skin or clothing.

o. All parts that are being cut must be supported in such a manner as to prevent them from falling during or at completion of the cut.

6) Storage and Handling of Compressed Gas Cylinders:

a. Compressed gas cylinders shall be legibly marked with either the chemical or trade name of the gas. Such markings shall be stenciled, stamped, or labeled and are not easily removable. The marking shall be located on the shoulder of the cylinder.

b. Compressed gas cylinders shall be equipped with approved connections.

c. Acetylene cylinders shall always be used and stored in an upright position (valve end up) to prevent the acetone (a stabilizing agent) from draining into the valves or fittings. Acetylene should never be used at a hose pressure exceeding 15 pounds per square inch (psi). Above 15 psi, acetylene is extremely unstable, and the possibility of an explosion exists.

d. Oxygen cylinders shall not be stored near oil or grease or other highly combustible/flammable materials.

e. Oxygen cylinders in storage shall be separated from fuel gas cylinders by a minimum distance of 20 feet, or by a noncombustible barrier at least 5 feet high and having a fire resistance rating of at least 1/2 hour.

f. Cylinders shall not be dropped, struck by objects, or permitted to strike against each other violently.

g. Cylinder valves shall be closed before moving cylinders, at the end of the shift, or when work is finished.

h. Valves of empty cylinders shall be closed.

i. Cylinders shall be kept far enough away from the actual welding/cutting operation so that sparks, hot slag, or flames will not reach them.

j. Cylinder valves shall be opened slowly.

k. Acetylene cylinder valves shall not be opened more than one and one half turns of the valve stem and preferably no more than three fourths of a turn.

l. Where a special wrench is required, it shall be left in position on the stem of the valve while the cylinder is in use. In the case of manifolded or coupled cylinders, at least one such wrench shall be available for immediate use.

m. Regulators are removed, valve caps are in place, and valves closed when cylinders are transported by vehicles. All vehicles used to transport cylinders shall have a proper support rack installed.

n. A suitable cylinder truck, chain, or other steadying device shall be used to prevent cylinders from being knocked over while in use or storage.

o. Cylinders shall not be placed where they may become part of an electric circuit. Tapping of an electrode against a cylinder to strike an arc is prohibited.

p. Cylinders shall be stored in shaded areas and secured in upright position with protector caps in place.

q. Cylinders shall never be used as rollers or supports.

r. Oxygen cylinders, when full, contain 2,400 psi at 70°F and must be treated with respect for the high pressure. The valve protector cap must always be in place when moving the cylinder.

s. A spontaneous explosion is likely to occur when oxygen comes in contact with hydrocarbons. Keep oxygen and hydrocarbons separated. Never lubricate or allow oil or grease to get oxygen connections or use oxygen for compressed air or pressure.

t. When handling cylinders by powered vehicles, they shall be secured in a vertical position. Unless cylinders are firmly secured on a special carrier intended for this purpose, regulators shall be removed and valve protection caps put in place before cylinders are moved.

u. Oxygen and acetylene must be stored separately or separated by a fire wall rated for a minimum of 30 minutes resistance. Plate steel may be used to separate cylinders in this manner.

7) Manifolding of Cylinders:

a. Cylinder manifolds shall be installed under the supervision of an experienced person(s) and must comply with proper practices in construction and use.

b. All manifolds and parts shall be appropriate for the gases for which they are approved.

c. When acetylene cylinders are manifolded, approved flash arresters shall be installed between each cylinder and the coupler block. One flash arrestor installed between the coupler block and regulator is acceptable for outdoor use only if the number of cylinders coupled does not exceed three.

d. Each cylinder lead shall be provided with a backflow check valve.

8) Welding/Cutting on Containers:

a. Used Containers: No welding, cutting, or other hot work shall be performed on empty drums, barrels, tanks, or other containers until they have been cleaned thoroughly. (This is to ensure that there are no flammable materials present or any substances such as greases, tars, acids, etc., which might produce a hazard when subjected to heat.) Any connection to the drum or vessel shall be disconnected or blanked off.

b. Venting and Purging: All hollow spaces, cavities, or containers shall be ventilated to remove gases before preheating, cutting, or welding. Purging with inert gas is recommended.

c. All enclosed spaces to be welded on will be checked for flammability and oxygen content prior to any hot work.

9) Fire Protection During Welding:

a. Objects to be welded, cut, or heated shall be moved to a designated safe location. If this is not possible, all movable fire hazards in the work space shall be taken to a safe place.

b. If the object to be welded, cut, or heated cannot be moved and all fire hazards cannot be removed (e.g., equipment, walls, floors, etc.), positive means shall be taken to confine the heat, sparks, and slag to protect the immovable fire hazards.

c. Welding, cutting, or heating shall not be performed where the application of flammable paint, the presence of other flammable compounds, or heavy dust concentration create a possible hazard.

d. Openings or cracks in floors, walls, ducts, tanks, etc., shall be closed. Where openings or cracks cannot be closed, additional precautions shall be taken to prevent sparks from penetrating the openings. The same precautions shall be taken in the presence of open doorways and open or broken windows.

e. Approved fire extinguishing equipment shall be present in the immediate work area.

f. Fire Watch:

i. A fire watch shall be maintained for at least 30 minutes after completion of welding/cutting operations so that possible smoldering fire can be detected and extinguished.

ii. Fire watch personnel shall be instructed in the selection and use of appropriate fire extinguishers.

iii. Fire watch personnel shall be familiar with facilities and the procedures to be followed in the event of a fire. They watch for fires in all exposed areas and attempt to extinguish fires only when obviously within the capacity of the equipment available.

iv. The requirement for a fire watch may be waived when, after completion of the Welding, Cutting, and Heating Permit, it has been determined that there is no possibility of sparks, slag, hot material, etc., coming into contact with flammable or combustible solids, vapors, liquids, or residues.

G.9. Lifting Heavy Objects

Heavy objects will be lifted using appropriate machinery or enough manpower as is required. Employees will be specifically instructed to seek assistance in lifting heavy objects.

G.9.a. Lifts Using Rigging

Lifts utilizing cranes, hoists, and other similar mechanical lifting devices shall:

1) A competent person shall conduct a lift assessment prior to the lift.

2) A written assessment and lift plan shall be developed for critical lifts (refer to Site Procedure 1403.105 Hoisting and Rigging Guidelines).

3) A critical lift is defined as follows:

    a. A critical lift is any lift which meets the definition established for this site by the facility owner/manager.

    b. A critical lift is any lift which:

        i. Involves lifting of personnel;

        ii. Involves loads greater than 30,000 lbs;

        iii. Involves loads greater than 75% of the crane capacity in the boom configurations potentially required;

        iv. Involves lifts for which the path of load travel is at any point out of the view of the crane operator;

        v. Involves the use of two or more cranes or lifting devices;

        vi. Involves non-routine or unusual rigging;

        vii. Involves the potential for damage that would result in unacceptable delay to schedule or significant program impact;

        viii. Involves the potential for a significant release of hazardous materials, radioactive materials, or other undesirable conditions;

        ix. Involves the potential for unacceptable risk of personnel injury or significant adverse health impact (on-site or off-site); or

        x. Any lift which the lifting equipment operator determines to be critical.

G.9.b. Manual Lifting

1) Before lifting:

    a. Determine if the object can be moved by some other means (mechanical device).

    b. Determine if the object is too bulky and would obscure vision; if so, get another person to help carry it. When handling material with others, everyone should agree on who will act as leader and give the signals. Loads should not be released until everyone is ready. Teamwork is important.

    c. Determine if the object is within the lifter's capability (a preliminary "heft" will indicate this).

    d. Determine if the footing around the object is solid.

2) Lifting:

    a. Legs should be bent at knees, back nearly vertical, body as close to the object as possible, feet apart but not further than shoulder width. Take a firm hold and straighten knees. Back is still straight and upright. Pull load close to body and lean back slightly to keep center of gravity over feet.

    b. Avoid twisting the body when lifting or carrying loads.

G.10. Environmental Hazards

G.10.a. Hanta Virus or Four Corners Disease

Hanta virus is associated with fecal and nesting materials of rodents. The following controls and information is based on guidelines from the Centers for Disease Control (CDC) and should be followed when working in areas of concern.

1) Use of wet methods would include simple dust control (no dry sweeping, no use of pressurized air, use water to keep surfaces from shedding dust).

2) Sanitizing methods are the same as above. Use a mixture of soap, water and bleach (e.g., chlorine bleach mixed in water with soap). Depending on the size of the operation this can be applied by hand held spray bottle, Hudson-type sprayer, back pack sprayer etc. Allow it to sit for 15 minutes for small scale work or longer for larger scale work. For extreme cases, a shock strength of 10% hypochlorite might be considered. Use of hypochlorite will normally require upgrading respiratory protection to full face respirators fitted with cartridges rated for chlorine as well as the requirements for the hanta virus itself.

3) Guidelines call for "HEPA" filters which have been replaced by new NIOSH designations. Any of the new respirator cartridge types may be used. These include N100 cartridges which must be discarded at the end of each day and cannot be used in oily environments. R100 cartridges must also be discarded at the end of each day's use but may be used in oily environments. P100 cartridges may be used in oily environments and

can be used until breathing resistance is uncomfortable to the wearer. For purposes of this application, they should be discarded at the end of each work week regardless of resistance.

4) Suspect areas should be cleaned under these guidelines before beginning other work.

5) This control will be determined by medical consultation.

Table G.10.a. Hanta Virus Control

Controls	Small Scale Cleanups or Exposures	Moderate Exposure	High Risk of Exposure
Use wet methods.	X	X	X
Pre-work sanitizing.	X	X	X
Respirators		X	X
Pre-work cleanup.		X	X
PPE (1)	Gloves	Gloves and boot covers (face protection for application of disinfectants)	Gloves, boots, face shields (or full-face respirators), water resistant coveralls.
Baseline Serum Sample			Case-by-case

G.10.b. Ticks and Spiders

1) Insect bites may cause localized pain, and in some cases an allergic reaction. Of greatest concern is tick bites (deer ticks carrying Lyme disease, and wood ticks carrying Rocky Mountain Spotted Fever), poisonous spider bites (black widows marked with a red hour-glass under the abdomen and brown recluse marked with a violin on their back) and scorpion stings.

2) Controls:

    a. Repellents.

        i. Use DEET repellents to avoid ticks.

        ii. Do not apply to open wounds.

        iii. Do not spray repellents onto face (spray on hands to apply to face or use liquid).

        iv. Wash hands and clothing at the end of the day's use.

    b. Long sleeved shirts and full length pants.

        i. Wearing long sleeved shirts and full length pants will help to avoid all of the above.

        ii. Wear light colored clothing to better see insects on your clothing.

    c. Wear bands to seal pant legs at the sock.

    d. Avoid or clean out their living areas.

i. Proper clearing and grubbing helps to remove hiding and nesting locations.

ii. Poisonous spiders will normally be found in quiet, secluded, dark, moist areas such as underneath trailers.

iii. When entering or working near these locations clean them out first using a broom or other long handled device.

3) Signs and symptoms of injury:

a. Poisonous spider bites:

i. Bite marks;

ii. Swelling;

iii. Pain;

iv. Nausea;

v. Difficulty breathing;

vi. Difficulty swallowing.

b. Ticks:

i. Body of tick remains;

ii. Painful joints;

iii. Fever;

iv. Unusual rashes;

v. Flu-like symptoms.

4) First Aid:

a. Poisonous spider bites and scorpion stings:

i. Wash the wound;

ii. Apply cold pack;

iii. Seek medical attention.

b. Ticks:

i. Use a tweezers to SLOWLY pull tick out of skin;

ii. Grasp tick as close to the skin as possible before removing;

iii. DO NOT attempt to burn tick off with matches or hot objects;

iv. DO NOT attempt other home remedies such as coating ticks with Vaseline®;

v. Seek medical attention at the first signs or symptoms;

vi. Seek medical attention if you have difficulty removing tick.

G.10.c. Insect Stings (Bees, Wasps, Hornets, Mosquitos)

1) Insect stings can be very painful.

2) For those with allergic reactions to bees or wasps, a bite may be fatal.

3) Control (insect stings).

   a. Thorough clearing and grubbing of work areas will help to reduce nesting areas. Use insect control sprays to clear out nesting areas.

   b. If work is conducted near nesting areas. Personnel should be requested to identify allergies before entering the site.

   c. Antivenin must be individual prescribed for sensitive individual and must be carried at all times. All personnel entering the site must complete the emergency medical information data sheet.

4) Signs and symptoms:

   a. Stinger may be present;

   b. Pain;

   c. Swelling;

   d. Allergic reaction (extreme symptoms).

5) First Aid:

   a. Remove stingers by scrapping it out with the edge of knife blade, tweezers tips (DO NOT SQUEEZE the stinger), credit card, or similar device.

   b. DO NOT use a tweezers to grasp a stinger to remove it (this may inject more poison).

   c. Wash wound.

   d. Cover.

e. Apply cold pack.

f. Watch for allergic reaction.

g. Use Benadryl® or other non-prescription antihistamines and seek medical attention if allergic reaction develops.

6) Mosquitoes (*West Nile Encephalitis or Meningitis Carriers [WNV]*) – 80% of people infected with WNV will not show any symptoms at all. There is no specific treatment for WNV infection. In the case with mild symptoms, they tend to pass on their own. In more severe cases people need to go to the hospital where they can receive supportive treatment (i.e., intravenous fluids, breathing, nursing care).

G.10.d. Poisonous Plants

1) Poison ivy, poison oak, and poison sumac may cause varying degrees of allergic reaction in different individuals.

2) Control:

a. Staying in cleared areas should help prevent contact with cactus and poisonous plants.

b. Proper clearing and grubbing will help to minimize this hazard.

c. Heavy equipment should be used for clearing vegetation to the extent possible.

d. Equipment operators must also be protected during this operation.

e. Wearing long sleeves and pants legs can minimize skin contact with poisonous plants but offers little protection from cactus needles.

3) Signs and symptoms:

a. Itching;

b. Rash;

c. Weeping sores.

4) First Aid:

a. Gently but thoroughly wash the affected area and all around it.

b. Baking soda paste may be applied to sores.

c. Calamine or Caladryl® lotions helps soothe irritation.

d. Benadryl® or other non-prescription antihistamines help dry up sores.

e. If condition continues to get worse or affect large portions of the body, seek medical attention.

G.10.e. Domestic and Wild Animal Bites, Rabies, and Plague

1) Bites inflicted by domestic and wild animals primarily pose a serious risk of infection. In some cases they may carry rabies as well.

2) Controls:

   a. In order to prevent problems arising from these bites it is essential that site personnel stay away from all wild or domestic animals.

   b. Dead animals shall be handled using equipment whenever possible.

   c. Sanitize equipment or handle remains using the PPE and sanitizing practices.

3) First Aid (domestic and wild animal bites):

   a. If bleeding is minor—wash the wound.

   b. Control bleeding.

   c. Apply antibiotic ointment.

   d. Cover the wound.

   e. Get medical attention.

G.10.f. Work Near, On, or In Water

Work near water is that work which involves a danger of drowning. As a rule of thumb work that is conducted within 6 feet of water more than 3 feet deep. It is anticipated that a significant portion of the work on this project will take place on or in water. An example list of anticipated JSAs for dredging activities for the Phase 2 Wet Dredge project is presented below. A program of rigorous planning is utilized for water work as well as water quality monitoring activities, dredging, barge movement, and barge unloading/loading activities. Since the Chequamegon Bay is an active waterway, attention is given to loading of materials on/off barges to ensure proper control. In addition, it is noted that any time a person is in the water diving, it increases the work-related hazards. Marine Contractor's site-specific HASP is provided as Appendix A further detailing work near, on, or in water. Personnel are expected to be trained, seasoned professionals with extensive experience complying with the following regulations:

- EPA Dive Safety Manual (April 2001)
- EPA Region 10 Dive Safety Plan (October 2011)
- OSHA commercial diving regulations 29 CFR 1910 Subpart T
- USCG commercial diving regulations 46 CFR Part 197
- USACE EM 385-1-1, Section 30 Diving Operations (revised March 17, 2008)

- Excerpts from preliminary JSA that will be required for the dredging project are presented in the table below.

Table G.10.b. Dredging JSA Examples

Activity Hazard Analyses
Coordination with Marine Traffic
Work on Water
Dredging Setup Operations and Breakdown
Dredging from Barge
Removing Materials from Barge
Water quality monitoring from boat
Restorative Layer Placement from Barge
Core Sampling from Barge
Diver Assisted Hydraulic Dredging

Personnel will "dirty up" the JSA as the task proceeds identifying new hazards and controls. Periodically, the "dirtied up" JSA will be turned in to the HSO who will revise the JSA (including the workers notes) and reissue the JSA with a revision number. The JSA will serve as the document record to ensure only trained signatories work at a given activity. FE JV ssupervisors and management will be responsible for identifying new activities or changes in activities requiring a task analysis:

1) Additional considerations may affect the need for these types of controls.

    a. Wind conditions and wave height of the water.

    b. Work on/near thin ice should also be considered a drowning hazard.

    c. Potential for flooding and severe weather.

2) Related standards include:

    a. Refer to the requirements of 29 CFR 1926.106.

    b. U.S. Coast Guard standards for approved lifesaving equipment are defined in 46 CFR Part 160.

3) Personnel exposed to water related hazards shall be provided with radio communications and/or cell phones.

4) Strict adherence to the buddy system must be maintained in these areas.

5) Throwing rings:

a. Type IV Personal Flotation Devices (PFD) are U.S. Coast Guard-approved "ring life buoys" typically referred to as "life rings" or "throwing rings."

b. These devices are required for work near water.

c. The interval between rings shall not exceed 200 feet.

d. Throwing rings must be within 100 feet of work.

e. Maintain 90 feet of retrieval line attached to throwing rings.

6) Wear U.S. Coast Guard approved work vests and inspect work vests before each use.

a. DO NOT use recreational boating PFDs such as ski jackets for work applications.

b. PFDs used as work vests may be Type I, II, III, or V PFDs. A Type V PFD, including Type V Hybrid PFDs, is acceptable only if it is U.S. Coast Guard approved and marked for use as a work vest, for commercial use, or for use on commercial vessels.

c. PFDs shall be fitted with a SOLAS (Safety of Life At Sea convention) compliant whistle or noise making device.

d. When worn at night, PFDs shall have SOLAS rated reflective tape/materials affixed to the PFD.

e. Safety nets, rope grab systems, or similar fall protection or positioning devices may be used in place of PFDs.

f. The use of PFDs is generally NOT appropriate for entrapment hazards such as deep muds.

g. In hypothermia conditions, PFDs should be insulated (e.g., "mustang suits").

7) Rescue Skiffs:

a. Rescue skiffs should be used judiciously and may pose an additional drowning risk for rescue personnel. Throwing rings should generally be used before launching a boat.

b. A flat bottom rescue skiff should also be used for rescue on thin ice. Rescue personnel should stay in the boat and slide it over the top of thin ice. Ropes from shore or stable ice may be used to help guide the boat.

c. The skiff must be in the water or capable of being quickly launched by one person.

d. There must be at least one person present and specifically designated to respond to water emergencies and operate the skiff at all times when there are employees above water.

    i. When the operator is on break another operator must be designated to provide the requisite coverage while employees are above water.

    ii. The designated operator must either man the skiff at all times or remain in the immediate area such that the operator can quickly reach the skiff and get underway.

    iii. The skiff operator may be assigned other tasks provided the tasks do not interfere with the operator's ability to quickly reach the skiff and get underway.

    iv. If visual contact is not maintained by the skiff operator, a communication system, such as a walkie-talkie, must be in use to inform the skiff operator of an emergency and to inform the operator where the skiff is needed.

    v. Skiff operators shall be qualified and shall operate the rescue skiff in a non-emergency situation before being qualified.

e. Equipment in the skiff:

    i. At least one paddle, attached by lanyard to the skiff (or a fixed oar) shall be included in the skiff (regardless of whether the skiff is powered or unpowered).

    ii. At least one PFD for each rescue person.

    iii. At least one throwing ring or throwing bag.

G.10.g. Crew Boat and Dredge-Barge Operations

a. Operating crew boats and floating plants on the water carries the risk of having a crew member fall overboard and possibly drown, striking or being struck by other vessels operating in the area, losing power or steering and drifting into hazardous areas (i.e. shore, marine facilities etc.) and encountering severe weather and dangerous seas, to name a few. The risk of a boating accident can be reduced by ensuring that boat operators are experienced, and when applicable, licensed; operating the vessel in compliance with U.S. Coast Guard rules and regulations; maintaining the vessel in good mechanical order; avoiding bad weather and dangerous seas; and ensuring emergency equipment is available on-board (i.e. life vests, life rings, life boats, fire extinguishers, communication equipment etc.). A Float Plan will be filed with the FE JV HSO. A copy of the daily Float Plan will be posted on shore in a conspicuous area for inspection.

b. To address these concerns, all work conducted from the excavator/restorative layer placement barges, hydraulic dredge, material barges and small vessels (crew,

monitoring, and work boats) will comply with applicable U.S. Coast Guard regulations. Crew. monitoring and work boats, excavator/restorative layer placement barges, hydraulic dredge, and material barges will be operated by experienced crew members and all equipment will be inspected prior to use to ensure that it is in proper working order. Vessel inspections will be conducted by the HSO initially at the start of the work and periodically thereafter throughout the duration of the project. Ultimately, though, the dredge superintendent and boat operators will be responsible for the safety and the integrity of their vessels.

c. Prior to the start of field activities, the excavator/restorative layer placement barge, hydraulic dredge, material barge, and crew, monitoring, work boat operators will give a detailed health and safety briefing on the location and use of all vessel safety equipment and the procedures for addressing on-board emergencies (i.e. fire, mechanical failure, man overboard situation, etc.). Excavator/restorative layer placement barges, hydraulic dredge, material barges, and crew, monitoring, and work boats will meet U.S. Coast Guard license and registration requirements and be equipped to safely support maximum rated crew and passenger sizes. The maximum number of passengers and weight shall be conspicuously posted on each vessel. The number of passengers shall not exceed the number of available PFDs (personal flotation devices). Personnel riding in the crew, monitoring, and work boats and working in unguarded areas on the excavator/restorative layer placement barges and material barges will be required to wear a PFD at all times. During evening operations, the PFDs will be equipped with reflective tape, flashing beacons and whistles.

d. The crew, monitoring, and work boats will have at least one sound signaling device (air horn), a fire extinguisher, sufficient number of PFDs for all passengers and crew, and a hand-held radio to communicate with shore-based support facilities. The excavator, restorative layer placement, and material barges and hydraulic dredge will be similarly equipped with portable fire extinguishers conspicuously staged at various locations throughout the vessel and inside the cab of the excavator. The material, restorative layer placement, and excavator barges and hydraulic dredge will also have a minimum of two (port and starboard side) throwable life rings with flashing beacon lights attached to 90 ft. of rope, one sound signaling device (air horn), and sufficient number of PFDs. The crew superintendent and operators will have portable radios for communicating with each other and with FE JV's site office. If it is necessary for a crewmember to approach the excavator while it is operating, the crew supervisor will call the operator and have him shut down the excavator (lower the bucket into the water, disengage the power drive, and set the brakes on the turntable) and make eye contact with the crewmember. At that point, the crewmember may approach the excavator. The area around the swing radius of the excavator's bucket and counter-weight will be roped off or otherwise demarcated with barriers and/or warning signs to alert crew of the struck by/crush hazard.

e. To avoid collision with other vessels operating in the area, boat operators will review the schedule of vessel activity in the waterway before beginning work and notify applicable port authorities of their intended work location and activities, if

feasible. The excavator and restorative layer placement barges, material barges, and crew, monitoring, and work boats will also be equipped with regulation position lights and running lights as appropriate. The decks on these vessels will also be adequately illuminated (minimum 5 foot candles). Boat operators will also look for and avoid other vessels operating in the area at all times. Dredging operations will be suspended during severe weather or rough seas.

G.11. Sanitation and Hygiene

G.11.a. Drinking Water

1) An adequate supply of potable water will be provided on site.

2) Portable water containers will be capable of being tightly closed and equipped with a tap.

3) Water shall not be dipped from containers for drinking purposes. Single service, disposable drinking cups will be provided.

4) No one shall place any objects (e.g., soda pop, ice tea, etc.) in coolers.

G.11.b. Restrooms and Hygiene Facilities

Table D-65.2 Toilet Facilities

Number of Employees	Minimum Number of Facilities
20 or fewer	One
21 to 199	One toilet seat and one urinal per 40 employees
200 or more	One toilet seat and one urinal per 50 employees

Toilet facilities (sanitary sewer w/flushing toilets, chemical toilets, recirculating toilets, or combustion toilets) including hand washing stations will be provided in accordance with 29 CFR 1926.65(n) and Table D 65.2.

H. Recordkeeping

The health and safety-related documents for the project will be handled in the following manner:

H.1. Training and Safety Meeting Records

Certificates of completion for all mandatory training for FE JV and lower tier subcontractor employees will be maintained on site at this site. Minutes for safety and health meetings, including daily safety briefings, will also be maintained on site. These records are located in Envirocon's safety trailer office.

H.2. Injury/Illness

Copies of "Supervisor's Report of Injury or Illness" will be maintained on site. The official OSHA 300 log is maintained at the corporate office. See the emergency procedures below for accident reporting procedures. A first aid log will be used to document first aid cases as described below in the log keeping section.

H.3. Accident Reports

Accident investigation reports will be maintained on site. All injuries will be reported to the client as well. See the emergency procedures below for accident reporting procedures.

H.4. Medical Surveillance Records

All medical records received on site will be forwarded to the corporate office after review. No medical records will be maintained on site; Fitness for Duty forms, however, will be available on site for all personnel.

H.5. Written Programs

Written programs for compliance with the OSHA standards, such as respiratory protection, hearing conservation, and certain chemical exposure are maintained at the corporate office.

H.6. Health and Safety Plans

At least one copy of the plan and any amendments will be maintained on site.

H.7. Employee Access

All employees have a right to access most of the documents related to health and safety. Medical and training records are available only to individuals requesting their own records. Employees can receive copies of their medical records or air monitoring exposure records upon written request. Medical information can only be released upon the written consent of the individual.

H.8. Health and Safety Related Logs

The HSO is responsible for maintaining logs of health and safety activities, including safety inspections.

H.8.a. Health and Safety Log

This is a bound log of daily inspections and health and safety issues kept by the project HSO.

H.8.b. First Aid Log

Employees are required to report all injuries and illness regardless of how minor the incident may seem. These reports shall be documented on an injury/illness report form, or in the project first aid log where diagnosis and treatments involve only simple first aid diagnosis and/or treatments.

1) Treatment/diagnosis by third-party EMTs, physicians, nurses, or other medical professionals shall be reported using the injury/illness reporting procedures. Determination of OSHA recordable/first-aid shall be determined by the Corporate Director of Health and Safety in these cases.

2) This First Aid Log is a log of all reported injuries and/or illnesses reported to supervisors and/or the HSO. This log shall document the report, date, name of the injured employee, nature of the injury/illness, diagnosis and the treatment given.

3) If no treatment is given the incident shall still be noted in the log. This shall include any dispensing of first aid supplies or administered by a supervisor, HSO or other first aid trained employee.

4) Non-work related injuries/illness reports and use of prescription drugs should also be noted in this log.

5) Self-medication by employees with respect to non-prescription (i.e., Over-the-Counter [OTC]) pharmaceuticals, unrelated for colds headaches or other non-work related ailments, need not be documented.

H.8.c. Equipment Free Release Decontamination Log

Decontamination and release of equipment from site shall be logged. Use of the Equipment Decontamination Log, Appendix E, may be used for this purpose.

I. Incident and Emergency Procedures

This section documents procedures to be followed in the event of incidents and certain emergencies. Where possible these have been formatted to individual sheets for response training and ready reference when needed.

I.1. General Emergency Procedures

This subsection describes procedures which are common to a variety of incidents.

I.1.a. Responsibilities

1) The site supervisor is responsible for the overall conduct of emergency procedures. This includes maintaining an orderly succession of supervision; making necessary reports to all concerned parties; ensuring that the causes of accidents are identified and corrected; and ensuring that injured personnel (with or without life threatening injuries) are escorted to medical treatment by the HSO or other supervisory personnel.

2) The HSO has the responsibility for ensuring that the provisions of this *HASP* are adequate and implemented in the field. Changing field conditions may require decisions to be made concerning adequate protection procedures. The HSO is also responsible for conducting site inspections on a regular basis to ensure the emergency readiness. The HSO shall be notified of any on-site emergencies and shall be responsible for ensuring that the appropriate procedures are followed.

I.1.b. First Aid

1) First Aid Kits are located in each FE JV pickups, trailers; and decontamination facility.
2) A first aid trained individual will be on site at all times.
3) Emergency eye wash will be located at the decontamination facility.

I.1.c. Evacuation Procedures

The HSO shall select and maintain appropriate assembly points for evacuations. These shall be posted and employees informed of their locations. At least one primary and one secondary assembly point shall be established.

1) When an evacuation is called for, employees shall proceed in an orderly fashion to the primary or secondary evacuation assembly points.

2) Turn off equipment whenever possible. Avoid leaving hazardous conditions in the process of evacuating.

3) Evacuate in the safest direction indicated by wind, smoke, fire, or other hazards.

4) Take a head count and report to the supervisor.

5) Do not leave the assembly area without reporting to the supervisor.

I.2. Reporting and Investigating Incidents

All incidents at the site shall be reported. It is hoped that most incidents will be small and/or near misses. It is essential that these events be reported as well more serious incidents in order to learn from them and avoid the more serious accidents.

I.2.a. Project and Facility Requirements

1) An incident is defined as follows:

    a. A work-related injury or illness;

    b. An exposure to a hazardous substance above the allowable exposure limit;

    c. Property/vehicle/equipment damage;

    d. An uncontrolled fire or explosion;

    e. An unplanned spill or release (including air releases) to the environment;

    f. A permit exceedance;

    g. Any unexpected contact or damage to aboveground or below ground utilities; and

    h. A "near miss" or an unplanned event that has a reasonable probability in resulting in one of the outcomes described above had the circumstances been different and for which modifications to management programs will reduce the probability of occurrence or the severity of the outcome.

2) Verbal Notifications

    a. In addition to immediate verbal (oral) reporting of all incidents to the client's Project Manager.

    b. A "serious" incident includes the following:

        i. Imminent danger safety violations;

        ii. Any incident involving the general public or visitors;

        iii. Exposure to a hazardous substance above the allowable exposure limit;

        iv. Work related injury requiring more than First Aid;

        v. Work related illness;

        vi. Spills of hazardous material in excess of 1 gallon or Reportable Quantity (RQ); and

        vii. Any unplanned fire on the facility property.

3) Incident investigations. An incident investigation shall be performed for all incidents for which a report is required. The supervisor and the designated HSO shall perform the investigation and shall include participation by others as necessary. The investigation is to be initiated as soon as possible after the incident.

I.2.b. Reporting Incidents

Report all unplanned, unexpected, events or changes in conditions. Some examples include:

1) Personnel incidents, such as:

    a. injuries;

    b. Illnesses;

    c. First aid cases;

    d. Fights or other acts or threats of violence;

    e. Fatalities; or

    f. Any personnel injuries or incidents which might be the result of acts of other contractors, subcontractors, or facility personnel.

2) Accidents such as:

    a. Motor vehicle accidents (with or without damages);

    b. Equipment accidents (with or without damages); or

    c. Property damage (including fires).

3) New, previously unknown, or unexpected potential hazards such as:

    a. Buried drums, cylinders, or hazardous materials containers;

    b. Unusual soil conditions (e.g., previously disturbed soils, soils with unusual odors, soils with unusual coloration);

    c. Floating contaminants (e.g., oil, chemicals, or sheens on water).

4) Environmental incidents such as:

    a. Oil or chemical spills;

    b. Dead or injured wildlife on the site; or

    c. Disturbed habitats.

5) Objects of potential cultural or historical importance such as:

    a. Bones;

    b. Buried coins or money;

    c. Arrow heads;

    d. Possible burial sites; or

    e. Finding articles of any potential cultural significance.

6) Unauthorized personnel in work areas such as:

    a. Unauthorized workers on site;

    b. Unescorted public visitors;

    c. Media personnel; or

    d. Unescorted government visitors.

I.2.c. Procedures for Reporting Incidents

1) First Responder's Report

    a. If your work is involved with the incident of interest, STOP WORK IMMEDIATELY.

    b. Ensure the safety of the area from any imminent hazards.

    c. Report to your immediate supervisor by radio or phone if at all possible.

    d. If you must leave the area to make a report, find someone to help secure the area if at all possible.

2) Supervisors

    a. Control imminent hazards as necessary.

    b. Ensure that injuries are being taken care of, and assign someone to escort injured employees leaving the site for medical evaluation/treatment.

    c. Ensure that the area is adequately secured.

    d. Ensure that the scene is not further disturbed.

    e. Visit the accident scene as soon as possible.

    f. Interview injured workers and witnesses as soon as possible.

3) Reporting requirements

    a. Report all incidents verbally to the client as soon as the area has been secured.

    b. Follow up with a written report before the close of business.

    c. Follow up with a written investigation report within 48 hours.

I.3. Personnel Injury

I.3.a. First Aid

1) The Project Manager (or senior supervisor on site) and/or HSO shall ensure necessary first aid or medical attention is obtained. First aid shall be provided by qualified first aid providers or site Fire Department EMTs.

2) If personnel need medical evaluation, ensure that an HSO or supervisor is assigned to escort the employee.

3) Do not allow injured personnel to drive themselves unless a doctor determines they are fit to do so.

4) If a doctor prescribes medication determine if that medication limits ability to drive. Do not allow employees to drive themselves if the medication impacts on driving safety. (If an employee wants to drive themselves and has been prescribed medication that will impact on driving safety the employee can wait to take the medicine at home if the doctor allows this.)

I.3.b. Hazard Assessment

The Project Manager (or senior supervisor on site) and/or HSO shall immediately investigate the nature and cause of injury in order to assess the hazard to ongoing site work. This should include consideration of working short-handed if the injured person cannot resume work right away. It is the senior supervisor's responsibility to stop work if necessary to make corrective changes.

I.4. Heat Stress

I.4.a. Signs and Symptoms

1) The incidence and severity of heat strain will vary widely among people, even under identical heat stress conditions. Disabilities often arise from the combined effects of environmental heat loading and metabolic heat production.

2) Prolonged increases in deep body temperature during the first trimester of pregnancy may endanger the fetus and are associated with temporary infertility for people of both genders.

3) Profuse and extended sweating produces dehydration and loss of body electrolytes and may lead to heat exhaustion or muscle cramps.

    a. Cold clammy skin is a sign of heat stress.

b. Hot and dry skin is a sign of HEAT STROKE, a medical emergency.

4) Oral or tympanic temperature exceeds 99.6°F is an early warning sign and monitoring should be increased. If temperature exceeds 100.6°F remove the employee and rehab.

5) A prime objective of heat stress management must always be preventing heat stroke, which is life threatening and is the most serious of the heat-induced disabilities.

   a. The **heat stroke** victim is often manic, disoriented, confused, delirious, or unconscious.

   b. The victim's skin is hot and dry, sweating has ceased, and the body temperature is 40°C (104°F) or higher.

   c. Immediate emergency care and hospitalization are essential if signs of heat stroke develop.

I.4.b. Treatment

1) Heat Stress:

   a. Force fluids.

   b. Remove PPE to allow evaporative cooling.

   c. Seated rest (or lie down).

   d. Rest in the shade to ensure removal from radiant heat.

   e. Carefully monitor pulse to ensure that pulse is lowering.

   f. If treatment fails to reduce pulse and temperature, or if these measures continue to increase, treat as a potential medical emergency, and call 911 for first responders.

2) Heat Stroke:

   a. This is an extremely serious medical condition.

   b. Treat as a medical emergency.

   c. Remove PPE.

   d. Lie down.

   e. Watch for signs of shock and treat accordingly.

   f. Keep skin moist with room temperature water (do not apply chilled water to skin surfaces unless instructed by emergency medical personnel).

I.5. Heavy Weather

I.5.a. High Winds

Outdoor equipment operations will be suspended as follows:

1) Sustained wind speeds of 40 mph;
2) Gusts exceeding 60 mph;
3) When dust control measures are no longer effective.

Wind risk operations at 25 mph:

1) Crane operations;
2) Work with sheet materials such as liners; or
3) Work with large-profile materials such as panels.

I.5.b. Lightning

Outdoor operations will be suspended when lightning is within a 20 second count of the site (i.e., the time difference between seeing a lightning strike and hearing the sound). High profile equipment operations shall be suspended when lightning is within 30 seconds or 10 miles of the site.

1) High profile operations include crane operations, drilling operations, or electrical wiring tasks.

2) Equipment operators shall stop their equipment and park it safely before heading for shelter.

3) No personnel will be left on the ground in an exposed location.

4) Preferred shelter is a permanent building. Personnel may also take shelter in trailers or low profile rubber tired equipment (e.g., pickups). Avoid driving pickups or any other equipment except to help evacuate personnel.

5) Work will resume after a 30-minute period without lightning.

I.5.c. Tornadoes

The supervisor will ensure that a dedicated watch is posted during periods of tornado watch or warning. Get clear of trailers and evacuate to the closer of the following:

1) The LTWTP, NSPW's main office building, or the basement of the Our Lady of the Lake School. If the above cannot be reached in time, lay low in nearest ditch or sunken area. Specific locations will be identified (e.g. signs) and discussed during site orientation.

I.6. Domestic and Wild Animal Bites, Rabies, and Plague

Bites inflicted by domestic and wild animals primarily pose a serious risk of infection. In some cases they may carry rabies as well.

I.6.a. First Aid (Domestic and Wild Animal Bites)

1) If bleeding is minor, wash the wound.
2) Control bleeding.
3) Apply antibiotic ointment.
4) Cover the wound.
5) Get medical attention.

I.7. Phone Threats

This includes bomb threats, threats against personnel, threats of violence or any other threatening communications made by phone or radio.

I.7.a. Do Not Hang Up

Try to remain calm. It is important not to hang up on threatening callers. This may provoke an act of violence.

1) Listen carefully to background noises or conversations.

2) Take notes on the callers exact words if possible.

3) Try to get someone else to report the call immediately to the phone company on another line before the caller hangs up.

I.7.b. Report the Call Immediately to the Senior Envirocon Supervisor On-Site

1) DO NOT discuss the call with anyone else.

2) The Envirocon supervisor shall immediately bring the call to the attention of the senior client's representative.

3) The senior supervisors from Envirocon and the client's Project Manager shall be responsible for determining if an evacuation will be called.

I.8. Emergency Contacts for Site

Table I.8. Important/Emergency Contacts

Fire Department	Ensure dispatcher is COA and not Ashland County	Emergency 911
Ambulance	Ensure dispatcher is COA and not Ashland County	Emergency 911
Police Department	Ensure dispatcher is COA and not Ashland County	Emergency 911
Utility Locate	Wisconsin Digger's Hotline	(800) 242-8511
Hospital: **Memorial Medical Center - Ashland Wisconsin** ·	1615 Maple Lane · Ashland, WI 54806 Directions: See Appendix I for Map and Directions	Phone: (715) 685-5500
Envirocon Work Comp	Montana State Comp Fund 5 South Last Chance Gulch P.O. Box 4759 Helena, MT 59604	Zurich American Phone: (877) 405-9045 Fax: (800) 622-8081 Email: USZ Care Center@zurichna.com
FE JV RA Project Manager	Denis Roznowski	(920) 496-6756
FE JV Site Supervising Construction Manager	Brad Hay	(678) 822-3568
FE JV Project Health & Safety Supervisor	Dan Allen	(720) 404-6325
Envirocon Corp. Dir Health & Safety	Frank Sullivan	(509) 0460-0798
Envirocon Loss Control and Investigations	Mel Lockridge	(406) 523-1179
Medical Monitoring	Melissa Barkell	(406) 523-1192
WorkCare Medical Monitoring	Ana Martinez	(800) 455-6155 x118
WorkCare Early Return To Work	WorkCare II (Incident Intervention)	**1(888) II-XPRTS OR 1(888) 449-7787**
Envirocon Corp Ofc. Missoula, MT		(406) 523-1150
Xcel Construction Manager (Site Primary Contact)	Tom Perry 301 Lake Shore Drive E Ashland, WI 54806	(906) 204-6680
Xcel Asst. Construction Manager (Site Secondary Contact)	Pat Carr	(218) 343-4471
Xcel Project Coordinator	Eric Ealy	(763) 276-6476
ENVIROCON SAFETY HOTLINE		(800) 224-7389

Foth Infrastructure & Environment, LLC Members

Name	Cell Phone	Function
Denis Roznowski	(920) 819-3513	Project Manager
Chris Seider	(920) 277-3613	Project Health & Safety Officer
Bellin OCC Health	(920) 430-4560	Consulting Physician

Appendix A

JF Brennan's Health and Safety Plan

Health and Safety Plan

Prepared for:

Ashland/NSP Lakefront Site Phase 2 Wet Dredge

Ashland, WI

Reviewed and Approved by:

Project Manager / Tyler Lee	_____	11/27/2016
Position / Name	Signature	Date

Table of Contents

1. Site Description/ History/ Evaluation

The Ashland/NSP Lakefront Project Site (CERCLIS # WISFN0507952) is located in Ashland, WI. The site consists of land located along the shore of Lake Superior and is owned by Xcel Energy. The site is bounded by US Highway 2 (Lake Shore Drive) to the south. Ellis Avenue and its extension to the City Marine to the west, Prentice Avenue and its extension to a boat launch to the east. The property is also known as Kreher Park. The project for which this Health and Safety Plan is implemented is for the Phase 2 Wet Dredge.

The upland site and near shore sediment deposits consist of soils, sediments, and groundwater contaminated by polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs). The most abundant constituents in each of these compounds include benzene, VOC, Naphthalene, and PAH. Additionally, free phase hydrocarbons derived from tars are present as non-aqueous phase liquids (NAPL). The free product, or NAPL, is present in underground pockets of tar and other materials and do not readily mix with water. Sediment contamination tends to be higher with depth below the sediment water/interface and is highest at the near shore area, decreasing with distance away from the shoreline towards the breakwater footprint.
In the event contaminants are encountered in heavy concentrations, proper procedures and personnel are in place with the necessary credentials to handle it accordingly.

Prevailing Weather:
Figures 1-3 provide the yearly temperature, precipitation, and wind trends for Ashland, WI. The source of the data for Figures 1-3 is Weatherspark.com.

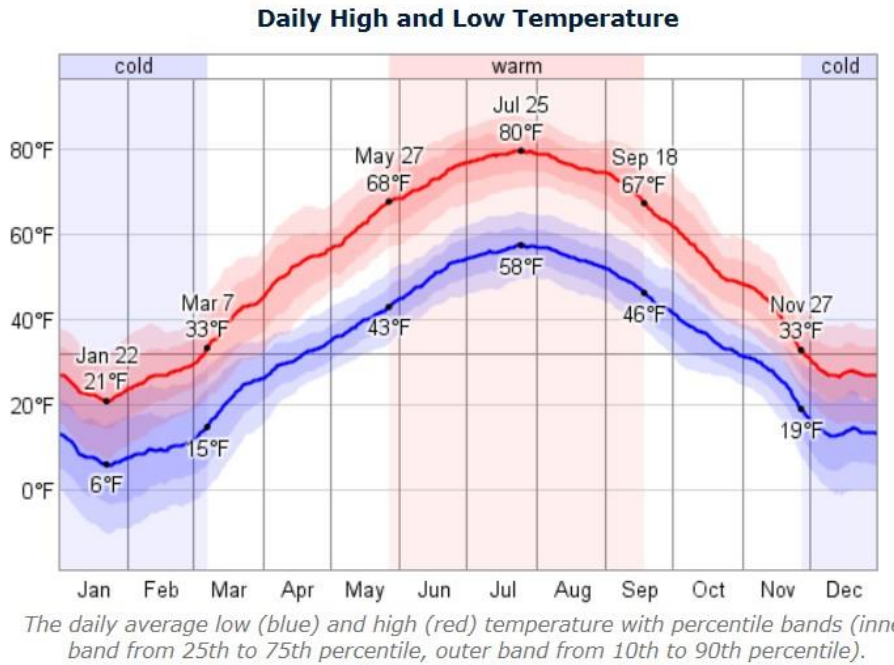
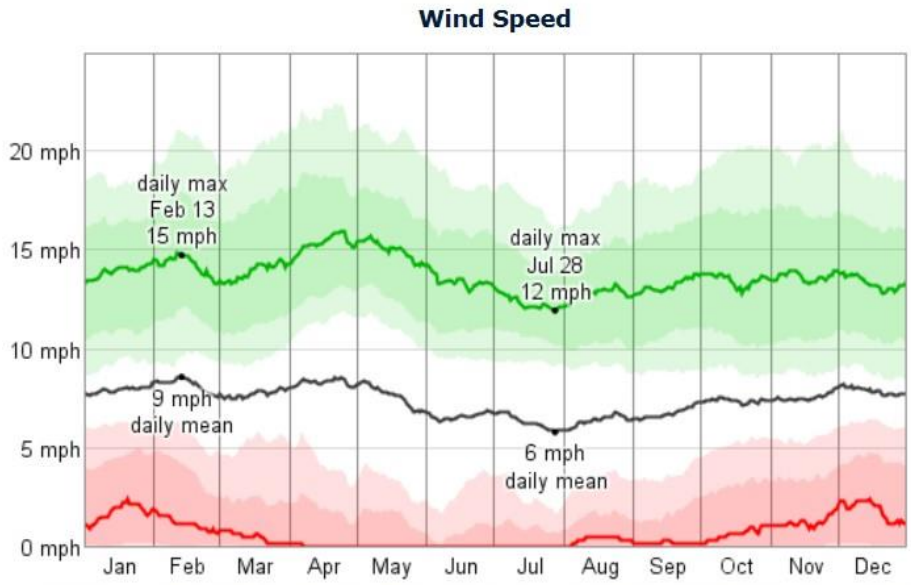


Figure 1. Average temperatures for Ashland, WI



The average daily minimum (red), maximum (green), and average (black) wind speed with percentile bands (inner band from 25th to 75th percentile, outer band from 10th to 90th percentile).

Figure 2. Average wind speeds for Ashland, WI

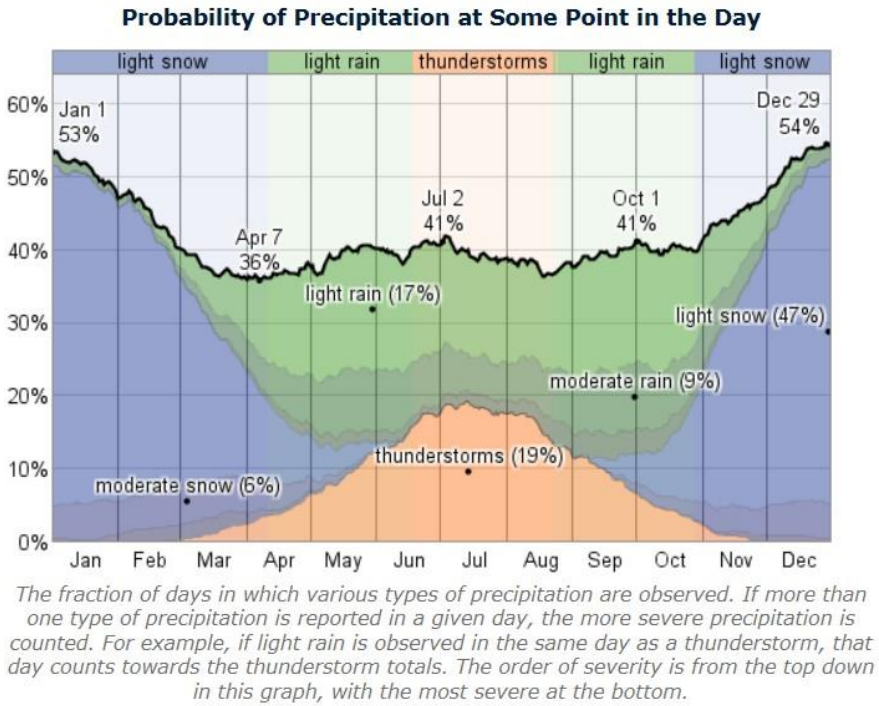


Figure 3. Average Precipitation Chances for Ashland, WI

2. Health and Safety Organization (responsibilities, qualifications, and chain of command)

This Health and Safety Plan (HASP) will be kept on the site during dredging activities and will be reviewed as necessary. The plan will be amended or revised as project activities or conditions change or when supplemental information becomes available. The below listed personnel comprise the Phase 2 Wet Dredge project leadership. All Brennan employees have completed a 40 hour Hazwoper course with the requisite 8 hour yearly refresher course.

Employee Name	Office	Responsibility
Tyler Lee	JFB	Project Manager (PM)
Steve Skau	JFB	Site Safety Coordinator (SSC)

Luke Ploessl	JFB	Brennan Corporate Health and Safety Manager (CHSM)
Dezy D Hajos	JFB	Brennan Safety Coordinator (SC)
Chad Defoe	JFB	Project Superintendent
Ross Johnson	JFB	Quality Control Technician

On a daily basis, the SSC will work in conjunction with Brennan Project Superintendent, administering the content of this site specific HASP. The SSC duties will include conducting daily tail-gate safety meetings, pre-task safety meetings, and updating Activity Hazard Analysis (AHAs) when unidentified tasks arise or when changes to identified tasks are appropriate. Furthermore, the SSC will interact on a daily basis with safety personnel reviewing safety document updates. Finally, on a frequent basis, Luke Ploessl (CHSM) will visit the site to ensure that this HASP is implemented in accordance with solicitation directives. Additionally Brennan's shift foreman will act as Site Safety Coordinators when the Site Safety Coordinator is offsite. All personnel will attend the daily plan-of-day meeting conducted by Foth Infrastructure & Environment/Envirocon Joint Venture (FE JV) personnel.

Crews have received training based on their designated assigned tasks within the Brennan Health and Safety Program in addition to third party OSHA 10 hour, Hazwoper, First Aid/CPR/AED and Blood Borne Pathogen training. At a minimum two on site employees will have this training.

3. Site Control

As described above, Brennan and the FE JV will establish work zones controlling access to areas of operations. Only personnel pre-approved by the Brennan SSC will be allowed to enter Exclusion or Work Zones. Furthermore, all personnel required to enter either an Exclusion or Work Zone shall have the requisite 40 hour Hazwoper training. All visitors must receive prior approval from the client or their designee to enter the site.

All visitors to the project site will be required to contact the PM prior to arriving at the site. Once on site, all individuals will be directed to immediately report to the project office, so that site specific training and visitor sign-in may occur. The Brennan PM will maintain logs of site visitation for inspection.

4. Features of Work Activity

Project

1. Mobilization of equipment
2. Installation of water quality barriers
3. Mechanical dredging
4. Hydraulic dredging
5. Restorative layer installation
6. Demobilization of equipment

5. Hazard Assessment

This section provides safe work practices and control measures for identified hazards to reduce or eliminate potential risk to personnel and equipment. Upon initiation of work at the site, Brennan will manage all hazards in accordance with this HASP and associated AHA forms. Furthermore, newly identified hazards will also be included within the below list after the start of operations. All newly identified hazards affecting activities at the site shall have corresponding AHA's constructed and reviewed with project personnel that will be performing the work.

One of the primary hazards on this particular site has been identified as Adverse Weather Conditions. The exposure to open water with heavy marine equipment will be managed with preemptive shutdowns. In other words, constant monitoring of weather conditions will be performed in order to complete the shutdown and cover procedures as adverse weather moves through the area.

All hazards shall be identified and/or mitigated according to the following procedures:

- When observed or discovered.
- When an imminent hazard exists that cannot be immediately abated without endangering employees or property, Brennan will remove all exposed workers from the area except those necessary to correct the hazardous condition.
- All such actions and dates completed shall be documented on Hazard Analysis Forms.

If an incident or injury were to occur due to any of the listed hazards or due to an un-identified hazard, initiate primary care and notify the Brennan SSC immediately. All contractors, subs, and visitors are to report incidents immediately to onsite FE JV management and Xcel field representatives. The contact numbers for all onsite personnel to be informed can be found in the jobsite trailers or with one of the foreman.

Chemical Hazards and Controls
All chemicals employed at the site by Brennan personnel will be accompanied by the relative SDS and handled in accordance with product specific information. Chemicals will not be allowed onsite until the SDS is made available.

Biological Hazards and Controls
The following lists hazards associated with biological organisms possibly present at the worksite. When an employee encounters one of the following biological hazards, the prescribed actions described below should be initiated. In addition, any workers allergic to plants or insects should report such conditions to the SSC prior to working at the site.

Bacteria/Fungi
Bacteria/ fungi are natural inhabitants of soil and are readily introduced into cuts and scrapes. Any injuries involving the possible introduction of soil into a wound should be cleaned as soon as possible, disinfected, treated with antibiotic ointment, and personal protective equipment (PPE) applied to prevent further exposure to soil. Seek medical attention immediately if the area becomes warm and/or reddened. Complete a minor injury report.

Snakes
Snakes typically are found in underbrush and tall grassy areas such as the marsh like conditions. If you encounter a snake, stay calm and be aware, as there may be other snakes in the area. Turn around and walk away on the same path you used to approach the area. It should be noted that there are no known poisonous or venomous snakes at this geographical location.

Poison Ivy and Poison Sumac
Poison ivy, poison oak and poison sumac typically are found in brush or wooded areas. Poison ivy and poison oak are most commonly found in moist areas or along the edges of wooded areas. During toolbox safety meetings, photos of poison ivy and poison oak will be distributed, so that personnel may become familiar with the plants.

If skin comes in contact with either plant, wash the area with soap and water immediately. If a reaction occurs (e.g. redness, blistering, itching), the reaction and is severe, seek medical attention.

Ticks
Ticks are typically found in wooded areas, bushes, tall grass and brush. Ticks are black, red or brown and can be up to ¼-inch in size. Wear tightly woven light-colored clothing with long sleeves and pant legs tucked into boots. Spray **only outside** of clothing with permethrin or permanone and spray skin with DEET only. Check yourself frequently for ticks.

If bitten by a tick, grasp it at the point of attachment and carefully remove it. After removing a tick, wash your hands, disinfect and press the bite area(s). Save the removed tick. Report the bite to the SSC for further medical attention if necessary.

Bees and Other Stinging Insects
Bees and other stinging insects may be encountered almost anywhere and may present a serious hazard, particularly to people with allergies. Watch for and avoid nests. Keep exposed skin to a minimum. Carry a kit if you have had allergic reactions in the past, and inform the SSC and/or co-worker. If

stung, and a stinger is present, remove it carefully with tweezers. Wash and disinfect the wound, cover it and apply ice. Seek medical attention if a reaction develops.

Blood-Borne Pathogens
Exposure to blood-borne pathogens may occur when rendering First Aid, CPR or when coming into contact with waste streams containing potentially infectious material. Exposure controls and personal protective equipment (PPE) are required as specified in the Brennan Health and Safety Manual.

Human illness from West Nile Virus is rare, even in areas where the virus has been reported. On rare occasions, West Nile Virus can result in a severe and sometimes fatal illness known as West Nile Encephalitis (an inflammation of the brain). The risk of severe disease is higher for persons 50 years of age and older.

Most infections of West Nile Encephalitis are mild and symptoms include fever, headache, body aches occasionally skin rash and swollen lymph glands. More severe infection may be marked by headache, high fever, neck stiffness, stupor, disorientation, coma, tremors, convulsions, muscle weakness, paralysis, and in some cases death. The incubation period in humans (i.e., time from infection to onset of disease symptoms) for West Nile encephalitis is usually 3 to 15 days. If symptoms occur, see your doctor immediately.

Physical Hazards and Controls

The following is a list of physical hazards and controls associated with work being performed at this jobsite.

Marine Operations
- All marine work will follow all navigational rules and give right of way to vessels accessing the area. During the evening hours all marine equipment will employ fleet lighting as prescribed by the U.S. Coast Guard (USCG).
- All operations involving boating will be performed by a certified operator.
- Per Brennan's Corporate policy, all personnel operating a boat at the site must have completed the Coast Guard Auxiliary Boaters safety course and be approved for operating a boat by the SSC.
- All personnel shall wear their Personal Floatation Device Type III (PFD) at all times while they are on the water or within 10' of the water's edge. (Inspect PFDs prior to use and do not use defective or damaged ones). Personnel working in the confines of a piece of machinery while on the water are exempted from this requirement. If working after dusk hours, PFDs should be equipped with strobe light and whistle.
- All personnel shall wear bright colors (for example: Hi-Vis with reflective strips orange, green, etc.) to enhance their visibility to one another.
- The Superintendent has final authority on operations with regards to weather and water conditions.
- One life ring buoy will be provided on all floating equipment for emergency rescue.
- Public exposure shall be minimized through the use of warning buoys, lights and signage. Underwater hazards shall be marked at the surface.
- Boats will be boarded from dock or pier unless suitable walking surface is available.
- Any boats operating in contaminated areas requires personnel to wear Tyvek when potential for dermal contact exists.
- The marine equipment must be operated according to U.S. Coast Guard (USCG) regulations for speed, lighting, right-of-way, etc.

Survey Lasers

- Laser beams used in surveying may be hazardous to the eyes.
- The severity of the hazard depends on the type of laser and its power.
- Avoid direct eye contact with the beam.
- This is most important when wearing corrective eyeglasses, which can intensify the beam's focus on the retina.
- Lasers used in surveying are usually low power.
- Lasers must be posted with safety warning signs.

Working on or over Water

- Fall protection should be provided to prevent personnel from falling into water. Where fall protection systems are not provided and the danger of drowning exists, U.S. Coast Guard-approved PFDs, shall be worn.
- Inspect PFDs prior to use. Do not use defective PFDs.
- A life-saving skiff or life raft must be provided for emergency rescue.
- A minimum of one ring buoy with 70 feet of 3/8-inch solid-braid polypropylene (or equal) rope must be provided for emergency rescue.
- Use all equipment according to the manufacturers' instructions and intentions.

Aerial Lifts

- Only authorized and trained personnel are permitted to operate aerial lifts.
- Inspect aerial lifts and test lift controls prior to use.
- Wear a full body harness with lanyard attached to the boom or platform. For scissors lifts where a standard guardrail system is installed and you are working within the confines of such a system, full body harness and lanyard are not required. Working over the water in a boom lift or similar will be discussed as agreed to as appropriate by on site management. If the discussion has not taken place prior to using the boom lift, the harness should always be worn.
- Do not attach lanyard to any adjacent structures or equipment while working from an aerial lift.
- Stand firmly on the floor of the platform and do not sit or climb on the railings of the platform or use planks, ladders, or other devices to increase working height.
- Remain in the platform at all times and do not leave the platform to climb to adjacent structures.
- Position aerial lifts on firm, level surfaces when possible, with the brakes set. Use wheel chocks on inclines. If outriggers are provided, position on solid surfaces or cribbing.
- Maintain safe clearance distances between overhead power lines and any part of the aerial lift or conducting material unless the power lines have been de-energized and grounded, or where insulating barriers have been installed to prevent physical contact. Maintain at least 10 feet from overhead power lines for voltages of 50 kV or less, and 10 feet plus ½ inch for every 1 kV over 50 kV (Reference Table 9-1).
- Do not exceed the boom and basket load limits.

- Do not use aerial lifts as cranes.
- Do not work or stand below aerial lift operations.
- Do not use aerial lifts when winds exceed 20 miles per hour.

Cranes, Hoists, and Rigging

- Only Certified Crane Operators are permitted to operate cranes.
- Prior to any use, cranes shall be inspected in accordance with all applicable regulations.
- Prior to any lifting operations, the SSC and the certified crane operator shall determine the necessary outrigger pad size/mats to prevent settling.
- Lifts plans shall be in place prior to utilizing the cranes.
- All rigging and use of rigging must be done under the supervision of a qualified rigger.
- At all times cranes shall maintain safe operating distances from energized power lines in accordance with Table 9-1.
- Maintain a safe distance from operating cranes and stay alert for crane movements. Avoid positioning between fixed objects, operating cranes and crane pinch points. Remain outside of the crane swing and turning radius. Crane swing radius shall be delineated with caution tape, signs, or barricades whenever possible to keep personnel out of the danger zone.
- Approach cranes only after receiving the operator's attention. The operator shall acknowledge your presence and stop movement of the crane. Never approach operating cranes from the side or rear where the operator's vision is compromised.
- When required to work in close proximity to operating cranes, wear high-visibility vests with reflective strips to increase visibility to operators.
- Stay clear of all hoisting operations. Loads shall not be hoisted over personnel.
- Cranes shall not be used to lift or lower personnel.
- The Utility Company or appropriate party will be notified to de-energize electrical lines near crane operations prior to working near them. If a crane becomes electrically energized, personnel shall not touch any part of the crane or attempt to touch any person who may be in contact with the electrical current. <u>If at all possible, the operator should remain in the crane cab until the contacted line is de-energized.</u>
- Do not exceed hoist load limits. When reviewing hoist limits the competent operator shall consider wind load, weather conditions, and ground pitch (angle).
- Insure load is level and stable before hoisting.
- Inspect all rigging equipment prior to use. Do not use defective rigging for any reason.
- Only use rigging equipment for the purpose it was designed and intended.
- Rigging shall be inspected and documented prior to use by a qualified rigger, signal person, or operator.
- Critical lifts will be performed in accordance with regulatory requirements.

Lockout/Tag-out

- Lock out/Tag out will follow procedures set forth in the Brennan Health and Safety Manual.
- Do not work on equipment when the unexpected operation could result in injury, unless lockout/tag-out procedures are implemented.

- Staff working under a lockout/tag-out procedure must complete the Brennan Lockout/Tag-out training course. Project-specific training may also be required on site-specific lockout/tag-out procedures.
- Standard lockout/tag-out procedures include the following six steps:
  - Notify all personnel in the affected area of the lockout/tag out
  - Shut down the equipment using normal operating controls
  - Isolate all energy sources
  - Apply individual lock and tag to each energy isolating device
  - Relieve or restrain all potentially hazardous stored or residual energy
  - Maintain a lockout/ tag out log.
  - Verify that isolation of the equipment has been accomplished. Once verified that the equipment is at the zero energy state, work may begin.
- Do not remove another person's lock or tag. Only a Brennan Supervisor, in conjunction with the SSC, may remove another person's lock or tag.

Welding and Cutting

- Only authorized and trained personnel are permitted to operate welding/cutting equipment.
- Prior to initiation of welding or cutting work, personnel must obtain hot work permits.
- Welding and cutting within a confined space is not allowed on this project.
- Do not enter areas where welding/cutting operations are taking place unless completely necessary and only after receiving permission from the welding/cutting operator.
- If you must be present in an area during welding/cutting operations, position yourself behind flash screens or wear glasses/goggles with lenses of appropriate tint.
- Do not look directly at the welding/cutting flash or at reflective surfaces surrounding welding/cutting operations.
- Avoid contacting compressed gas cylinders. Cylinders should be firmly secured in an upright position at all times.
- Prior to use and after a compressed gas cylinder has been spent, it shall be securely placed in an upright position, capped, and locked within a storage rack.
- Be aware of trip hazards created by welding hoses, power cables, leads and cords positioned on walking surfaces.
- Flashback arrestors are required on all torch equipment.
- Regulators shall be bled off when equipment is not in use.
- Hot work permits are required when on site.
- FIRE WATCH: must be present during the burning and 30 minutes after the last burn. This person shall have no others duties than maintaining fire watch.

Compressed Gas Cylinders

- Regulator must be removed and valve caps must be in place when cylinders are unused, transported, moved or stored.

- Prior to acceptance of any type of gas cylinders at the project location, personnel shall insure that cylinders are properly coded and labeled by the vendor.
- Cylinders must be secured in an upright position at all times.
- Cylinders must be shielded from welding and cutting operations. They must also be positioned to avoid being struck or knocked over, contacting electrical circuits or exposed to extreme heat sources.
- Cylinders must be secured on a cradle, basket or pallet when hoisted; they may not be hoisted by choker slings.
- When not in use cylinders must be separated a minimum of 25' or by a fire barrier.

Fall Protection

- Fall protection systems must be used to eliminate fall hazards when performing construction activities at a height of 4 feet or greater.
- The SSC shall act as competent person and shall inspect and oversee the use of fall protection systems. Follow all requirements established by the Brennan Corporate Health and Safety Manual for the use and limitation of fall protection systems.
- Remain within the guardrail system when provided. Leaning over or stepping across a guardrail system is not permitted.
- Do not stand on objects (boxes, buckets, bricks, blocks, etc.) or ladders to increase working height on top of platforms protected by guardrails.
- Inspect personal fall arrest systems prior to each use. Do not use damaged fall protection systems at any time, or for any reason.
- Set-up personal fall arrest systems so that you cannot free-fall more than 4 feet.
- Only attach personal fall arrest systems to anchor points capable of supporting at least 5,000 pounds.
- Use fall protection equipment for fall protection only. Never use fall protection equipment to hoist materials. Do not use personal fall arrest systems that have been subjected to impact loading.
- All personnel working in a man basket are required to tie-off within the confines of the basket.

Hand Tools

- Operate all tools according to the manufacturer's instructions and within design limitations.
- All hand and power tools shall be maintained in a safe condition.
- Tools are to be inspected and tested before use. If a tool is found to be defective, it is to be tagged "Do Not Use" and removed from service until repaired.
- Personal protective equipment, such as gloves, safety glasses, earplugs and face shields are to be used when exposed to a hazard from the tool.
- Power tools are not to be carried or lowered by the cord or hose.
- Disconnect tools from energy sources when not in use, before servicing and cleaning, and when changing accessories such as blades, bits and cutters.
- Safety guards on tools are to remain installed while the tool is in use and promptly replaced after repair or maintenance has been performed.
- Tools are to be stored properly where they will not be damaged or come in contact with hazardous materials.
- If a cordless tool is connected to its recharge unit, both pieces of equipment must conform strictly with electrical standards and manufacturer's specifications.

- Tools used in an explosive environment must be rated (i.e., intrinsically safe, spark proof, etc.) for work in such an environment.
- Impact tools, such as drift pins, wedges and chisels shall be kept free of mushroomed heads.
- Manual and pistol-grip hand tools may involve work with highly repetitive movement, extended elevation, constrained postures or positioning of body members (e.g., hand, wrist, arm, shoulder, neck, etc.). Consider alternative tool design, improved posture, selection of appropriate materials, work organization and sequencing to prevent muscular skeletal, repetitive motion and cumulative trauma stressors.
- Tools shall be tested each day before use to insure that safety devices are in proper working condition. The method of testing shall be in accordance with the manufacturer's recommended procedure.
- Belts, gears, shafts, pulleys, sprockets, spindles, drums, fly wheels, chains or other reciprocating, rotating or moving parts of equipment shall be guarded if such parts are exposed to contact by employees or otherwise create a hazard.
- All liquid fuel-powered tools shall be stopped while being refueled, serviced or maintained.
- All portable electrical tools and equipment shall be used in conjunction with a GFCI device or circuit.
- Chords and hoses associated with electrical hand tools shall be inspected prior to use.

General Practices and Housekeeping

- Good housekeeping must be maintained at all times in all project work areas.
- Nails will be bent over or removed from boards or loose stock.
- Common paths of travel should be established and kept free from the accumulation of materials.
- Keep access to aisles, exits, ladders, stairways, scaffolding and emergency equipment free from obstructions.
- Provide slip-resistant surfaces, ropes and/or other devices to be used.
- Specific areas should be designated for the proper storage of materials.
- Tools, equipment, materials and supplies shall be stored in an orderly manner.
- As work progresses, scrap and unessential materials must be neatly stored or removed from the work area.
- Containers should be provided for collecting trash and other debris and shall be removed at regular intervals.
- All spills shall be quickly cleaned up. Oil and grease shall be cleaned from walking and working surfaces.

Hazard Communication

- All chemicals brought on site by Brennan shall be accounted for on a list which is cross referenced to respective safety data sheets (SDSs).
- Confirm that an inventory (i.e. a list) of chemicals brought on site by Brennan subcontractors is available.
- Request or confirm locations of SDS from the client, contractors, and subcontractors for chemicals to which Brennan employees potentially are exposed.
- Before, or as the chemicals arrive onsite, obtain an SDS for each chemical and retain a copy for submission to the Brennan CSM.
- Label portable chemical containers (i.e. chemicals transferred from a manufacturer’s container to a smaller volume container for individual use) with the identity of the chemical and hazard warnings. Store all chemicals properly as directed by the SDS, paying special attention to 1)

compatibility (i.e. keeping acids separated from bases/caustics, and oxidizers from fuels, etc.), 2) quantity limits, 3) secondary containment, 4) fire prevention and 5) environmental conditions and restrictions.

Lifting

- Proper lifting techniques must be used when lifting any object.
  - Plan storage and staging to minimize lifting or carrying distances.
  - Split heavy loads into smaller loads.
  - Use mechanical lifting aids whenever possible.
  - Have someone assist with the lift—especially for heavy or awkward loads.
  - Make sure the path of travel is clear prior to the lift.
  - Use Brennan supplied work gloves when lifting objects.
  - The allowable individual weight limit on any given lift is 50 lbs.

Fire Prevention

- A-B-C Type Fire extinguishers shall be provided so that the travel distance from any work area to the nearest extinguisher is less than 100 feet. Extinguishers must:
  - be maintained in a fully charged and operable condition
  - be visually inspected each month
  - undergo a maintenance check each year
  - must be stored in a manner that does not allow for damage due to falling or contact with moving vehicles
- The area in front of extinguishers must be kept clear.
- Combustible materials stored outside should be at least 10 feet from any building.
- Solvent waste and oily rags must be kept in a fire resistant covered container until removed from the site.
- Flammable/combustible liquids must be kept in approved containers and must be stored in an approved storage cabinet.
- Flammable liquid storage containers (i.e. 55 gallon drums or larger) shall be grounded, and portable metal containers shall be bonded to the main storage container prior to transferring flammable liquids.

Electrical

- Only qualified personnel are permitted to work on unprotected energized electrical systems.
- Only authorized personnel are permitted to enter high-voltage areas.
- Do not tamper with electrical wiring and equipment unless qualified to do so. All electrical wiring and equipment must be considered energized until lockout/tag-out procedures are implemented and potentially energized electrical equipment has been verified as de-energized.
- Inspect electrical equipment, power tools and extension cords for damage prior to use. Do not use defective electrical equipment. All defective equipment shall be removed from service immediately and tagged as “out of service”.

- All temporary wiring, including extension cords and electrical power tools, must have ground fault circuit interrupters (GFCIs) installed.
- Extension cords must be:
  - Equipped with third-wire grounding
  - Covered, elevated or protected from damage when passing through work areas
  - Protected from pinching if routed through doorways, windows, wall openings or any other through any other structural penetration
  - Not fastened with staples, hung from nails, secured with plastic zip-ties, or suspended with wire
- Electrical power tools and equipment must be effectively grounded or double-insulated and UL approved.
- Operate and maintain electric power tools and equipment according to manufacturers' instructions.
- Maintain safe clearance distances between overhead power lines and any electrical conducting material unless the power lines have been de-energized and grounded, or where insulating barriers have been installed to prevent physical contact. Maintain at least 10 feet from overhead power lines for voltages of 50 kV or less, and 10 feet plus ½ inch for every 1 kV over 50 kV (See Table 9-1).
- Temporary lights shall not be suspended by their electric cord unless designed for suspension. Lights shall be protected from accidental contact or breakage.
- Protect all electrical equipment, tools, switches and outlets from environmental elements.

Stairways and Ladders

- Personnel should avoid using both hands to carry objects while on stairways; if unavoidable, use extra precaution. Every effort must be considered before using a ladder. SSC/HSO will have to evaluate the use and preform a risk assessment. In addition to OSHA guidelines, ladders will not be use more than 30 minutes.
- Personnel must not use pan and skeleton metal stairs until permanent or temporary treads and landings are provided the full width and depth of each step and landing.
- Ladders must be inspected by a competent person for visible defects prior to each day's use. Defective ladders must be tagged and removed from service.
- Ladders must be used only for the purpose for which they were designed and shall not be loaded beyond their rated capacity.
- Only one person at a time shall climb on or work from an individual ladder.
- User must face the ladder when climbing and descending the ladder, keeping the belt buckle between side rails.
- Ladders shall not be moved, shifted or extended while in use.
- User must use both hands to climb. Materials and equipment should be raised and lowered using rope.
- Straight and extension ladders must be tied off to prevent displacement.
- Ladders that may be displaced by work activities or traffic must be secured or barricaded.
- Portable ladders must extend at least 3 feet above landing surface.
- Straight and extension ladders must be positioned at such an angle that the ladder base to the wall is one-fourth of the working length of the ladder.
- Stepladders are to be used in the fully opened and locked position and must have one person holding the ladder to prevent movement.

- Users are not to stand on the top two steps of a stepladder; nor are users to sit on top or straddle a stepladder.
- Fixed ladders > 24 feet in height must be provided with fall protection devices.
- Fall protection should be considered when working from extension, straight, or fixed ladders greater than six feet from lower levels and both hands are needed to perform the work, or when reaching or working outside of the plane of ladder side rails.

Heat Stress

- Drink 16 ounces of water before beginning work. Disposable cups and water will be available. Under severe conditions drink 1 to 2 cups of water every 20 minutes, for a total of 1 to 2 gallons per day. Do not use alcohol in place of water or other nonalcoholic fluids. Decrease your intake of coffee and caffeinated soft drinks during working hours.
- Acclimate yourself by slowly increasing workloads (e.g., do not begin with extremely demanding activities).
- Use cooling devices, such as cooling vests, to aid natural body ventilation. These devices add weight, so their use should be balanced with efficiency.
- Use mobile showers or hose-down facilities to reduce body temperature and cool protective clothing.
- If possible, conduct field activities in the early morning or evening and rotate shifts of workers.
- Avoid direct sun whenever possible. Exposure to direct sun can decrease physical efficiency and increase the probability of heat stress. Take regular breaks in a cool, shaded area. Use a wide-brim hat or an umbrella when working under direct sun for extended periods.
- Provide adequate shelter/shade to protect personnel against radiant heat (sun, flames, hot metal).
- Maintain good hygiene standards by frequently changing clothing and showering.
- Observe one another for signs of heat stress.

SYMPTOMS AND TREATMENT OF HEAT STRESS					
	Heat Syncope	**Heat Rash**	**Heat Cramps**	**Heat Exhaustion**	**Heat Stroke**
Signs and Symptoms	Sluggishness or fainting while standing erect or immobile in heat.	Profuse tiny raised red blister-like vesicles on affected areas, along with prickling sensations during heat exposure.	Painful spasms in muscles used during work (arms, legs, or abdomen); onset during or after work hours.	Fatigue, nausea, headache, giddiness; skin clammy and moist; complexion pale, muddy, or flushed; may faint on standing; rapid thread pulse and low blood pressure; oral temperature normal or low	Sweating has stopped and skin is red, hot and dry; dizziness; confusion; rapid breathing and pulse; high oral temperature.
Treatment	Move to a cooler area, Rest lying down, Increase fluid intake, Recovery usually is prompt and complete.	Use mild drying lotions and powders, and keep skin clean for drying skin and preventing infection.	Move to a cooler area, Rest lying down, Increase fluid intake.	Move to a cooler area. Rest lying down, with head in low position. Administer fluids by mouth. Seek medical attention.	Cool rapidly by soaking in cool—but not cold—water. Call ambulance, and get medical attention immediately

Monitoring Heat Stress

These procedures should be considered when the ambient air temperature exceeds 70^{o}F, the relative humidity is high (>50 percent), or when workers exhibit symptoms of heat stress.

- The heart rate (HR) should be measured by the radial pulse for 30 seconds, as early as possible in the resting period.
- The HR at the beginning of the rest period should not exceed 100 beats/minute, or 20 beats/minute above resting pulse.
- If the HR is higher, the next work period should be shortened by 33 percent, while the length of the rest period stays the same.
- If the pulse rate still exceeds 100 beats/minute at the beginning of the next rest period, the work cycle should be further shortened by 33 percent.
- The procedure is continued until the rate is maintained below 100 beats/minute, or 20 beats/minute above resting pulse.

Cold Stress

- Be aware of the symptoms of cold-related disorders. Wear proper layered clothing for the anticipated fieldwork. Appropriate rain gear is a must in cool weather.
- Wind-Chill Index is used to estimate the combined effect of wind and low air temperatures on exposed skin. The wind-chill index does not take into account the body part that is exposed, the level of activity or the amount or type of clothing worn. For those reasons, it should only be used as a guideline to warn workers when they are in a situation that can cause cold-related illnesses.
- Persons who experience initial signs of immersion foot, frostbite, hypothermia should consult the Brennan SSC to avoid progression of cold-related illness.
- Observe one another for initial signs of cold-related disorders.
- Obtain and review weather forecast—be aware of predicted weather systems along with sudden drops in temperature, increase in winds and precipitation.

SYMPTOMS AND TREATMENT OF COLD STRESS			
	Immersion (Trench) Foot	**Frostbite**	**Hypothermia**
Signs and Symptoms	Feet discolored and painful; infection and swelling present.	Blanched, white, waxy skin, but tissue resilient; tissue cold and pale.	Shivering, apathy, sleepiness; rapid drop in body temperature; glassy stare; slow pulse; slow respiration.
Treatment	Seek medical treatment immediately.	Move victim to a warm place. Re-warm area quickly in warm– but **not** hot– water. Have the victim drink warm fluids, but **not** coffee or alcohol. Do not break blisters. Elevate the injured area, and get medical attention.	Move victim to a warm place. Have victim drink warm fluids, but **not** coffee or alcohol. Get medical attention.

Procedures for Locating Buried Utilities

- Utility services will be contacted prior to Pilot Study activities in order to locate utilities within the vicinity of operations. Once utilities are located, as-built drawings will be created by survey personnel who will place 50 foot offsets from the utilities on the drawings. These drawings will then be given to dredge operators prior to performing their activities in order for them to be aware of the existence of utilities and to maintain adequate distances to prevent potential hazards.
- Review locations of sanitary and storm sewers, electrical conduits, fuel tanks and lines, water supply lines and natural gas lines.

- Review proposed locations of intrusive work with facility personnel knowledgeable of locations of utilities. Check locations against information from utility mark-out service.
- When uncertain about a utility location within an area proposed for excavation, manually remove material if the utility is suspected to be within 3' of the surface.
- Monitor for signs of utilities during advancement of intrusive work (e.g., sudden change in advancement of auger or split spoon).
- When the client or other onsite party is responsible for determining the presence and locations of buried utilities, the SSC should confirm that arrangement.

Vehicle Safety—Operator Safety

- Operate vehicle only when in possession of valid driver's license.
- Prior to operating a vehicle, perform a localized inspection in the vicinity of the vehicle to insure that hazards do not exist or that there has not been a change in conditions.
- When operating a vehicle in tight spaces or operating a vehicle with a trailer use a spotter for additional guidance purposes.
- Do not use a cell phone or similar personal electronic device while driving.
- Employees shall not operate vehicles while under the influence of drugs or alcohol. Consumption of drugs or alcoholic beverages before or during work shift/driving is prohibited, as is possession of them within vehicle.
- All vehicle occupants must use seat belts at all times. Familiarize yourself with rental vehicle features (e.g., mirror & seat adjustments).
- Always drive within the speed limit.
- Do not drive if you are fatigued.
- Use tie-downs to secure equipment in large-cab vehicles such as vans.
- Exercise caution when entering or exiting a traveled way or parking along street—avoid sudden stops, use hazard lights when locating or stopping at work areas.
- Park in a manner that will allow for safe exit from vehicle, and if possible, park vehicle so that it can serve as a barrier.
- Before talking on a mobile phone, pull off of the roadway and park. Utilize hazard lights to make traffic aware.
- Park vehicles in a location where it can be accessed easily in the event of an emergency.

Working/Walking Adjacent to Vehicle Traffic

- All staff working adjacent to a traveled way or within work area must wear reflective strip/high-visibility ANSI Class 2 safety vests.
- When working next to an active roadway deploy cones, signs, or flagging to control the flow of traffic.
- Work as far from a road or traveled way as possible to avoid creating confusion for drivers.
- Remain aware of factors that influence traffic related hazards and require controls—sun glare, rain, wind, flash flooding, limited sight-distance, hills, curves, guardrails, width of shoulder (i.e., breakdown lane), etc.
- Always remain aware of an escape route.
    - Examples: behind an established barrier, parked vehicle, guardrail, etc.

- Always pay attention to moving traffic and do not assume drivers are looking out for you.
- Remain aware of approaching traffic for signs of erratic driving behavior.
- When workers must face away from traffic, a "buddy system" should be used. One worker should always be facing in the direction of oncoming traffic. Minimize the amount of time that you will have your back to oncoming traffic.
- Lookouts should be used when physical barriers are not available or practical. The lookout continually watches approaching traffic for signs of erratic driver behavior and warns workers. Vehicles should be parked at least 40 feet away from the work zone and traffic.

Vehicles Entering/Exiting Site

- A trained or qualified flagman must be used when backing heavy equipment onto the jobsite.
- If the vehicle will impede the normal flow of traffic when pulling into/out of the site, a flagman must also be used. Once the vehicle is on the road way, a field vehicle equipped with flashing lights will follow the heavy equipment vehicle.
- It is imperative that truck operations do not pose a traffic hazard to pedestrians and normal road traffic.

Uneven Walking Surfaces

- Employees walking in ditches, swales and other drainage structures adjacent to roads or across undeveloped land must use caution to prevent slips and falls. Failure to use caution in these areas can result in twisted or sprained ankles, knees, and backs.
- Whenever possible observe the conditions from a flat surface and do not enter a steep ditch or side of a steep roadbed.
- If steep terrain must be traveled, sturdy shoes or boots that provide ankle support should be used.

Slips, Trips, and Falls

- Institute and maintain good housekeeping practices.
- Keep hands out of pockets when walking, so that they may be used to break a fall.
- Install proper illumination to areas when working inside or during the evening hours.
- Pick up tools and debris in the work area.
- Walk or climb only on equipment and/or surfaces designed for personnel access.
- Be aware of poor footing and potential slip and trip hazards in the work area.

Pressure Washing Operations

- Wear modified level D personal protective equipment when operating a pressure washer including steel-toed safety shoes or boots, face shield, hearing protection and protective clothing (PPE). Do not tie the dead man control in the "on" position
- Never spray yourself or another individual.
- When using a pressure washer for the purpose of cleaning contaminated equipment, insure to don the proper PPE (Tyvek) and that all rinse water is collected for post treatment.
- Prior to use of a pressure washer inspect the immediate vicinity for any electrical hazards.

- Follow manufacturer's safety and operating instructions.
- Inspect pressure washer before use and confirm the "dead man" switch is fully operational.

Inclement Weather

Adverse weather conditions have the ability to present sudden hazards to the worksite. It is critical that every step be taken to prepare and plan for an emergency situation resulting from adverse conditions. Upon startup of the project, an emergency action plan will be developed based on the layout of the worksite and critical areas of operation. Emergency procedures will be clearly defined and emergency shelters identified for all marine equipment.

Adverse weather conditions requiring immediate suspension of field work activities are defined as the following:

Lightning- Lightning watches or warning shall be enacted as the situation warrants. When electrical activity is detected in the area, a 30-minute stand-down will occur to allow the storm cell to pass the area. If lightning is observed within the stand down period, the 30-minute time frame is extended until 30 minute after the last observed electrical activity. If on barge lighting shelter is considered, careful on board structure evaluation and agreement should addressed.

- Boat operations during inclement weather will be reduced to only essential tasks. In the case of the small craft advisory boat operations will be limited to larger vessels or shutdown. If wave action effects sediment removal the marine equipment will be moved to a protected area to dredge.
- Local Tornado warnings or watches must be monitored to determine if a complete stoppage of work is needed.
- Tornados or Severe weather are likely to bring strong winds into the bay that will present safety concerns. It will be important to takes steps to secure work areas and take shelter in a secure location.
- The SSC can monitor multiple sources to track developing potential for lightning. These are the following:
  - Doppler radar reports from the internet
  - National Weather Service radio reports
- Field crews shall report any observations of lightning or thunder in their area to the SSC.
- If you are inadvertently caught outside in a thunder/lightning storm, take the following precautions:
  - Seek shelter among an area that provides the substantial protection
  - Avoid lone trees as shelter.
  - Avoid open, bare areas.
  - Do not cross water bodies.
- If caught in an open area, place feet close together and crouch down, without lying on the ground.

When working on the Water: the weather forecasts and radar should be regularly monitored to prepare for adverse conditions. Some of the following steps should be taken to prepare for severe weather:

- If the marine equipment is capable of being spudded down on the water, this should be done to stabilize the vessel. The spuds may help protect workers and act as a grounded method for the vessel in lighting situations.

- Shelter should be provided on all marine equipment to provide additional protection. If shelter is not available, personnel should remove themselves from the marine equipment and seek the closest safe shelter. If vessels or barges are not capable of being spudded down, they should be moored in a safe area at the captain's discretion.
- All marine equipment should be secured prior to the approach of the storm.
- The number one priority in any severe weather conditions is employee safety. All required marine safety equipment shall be utilized to protect against water hazards.
- Caution should be taken in low lying areas for potential flash flooding conditions. High ground should be sought if conditions are present.

6. Training

General Training Requirements
Prior to initiation of site work, all personnel shall be properly indoctrinated in site health and safety regulations. Furthermore, personnel shall receive appropriate training to safely perform work at the site. General training required to perform work at the site within an exclusion zone will include successful completion of a 40 hour Hazwoper course with requisite 8 hour yearly refresher courses. Additionally, all crane operators performing work at the site shall attain Certified Crane Operator status and obtain fork lift certification if a fork lift is required for project work. When occupying Bay Front for staging or launching equipment, plant orientation training will be required.

Site Specific Requirements
All leadership involved in day to day operations at the site, including the PM, Superintendents, Foreman, and Safety Personnel will coordinate a site specific orientation for those employees working under their supervision.

All personnel, leadership and professional craft, shall undergo the following site specific training prior to working at the site:

- **Operations Training-** Operations training will initially be enacted by the Brennan PM with subsequent training directed by the SSC. Training will include an overview of on-going operations, review of AHA sheets, verify successful completion of general training requirements, and review in emergency response training.

Daily and Weekly Safety Meetings
Each day, prior to the start of operations or shift, Brennan personnel and subcontractors will meet to discuss and coordinate upcoming work activities. The Brennan SM or Superintendent will perform all pre-work safety meetings. When a change in work arises or a new phase of work is set to begin, the SSC will use the daily operational meetings to discuss potential hazards associated with the new phase of work.

Before each start of work activity, a Weekly Toolbox Safety Meeting will occur at the project site. Weekly Toolbox safety meetings will entail discussion of site specific safety related issues, additional site specific training, and also additional safety related topics.

Refresher Training
As required by OSHA, all individuals performing work at the site will have completed yearly eight hour refresher training prior to beginning work at the site.

Records
Records of all site specific training, safety related meetings, personnel safety training credentials, and operator credentials shall be kept at the site for periodic inspection or as requested the FE JV.

First Aid/ Injuries
As stated above, Brennan employs the Zero Injury Philosophy within its safety program. Brennan is committed to providing the safest working environment, proper tools and training to its employees in order to achieve zero injuries Accordingly, all operational or safety related incidents and near misses are reported, regardless of size and severity. Furthermore, in any instance where First Aid is required, reports are generated detailing the nature, root causes, involved personnel, severity of the incident, and corrective actions to prevent future occurrences. All injuries no matter how minor will be reported to the FE JV at the earliest opportunity.

Lost Time Injuries
All severe injuries that may preclude lost work time shall receive initial medical care at the Memorial Medical Center. Lost time injury documentation shall include a full investigation of the incident or accident leading to the loss time injury including personnel involved, equipment involvement, personnel interviews, and methods to prevent future loss time injuries. A pre-final report will be available for the FE JV inspection within 24 hours of the incident with a final report issued within five business days.

Individuals involved in a loss time incident shall not return to work until receiving clearance from a medical doctor or physician's assistant.

7. Industrial Hygiene Monitoring

Industrial hygiene monitoring will be performed on an as needed basis based on the exposures presented in the work tasks. The Brennan safety department will conduct sound monitoring of equipment as needed to identify any potential noise issues. Brennan will follow the FE JV site Health and Safety Plan to determine the proper level of PPE for the potential airborne contaminates.

8. Standard Operating Procedures/Engineering Controls/Work Practices

Throughout this Health and Safety Emergency Response Plan details have been prescribed for standard site operating procedures. Additionally, the following work restrictions and procedures shall be enacted during site operations.

Confined Space Entry System

Brennan will label all hatches and areas that meet the requirements of a confined space. When access is needed to these areas a confined space entry permit will be filled out prior to entry.

Personnel Teaming/ Buddy System

Brennan will maintain radio communication with each member of the crew on that shift during operations and use of the buddy system during certain hazardous operations. All individuals on each crew shall be responsible for assuring that crew members are accounted for during emergency situations.

Overhead Electrical Hazards

Prior to the start of Brennan operations, Brennan superintendents, crane operators, safety personnel, and site management will perform a site investigation to determine the extent of electrical hazards as they pertain to anticipated crane operations. Brennan site safety personnel will document the pre-work electrical hazard investigation and will periodically review results of the investigation with personnel. Additionally, as operations approach areas identified as potential hazards, pre-work meetings will specifically address overhead electrical hazards, hazard mitigation methods, and operating procedures required while working in the vicinity of overhead power lines.

At all times personnel shall not violate the standards set forth in ANSI B.30 2004, which governs crane operation near power lines. All operations need to stay 20 feet away from power lines unless the voltage in known and then follow Table 9-1.

Table 9-1: Minimum Safe Working Distances to Overhead Power Lines

Normal Voltage (kV) Operation Near High Voltage Power Lines	Minimum Required Clearance (feet)
Up to 50	10
Over 50 to 200	15
Over 200 to 350	20
Over 350 to 500	25
Over 500 to 750	35
Over 750 to 1000	45
Over 1000	As established by the utility owner/operator or registered professional engineer

Loading and Unloading of Trucks

Loading and unloading of trucks will include equipment deliveries, and removal of any additional items. Equipment loading/ unloading and clean material deliveries will be coordinated prior to arrival of delivery trucks to the site. Trucks arriving to the site will meet Department of Transportation (DOT) standards. All unloading of equipment and material will be performed by competent individuals trained in proper techniques for safely removing equipment and materials from a truck.

Ignition Sources

Smoking will only be allowed in designated areas. However, cutting torches and welding equipment, may be used to facilitate welding and cutting of materials and other miscellaneous tasks at the site. All required "hot work permits" will be in place prior to the start of the work day. It shall be the responsibility of the Site Superintendent to attain all required "hot work permits" prior to the start of each work day.

Electrical Construction

Brennan will not perform any site electrical construction.

9. Personal Protective Equipment (PPE)

It is Brennan's standard practice to provide required PPE to all individuals working on company projects excluding steel toed shoes and clothing. In accordance with Brennan's practice, the following pieces of equipment shall be issued to project personnel:

1. Hard hat
2. Safety glasses with side shields
3. Hi-vis vests or shirts with reflective markings
4. Work gloves

Skin Protection

Personnel will employ the use of standard construction personnel protection equipment throughout the project period. On a daily basis steel toed boots, hard hats, eye protection, and gloves shall be required for work at the site. All items, except steel toed boots, shall be provided to individuals prior to site work. Employees will also be required to wear long pants and at minimum short sleeve shirts.

Working Over or Near Water

When operations require that personnel work over or near water at depths that could warrant hazardous conditions, personal flotation devices shall be required within 10 feet of the water.

10. Personnel Hygiene and Decontamination

All equipment and material that may have come into contact with the sediment must be decontaminated, inspected and documented prior to leaving the worksite. During removal of piling, laborers will wear proper level D protection to protect against dermal exposure.

The foremost area for worker exposure would be through dermal contact. Therefore, employees shall maintain good personal hygiene. Breaks and lunch shall be taken in the designated clean areas. If skin contact is made with the sediment, it should be cleaned off before eating, drinking or smoking.

11. First Aid Provisions and Emergency Equipment

Brennan personnel working at the site shall receive training in the use of Emergency First Aid kits to include deployment and location information. At a minimum, Brennan shall maintain routinely inspected Emergency First Aid kits at the following locations:

1. Marine Equipment
2. Inside the cabs of all heavy equipment
3. Inside the cabs of all company pick-ups located at the jobsite
4. Project specific field office

Fire extinguishers shall also be placed and secured throughout the jobsite at the following locations:

1. Marine Equipment
2. Inside the cabs of all heavy equipment
3. Inside the cabs of all company pick-ups located at the jobsite
4. Project specific field office
5. Near any flammable or combustible material

Life rings with lifelines shall be located at each location:

1. Barge/Marine plant
2. Site access to water
3. Crew, work, and survey boats

12. Emergency Response/ Contingency Plan and Procedures

In accordance with solicitation directives, Brennan has prepared the following emergency response procedures in the event of First Aid requirements, fire, or chemical exposure. Accordingly, the following plan is provided:

Pre-Emergency Planning

Prior to the first day of work, all Brennan and subcontractor personnel will undergo site orientation and site specific emergency response training. Pre-emergency planning shall be included with training procedures and consist of orientation on evacuation routes, emergency medical notification and procedures, emergency response to medical or fire instances and evacuation procedures and routes. A man overboard emergency drill will be performed at startup of activities along with periodic drills throughout the project.

Local Emergency Services

Medical Care Facility

Brennan has identified the nearest medical facility to be:

Memorial Medical Center
1615 Maple Lane
Ashland, WI 54806

Please see Appendix A for the route map from Kreher Park to the Memorial Medical Center East. In the event that an individual is taken to emergency care in a company vehicle, two individuals may be needed to accompany the patient if there is a likelihood of the patient going into shock. This facility will be used for all employee medical needs.

Fire Department

Ashland Fire Department
122 Lake Shore Drive East
Ashland, WI 54806

Police Department

Ashland Police Department
601 Main Street West
Ashland, WI 54806

Personnel Roles, Lines of Authority, Training and Communication

In the event of an emergency response, work shall cease and responding personnel shall notify a supervisor in the immediate vicinity prior to initiating response activities. The responding supervisor shall immediately notify the Brennan SSC who will notify the FE JV. Once immediate response or care has been given and the incident has been mitigated to the extent that personnel may return to work, the Brennan SSC shall submit a preliminary report to the FE JV followed within twenty four hours of the incident.

Similar to training provided for pre-emergency planning, all personnel will receive training in proper communication and notification techniques and requirements in the event of an emergency. All training shall be conducted prior to the first day of work at the site by Brennan or subcontractor personnel.

Emergency Recognition and Prevention

All personnel working at the site on behalf of Brennan and its subcontractors are trained union professionals knowledgeable in the identification of emergency situations.

On a weekly basis, Brennan's SSC will perform inspections of the all work areas in an effort to identify and mitigate situations that may lead to an emergency response.

Safe Distances and Places of Refuge

Prior to the initiation of site activities, Brennan personnel will meet with the FE JV safety personnel to identify appropriate muster locations in the event of an emergency. Furthermore, Brennan personnel will review survey findings with respect to utilities and overhead power lines and anticipated effects on machinery movement and project operations.

Evacuation Routes and Procedures

Prior to initiation of site activities, Brennan personnel will meet with the FE JV personnel to identify emergency evacuation routes and procedures. Subsequent to procedure and route identification, Brennan will incorporate routes and procedures into site personnel training.

Emergency Alerting and Response Procedures

In the event of an emergency that requires medical attention or professional response, personnel will first contact a supervisor in the immediate vicinity prior to initiating emergency response actions. Notified supervisors will immediately inform Brennan's SSC, through radio communications, prior to assisting with emergency response procedures. Brennan's SSC shall be responsible for notifying the FE JV personnel.

Critique of Response and Follow-Up

Within a week of an incident requiring an emergency response, the Brennan SSC shall submit a full report detailing the emergency response and factors that have been subsequently implemented to mitigate future events.

Emergency Fire Response

Fire extinguishers shall be placed at various designated locations throughout Brennan's work area. In the event of a "small fire", i.e. a fire which can be mitigated through the use of fire extinguishers, personnel shall be allowed to operate a fire extinguisher to engage the area of concern. However, in the event that it is questionable whether a fire extinguisher can affirmatively negate a fire, personnel will be directed to immediately leave the vicinity and make the proper notifications.

13. Heat and Cold Stress Monitoring

The SSC, Site Superintendent, and Foreman shall be trained in the recognition of heat stress and heat fatigue. Work may be performed during the summer months when the level of heat is at its highest. Therefore, throughout site work, water shall be readily available to project personnel. Furthermore, a cooling area will be provided in the work Support Zone for each crew performing work at the site, so that individuals may exit from direct sunlight. At a minimum, personnel shall take two fifteen minute and one half-hour break per ten hour day.

During the fall and spring, crews may be presented with the hazards that lead to cold stress. If these circumstances arise, personnel will be instructed to dress for the tasks assigned. In addition, designated break areas will be made available for use during to work day to reduce the likelihood of cold stress.

Drinking water shall be supplied to all areas of the site under Brennan control and refreshed daily to prevent employees from experiencing dehydration.

14. Hazard Communication Program

Brennan participates in an electronic Hazard Communication Program as a component of the OSHA Global Harmonization Program and SDS, where all personnel have immediate access to SDS data for chemicals employed at the site. As such, all routine chemicals envisioned for use at the site are catalogued prior to work. In the event that a chemical is brought to the site, which has not been pre-identified, Brennan's SSC will download all required SDS information through the Brennan electronic program. Finally, the electronic SDS program, including all anticipated site chemicals, is available for the FE JV inspection upon request.

15. Accident Prevention Plan

Safety Hazards

The anticipated safety hazards with hazard mitigating operations have been included as part of Section 5 of this HASP. Furthermore, AHAs for all anticipated and unanticipated tasks (as they occur) will be submitted to the FE JV for approval prior to the start of a task.

Corporate Safety Program Philosophy and Mission

The philosophy of the Brennan Corporate Safety Program is to ensure that all employees have the proper equipment, training, and atmosphere to safely perform their work. Without exception, ensuring that each individual can safely return home to his or her family is the primary mission of the Brennan Corporate Safety Program.

Corporate Safety Program Objective

Brennan's objective is to create a Culture of Safety, where all incidents, accidents, and injuries are eliminated from the workplace. A Culture of Safety can only be created when managers, superintendents, foremen, and employees receive necessary training, and apply it to field operations.

Each day safe work practices need to be communicated and reiterated to all employees. Before work starts, hazards need to be identified through the Activity Hazard Analysis process. All team members need to be clear on what is expected of them to perform work for Brennan and other team members.

All personnel are assigned responsibility for safe and healthy operations. This concept is the foundation for involving all employees in identifying hazards and providing solutions. For any operation, individuals have full authority to stop work and initiate immediate corrective action or control. In addition, each worker has a right and responsibility to report unsafe conditions/practices. This right represents a significant facet of worker empowerment and program ownership. Through shared values and a belief that all accidents are preventable, our employees accept personal responsibility for working safely.

Each project team member is responsible for the following performance objectives:

- All employees are required to treat safety as value. During any task, employees must consider the possible effects of their actions on themselves and others and take appropriate protective measures.
- All personnel are charged with aiding in the protection of the public including, as your job description dictates, installation and maintenance of signs, signals, buoys, lights, fences, guardrails, ramps, temporary sidewalks, barricades, and overhead protection, as may be necessary.
- Security fencing protects employees, the company and the general public. All fencing must be maintained by all employees to the extent of their job description. Report to your supervisor defects beyond your ability to repair.
- Complete an orientation prior to being authorized to enter the project work areas
- Employees are required to review, be familiar with, and adhere to site-specific jobsite health and safety plans, procedures, practices, precautions, and permits.
- Use only safe means of access to and from work areas.
- Perform work in a safe manner and produce quality results; complete work without injury, illness, or property damage.

Corporate Management and Division Manager Responsibility

Corporate Management and Division Managers are the basis for adherence to the Corporate Safety Policy. It is their responsibility to ensure each project is adequately staffed and equipped with proper safety items. Furthermore, it is the responsibility of Corporate Management and Division Managers to implement disciplinary actions, should they become necessary. The following list is a summary of individual duties for Senior Management and Divisional Managers:

1. Ensure each project's safety reviews have been completed prior to the start of a project.
2. Assure each project estimate properly captures required safety needs, i.e. equipment, safety personnel, competent people, training, certifications.
3. Staff each project with properly trained personnel.
4. Actively involve one's self with project Toolbox Safety Meetings when visiting a project.
5. Perform a quarterly safety review with each Project Manager or Superintendent.
6. Implement disciplinary procedures when required.
7. Perform follow-up with each new hire to insure that a safety orientation was performed.

Health and Safety Department

It is the primary function of the Corporate Safety Department to implement and enforce the Brennan Inc. Safety Policy. The Corporate safety department will report directly to the COO of Brennan with the following specific work objectives:

1. Understand and implement all safety requirements as they pertain to OSHA, U.S. Corps of Engineer, or other client standards.
2. Properly train personnel as necessary to meet all OSHA, U.S. Corps of Engineer, or other client standards.
3. Review site specific or project specific safety plans for adherence to OSHA, U.S. Corps of Engineer, or other client standards.

4. Maintain records of corporate safety performance.
5. Perform periodic safety reviews of project locations. Review project safety reviews with project, divisional, or senior management.
6. Maintain site specific project safety staffs as necessary.
7. Review quarterly corporate safety performance with CFO, COO, and CEO.
8. Semi-annually review new hire safety performance and make recommendations as to full-time hiring.

Project Management

Each individual working in project management, as a Project Engineer, or as a Project Manager is expected to implement the Corporate Safety Policy at his or her site. Proper documentation of skills, training, and orientation are performed at the project level, so it is imperative that project management personnel properly communicate all requirements to field personnel. Project management personnel are expected to perform the following specific work objectives:

1. Insure that each individual at the site is performing tasks commensurate with their capabilities.
2. Insure that the project specific Health and Safety Plan is consistent with project risks.
3. Ensure that the project site is properly equipped with personal protective equipment.
4. Perform new hire orientation or site-specific orientation to all employees prior to the start of a project.
5. Evaluate new hire safety performance and make recommendations as to full time employment.
6. Insure that toolbox meetings are being performed at the site and actively participate in toolbox safety meetings.
7. Enforce all safety regulations and the Corporate Safety Policy.
8. Continually inspect for unsafe work practices and correct all unsafe work practices.

Superintendent Responsibility

The success of our accident program depends on the sincere, constant, and cooperative effort of all Superintendents. A Superintendent, in many cases, represents the highest field level of leadership. Strict adherence to safety protocol and enforcement by a Superintendent is critical to the success of the Corporate Safety Program. A Superintendent will:

1. Lead by Example
2. Perform new hire orientation in the absence of a site safety manager or project manager.
3. Make recommendation as to full time employment for newly hired personnel after the 120 day initiation period as specified in the Employee Handbook.
4. Teach each employee what the hazards are on the job and how to avoid them.
5. Create, edit, or review Activity Hazard Analysis for each operation.
6. Enforcement of all safety regulations.
7. Continuous inspection for unsafe practices and conditions and prompt corrective action to eliminate causes of accidents.
8. Investigate all accidents promptly in order to discover their cause and provide proper corrective action.
9. Management of Toolbox Safety meetings.

10. Maintain a current First Aid and CPR card
11. See that needed safety equipment and protective devices are provided for each job.
12. Instruct new employees and review job safety practices.
13. Set the proper safety example.

Foreman's Responsibility

Effective and safe work can be accomplished when the foreman cooperates sincerely within the safety program. Foremen must consistently implement and enforce corporate safety polices. Foremen will:

1. Familiarize themselves with the company policy and safety program responsibilities.
2. Have the same responsibility for safety as for any other part of operations.
3. Instruct all new employees on the reporting of all accidents, first aid procedures and the use of safety devices and equipment.
4. Be responsible for the regular inspection of all tools and equipment used on work under his supervision.
5. Make certain that no work is assigned to an individual who is unqualified or incapable of doing the work safely.
6. Make certain that the project is in as safe a condition as possible, before leaving a job. They shall arrange adequate warning of any condition, which might endanger workers or the public.

Employee Responsibility

Your cooperation is necessary for the protection of yourself and fellow workers. All employees will:

1. Make safety job #1. Any employee at any time may stop work for an unsafe condition.
2. Strictly adhere to Corporate Safety Policy
3. Understand Corporate Safety Policy as it applies to their work.
4. In the case of an accident, inform the Foreman immediately, and seek first aid or medical assistance without delay.
5. Report any hazardous conditions to the Foreman.
6. Submit recommendations for safety.
7. Know your responsibilities in the case of an emergency.
8. Be familiar with and comply with safety practices listed in this manual.
9. Attend weekly safety meetings and comply with safety items discussed.
10. Properly handle, use and store all safety equipment and company tools.
11. Use the required safety equipment and wear the proper clothing.

Safety Meetings

Pre-Task Safety Meetings

Pre-task safety meetings are held when a new activity or a change in daily work activities is presented. A plan devised for the work and safety hazards are briefly discussed.

Daily Safety Meetings
Prior to the start of daily activities, a safety meeting shall be enacted to discuss upcoming work operations. Also, in addition to the job site related safety functions, daily safety meeting may include corporate or jobsite safety training.

Weekly Safety Meetings
Weekly safety meetings may be held with all crews collectively. The weekly meetings provide all crews with a chance to discuss scheduling for the following two weeks. As the schedule develops, safety hazards are identified and control measures are implemented. During this time, infractions from the previous week are discussed and how the situations were remedied. Additionally, as required weekly safety meetings may include corporate or jobsite training.

Subcontractor Supervision
Prior to a subcontractor's inclusion in work for Brennan, a Subcontractor Prequalification form must be completed and submitted to the Brennan Corporate Controller. At its sole discretion, Brennan may elect to contract work with a subcontractor based upon its prequalification information.

Brennan requires each of its sub-contractors to have a written safety policy specifically tailored to the sub-contractor's business. Furthermore, Brennan expects adherence to the following key safe work components:

Subcontractor Competent Individual
The sub-contractor is required to maintain a Competent Person on site at all times during sub-contractor work. The Competent Individual shall have a full understanding of project specific and construction industry safety practices.

Personal Protective Equipment
All Brennan subcontractors are, at a minimum, to have the following pieces of Personal Protective Equipment:

a. Hard hats
b. Steel-toed boots
c. Life jacket (when working near the water)
d. Eye protection with side shields
e. Gloves
f. Full-face shields (when grinding or using cutting equipment)

Subcontractor Medical Facilities
Prior to beginning work on a Brennan site, subcontractors are required to identify the nearest medical treatment facilities and contact means for use in the event of an emergency. Furthermore, Brennan requires that subcontractors provide their own First Aid equipment at the worksite.

Subcontractor Fire Prevention
Subcontractors must provide their own fire protection and suppression equipment. Furthermore, each piece of spark inducing equipment that a subcontractor brings to the site must have a clearly identified fire extinguisher, with a current inspection tag, dedicated to that piece of equipment.

Subcontractor Housekeeping
All Brennan subcontractors are required to keep their work areas neat and orderly.

Subcontractor Fall Protection
All Brennan subcontractors are expected to comply with OSHA fall protection standards. Any specific item not expressly identified above, shall not preclude the subcontractor from compliance. OSHA, U.S. Corps of Engineer, or private client standards, whichever is more stringent, shall govern subcontractor compliance standards.

Pre-Construction Subcontractor Safety Meeting
Prior to the initiation of onsite subcontractor work, a meeting shall take place between Brennan and the subcontractor to discuss safety and operational issues. At a minimum, the following individuals are required to attend the Pre-Construction Safety Meeting:

1. Brennan Division or Project Manager
2. Brennan Corporate Safety Director or Site Specific Safety Individual
3. Subcontractor Competent Individual

Daily and Weekly Subcontractor Safety Meetings:
Subcontractors working under Brennan are required to perform a daily Toolbox Safety Meeting with their employees. Documentation of topics, issues, and a personnel attendance list shall be submitted to Brennan immediately after the meeting on a weekly basis.

Additionally, throughout a subcontractor's work at the jobsite, all subcontractor personnel will attend the daily Brennan safety meeting prior to the start of work operations.

16. Cutting, Brazing and Welding Procedures

All Brennan personnel and Brennan subcontractor personnel shall strictly adhere to the requirements of the Brennan hot work program. It shall be the responsibility of the Brennan Site Superintendent or the Subcontractor Superintendent to ascertain required hot work permits each day before crews under their leadership begin work. The Brennan SSC shall enforce all permit requirements.

Hot Work Personal Protection Equipment

- Impact and heat resistant goggles or eye protection, in many cases, helmets.
- Lenses and filters in eye wear to protect against intense light or ultraviolet (UV) radiation.
- Gloves to be thermal and flame-resistant (leather preferred).
- Protective clothing to guard exposed skin from thermal and UV radiation.
- Flame-resistant leggings may be appropriate for additional leg protection.
- Other personal protective equipment, such as hearing protective devices may be appropriate.
- Individuals performing hot work at a location other than a permanent hot work station shall position at least one person (fire watch) to watch for and extinguish any blaze that starts.
- If hot work is being performed in an unoccupied area where combustible materials are present, a person shall remain for 20 minutes after completion of the operation and during operator's breaks (i.e. – lunch, coffee) to ensure that sparks do not start a fire.
- Fire watch shall warn the operator if hazardous conditions develop in the area affecting fire safety or personal safety of the operator.
- Fire watch shall have the appropriate fire extinguisher and shall be knowledgeable in its use.

Oxygen-Fuel Gas Welding and Cutting

- Hoses must be properly rated for the designed service, properly connected, and do not use clamps or wire for connections.
- All oxygen-acetylene or other fuel gas torch systems have a:
    - Flashback protection device between the hoses and the regulator on the bottle side to prevent flashback from passing the point where the protection device is installed on a torch.
- Operators shall use the manufacturer's recommended procedure for shutting off the torch being used.
- Operators shall inspect hot work equipment, including PPE, before use and replace defective equipment before proceeding.
- Regulators shall be bled off when the equipment is not being used.

Fire- High Risk Locations

Potential cases would include:

- Fuel gas generator tanks and piping in rooms where fuel gas is generated.
- Exhaust ducts attached to wood, rubber, or fiber working machines and other ducts that may be coated on the inside with a flammable residue.
- Ducting in which flammable, toxic, or explosive vapors have been, or may be present.
- Area where combustible fibers are used or stored or in woodworking areas.
- Any area where wet-cell batteries are present.

Combustible Metals (or Alloys)

- Weld combustible metals, and alloys of combustible metals, only in areas specifically established for that purpose and equipped with inert arc welding equipment and special magnesium firefighting equipment.

- Place combustible metal dust, filings, and chips in closed, noncombustible containers, or remove them from the welding area before any welding begins.

Welding Procedures
Prior to initiation of welding operations, personnel must become familiar with types of materials on which weld work occurs. Vapors associated with welding operations may pose health risks to personnel. Accordingly, if an individual is not familiar with the types of material on which weld work occurs or the weld material itself, Brennan's SSC should be contacted for a task review.

17. Spill Control Provisions

Brennan and its subcontractors shall maintain the means at the project location to contain and mitigate fuel, oil, or chemical spills. In the event that a spill occurs, all mitigation efforts and reporting procedures shall strictly comply with Coast Guard, Department of Natural Resources, EPA, and the Ashland Bay Port District. Brennan will follow the Environmental Protection Plan (EPP) developed specifically for this site when handling spill prevention and environmental issues.

Spill kits shall be located within work areas near spill potential equipment. All spill kits shall include sorbent pads, containment booms, and sweeps. On a quarterly basis, spill kits shall be inspected by Brennan's SSC to ensure that degradation of containment equipment has not occurred.

Oil Spill Response Actions
1. Assess conditions in the area, and determine if there are injured persons, or if the situation makes it too hazardous to enter the area. Attempt to stop the source of the spill.
2. If the barge is leaking, make arrangements to remove the oil from the affected compartment. If possible, transfer the oil into another compartment on the barge. If this is not possible, make arrangements to off load the barge's contents into another barge, or facility.
    - Federal regulations require that a licensed tankerman supervise all cargo transfer on tank barges.
    - When transferring products from or within the tank barge, always follow the vessel transfer procedure on board.
3. Use absorbents and pads to prevent spilled oil from entering the water.
4. After attempting to stop the spill, contact the FE JV and the Qualified Individual. If unable to contact those individuals contact the National Response Center at 1-800-424-8802.

Incident Notification Procedures
After initial mitigation techniques have been enacted to contain a spill, contact Brennan's SSC who will enact notification procedures through the proper channels. As a matter of federal law, the National Response Center must be contacted after a spill event.

18. Water/ Boater Safety

Brennan will maintain various work boats at the site at all times. All individuals using work boats must have completed the Coast Guard Boaters safety course and be approved for operation by Brennan's SSC or Superintendent. Prior to operation, personnel must employ the use of a personal flotation device. Furthermore, at all times while the boat is in operation, personnel must fasten the emergency shutdown chord to their personnel flotation device.

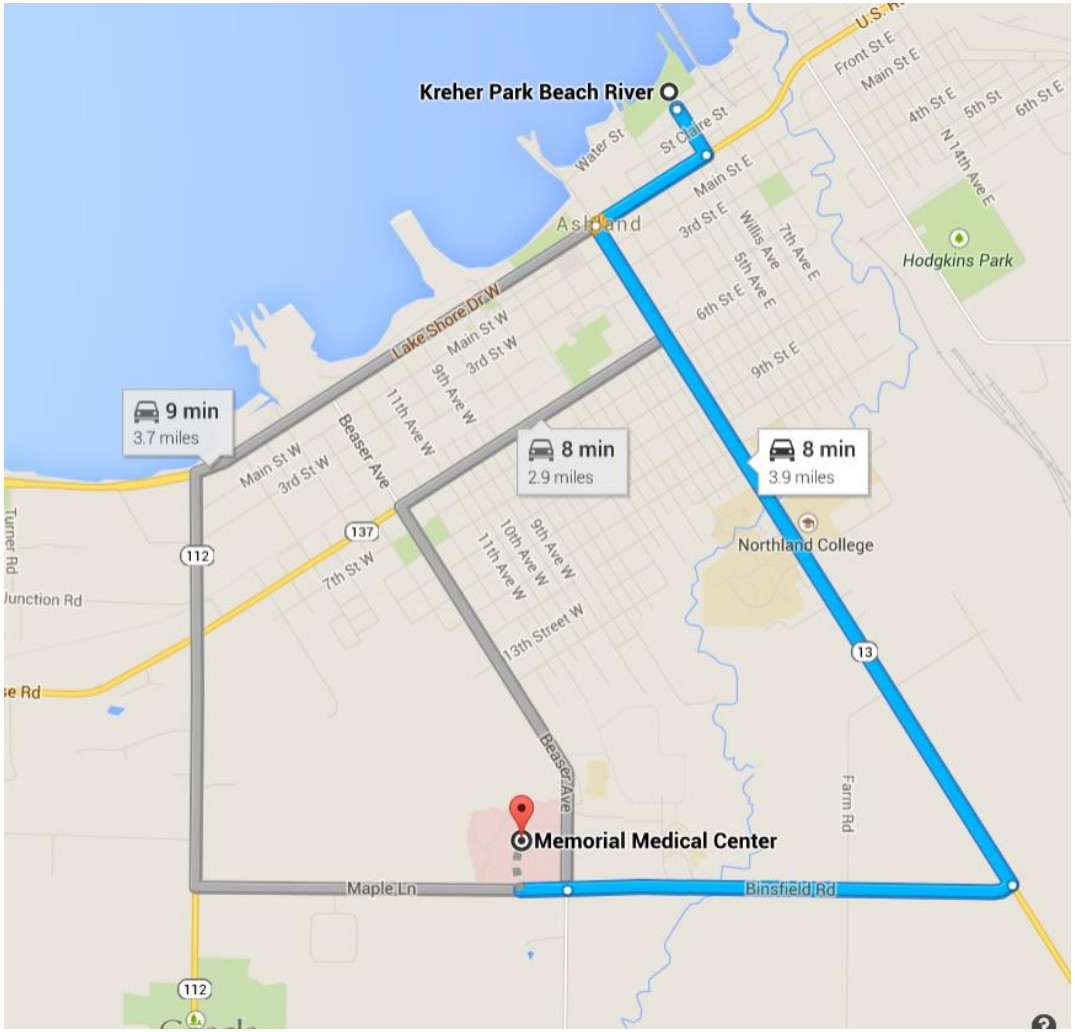
All work boats at the site shall have oars, fire extinguisher, horn, throw ring, and battery box, per Brennan policy and US Coast Guard (USCG) regulations. Boats should be inspected periodically, in the event that required items are missing, personnel should report deficiencies immediately.

Personal flotation devices shall not be required if the work area is contained within hand railing or the depth of water adjacent to the pier or dock would preclude drowning.

19. Dredging Around Utilities

Brennan will locate all utilities before dredging work starts. The individual utility companies will be contacted to located and provide as built drawings of the utilities. Once utility locations have been confirmed a 50 foot buffer will be put on both sides of the utility. The location of the utility and the buffer area will be displayed on the dredge computer so that the dredge does not dredge or spud into the utility area.

20. Appendix A – Emergency Facility Map



Appendix B

Voluntary Employee's Emergency Information Data Sheet

Voluntary Employee's Emergency Information Data Sheet

The following information is being gathered to help us respond to an emergency. **All questions are optional.** You may answer any of the questions you like or leave any blank. The original copy is sent to the Corporate safety office, and a copy will be maintained on site. If the information provided changes, you should submit a new sheet.

Employee Name (please print clearly): _____

Emergency Contacts (name as many as you like)
In the event of an emergency who should we contact to let them know? _____

_____

What City and State do they live in?_____

What is their phone number? _____

What is their relationship to you? _____

Emergency Contact for YOU

How can we get in touch with you for project recalls, shutdowns, emergencies etc.?

_____

Where are you staying while on site? _____

What is the phone number there? _____

Medical Conditions

Are you allergic to any medications? □yes/□no What are they?_____

Are you allergic to insect bites or stings? □yes/□no What are they?_____

Do you carry treatments or medicine(s) (e.g., insulin, sugar/candy/food, bee sting kits) that needs to be given in an emergency? □yes/□no What are they?_____

Where is it kept?_____

Are you or do you have:

- □yes/□no: Hypertension (Is it uncontrolled? □yes/□no)
- □yes/□no: Asthma (Is it uncontrolled? □yes/□no)
- □yes/□no: Diabetes (Is it uncontrolled? □yes/□no)
- □yes/□no: Hypoglycemia
- □yes/□no: Epilepsy/seizures
- □yes/□no: Fainting spells
- □yes/□no: Irregular heart beat
- □yes/□no: Narcolepsy (sleeping spells)

What company do you work for? _____

Safety Officer's Notes:

Appendix C

Authorization to Work Form

Envirocon

Daily Safety Meeting, Plan of the Day and Authorization to Work Form

Project Name/Location: | **Project Number:** |

Today's Date and Time:

Describe the Envirocon Plan of the Day (POD), Including Subcontractor Work

Other Work Activities: other contractors on site, deliveries, new equipment, equipment servicing, etc.

Today's Safety Topics

Site/Personnel IH Monitoring

Today's Assigned Behavior Observer(s)

Applicable Permits & Plans (check off)

	Confined Space
	Critical Lift
	Hot Work
	LO/TO Checklist
	Rigging
	Other

Previous Day's Stop Works/Safety Observations/Suggestions:

AHAs, JSAs or JHAs Applicable to Today's Work (check off)

✓	Add AHA name and number (below)	✓	Add AHA name and number (below)

New Site Hazards from Previous Day

Muster Points/Emergency Contact Number

1) 2)

Emergency Contact Number:

Changing Conditions from Previous Day (e.g., traffic patterns, zones, weather, etc.)

Supervisor and Safety Competent Person Authorization to Work (ATW)

Supervisor: *Signature:*

SCP: *Signature:*

Date:	Project Name:	Project No:
Envirocon	**Safety Meeting and POD Acknowledgement**	Page 2 of 3

Signature of Personnel

I understand the Plan of the Day and topics associated with this safety meeting. I am also aware of my authority to stop work. I will report all incidents and illness to the site management. AHAs, JSAs or JHAs and Field Activity Plans pertaining to my tasks have been reviewed. I will update these plans as needed when my task changes or if I find a safer way to perform my work.

Name:	Company:	Signature:	Time In:	Time Out:

Date:	Project Name:	Project No:
Envirocon	**Safety Meeting and POD Acknowledgement**	Page 3 of 3

Signature of Personnel

I understand the Plan of the Day and topics associated with this safety meeting. I am also aware of my authority to stop work. I will report all incidents and illness to the site management. AHAs, JSAs or JHAs and Field Activity Plans pertaining to my tasks have been reviewed. I will update these plans as needed when my task changes or if I find a safer way to perform my work.

Name:	Company:	Signature:	Time In:	Time Out:

Appendix D

Job Safety Analysis
(to be constructed in the field)

Appendix E

Decontamination Report/Log for Release of Equipment

Decon Report/Log for Release of Equipment

Method	Decon Method Description:	
Method 1	Dry decon using shovels, brooms, etc.	Project Name: Ashland/NSP Lakefront Site
Method 2	Wet decon using high pressure washer	Project Number: 16X002
Method 3	Wet decon using low pressure water hoses, hotsy and scrub brushes	Contaminants: BTEX, naphthalene, PAHs

DECONTAMINATION ACTIVITIES							INSPECTION ACTIVITIES	
date & time	Equipment Description, Model, and serial number Owner			Decon Method	Decon Supervisor		Inspector	Notes
date	Description			☐ Method 1	name		name	☐sat ☐unsat
	Owner	Make	Model	☐ Method 2	sig		sig	
time		serial		☐ Method 3				
date	Description			☐ Method 1	name		name	☐sat ☐unsat
	Owner	Make	Model	☐ Method 2	sig		sig	
time		serial		☐ Method 3				
date	Description			☐ Method 1	name		name	☐sat ☐unsat
	Owner	Make	Model	☐ Method 2	sig		sig	
time		serial		☐ Method 3				
date	Description			☐ Method 1	name		name	☐sat ☐unsat
	Owner	Make	Model	☐ Method 2	sig		sig	
time		serial		☐ Method 3				
date	Description			☐ Method 1	name		name	☐sat ☐unsat
	Owner	Make	Model	☐ Method 2	sig		sig	
time		serial		☐ Method 3				
date	Description			☐ Method 1	name		name	☐sat ☐unsat
	Owner	Make	Model	☐ Method 2	sig		sig	
time		serial		☐ Method 3				

Appendix F

Contaminants of Concern

Contaminants of Concern

Contaminants	OSHA PEL	ACGIH TLV	Exposure Routes	Acute Symptoms	Chronic Symptoms	Target Organ	IP	Spec. gravity	V.P. mmHg	Flash point deg F	LEL %	UEL %
acenaphthene	?	?	Inhalation of aerosols and contact	eye irritation primarily a chronic skin and respiratory hazard	Cancer Cardiovascular disease	skin respiratory sys bladder kidneys skin	?	1.2	0.3	350		
benzene	1 ppm	0.5 ppm skin	Inhalation contact absorption	Irritation of eyes, nose, and respiratory system dermatitis, headache, nausea	Bone marrow depression anorexia, leukemia	Blood, CNS. skin, bone marrow, eyes, respiratory tract	9.24	0.88	75	12	1.3	7.9
coal tar pitch volatiles {polynuclear aromatic hydrocarbons (PNA); poly aromatic hydrocarbons (PAH)} {e.g., pyrene, phenanthrene, acridine, chrysene, anthracene, benzo(a)pyrene, and benzene soluble or benzene insoluble fractions}	0.2 mg/m3 see OSHA 1910. 1002	0.02 mg/m3	Inhalation of aerosols and contact	eye irritation primarily a chronic skin and respiratory hazard	dermatitis, bronchitis, some are carcinogens for lung, skin, and kidney cancers	skin respiratory sys bladder kidneys	properties vary depending on individual compound					

Contaminants	OSHA PEL	ACGIH TLV	Exposure Routes	Acute Symptoms	Chronic Symptoms	Target Organ	IP	Spec. gravity	V.P. mmHg	Flash point deg F	LEL %	UEL %
ethyl benzene	100 ppm	100 ppm	Inhalation Ingestion Contact	irritation of eyes skin and mucus, headaches, coma, narcosis	dermatitis	CNS, eyes, respiratory system, skin, CNS	8.76	0.87	7	55	0.8	6.7
naphthalene	10 ppm	10 ppm skin	Inhalation Ingestion Contact Absorption	Irritation of eyes, Headache, Confusion, malaise, Nausea, vomiting, Abdominal pain, Irritated bladder, Profuse sweating,	Jaundice, hematuria (blood in the urine), hemoglobinuria, renal shutdown; dermatitis, optical neuritis, corneal damage	Skin, CNS, Eyes Liver Kidneys Blood	8.12	1.15	0.08	174	0.9	5.9
toluene	200 ppm	50 ppm	Inhalation Ingestion Contact	dermatitis, fatigue, weakness, confusion, muscular, fatigue	insomnia	CNS, liver, kidneys, skin	8.82	0.87	20	40	1.2	7.1
trichlorobenzene (syn: 1,2,4-trichlorobenzene)	? ppm	5 ppm ceiling	Inhalation Ingestion Contact Absorption	irritation of the eyes skin; and mucus membrane liver and kidney damage in animals	liver and kidney damage in animals	eyes, skin, respiratory system, liver, possible teratogen	?	1.45	1			10.5

Contaminants	OSHA PEL	ACGIH TLV	Exposure Routes	Acute Symptoms	Chronic Symptoms	Target Organ	IP	Spec. gravity	V.P. mmHg	Flash point deg F	LEL %	UEL %
Trimethylbenzene (mixed isomers)	? ppm	25 ppm	Inhalation Ingestion Contact	irritation of the eyes and Skin, nose, throat; Lassitude, dizziness nausea, vomiting,	liver injury	eyes, skin, respiratory system, CNS blood	~8.4	~0.88	1	120	0.9	6.4
xylene (mixed isomers)	100 ppm	100 ppm	Inhalation Ingestion Contact absorption	drowsiness, incoherence, anorexia, confusion, abdominal, pain, irritation of eyes skin, nose, throat, dizziness, excitement,	liver and kidney disease	CNS, liver, kidneys, skin G.I. tract blood	8.56 to 8.44	0.88 to 0.86	9 to 7	90 to 81	1.1 to 0.9	7.0 to 6.7

Appendix G

Excavation and Trenching Plan

Table of Contents

A. Purpose

The purpose of this plan is to help the site competent person comply with the requirements of 29 CFR 1926, Subpart P--Excavations, related safety issues such as heavy equipment use, the Ashland/NSP Lakefront Site Health and Safety Plan (HASP).

B. Applicability

This plan is intended to be used for all excavations and trenches. The competent person must decide specifically which sections apply and how all hazards presented by the excavation are being controlled.

B.1. Basis

B.1.a. Project HASP

The basis for this plan is the Ashland/NSP Lakefront Site Health and Safety Plan. This plan is considered to be an attachment to that plan and mandatory in the same manner as the project HASP.

B.1.b. NSPW Contractor Safety System

The NSPW Contractor Safety System also governs work on this facility and must be complied with.

B.1.c. ANSI Z 10.12

Where appropriate this procedure may also reference ANSI Z 10.12 Standards for Excavation in lieu of federal or state regulations.

B.1.d. OSHA Regulations

The primary applicable regulations governing the specific hazards addressed in this plan are 29 CFR 1926, Subpart P, applicable to excavations and trenches; and 29 CFR 1926, Subpart O, applicable to heavy equipment safety.

B.2. Conflicting Requirements

In general the intention of this plan is to comply with all of the basis requirements. In the event where this would result in a conflict (i.e., where following all of the requirements cannot be accomplished because one requirement precludes following of the other(s)) the basic hierarchy is as follows:

B.2.a. Hierarchy

1) Federal and state regulations preempt the others.

2) NSPW requirements will generally preempt Envirocon's is stricter.

3) Envirocon procedures must be followed to the extent that this does not produce a conflict with the above requirements.

B.2.b. Hierarchy Results in a Reduction of Protection

In the event that a supervisor, competent person, or employee believes that the above hierarchy will result in a reduction of employee protection, a resolution shall be considered with the appropriate client representative. If this fails to resolve the conflict, notify the Envirocon Director of Health and Safety.

C. Excavation Competent Person(s)

A competent person must be designated before any excavation or intrusive work activity begins. This plan applies regardless of whether personnel will enter a trench or an excavation. The competent person will determine the safety measures needed.

C.1. Designation and Approval

Excavation competent persons at this project must be designated on the form attached at the end of this plan.

C.2. Competent Person Responsibilities

The competent person is defined as one who is capable of identifying existing and predictable hazards in the surroundings, or working conditions which are unsanitary, hazardous, or dangerous to employees, and who has authorization to take prompt corrective measures to eliminate them.

C.2.a. Availability of Competent Person.

The competent person must be on-site during any excavation or intrusive work activity for which he is responsible.

C.2.b. Competent Person Tasks.

The competent person must also perform or be capable of performing the following tasks:

1) Application of 29 CFR 1926 Subpart P to the excavation or intrusive work activity;

2) Daily inspections of the excavation or intrusive work including an inspection after a hazard increasing event such as a thunderstorm;

3) Classifying soil at the excavation or intrusive work;

4) Determining proper protective requirements;

5) Determining the need for excavation or intrusive work de-watering operations and monitoring all de-watering activity;

6) Coordinate completion of any necessary local permits with a project engineer.

D. Soil Classification and Type

Appendix A of 29 CFR 1926 Subpart P outlines the minimum requirements for the classification of soil. Upon determining the soil type, the competent person must then determine the protection system which will be used to protect any employee or lower tier subcontractor who may enter the excavation.

D.1. Competent Person

In a designed excavation, one where a PE certified engineer has designed the sloping and protective system requirements, the competent person is responsible for ensuring that the specified sloping/protective systems are followed on a daily basis and to conduct daily inspections for unexpected hazards or changes in conditions.

Where a PE has not determined protective systems, the competent person is responsible for determining soil classification.

Only a PE or qualified geologist, or similarly qualified person shall determine soil type of "stable rock."

D.2. OSHA Soil Classifications.

The following are the soil classifications recognized by OSHA in 29 CFR 1926 Subpart P. The competent person must classify the soil based on the manual and visual tests conducted at the excavation site. OSHA's Subpart B assumes that a Type C soil unless a written classification documents another classification.

D.2.a. Requirements.

OSHA requires written documentation of soil classifications other than Type C soils.

D.2.b. Type A soil means:

1) Cohesive soils with an unconfined compressive strength of 1.5 ton per square foot (tsf) (144kPa) or greater.

2) Examples of cohesive soils are: clay, silty clay, sandy clay, clay loam and, in some cases, silty clay loam and sandy clay loam.

3) Cemented soils such as caliche and hardpan are also considered Type A. However, no soil is Type A if:

a) The soil is fissured; or

b) The soil is subject to vibration from heavy traffic, pile driving, or similar effects; or

c) The soil has been previously disturbed; or

d) The soil is part of a sloped, layered system where the layers dip into the excavation on a slope of four horizontal to one vertical (4H:1V) or greater; or

e) The material is subjected to other factors that would require it to be classified as a less stable material.

D.2.c. Type B soil means:

1) Cohesive soil with an unconfined compressive strength greater than 0.5 tsf (48 kPa) but less than 1.5 tsf (144 kPa); or

2) Granular cohesionless soils including: angular gravel (similar to crushed rock), silt, silt loam, sandy loam and, in some cases, silty clay loam and sandy clay loam.

3) Previously disturbed soils except those which would otherwise be classed by Type C soil.

4) Soil that:

a) meets the unconfined compressive strength or cementation requirements for Type A, but is fissured or subjected to vibration; or

b) Dry rock that is not stable; or

c) Material that is part of a sloped, layered system where the layers dip into the excavation on a slope less steep than four horizontal to one vertical (4H:1V), but only if the material would otherwise be classified as Type B.

D.2.d. Type C soil means:

1) Cohesive soil with an unconfined compressive strength of 0.5 tsf (48 kPa) or less; or

2) Granular soils including gravel, sand, and loamy sand; or

3) Submerged soil or soil from which water is freely seeping; or

4) Submerged rock that is not stable; or

5) Material in a sloped, layered system where the layers dip into the excavation or a slope of four horizontal to one vertical (4H:1V) or steeper.

D.2.e. Stable Rock – Refer to Soil Types

Stable Rock is not a soil classification. Stable Rock is a soil type (see the OSHA soil type discussions below). A "stable rock" determination shall be determined by a qualified person as described in D.1 above.

D.3. Soil Classification Requirements.

The competent person must be able to classify each soil and rock deposit associated with a trench or excavation as to stable rock, Type A, Type B, or Type C soil.

D.3.a. Basis of Classification.

The classification of soil type must be accomplished by at least one visual and one manual test. There are several allowable tests that can be used to determine soil type. This testing must be done by the competent person and performed prior to and during the job. Refer to Appendix A of Subpart P for manual and visual test procedures.

D.3.b. Reclassification.

If, after the soil has been classified, conditions change, the competent person is responsible for evaluating the situation and, if necessary, change the classification.

D.4. OSHA Soil Types.

D.4.a. Stable Rock.

1) A "stable rock" determination shall be determined by a qualified person as described in D.1 above.

2) Stable rock is not one of the texture classes. However, it is one of the OSHA classifications of soil.

3) Stable rock is solid mineral material which can be excavated; and the sides stand vertical and remain stable and vertical throughout construction.

4) Coral is not considered stable rock.

D.4.b. Cemented Soil.

1) Cemented soils are soils that are held together by a chemical agent such as calcium carbonate.

2) Examples of cemented soils would include caliche and hardpan. Cemented soils are classified as Type A soils with an unconfined compressive strength greater than 1.5 tsf.

D.4.c. Cohesive Soil.

1) Cohesive soils are basically fine grained soils. Cohesive soils range from clay through clay loam.

2) A cohesive soil will stand unsupported when excavated and is plastic when moist. That is, cohesive soil can be rolled into a ribbon.

3) A cohesive soil is hard to break up when it is dry.

4) Cohesive soils are classified as Type A soils with an unconfined compressive strength greater than 1.5 tsf.

D.4.d. Granular Soil.

1) Granular soils are composed of coarse grained material that has very little cohesive strength.

2) Granular soils include loamy sand, sand and gravel.

3) A soil is classified as granular if more than 65% of the grains are distinguishable with the unaided eye.

4) Granular soils, when excavated will not stand and the walls of the excavation can crumble easily.

5) CAUTION:

a) Some granular soils will exhibit cohesion when wet, but when dry will fall apart.

b) This type of soil is especially dangerous when found at a construction site. The walls of a trench appear to stand with no support, however, when they dry they could crumble and fall into the trench bottom.

6) Granular soils are classified as soil Type B or C, and may require the highest degree of protection. Type C soils would have an unconfined compressive strength of less than 0.5 tsf.

D.4.e. Granular Cohesionless.

1) Soils that range from silt through sandy loam or are composed of angular particles are said to be granular cohesionless soils.

2) These are difficult soils to work with because the group ranges from a very stable Type B to the unstable Type C soil.

3) Course angular granular soils are classified as Type B soils and have an unconfined compressive strength range from 0.5 tsf to 1.5 tsf.

D.4.f. Layered Soil System.

A layered soils system is composed of two or more distinctly different soil or rock types arranged in layers. Micaceous seams or weakened planes in rock or shale are considered layered. The layers may lay on a horizontal plane or be sloped. When they are sloped into the excavation they represent a collapse hazard to the trench wall. A slope greater than 4H:1V would classify any soil as Type C. Sloped layers less than 4H:1V would be classified as Type B soil. No layered system can be Type A soil.

E. Protective Systems

29 CFR 1926.652 requires that each employee in an excavation be protected from cave-ins by an adequate protective system unless excavations are made in stable rock or are less than five feet in depth and examination by the competent person provides no indication of potential cave-in. Additionally, whichever protective system is chosen must have the capacity to resist without failure all loads that are intended or could reasonably be applied to the system.

E.1. Design of Sloping and Benching Systems.

The slopes and configurations of sloping and benching systems must be determined by the competent person in accordance with the requirements of 29 CFR 1926(b)(1) through (b)(4) as well as 29 CFR 1926 Subpart P-Appendix B.

After the competent person has determined the soil type based on one visual and one manual test, the competent person may design the sloping and benching system for excavations that are less than 20 feet deep using the following table.

SOIL OR ROCK TYPE	EXAMPLES	MAXIMUM ALLOWABLE SLOPES HORIZONTAL TO VERTICAL FOR EXCAVATIONS LESS THAN 20 FEET DEEP *
Stable Rock	A "stable rock" determination shall be determined by a qualified person as described in D.1 above.	Vertical (90 Degrees)
Type A Cohesive	Clay, Hardpan, Silty Clay	3/4 : 1 (53 degrees)
Type B Cohesive/Granular	Silt, Unstable Rock, sandy Loam, Fissured type A	1 : 1 (45 degrees)
Type C Granular	Gravel, Submerged, Loamy, Sand	1.5 : 1 (34 degrees)

Notes:

* The design of any protective system, including benching or sloping systems, must be approved by a registered Professional Engineer (PE) for excavations deeper than 20 feet.

A "stable rock" determination shall be determined by a qualified person as described in D.1 above.

E.2. Support Systems.

E.2.a. Design of support systems, shield systems and other protective systems.

If the competent person determines that personnel will be protected from cave-ins by a protective system other than sloping and benching, the design of the support systems, shield

systems, and other protective systems be based on the conditions at the project site and data provided by an Envirocon or subcontracted registered professional engineer or from tabulated data provided by the manufacturers of the protective systems.

E.2.b. OSHA requirements.

The design of the protective system must be in accordance with the requirements of 29 CFR 1926.652(c)(1) through (c)(4) and 29 CFR 1926 Subpart P-Appendices C, D, E respectively.

E.2.c. Protection for Exceptional Conditions.

In large/deep excavations where traditional shoring and sloping are not practical, alternate protective measures may be implemented to protect personnel in the excavation.

1) Additionally, the top of the excavation must be protected with stop logs, earthen berms, or other types of protective barriers which will keep pedestrians and vehicles from approaching the edge of the excavation.

2) Approvals.

a) Any deviations from traditional protective systems must be approved by a registered Professional Engineer (PE), or the Envirocon Director of Health and Safety.

b) Such protective systems shall be documented and submitted to the client's representative.

F. Excavation Safe Work Practices

Excavation activity exposes Envirocon personnel and lower tier subcontractors to many dangers which, if not recognized, can cause death or serious injury.

F.1. Surface Hazards.

The excavation area should be inspected and any debris, structures, and surface protrusions that are located so as to create a hazard to employees shall be removed as necessary to safeguard employees. Any buildings on the site should be evaluated for structural integrity and supported if necessary.

F.2. Underground Installations/Utility Locations.

Before conducting any excavation work, the location of utility installations, such as sewer, telephone, fuel, electric, water lines, or any other underground installations that reasonably may be expected to be encountered during excavation work, shall be determined.

F.2.a. Contacting Utility Companies.

Utility companies or the state utility protection service shall be contacted at least two working days prior to excavation activities to be advised of the proposed work, and asked to establish the location of the utility underground installations prior to the start of actual excavation.

F.2.b. Protection of Locate Markers.

Envirocon personnel and sub-contractors should be careful to protect and preserve the markings of approximate locations of facilities until the markings are no longer required for safe and proper excavations.

1) If the markings of utility locations are destroyed or removed before excavation commences or is completed, the Envirocon competent person must notify the utility company or other cognizant facility personnel.

2) Envirocon equipment operators shall maintain at least 3-feet clearance between any underground utility and the cutting edge or point of powered equipment.

3) Excavating within 18 inches of a utility locate should be avoided if possible (additional distance must be added for the dimensions of the utility as well). If materials must be excavated within two feet of a utility locate line it should be hand excavated (also referred to as "potholing"). Other acceptable means of excavation may be acceptable such as vacuum excavation. Refer to 29 CFR 1926.651(b)(3), ANSI Z 10.12 paragraph 2.5.3; and the applicable state laws governing one-call excavation procedures.

F.2.c. Supporting Utilities.

While the excavation is open, underground installations shall be protected, supported or removed as necessary to safeguard employees.

F.3. Access and Egress.

Envirocon will provide a safe means of access to and egress from all excavations. The following are considered acceptable methods of entering and exiting excavations.

F.3.a. Structural Ramps

Structural ramps that are used solely by employees as a means of access or egress from excavations shall be designed by the competent person. Structural ramps used for access or egress of equipment shall be designed by a competent person qualified in structural design or structural engineering, and shall be constructed in accordance with the design.

Structural members used for ramps and runways shall be of uniform thickness. Cleats or other appropriate means used to connect runway structural members shall be attached to the bottom of the runway or shall be attached in a manner to prevent tripping. Structural ramps used in lieu of steps shall be provided with cleats or other surface treatments on the top surface to prevent slipping.

F.3.b. Ladders and Stairways.

Ladders or stairways constructed in accordance with OSHA standards may also be used.

F.3.c. Trenches.

A stairway, ladder, ramp or other safe means of egress shall be located in trench excavations that are 4 feet or more in depth so as to require no more than 25 feet of lateral travel for employees. Any ramp used for employee egress must be sloped at an angle which would allow employees to walk upright out of the excavation.

F.4. Exposure to Vehicular Traffic.

Envirocon and subcontract personnel who may be exposed to vehicular traffic both on projects and public highways shall be provided with and shall wear warning vests or other suitable garments marked with or made of reflectorized or high-visibility material.

F.5. Exposure to Falling Loads.

No Envirocon employee or lower tier subcontractor shall be permitted underneath loads handled by lifting or digging equipment. Personnel must stand away from any vehicle being loaded or unloaded to avoid being struck by any spillage or falling materials. Truck drivers may remain in the cabs of vehicles being loaded or unloaded when the vehicles are equipped with over-cab protective structures, in accordance with 29 CFR 1926.601(b)(6), to provide adequate protection for the operator from falling objects during loading and unloading operations.

F.6. Warning System for Mobile Equipment.

When heavy equipment and trucks operate adjacent to an excavation or when such equipment is required to approach the edge of an excavation, and the operator does not have a clear and direct view of the edge of the excavation, a warning system shall be utilized such as barricades, hand or mechanical signals or stop logs. If possible, the approach grade should be away from the excavation.

F.7. Hazardous Atmospheres.

Because there is a likelihood that excavation activity at this site involve hazardous materials, the Envirocon competent person must ensure that acceptable atmospheric conditions exist.

F.7.a. Airborne Hazards Associated With This Project Include:

1) Radioactive Materials
2) Organic Hydrocarbons

F.7.b. Air Monitoring.

Air monitoring shall be conducted in accordance with the Envirocon project HASP.

1) The Envirocon competent person shall coordinate with the project health and safety officer to ensure that excavation monitoring is performed in accordance with the site-specific monitoring requirements.

2) Typically this monitoring will require direct reading atmospheric monitoring to determine entry requirements and TWA personal exposure monitoring to confirm direct reading results.

3) When atmospheric monitoring is required, the site safety officer must check the atmosphere for the following in the order shown, or as directed by the site-specific monitoring requirements:

a) Oxygen Content

i) acceptable conditions: 21% (i.e., ambient oxygen conditions)

ii) Conditions other than normal/ambient shall be evaluated to determine the reason for the difference. Controls shall be established accordingly.

iii) In any case where oxygen is 19.5% or less, it shall be considered IDLH (Immediately Dangerous to Life or Health in accordance with the requirements for respiratory protection).

b) Flammable Conditions

i) acceptable conditions: ambient (i.e., no deflection above normal background)

ii) Conditions other than ambient shall be evaluated to determine the potential source of flammable vapors and appropriate controls established.

iii) In any case where flammable vapors exceed 10% LEL work shall be stopped until appropriate controls can be established.

c) Toxic Atmospheres: Refer to site monitoring procedures.

F.7.c. Confined Space Conditions.

Any excavation or trench deeper than four (4) feet meets the definition of a confined space if a hazardous atmosphere exists or could reasonably be expected to exist, such as in excavations where contaminants of concern are recognized as being present. . Excavations over 4 feet in depth should be considered as confined spaces until all of the potential, associated hazards have been ruled out by a competent person.

F.7.d. Changing Conditions.

Based on the competent person's visual observation of the excavation and the soil and/or fill material, atmospheric monitoring may not be necessary. However, if conditions change, the competent person must re-evaluate whether atmospheric monitoring is required.

F.7.e. Ventilation

Adequate precautions shall be taken, for example providing ventilation to prevent employee exposure to harmful atmospheres. When controls are used that are intended to reduce the level of atmospheric contaminants to acceptable levels, direct reading air monitoring shall be conducted periodically to ensure that the atmosphere remains safe.

F.7.f. Emergency Rescue Equipment

Emergency rescue equipment, such as self-contained breathing apparatus (SCBA), a safety harness and line, or a basket stretcher, shall be readily available where hazardous atmospheric conditions exist or may reasonably be expected to develop during work in an excavation. This equipment shall be kept close to the excavation for use in an emergency.

F.8. Water Accumulation.

Employees shall not work in excavations in which there is accumulated water, or in excavations in which water is accumulating, unless adequate precautions have been taken to protect employees against the hazards posed by water accumulation.

F.8.a. General.

The precautions necessary to protect employees adequately vary with each situation, but could include special support or shield systems to protect from cave-ins, water removal to control the level of accumulating water, or use of a safety harness and lifeline.

F.8.b. Monitoring.

If water is controlled or prevented from accumulating by the use of water removal equipment, the water removal equipment and operations shall be monitored by a competent person to ensure proper operation.

F.8.c. Surface Water Controls.

If excavation work interrupts the natural drainage of surface water (such as streams); diversion ditches, dikes, or other suitable means shall be used to prevent surface water from entering the excavation and to provide adequate drainage of the area adjacent to the excavation.

F.8.d. Heavy Rain Inspections.

Excavations must be inspected after heavy rain that could impact on the excavation. Inspections are discussed below.

F.9. Stability of Adjacent Structures.

Where the stability of adjoining buildings, walls, or other structures is endangered by excavation operations, support systems such as shoring, bracing, or underpinning shall be provided to ensure the stability of such structures for the protection of employees.

F.9.a. Excavation below the level of the base or footing of foundations.

Excavation below the level of the base or footing of any foundation or retaining wall that could be reasonably expected to pose a hazard to employees shall not be permitted except when:

1) A registered professional engineer has approved the determination that such excavation work will not pose a hazard to employees.

2) A support system, such as underpinning, designed by a registered professional engineer is provided to ensure the safety of employees and the stability of the structure; or

3) The excavation is in stable rock; or

4) A registered professional engineer has approved the determination that the structure is sufficiently removed from the excavation so as to be unaffected by the excavation activity; or

5) If a support system has been put in place to stabilize an adjacent structure, it must be inspected for movement and structural integrity daily by the competent person.

F.9.b. Undermining Structures.

Sidewalks, pavements, and other structures shall not be undermined unless a support system or another method of protection is provided to protect employees from the possible collapse of such structures.

F.10. Fall Protection

Where employees or equipment are required or permitted to cross over excavations; walkways, or bridges with standard guardrails shall be provided.

F.11. Edges

F.11.a. Fall Protection

1) Walkways shall be provided where employees or equipment are required or permitted to cross over excavations. Guardrails, which comply with 1926.502(b), shall be provided where walkways are 6 feet (1.8 m) or more above lower levels.

2) Keep people and equipment away from excavation edges.

a) When mobile equipment is operated adjacent to an excavation, or when such equipment is required to approach the edge of an excavation, and the operator does not have a clear and direct view of the edge of the excavation, a warning system shall be utilized such as barricades, hand or mechanical signals, or stop logs. If possible, the grade should be away from the excavation.

b) Adequate barrier physical protection shall be provided at all remotely located excavations.

c) All wells, pits, shafts, etc., shall be barricaded or covered.

d) Upon completion of exploration and other similar operations, temporary wells, pits, shafts, etc., shall be backfilled.

3) The competent person must determine a safe distance for personnel approaching the edges of excavations based on a careful inspection of the materials and conditions of the materials forming the edge. As a general rule these distances should not exceed the following:

a) For edges along 6 foot vertical drops or less (including benched excavations):

i) Keep personnel at least 3 feet away from the edge of the excavation.

ii) Where there are cracks, fissures, or subsidence depressions indicating and unstable edge keep back at least 3 feet from the crack, fissure, or depression.

b) For edges along vertical drops greater than 6 feet where soils are cohesive:

i) Keep personnel at least 3 feet away from the edge of the excavation.

ii) Where there are cracks, fissures, or subsidence depressions indicating and unstable edge keep back at least 3 feet from the crack, fissure, or depression.

c) For edges along vertical drops greater than 6 feet where soils are non-cohesive:

i) Keep personnel at least 6 feet away from the edge of the excavation.

ii) Where there are cracks, fissures, or subsidence depressions indicating and unstable edge keep back at least 6 feet from the crack, fissure, or depression.

F.11.b. Highwalls

1) Employees shall be kept out of the areas below highwalls or excavation faces that are not stable rock, benched or sloped. As a general rule, employees on foot shall keep clear for a distance greater than or equal to the height of the wall face.

2) Equipment operating below highwalls that are not stable rock, benched or sloped shall keep cabs out from under overhanging cuts.

F.11.c. Protection of Employees From Loose Rock or Soil.

Adequate protection shall be provided to protect employees from loose rock or soil that could pose a hazard by falling or rolling from an excavation face.

1) Protective Systems. Such protection shall consist of scaling to remove loose material; installation of protective barricades at intervals as necessary on the excavation face to stop and contain falling material; or other means that provide equivalent protection.

2) Spoils and Other Materials Near Excavation Edges.

a) Employees shall be protected from excavated or other materials or equipment that could pose a hazard by falling or rolling into excavations.

b) Protection shall be provided by placing and keeping such materials or equipment at least 2 feet from the edge of excavations, or by the use of retaining devices that are sufficient to prevent materials or equipment from falling or rolling into excavations, or by a combination of both if necessary.

c) In accordance with the site HASP, in instances in which overpressure (the weight of nearby construction equipment, materials or existing buildings) a distance of 4 feet, measured from the edge of the cut to the bottom of the sloughing pile, shall be used.

F.12. Inspections.

Excavations, the adjacent areas, and protective systems shall be inspected by a competent person for evidence of a situation that could result in possible cave-ins, indications of failure of protective systems, hazardous atmospheres, or other hazardous conditions.

F.12.a. Documentation.

All inspections shall be documented by the competent person. This may be documented in the site safety log or use the attached inspection form.

F.12.b. Daily/shift Inspections.

An inspection shall be conducted by the competent person prior to the start of work and as needed throughout the shift.

F.12.c. Stop Work Conditions.

Where the competent person finds evidence of a situation that could result in a possible cave-in, indications of failure of protective systems, hazardous atmospheres, or other hazardous conditions, exposed employees shall be removed from the hazardous area until the necessary precautions have been taken to ensure their safety.

F.12.d. Post-event Inspections.

Any event which potentially threatens the stability of protective systems requires an inspection by a competent person.

1) Heavy rain that could impact on the excavation is a common example.

2) Snow, snow melt, earthquakes, or use of explosives nearby would be other examples.

F.13. Protection of the Public.

Since open excavations are often an attractive nuisance to the public, adequate barrier for physical protection shall be provided at all excavations. Remotely located excavations may require special protection including, but not limited to, highly visible snow fence, concrete barriers, chain link fence and flashing warning light. All wells, pits, shafts, etc., shall be barricaded or covered. Upon completion of exploration and similar operations, temporary wells, pits, shafts, etc., shall be covered or backfilled.

F.14. Stop work conditions.

Excavations often occur in areas where articles, materials, or conditions may arise or be discovered in the process of excavating. All personnel must be aware of this potential and immediately stop work and report the circumstances in accordance with incident reporting procedures when these conditions arise.

F.14.a. New, previously unknown, or unexpected potential hazards such as:

1) buried drums, cylinders, or hazardous materials containers,

2) possible unexploded ordinance,

3) unusual soil conditions (e.g., previously disturbed soils, soils with unusual odors, soils with unusual coloration, soils which appear to be backfill, etc.), or

4) floating contaminants (e.g., oil, chemicals, or sheens on water).

F.14.b. Environmental incidents such as:

1) oil or chemical spills,

2) dead or injured wildlife, or

3) disturbance of protected habitats.

F.14.c. Objects of potential cultural or historical importance such as:

1) bones,

2) buried coins or money,

3) arrow heads,

4) possible burial sites, or

5) finding articles of any potential cultural significance.

F.14.d. "Time-out" for Safety Authority.

Envirocon personnel are required to take personal responsibility for their safety, the safety of their buddy, and the safety of all others on/near the site. The "time-out" for safety is Envirocon's authorization to employees to take a moment to correct an unsafe condition, or contact their supervisor for clarification if they encounter a condition that they believe may be potentially hazardous.

G. Excavation Inspection Checklist

The following checklist shall serve as a partial guideline for the competent person inspections.

Yes/Sat	No/Unsat	N/A	Competent Person: / Date: / Time: / Excavation Location: / Scope of Work: / Personnel will enter this excavation? ☐ yes ☐ no **Inspection items**	**Notes/Corrections**
			Wisconsin one Call has been notified? Diggers Hotline: Wisconsin's One-Call Center CALL 811 or (800) 242-8511	
			Does this job require special training? Describe	
			• personnel have received necessary training.	
			What is the soil classification? _____	
			• Will the soil be classified based on its properties and site conditions? • If the answer is "NO" soil should be classified type C. • If the answer is yes proceed with the remaining soil classification item below.	
			• Based on visual observation, which best describes the soil in this excavation? ☐ Stable Rock; ☐ Cemented Soil; ☐ Cohesive Soil; ☐ Granular Soil ☐ Granular Cohesionless; ☐ Layered System	
			• Based on visual observation, what is the moisture condition of the soil? ☐ Dry Soil; ☐ Moist Soil; ☐ Wet Soil; ☐ Saturated Soil	
			• Pocket penetrometer readings (if available) in tsf (tons per square foot): ☐ > 1.5 tsf (type A); ☐ 0.5 – 1.5 tsf (type B); ☐ < 0.5 tsf (type C)	
			• What manual test was used to determine the soil type? ☐ plasticity; ☐ dry strength; ☐ thumb penetration; ☐ other	
			• Based on at least one manual test, what classification is the soil in this excavation? ☐ Stable Rock; ☐ Type A Soil; ☐ Type B Soil; ☐ Type C	
			Are slopes, benches, or other protective systems as required for trenches?	
			• Shoring / protective systems have been designed by a registered professional engineer or accompanied by tabulated data from the manufacturer?	
			• Shoring and other protective system checked/measured each day to detect movement and possible failure?	
			• Are stock pile slopes showing signs of instability and are people and equipment protected from such conditions?	
			• Are people and equipment adequately protected from, or kept away from excavation cuts that may slough or cave in non-trench excavations?	
			Electrical Safety	

TITLE: Excavation and Trenching Safety Plan and Inspection Form	Reviewed and Approved By: David Hardy, CHST, PHSM

Yes/Sat	No/Unsat	N/A	Competent Person: / Date: / Time: / Excavation Location: / Scope of Work: / Personnel will enter this excavation? ☐ yes ☐ no **Inspection items**	**Notes/Corrections**
			• Are all electrical devices grounded and/or GFCI protected?	
			• Temporary electrical cords are rated (e.g. JS, S, JSO, SO, JSOW, SOW)?	
			Surface Encumbrances and Adjoining Structures	
			• Surface encumbrances located so as to create a hazard to employees have been removed or supported, as necessary, to safeguard employees?	
			• Are support systems such as shoring, bracing, or underpinning provided to ensure stability of adjoining structures (i.e., buildings, walls) endangered by excavation activities?	
			• Support system(s) have been designed by a registered professional engineer?	
			Utilities	
			• OVERHEAD utilities that may pose a hazard have been identified and marked? (NOTE: Marking overhead hazards on the ground may be more effective than elevated markers!)	
			• Have utility companies been contacted and advised of proposed work?	
			• Have the estimated locations of all underground installations been identified and marked prior to excavation?	
			• If underground installations are exposed, are they protected, supported or removed while excavation is open?	
			Access and Egress	
			• Are safe stairways, ladders, or ramps provided for worker access/egress (must be within 25' of travel for personnel in trenches)?	
			• Are structural ramps that are used for access and egress of equipment and/or personnel designed by a competent person qualified in structural design and constructed in accordance with the design?	
			Is the equipment and vehicular traffic safe?	
			• Are traffic patterns and speeds safe?	
			• Are warning systems utilized when mobile equipment is operated adjacent to or at the edge of an excavation? If yes, which type is being used? ☐ Hand Signals; ☐ Stop Logs; ☐ Earthen Berm; ☐ Other	
			• Are personnel exposed to public or project vehicular traffic wearing reflectorized or high visibility vests?	

Appendix G

Foth | Envirocon Joint Venture

Ashland/NSP Lakefront Excavation Trenching Plan

TITLE: Excavation and Trenching Safety Plan and Inspection Form	Reviewed and Approved By: David Hardy, CHST, PHSM

Yes/Sat	No/Unsat	N/A	Competent Person: / Date: / Time: / Excavation Location: / Scope of Work: / Personnel will enter this excavation? ☐ yes ☐ no **Inspection items**	**Notes/Corrections**
			Overhead Hazards	
			• Employees are not exposed to overhead loads handled by lifting or digging equipment?	
			• Are employees protected from rock falls and sloughing soils?	
			• Are employees protected from excavated or other material and equipment by placing this material a minimum of two (2) feet from the edge of excavations or by the use of retaining devices?	
			Is there a potential for hazardous atmospheres? Or, is this excavation deeper than 4-feet and considered a confined space?	
			• Confined Space Permit is appropriate?	
			• Are atmospheric hazards adequately tested/controlled? Attach or reference necessary monitoring results data sheets.	
			• Is emergency rescue equipment such as SCBA, safety harness and line, or basket stretcher readily available and attended when hazardous atmospheric conditions exist?	
			Water Accumulation Hazards	
			• Has water accumulation been factored into the soil classification?	
			• Is water being controlled or prevented from accumulating in excavation by the use of water removal equipment?	
			• Is water control equipment operation being monitored by a competent person?	
			Slips, Trips, Falls	
			• Are standard guardrails provided on walkways/bridges that cross excavations?	
			• Are all remotely located excavations adequately barricaded or covered?	
			• Are rope grabs or footing controls provided for steep/slippery slopes?	
			• Housekeeping is adequate?	
			Other notes:	

Appendix G

Foth | Envirocon Joint Venture

Ashland/NSP Lakefront Excavation Trenching Plan

TITLE: Excavation and Trenching Safety Plan and Inspection Form	Reviewed and Approved By: David Hardy, CHST, PHSM

Yes/Sat	No/Unsat	N/A	Competent Person:	Date: Time:	Notes/Corrections
			Excavation Location: Scope of Work: Personnel will enter this excavation? ☐ yes ☐ no		
			Inspection items		

Name of Competent Person:

Verification Excavation is Safe for Activities and Conditions and Controls Noted: ☐ yes

Signature:

Appendix H

Confined Space Plan

Appendix H	
Foth | Envirocon Joint Venture	**Ashland/NSP Lakefront Confined Space Entry Plan**
TITLE: **Confined Space Entry Plan**	Reviewed and Approved By: David Hardy, CHST, PHSM

Table of Contents

A. Purpose / Scope

The purpose of this program is to establish a minimum compliance program for Foth Infrastructure & Environment/Envirocon Joint Venture (FE JV) personnel to comply with OSHA's Confined Space Standard (29 CFR 1910.146).

In most confined space entry situations, FE JV personnel will be entering the confined spaces "host employer" NSPW (see 29 CFR 1910.146(c)(8)). In such cases, it is FE JV's intention to meet and/or exceed the requirements of NSPW Contractor Safety System as well as the OSHA Confined Space Entry Standard. With regard to permit forms, postings, labels, logs, and other administrative processes, FE JV will defer to NSPW forms and processes provided they comply with Envirocon's program and the OSHA standard(s).

Regardless of the of the host facility procedures, FE JV will designate a confined space supervisor for all confined space entries. This supervisor must be familiar with the host facility requirements as well as Envirocon's procedures; and ensure that the process practiced on the job site meets or exceed the requirements of both.

B. Reference Documents

- Federal OSHA Confined Space Standard 29 CFR 1910.146.
- NIOSH Criteria Document "Working in Confined Spaces" Dec. 1979
- American Petroleum Institute Publications 2217, 2217A and 2015.
- NSPW Contractor Safety System

C. Definitions

1. Atmosphere

Generic term for gases, vapors, mists, fumes, and dusts within a confined space.

2. Atmosphere Testing/Air Monitoring

The use of a combustible gas/oxygen meter and/or a gas-specific instrument to monitor the atmosphere inside a confined space.

3. Attendant

Attendant as defined in OSHA 29 CFR 1910.146, means an individual stationed outside the permit-required confined space who is trained as required by this standard and who monitors the authorized entrance inside the permit-required confined space. This person does not have duties that will take him/her away from the confined space while workers are inside.

4. Confined Space

A space with one or more of the following traits:

a. Limited openings for entry and exit

b. Limited natural ventilation

c. Toxic or oxygen-deficient atmospheres

d. Potential for engulfment or entrapment

e. An area that is not designed for continuous occupancy

f. An excavation deeper than 4-feet

Examples are storage tanks, underground sumps, pipelines, pits, trenches, tunnels, ship holds, etc.

5. Confined Space Entry Permit

a. A NSPW Contractor Safety System form which needs to be filled out prior to any confined space entry. Complete use of the form will insure that all health and safety considerations have been addressed prior to entry.

b. This form is signed by the Confined Space Supervisor, attendant, and authorized entrants and acts as a permit for the entry.

c. The second side of the form contains a section for recording air monitoring and equipment calibration data (see Section 28, Forms).

d. This permit must be saved for 1 year.

6. Downgraded Space

Confined spaces may be downgraded to a non-permit space permanently or temporarily using one of the following means.

a. (c)(7) downgrade to non-permit status

   This is a permanent downgrade by reclassification of a confined space previously classified as a permit required confined space. This downgrade is accomplished in accordance with 29 CFR 1910.146(c)(7).

b. (c)(5) downgrade space

   A confined space which has been downgraded to a non-permit status based on the requirements of 29 CFR 1910.146(c)(5).

   FE JV personnel will only downgrade a space under this rule on a temporary basis for a certain period of time. This downgrade must be documented in accordance with the host facility requirements OR by noting the downgrade status on an issued

confined space entry permit. (e.g., under the rescue provisions of the permit indicate the use of (c)(5) alternate procedures.

7. Engulfment

The surrounding and effective capture of a person by a liquid or flowable solid substance with sufficient force to cause death by strangulation, constriction, or crushing.

8. Entry

The action by which a person passes through an opening into a permit-required confined space. Entry includes ensuing work activities in that space and is considered to have occurred as soon as any part of the entrant's body breaks the plane of an opening into the space.

9. Entry Supervisor

The person (such as the employer, foreman, Project Manager, etc.) responsible for determining if acceptable entry conditions are present at a permit space where entry is planned, for authorizing entry and overseeing entry operations, and for terminating entry as required by this section.

10. Fall Protection

Equipment and procedures utilized to prevent falls while entering and exiting a confined space.

11. Hot Work

Any work being performed that presents an ignition or heat source. Examples are welding, grinding, burning, chop saw, abrasive disk usage, chipping, etc.

12. Inerting

a. The process of purging the atmosphere of a space with an inert gas (one which will not support combustion) to eliminate the potential for fire or explosion.

b. The typical gas used will be either carbon dioxide or nitrogen.

c. Inerting does not remove the source of flammable vapor (i.e., flammable liquids), but instead removes the oxygen/flammable vapor **above the liquid.**

13. Intrinsically Safe/Explosion Proof

a. Electrical equipment which does not present the potential for electrical spark and/or which is designed and constructed to contain any fire or explosion inside the unit preventing propagation of fire back into the general environment. This equipment has been certified as safe for use in flammable atmospheres.

b. The majority of equipment is certified by Underwriter Laboratories (UL) or Factory Mutual (FM).

c. At a minimum, equipment must be rated as Class 1, Division 1 for use around flammable vapors.

d. In addition, the equipment must be rated for the group type of atmosphere present. See Atmosphere Group definitions.

e. At a minimum, all electrical equipment taken into a space containing (or previously containing) flammable liquids or vapors (in excess of 10% LEL) will be certified by the manufacturer for that purpose.

14. Isolation

The act of ensuring that the space cannot be accidentally refilled with product and/or re-energized electrically or mechanically while personnel is inside.

15. Local Exhaust Ventilation

The use of an exhaust system, at the point of contaminant generation to capture generated contaminants and keep them from dispersing into the overall area. Discharge from this system must be directed to a safe location. Note: some discharge airborne contaminants (i.e., asbestos, PCBs, lead) and will require HEPA filtration.

16. Lockout

a. The act of physically locking out electrical, hydraulic, or pneumatic controls and/or mechanical linkage to ensure isolation.

b. Typically performed by lock and key or the physical removal of key components that make it impossible for a system to be restarted while personnel are working on or inside the system.

17. Mechanical Ventilation

A method of providing dilution ventilation into a confined space. Typically provided by electrically powered or air-driven blowers.

18. Natural (Gravity) Ventilation

Ventilation provided to a space by nonmechanical means. Air diffusing into a space opening (without aid of blowers or fans) is considered natural ventilation. This is **not** an effective method for ensuring the safety of personnel and/or reducing the flammability potential inside the confined space.

19. Non-Permit Confined Space

"Non-permit confined space" means a confined space that does not contain or, with respect to atmospheric hazards, have the potential to contain any hazard capable of causing death or serious physical harm.

20. Oxygen Deficiency

An atmosphere where oxygen concentration is less than 19.5% by volume. State and federal safety regulations require that personnel wear air-supplied respirators in oxygen-deficient atmospheres.

21. Oxygen Enriched

An atmosphere where oxygen concentration is greater than 23.5% by volume. Fire and explosion potentials are increased greatly.

22. Permit-required confined space (permit space)

A permit space means a confined space that has one or more of the following characteristics:

a. Contains or has a potential to contain a hazardous atmosphere;

b. Contains a material that has the potential for engulfing an entrant;

c. Has an internal configuration such that an entrant could be trapped or asphyxiated by inwardly converging walls or by a floor which slopes downward and tapers to a smaller cross-section; or

d. Contains any other recognized serious safety or health hazard.

23. Rescue Person

a. A rescue team will be required for all permit-required confined space entries.

b. A person trained in accordance with the requirements of 29 CFR 1910.146 for the purpose of conducting rescue.

24. Retrieval Equipment

a. Mechanical hoist equipment designed to raise and lower personnel from a space. This equipment is attached to a tripod or other supporting structure which is capable of being a support platform for other fall protection equipment.

b. All equipment used for raising or lowering personnel will be rated for such operations by the manufacturer.

25. Saddle Vent

A piece of equipment that allows a ventilation duct to be placed in a manhole and still allow personnel to enter/exit without the duct being removed. This allows continuous ventilation inside the space.

26. Unknown Hazard

A space where the hazard potential is unknown. Air monitoring from outside the space is unable to determine if all areas inside are free of hazard. In these cases, personnel will consider the space high hazard.

27. Zero Mechanical State (ZMS)

The point where all power sources, that can produce a hazard to an employee, have been neutralized. This includes all pneumatic, electrical, and mechanical components.

D. Host Facility Requirements

The host facility requirements are documented in the OSHA standard beginning at 29 CFR 1910.146(c)(8).

"When an employer (host employer) arranges to have employees of another employer (contractor) perform work that involves permit space entry, the host employer shall:

- Inform the contractor that the workplace contains permit spaces and that permit space entry is allowed only through compliance with a permit space program meeting the requirements of this section;
- Apprise the contractor of the elements, including the hazards identified and the host employer's experience with the space, that make the space in question a permit space;
- Apprise the contractor of any precautions or procedures that the host employer has implemented for the protection of employees in or near permit spaces where contractor personnel will be working;
- Coordinate entry operations with the contractor, when both host employer personnel and contractor personnel will be working in or near permit spaces, as required by paragraph (d)(11) of the standard; and
- Debrief the contractor at the conclusion of the entry operations regarding the permit space program followed and regarding any hazards confronted or created in permit spaces during entry operations.

E. Training

A FE JV Competent Person will provide training to all personnel whose duties involve entry, supervision, or support duties for confined space entry.

1. Training will be provided:

a. Before the employee is first assigned duties;

b. Before there is a change in assigned duties (this includes in particular a change in host employer confined space entry program);

c. Whenever there is a change in permit space operations that presents a hazard that the employee has not been trained in;

d. Whenever there are deviations from the permit space entry procedures or inadequacies in the employee's knowledge.

2. Contents

FE JV 's training will contain the following:

a. Respirator use (job specific);

b. 29 CFR 1910.146;

c. Envirocon's Confined Space Policy;

d. Permit conditions at jobsite;

e. Use of Ventilation System at jobsite;

f. Atmospheric sampling and test devices:

g. Combustible Gas Indicator; and

h. Use of a PID.

i. Use of rescue and support equipment;

j. Emergency rescue procedures/practice;

k. Duties of entrants

l. Duties of attendants

m. Duties of supervisors

n. Required personal protective equipment; and

o. Communication systems

3. Rescue Training

Rescue teams will receive special additional training in accordance with the standard, and shall be certified accordingly.

4. Site-specific Training

In addition to the above listed training, employees shall also receive a site-specific training in the applicable host-employer's confined space entry program requirements for the work tasks to be performed on that facility.

5. Certification

Each employee will be issued a certificate upon completion of this training. The certificate will contain the following information:

a. Name of employee trained;

b. Date of training; and

c. Signature of person who conducted the training.

F. Potential Hazards

The following represent the general hazards that can be expected in the variety of confined space jobs FE JV personnel have or will be exposed to. Each hazard must be assumed until proved otherwise:

1. Atmosphere

a. Insufficient or enriched oxygen.

b. Toxic dusts, mists, fumes, smoke, vapor, and gas.

c. Flammable and explosive gases, liquids, vapors, and dusts.

2. Access

a. Inadequate access opening for entry/egress and internal obstructions hampering movement.

b. Inadequate illumination.

c. Slippery surfaces including ladder rungs, baffles, and tank floors.

3. Mechanical

a. Start up of agitators, tumblers, crushers, mixing blades, screw conveyors, saws, etc.

b. Opening of feed lines which introduce corrosives, heated or gaseous substances such as steam, water, blast furnace gas, or other substances hazardous to health.

4. Engulfment

a. Avalanche of materials or falling objects.

b. Pressurized lines containing hydraulic oil, gas, or other fluids.

5. Electrical

Electrical shock or electrocution from plug-in lights, tools, or other portable equipment.

6. Physical

a. Temperature extremes.

b. Naturally occurring radioactive materials (NORM).

c. Bites from snakes, spiders, insects, and/or rodents.

7. Chemical

a. Contact with contaminated soil or water

G. FE JV Procedures

Failure to follow this policy will be considered a serious violation of FE JV safety policy and will result in disciplinary action.

1. NSPW Facility Procedure

Follow all NSPW procedures at a minimum. Where FE JV procedures are more protective, follow FE JV procedures. Where FE JV procedures are more protective, and following the FE JV procedures would result in a conflict with the host facility procedures, notify your supervisor immediately and do not proceed with entry until a FE JV CIH or CSP has resolved the conflict.

2. Training

a. Every person tasked with working in or providing support for confined space entries shall have training in the hazards and correct procedures before initial entry into confined spaces.

b. Project Managers are responsible for ensuring that all personnel entering a space are thoroughly trained in this procedure. Special emphasis must be placed on ensuring that personnel can perform rescue operations efficiently.

3. Classification

The host facility will have classified their confined spaces in accordance with their procedures and program. The designated FE JV safety competent person (e.g., site safety officer) shall independently re-assess client postings prior to allowing FE JV personnel to enter a potential confined space.

a. A confined space entry decision must be based upon the results of air monitoring and knowledge of chemical properties (odor thresholds and other warning properties) and the limitations or respiratory protection (cartridge maximum allowable concentrations and breakthrough times).

b. Lack of knowledge concerning the airborne concentrations of contaminants or the type of contaminant present will be reason to classify the space as most hazardous.

c. OSHA stipulates that a confined space is categorized as permit or non-permit required. **FE JV considers all confined spaces as permit required, until a hazard evaluation form has been completed to downgrade the space to a non-permit required space.**

d. In most cases it is preferable to downgrade spaces temporarily using the (c)(5) rules. Even though the space is technically a non-permit space, a confined space permit shall be used to document the applicable period of temporary downgrade, to document that the downgrade conditions have been tested and met, and to control entry into the space.

4. No Entry Conditions

Envirocon's policy forbids entry into confined spaces under any one of the following conditions:

a. LEL > 10%; or

b. Oxygen < 19.5% or > 23.5% (no entry into inerted or enriched spaces); or

c. Unable to monitor space prior to entry; or

d. Entry sizes that require PPE removal; or

e. Spacial configurations that prevent rescue.

5. IDLH Atmospheres

a. Oxygen Deficient Atmospheres

Any oxygen concentration less than 19.5% by volume could be considered IDLH because:

(a) Some LEL meters will not function below 19.5%, and therefore will not give accurate readings.

(b) In the event of airline failure, individual would have limited time to accomplish self-rescue.

FE JV personnel are not to enter (the whole body passing through the Plane of Entry) oxygen IDLH atmospheres, including tanks that have deliberately been inerted by removing oxygen for the purpose of making them safe for hot work, **until oxygen levels are brought up to at least 19.5%.** Note that 19.5% is safe for entry, but would still require Level B respiratory protection.

b. Toxic Gas or Vapor Atmospheres

Decisions to enter a space deemed IDLH (referring to a toxic gas or vapor) must be made in conjunction with the Envirocon Industrial Hygienist or Corporate Health and Safety Director.

As a general rule, Envirocon policy will be to avoid entry in these conditions. However, many chemicals have extremely low IDLH levels that cannot feasibly be lowered by ventilation.

Note that an IDLH atmosphere resulting from a toxic gas or vapor does not necessarily offer the same immediate hazard as extreme oxygen deficiency

6. Ventilation

a. The need for ventilation will be dependent upon LEL/PEL levels.

b. All ventilation and pumping equipment will be bonded and grounded.

c. Mechanical ventilation will be initiated prior to entry in any spaces to dilute or maintain flammable levels at 10% LEL or less or reduce purge/dilute toxic atmospheres below IDLH.

7. Entry Requirements

All entries into spaces with known or potentially hazardous conditions will be directly supervised by a FE JV Manager completely familiar with this procedure. This Manager will be in attendance whenever personnel are inside the space and is responsible for enforcing all the provisions contained in this procedure, host facility requirements, and 29 CFR 1910.146.

a. Entry Opening Size

An 18- to 24-inch diameter opening will be the minimum size for the majority of personnel.

In no case will it be acceptable that personnel remove protective equipment (with the intent on donning it once inside) to facilitate entry into a small opening.

And in no case will a person be allowed to enter if, by virtue of their size, they are the only employee small enough to enter.

b. Fire and Explosion Prevention

No matches, lighters, items capable of producing a spark or flame, non-approved radios or monitoring equipment, flashlights, lanterns, etc., shall be used in or within 25 feet of a confined space containing or potentially containing flammable vapors or gases.

c. Termination of Operation

Entry operations will be terminated (or not started) in the event of failure of:

Air monitoring equipment

PPE including respiratory protection; and

Rescue equipment.

Operations will not resume until all repaired equipment is repaired or replaced.

d. Any deviations from this procedure will require the approval of the Corporate Safety Manager.

H. Entry Procedure

1. Confined Space Hazard Identification

a. Before employees are permitted to enter a confined space, the hazards must be identified and evaluated.

b. The severity of hazards will be determined in order to classify the confined space entry as a high hazard or low hazard entry.

c. Each space will be monitored prior to entry.

d. A space will always be classified as worse case if air monitoring data is not available.

2. Required Level of Protection

Will follow standard 29 CFR 1910.120 guidelines and the Ashland/NSP Lakefront Site HASP.

a. Classification of contaminant environment regarding chemical properties and routes of entry, IDLH, and cartridge limitations. .

b. Level C or D respiratory protection will require supportive air monitoring documentation.

3. Confined Space Entry Permit System

Where required, FE JV will use the established host facility permit system. When allowed by NSPW, FE JV will use its own permit forms.

a. FE JV permits shall be used for the following:

Authorizing entry into a permit-required confined space.

Temporarily (for a specified period of time) downgrading a space under the 29 CFR 1910.146(c)(5) rules.

b. A FE JV Entry Permit shall be completed prior to entry into any confined space.

c. This permit must be signed by the responsible FE JV Supervisor.

d. The permit shall be available at the worksite location of the confined space and shall be dated and valid for one shift only. Contact Corporate Health and Safety for additional copies.

e. All questions on the form must be filled out.

f. When answering the questions on side 1 of the permit:

In some cases, a "n/a" is appropriate and would indicate that the specific item does not apply to the situation. Use caution when deciding that the item is "n/a"; and

Special attention must be directed to any question where the answer is "no". A "no" answer may indicate that adequate precautions have not been taken or that a hazard possibly continues to exist.

g. The Entry Permit cannot be completed until all pre-entry testing and sampling have been accomplished. **The permit must be filled out at the site under actual working conditions.**

h. The project Safety Officer, as named on the entry permit, shall evaluate, plan, and implement the procedures necessary to safeguard the personnel assigned to the job. He/she has responsibility to evaluate/approve any "n/a" or "no" answers on the permit.

i. OSHA 29 CFR 1910.146 requires that all permits be saved for 1 year.

4. Required Personnel

a. Entry Supervisor

FE JV Project Manager is responsible for evaluation of the confined space and authorization of personnel to enter. Duties include:

Enforcing the confined space procedures and permit requirements;

Ensuring Confined Space Entry Permits are posted and that a confined space authorized Attendant is present during all entry activities;

Ensuring that all personnel have received proper training in confined space entry procedures and proper use of safety retrieval equipment in an emergency;

Ensuring that all necessary safety retrieval equipment is on site, operational, and properly deployed prior to entry;

Ensuring that appropriate measures are implemented so that confined spaces will not be inadvertently entered by employees in the area; and

Authority must be documented in writing on the confined space permit.

b. Support Personnel

Entry into a confined space shall be made only when enough outside support personnel are available to handle communication, support equipment, and to provide assistance or emergency aid as necessary.

The number of personnel needed for support will be based on the complexity of the project.

Complex projects can require five supporting personnel for one entry person.

c. Attendant

All space entries require an Attendant assigned to the project. This person's duties include maintaining communication and providing necessary assistance to workers inside.

Communications with inside personnel **must be direct** (either radio or audible voice).

This individual's primary responsibilities are:

(a) Remain outside the space;

(b) Know hazards that may be present;

(c) Maintain count and communication with entrants;

(d) Observe space for changing conditions;

(e) Prevent unauthorized entry while space is open; and

(f) Calls for rescue if emergency occurs.

The assigned Attendant(s) cannot leave a confined space area unless they are immediately replaced with another attendant.

d. Authorized Entrant(s)

Specific employees (named on the Confined Space Permit) that are trained, correctly attired, and authorized by the supervisor to enter the confined space.

e. Rescue Person/Team

A team of qualified rescuers is required to be specifically identified and provided for in accordance with 29 CFR 1910.146 for all permit-required spaces.

For circumstances where an IDLH or flammable atmosphere may be encountered; and for entries into unknown atmospheres, and awkward spacial configurations preventing unaided remote rescue the following additional requirements shall be met:

This individual must be dressed in the same level of protection as the entry person.

He/she must be stationed at the opening to the space **in direct line of sight** or contact with those inside.

This person will be on station the entire time that operations are being conducted.

Complex entries **may require** two Rescue Persons; this person will be equipped with supplied air respirator and harness/retrieval line.

5. Atmosphere Air Monitoring

a. Prior to entry, all spaces will be initially tested for flammable gases, vapors, and oxygen deficiency, plus toxic vapor or gases (based on the potential for toxics being present).

b. OSHA requires that the monitoring be conducted in the following specific order:

Oxygen;

LEL; and

Toxic gases and vapors.

c. The person assigned the task of monitoring shall know the proper procedure for calibration and operation of all sampling equipment in accordance with manufacturer's or Envirocon's Standard Operating Procedures for Combustible Gas/Oxygen Meters and Toxic Gas Specific Monitoring Instruments.

d. Each instrument used will be thoroughly tested prior to daily use to ensure that it is properly calibrated and that it is functioning properly.

e. CGIs or direct reading Toxic Gas Meters will **not** be used for certifying an area "safe for entry" if their calibration has not been confirmed with the appropriate calibration gas.

f. Monitoring readings will be made from bottom to top and in all remote sections of the space.

Remote monitoring lines will be utilized to negate the need to enter the space for monitoring.

g. Monitoring personnel must always confirm that a lack of LEL reading is not caused by low oxygen concentrations.

h. All air monitoring results and equipment calibrations will be recorded on the back of the FE JV Entry Permit Form.

i. It is recognized that the condition in some spaces may change over time. Initial testing may underestimate hazards in these situations.

j. Continuous monitoring inside the space for flammables, oxygen deficiency, and/or toxic gas and vapors:

Will be necessary where inside conditions could rapidly change.

Example situations would include when welding or cutting inside the space; using solvents to clean inside surfaces; cleaning operations disturb contaminants so that previously covered contaminants could become airborne; dismantling pipe work or other structures that could contain contaminants; etc.

k. Once ventilation is started, periodic checks should be made of the surrounding area (where the contaminated air is exhausted) to ensure that no hazard is presented to people or equipment.

l. Personnel will be removed from the area if monitoring demonstrates that ventilation is not sufficient to maintain the atmosphere below 10% LEL or if oxygen levels dip below 19.5%.

6. Isolation/Lockout/Zero Mechanical State (ZMS)

a. Before entering any confined space, personnel will take sufficient steps to ensure that it is impossible for toxic contaminants or potentially hazardous products to re-enter a space and that all potentially hazardous conditions (involving electricity or other stored energies) are brought to a ZMS.

b. All requirements of the OSHA Lockout/Tagout Operating Procedure will be followed.

c. While performing work at a non- FE JV location, it is not always possible to have total control over a client's employees or property. The Project Manager will stop operations if there is any doubt concerning employee safety and will contact the Corporate Health and Safety Manger to ensure that adequate steps are being taken.

7. Mechanical Ventilation

a. The method chosen to ventilate the space (making it positive pressure by blowing air into it or making it negative pressure by drawing air out of the space) will be made based on site conditions. Either method can effectively dilute contaminant concentrations to acceptable levels.

b. Any ventilation equipment or duct work exposed to flammable gases or dusts **must** be bonded and grounded prior to use.

c. Electrical fans

Will not be placed inside a space that contains flammable vapors.

Do not draw (suck) flammable vapors from a space through a fan regardless of the distance of the motor from the confined space. This presents a hazard of drawing flammable vapors through an ignition source producing an explosion or flashback.

When using fans, flexible tubing or duct work will be used to distribute air into the space.

d. Continuous ventilation criteria

General dilution ventilation will be continuous at a minimum rate of five (5) air changes per hour for oxygen deficiency and 10 air changes per hour for toxic or flammable atmospheres.

Dilution ventilation is not always sufficient to ensure that toxic environments are rendered safe (below PEL or IDLH concentrations).

Initial or continuous ventilation is not needed if there is NO possibility of contaminant generation while personnel are inside.

e. Contaminants displaced from a space:

Will present exposure potentials to outside personnel;

This discharge can possibly accumulate and form flammable or explosive concentrations;

Any potential exposure must be monitored with appropriate PPE upgrades being made as necessary;

Contaminated air needs to be discharged in an area that is not occupied and/or in an downwind location. This is accomplished by directing the exhaust from the space through plastic flex hose to a safer area; and

Be aware of local air pollution district requirements prior to tank ventilation.

f. Local exhaust ventilation (inside the space at the point of contaminant generation) shall be provided when mechanical dilution ventilation is not capable of preventing the point source contaminant from producing unacceptable high concentrations throughout the area. Example: spreading a flammable solvent on a surface inside a tank.

g. **It is not acceptable that ventilation equipment block the entrance of a confined space.**

When entering manholes or other small openings, a saddle vent can be utilized if the duct work will interfere with entry/egress.

An alternative is to use flexible poly tubing which can be easily compressed which will allow passage without removal.

h. Fans or blowers used for mechanical ventilation shall be located so they will not discharge exhaust gases from vehicles, heaters, furnaces, or adjacent operations capable of generating airborne contaminants into the space.

i. Duct work should be placed so that unnecessary bends are eliminated. Metal elbows or corners may be purchased to avoid pinching the airflow.

j. Negative pressure can be provided by placing the inlet of the blower inside the space with the discharge directed outside. This method is effective in drawing clean air into the space, but is not as effective (in producing uniform dilution of contaminants) as blowing directly into the space.

8. Safety Equipment

The following equipment requirements are to be considered minimum. The equipment must be present and operational prior to start up and initial entry of the individual.

a. Oxygen and Combustible Gas Indicators, calibration kit, all accessories including remote sample line and in-line filters, instruction manual, and response charts and graphs to test for and interpret the flammable atmosphere.

b. Photo Ionizing Detector, detector tubes, or direct reading toxic gas meters as appropriate to determine toxic content of atmosphere.

c. Mechanical ventilation equipment, i.e., blowers, compressor, hoses, and auxiliary equipment as designated for the confined space.

d. Respiratory/face protection

The exact level and type shall be determined by the Project Health and Safety Officer based upon the conditions and test results of the confined space and the work activity performed.

All respirators shall be NIOSH/MSHA-approved devices and shall be fitted and maintained in accordance with the Envirocon Respiratory Protection Policy.

Eye protection will always be worn when a splash or flying object hazard exists.

An additional standby air source with attached airline and regulator

Will be necessary for entries into Restricted Entry spaces, where there is any possibility that the 5-minute egress will not provide a good margin of safety for getting out in an emergency. Lines will be coiled and ready for immediate use near the opening.

e. Body/hand/foot protection

All workers entering a confined space shall wear protective clothing sufficient to protect the wearer against known or suspected toxic or irritating materials.

Specific types of suit material will be described in the Confined Space Permit.

f. Hearing protection

Equipment operation and ventilation system operation results in increased noise levels in confined spaces. Hearing protection shall be used when elevated noise levels are present.

g. All workers shall wear a hard hat.

h. Rescue equipment

The specific type and degree of rescue equipment will depend upon the nature of the confined space with regard to access/egress. This decision would take into account the exact manner in which the individual can be feasibly extracted (i.e., by the wrists, waist, straight up) and the accompanying strain to the persons body.

A body harness/belt is required when an employee is working in an area that, for purposes of rescue, is considered restricted and when any failure of ventilation could allow the build-up of toxic or explosive gases within the time necessary to vacate the area.

A full-body harness is required for any vertical entry greater than 5 feet.

An ANSI-approved restraint belt will usually be satisfactory for horizontal entry.

If the worker in the confined space is required to wear a harness, the Rescue Person shall also have a safety harness and air supplied respirator immediately available.

Mechanical rescue/extraction equipment:

Such as tripod, block and tackle, and lifelines will be available, set-up, and in working order prior to entry if needed to remove a worker from a confined space; and

This equipment must be capable of being hand operated and reversible.

The Safety Officer on the project can make a decision to disconnect lifelines if it is felt that the lines present an undue hazard or hindrance to routine operations.

i. Radio communication

Radios should be provided as the primary means of direct communication with personnel inside a confined space if direct visual contact is impractical.

Foth | Envirocon
Joint Venture

Confined Space Entry Permit

JOB NAME: _____ Location: _____
DESCRIPTION OF SPACE: _____
TASK: _____
CONTAMINANTS: _____
SPECIAL HAZARDS: _____

	Print Name:	Pre-entry Briefing Signature
Supervisor:		
Attendant:		
Entrants:		

Classification of Space:

☐ NO ENTRY: if any of the following conditions:
____ LEL > 10% ____ Oxygen < 19.5% or > 23.5% ____ Unable to monitor ____ > IDLH
☐ PERMIT REQUIRED CONFINED SPACE (RESTRICTED ENTRY): Requires Escape Provisions
☐ (c)(5) Alternate rules
(temporary downgraded of space, rescue provisions not required). Document/monitor conditions as follows):
☐ space has been ventilated to airborne hazards less than established exposure limits
☐ no other serious (i.e., confined space) hazards exist (e.g, engulfment hazards or converging walls).
☐ NON-PERMIT CONFINED SPACE
☐ ENCLOSED SPACE

PRE-ENTRY CHECKLIST		YES	NO	N/A
Training:	All workers have completed training in Confined Space Procedure?			
	All personnel listed above have been briefed on permit procedures prior to entry?			
	Communication procedures are thoroughly understood?			
Permits:	All chemical and gas delivery lines are disconnected and/or capped?			
	Stored electrical, mechanical, pneumatic power sources reduced to zero energy?			
	All Lockout/Tagouts in place and permits issued as needed?			
	Gas hazard addressed and hot work permits issued as needed?			
Monitoring:	Monitoring equipment has been calibrated/span checked?			
	Initial Testing Completed (19.5%<O2<23.5% and LEL < 10%)			
Ventilation has been established for and adequate or work which may generate gas hazard?				
	Exhausted air is ducted to a safe location?			
Gas Hazardous locations have adequate ventilation to control vapor production?				
	Ventilation and liquid pumping equipment is bonded and grounded?			
	Is adequate explosion-proof lighting available?			
All required safety equipment is available, tested - functional?				
Rescue Procedure (if required for space classification) has been established?				
	Is there non-entry extraction for vertical depths >5 feet as part of plan?			
	Rescue personnel notified or standing by?			
	Support personnel trained in CPR/First Aid if rescue provisions required?			

Foth | Envirocon Joint Venture

Confined Space Entry Permit

PPE Requirements	**Respiratory Protection** Requirements
☐ hard hat ☐ safety glasses ☐ face shield	☐ SCBA, ☐ Airline respirator, ☐ with escape air
☐ steel toed safety boots ☐ flashlight ☐ radio ☐ emergency whistle/horn/other:	☐ Air Purifying Respirator, ☐ full face, ☐ full face or half mask
Chemical Protective Clothing (CPC). ☐ outer garment	☐ Cartridge type: ☐P100/HEPA, ☐ organic vapor, or ☐ other/combination:
☐ inner garment: ☐ outer gloves: ☐ inner gloves: ☐ inner boots: ☐ outer boots: ☐ other:	Cartridge change schedule: ✓ change if odors detected or if difficult to breath ☐ change cartridges beginning of each week ☐ change cartridges daily ☐ change cartridges as follows:
	☐ Voluntary use for comfort of employee from odors or nuisances.

Rescue Provisions (Optional for non-permit spaces and (c)(5) downgrade spaces.)

☐ Tripod with Winch	☐ Auxiliary Fall Block	Fire Department:
☐ Full body harness	☐ Waist Belt	Hospital:
☐ Ankle Cuff	☐ Wrist Cuff	Ambulance:
☐ Rope Grab/Life Line		Emergency Decon:
☐ (c)(5) downgraded space alternate rules		

Monitoring Requirements

Air Monitoring Requirements (initial and follow-up air monitoring must be documented on data form):

	initial	during entry	action level
oxygen (first test)	☑	☐ continuous ☐ before re-entry ☐ other:	< 19.5% or >23.5% requires special permit
combustible gas (2nd)	☐	☐ continuous ☐ before re-entry ☐ other:	> 10 % LEL requires special entry permit
toxic (specify):	☐	☐ continuous ☐ before re-entry ☐ other:	
		☐ continuous ☐ before re-entry ☐ other:	

APPROVAL: _____ _____ / _____

supervisor's signature and name — date / time

This permit expires at the end of the shift issued, or ☐ other:

Appendix I

Map to Hospital

Emergency Routes

Directions for medical evacuation and hospital routes: (see attached map)

301 Lake Shore Drive East, Ashland, Wisconsin 54806

Depart US-2 / Lake Shore Drive east toward 3rd Avenue East

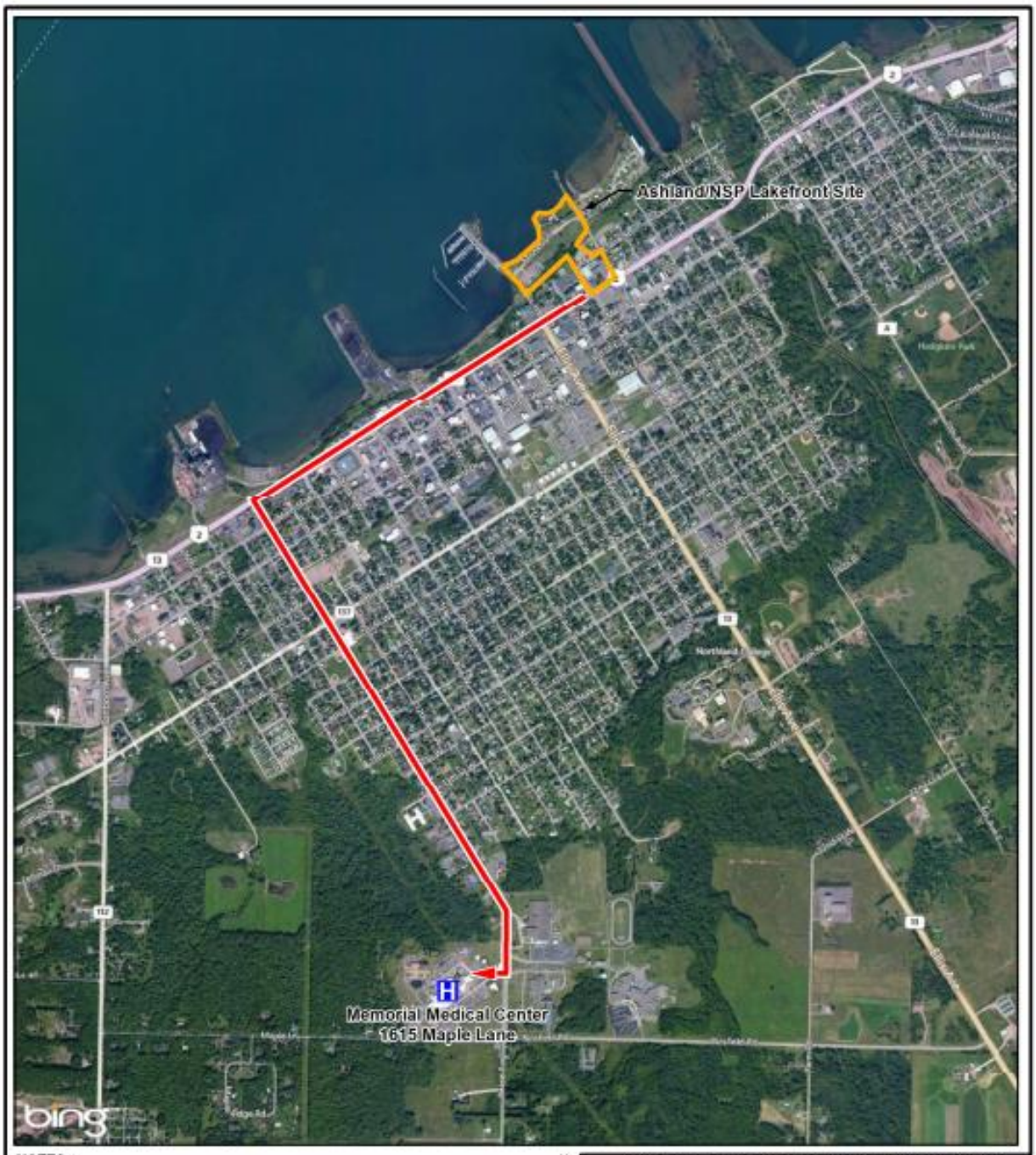
Turn left onto WI-13 / Ellis Avenue

Turn right onto 22nd / Ellis Avenue

Road name changes to Farm Road

Turn right onto Binsfield Road

Arrive at 1615 Maple Lane, Ashland, Wisconsin 54806



NOTES:
1. Base map from esri.com, courtesy of the Microsoft Corporation and its data suppliers.

N

Foth | Envirocon
Joint Venture

This drawing is neither a legally recorded map nor a survey and is not intended to be used as one. This drawing is a compilation of records, information and data used for reference purposes only.

0 800 1,600
Feet

NORTHERN STATES POWER COMPANY

FIGURE 1
HOSPITAL ROUTE MAP
HEALTH AND SAFETY PLAN - ADDENDUM 1
ASHLAND/NSP LAKEFRONT SITE

Date: DECEMBER 2013	Revision Date:	
Drawn By: BJW1	Checked By: JSK	Scope: 12X001

Path: X:\GB\IE\2012\12X001\GIS\mxd\hospital_route_map_a-size.mxd Date: 12/13/2013

Appendix H

Specifications

TECHNICAL SPECIFICATIONS

TABLE OF CONTENTS

SECTION 01 10 00

SUMMARY

PART 1 - GENERAL

1.1 SUMMARY

A. Section Includes
1. References
2. Specification Formats and Conventions
3. Work Covered by the Contract Documents
4. Work Sequence
5. Use of Premises
6. Work By Others
7. Future Work
8. Contractor-Furnished Products
9. Partial Contractor Occupancy
10. Project Utility Sources
11. Miscellaneous Provisions

1.2 REFERENCES

A. Definitions
1. Basic Contract definitions and terminology are included in the Agreement.
2. The term "approved," when used to convey Contractor's action on Subcontractor's submittals, applications, and requests, is limited to Contractor's duties and responsibilities as stated in the Agreement.
3. The term "regulations" includes laws, ordinances, statutes, and lawful orders issued by authorities having jurisdiction, as well as rules, conventions, and agreements within the construction industry that control performance of the Work.

B. Industry Standards
1. Unless the Contract Documents include more stringent requirements, applicable construction industry standards have the same force and effect as if bound or copied directly into the Contract Documents to the extent referenced. Such standards are made a part of the Contract Documents by reference.
2. Comply with standards in effect as of date of the Contract Documents, unless otherwise indicated.
3. If compliance with two or more standards is specified and the standards establish different or conflicting requirements for minimum quantities or quality levels, comply with the most stringent requirement.
4. The quantity or quality level shown or specified shall be the minimum provided or performed. The actual installation may comply exactly with the minimum quantity or quality specified, or it may exceed the minimum within reasonable

limits. To comply with these requirements, indicated numeric values are minimum or maximum, as appropriate, for the context of requirements.

5. Each section of the specifications generally includes a list of reference standards normally referred to in that respective section. The purpose of this list is to furnish the Subcontractor with a list of standards normally used for outlining the quality control desired on the project. The lists are not intended to be complete or all inclusive, but only a general reference of standards that are regularly referred to.
6. Each entity engaged in construction on the Project shall be familiar with industry standards applicable to its construction activity. Copies of applicable standards are not bound with the Contract Documents. Where copies of standards are needed to perform a required construction activity, obtain copies directly from the publication source and make them available on request.

1.3 SPECIFICATION FORMATS AND CONVENTIONS

A. The Specifications are organized into Divisions and Sections using the 50-division format and CSI's "MasterFormat" numbering system.

B. The Specifications use section numbers and titles to help cross-referencing in the Contract Documents. Sections in the Project Manual are in numeric sequence; however, the sequence is incomplete. Consult the table of contents at the beginning of the Project Manual to determine numbers and names of sections in the Contract Documents.

1.4 WORK COVERED BY THE CONTRACT DOCUMENTS

A. Project Identification
   1. Project location: Ashland/NSP Lakefront Site, Ashland, Wisconsin

B. The Work includes:
   1. Mobilization
   2. Site preparation
   3. East/West gap closures and water quality barrier system installation
   4. Mechanical dredging, off-loading, and transport to disposal site
   5. Hydraulic dredging, dewatering, and transport to disposal site
   6. Restorative layer placement
   7. Restoration
   8. Demobilization

1.5 WORK SEQUENCE

A. Conduct the Work in phases.

2017

1. Mobilization
2. Install all necessary marine safety features around working areas

3. Install east and west Breakwater gap closures
4. Install water quality barrier system
5. Perform mechanical dredging in DMU-1
6. Install isolation barrier between DMU-1 and DMU-2 and apply flocculent, as necessary
7. Perform hydraulic dredging in DMU-1 (including null areas)
8. Perform mechanical dredging in DMU-2 and apply flocculent, as necessary
9. Perform hydraulic dredging in DMU-2 (including null areas)
10. Winterization of site

2018

1. Mobilization
2. Access gap closures and repair/replace, if necessary
3. Install water quality barrier system, if necessary
4. Install restorative layer
5. Restoration
6. Demobilization

1.6 USE OF PREMISES

A. Subcontractor shall have full use of the premises for construction operations, including use of the Project Site, as allowed by law, ordinances, permits, easement agreements and the Contract Documents.

B. Assume full responsibility for site safety and protection of public.

C. Assume full responsibility for protection and safekeeping of material and products stored on or off premises.

D. Move any stored material or products which interfere with operations of Contractor or other Subcontractors.

E. Use of Site
1. Work can occur 12 hours per day for a maximum of 6 days per week. Hours of operation include all off-loading activities.

1.7 WORK BY OTHERS

A. Contractor will provide quality assurance testing as defined in the specifications.

B. Offloading of dredged material at sediment processing tent and processing of dredged material to be performed by Contractor.

1.8 CONTRACTOR-FURNISHED PRODUCTS

A. Water quality barrier system materials currently stored on-site for Subcontractor’s use.

1.9 PARTIAL CONTRACTOR OCCUPANCY

A. Subcontractor provide:
   1. Access for Contractor's personnel.
   2. Access for Contractor to perform all necessary inspections.

PART 2 - PRODUCTS (Not Used)

PART 3 - EXECUTION (Not Used)

END OF SECTION

SECTION 01 32 33

PHOTOGRAPHIC DOCUMENTATION

PART 1 - GENERAL

1.1 SUMMARY

A. Section includes administrative and procedural requirements for the following:
   1. Construction photographs.
   2. Construction video recordings.

1.2 INFORMATIONAL SUBMITTALS

A. Digital Photographs
   1. Photos shall be submitted as unaltered digital files with same aspect ratio as the camera sensor, uncropped, date and time stamp (preferred) in folder named by date of photograph.
   2. Provide the following information with each image description:
      a. Name of Project.
      b. Name and contact information for photographer.
      c. Date photograph was taken.
      d. Description of vantage point, indicating location, direction (by compass point), and elevation or story of construction, if building.
      e. Unique sequential identifier keyed to accompanying key plan.

B. Video Recordings
   1. Submit video recordings in digital video disc format acceptable to Owner/Engineer.
   2. With each submittal, provide the following information:
      a. Name of Project.
      b. Name and address of photographer.
      c. Date video recording was recorded.
      d. Description of vantage point, indicating location, direction (by compass point), and elevation or story of construction, if building.
      e. Description of activity being recorded and purpose of recording.

PART 2 - PRODUCTS

2.1 PHOTOGRAPHIC MEDIA

A. Provide digital images in .jpg or .tif format on digital CD, or equivalent. Images shall be contained in separate folders for each day photos were taken.

B. Digital Video Recordings
Provide digital video recordings in high-resolution, digital video disc, or equivalent.

PART 3 - EXECUTION

3.1 CONSTRUCTION PHOTOGRAPHS

A. General
1. Take photographs using the maximum range of depth of field, and that are in focus, to clearly show the Work.
2. Photographs with blurry or out-of-focus areas will not be accepted.
3. Maintain key plan with each set of construction photographs that identifies each photographic location.

B. Submit digital images exactly as originally recorded in the digital camera, without alteration, manipulation, editing, or modifications using image-editing software.
1. Include date and time in file name for each image.
2. Maintain one set of images accessible in the field office at Project site, available at all times for reference.

C. Preconstruction Photographs
1. Before starting construction, take photographs of Project site and surrounding properties, including existing items to remain during construction, from different vantage points, as directed by Engineer.
2. Take sufficient number of photographs to show existing conditions adjacent to property before starting the Work.
3. Take sufficient number of photographs of existing buildings either on or adjoining property to accurately record physical conditions at start of construction.
4. Take additional photographs as required to record settlement or cracking of adjacent structures, pavements, and improvements.
5. Provide video documentation of existing roadways which may be affected by construction activities.

D. Periodic Construction Photographs
1. Take sufficient number of photographs weekly, with timing each month adjusted to coincide with the cutoff date associated with each Application for Payment.
2. Select vantage points to show status of construction and progress since last photographs were taken.

E. Final Completion Construction Photographs
Take sufficient number of color photographs after date of Substantial Completion for submission as project record documents.

3.2 CONSTRUCTION VIDEO RECORDINGS

A. General
1. Display continuous running time and date.
2. At start of each video recording, record weather conditions.

3. Describe scenes on video recording by audio narration by microphone while video recording is recorded.
4. Include description of items being viewed, recent events, and planned activities.
5. At each change in location, describe vantage point, location, direction (by compass point), and elevation or story of construction, if building.
6. Include description of unusual or significant features.
7. Record settlement or cracking of adjacent structures, pavements, and improvements.
8. Confirm date and time at beginning and end of recording.
9. Begin each video recording with name of Project, Contractor's name, videographer's name, and Project location.

B. Preconstruction Video Recording

Before starting construction, record video recording of Project site and surrounding properties from different vantage points, as directed by Engineer.

1. Flag utility locations before recording construction video recordings.
2. Show existing conditions adjacent to Project site before starting the Work.
3. Show existing buildings either on or adjoining Project site to accurately record physical conditions at the start of construction.
4. Show protection efforts by Contractor.

END OF SECTION

SECTION 01 35 53.13

SAFETY AND ENVIRONMENTAL PROCEDURES FOR HAZARDOUS MATERIAL SITES

PART 1 - GENERAL

1.1 SUMMARY

A. Section Includes
   1. Site-specific *Health and Safety Plan for Phase 2 Wet Dredge (HASP)* (FE JV, 2016).
   2. Personal injury and property damage prevention
   3. Personnel organization, qualifications and responsibilities

1.2 REFERENCES

A. Code of Federal Regulations
   1. 29 CFR 1910 Occupational Safety and Health Standards
   2. 29 CFR 1926 Safety and Health Regulations for Construction

B. Existing *HASP* (FE JV, 2016)

1.3 SUBMITTALS

A. Submit site-specific *HASP*, not for approval, but as evidence of compliance with state and federal requirements. Include resumes of the proposed Safety Representative(s) to be used on the Project.

1.4 SITE SAFETY AND HEALTH PLAN

A. Develop and implement a site-specific *HASP* meeting the requirements of 29 CFR 1910.120, 29 CFR 1926 and other applicable federal, state and local regulations. *HASP* must be consistent with (and not less restrictive than) all requirements listed in the existing *HASP* referenced in Section 1.2 (B).

B. Prepare the *HASP* specifically for the site and the anticipated activities based on available information on site conditions and hazards.

C. The *HASP* shall be considered a living document, updated as conditions change during Project execution.

D. On-site work shall not begin until the *HASP* has been prepared and implemented.

E. Include the following in the implementation portion of the *HASP*:
   1. Monitoring for hazards commonly associated with construction activities.

1.5 PERSONAL INJURY AND PROPERTY DAMAGE PREVENTION

A. Provide necessary protection to prevent damage, injury or loss to:
   1. Persons on the Site or who may be affected by the Work.
   2. Materials and equipment to be incorporated in the Work.

B. Comply with all applicable laws, ordinances, rules and regulations affecting the safety of persons or property providing any necessary safeguards for such safety and protection.

C. Notify the Contractor of any properties or utilities that are affected by the Work.

D. The duties and responsibilities of the Subcontractor for the safety and environmental protection of the workers and the site shall continue until final payment is made by the Contractor to the Subcontractor.

1.6 PERSONNEL ORGANIZATION, QUALIFICATIONS AND RESPONSIBILITIES

A. Designate the Safety Representative, a Site Health and Safety Officer, and at least one alternate.

B. Subcontractor shall have a full time dedicated Safety Representative on site while Work is being performed.

C. The Site Health and Safety Officer shall:
   1. Implement and enforce the site-specific *HASP*.
   2. Provide hazard communication information.
   3. Be responsible for any safety environmental monitoring.
   4. Have the authority to stop work activities if unacceptable health or safety conditions exist.
   5. Coordinate and recommend corrective actions for identified health and safety deficiencies and oversee the corrective actions.

PART 2 - PRODUCTS (Not Used)

PART 3 - EXECUTION

A. Comply with existing site-specific *HASP* (Section 1.2 B).
B. Implement Subcontractor’s Health and Safety Plan.

END OF SECTION

SECTION 01 50 00

TEMPORARY FACILITIES AND CONTROLS

PART 1 - GENERAL

1.1 SUMMARY

A. Provide temporary facilities and controls required for construction activities and:
   1. Include costs in total price of contract.
   2. Maintain until final completion of project.

1.2 UTILITY USE CHARGES

A. Include cost or use charges for temporary facilities in the Contract Sum.

B. Pay sewer service use charges for sewer usage (portable toilet) by all parties engaged in construction at Project site.

C. Pay water service use charges whether metered or otherwise, for water used.

1.3 QUALITY ASSURANCE

A. Comply with industry standards and with applicable laws and regulations of authorities having jurisdiction, including but not limited to the following:
   1. Health and safety regulations.
   2. Utility company regulations.
   3. Police, fire department and rescue squad rules.
   4. Environmental protection regulations.
   5. NFPA 241 "Standards for Safeguarding Construction, Alterations and Demolition Operations".
   6. ANSI-A10 Series standards for "Safety Requirements for Construction and Demolition".
   7. NECA Electrical Design Library "Temporary Electrical Facilities", NFPA 70, and NEMA, NECA and UL standards and regulations for temporary electric service.

B. Arrange for authorities having jurisdiction to inspect and test each temporary utility before use. Obtain required certifications and permits.

1.4 PROJECT CONDITIONS

A. The following conditions apply to use of temporary services and facilities by all parties engaged in the Work:
   1. Keep temporary services and facilities clean and neat.
   2. Relocate temporary services and facilities as required by progress of the Work.

PART 2 - PRODUCTS

2.1 MATERIALS

A. Provide undamaged materials in serviceable conditions and suitable for use intended.

2.2 EQUIPMENT

A. Provide undamaged equipment in serviceable conditions and suitable for use intended.

B. Provide temporary self-contained toilet units of temporary single-occupant toilet units of the chemical, aerated recirculation, or combustion type for use by all construction personnel. Units shall be properly vented and fully enclosed with a glass-fiber-reinforced polyester shell or similar nonabsorbent material.

A. Field Office
   1. Provide insulated weathertight manufactured mobile unit which includes:
      a. Heating and air conditioning system.
      b. Lockable entrances.
      c. Operable windows with insect screens.
      d. Minimum 240 sq. ft. floor space.
      e. First aid kit.
   2. A hand carried, portable, UL rated fire extinguisher complying with NFPA 10 and NFPA 241 for classification, extinguishing agent, and size required by location and class of fire exposure.
   3. Bottled-water drinking-water unit.

PART 3 - EXECUTION

3.1 INSTALLATION, GENERAL

A. Locate facilities where they will serve the Project adequately and result in minimum interference with performance of the Work. Relocate and modify facilities as required.

B. Provide each facility ready for use when needed to avoid delay. Maintain and modify as required. Do not remove until facilities are no longer needed or are replaced by authorized use of completed permanent facilities.

C. Temporary Electric Power Service
   1. Provide weatherproof grounded electric power service and distribution system of sufficient size, capacity and power characteristics for construction needs.
   2. Include meters, transformers, overload-protected disconnects, automatic ground-fault interrupters and main distribution switch gear.

D. Temporary Lighting
1. Install and operate temporary lighting that will fulfill security and protection requirements without operating the entire system.
2. Provide lighting that provides adequate illumination for construction operations and traffic conditions.

E. Temporary Heat and Ventilation
1. Provide temporary heat and ventilation required for the construction activities, including but not limited to curing or drying completed installations and protecting construction from adverse effects of low temperatures and high humidity.
2. Use safe equipment that will not have a harmful effect on elements being installed and on completed installations.
3. Coordinate ventilation requirements to produce the ambient condition required for the work and to minimize energy consumption, and to protect personnel from fumes and other harmful effects.

F. Heating Facilities
1. Provide vented self-contained heaters with individual space thermostatic control.
2. Do not use gasoline-burning space heaters, open flame or salamander-type heating units.

G. Temporary Sanitary Facilities
1. Provide for toilets, wash facilities and drinking water fixtures in compliance with regulations and health codes for type, number, location, operation and maintenance of fixtures and facilities.
2. Provide toilet tissue, paper towels, paper cups and similar disposable materials as appropriate for each facility, and provide covered waste containers for used materials.
3. Install separate self-contained toilet units for male and female personnel shielded to ensure privacy.
4. Install wash facilities supplied with potable water at convenient locations for personnel involved in handling materials that require wash-up for a healthy and sanitary condition.
    a. Dispose of drainage properly.
    b. Supply cleaning compounds appropriate for each condition.
    c. Include safety showers, eyewash fountains and similar facilities for the convenience, safety and sanitation of personnel.
5. Provide drinking water fountains or containerized tap-dispenser bottled-drinking water units, complete with paper cup supplies. Where power is accessible, provide electric water coolers to maintain dispensed water temperature at 45 to 55°F (7 to 13°C).

3.2 OPERATION, TERMINATION, AND REMOVAL

A. Supervision
1. Enforce strict discipline in use of temporary facilities.

2. Limit availability of temporary facilities to essential and intended uses to minimize waste and abuse.

B. Maintenance
1. Maintain facilities in good operating condition until removal.
2. Protect from damage by freezing temperatures and similar elements.
3. Maintain operation of temporary enclosures, heating, cooling, humidity control, ventilation, and similar facilities on a 24-hour basis where required to achieve indicated results and to avoid possibility of damage.
4. Prevent water-filled piping from freezing.
5. Maintain markers for underground lines.
6. Protect underground lines from damage during excavation operations.

C. Termination and Removal
1. Unless the Contractor requests that a temporary facility be maintained longer, each temporary facility shall be removed when the need for its service has ended and can be replaced by authorized use of a permanent facility.
2. Complete or, if necessary, restore permanent construction that may have been delayed because of interference with the temporary facility.
3. Repair damaged Work, clean exposed surfaces, and replace construction that cannot be satisfactorily repaired.
   a. Materials and facilities that constitute temporary facilities are the property of the Subcontractor, except the Owner reserves the right to take possession of project identification signs.

END OF SECTION

SECTION 35 20 23

DREDGING AND DEBRIS REMOVAL

PART 1 - GENERAL

1.1 SUMMARY

A. Work covered by this Section includes:
1. Mechanical removal of debris.
2. Mechanical dredging of Inventory and Residual Sediments.
3. Hydraulic dredging of Residual Sediments.
4. Barge dewatering.
5. Sediment offloading.

B. Related Requirements:
1. Water quality barrier system requirements are provided in Section 44 41 21.
2. Restorative Layer Placement requirements are provided in Section 35 53 00.
3. Work covered by this Section shall be in accordance with the Environmental Protection Agency- (EPA) approved *Final Design for Phase 2 Wet Dredge* (*Final Design*) (FE JV, 2016).

1.2 REFERENCES

A. Abbreviations:
1. cy – cubic yards
2. DMU – Dredge Management Unit
3. gpm – gallons per minute

B. Defined Terms:
1. Debris Removal: Clearing of large non-sediment objects and obstructions from the Phase 2 Wet Dredge Area and null areas prior to sediment dredging activities.
2. Inventory Sediment Dredging: Mechanical dredging conducted following debris removal; primary means of removing impacted sediment within the Phase 2 Wet Dredge Area.
3. Residual Sediment Dredging: Re-dredge passes using either mechanical or hydraulic dredging methods for areas not meeting cleanup goals or performance standards based on post mechanical/hydraulic interim and final confirmation sediment sampling.

1.3 OBJECTIVES OF THE WORK

A. The objective of the dredging Work covered by this Section is to evaluate the effectiveness and implementability of wet dredging to successfully achieve cleanup goals or performance standards for sediments within the Phase 2 Wet Dredge Area. Subcontractor is expected to participate in planning, design, and execution of the

Work as part of a design-build team in order to fully meet objectives of the Work.

B. Additional details regarding objectives of the Work are provided in the *Final Design*.

1.4 ADMINISTRATIVE REQUIREMENTS

A. Preconstruction Coordination: In order to successfully meet objectives of the Work, Subcontractor will be required to coordinate with the Contractor on the following items:
   1. Preconstruction design support: Subcontractor to provide technical and design support as part of the preconstruction activities. This effort will be directed and managed by the Contractor and will generally include support in the areas of planning, design, and determination of means and methods.
   2. Preconstruction meetings: Subcontractor is expected to participate in preconstruction meetings as requested by the Contractor.
   3. Subcontractor Project Team: Subcontractor shall identify key roles and responsibilities in support of the Work and shall identify a single point of contact for the preconstruction design support through which efforts of the Subcontractor will be managed and information disseminated.

B. Sequencing: Work identified in this Section is to be performed within the following general sequence:
   1. Planning and Final Design: Subcontractor to participate in planning and final design development during the preconstruction phase of the work.
   2. Installation of Water Quality Barrier System: Barrier system must be installed prior to any debris removal or sediment disturbance activities.
   3. Shoreline Debris Removal and Dredging: Initial dredging and debris removal from the shoreline will be required to create draft for the dredge and material transfer barges. Shoreline debris removal and dredging conducted from the shore will be performed by the Contractor.
   4. Marine-Based Dredging: Contemporaneously with shoreline debris removal and dredging, the marine-based dredging, to be performed by the Subcontractor, is to commence in the following sequence:
      a. Mechanically (Inventory) dredge DMU 1. Large debris and wood waste will be removed first in (including a minimum of 12 inches of material from the null areas within and adjacent to) each DMU, prior to the sediment, as necessary to promote appropriate segregation of the two materials.
      b. Install isolation barrier between DMU 1 and DMU 2.
      c. Apply flocculent, as necessary, to enhance water quality in DMU 1.
      d. Hydraulically (Residual) dredge DMU 1, including null areas. Contemporaneously, mechanically (Inventory) dredge DMU 2.
      e. Apply flocculent, as necessary, to enhance water quality in DMU 2.
      f. Hydraulically (Residual) dredge in DMU 2.
      g. Dredge sequencing may be altered if approved by the Contractor.
   5. Clearance: Once target depths have been achieved in each DMU and water quality meets the requirements of the *Monitoring Plan for Phase 2 Wet Dredge* (FE JV, 2016), final confirmation sediment samples will be collected to evaluate the

performance of the sediment removal. Final confirmation sediment sampling will be performed by the Contractor.

a. Re-dredge passes may be required based on results of final confirmation sampling.
b. Post-mechanical and hydraulic interim samples will be collected by the Contractor immediately following the mechanical and hydraulic dredging of each DMU to the targeted depths, prior to final confirmation sampling. Additional dredging (Inventory or Residual) within the DMU may be required based on the results of post-mechanical and hydraulic interim sampling.

6. Restorative Layer Placement: Once both DMUs have been cleared, a minimum 6 inch thick restorative layer, consisting of a clean sand/gravel mix, will be placed over the DMUs, including any sideslopes and null areas, as shown on the Drawings..

1.5 SUBMITTALS

A. Daily Dredging Reports:
1. Subcontractor shall submit reports summarizing daily dredging operations to the Contractor no later than 11:00 a.m. the following work day. Reports shall contain:
   a. Day and date of report;
   b. Project name;
   c. Weather conditions;
   d. Location/area of dredging (e.g., a figure);
   e. Crew size, assignments, and hours worked;
   f. Time and duration of any dredging work delay or shutdown and reason for the delay or shutdown.
   g. Approximate volumes and character of material dredged (including debris), particularly any changes in or other unusual observations of sediment characteristics or debris encountered;
   h. QC depth soundings taken;
   i. Accidents, spills, and mishaps, etc. and actions taken to respond to these incidents;
   j. Names of any visitors and time of their visit to the site; and
   k. Name of individual making report.

B. Weekly Reports:
1. In addition to the Daily Dredging Reports, Subcontractor shall also submit weekly reports summarizing weekly progress and productivity.
2. Construction drawings shall be utilized to reflect progress.

C. Survey:
1. Submit to the Contractor a listing of benchmarks and/or control points established (or occupied) at the site by Subcontractor and their horizontal and vertical positions.
2. Perform and submit preconstruction bathymetric survey to Contractor. Contractor will audit the preconstruction bathymetric survey of the Subcontractor.

3. All QC bathymetric surveys used to document existing conditions will be single-beam with surveying transect grids located no further than 25 feet apart.
4. Submit for Contractor QC bathymetric surveys of completed Work with quantity calculations for the following Work items:
   a. Mechanical (Inventory) dredging.
   b. Hydraulic (Residual) dredging
5. Survey submittals shall include electronic files (raw and processed data with 1x1 foot gridded data interpolation) in a format compatible with Contractor.

1.6 QUALITY ASSURANCE

A. Personnel Requirements: Provide competent personnel to perform the Work. Personnel shall be trained and have prior experience using all of the equipment, meeting environmental requirements, and achieving dredging tolerance limits.

B. Marine Requirements:
1. Subcontractor shall provide or make arrangements (in coordination with Contractor's operations) for all marine equipment and facilities, including staging areas, docks, and transportation of equipment, material, and personnel to and from offshore operations.
2. Subcontractor shall provide marine equipment that complies with all regulatory and safety requirements.
3. Subcontractor will provide Notice to Mariners to appropriate agencies one week prior to starting marine construction activities. Contractor will notify City of Ashland, Wisconsin Department of Natural Resources (WDNR), U.S. Environmental protection Agency (USEPA) and other necessary agencies when offshore operations are to commence.
4. All offshore operations shall comply with all applicable laws, rules, and customs, including those regarding lights, day signals, markers, etc. Offshore equipment shall comply with the requirements of the U.S. Coast Guard and U.S. Army Corps of Engineers.

C. Regulatory Requirements: Comply with conditions and substantive requirements of all applicable permits, and permit equivalency.

D. Dredge cut monitoring: Dredging shall be performed utilizing a real time positioning system capable of monitoring the position of the dredge bucket in relation to the dredge design elevations. Specific equipment and tolerances are specified in Article 3.4 of this Section.

E. Post-Dredge Bathymetric Survey:
1. Contractor will perform post-dredging bathymetric survey(s) that will serve as the basis for approval of achieving target dredge elevations. Contractor will audit the post-dredge bathymetric survey of the Subcontractor.
2. All QA bathymetric surveys will be single-beam with surveying transect grids located no further than 25 feet apart. Grid lines occupied are to be the same lines occupied for preconstruction surveys.

1.7 FIELD CONDITIONS

A. A significant amount of wood debris was present during pre-design poling and core sampling. Subcontractor shall be prepared to remove and manage debris in the sediment during dredging, and consider the effect of debris on dredge production rates. An approximate elevation of the bottom of the wood waste is presented in Drawing No. 13.

PART 2 - PRODUCTS - Not Used

PART 3 - EXECUTION

3.1 PREPARATION

A. Provide facilities as necessary to protect structures from damage during the dredging and debris removal operations.

B. Install water quality barrier system in accordance with requirements of Section 44 41 21 prior to executing debris removal or dredging activities.

C. Environmental Protection:
1. Wherever possible, use biodegradable hydraulic oil.
2. Provide necessary facilities/equipment to comply with Federal, State and local requirements concerning air, noise and water quality.
3. Protect against discharge of any oils, fuels, bitumens, garbage, trash, sewage, or other materials which may be harmful to fish, wildlife, or vegetation into the waters of the State. Should the Subcontractor spill, dump, lose, throw off the dredge or sink any material, plant, machinery or appliance, which in the opinion of the Contractor, may be dangerous to the environment or hazardous to navigation, the Subcontractor shall promptly recover or correct any such spills or dangerous discharges from equipment at Subcontractor expense.

D. Provide oil/absorbent boom and necessary associated equipment to continuously control and collect and remove as necessary, oil and sheen as encountered during dredging.

3.2 GENERAL DREDGING REQUIREMENTS

A. Perform work in a manner so that the structural integrity of existing shoreline structures is not compromised during dredging activities. Take care to avoid scratching of otherwise damaging the existing steel bulkhead wall along the south shoreline of the Project Area.

B. Dredged material and debris may only be stockpiled as indicated on the Drawings.

C. Dredging Limits and Target Depth:

1. The dredge area limits and approximate thicknesses are shown on the Drawings.
2. Preserve stable side slopes and avoid leaving residual sediment above the target elevations in any areas where dredging has been performed.
3. Subcontractor is allowed up to 0.5 foot of dredge overcut beyond the target elevations measured on the floor of the dredge cut only (excluding side slopes).
4. Sediment dredging will be considered complete when sediments have been removed to target elevations (or a maximum of 0.5 foot below target elevation), bathymetry surveys have been performed to document removal to target elevations over at least 90% of the subject area (excluding verified high subgrade areas), and when final confirmation sampling has shown that target total polynuclear aromatic hydrocarbon (tPAH) concentrations and non-aqueous phase liquid (NAPL) removal goals have been met.
5. If it is determined by post-dredge bathymetric survey that dredging has not achieved the target design elevation in at least 90% of the work area, additional dredging will be performed to reach the target elevation (excluding verified high subgrade areas).
6. Those areas that remain above the target design elevation shall be relatively isolated (i.e., non-contiguous). No areas remaining above the target elevation shall exceed the target elevation by greater than 0.5 foot, unless such areas are verified as being native hard lakebed material (i.e., rock, stiff clay, dense sand, gravel. etc.). In the event that limited areas are not able to meet the 0.5 foot tolerance due to physical constraints, Subcontractor and Contractor, in consultation with the Agencies, will determine the appropriate adaptive approach.
7. If it is determined through review of final confirmation sediment sampling results or visual post-mechanical and hydraulic interim sediment sampling results that removal requirements have not been met, additional dredging shall be performed to target elevations established by Contractor.
8. Overcut Penalty: Subcontractor shall pay for transportation and disposal costs of material dredged beyond the 0.5 foot vertical overcut allowance at an estimated unit rate to be determined at time of Contract award. Measurement of material dredged beyond the 0.5 foot overcut allowance, for each DMU, shall be based on the volumetric difference, determined by Contractor, between the post-dredge bathymetric survey and approved original (does not apply to new established target elevations) target elevations (including sideslope areas). This volumetric difference will be divided by the design dredge area (including sideslope areas) to determine the actual average overcut thickness that occurred, and then be compared to the 0.5 foot overcut allowance. Subcontractor shall endeavor to minimize overcut on sideslope areas, with the main focus being on achieving a stable condition. A density of 1.5 tons per cubic yard will be used to convert cubic yards to tonnage.

D. Dredging Operations:
1. Dredging operations are to be performed 12 hours per day and 6 days per week.
2. If working at night, Subcontractor shall provide and maintain adequate lighting from sunset to sunrise to allow for safe and proper observation and control of dredging operations.

3. Immediately stop dredging and notify the Contractor in the event that something is encountered which is unanticipated or outside the scope of this specification.
4. A Contractor representative will be present on site during dredging activities.
5. Control dredge speed and operations to minimize sheen and the re-suspension of sediment into the water column and to minimize the settling out of re-suspended solids in areas previously dredged.
6. Overlap dredge cuts to avoid leaving ridges or windrows of sediment between adjacent cuts.
7. Establish final side slopes to the angle of repose shown on the Drawings that assures stability and avoids subsequent sloughing of residual material.
8. Minimizes generation of sheen and resuspension of sediment between dredge plant moves.

3.3 DEBRIS REMOVAL

A. Large debris removal shall be conducted using an excavator equipped with a grapple, thumb, or rake attachment, a standard dredge bucket, or an environmental bucket, as appropriate.

B. Large debris shall be removed prior to sediment in each DMU, when necessary, to facilitate handling at the offload site.

3.4 MECHANICAL (INVENTORY) SEDIMENT DREDGING

A. Mechanical (Inventory) Sediment Dredging shall be performed by wet excavation with a dredge equipped with an environmental bucket or other approved bucket. Means and methods shall be provided to move dredged sediments to the offload area.

B. Dredge bucket: An environmental dredging bucket designed to minimize loss of material during the lifting of the bucket through the water column shall be used. Buckets may include a lid, or “thumb” to close the bucket prior to lifting through the water column.

C. Dredge Monitoring Equipment: Dredging equipment shall be equipped with a real-time kinematic global positioning system (RTK-GPS) in conjunction with inclinometers and DREDGEPACK® software manufactured by HYPACK, Inc. (or equivalent) that continuously measures and records the horizontal and vertical position of the bucket in accordance with the following tolerance requirements:
1. Horizontal Tolerance: 3.0 ft.
2. Vertical Tolerance: 0.2 ft.
3. Any new site control points shall be established and be accurate within 0.05 ft horizontally and 0.1 ft vertically as determined by GPS equipment using static observations or by kinematic techniques.
4. New site control points shall be clear of obstacles that may cause GPS multi-path problems or radio signal interference such as fences, buildings, and radio masts to the extent possible.

5. Horizontal positions shall be referenced to Wisconsin State Plan, North Zone (U.S. Feet), NAD83.
6. Elevations shall be referenced to the North American Vertical Datum of 1988 (NAVD88 Geoid 12a).
7. Subcontractor shall demonstrate compliance daily with specified tolerance intervals as directed by Contractor, by calibration with a site benchmark or control point.

D. Mechanical Dredging Productions Rates: Subcontractor shall target dredging production rates of 1,200 cy/day average . This production rate may be modified in the field to account for unforeseen circumstances, changes in schedule, or operational control purposes.

E. Material Barges: Subcontractor shall deploy shallow draft barges to be maintained inside the barrier system to transport dredged material from the area being dredged to the off-loading area. The quantity of barges shall be sufficient to ensure no interruption in production.

F. Barge Dewatering: Decant water from the material barges shall be pumped to a geotextile bag located in the sediment processing tent. Contractor will be responsible for operating and maintaining the geotextile bag, Subcontractor shall be responsible for pump and piping.

3.5 RESIDUAL SEDIMENT DREDGING

A. Residual sediment dredging will be performed as directed by Contractor. Subcontractor, in consultation and with approval of the Contractor, shall select the appropriate dredging method:

1. Mechanical dredging may be used for dense material and will be the same as that specified for inventory dredging (Section 3.4).
2. Hydraulic dredging shall be plain suction or specialty dredge head intended to minimize overdredging and re-suspension, subject to approval of Contractor. Dredged materials will be pumped to the geotube pad, where dewatering will occur by the Contractor via the use of geotextile tubes.

B. Contractor will be responsible for providing, operating, and maintaining the geotextile tubes for dewatering of hydraulically dredged sediments. Subcontractor shall provide pump and piping equipment to deliver dredged material to dewatering area. Pumping requirements for the dewatering operation are provided in Section 3.5 C.

C. Hydraulic Dredging Processing Limits: Subcontractor's means and methods for hydraulic dredging shall be limited to the following flow conditions:
1. Production rate: Not to exceed 10,000 square feet per day unless otherwise directed by Contractor.
2. Flow rate: 1,000 gpm (based on 10-hour 'up-time' operational day) or as directed by Contractor.

3.6 OFFLOAD OF DREDGED MATERIAL

A. The Contractor will manage material from barge offloading to final disposal.

B. Subcontractor will coordinate movement of barges to and from the offloading site so as to not impede dredge production rates and efficient movement of dredged material.

3.7 QUALITY CONTROL

A. Subcontractor Bathymetric Surveys:
   1. Subcontractor to provide the following bathymetric surveys:
      a. Pre-dredge: Establish baseline from which to quantify work.
      b. Post mechanical and hydraulic: Perform to track progress in achieving target elevations.
      c. Post-dredge: Establishes final condition for verification of work and quantities.
   2. All bathymetric surveys will be single-beam with survey grid transects located no further than 25 feet apart. If there are portions of the project area that are not accessible for the marine survey equipment (i.e., water is too shallow), bathymetric measurements may be collected using conventional survey methods (e.g., a survey rod and total station).
   3. Survey data (point files as specified in Section 1.5 D) shall be provided to Contractor. Contractor may independently generate surfaces and volume take-offs as a check on Subcontractor's calculations.
   4. Contractor will audit Subcontractor’s bathymetric survey.

3.8 CLEANUP

A. Upon completion of the Work, pressure-wash all equipment that has handled or made contact with sediments, including, but not limited to the dredge bucket, dredge head, material barges, and material handlers. Wash water shall be appropriately handled and disposed in accordance with Contractor requirements, and material residue (solids) shall be disposed with the stabilized sediments.
   1. Subcontractor may utilize offloading and/or geotube pad for decontamination of equipment in coordination with Contractor operations and requirements.
   2. Subcontractor to provide information regarding planned detergent or cleaning agents including, but not limited to, safety data sheets, for Contractor approval.

B. Cleaning of Sediment from existing Shoreline Bulkhead Wall: Subcontractor shall clean sediment from the existing steel sheet pile bulkhead wall where exposed by dredging operations. Sheet pile is coated with epoxy coating (Fast Clad ® – Brush Grade Epoxy, Sherwin Williams) for protection from biological degradation. For this Work, the following shall apply:
   1. Sediment shall be removed from the sheet pile, as technologically practicable, to the target elevation without damage to the coating.

2. Subcontractor may use high pressure water or scraping with materials not detrimental to the coating to separate the sediment.
3. Any damage caused to the coating by Subcontractor's Work shall be repaired at Subcontractor's expense. Coating and application shall be approved by Contractor.
4. Existing condition of sheet pile coating will be observed following the protocols defined in Section 5.8 of the *Final Design*.

C. Cleaning of Staining from existing Shoreline Bulkhead Wall: In a dry state, the stain on the sheet pile will have a solution of citrus cleaner applied. The citrus cleaner will be allowed to soak and then the stain will be worked with scrapers and/or brushes. Additional application of the citrus cleaner may be necessary during this step. If the stain is thick it may be scraped for gross removal prior to cleaner application. Power washing of the sheet pile will remove the dissolved stain and prepare the sheet pile for coating inspection. All scrapings and liquids resulting from the cleaning operation will be collected in the coffer dam sump and transferred to the Dredge Water Treatment System (DWTS) for treatment.

D. Marine equipment removed from the lake shall be cleaned in accordance with WDNRs' requirements before leaving the site to prevent the spread of viral hemorrhagic septicemia (VHS) and invasive species.

E. Contact the Contractor for inspection and approval of intermediate and final clean-up of equipment and work areas.

END OF SECTION

SECTION 35 53 00

RESTORATIVE LAYER PLACEMENT

PART 1 - GENERAL

1.1 SUMMARY

A. Section Includes:
   1. Placement of restorative layer within dredged and null areas.

1.2 SYSTEM DESCRIPTION

A. Restorative Layer: 6-inch thick layer of clean coarse sand placed within the dredged and null areas. Restorative layer is intended to provide stabilization of the lakebed and suitable habitat for benthic recolonization.

1.3 QUALITY CONTROL

A. Restorative Layer Thickness: Subcontractor shall develop and implement quality control measures for placement of restorative material to required thickness. Plan may include measures such as poling, sounding, or core sampling to ensure material is placed as specified.

PART 2 - PRODUCTS

2.1 RESTORATIVE LAYER MATERIAL (PROVIDED BY CONTRACTOR)

A. Contractor will supply Restorative Layer Material to Subcontractor for placement.

B. Material specifications provided in this Article are intended to provide Subcontractor information needed for planning and execution of the work described in this Section.

C. Restorative layer material shall be coarse sand material free from organic impurities and debris meeting graduation shown in Section 2.1 E.

D. Contractor shall require sand supplier to provide test results to certify the restorative layer material as clean (total polynuclear aromatic hydrocarbon [tPAH] analytical results).

E. Gradation:

Sieve Size	Percent Passing (by Weight)
1.5-inch	100
No. 4	60-100
No. 10	45-85
No. 40	5-25
No. 200	0.5 or less

F. As delivered moisture content (ASTM D2216) of 5% or less.

PART 3 - EXECUTION

3.1 INSTALLATION

A. Approval Prior to Placement: Subcontractor shall coordinate all aspects of placement activities with Contractor and ensure areas to receive restorative layer material have been approved.

B. Placement: Place restorative layer in one 6-inch lift. For side slopes, place material from the toe of the slope upward. Placement technique should minimize disturbance of bed sediments by limiting fall velocity of material.

C. Equipment: Restorative layer material may be placed using the same equipment deployed for mechanical dredging, provided it has been cleaned and decontaminated. Subcontractor may propose alternate placement equipment for approval by Contractor.

3.2 TOLERANCE

A. Restorative Layer Thickness:
1. Minimum: 6 inches
2. Maximum: 9 inches

B. The restorative layer material will be placed to achieve a 6-inch thickness. The placed thickness of the restorative layer at all sampling points shall demonstrate a minimum thickness of 4 inches of the unmixed restorative material. One half of the thickness of any underlying mixed zone (where> 50% of the material is restorative layer material, mixed into pre-existing sediment) may be considered as additional thickness of the placed restorative layer, and used as the total basis of comparison against the specified 6 inch total thickness, up to a maximum 2 inches credited to the restorative layer.

C. Over Placement Penalty: Subcontractor shall pay for transportation and cost of material placed beyond the 9-inch maximum thickness over the entire planned area of

restorative layer placement at a unit price to be determined when the source of restorative layer material has been determined by Contractor. Measurement of thickness will be based on Contractor's restorative layer thickness verification core collection as specified in Section 4.3 of the *Monitoring Plan for Phase 2 Wet Dredge* (*Monitoring Plan*) (FE JV, 2016, which is Appendix C of the *Final Design for Phase 2 Wet Dredge* (FE JV, 2016. Quantity of material will be determined by multiplying thickness of restorative layer beyond 9 inches by the area of the sampling cell as shown on Drawing No. 13. This volume will be converted to tonnage based on a density of 1.3 tons per cubic yard. The basis for the over placement calculation will be the entire planned area of restorative layer placement (floor and sideslopes of dredged and null areas) multiplied by 9 inches.

3.3 FIELD QUALITY CONTROL

A. After the restorative layer is placed, restorative layer verification thickness core collection will be conducted by the Contractor to ensure the 6-inch thickness has been met.

B. Non-Conforming Work: Subcontractor will be required to place additional material within areas determined to be less than 6 inches in thickness as determined through Contractor restorative layer verification thickness core collection.

END OF SECTION

SECTION 44 41 13

DREDGE WATER TREATMENT SYSTEM

PART 1 - GENERAL

1.1 SUMMARY

A. Section Includes:
This Section covers the furnishing of dredge water treatment system equipment. System shall be complete with all equipment shown, including, but not limited to, open top tanks, fixed axle frac tank, pumps, Dissolved Air Flotation (DAF) unit, electric centrifugal pumps, filter press, sand filter, bag filters, granular activated carbon vessels, flow meter, and turbidity meter.

B. The fixed angle frac tanks, pumps, air operated diaphragm pumps, filter press, sand filter, bag filters, granular activated carbon vessels, flow meter, and turbidity meter will be housed in an Allsite structure.

C. Frac tanks and water transfer pumps will be installed on the ground surface.

D. All piping shall be furnished to a quick-disconnect connection outside of the tank or equipment container, from which point the Contractor will make his connections.

E. The following Work is not included:
1. Power supply to all electrical equipment.
2. Control circuit wiring.
3. Water transfer piping between system components outside the system container.
4. All stub-outs for process inlet and effluent piping shall be furnished and set under another division of Work.

1.2 DESIGN DATA

A. The plant design shall meet the following conditions.
1. Design Average Daily Flow: 600 gallons per minute (gpm)
2. Maximum Hourly Flow: 600 gpm
3. Available Power Supply: three phase 480 volts; single phase 240 volt
4. Water influent quality as noted in Section 8 of the *Final Design for Phase 2 Wet* (FE JV, 2016).

B. The plant design shall meet the water effluent quality limits as noted in the *Temporary Water Treatment System Operations, Maintenance, and Monitoring Plan*, which is Appendix P of the *Final Design for Phase 1 Remedial Action* (FE JV, 2015).

C. The plant equipment shall be installed by the Contractor under the direct supervision of the manufacturer.

1.3 QUALITY ASSURANCE

A. It is the intent of these specifications to procure a quality product by an established manufacturer of the latest design. The cost of the equipment shall include all royalties and costs arising from patents and licenses associated with furnishing the specified equipment.

B. All materials shall be designed to withstand stresses encountered in operation, fabrication, and erection.

1.4 PROTECTION, DELIVERY, AND HANDLING

A. Shipment shall be made from the manufacturer in such a way as to prevent damage to any parts of the equipment during shipping and storage.

B. Special handling and storage instructions shall be forwarded in a separate transmittal to insure against damage during long periods of storage.

PART 2 - PRODUCTS

2.1 SCHEDULE OF EQUIPMENT AND MATERIALS

A. The following are the main items of equipment, as noted on the *95% Design for Phase 2 Wet Dredge* Drawings (FE JV, 2016) and Attachment 1 – Equipment Cut Sheets, to be furnished with the package plant.

1. Geotextile tubes
2. Chemical Injection system (tank and pump)
3. DAF unit with sludge collection and AOD pump (2)
4. Filter press with AOD pumps
5. Weir Tank (4)
6. Open-top tanks (3)
7. Fixed Axle Frac Tank (2)
8. 6-inch centrifugal pumps (5)
9. Four-Pod sand filter (2)
10. Dual bag filter system- 1 micron (6 vessels, 12 bag each vessel)
11. Dual Granular activated carbon (GAC) vessels (6); (10,000 lb. GAC each)
12. Flow meter (2)
13. Turbidity meter

2.2 PROCESS PIPING

A. All process piping and fittings shall be 3-inch diameter lay-flat PVC.

PART 3 - EXECUTION

3.1 INSPECTION

A. The equipment installer shall be responsible for the following:
   1. Verify all structural dimensions.
   2. Verify centerline grades of all pipes sleeves and/or pipes passing through walls.

3.2 PERFORMANCE

A. The manufacturer shall furnish shop drawings showing the location and elevation of all inserts, pipe sleeves, anchor plates, and any other appurtenances required for installing the package plant equipment.

B. The equipment manufacturer shall guarantee all equipment free from defects in material and workmanship for one year from start up, and shall replace any component part proven defective during the guarantee period.

3.3 SUPERVISION OF ERECTION, START-UP, AND TRAINING

A. The Contractor will be responsible for supervision of erection, start-up, and operator training. However, the equipment manufacturer's representative must be available by phone and e-mail for technical assistance, as needed.

END OF SECTION

ATTACHMENTS

to

SECTION 44 41 13

DREDGE WATER TREATMENT SYSTEM

PRODUCT DATA SHEET

January, 2007

FLIP TOP WEIR TANK

(VE ENTERPRISES VERSION)

GENERAL INFORMATION

This fixed-axle tank is fitted with two internal weirs and 14 top inspection doors.

WEIGHTS AND MEASURES

» **Capacity:**	20,000 gallons
» **Height:**	8'-6¼" (grade to tank roof) 12'-8½" (grade to top of handrails when up)
» **Width :**	8'-6"
» **Length:**	45'-7½" (tank only), 50'-0" (nose-to-bumper)
» **Weight:**	33,000 lbs.

STRUCTURAL DESIGN

» **Floor:**	¼" ASTM A36 carbon steel. "V" bottom sloping from each side to centerline of tank
» **Sides/Ends:**	¼" ASTM A36 carbon steel, corrugated shape
» **Roof Deck:**	¼" ASTM A36 carbon steel
» **Wall Frame:**	Corrugations only, no internal frame
» **Internal Weirs:**	Two internal steel weirs equally spaced to create three compartments inside tank. Overflow weir (forward weir) extends from floor up to one foot from top of tank. Underflow weir extends down from roof and terminates one foot from floor seam at sidewalls. Designed for 16 lbs. per gallon liquid on one side of weir and no liquid on the other side.

FEATURES

» **Relief Valve:**	None
» **Valves:**	(2) 4" wafer style butterfly valve, Bray series 30 or equivalent, with cast iron body, Buna-N seat and seals, 316 SS stem, Nylon 11 coated ductile iron disk

FEATURES – cont.

» **Fill Line:**	One 3-inch schedule 40 ASTM A106B pipe with cap and securing chain. Line enters front of tank near top with dip tube into first compartment down approx. halfway from bottom of tank where it 90° elbows into compartment.
» **Front Drain:**	One 4" wafer style butterfly valve. Mounted on 150# weld neck flange on tank side and 150# FPT flange on outside with plug and chain.
» **Rear Drain:**	One 4" wafer style butterfly valve. Mounted on 150# weld neck flange on tank side and 150# FPT flange on outside with plug and chain. Remote-operation handle.
» **Rear Process Outlet:**	One (1) 4" flanged and blinded nozzle 18" below roof deck
» **Top Doors:**	14- 51"x39"x10ga plate lids
» **Manways:**	Three (3) 22" diameter, passenger side
» **Manway Seals:**	Buna-N (NBR)
» **Stairway:**	OSHA compliant non-slip stairway with handrails and guardrails
» **Walkway:**	Full length of tank with guardrails on both sides; door handles accessible

SURFACE DETAILS

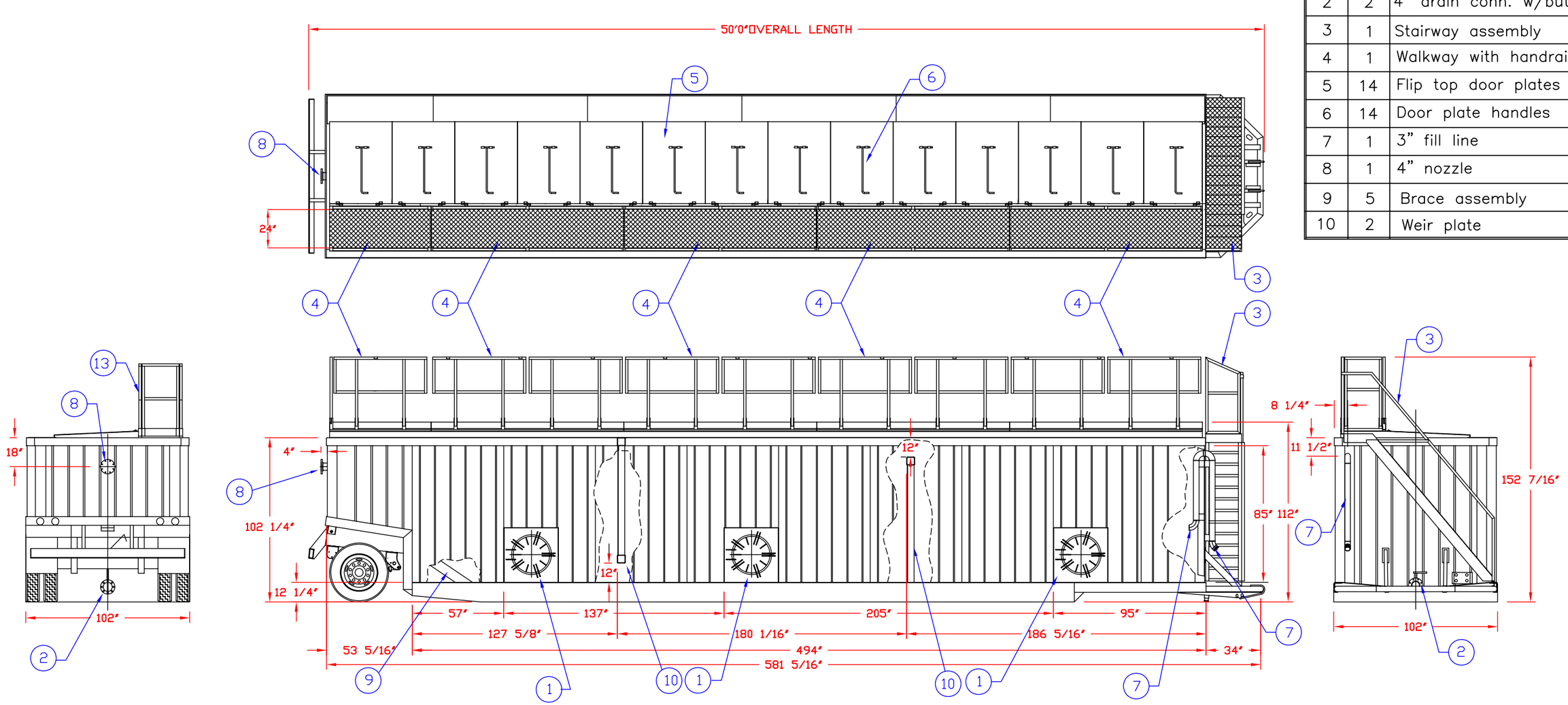
» **Exterior Coating:**	High gloss polyurethane
» **Interior Coating:**	Chemical resistant lining

TESTS/CERTIFICATIONS

» **Test Performed:**	100% water-tested to full capacity by OEM, plus level 1, 2 &3 QMS inspections by Baker Tanks

BAKERCORP™

ITEM	QTY	DESCRIPTION
1	3	22" diameter manway
2	2	4" drain conn. w/butterfly valve
3	1	Stairway assembly
4	1	Walkway with handrail
5	14	Flip top door plates
6	14	Door plate handles
7	1	3" fill line
8	1	4" nozzle
9	5	Brace assembly
10	2	Weir plate



SPECIFICATIONS:
1) Tank Capacity: 20,000 gallons (476 BBL)
2) Tank Weight: 33,000 lbs. (empty)

NOTES:
1. This drawing is a baseline representation for this model of tank. Variations between this drawing and the actual equipment in the field can and do exist, primarily with appurtenance locations, sizes and quantities. Consult your local BakerCorp representative if specific needs exist.
2. THIS TANK IS *NOT DESIGNED FOR TRANSPORTING LIQUIDS*. It should be moved only when empty.
3. Tanks of this type have an internal lining (coating) on the wetted surfaces.
4. This tank is constructed from A36 carbon steel.

REV.	DESCRIPTION	DATE	BY
G			
F			
E			
D			
C			
B			
A	FIXED CUTAWAYS / LINEWEIGHT	7/12/05	Z.E.R

BAKERCORP™ 3020 OLD RANCH PARKWAY SEAL BEACH, CA 90740-2751

SCALE: DO NOT SCALE	SIZE B	ORIGINAL DWG. DATE 16JUL02
DRAWN BY: P.J.B.	APPROVED BY:	CAT/CLASS --
TITLE: VE ENTERPRISES FLIP TOP WEIR TANK		SHEET 1 of 1
DRAWING NO. S-2-M0005-1-		REV. A

PRODUCT DATA SHEET

January, 2007

MODERN FIXED AXLE TANK

(500 BBL ROUND BOTTOM VERSION)

GENERAL INFORMATION

This tank has a smooth interior wall and round bottom for easy cleaning.

WEIGHTS AND MEASURES

» Capacity:	500 BBL (21,000 gallons)
» Height:	10′-8″ (grade to roof plate) 13′-4″ (grade to upright guardrail
» Width :	8′-6″
» Length:	47′-2″ (nose to tail) 42′-11″ (end wall to end wall)
» Weight:	29,000 lbs. (est.)

STRUCTURAL DESIGN

» Floor:	¼″thick ASTM A36 carbon steel round bottom
» Sides/Ends:	¼″ thick ASTM A36 carbon steel
» Top Deck:	¼″ thick ASTM A36 carbon steel
» Wall Frame:	6″ wide channel-shaped steel (on exterior side of walls)
» Roof Frame:	3″ wide x 1½″ tall channel-shaped steel (on exterior side of roof deck)
» Internal Cross Bracing:	None

FEATURES

» Valves:	2-Front &1-Rear: 4″- wafer butterfly valve. Cast iron body, Buna-N seat & seals, 416 SS stem, Nylon 11 coated ductile iron disk w/ plug and chain.
» Relief Valve:	16 oz./in^2 pressure setting, 0.4 oz./in^2 vacuum setting; Buna-N seal
» Front Inlet:	8″ connection, flanged on the inside and outside of the tank
» Front Drain:	4″-150# flanged connection with butterfly valve
» Rear Drain:	4″-150# flanged connection with butterfly valve and remote operation handle

FEATURES – cont.

» Fill Line:	3″ pipe, top of tank, with cap and chain
» Gel Line:	4″ sch. 40 pipe; flanged with butterfly valve
» Top Vapor Connection:	4″-150# weld neck flange with blind flange (chained) and Buna N gasket
» Top Manway:	One - 21½″ I.D. domed lid w/anti-personnel bars, slotted hinges and 5 - ¾″ T or eye bolt with wing nut fasteners, hinged to side of tank. Buna-N (NBR) gasket.
» Front Manway:	One - 21½″ I.D. domed lid, slotted hinges and 5 - ¾″ T or eye bolt with wing nut fasteners,, hinged away from stairs. Buna-N (NBR) gasket.
» Side Manway:	One - 21½″ I.D. domed lid, slotted hinges and 5 - ¾″ T or eye bolt with wing nut fasteners,, mounted on passenger side and hinged to front of tank. Buna-N (NBR) gasket.
» Stairway:	Front-mounted with access from driver's side of tank
» Level Gauge:	Ball style with 2-8″ 304 SS floats. Floor supports hold floats ½″ off floor.
» Tires:	11.00 x 22.5 (nylon tubeless)
» Axles:	25K axle, automatic slack adjusters, top mounted 30 service chambers, outboard drums

SURFACE DETAILS

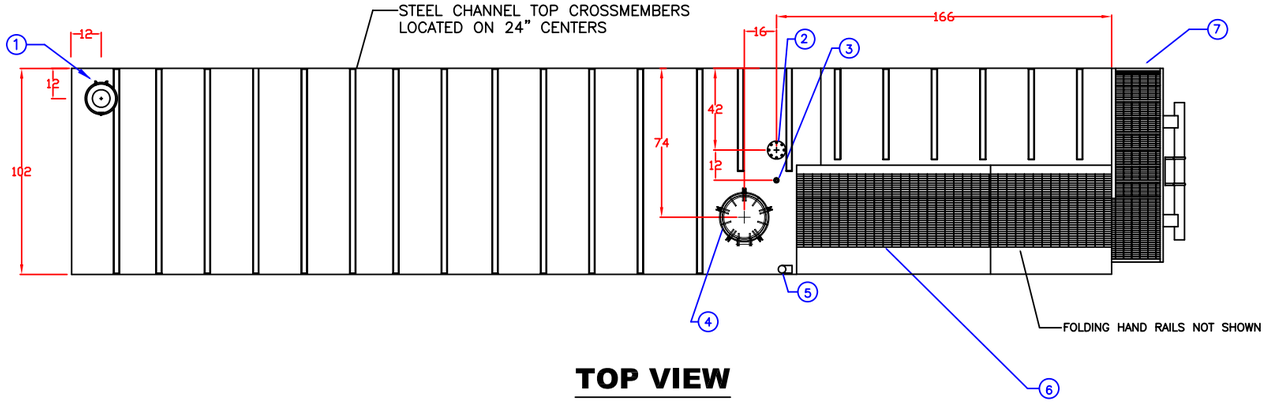
» Exterior Coating:	High gloss polyurethane paint
» Interior Coating:	Chemical resistant lining
» Safety Paint:	Safety yellow – handrails, hatch covers and trip hazard surfaces
» Placard Mounts:	Removable 10-gauge steel, 48″x48″, both sides of tank at top rear. Secured with nylock nuts or bolts with lock washers.

TESTS/CERTIFICATIONS

» Test Performed:	100% water tested to full capacity, 3 psi – 20 min test; Level I, II and III inspections on a scheduled basis

BAKERCORP™

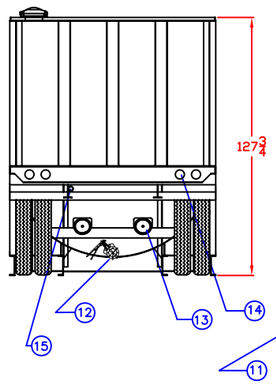
3020 OLD RANCH PARKWAY • SUITE 220 • SEAL BEACH, CA • 562-430-6262



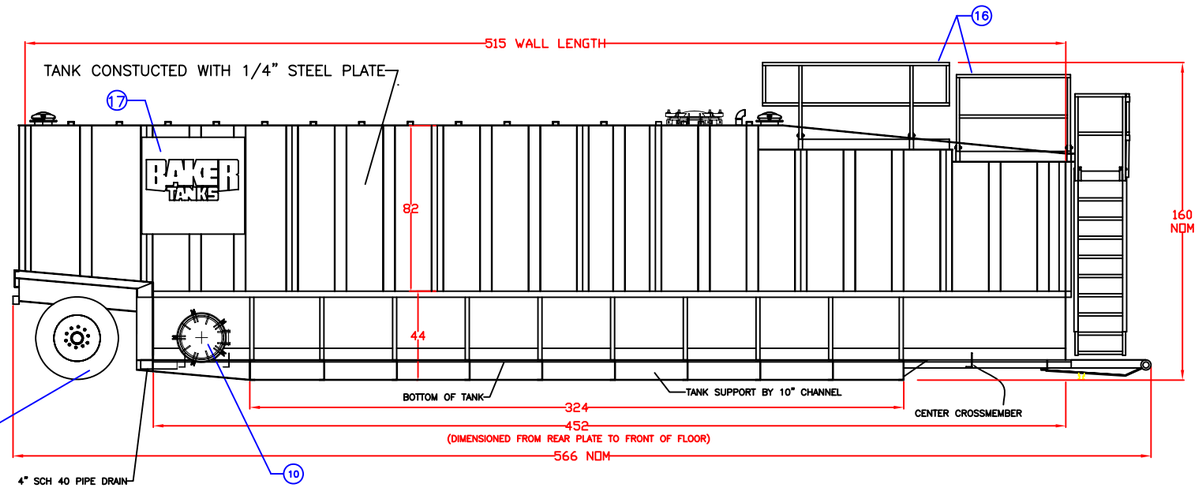
TOP VIEW

1) FLANGE MOUNT BLAYLOCK LL10 P/V VENT 16OZ SETTING, BAKER SPEC
2) 4" FLANGE WITH BLIND CAP AND CHAIN
3) 2" COUPLING WITH PLUG
4) MANWAY WITH INTERNAL BARS, 21 1/2"ID, DOMED LID
5) 3" NIPPLE WITH CAP AND CHAIN
6) SAFETY WALK WAY
7) ACCESS STAIRS
8) LEVEL GAUGE W/2-8" STAINLESS STEEL BALL "Y" SUPPORT HOLDS BALLS 1/2" OFF FLOOR
9) FRONT DRAIN W/VALVE, PLUG, CHAIN
10) MANWAY, 21 1/2"ID, DOMED LID (2)
11) 11.00 X 22.5 TUBLESS TIRE ON 10 HOLE STEEL WHEEL
12) 4" FLANGE, VALVE, THREADED FLANGE, PLUG, CHAIN REMOTE OPERATION HANDLE
13) 25K AXLE, AUTOMATIC SLACK ADJUSTERS, TOP MOUNTED 30 SERVICE CHANBERS, OUTBOARD DRUMS, HUTCH 9700 SUSPENSION, 3 LEAF HIGH ARCH SPRINGS
14) DOT TAIL LIGHTS AND LOWER MARKER LIGHTS, NO TOP LIGHTS
15) 1" X 6" PIPE W/WELDED CAP & THREADED CAP
16) FOLDING HAND RAILS
17) 48x48 BOLTED PLATE (for Baker Decal)

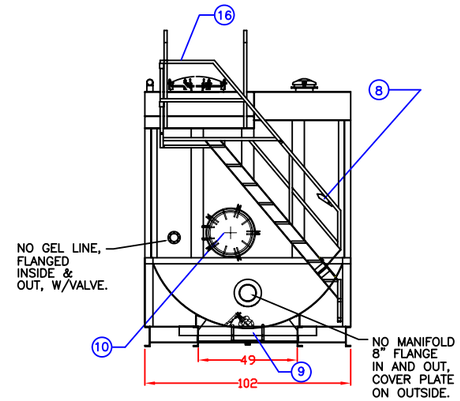
NOTE:
ALL VALVES BRAY SERIES 30, CAST IRON BODY, 416SS STEM, BUNA-N SEAT, NYLON 11 COATED DUCTILE IRON DISC, HANDLES AS SHOWN.
ALL WALL AND ROOF RIBS TO BE CONTINUOUSLY WELDED, ALL TANK SHELL SEAMS TO BE WELDED ON BOTH SIDES.
100% CAPACITY WATER TEST @ 3 PSI
SOME ITEMS MAY NOT BE SHOWN IN ALL VIEWS



REAR VIEW



SIDE VIEW



NOTES:
STAIRS FITTED WITH LOWER 1/2 WIDTH SECTION REMOVABLE TO REPLACE WITH FULL WIDTH STEP OPTION

FRONT VIEW

SPECIFICATIONS:
1) Tank Capacity: 20,100 gallons (500 BBL)
2) Tank Weight: 28,800 lbs. (empty)

NOTES:
1. This drawing is a baseline representation for this model of tank. Variations between this drawing and the actual equipment in the field can and do exist, primarily with appurtenance locations, sizes and quantities. Consult your local BakerCorp representative if specific needs exist.
2. THIS TANK IS *NOT DESIGNED FOR TRANSPORTING LIQUIDS*. It should be moved only when empty.
3. Tanks of this type have an internal lining (coating) on the wetted surfaces.
4. This tank is equipped with a pressure/vacuum relief valve set at 1.0 1bs/sq. in. pressure and 0.4 oz/sq.in. vacuum.

REV.	DESCRIPTION	DATE	BY
G			
F			
E			
D			
C			
B			
A	fixed text	7/12/05	ZER

BAKERCORP™
3020 OLD RANCH PARKWAY
SEAL BEACH, CA 90740-2751

SCALE: Do Not Scale	SIZE B	ORIGINAL DWG. DATE 27SEP04
DRAWN BY: V.A.W.	APPROVED BY: –	CAT/CLASS ––
TITLE: MODERN MFG. ROUND BOTTOM FIXED AXLE TANK – 500BBL		SHEET 1 OF 1
DRAWING NO. S-2-M0006-2-		REV. A

Environmental Treatment Systems, Inc.
4310 McEver Industrial Drive
Acworth, Georgia 30101

RT-100A Rental DAF Specifications

SCOPE OF SUPPLY

1) **Dissolved Air Flotation System**
Environmental Treatment Systems, Inc. (ETS) will supply the RT-100A dissolved air flotation system which includes the following features:

a) Flotation Tank: The unit consists of a rectangular flotation tank constructed of 304 stainless steel plate reinforced with 304 stainless steel tubular vertical wall structural supports. The unit is supported on a stainless steel base consisting of horizontal beams across the width of the unit and a continuous beam structure down both sides of the length of the unit. The base is constructed to allow for easy cleaning around and under the unit. The unit is designed for above-ground positioning on a suitable concrete pad or steel frame and is constructed for indoor or outdoor conditions.

b) Contact Chamber: Influent wastewater enters the DAF unit through a flanged influent header into the contact chamber. The recycle (whitewater) stream is mixed with the influent through a series of injection ports in the contact chamber and the influent header. The contact chamber serves as an internal weir which provides even distribution and mixing of the process flow across the width of the unit. The contact chamber has two cutouts in the bottom to allow settled solids to drain to the bottom of the DAF.

c) Float Removal System: The unit is equipped with a chain and flight top float (skimmings) removal system driven by a low speed, gear reducer with motor assembly. The float material is removed in a con-current direction. This design involves moving the float bed on the surface down the length of the unit in the direction of flow and allows for longer float residence time prior to removal, resulting in drier float material.

i) The top skimmer system consists of double strands of 304 stainless steel double pitch roller chain, supported by UHMW shoes on stainless steel guide angles. The chain supports adjustable skimmer blades retained on 304 stainless steel angle plates with stainless steel fasteners. The skimmer blades are spaced approximately every 3-5 ft. along the chain length. The chain system operates on single duty, stainless steel sprockets mounted on stainless steel shafts turning in adjustable bearing supports. The correct chain tension is indicated by a chain tensioning indication system that shows when the chain tension requires adjustment. The system is driven by a geardrive with TEFC motor through a chain and sprocket system. Adjustable timer controls in control panel provide for intermittent skimmer operation which allows for flexibility in the removal of float material from the unit.

ii) On the effluent end, the skimmer pulls the collected surface material (float) up a curved beach and into an internal float hopper. The beach is curved to allow for efficient removal of float material by the skimmer wiper. The internal float hopper is sized to allow intermediate storage of the material prior to discharge through a flanged nozzle for pumping to storage for dewatering or transport.

d) Settled Solids Removal System: Full-length sloped side walls channel settleable material to a trough in the bottom of the tank for removal by an auger system pulling the material towards the influent end of the unit (counter-current). The counter-current design removes settled material quickly from the unit at the opposite end from the treated water discharge. The material is discharged through a flanged nozzle located in the influent end of the unit base. The auger system consists of a 6" diameter, 6" pitch 304 stainless steel auger in the trough located in the V-shaped bottom of the unit. The auger extends the full length of the DAF. The system is driven by a heavy duty gear drive assembly connected to a 0.25hp/460V/TEFC motor with a shear coupling for overload protection. Adjustable timer controls in control panel provide for intermittent auger operation which allows for flexibility in the removal of settled material from the unit.

Environmental Treatment Systems, Inc.
4310 McEver Industrial Drive
Acworth, Georgia 30101

RT-100A Rental DAF Specifications

e) Effluent Discharge: At the effluent end, a vertical baffle directs the clarified effluent up into a header box and through an adjustable weir system. The weirs are adjustable to determine the optimum liquid level in the unit and are designed to provide minimum fluctuation of the tank liquid level with the variation of influent flow. Clarified effluent overflowing the weirs collects in an internal trough and is discharged through a flanged nozzle.

f) Recirculation (Whitewater) System: The recirculation system is designed to saturate, under pressure, a clarified effluent stream with air to create a dissolved air solution or whitewater. When the whitewater stream is introduced into the contact chamber of the DAF unit, fine, micro-bubbles are released to make contact with flocculated contaminants which rise to the surface within the flotation tank for removal.

   i) Clarified wastewater from the effluent discharge is recycled through the unit by a HELLBENDER™ DAF pump designed to operate at pressures in excess of 85 psi. The pump features a 316 stainless steel casing and impeller, stainless steel shaft, mechanical seal with seal flush, and a premium efficiency 460 V/3 ph/60 Hz/TEFC motor.

   ii) Air is supplied into the recycle stream via an eductor loop from the discharge of the pump to the pump intake, drawing in ambient air and forcing it into solution with the recycle stream under pressure from the pump. This makes an outside compressed air supply unnecessary; however, compressed air can be added through this system. Air flow into the pump is regulated by an air rotameter with a needle valve. All recirculation piping is Sch. 80 CPVC and 304SS.

   iii) The recycle stream is routed through an Air Dissolving Pipe (ADP) that provides additional hydraulic retention time under pressure and allows the separation and removal of large, undissolved air bubbles. The ADP is a vertical section of stainless steel pipe in the recycle piping system that is equipped with a bottom valve for draining and servicing. Liquid level in the ADP is automatically maintained by an air release valve with an in-line equalizer.

   iv) Discharge pressure from the recycle pump and the ADP is controlled by a series of whitewater injection points into the contact chamber and influent header through stainless steel ball valves. A mid-tank injection system provides the option of adding whitewater into the flotation cell just downstream of the contact chamber. A liquid filled pressure gauge is provided for monitoring recycle pressurization performance.

   v) The recirculation pump, ADP, and all recirculation piping are mounted to the flotation tank.

g) Paint and Coatings: All motors, pumps, drives, control panels, and valves are shipped with the manufacturer's standard coatings.

h) Special Conditions: Refer to the body of the proposal for any changes to the specifications of this system. These Special Conditions take precedence over the general specifications in this section.

Environmental Treatment Systems, Inc.
4310 McEver Industrial Drive
Acworth, Georgia 30101

RT-100A Rental DAF Specifications

SPECIFICATION SUMMARY SHEET
DAF MODEL RT-100A Rental (with Integral Floctube)

Dimensions, Weights, and Capacities

Length, overall[2]	20'-7"	Nominal water volume	2,400 gallons
Width, overall[2]	8'-5"	Float hopper capacity	170 gallons
Height, overall[2]	8'-2"	Empty weight	8,000 lb
Min water elevation	5'-7"	Operating weight	31,400 lb
Max water elevation	6'-0"	Tank materials	Type 304 stainless steel
Active surface area	101 ft^2	Base materials	Type 304 stainless steel

Recirculation System

Recycle pump HP	15 HP	Air flow rate	54 – 72 scfh[1]
Recycle pump model	Hellbender HB-90	Air Dissolving Pipe volume	33 gallons
Recycle flow (nominal)	90 gpm	Recycle pressure	90 – 100 psig

Float Removal System

Direction	With flow	Splash and drive guards	304 SS
Skimmer drive HP	0.5 HP	Chain	2060 304 SS roller chain
Skimmer speed	4.6 – 12.2 ft/min	Skimmer shafts	2" Φ, 303 SS
Speed Control	VFD	Skimmer blade construction	Formed 304 SS flights w/ UHMW/PVC wipers

Settled Solids Removal System

Direction	Against flow	Auger diameter	6"
Auger drive HP	0.25 HP	Auger pitch	6"
Auger speed	3.6 ft/min	Auger construction	304 SS

Piping Connections and Specifications

Influent connection	8" 150# flange	Recirculation piping	3" Sch 80 CPVC
Effluent connection	8" 150# flange	Air Dissolving Pipe Drain	1½" FPT Ball Valve
Float discharge	6" 150# flange	Air Dissolving Pipe	12" Φ x 60" ht, 304 SS
Settled solids discharge	4" 150# flange	Effluent weirs	(4) 8" Φ, 5" adjustment

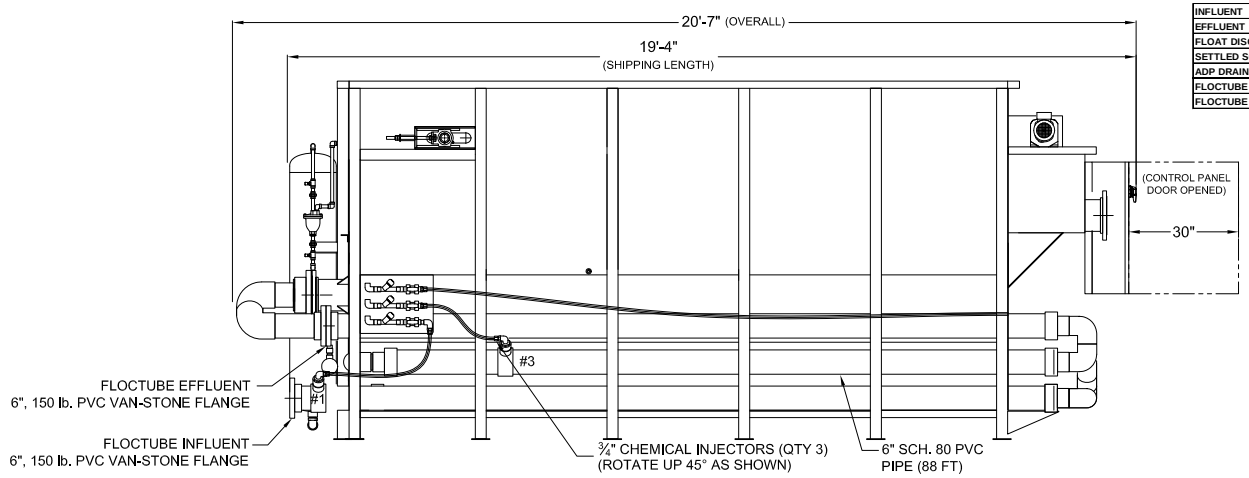
Control Panel

Enclosure	304SS NEMA 4X	Location	Mounted on DAF (effluent end)
Power	460V/3ph/60Hz/60A	Installation	Pre-wired to DAF

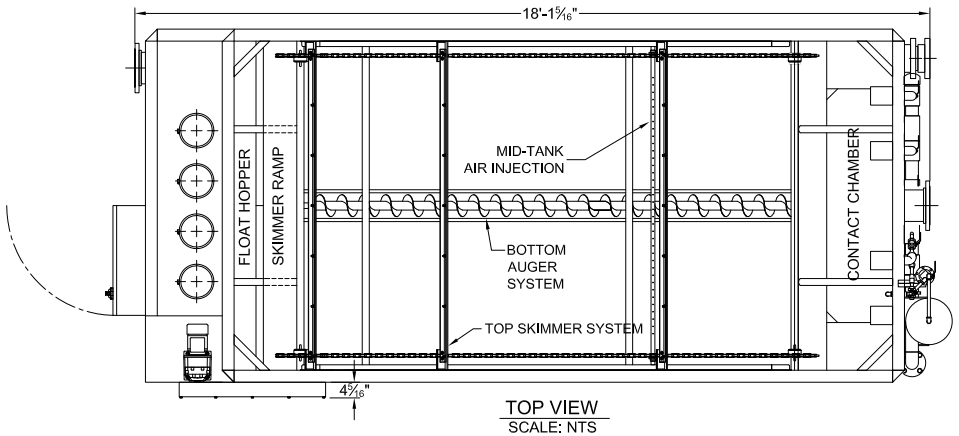
[1] Air flow rate using ambient air eduction.
[2] Values rounded up to nearest inch.

PIPING CONNECTIONS (RT-100 w/ Integral FT-64 Floctube)	
INFLUENT	8" ASME 150 lb. FLANGE - PRE-PIPED TO FLOCTUBE
EFFLUENT	8" ASME 150 lb. FLANGE - PIPE AS REQUIRED
FLOAT DISCHARGE	6" ASME 150 lb. FLANGE - PIPE AS REQUIRED
SETTLED SOLIDS DISCHARGE	4" ASME 150 lb. FLANGE - VALVE INDEPENDENTLY AND PIPE TO TRENCH (FLOOR) DRAINS
ADP DRAIN	1¼" FPT BALL VALVE - NO CONNECTION REQUIRED
FLOCTUBE INFLUENT	6" ASME 150 LB. FLANGE - PIPE AS REQUIRED
FLOCTUBE EFFLUENT	6" ASME 150 LB. FLANGE - PRE-PIPED TO DAF INFLUENT

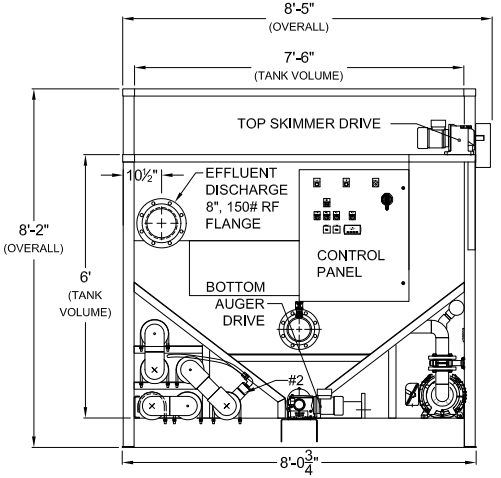
TANK DATA (RT-100 w/ Integral FT-64 Floctube)	
TOTAL WEIGHT EMPTY (APPROX.)	8,000 LBS.
TOTAL WEIGHT FULL (MAX. OPERATING LEVEL)	31,400 LBS.
TOTAL VOLUME (OPERATING LEVEL)	2,400 GALLONS
CONTACT CHAMBER CAPACITY	250 GALLONS
FLOAT HOPPER CAPACITY	170 GALLONS



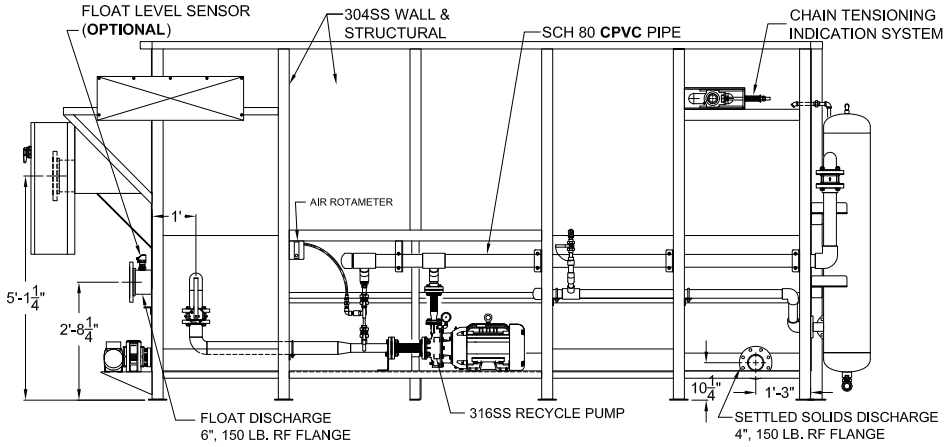
RIGHT SIDE VIEW
SCALE: NTS



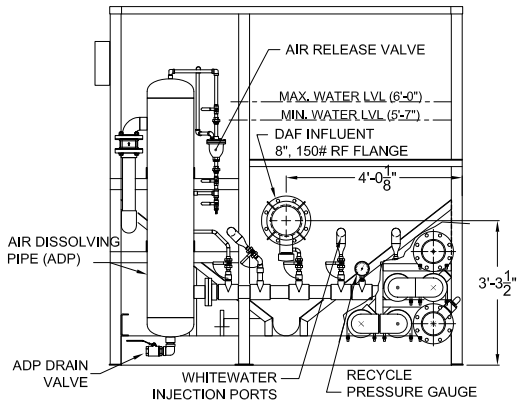
TOP VIEW
SCALE: NTS



REAR VIEW
SCALE: NTS



LEFT SIDE VIEW
SCALE: NTS



FRONT VIEW
SCALE: NTS

Title: RT-100LA DAF W/ FT64-XM FLOCTUBE & PANEL OVERVIEW DRAWING

Project: ENVIRONMENTAL TREATMENT SYSTEMS ACWORTH, GA

Drwn By: PK/DY
Apprvd By:
Date: 5/24/2012
File: rt100a-rental-1_CP
Sheet No. 1 of 1

ENVIRONMENTAL TREATMENT SYSTEMS INC.
4310 McEver Industrial Drive
Acworth, GA 30101
TEL. (770) 384-0602
FAX (770) 384-0603

Rev. | Description | Date | By

Size: ANSI A

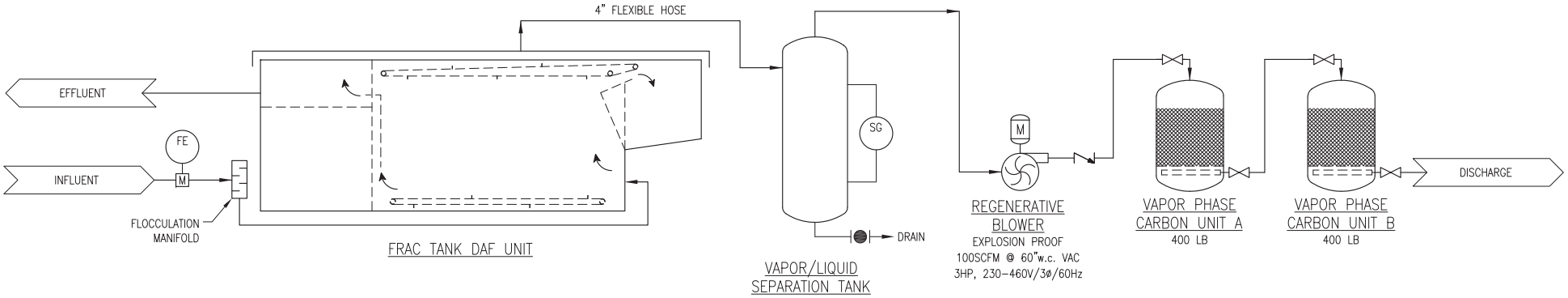
DAF Off-gas Emissions Treatment System

The open top of the dissolved air flotation (DAF) unit will be enclosed with a tarp and plywood cover system and secured. The DAF headspace will be ventilated using an explosion-proof blower moving approximately 150 CFM air flow. Air flow will be routed through a knock-out box to remove entrained water droplets, and subsequently through two vapor phase granular activated carbon (GAC) adsorbers in series. Any residual amounts of Volatile Organic Compounds (VOCs), Semi-volatile Organic Compounds (SVOCs) and odiferous compounds in the ventilated DAF air will be removed by the vapor phase GAC. These GAC adsorbers will be located outside the STWTS building. The exhaust of the treated air stream will be vented to the atmosphere through a PVC stack.

The system is comprised of the following:

- Tarp and plywood DAF cover system
- One (1) steel knock out tank
- One (1) electric blower with local on/off control panel
- Two (2) 400-lb drum type, vapor phase carbon adsorbers
- One (1) PVC effluent stack terminating 10 feet above grade
- Interconnecting fittings and suction hoses

More details about the vapor phase treatment system including a Process Flow Diagram, blower specification and GAC vapor phase drum specification follow.



NO.	REVISIONS	BY	DATE
A	PRELIMINARY DESIGN	MSM	01/28/16

CUSTOMER:

SITE:

TITLE: FLOW DIAGRAM
FRAC TANK
DAF UNIT

SCALE: NTS	APPROVED BY:	DRAWN BY: MSM
DATE: 01/28/16		

GWTT
Ground/Water Treatment & Technology, LLC
627 MOUNT HOPE ROAD - WHARTON, NJ 07885
PHONE: 973-983-0901 - FAX: 973-983-0903
www.gwttllc.com

DWG SIZE: A	SHEET: 1 OF 1	DRAWING NO.: XX-XXXXXX-XXXXX	X

EN 606
Explosion-Proof Regenerative Blower

FEATURES

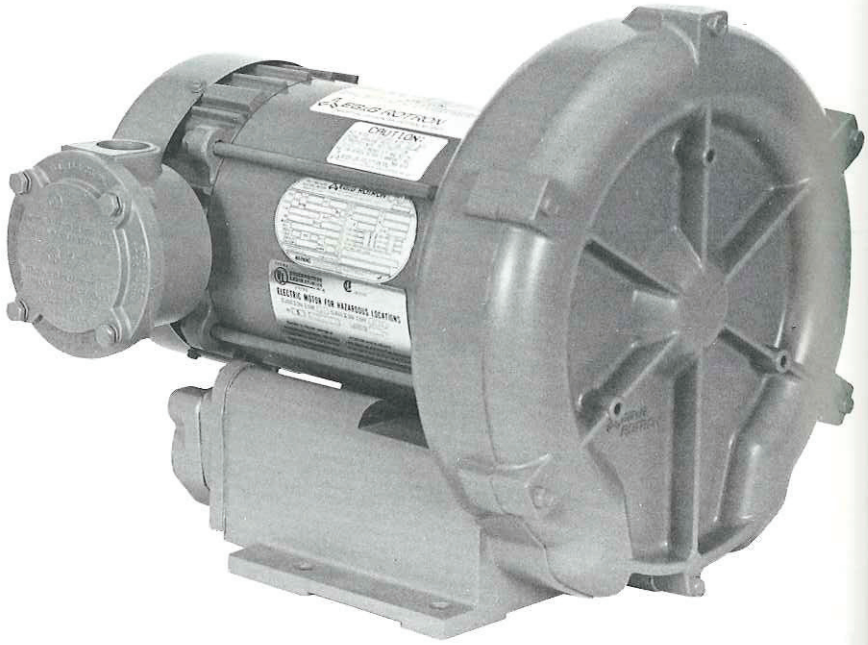
- Manufactured in the USA
- Maximum flow: 200 SCFM
- Maximum pressure: 75″ WG
- Maximum vacuum: 75″ WG
- Standard motor: 3.0 HP
- Blower construction — cast aluminum housing, cover, impeller & manifold; cast iron flanges
- UL & CSA approved motors for Class I, Group D atmospheres
- Sealed blower assembly
- Quiet operation within OSHA standards

OPTIONS

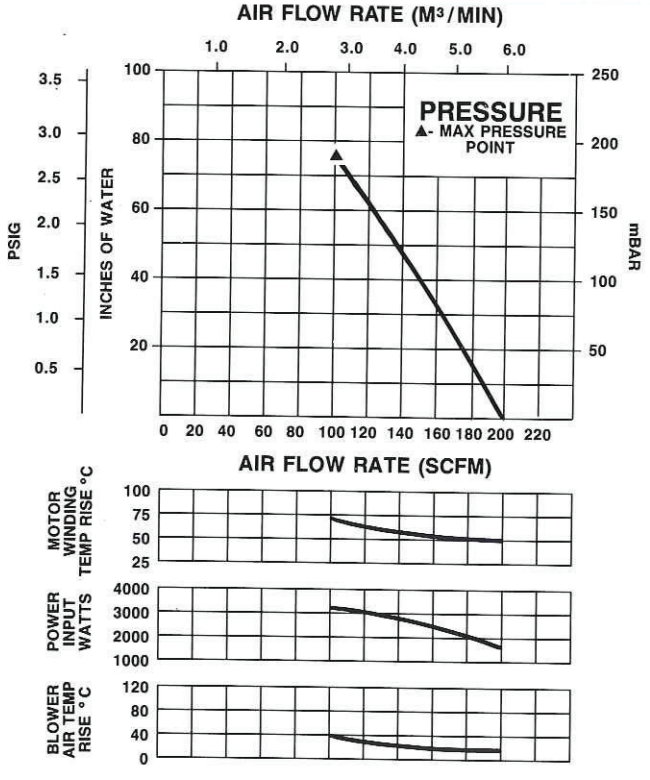
- TEFC motors
- 50 Hz motors
- International voltages
- Other HP motors
- Corrosion resistant surface treatments
- Remote drive (motorless) models

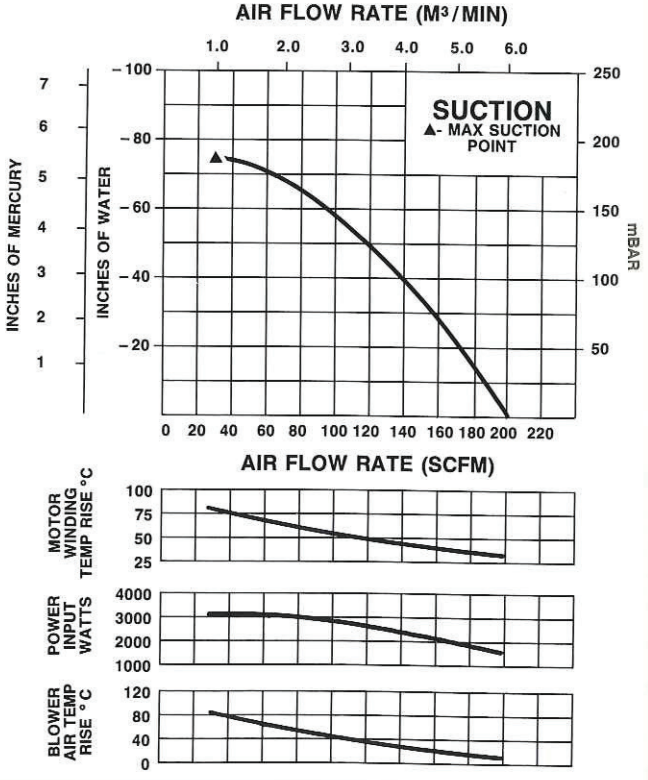
ACCESSORIES

- Moisture separators
- Explosion-proof motor starters
- Inline & inlet filters
- Vacuum & pressure gauges
- Relief valves
- External mufflers



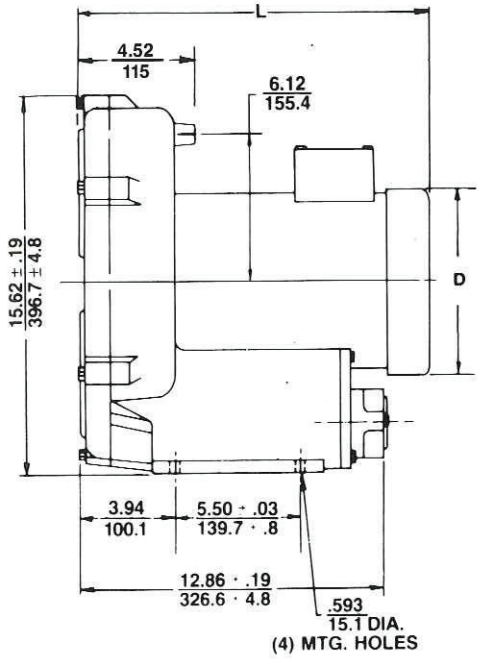
BLOWER PERFORMANCE AT STANDARD CONDITIONS

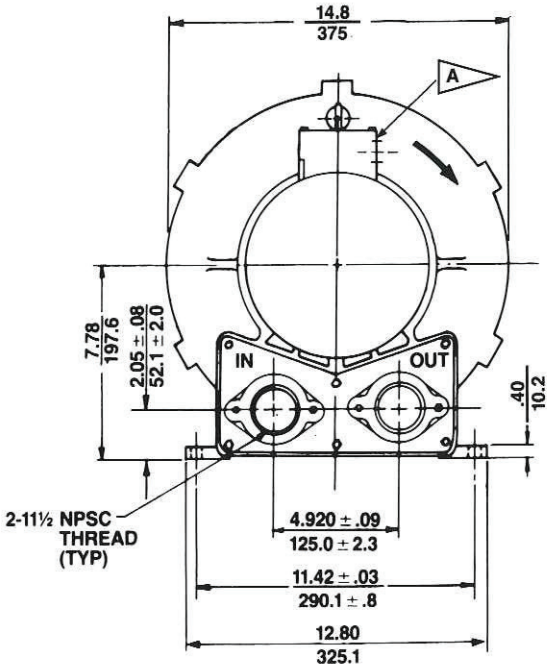




EG&G ROTRON, SAUGERTIES, N.Y. 12477 • 914/246-3401 • FAX 914/246-3802

EN 606
Explosion-Proof Regenerative Blower





DIMENSIONS: IN / MM
TOLERANCES: .XX ± .1 / 2.5
(UNLESS OTHERWISE NOTED)

MODEL	L (IN) ± .3	L (MM) ± 8	D (IN) ± .1	D (MM) ± 3
EN606M72L	17.7	456	7.2	182
EN606M5L	19.9	505	8.5	216

A 0.75" NPT CONDUIT CONNECTION

SPECIFICATIONS

MODEL	EN606M5L	EN606M72L		EN606M86L
Part No.	038222	038179		038437
Motor Enclosure Type	Explosion-proof	Explosion-proof		Explosion-proof
Horsepower	3.0	3.0		3.0
Phase — Frequency	Single — 60 Hz	Three - 60 Hz		Three - 60 Hz
Voltage [1]	208-230	230	460	575
Motor Nameplate Amps	15.5-14.5	7.4	3.7	3.0
Maximum Blower Amps [3]	18.1-16.7	7.6	3.8	3.1
Inrush Amps	94-88	65	32.5	26
Starter Size	1	0	0	0
Service Factor	1.0	1.0		1.0
Thermal Protection [2]	Pilot Duty	Pilot Duty		Pilot Duty
Bearing Type	Sealed, Ball	Sealed, Ball		Sealed, Ball
Shipping Weight	130 lb (59 kg)	106 lb (48 kg)		106 lb (48 kg)

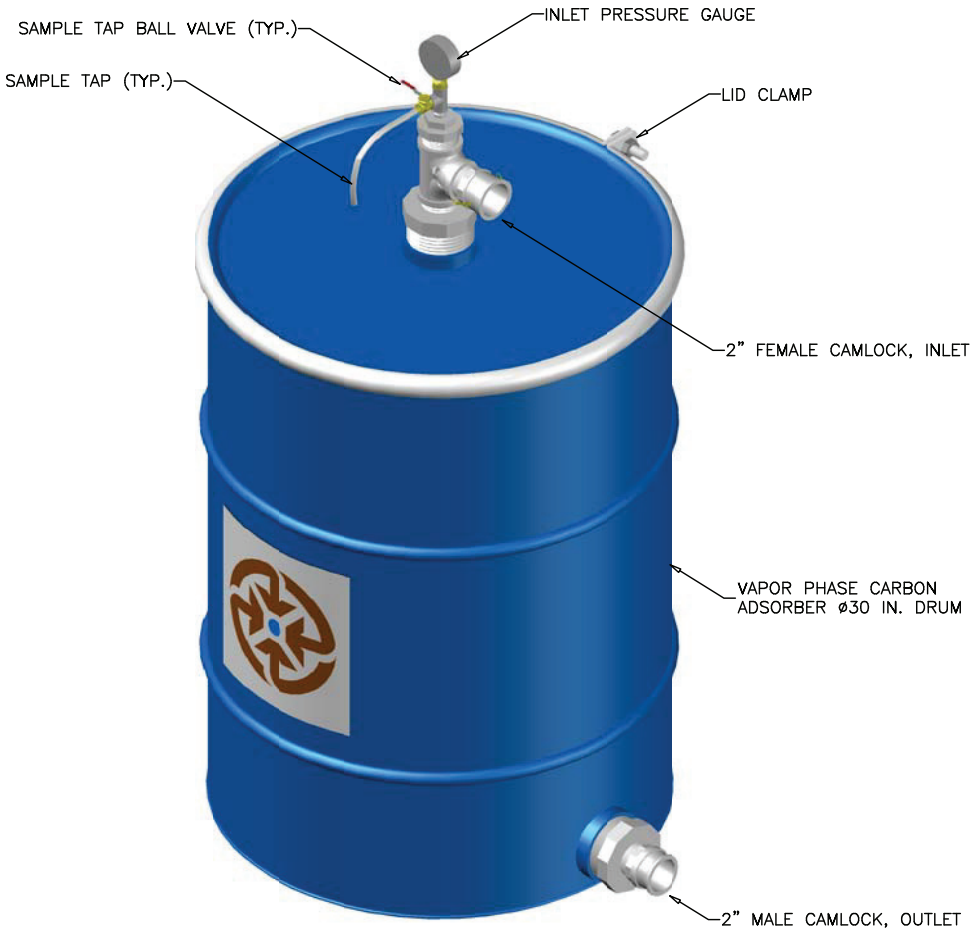
BLOWER LIMITATIONS

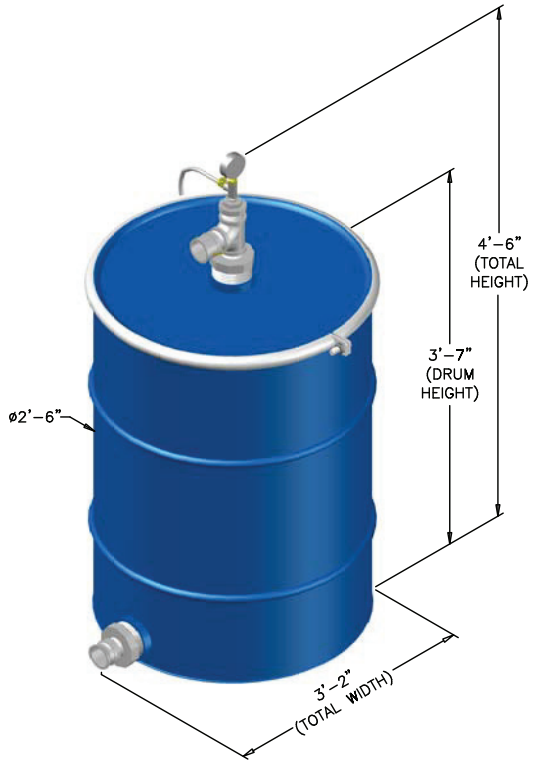
Min. Flow @ Max. Suction	30 SCFM @ –75" WG	30 SCFM @ –75" WG	30 SCFM @ –75" WG
Min. Flow @ Max. Pressure	105 SCFM @ 75" WG	105 SCFM @ 75" WG	105 SCFM @ 75" WG

[1]All dual voltage 3 phase motors are factory tested and certified to operate on 200-230/400-460 VAC-3 ph-60 Hz. All dual voltage 1 phase motors are factory tested and certified to operate on 110-120/200-230 VAC-1 ph-60 Hz.
[2]Maximum operating temperatures: Motor winding temperature (winding rise plus ambient) should not exceed 140°C for Class F insulation or 120°C for Class B insulation. Blower outlet air temperature should not exceed 140°C (air temperature rise plus ambient).
[3]Corresponds to the performance point at which the blower and/or motor temperature rise reaches the limit of the thermal protection in the motor.

Specifications subject to change without notice. Please contact factory for specification updates.

T:\Cad Files\Rentals - STANDARD DRAWINGS\EQUIPMENT SPECIFICATION\VAPOR PHASE ADSORBERS\ST-0076-SPC Rev-A 400 Vapor Phase Carbon Adsorber.





NOTE: THIS DRAWING DEPICTS A "TYPICAL" SKID. ACTUAL DETAILS AND DIMENSIONS MAY VARY.

400 POUNDS CARBON ADSORBER SPECIFICATIONS

– CARBON FILL:	400 Lbs.
– MAX. OPERATING PRESSURE:	3 PSI
– MAX. FLOW RATE:	300 CFM
– HOUSING CONSTRUCTION:	CARBON STEEL
– INLET CONNECTION:	2" FEMALE CAMLOCK
– OUTLET CONNECTION:	2" MALE CAMLOCK
– DRAIN:	NONE
– CARBON FILL VOLUME:	14 Cu.ft.
– CARBON ADSORBER WEIGHT	
EMPTY:	500 Lbs.
SHIPPING (W/CARBON):	900 Lbs.
OPERATING:	900 Lbs.

NO.	REVISIONS	DATE
A	TYPICAL	03/09/09

400 Lb. CARBON ADSORBER STANDARD EQUIPMENT SPECIFICATION

SCALE: NTS	APPROVED BY: JB	DRAWN BY: AAV	
DATE: 03/09/09			

GROUND/WATER TREATMENT & TECHNOLOGY
P.O. BOX 1174
DENVILLE, NJ 07834

DWG SIZE: A	SHEET: 1 OF 1	DRAWING NUMBER: ST-0076-SPC	A

PRODUCT DATA SHEET

January, 2007

YARDNEY 4-POD SAND FILTER

(Equip. # SFL21988 and earlier)

GENERAL INFORMATION

Skid mounted high rate automatic backwashing sand media filter (4 tanks (pods)) designed for general-purpose water filtration of organic and inorganic solids (Yardney Model # IL5424-4AS2). Powered by 110 V external power supply, or battery with solar cell recharge for remote operation.

WEIGHTS AND MEASURES

» **Capacity:**	504 – 756 gpm (Normal flow range) 1000 gpm (Peak flow)
» **Design Press:**	80 psi maximum
» **Temperature:**	Limit to ambient. Consult BakerCorp if temperature exceeds 100 degrees.
» **Filtration:**	To 50 microns
» **Height:**	8'-11" (overall)
» **Width :**	6'-3"
» **Length:**	20'-1"
» **Weight:**	6,326 lbs. – equipment only 14,500 lbs. – media only 28,000 lbs. - operational
» **Backflush:**	240 gpm, automatic

OPERATING REQUIREMENTS

» **Compressed Air:**	5 cfm minimum at 60 psi **[Note: external air supply required]**
» **Sand Media:**	Crushed silica, 0.47MM (#80 grit)
» **Gravel Media:**	#3 crushed rock, ½" x ¾"
» **Input Power:**	Selectable input power of customer supplied 110 V AC, or 12V DC from a unit mounted solar package.
» **Output Power:**	12V DC

FEATURES

» **System Controller:**	Automatic Filter Controller. Flush activation based on elapsed time and/or pressure differential.
» **Piping:**	Inlet & outlet pipe is 6" A53B, 3/16" wall; weld fittings are A234; flanges are A106. Backflush piping is 4" schedule 40 PVC.
» **Solar Panel:**	Uni-Solar Model UA-5 (5 watts) module.

FEATURES – con't

» **Press. Gauge:**	2" face, ¼" NPT bottom connection, stainless steel case, plexiglass lens, brass bourdon tube, 0-100 psi range.
» **Flowmeter:**	Six-inch propeller type meter, AWWA C704-92 compliant. Instantaneous flowrate indicator and six-digit totalizer. Accuracy is ±2% of reading. Repeatability of 0.25%. Rated at 90-1200 gpm, 150 psi, 160°F. Tube: epoxy-coated carbon steel; Impeller: high-impact plastic.
» **Butterfly Valves:**	Effluent / Influent: 6" with cast iron body (epoxy coated), EPDM seat, 304 SS stem and aluminum bronze disc. Tank Isolation: 4" grooved ends, EPDM disc coating
» **Ball Valves:**	Four-inch, bronze body and brass ball; seat is carbon/glass-filled PTFE. ¼ turn open or close.
» **Solenoid Valve:**	12V DC, normally closed type 7121V (energizing opens valve).
» **Differential Press. Switch:**	0-30 psid. Two-inch dial, plated steel case, ±3% accuracy.
» **Air / Vacuum Release Valve:**	2" Bernard Model 4415 valve, mounted on backwash, influent and effluent lines
» **Battery:**	Sealed rechargeable lead-acid, 12V, NP2.6-12
» **Battery Charger:**	Power-Sonic Model PSC-12500A, 12 volts.
» **Tubing:**	Pressurized – ¼" 304 ss w/ Hoke fittings; Drain - ¼" polypropylene; Vent – schedule 80 PVC

SURFACE DETAILS

» **Interior Coating:**	3M Skotchkote 134
» **Exterior Coating:**	High Gloss Polyurethane

TESTS/CERTIFICATIONS

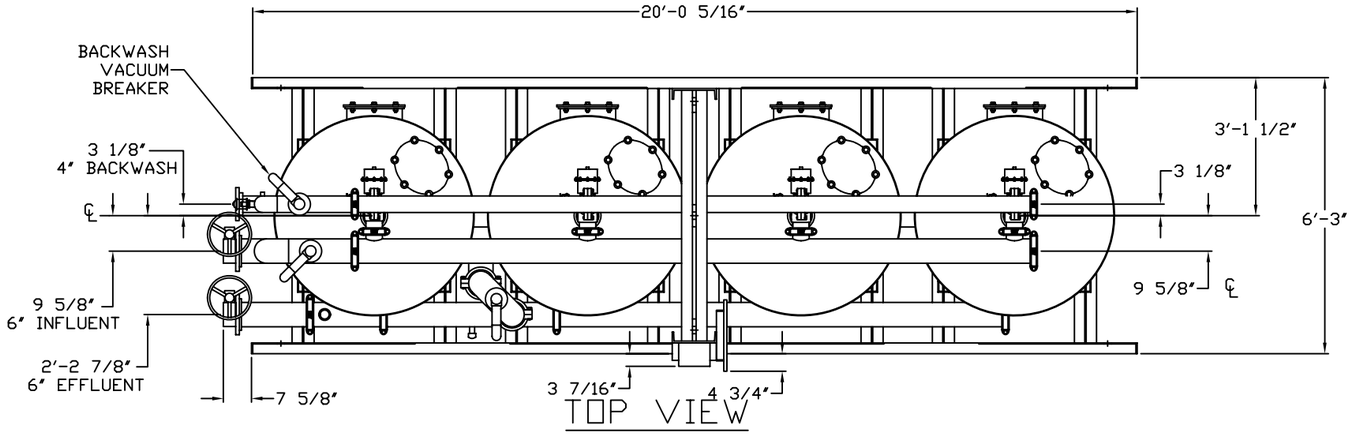
» **Tests Performed:**	OEM pressure tested. BakerCorp performs scheduled QMS inspections.

BAKERCORP™

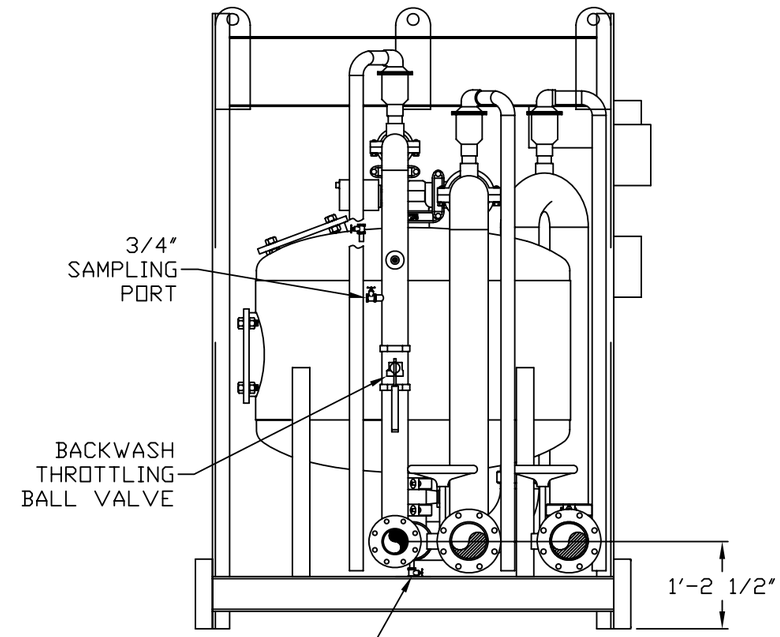
3020 Old Ranch Parkway • Suite 220 • Seal Beach, CA • 562-430-6262

NOTES:

1. This drawing is a baseline representation for this size skid. Variations between this drawing and the actual equipment in the field may exist, primarily with appurtenance locations. Consult your local BakerCorp representative if specific needs exist.

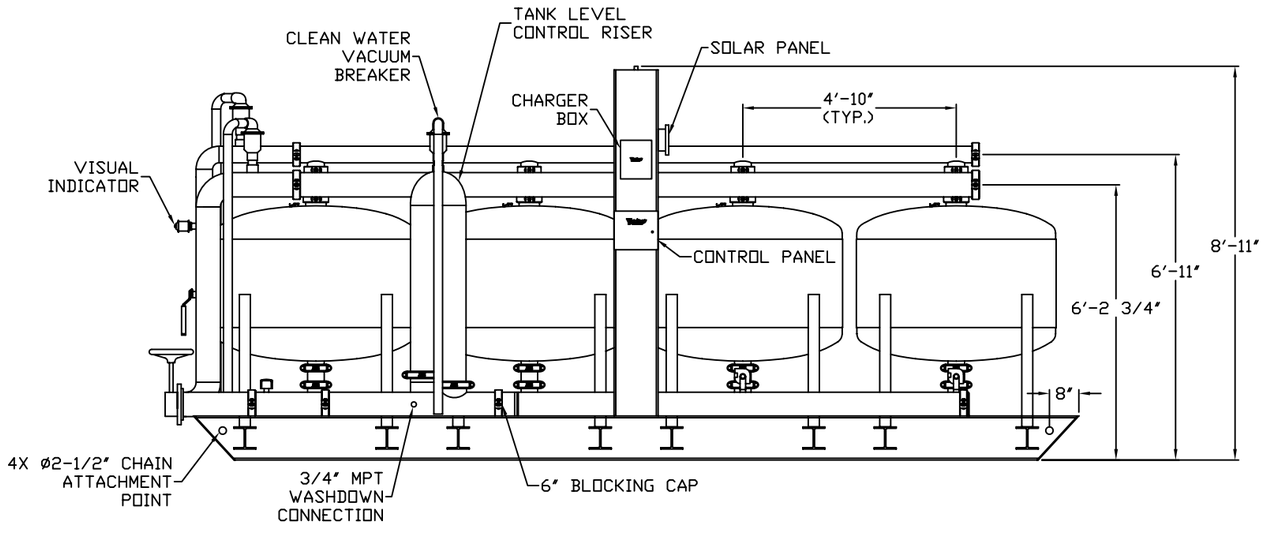


TOP VIEW



END VIEW

MODEL IL54244AS2 (B)



SIDE VIEW

NOTES:

1. FLOW RATE DESIGN - 1000 GPM
2. MAXIMUM WORKING PRESSURE - 80 PSI .
3. ELECTRICAL:
   - CONTROLLER 120V / SOLAR
4. WEIGHT (APPROX.)
   A. EQUIPMENT - 6,326 LBS.
   B. MEDIA - 14,500 LBS.
   C. OPERATION - 28,000 LBS.
   D. DRAINED & WET - 23,800 LBS.
5. BACKWASH RATE: 15 GPM/FT^2 - 240 GPM.
6. SOLAR PACKAGE.
7. HYDRAULICALLY ACTIVATED VALVES. W/ SS TUBE
8. STEEL CONDUIT
9. TUBE TANK VENT VALVES TO GROUND

REV.	DESCRIPTION	DATE	BY
G			
F			
E			
D			
C			
B	Changed drawing title and model number	4/17/05	PJB
A	Added note	6/13/03	PJB

BAKERCORP™ 3020 OLD RANCH PARKWAY SEAL BEACH, CA 90740-2751

SCALE: Do Not Scale	SIZE B	ORIGINAL DWG. DATE 06SEP02
DRAWN BY: P.J.B.	APPROVED BY: –	CAT/CLASS ––
TITLE: YARDNEY 4–POD SAND FILTER (Equipment No. SFL21988 and lower)		SHEET 1 OF 1
DRAWING NO. S-9-M0005-1-		REV. B

PRODUCT DATA SHEET

March, 2008

8" 304 STAINLESS STEEL 12-BAG FILTER SYSTEM

GENERAL INFORMATION

Single vessel mounted on a forkliftable skid. Housing is not ASME code stamped. Different filter elements are available depending on job requirements and should be specified by the customer prior to use.

WEIGHTS AND MEASURES

» **Capacity*:**	1200 – 2000 gpm (@ 1 micron and up)
» **Design Press:**	150 psig
» **Design Temp:**	225°F max. (gasket dependent)
» **Height:**	7'-5" (overall)
» **Width:**	4'-11"
» **Depth:**	7'-5"
» **Weight (dry):**	1075 lbs. (approx.)

*Capacity (flowrate) depends on factors such as liquid viscosity, micron value of the filter media, solids loading etc. Assuming water as a filtrate and factoring in pressure drop only, 2000 gpm is a practical upper limit for a size #2 bag with a 100 micron rating; 1200 gpm with 1-micron rated bags.. Clean pressure drop would be 2-3 psi. Lowering the micron rating increases the pressure drop. The minimum pressure drop for this unit at higher micron ratings is 1-2 psi. Filter bags should be changed out at 15-18 psid, or earlier if the process requires it.

SKID DESIGN

» **Skid:**	2"x2"x0.25" A36 c.s. structural tubing
» **Vessel Leg Supports:**	3x3x.375 angle, SA-36
» **Forklift Pockets:**	Through front and rear framing channels

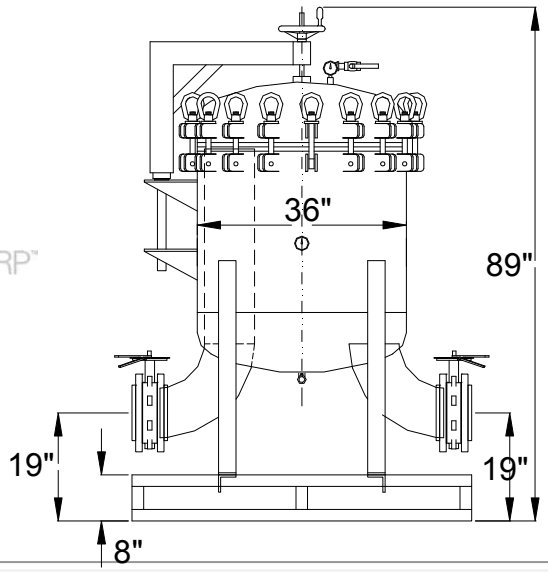
FILTER DESIGN

» **Assembly Number:**	Krystil Klear LR12-36-30-8F-A-4-15-SP
» **Top Head:**	(17) closure bolts and nuts with davit lift assembly. 36" O.D., 0.25" thk, SA-240 Gr. 304 stainless steel
» **Shell:**	36" O.D., 0.25" thick x 28" L . R & T, SA-240 Gr. 304 stainless steel
» **Inlet & Outlet:**	8" 150# RFSO flanges, SA-182 Gr. 304 S.S.
» **Bag Elements:**	12 required: size #2, 7-1/16" snap ring & 30" length required; Available fibers range from 1 to 1500 microns.
» **Lid Seal:**	Buna N O-ring
» **In/Out Valves:**	8" 150" butterfly with Buna seat
» **Internal Hardware:**	SA-240 Gr. 304 S.S. tube sheet

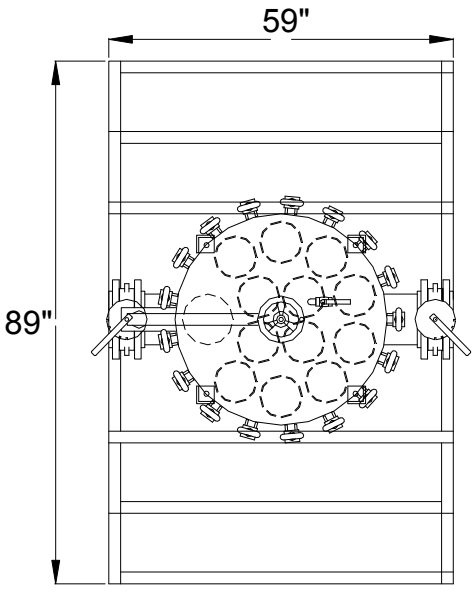
TESTS / CERTIFICATIONS

» **Test Performed:**	OEM Hydrotested @ 195 psi. Scheduled QMS inspections after purchase by BakerCorp.

BAKERCORP™



BAKERCORP™



PRODUCT DATA SHEET

April, 2010

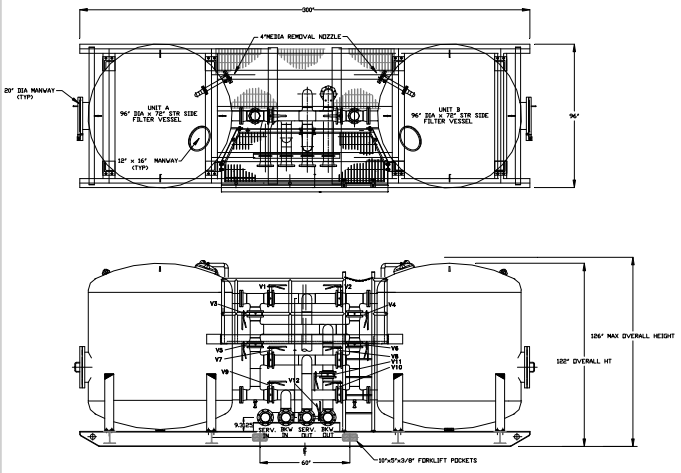
D-KLEEN.WATER 10K

GENERAL INFORMATION

This system is designed for continuous aqueous phase treatment of groundwater or wastewater, and has the ability to remove contaminants to non-detectable levels. The influent stream may be drawn in through the system in either series or parallel flow, and can operate on one vessel only while the other is in backwash mode. BakerCorp can provide a number of service and disposal options for the spent media,

WEIGHTS AND MEASURES

»Max. Flowrate:	Up to 600 gpm in series or 1200 gpm in parallel (application dependent)
»Max. Pressure:	100 psi
»Max. Temp:	150°F
»Height:	10'-6" (overall)
»Width:	8'-0" (skid)
»Length:	25'-0" (skid)
»Diameter:	96" (each vessel)
»Shipping Weight: (empty)	40,000 lbs.(equipment – 20,000 lbs; activated carbon – 20,000 lbs)
»Operating Weight:	80,000 lbs. (including 40,000 lbs. water)



FILTER MEDIA

»Types:	•Activated Carbon •Organoclay •Ion Exchange Resin •Specialty Media
»Volume:	320 cu. ft per vessel (640 cu. ft. total)
»Weight:	~10,000 lbs. each vessel (20,000 lbs. total)

MISCELLANEOUS DATA

»Vessel Code:	ASME Code stamped for 100 psi @ 150°F.
»Service In/Out:	6" Flanged connection w/ sch. 40 piping
»Backwash In/Out:	6" Flanged connection w/ sch. 40 piping
»Manifold Valves:	6" Lever-operated cast iron butterfly
»Media Removal:	4" top-mounted nozzle with draw connection at grade
»Internals:	Lower Underdrain: 6" header/2"x1" drop strainer type constructed of 304 SS & 316SS nozzles Upper Distributor: 6" header/3" open end riser type constructed of 304 SS
»Platform:	Galvanized grating with perimeter guardrails
»Vessel Interior Access:	Top manway – 12"x16" elliptical Side manway – 20" round
»Manway Gaskets:	Neoprene
»Interior Coating:	Polyamine epoxy coating

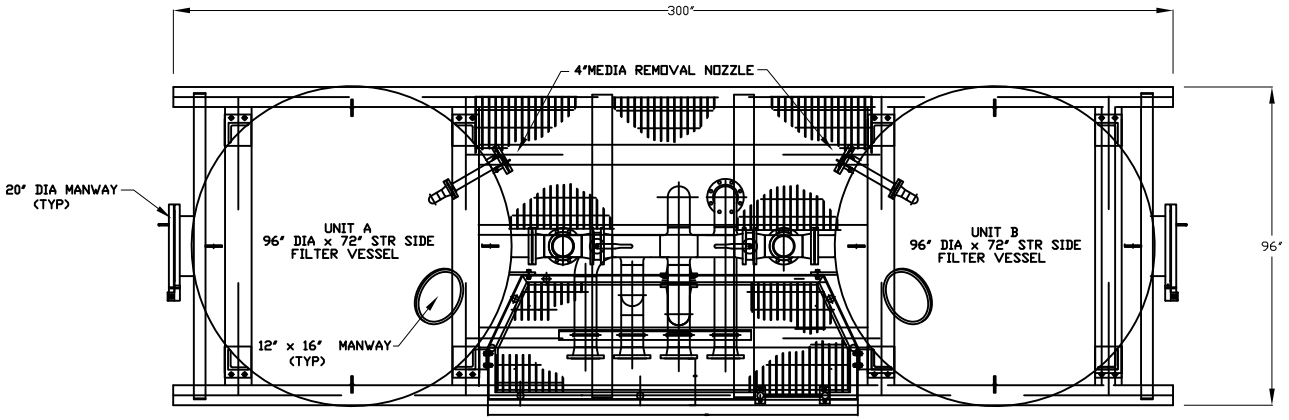
PRESSURE DROP DATA & OPTIONS AVAILABLE

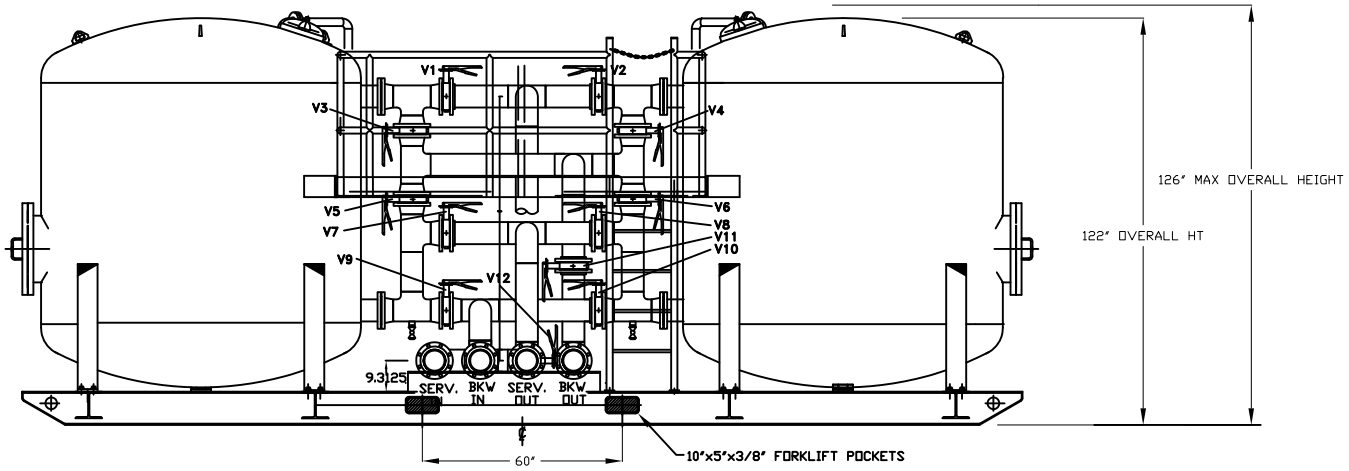
Contact BakerCorp

NOTE:
Wet activated carbon preferentially removes oxygen from air. In closed or partially closed containers and vessels, oxygen depletion may reach hazardous levels. If workers are to enter a vessel containing carbon, appropriate procedures for potentially low oxygen spaces must be followed, including all federal and state requirements.

BAKERCORP

3020 Old Ranch Parkway • Suite 220 • Seal Beach, CA • 562-430-6262





VALVE OPERATION CHART

FUNCTION	VALVES OPEN
SERVICE UNIT A	V1,V7
SERVICE UNIT B	V2,V8
PARALLEL SERVICE A&B	V1,V7,V2,V8
SERIES SERVICE A TO B	V1,V5,V4,V8
SERIES SERVICE B TO A	V2,V6,V3,V7
BACKWASH UNIT A	V9,V3,V11
BACKWASH UNIT B	V10,V4,V11
RINSE UNIT A	V1,V5,V11
RINSE UNIT B	V2,V6,V11
SERVICE BYPASS	V12

GENERAL CONSTRUCTION NOTES

1. VESSEL - ASME CODE STAMPED FOR A WORKING PRESSURE OF 100 PSI AT 150 DEGREES F.
2. SURFACE FINISH:
   VESSEL INTERIOR:
   PAINT: ONE COAT CARBOLINE PHENOLINE 309, F744 GREY, 25-30 MILS DFT
   EXTERIOR, VESSEL, SKID AND PIPING.
   PAINT: ONE COAT CARBOLINE CARBOZINC 858, 0300 GREEN, 3-5 MILS DFT
   ONE COAT CARBOLINE CARBOTHANE 134HG, BAKER GREEN, 2-3 MILS DFT
   EXTERIOR - PLATFORM, LADDER & HANDRAILS
   PAINT: ONE COAT CARBOLINE CARBOZINC 859, GRAY, 3-5 MILS DFT
   ONE COAT CARBOLINE CARBOTHANE 134HG, YELLOW, 2-3 MILS DFT
3. VESSEL INTERNALS:
   UNDERDRAIN COLLECTOR - 6" HEADER/2"x1" DROP STRAINER TYPE CONSTRUCTED
   UPPER DISTRIBUTOR - 6"HEADER/3" OPEN END RISER TYPE CONSTRUCTED OF 316SS.
4. FACE PIPING - 6" SCH 40 WITH 150# RFWN FLANGE TERMINATIONS
5. WEIGHTS:

EMPTY EQUIPMENT WEIGHT	21100 LBS
MEDIA, ACTIVATED CARBON (350 CU.FT)	20000 LBS
TOTAL TRANSPORT WEIGHT	41100 LBS
WATER FILL	40000 LBS
TOTAL OPERATING WEIGHT	81100 LBS

REV.	DESCRIPTION	DATE	BY
G			
F			
E			
D			
C			
B			
A			

BAKERCORP™ 3020 OLD RANCH PARKWAY SEAL BEACH, CA 90740-2751

SCALE:	SIZE: A	ORIGINAL DWG. DATE: 25JAN07
DRAWN BY: P.J.B.	APPROVED BY: –	CAT/CLASS: NA
TITLE: 10K DUPLEX FILTER SKID UNIT		SHEET: 1 OF 1
DRAWING NO.: S-9-M0023-1-		REV.: 0

PRODUCT DATA SHEET
October, 2007

EZ CLEAN FIXED AXLE MIX TANK

GENERAL INFORMATION

This tank has a smooth interior wall for easy cleaning.

WEIGHTS AND MEASURES

» Capacity:	480 BBL (20,160 gallons)
» Height:	11′-2″ (grade to roof deck) 14′-8″ (grade to top of upright guardrails)
» Width:	8′-6″ (between side runners)
» Length:	39′-9″ (front nose to outside of rear stairway) 37′-6″ (tank only)
» Weight:	31,650 lbs.

STRUCTURAL DESIGN

» Floor:	¼″thick ASTM A36 carbon steel (V-bottom)
» Sides/Ends:	¼″ thick ASTM A36 carbon steel
» Top Deck:	¼″ thick ASTM A36 carbon steel
» Wall Frame:	3/16″x3″x5″ ASTM A36 formed channel
» Roof Frame:	3/16″x3″x5″ ASTM A36 formed channel

FEATURES

» Relief Valve:	16 oz./in^2 pressure setting, 0.4 oz./in^2 vacuum setting; Buna-N seal.
» Valves:	1-Front &1-Rear: 6″- wafer butterfly valve. Cast iron body, Buna-N seat & seals, 316 SS stem, Nylon 11 coated ductile iron disk w/ plug and chain.
» Front Piping Connections:	Bottom Drain: 6″-150# flanged nozzle and butterfly valve Inlet/Outlet: 2 - 4″-150# raised face flange with blind flange (chained) Steam Coil: 2 - 3″-150# raised face flange with blind flange (chained) Thermowell: 2 – 2″-150# raised face flange (chained) with ¾″ threaded plugged coupling for probe insertion. One on lower vertical wall and one on upper vertical wall.
» Rear Piping Connections:	Bottom Drain: 6″-150# flanged nozzle and butterfly valve Inlet/Outlet: 2 - 4″-150# raised face flange with blind flange (chained)
» Roof Deck Connections:	Vapor Recovery: 4″-150# flange (blinded) Gauging Port: 4″ flange (blinded) with 2″ threaded plugged port in blind flange. Top Fill: 4″-150# flange (blinded)
» Heating Coils:	3″ sch. 80 pipe with 105 ft^2 of surface area
» Guardrails:	Top deck, fold-down, 1¼″ x 1¼″ square tubing.

FEATURES – cont.

» Interior Access:	2-50″ long x 32″ wide hinged vapor-proof marine-style hatches with neoprene gaskets and removable fall protection grid.
» Roof Access Stairway:	Rear mounted – lower section folds up for transport and down for use. Stairway includes handrails.
» Internal Ladder:	One; mounted below front-end interior access hatch on roof deck.
» Level Indication:	Ball style with 2-8″ 304 SS floats with pointer-indicator on front endwall. Floor supports hold floats ½″ off floor. *[One 2″ plugged connection for optional electronic gauge on top deck.]*
» Electric Motors:	Four Marathon 10 hp., type TGS, 215TC frame, 230/460 volts, 60 HZ, 3 phase, 1755 RPM, 25/12.5 F.L. amps, 1.0 service factor, EPFC enclosure, 60°C max. ambient temperature.
» Gearboxes:	Model KAF87AM215TC, reduction ratio 24.92:1 (Input speed:1744 RPM, Output speed: 70 RPM). 2-3/8″ dia. output shaft.
» Mixer Shafts:	4- 80″ long x 2-3/8″ diameter, ASTM A1018.
» Mixer Blades:	Long (bottom) Blades: 1/2″ thk. X 6″ wide x17″ long (41″ swing path dia.) Short (upper) Blades: 1/2″ thk. X 6″ wide x 11-5/8″ long (30-3/8″ swing path dia.) One set of each per each mixer shaft. Material is ASTM A514.(Flow direction is downward)
» Axle:	77½ track straight, non steer, 19,000# capacity.
» Suspension:	Silent Drive, 3 air-bags with manual release.

SURFACE DETAILS

» Exterior Coating:	High gloss polyurethane
» Interior Coating:	None

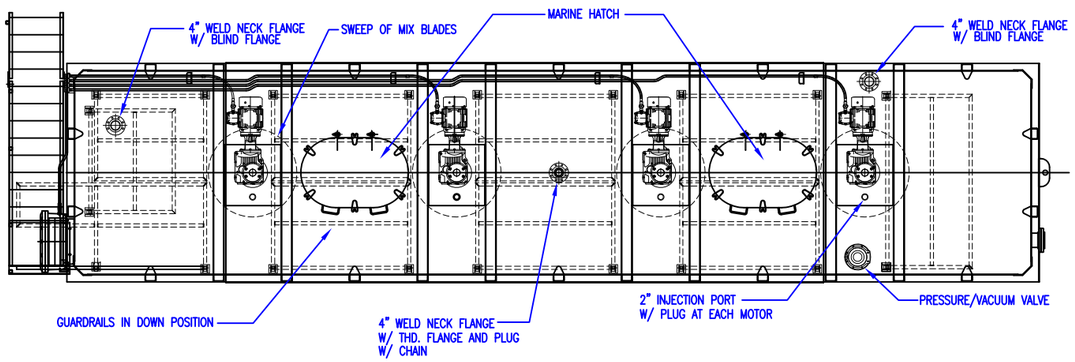
ELECTRICAL SPECIFICATIONS

» Power Supply:	480V ±5%, 3-phase regulated voltage & current supply capable of supplying 60A min. (by customer)
» Motor Control:	NEC and OSHA compliant control panel on front wall of tank.

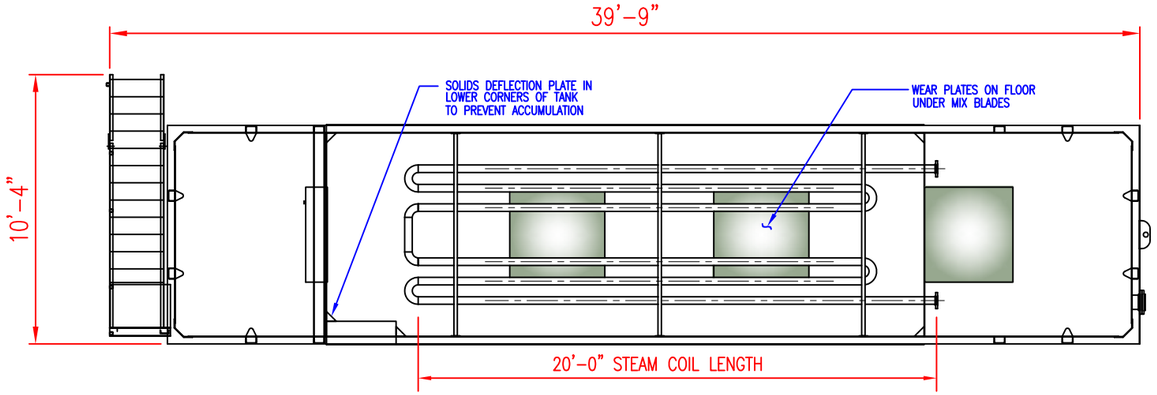
TESTS/CERTIFICATIONS

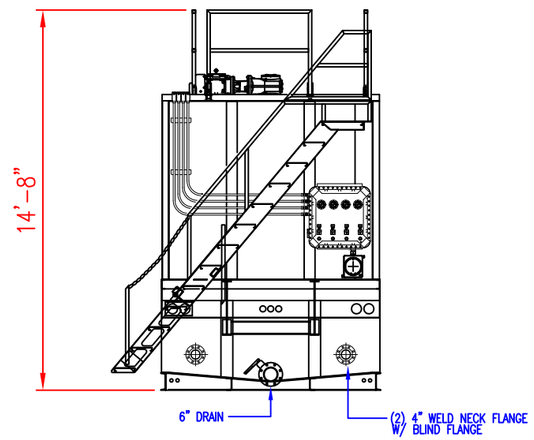
» Tests Performed:	Hydrotest, electrical checks, and air pressure test of coil by mfr. Level I, II and III inspections on a scheduled basis by Baker.

TOP VIEW - ROOF DECK

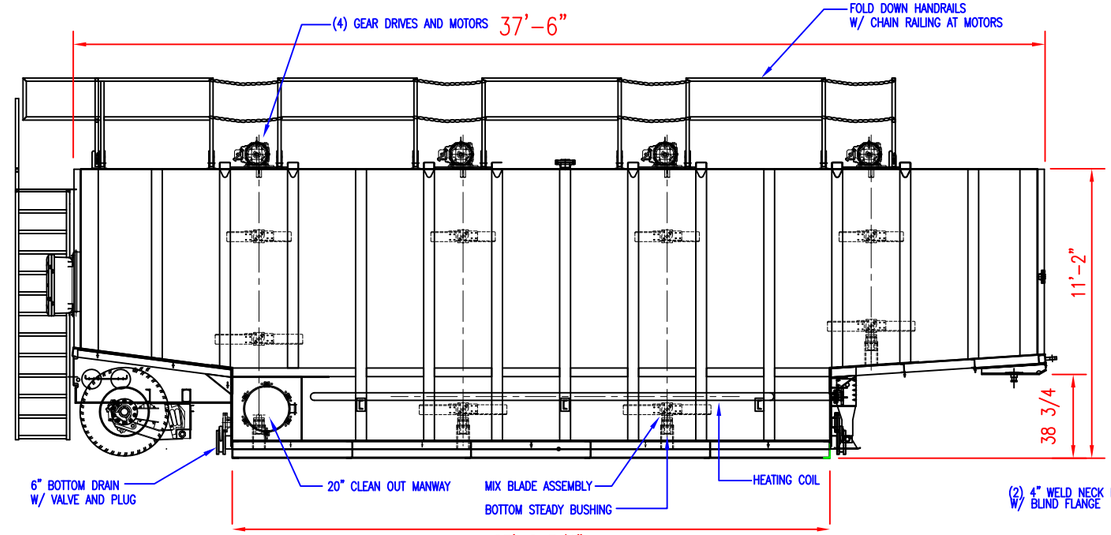


INTERIOR VIEW

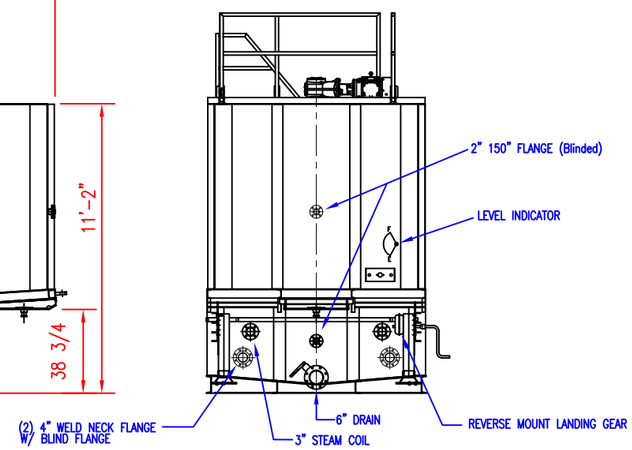




REAR VIEW



CURBSIDE VIEW



FRONT VIEW

SPECIFICATIONS:

1) Tank Capacity: 20,160 gallons (480 BBL)
2) Tank Weight: 32,000 lbs. approx (empty)

NOTES:

1. This drawing is a baseline representation for this model of tank. Variations between this drawing and the actual equipment in the field can and do exist, primarily with appurtenance locations, sizes and quantities. Consult your local BakerCorp representative if specific needs exist.
2. THIS TANK IS *NOT DESIGNED FOR TRANSPORTING LIQUIDS*. It should be moved only when empty.
3. This tank is equipped with a pressure/vacuum relief valve set at 1.0 1bs/sq. in. pressure and 0.4 oz/sq.in. vacuum.

REV.	DESCRIPTION	DATE	BY
G			
F			
E			
D			
C			
B			
A			

BAKERCORP™ 3020 OLD RANCH PARKWAY SEAL BEACH, CA 90740-2751

SCALE: Do Not Scale	SIZE B	ORIGINAL DWG. DATE 30MAY07
DRAWN BY: P.J.B.	APPROVED BY: –	CAT/CLASS ––
TITLE: EZ CLEAN FIXED AXLE MIX TANK		SHEET 1 OF 1
DRAWING NO. S-2-M0016-1-		REV. 0

SECTION 44 41 21

WATER QUALITY BARRIER SYSTEM

PART 1 - GENERAL

1.1 SUMMARY

A. Section Includes:
1. Rock Berm and Gap Closures
2. Breakwater and Gaps Barrier System
3. Isolation Barrier System
4. Interim Near-Shore Barrier System
5. Rock Protection Barrier System
6. Absorbent Boom
7. Oil Boom

B. Related Requirements:
1. Work covered by this Section shall be in accordance with the Environmental Protection Agency- (EPA) *Final Design for Phase 2 Wet Dredge* (*Final Design*) (FE JV, 2016) and the *Monitoring Plan for Phase 2 Wet Dredge* (*Monitoring Plan*) (FE JV, 2016), which is Appendix C of the *Final Design for Phase 2 Wet Dredge* (FE JV, 2016).

1.2 REFERENCES

A. Abbreviations:
1. DMU – Dredge Management Unit

1.3 SYSTEM DESCRIPTION

A. The Water Quality Barrier System described in this Section is a system of curtain-type barriers installed behind the existing breakwater structure to control the transport and migration of sediment, contaminants of concern (COC), and other potential water impacts (such as surface sheens and non-aqueous phase liquid [NAPL] migration) from the Phase 2 Wet Dredge Area during dredging and debris removal activities. The Water Quality Barrier System, depicted on Drawing Nos. 15, 16, 17, and 18, includes a rock berm and geotextile tube gap closures, breakwater and gaps barrier system, isolation barrier system, rock protection barrier system, interim near-shore barrier system, and multiple oil booms.

1.4 SUBMITTALS

A. Product Data: Submit manufacturers' printed data sheets or catalog pages illustrating products specified in this Section.

1.5 QUALITY ASSURANCE

A. Pre-installation Meeting:
   1. Meet at least once prior to installation of the Water Quality Barrier Systems.
   2. Attendees:
      a. Subcontractor's designated quality control representative.
      b. Contractor.
      c. Others requested by Contractor.
   3. Topics:
      a. Specifications and Drawings.
      b. Submittal requirements and procedures.
      c. Schedule for beginning and completing installation.
      d. Training for installation personnel.
      e. Installation crew size.

1.6 DELIVERY, STORAGE AND HANDLING

A. Store unused equipment in secure upland location. Unused and reclaimed equipment shall be stored and protected per manufacturer’s requirements and at Contractor direction for later phases of the dredging work.

B. Handle equipment in a manner to prevent impact blows, abrasion damage, gouging or cutting.

PART 2 - PRODUCTS

2.1 CONTRACTOR FURNISHED PRODUCTS

A. Contractor will supply Base Stone (2-inch minus), Core Stone, Restorative Layer Material to Subcontractor for filling Geotextile Tubes, and Geotextile Tubes.

B. Material specifications provided in this Article are intended to provide Subcontractor information needed for planning and execution of the work described in this Section.

   1. Base Stone shall be a 2 inch minus stone.
   2. Core Stone shall meet the gradation listed below, be well graded and not exhibit gap grading or scalping from individual size ranges.
   3. Restorative Layer Material shall be coarse sand material as described in Section 35 53 00.
   4. Core Stone Gradation:

Core Stone Weight (lbs.)	Percent Less Than by Weight	
	(Upper) Limit	(Lower) Limit
1	10	0
10	35	5
25	60	15
75	100	50
300	-	100

5. Geotextile Tubes shall be GT1000M Geotube® or equivalent.

2.2 ROCK BERM AND GAP CLOSURES

A. Description: A rock berm consisting of Core Stone placed on a layer of Base Stone and gap closures consisting of stacked geotextile tubes as shown on Drawings 15 and 16.

2.3 BREAKWATER AND GAPS BARRIER SYSTEM

A. Description: A dual barrier system consisting of two curtain sets, spaced approximately 15 feet apart, of a full-depth curtain extending from the water surface downward to the lakebed, and an accompanying submerged bedload baffle curtain, extending from lakebed upward (four curtains total); together covering the entire water column but allowing water to flow between them (see Details 1 and 2 on Drawing No. 17 and Detail 1 on Drawing No. 18).

B. Manufacturers: Spilldam Environmental, Inc., or equal.

C. Curtain Material Performance Criteria:
1. Puncture Strength: 400 pounds
2. Tear Strength: 110 pounds

D. Specifications:
1. Common:
   a. Curtain Material: 22 ounce per square yard, polyvinyl chloride- (PVC) coated polyester.
   b. End Connectors: Tool free, aluminum, universal end connectors with Velcro® flaps.
2. Impermeable Turbidity Curtain:
   a. Float: 12-inch closed cell foam flotation.
   b. Bottom Ballast: double 5/16-inch galvanized steel chain.
   c. Upper Ballast: single 5/16-inch galvanized steel chain.
   d. Tension Cable: 5/16-inch PVC-coated steel aircraft cable.
   e. Provide adjustable line skirt reefing with anchor points.

3. Bedload Baffle:
    a. Float: 3-inch closed cell foam flotation.
    b. Bottom Ballast: double 1/2-inch galvanized steel chain.

E. Factory Assembly:
1. Length of the curtain will be dependent on the water depth and will vary over the length of the barrier curtain. Each section shall be specifically manufactured based on location and depth.

2.4 ISOLATION BARRIER SYSTEM

A. Description: A barrier curtain system, same as breakwater and gaps barrier system, consisting of one set, spaced 15 feet apart, of a full-depth curtain extending from the water surface downward to the lakebed, and an accompanying submerged bedload baffle curtain, extending from the lakebed upward (two curtains total). Together, covering the entire water column but allowing water to flow between them (see Details 1 and 2 on Drawing No. 17 and Detail 1 on Drawing No. 18). The isolation curtain will be installed following the completion of mechanical dredging in DMU-1 and will separate ongoing dredging operations in the two DMUs.

B. Product specification for Isolation Barrier System shall meet requirements of Article 2.1 of this Section.

2.5 INTERIM NEAR-SHORE BARRIER SYSTEM

A. Description: A barrier system consisting of a full-height impermeable curtain will be deployed approximately 50 feet from the shoreline during land-based removal of nearshore sediments (see Detail 1 on Drawing No. 17).

B. Manufacturers: Spilldam Environmental, Inc., or equal.

C. Curtain Material Performance Criteria:
1. Puncture Strength: 400 pounds
2. Tear Strength: 110 pounds

D. Specifications:
1. Common:
    a. Curtain Material: 22 ounce per square yard, polyvinyl chloride- (PVC) coated polyester.
    b. End Connectors: Tool free, aluminum, universal end connectors with Velcro® flaps.
2. Impermeable Turbidity Curtain:
    a. Float: 12-inch closed cell foam flotation.
    b. Bottom Ballast: double 5/16-inch galvanized steel chain.
    c. Upper Ballast: single 5/16-inch galvanized steel chain.

d. Tension Cable: 5/16-inch PVC-coated steel aircraft cable.
e. Provide adjustable line skirt reefing with anchor points.

E. Factory Assembly:
1. Length of the curtain will be dependent on the water depth and will vary over the length of the barrier curtain. Each section shall be specifically manufactured based on location and depth.

2.6 ROCK PROTECTION BARRIER SYSTEM

A. Description: Partial-height curtain extending from the water surface downward.

B. Manufacturers: Spilldam Environmental, Inc., or equal.

C. Curtain Material Performance Criteria:
1. Puncture Strength: 400 pounds
2. Tear Strength: 110 pounds

D. Specifications:
1. Curtain Material: 22 ounce per square yard, PVC-coated polyester.
2. End Connectors: Tool free, aluminum, universal end connectors with Velcro® flaps.
3. Float: 12-inch closed cell foam flotation.
4. Bottom Ballast: double 5/16-inch galvanized steel chain.
5. Upper Ballast: single 5/16-inch galvanized steel chain.
6. Tension Cable: 5/16-inch PVC-coated steel aircraft cable for Rock Protection Barrier; 5/8-inch PVC-coated steel aircraft cable for Breakwater Gap Barrier.
7. Provide adjustable line skirt reefing with anchor points.

2.7 OIL BOOM

A. Description: Heavy-duty type oil containment boom.

B. Manufacturers: Spilldam Environmental, Inc., or equal.

C. Curtain Material Performance Criteria:
1. Puncture Strength: 400 pounds
2. Tear Strength: 110 pounds

D. Specifications:
1. Curtain Material: 22 ounce per square yard, PVC-coated polyester.
2. End Connectors: Tool free, aluminum, universal.
3. Height: 21 inch overall height
4. Draft: 12-inch skirt depth
5. Ballast/Tension: 5/16 inch galvanized ballast chain

6. Float: 6 inch diameter, flexible, closed cell foam

PART 3 - EXECUTION

3.1 INSTALLATION

A. General Installation Notes:
   1. Care during Installation: Subcontractor shall take care during installation and removal process so all system elements, especially the barrier fabric, are not damaged during deployment, and may be used for subsequent planned remedial action work.
   2. Curtain barrier sections shall be connected together on shore at the lacing grommets, and PVC flaps secured over the grommets using Velcro®.
   3. Curtains shall be furled for placement in the water and unfurled after proper placement and anchoring.
   4. Barrier systems shall be installed before on-the-water activities are initiated in, or adjacent to the water.
   5. Install barrier systems as close to the construction as shown on drawings. The barrier shall remain in place and be maintained until the on-the-water activities are completed and shall not be removed or otherwise opened without approval of Contractor.
   6. The ends of the barriers shall be securely anchored and keyed into the shoreline to fully enclose the Work area.

B. Breakwater, Gaps, Isolation, and Interim Near-Shore Barrier Systems:
   1. Curtain Anchoring: Affix to fence posts spaced and driven as necessary to keep barrier in general alignment as shown on drawings. If fence post cannot be driven due to lakebed constraints, use appropriated weighted mushroom anchor to secure curtain.

C. Oil Boom: Deploy oil boom and absorbent materials, as shown on the Drawings, and as needed to control sheen in the dredge work area.

D. Sequences of Operation: Installation of the barrier system will be conducted by working progressively from offshore to nearshore in the following order:
   1. Rock Berm and Gap Closures
   2. Rock Protection Barrier System
   3. Breakwater and Gaps Barrier System
   4. Floating absorbent oil booms (shall be placed as needed throughout the installation process)
   5. Isolation Barrier System upon completion of mechanical dredging in DMU 1.
   6. Interim Near-Shore Barrier System, as necessary, to align with shoreline material removal schedule.

3.2 MAINTENANCE

A. Additional material for each barrier system component shall be manufactured in the event replacement is required. The extra material shall be stored on site in a dry upland facility providing easy access in the event that maintenance and replacement is necessary. Subcontractor shall propose quantity of additional material to have on hand at start of project to ensure no schedule interruptions.

B. Inspect barrier system daily during operations and after storm/wave events for damage or deficiencies, this includes flying drone weekly to observe barrier system condition, function, and alignment. Make repairs/adjustments immediately. Dredging activities shall not be performed without fully functioning barrier system in place and operational.

C. Immediately correct any bypassing or under performance issues identified.

D. Clean or replace boom material that shows visible contamination of material.

3.1 REMOVAL AND CLEANING

A. The Water Quality Barrier System curtains and geotextile tubes shall be removed by Subcontractor at Contractor direction in a systematic manner once water quality in situ monitoring or sampling results confirm that water quality meets the conditions defined in Section 2.6 of the *Monitoring Plan*.

B. Care shall be taken when removing the barrier system to minimize the release or re-suspension of accumulated sediment.

C. Once removed, at Contractor direction, all system components shall be decontaminated and disposed of in accordance with disposal facility requirements or stored for future reuse.

END OF SECTION

SECTION 44 60 03

ALLSITE TENT STRUCTURE

PART 1 - GENERAL

1.1 SUMMARY

A. Section Includes:
1. Requirements for procurement and installation of the Allsite tent structure.
2. Fabrication, shop assembly, testing, operation, and demobilization of a tent structure by Allsite Fabric Structures of Memphis, Tennessee.

1.2 GENERAL REQUIREMENTS

A. The Allsite structure will serve several key functions:
1. Provide an enclosed environment wherein potential emissions of particulates and volatile organic compounds/semi-volatile organic compounds (VOC/SVOC) can be contained and controlled.
2. Provide an enclosed environment suitable for management of sediment and debris including a safe environment for working inside the structure.

1.3 MANUFACTURERS' DRAWINGS AND DATA

A. Shop drawings and vendor data are provided in the *Final Design* Drawings.

1.4 OPERATIONS AND MAINTENANCE

A. Operations and maintenance shall be in accordance with manufacturer’s recommendations.

PART 2 - PRODUCTS

2.1 ALLSITE TENT STRUCTURE MATERIALS AND EQUIPMENT

A. Allsite Fabric Structures shall supply all the components of the tent structure.

B. The Contractor will supply ventilation fans.

2.2 VENTILATION TREATMENT

A. For odor control purposes, treatment of exhaust air from the ventilation system will be required.

2.3 ELECTRICAL EQUIPMENT/INSTRUMENTATION AND CONTROLS

A. The power supply to the system shall be 480 volt, three-phase. The Contractor shall provide the necessary transformers for any other power requirements.

2.4 FOUNDATION REQUIREMENTS

A. The foundation for installation of the Allsite tent structure will be at the elevations noted on the *Final Design for Phase 2 Wet Dredge* (*Final Design*) Drawings (FE JV, 2016).

B. The finished surface will be bituminous asphalt concrete.

C. The subgrade and finished surface components and thicknesses are noted on the *Final Design* Drawings.

PART 3 - EXECUTION

3.1 ASSEMBLY AND SHIPPING

A. The Allsite tent structure materials will be inspected at the manufacturer's shop prior to shipment. Machined surfaces shall be protected from damage. Loose parts shall be shipped with the unit and clearly marked with part number that is consistent with field assembly instructions.

3.2 ON-SITE STRUCTURE INSTALLATION

A. The Allsite tent structure shall be installed in accordance with the manufacturer-supplied erection plan and in conformance with the manufacturer-supplied drawings, specifically Drawing Nos. 20, 21, 28, and 29, which are provided in the *Final Design* Drawing set.

END OF SECTION

SECTION 44 61 01

SEDIMENT PROCESSING TENT VENTILATION AND TREATMENT SYSTEM

PART 1 - GENERAL

1.1 SUMMARY

A. Section Includes:
This Section covers the furnishing of a temporary sediment processing tent ventilation system. System shall be complete with all equipment shown, including, but not limited to 5 modules, each containing, ductwork, blower, particulate filters, granular activated carbon (GAC) adsorption bed, and stack discharge.

B. The 5 modules, each containing ductwork, blower, particulate filters, GAC adsorption bed, and stack discharge will be located outside the Allsite sediment processing tent with ventilation intake ductwork located inside the sediment processing tent.

C. Sediment processing tent ventilation system will be installed on the ground surface.

D. The following Work is not included:
1. Power supply to all electrical equipment.
2. Control circuit wiring.
3. Ductwork and blower collecting emissions at the dredge off-loading equipment and slot conveyor.

1.2 DESIGN DATA

A. The plant design (for each of five modules) shall meet the following conditions.
1. Design Average Daily Flow (during day shift): 32000 CFM @ 3.1 TSP and 22.1 fan HP.
2. Expected Average Daily Flow (during night time hours): 16000 CFM @ 1.0 TSP and 3.4 fan HP.
3. Expected Daily Maximum: 38000 cfm @ 6.0 TSP and 40 fan HP.
4. Available Power Supply: three phase 480 volts; single phase 240 volt
5. Air influent quality as noted in Appendix D.

B. The total air flow rate to be ventilated and treated is 160,000 acfm. Air Filters provides five modular units each at 32,000 acfm for a total of 160,000 acfm capacity. Each unit will measure 8 feet wide x 10 feet tall and 17.5 feet long with a 42 inch spiral duct stack, 20 foot long with a rain cap. A stack will be mounted on top of each modular unit and guide wires will be attached to each unit to steady the stack. The stacks will exhaust at 29.5 feet above ground surface.

C. The carbon beds will use 304 SS perforated sheets 48 inches x 104 inches x 6 inches deep or about 17.3 cubic feet (cf) of carbon per bed and 6 beds per unit for a total volume of 103.8 cf. At an average weight of 32.5 lbs. per cubic foot, a total carbon

weight per unit minimum is 3,400 lbs. At a 30% adsorption factor and 8.8 lbs. of contaminants per hour for a 12-hour day run time, the carbon should last (conservatively) about 48 days. The face velocity for six beds at 34.6 foot square (ft sq.) each for a total of 207.6 sq. ft. per unit and 32,000 acfm flow gives a 155 foot/minute bed velocity and a residence time of 0.19 seconds. The pressure drop for the carbon bed should be 2.7 inches of water gauge.

D. Each modular unit is constructed of 14-gauge G-90 galvanized metal on a six channel epoxy-coated base. Carbon removal and fill will be from the top through two flip up panels. The bag filters will each have a magnehelic gauge to measure the pressure loss. Controls for the 40 horsepower (HP) motor would be mounted in a 3R control box for a VFD, start-stop station and disconnect pre-wired. The Fan Section would be insulated with duct board to reduce noise.

E. The plant design shall reduce potential nuisance odors contained in the sediment processing tent ventilation exhaust.

F. The plant equipment shall be installed by the Contractor under the direct supervision of the manufacturer.

1.3 QUALITY ASSURANCE

A. It is the intent of these specifications to procure a quality product by an established manufacturer of the latest design. The cost of the equipment shall include all royalties and costs arising from patents and licenses associated with furnishing the specified equipment.

B. All materials shall be designed to withstand stresses encountered in operation, fabrication, and erection.

1.4 PROTECTION, DELIVERY, AND HANDLING

A. Shipment shall be made from the manufacturer in such a way as to prevent damage to any parts of the equipment during shipping and storage.

B. Special handling and storage instructions shall be forwarded in a separate transmittal to insure against damage during long periods of storage.

PART 2 - PRODUCTS

2.1 SCHEDULE OF EQUIPMENT AND MATERIALS

Each of the 5 air filter units consists of:

- 32,000 ACFM unit at 6-inch TSP
- A 14 ga. G-90 Cabinet setting on a 6-inch channel base, the black iron will be cleaned and epoxy coated.

- The pre-filters are a 16 inch stiff-pocket bag. An original set of 16 filters per unit is included and 6 additional filter changes are expected.
- The Carbon media holding cells are of 304 SS, with 20 ga. SS perforated material on both the in and out sides. Six cells of about 48W x 104 tall and 6 inches deep will be in each unit.
- One charge of virgin carbon (Granular 4 x 8 mesh) sent separately. An estimated 3 additional carbon changes are expected for the project.
- The post filters are stiff pocket bags 24 x 24 x 26 deep with 8 pockets, MERV 15 rating. An original set of 16 filters per unit is included and is expected to last the project duration.
- Magnehelic gauges are built into the unit to measure each of the two filter banks pressure drop.
- The Plenum fan is mounted with a 40 hp 230/460 TEFC fan motor on a common base with spring vibration isolators.
- The fan motors are pre wired to an external 3R Control box that contains a VFD for 460 volt, start-stop station and disconnect, with additional fans and vents for the VFD cooling.
- The internal fan compartment will be insulated inside with 1-inch foil faced duct board to reduce sound external to the unit.
- The cabinet top will have a 42-inch safety rail around the perimeter and a ladder to reach the top. These two items will be fitted and shipped KD.
- A 42-inch diameter by 20 foot tall discharge stack with guide wires and rain cap will be shipped separately, mounted on the top of the unit. The stock exhaust height is 29.5 feet above ground surface.

2.2 PROCESS DUCTWORK

A. All process ductwork is provided by Air Filters, Inc. and Tony Brown HVAC. Refer to Drawing No. 27 for ductwork to be installed.

PART 3 - EXECUTION

3.1 INSPECTION

A. The equipment installer shall be responsible for the following:
   1. Verify all structural dimensions.

2. Verify centerline grades of all duct work passing through walls.

3.2 PERFORMANCE

A. The manufacturer shall furnish shop drawings showing the location and elevation of all inserts, blower units, duct work, anchor plates, stacks, and any other appurtenances required for installing the package plant equipment.

B. The equipment manufacturer shall guarantee all equipment free from defects in material and workmanship for one year from start up, and shall replace any component part proven defective during the guarantee period.

3.3 SUPERVISION OF ERECTION, START-UP, AND TRAINING

A. The Contractor will be responsible for supervision of erection, start-up, and operator training. However, the equipment manufacturer's representative must be available by phone and e-mail for technical assistance, as needed.

END OF SECTION

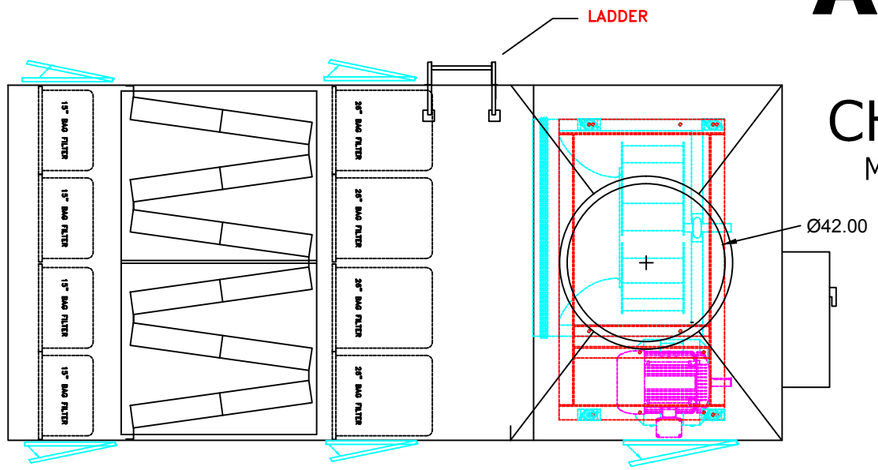
ATTACHMENTS

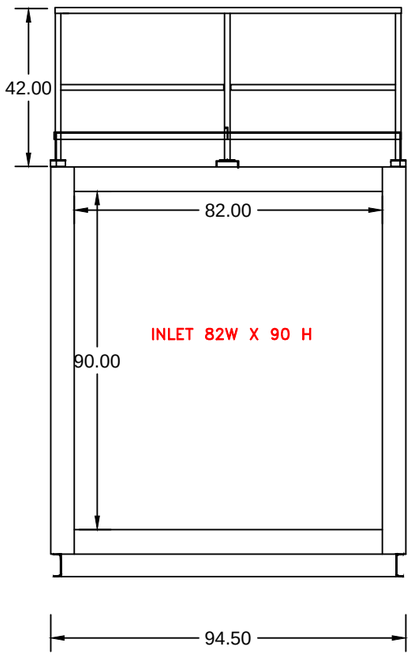
to

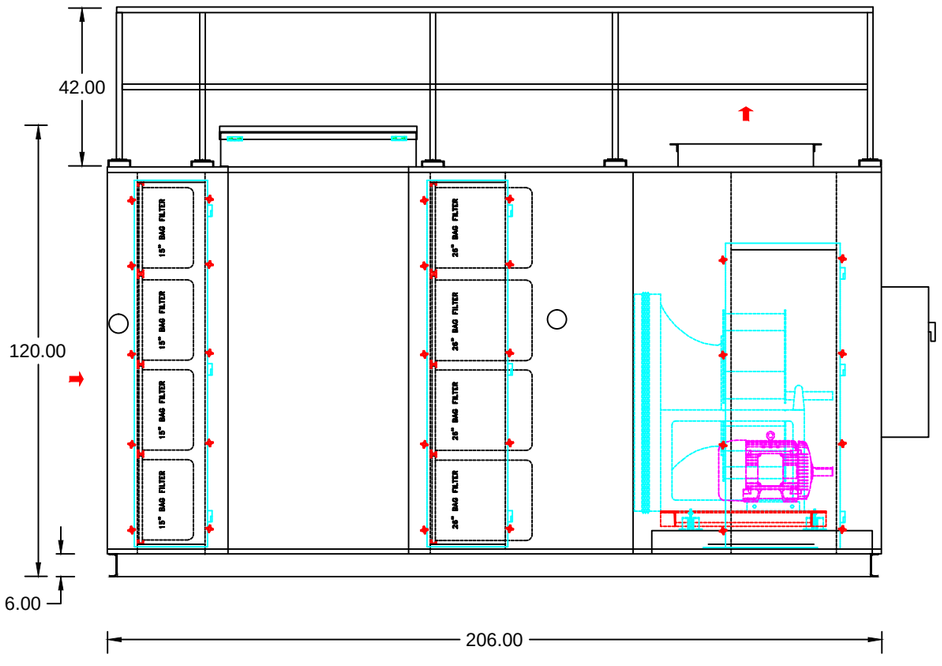
SECTION 44 61 01

SEDIMENT PROCESSING TENT VENTILATION AND TREATMENT SYSTEM

☐ APPROVED PER _____
☐ APPROVED AS NOTED
☐ CORRECT AND RE-SUBMIT







Air Filters, Inc.

CHEMICAL MEDIA UNIT

MODEL: HSG-FFU-3S-BCMW48X6B-4H4W

THREE STAGE FAN PACK

WEATHERPROOF CONSTRUCTION

NOTES

14 GAUGE GALVANIZED STEEL CONSTRUCTION
6 INCH CHANNEL IRON BASE, EPOXY COATED

EXTRUDED ALUMINUM FILTER TRACKS WITH WOVEN NYLON PILE SEAL.

MAGNEHELIC GAUGE OF EACH FILTER BANK

DOORS DEALED WITH CLOSED CELL NEOPRENE GASKET.

DUCT BOARD LINER AROUND THE FAN COMPARTMENT WALLS

METAL TO METAL COMPONENTS SEALED WITH SILICONE COMPOUND.

DOORS FITTED WITH KNURL KNOB – BOLT DOWN LATCHES.

CONTROL BOX 3R, WITH VFD, DISCONNECT AND STOP-START STATION

20 FOOT SECTION OF 36 INCH DIA. SPIRAL DUCT WITH RING FLANGES AND RAIN CAP

BLOWER: 32,000 CFM @ 6" TSP (PLN-44) CL-II

MOTOR: 40 HP / 3 PH / TEFC / 460 V.

FILTER SCHEDULE

	NO.	FILTER DIMENSIONS	
PRE FILTER	16	NOMINAL SIZE: ACTUAL SIZE:	24" X 24" X 16" 23.38" X 23.38" X 16"
FINAL FILTER	16	NOMINAL SIZE: ACTUAL SIZE:	24" X 24" X 26" 23.38 X 23.38 X 26

Air Filters, Inc.
A DIVISION OF B&B TECHNOLOGY, INC.
8282 Warren Rd. * Houston, TX 77040
(713) 896-8901 Phone (713) 896-8912 Fax
www.airfilterusa.com sales@airfilterusa.com

PROJECT: ASHLAND, WI.	UNIT TAG: PRELIMINARY DWG.	QTY:	DATE: 09/15/2016	
	DESIGNED BY: VBS	PURCHASE ORDER No.:		
SIZE: 4 HIGH X 4 WIDE	ENGINEER:	REPRESENTATIVE:	DRAWING NAME: HSG-FFU-3S-BCMW48X6B-4H4W	REV. B

Appendix I

Site Mass Balance

Full-Scale Dredging and Sediment Processing – Site Material Mass Flow Balance for Solids and Contact Water

The following are salient assumptions used for Solids and Contact Water Mass Flow Balances expected to be generated during full-scale dredging operations. Non-contact site water is not included in this evaluation. The Mass Flow Balances are provided separately as a solids and contact water flow balance. The flow balances are provided as an example based on assumptions and best available information. The results are used in basis of design, site support operations and facilities optimization. A short-list of assumptions and basis for calculations is provided below.

1. Flow Mass Balances are based on the following concurrently generated sources: mechanical dredging averaging 1,200 cubic yards (cy) of in-place sediments per day; 10 hours operational up-time of hydraulic cleanup dredging at 1,000 gpm per day (600,000 gallons per day); and accommodating a 4.2 inch rain event (25-year storm event) while collecting and storing precipitation contact water for treatment. Operating two 10-hour up-time shifts for hydraulic dredging of DMU-2 is addressed in the DWTS through use of the redundant carbon units that are on-site. Instituting this measure will increase the DWTS treatment capacity to 1,000 gpm.

2. The mechanical dredge component assumes sediment and debris characteristics corresponding to approximately 61% in-place solids content by weight, and approximately 39% in-place water content by weight (wet weight basis).

3. According to sediment cores, the specific gravity average of in-place sediments and water is approximately 1.9 not including woody waste or other debris. An in-place density average of approximately 118 pcf is a result.

4. Roughly half the sediment and debris total off-loaded and processed is comprised of debris (that is removed in the grizzly and finger deck) while half is sediment less than 2-inch in size.

5. The dredge haul barge is expected to contain the same average solids and water percentage as in-place sediments.

6. Approximately half the water content from the dredge haul barge is expected to be pumped to geobags or geotextile tubes in the sediment processing tent, then filtrate pumped to a Modutank, while half will be off-loaded with sediment and debris.

7. After grizzly and finger deck initial processing, approximately one-half of available water content will be recovered or lost from pre-screened sediment.

8. Roughly 3% - 5% of pebble lime will be used for fine sediment stabilization. An additional amount may be used for smaller debris stabilization (debris removed by pre-processing) if necessary.

9. The final average waste product that will be transported to VONCO will have an average moisture content of approximately 18.5 % (wet weight basis), and an average conversion of approximately 1.4 tons per in-place surveyed cubic yard of sediment, debris and water content.

10. Hydraulic clean-up dredging is expected to have up to 2% in-line vol/vol solids content.

11. Precipitation contact water will be collected from contact water collection areas indicated on Drawing No. 6. The overall system is sized to accommodate a 25-year precipitation event of up to 4.2 inch. Over 24-hour duration, a total of up to 205,100 gallons precipitation contact water may be collected for storage and subsequent treatment in DWTS.

12. The Modutank sizing to accommodate all contact water generation sources (see Appendix B-4) at one time will be approximately 800,000 gallons.

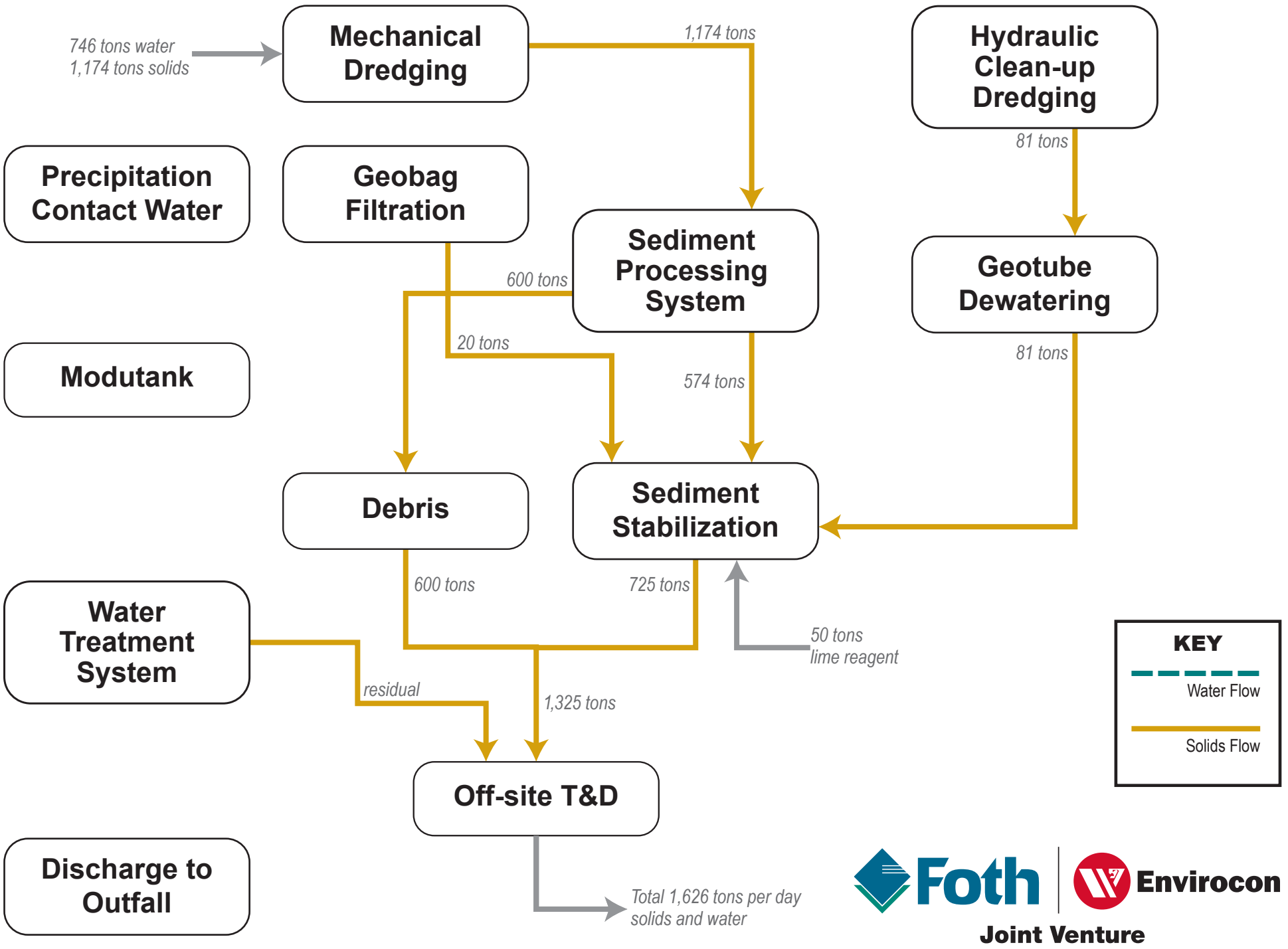
13. The DWTS will treat all contact water generated from the various sources. With a large Modutank storage capacity of up to 800,000 gallons (specifically for large precipitation events storage and for residual hydraulic dredging carriage water storage), the DWTS average flow rate necessary to accommodate all contact water sources listed is 600 gpm (with up to 750-gpm maximum flow rate, available as a contingency factor). By bringing on the redundant additional carbon units on-site, the flow capacity is increased to 1,000 gpm

14. Routinely, combined mechanical and hydraulic dredging operations will contribute approximately 711,000 gallons per day, a maximum of 6 days per week, while the DWTS can treat at least 720,000 gallons per day, 7 days per week at 600 gpm flow rate, with 83% operational up-time factor. By bringing on the redundant additional carbon units on-site, the flow capacity is increased to 1,000 gpm.

The Solids Flow Balance Diagram is indicated on Figure 1, and the Water Flow Diagram is included on Figure 2.

FIGURE 1: SOLIDS FLOW BALANCE

1,200 CY/DAY DREDGE RATE (TOTAL)

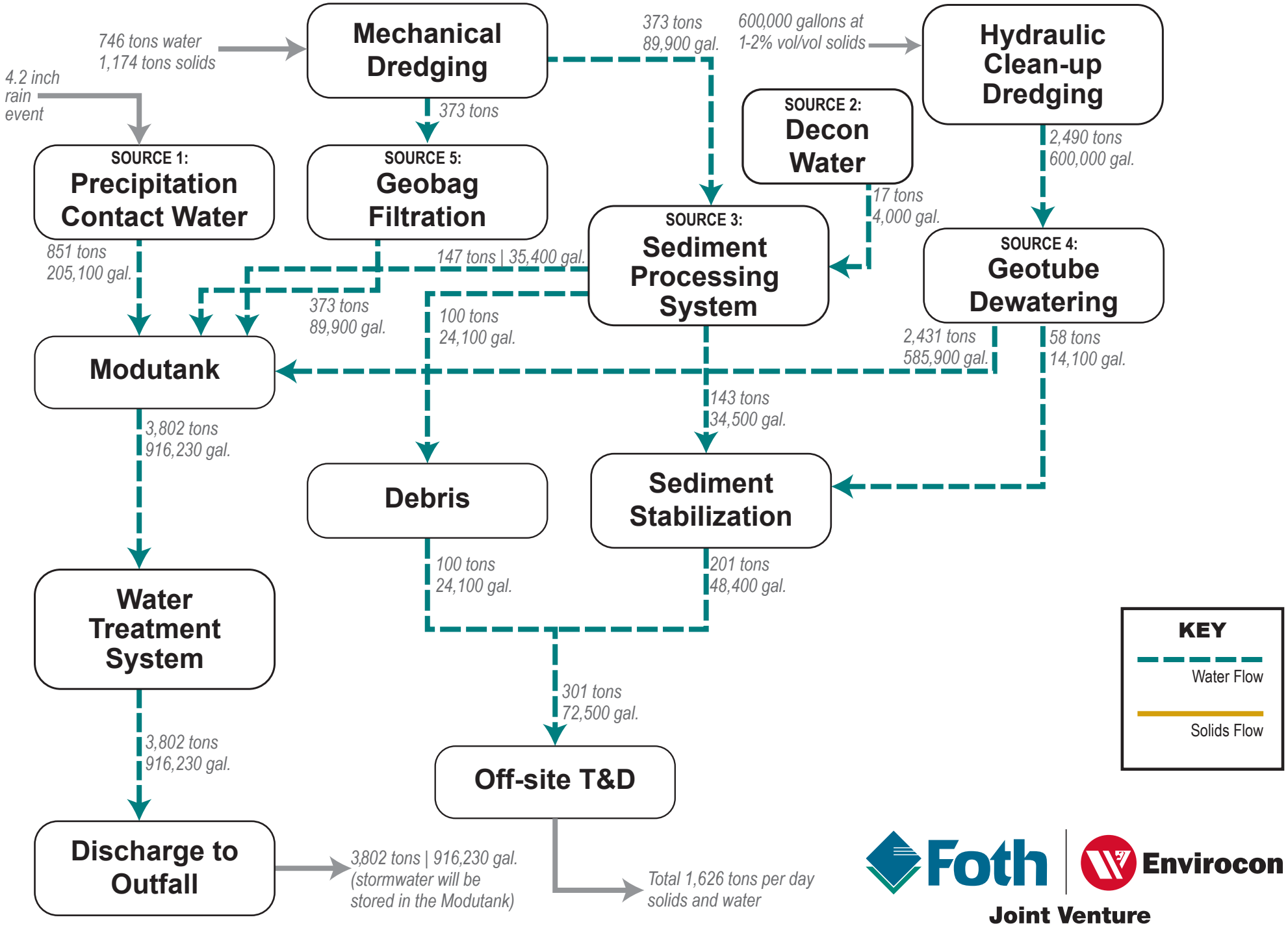


Foth | Envirocon

Joint Venture

FIGURE 2: WATER FLOW BALANCE

1,200 CY/DAY DREDGE RATE (TOTAL)



Foth | Envirocon

Joint Venture