Memorandum

October 7, 2016

To:	Shawn Wenzel, WDNR	Ref. No.:	058505
From:	Glenn Turchan, Nicole Knezevich/jp/67		
CC:	Kim Tucker Billingslea, GM; Linda Hanefield, WDNR; James Killian, WDNR; William Fitzpatrick, WDNR; Donalea Dinsmore, WDNR; Steve Song, Ramboll Environ; Mark Nielsen, Ramboll Environ; Renee Sandvig, Ramboll Environ; Phyllis Fuchsman, Ramboll Environ; Pieter Booth, Ramboll Environ; Margaret McArdle, Exponent; William Goodfellow, Exponent; Mauricio Barrera, GHD; Tom Kinney, GHD		
Subject:	**Response to WDNR Comments (09/28/2016 Conference Call) Supplemental Rock River (Mile 178.5 to 180.5) Investigation GM Janesville Assembly Plant 1000 General Motors Drive Janesville, Wisconsin**		

During a conference call on September 28, 2016 with General Motors LLC (GM) and the GM Team (GHD Services Inc. [GHD]; Exponent, and Ramboll Environ), the Wisconsin Department of Natural Resources (WDNR) provided additional general comments regarding the Supplemental Rock River (Mile 178.5 to 180.5) Investigation Work Plan (Work Plan) that was submitted to the WDNR for review on September 9, 2016. Additional clarification has been added to several comments previously received by the WNDR via e-mail on September 22, 2016 and September 26, 2016. GM's responses to the comments are provided below:

General Comments

WDNR Comment No. 1:

In general, the WDNR requested additional information regarding laboratory quality assurance (QA)/quality control (QC) information.

GM Team Response:

Table 1 provides a summary of the chemical and geotechnical analyses proposed in the Work Plan, which identifies the specific laboratory conducting the analysis, chemicals for analysis, and methods for each environmental medium being collected.

Additional Standard Operating Procedures (SOPs) for TestAmerica, as specified in Table 1, have been provided in Attachment A. Please note that TestAmerica has given the GM Team permission to provide the laboratory SOPs found within Attachment A to the WDNR for review purposes only. GM agreed to request that these SOPs not be released by the WDNR without written permission from TestAmerica.

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The Work Plan has been revised to indicate that the specified QA/QC samples will be taken throughout the Rock River Investigation to ensure that representative QA/QC samples are located within all of the target areas within the Rock River (e.g., embayment, impoundment, adjacent to the Site, and upstream controls).

WDNR Comment No. 2:

The WDNR requested that any conditions of the Rock River that may delay the proposed schedule for the Rock River Investigation be identified and discussed within the Work Plan (e.g., significant rain event and/or flood stage). The unusual seasonal weather conditions should be considered and discussed in the resulting report.

GM Team Response:

The Work Plan has been revised to identify and discuss conditions that may delay the proposed schedule for the Rock River Investigation. These conditions include a significant rain event and/or flood stage that may pose a health and safety concern to GM Team personnel conducting the sampling and/or impact the quality of the resulting data.

Additional Clarification for Specific Comments (09/22/16)

WDNR Comment No. 2:

Page 5, # 15: uncertain how water elevation is to be determined. Shore-based staff gage, or RTK GPS?

GM Team Response:

The water elevation of the Rock River will be determined by Real Time Kinetic (RTK) Global Positioning System (GPS) at each sample location. This is consistent with the methodology used during the first round of sediment testing reported on in March 2016. The water elevation is determined by taking the elevation measurement directly at the surface water level.

As indicated in the Work Plan, whenever possible sample points will be located using sub-meter DGPS and R8 GNSS RTK GPS and coordinates provided to WDNR (referenced to NAVD88 vertical datum and NAD 83 horizontal datum). However, the powerlines which run over the Rock River in the study area have been interfering with the radio link between the base station and the mobile unit of the DGPS and R8 GNSS RTK GPS unit for many of the downstream locations. In these instances, a Trimble® GeoExplorer® 6000 series GeoXH™ handheld GPS is being used to determine the sample locations and surface water elevation. The datasheet for this alternate GPS unit has been provided in Attachment B.

WDNR Comment No. 6:

Page 7, core sectioning. If visual inspection notes distinct stratigraphic or lithological breaks in the >.5' to 2' and 2' to refusal intervals, an aliquot of that interval should be analyzed separately and in addition to the planned segments.

GM Team Response:

Agreed. If distinct or lithological breaks in the sediment are noted, additional samples will be collected in addition to the planned segment.

A photographic log will be provided in the Supplemental Rock River (Mile 178.5 to 180.5) Investigation Report of the collected sediment cores. Markers will be placed on the exterior of the sediment cores to clearly indicate stratigraphic or lithological breaks.

WDNR Comment No. 12:

The calculation for total PAHs needs to be documented in the work plan/ QAPP. DNR staff were unable to reproduce the calculated concentrations in the previous data report (suspect there were substitutions for non-detected values which may lead to higher calculated values.)

GM Team Response:

The calculation for total polycyclic aromatic hydrocarbons (PAHs) has been documented in the Work Plan. For the current Work Plan, the toxicity test samples will have PAHs reported from two different methods: the EPA 8270 semi-volatile organic compound (SVOC) method and the select ion mode [SIM] parent + alkylated PAHs method. The initial expedited analysis of SVOC PAHs, which include mostly parent PAHs, will be used only for the purpose of identifying which sediment samples should be carried forward for toxicity testing. The risk analysis will rely on the SIM analyses of parent and alkylated PAHs.

To calculate total PAHs, the following rules will be applied:

- When SIM analysis of parent and alkylated PAHs are analyzed, they are included in the summation and the parent PAHs from the SVOC analysis are not included.
- When a PAH is non-detected, then one-half the detection limit is used.
- The limit used to calculate the total PAH concentrations are the quantitation limit.

The Supplemental Rock River (Mile 178.5 to 180.5) Investigation Report will consider all of the previously collected sediment data from the March 2016 Sediment Investigation in addition to the investigational activities proposed in the current Work Plan. Table 2 presents a sub-set of the revised total PAH concentrations from the Sediment Investigation and Data Evaluation and Data Report using this approach. Revised total PAH concentrations have been provided for all surface sediment samples (0 – 0.5 feet [ft]), and a representative deep (0.5 – 2 ft) and composite sample. The revised total PAH concentrations do not change the conclusions presented in the Sediment Investigation and Data Evaluation Report submitted to the WDNR in May 2016.

WDNR Comment No. 14:

Reference sample locations should not be weighted to materials that are only similar to the characteristics of the GM depositional area. They should be representative of the sediments present upstream of the depositional area in question. Sample replicates (co-located cores) should be

incorporated in the design to assess variance within the depositional area and representativeness of the samples (i.e., nugget effect and range of influence).

GM Team Response:

Field duplicate samples from the reference area will be collected as specified in the Work Plan. While the GM Team understands the desire to incorporate sample replicates (co-located cores) into the sample design to assess variance within the depositional areas and representativeness of the samples, a composite of several sediment cores is required to achieve the sample volume requirements of the Work Plan for the proposed sediment sample intervals (0 - 0.5 ft and 0.5 ft to 2 ft). Therefore, this integration of variability, through the use of composites, reduces the value of adding field replicates (co-located cores). However, field replicates were previously built into the Work Plan for the 0 - 0.5 ft sampling interval, as proposed locations for sediment samples were co-located with the proposed locations for sediment sampling for benthic invertebrate toxicity testing. These co-located samples will be located approximately 5 ft apart, and will be analyzed for similar chemical analyses, and thus can be considered field replicates.

Additional Clarification for Additional Specific Comments (09/26/2016)

WDNR Comment No. 1:

The protocol for core corrections based on recovery rations needs to be included in the QAPP. All data presentation should include both raw and transformed values.

GM Team Response:

Acknowledged. Data presentation will include both raw and transformed values in the Supplemental Rock River (Mile 178.5 to 180.5) Investigation Report.

WDNR Comment No. 3:

Prey fish composites: to ensure consistency with WDNR and EPA methods/results, the length of the smallest fish should be with 75% of the length of the largest fish in a composite.

GM Team Response:

The actual composition of prey fish composite samples will depend on the fish captured. However, to the extent possible, composite samples of prey fish will include specimens that differ no more than 25 percent in length. If this is not possible based on fish specimens collected in the field, a conference call will be set up with the WDNR to provide input and advice on how to proceed with the prey-fish composite samples. Fish tissue collection will be taking place between October 10 and October 14, 2016.

Table 1

Summary of Analytical Information
GM Janesville Assembly Plant
Janesville, Wisconsin

Scope of Work Referenced in the Work Plan	Environmental Media	Laboratory	Chemicals for Analyses	Method for Analysis
Surface Water SOW (Section 2)	Surface Water	TestAmerica (Denver)	PAH	SW-846 8270C
		TestAmerica (Canton)	TAL Metals - less earth metals	SW-846 6020/7471
			PCB	SW-846 8082
			Water Hardness	SW-846-2340C-1997
Sediment Investigation SOW (Section 3)	Sediment	TestAmerica (Canton)	TAL Metals - less earth metals	SW-846 6020
			Mercury (CVAA)	7471B
			PCB	SW-846 8082
			Hexavalent Chromium	7196A
			Black carbon	Biogeochemical Cycles,
			Methyl mercury	EPA 1630
		TestAmerica (Denver)	PAH	SW-846 8270C
		TestAmerica (Knoxville)	Alkalated PAH	Isotope dilution
		Pace Analytical Services Inc.	AVS/SEM metals - Cd, Cu, Pb, Ni, Ag, Zn	EPA-1629/6010
		TestAmerica (Burlington)	TOC	Lloyd Kahn
			Grain Size Analysis	ASTM D422; sieve only
			Grain Size Analysis	ASTM D422; with hydrometer
			Total Solids and Water Content	ASTM D2216
			Bulk Density	ASTM D2937
			Atterberg Limits	ASTM D4318
		GeoTesting Express Inc.	Direct Shear Testing	ASTM D3080
Benthic Invertebrate Sediment Toxicity Testing SOW (Section 4)	Sediment (Section 4.1)	TestAmerica (Canton)	Expedited TAL Metals - less earth metals	SW-846 6020
			Expedited Mercury (CVAA)	7471B
			Methyl mercury	EPA 1630
		TestAmerica (Denver)	Expedited PAH	SW-846 8270C
		TestAmerica (Knoxville)	Alkalated PAH	Isotope dilution
		TestAmerica (Canton)	TAL Metals - less earth metals	SW-846 6020
			Mercury (CVAA)	7471B
			PCB	SW-846 8082
		Pace Analytical Services Inc.	AVS/SEM metals - Cd, Cu, Pb, Ni, Ag, Zn	EPA-1629/6010
		TestAmerica (Burlington)	TOC	Lloyd Kahn
			Grain Size Analysis	ASTM D422; sieve only
		Eurofins CalScience Labs Environmental	Pyrethroid Pesticdes	EPA 8270D (M)/TQ/EI
			Total Solids	SM 2540 B
		Energy & Environmental Research Center; University of North Dakota	PAH	SW-846 8270C SIM
			Alkyated PAH	
	Porewater (Section 4.3)	Energy & Environmental Research Center; University of North Dakota	PAH	ASTM D7363-13 and EPA 8272 SIM
			Alkyated PAH	
		TestAmerica (Canton)	Methyl mercury	EPA 1630
			Total Mercury LL	EPA 1631
	Toxicity Testing (Section 4.4)	Ramboll Environ: Port Gamble Environmental Laboratory	*Hyalella azteca* 42-d Test	EPA 600/R-99/064 100.4
			Chironomus dilutus 20-d Test	EPA 600/R-99/064 100.5
Aquatic Biota Tissue Investigation SOW (Section 5)	Benthic Invertebrate Tissue (Section 5.1)	TestAmerica (Pittsburgh)	Site Specific Metals (Cd, Cu, Pb, Zn)	SW-846 6020
			PAH	SW-846 8270C
			PCB LL	EPA 8082A
			Lipid Content	EPA 1980
		TestAmerica (Canton)	Methyl mercury	EPA 1630
			Total Mercury - LL	EPA 1631E
	Prey-Size Fish Composites (Section 5.2.1)	TestAmerica (Pittsburgh)	Site Specific Metals (Cd, Cu, Pb, Zn)	SW-846 6020
			PAH	SW-846 8270C
			PCB LL	EPA 8020
			Lipid Content	EPA 1980
			Total Solids	EPA 160.3
		TestAmerica (Canton)	Total Mercury - LL	1631E
	Game Fish (Section 5.2.2)	TestAmerica (Pittsburgh)	PCB LL	EPA 8020
			Lipid Content	EPA 1980
			Total Solids	EPA 160.3
		TestAmerica (Canton)	Total Mercury - LL	1631E

Table 2

Summary of Total PAH Calculations
GM Janesville Assembly Plant
Janesville, Wisconsin

Sample Location:		SS-1	SS-1	SS-1	SS-2	SS-2	SS-3	SS-4	SS-5	SS-6	SS-7	SS-9
Sample Identification:		SE-031016-JN-021	SE-031016-JN-023	SE-031016-JN-022	SE-031016-JN-017	SE-031016-JN-015	SE-031016-JN-019	SE-030916-JN-008	SE-031016-JN-012	SE-030916-JN-002	SE-030916-JN-005	SE-031016-JN-025
Sample Date:		3/10/2016	3/10/2016	3/10/2016	3/10/2016	3/10/2016	3/10/2016	3/9/2016	3/10/2016	3/9/2016	3/9/2016	3/10/2016
Sample Depth:		(0-0.5) ft BGS	(0-3.5) ft BGS	(0.5-2) ft BGS	(0-0.5) ft BGS	(0.5-2) ft BGS	(0-0.5) ft BGS	(0-0.5) ft BGS	(0-0.5) ft BGS	(0-0.5) ft BGS	(0-0.5) ft BGS	(0-0.5) ft BGS
Sample Type:		Shallow	Composite	Deep	Shallow	Deep	Shallow	Shallow	Shallow	Shallow	Shallow	Shallow
Compound		**PAH conc**	**Values for Total PAH Calculation**	**PAH conc**	**PAH conc**	**PAH conc**	**Values for Total PAH Calculation**	**PAH conc**	**PAH conc**	**PAH conc**	**PAH conc**	**PAH conc**	**PAH conc**	**PAH conc**
Semi-Volatile Organic Compounds (SVOCs) 8270														
Acenaphthene	mg/kg	--	<0.0017	0.00085	0.051	--	<0.0015	0.00075	--	--	--	--	--	--
Acenaphthylene	mg/kg	--	0.011 J	0.011	0.032	--	<0.00071	0.000355	--	--	--	--	--	--
Anthracene	mg/kg	--	0.025	0.025	0.15	--	0.0083 J	0.0083	--	--	--	--	--	--
Benzo(a)anthracene	mg/kg	--	0.086	0.086	0.31	--	0.024	0.024	--	--	--	--	--	--
Benzo(a)pyrene	mg/kg	--	0.082	0.082	0.24	--	0.019	0.019	--	--	--	--	--	--
Benzo(b)fluoranthene	mg/kg	--	0.1	0.1	0.27	--	0.025	0.025	--	--	--	--	--	--
Benzo(g,h,i)perylene	mg/kg	--	0.06	0.06	0.15	--	0.01 J	0.01	--	--	--	--	--	--
Benzo(k)fluoranthene	mg/kg	--	0.033	0.033	0.17	--	< 0.0014	0.0007	--	--	--	--	--	--
Chrysene	mg/kg	--	0.1	0.1	0.32	--	0.028	0.028	--	--	--	--	--	--
Dibenz(a,h)anthracene	mg/kg	--	<0.0015	0.00075	0.035	--	< 0.0013	0.00065	--	--	--	--	--	--
Fluoranthene	mg/kg	--	0.19	0.19	0.69	--	0.045	0.045	--	--	--	--	--	--
Fluorene	mg/kg	--	0.014 J	0.014	0.081	--	< 0.0011	0.00055	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene	mg/kg	--	0.052	0.052	0.12	--	0.012 J	0.012	--	--	--	--	--	--
Naphthalene	mg/kg	--	0.012	0.012	0.033	--	0.0017	0.00085	--	--	--	--	--	--
Phenanthrene	mg/kg	--	0.11	0.11	0.55	--	0.036	0.036	--	--	--	--	--	--
Pyrene	mg/kg	--	0.19	0.19	0.67	--	0.049	0.049	--	--	--	--	--	--
Selected Ion Monitoring (SIM) SVOCs														
Acenaphthene	mg/kg	0.0408	--	--	--	0.0248	--	--	0.124	0.512	0.994	0.381	0.237	0.413
Acenaphthylene	mg/kg	0.0873	--	--	--	0.0891	--	--	0.071	0.277	0.131	0.131	0.168	0.144
Anthracene	mg/kg	0.178	--	--	--	0.106	--	--	0.321	1.1	2.16	0.924	0.995	0.968
Benzo(a)anthracene	mg/kg	0.396	--	--	--	0.212	--	--	0.57	1.47	3.76	1.41	1.96	1.86
Benzo(a)pyrene	mg/kg	0.44	--	--	--	0.251	--	--	0.53	1.21	3.51	1.08	1.73	1.61
Benzo(b)fluoranthene	mg/kg	0.335	--	--	--	0.2	--	--	0.488	1.18	2.99	1.36	1.78	1.68
Benzo(e)pyrene	mg/kg	0.258	--	--	--	0.158	--	--	0.367	0.981	2.21	0.926	1.3	1.21
Benzo(g,h,i)perylene	mg/kg	0.24	--	--	--	0.152	--	--	0.313	0.707	1.87	0.708	1.1	1.08
Benzo(j)fluoranthene/Benzo(k)fluoranthene	mg/kg	0.349	--	--	--	0.196	--	--	0.442	1.1	3.14	0.97	1.48	1.38
C1-Benzo(a)anthracenes/chrysenes	mg/kg	0.169	--	--	--	0.149	--	--	0.622	3.47	1.73	1.73	2.5	2.18
C1-Fluoranthenes/Pyrenes	mg/kg	0.356	--	--	--	0.224	--	--	0.86	3.8	3.19	2.63	3.55	3.32
C1-Fluorenes	mg/kg	0.027	--	--	--	0.0239	--	--	0.138	1.27	0.392	0.96	1.11	0.893
C1-Naphthalenes	mg/kg	0.0189	--	--	--	0.0226	--	--	0.18	4.11	0.897	1.22	0.805	0.204
C1-Phenanthrenes/Anthracenes	mg/kg	0.218	--	--	--	0.181	--	--	0.992	6.58	2.98	6.15	4.98	4.9
C2-Benzo(a)anthracenes/chrysenes	mg/kg	0.0737	--	--	--	0.0961	--	--	0.552	3.76	1.21	2.48	2.65	2.55
C2-Fluorenes	mg/kg	0.0323	--	--	--	0.0515	--	--	0.406	4.27	0.904	3.16	3.85	2.66
C2-Naphthalenes	mg/kg	0.0408	--	--	--	0.0539	--	--	0.749	7.49	1.4	3.59	1.76	2.42
C2-Phenanthrenes/Anthracenes	mg/kg	0.111	--	--	--	0.174	--	--	1.71	14	3.36	10.6	11	8.95
C3-Benzo(a)anthracenes/chrysenes	mg/kg	0.0347	--	--	--	0.0641	--	--	0.426	2.89	0.911	1.99	2.04	1.94
C3-Fluorenes	mg/kg	0.0584	--	--	--	0.0921	--	--	0.665	7.94	1.85	4.5	6.36	4.78
C3-Naphthalenes	mg/kg	0.0386	--	--	--	0.0515	--	--	0.826	7.62	1.38	4.11	3.41	3.7
C3-Phenanthrenes/Anthracenes	mg/kg	0.0569	--	--	--	0.135	--	--	1.73	15.7	2.99	9.08	11.9	9.45
C4-Benzo(a)anthracenes/chrysenes	mg/kg	0.0254	--	--	--	0.0438	--	--	0.324	2.08	0.54	1.16	1.78	1.44
C4-Naphthalenes	mg/kg	0.0228	--	--	--	0.0589	--	--	0.503	6.92	1.38	4.39	3.95	3.88
C4-Phenanthrenes/Anthracenes	mg/kg	0.0327	--	--	--	0.0816	--	--	1.01	8.69	1.89	4.74	6.17	6.06
Chrysene/Triphenylene	mg/kg	0.433	--	--	--	0.252	--	--	0.761	2.76	4.22	2.37	3.06	2.82
Dibenz(a,h)anthracene	mg/kg	0.0667	--	--	--	0.0447	--	--	0.0929	0.222	0.572	0.195	0.292	0.258
Fluoranthene	mg/kg	0.879	--	--	--	0.445	--	--	1.25	3.2	9.63	4.22	4.93	4.79
Fluorene	mg/kg	0.0518	--	--	--	0.0289	--	--	0.136	0.876	1.31	0.837	0.506	0.596
Indeno(1,2,3-cd)pyrene	mg/kg	0.227	--	--	--	0.141	--	--	0.295	0.637	1.81	0.612	0.951	0.924
Naphthalene	mg/kg	0.0203	--	--	--	0.0236	--	--	0.332	1.87	1.23	0.489	0.37	0.24
Perylene	mg/kg	0.201	--	--	--	0.28	--	--	0.221	0.402	1.06	0.575	0.681	0.684
Phenanthrene	mg/kg	0.478	--	--	--	0.309	--	--	1.09	3.94	9.09	5.67	2.66	4.78
Pyrene	mg/kg	0.756	--	--	--	0.403	--	--	1.13	3.29	7.37	3.24	4.45	4.18
Total PAH-16[a]		5.0		1.1	3.9	2.9		0.3	7.9	24.4	53.8	24.6	26.7	27.7
Total PAH-34[b]		6.8				4.8			20.2	126.3	84.1	88.6	96.5	88.9

Notes:

a. Total PAH-16 includes the 16 Priority Pollutant PAHs, for comparability to screening values. Total PAH concentrations include one-half the detection limit for non-detected analytes.
b. Total PAH-34 includes parent and alkylated PAHs.
-- Not Analyzed
J - Estimated concentration.
< - Not detected at the associated reporting limit.
mg/kg - milligrams per kilogram
PAH - Polycyclic aromatic hydrocarbons

Attachment A
TestAmerica Standard Operating Procedures (SOPs)

Title: Particle Size Analysis (ASTM D 2217 and D422-63)

Approval Signatures:

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Brad W.Chirgwin
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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: Liquid Limit, Plastic Limit & Plasticity of Soils (ASTM D4318- 05)

Approval Signatures:

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Approval Date: 21 June 2016

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 liquid limit, plastic limit and plasticity index of soils. This analysis is amenable to soils with significant amounts of silt and clay particles. It is not recommended for coarse-grained or sandy soils.

- Samples containing few to no particles that will be retained by #40 sieve are prepared using the wet preparation method.
- Samples containing a large percentage of particles that would be retained on a #40 sieve are prepared using the dry preparation method.

2.0 Summary of Method

Wet Preparation: A 150 to 200 g representative portion of sample that would pass through the #40 (425 um) sieve is spread into the brass cup of a mechanical liquid limit device and divided in two parts with a groove tool. The cup is repeatedly lifted and dropped until 13 mm (½ in.) of the sample flows together. This test is repeated several times at different water contents. The plastic limit is determined by repeatedly pressing the soil into an ellipsoidal shape and then rolling the soil into a 3.2 mm (1/8 inch) diameter thread, until the thread crumbles and sample can no longer be rolled into a ball or thread. The water content of the soil at this point is considered the plastic limit. The plasticity index is calculated as the difference between the liquid and plastic limits.

Dry Preparation: A representative portion of the sample is dried, pulverized and passed though a #40 sieve and placed in a mixing dish. The material retained on the #40 sieve is soaked with reagent water to separate the fine particles from coarse particles, decanted through a #40 sieve and collected in collection pan. The rinse water is added to the dried material which passed the #40 sieve and mixed with more reagent water to get to the proper liquid limit. A portion of the sample is spread into the brass cup of a mechanical liquid limit device and divided in two parts with a groove tool. The cup is repeatedly lifted and dropped until 13 mm (½ in.) of the sample flows together. This test is repeated several times at different water contents. The plastic limit is determined by repeatedly pressing the soil into an ellipsoidal shape and then rolling the soil into a 3.2 mm (1/8 inch) diameter thread, until the thread crumbles and sample can no longer be rolled into a ball or thread. The water content of the soil at this point is considered the plastic limit. The plasticity index is calculated as the difference between the liquid and plastic limits.

This SOP is based on the following reference methods:

- ASTM Standard D 4318-05 “Standard Test Methods for Liquid Limit, Plastic Limit and Plasticity Index of Soils”. ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

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

Atterberg Limits: Liquid limit and plastic limit of soils.

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.

- Oven, 110°C (+/-5°C), Barnstead LC Oven Model# 3513 or equivalent.
- Top loading balance, Mettler Model# PB3002 or equivalent.
- Aluminum measuring pans, Fisher Scientific or equivalent.
- Stainless steel spatulas and spoons, Fisher Scientific or equivalent.
- Heat shield gloves / Oven Tongs, Fisher Scientific or equivalent.
- 250 mL glass beakers
- Liquid limit device meeting the requirements of ASTM D4318
- Metal gauge block for calibration of liquid limit device
- Flat grooving tool meeting the requirements of ASTM D4318
- Frosted glass plate that is 12 inches square and 3/8 inch thick
- #40 (425um) sieve and collection pan
- Aluminum pans with close-fitting lids
- Parafilm
- Rubber-tipped pestle and mortar

7.0 Reagents and Standards

Reagent Water

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection. Sample collection procedures are provided in this SOP for guidance only. The laboratory recommends that all samples be collected in accordance with a client specified sampling plan.

Listed below are recommended sample size, preservation and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time	Reference
Solid	Glass	500g	None	None	Method

Unless otherwise specified by client or regulatory program, after analysis samples are held for a minimum of 30 days and then disposed of in accordance with applicable regulations.

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.

10.1.1 Liquid Limit Device Calibration Check

Liquid Limit Devices are purchased certified annually.

10.1.2 Grooving Tool Critical Dimension(s) Check

The groove tool is checked daily prior to use using the metal groove calibration tool.

10.2 Liquid Limit Procedure

10.2.1 Sample Preparation for Material that Passes the #40 Sieve (Wet Preparation)

Determine by visual and manual methods that the material has few to no particles that would be retained on the #40 sieve. In this case the samples will be processed using the wet preparation method. If the sample has a large percentage of material that will be retained on a #40 sieve the laboratory will prepare the sample using the dry preparation method described in Section 10.2.2.

For wet preparation prepare 150 to 200g of sample by mixing thoroughly with reagent water on a glass plate or mixing dish using a spatula. If needed, the sample can be soaked in a mixing dish with a small amount of reagent water to soften the material before mixing. Adjust the water content of the material to bring it to a consistency that would require 25-35 blows of the liquid limit device to close the groove. If during mixing, a small percentage of material is encountered that would be retained on the #40 sieve remove these particles by hand. Place the prepared material in the mixing dish and cover with parafilm, allow the material to stand for a minimum of 16 hours. Before starting the test thoroughly remix the sample. Proceed to Section 10.2.3.

10.2.2 Sample Preparation for Material Retained on the #40 Sieve (Dry Preparation)

Determine by visual and manual methods that the material has particles that would be retained on the #40 sieve. In this case, the laboratory's default method is dry preparation.

Dry a representative portion of the sample at room temperature until soil clods will pulverize easily. Once dry in appearance pulverize the sample using a rubber-tipped pestle and mortar being sure not to breakdown individual particles. Sieve the dried material through a #40 sieve collecting the material passing the sieve. Place all material passing the #40 sieve into a mixing dish. When large coarse particles such as shells, concretions or other fragile particles are found during pulverization do not crush these particles to make them pass the #40 sieve.

Place any material retained on the #40 sieve in an aluminum dish and soak with reagent water. Stir this material to separate the fine material from the coarse material. Transfer the sample and water mixture to a #40 sieve with a collection pan being sure to capture the water and any suspended fines in the collection pan. Discard the material retained on the #40 sieve. Pour the water mixture from the collection pan into the mixing dish containing the material that passed through the #40 sieve.

Adjust the water content of the mixture by adding small increments of reagent water or by allowing the mixture to dry at room temperature while mixing on a glass plate. The material should be at a water content that would require 25-35 blows of the liquid limit device to close the groove. Place the prepared material in the mixing dish and cover with parafilm, allow the material to stand for a minimum of 16 hours. Before starting the test thoroughly remix the sample. Proceed to Section 10.2.3.

10.2.3 Analysis (Method A)

Place a portion of the sample in the cup of the liquid limit device, press, pat and spread the sample until it reaches a depth of approximately 10mm at its deepest point, tapering to form a horizontal surface. Take care to work air bubbles out of the sample, but try to form the soil pat using as few strokes as possible. Cover any unused soil in the beaker to retain moisture.

Form a groove in the sample by drawing the tool, beveled edge forward, through the soil on a line joining the highest point to the lowest point on the rim of the cup. When cutting the groove, hold the tool against the surface of the cup and draw in an arc, maintaining the tool perpendicular to the surface of the cup. If the soil cannot be cut without tearing, use several shorter strokes of the grooving tool, or cut a slightly smaller groove using a spatula and use the grooving tool to form the final dimensions. Use extreme care to prevent the soil pat from sliding in the cup.

Clean the underside of the cup and verify that there are no soil crumbs present on the base or cup. Lift and drop the cup by turning the crank at a rate of 2 drops per second, until the two

halves of soil come in contact across the groove along a distance of 13mm (1/2”).

Verify that an air bubble has not caused premature closing of the groove by comparing both sides of the groove. Both sides of the groove should flow together with approximately the same shape. If an air bubble is present, add a small amount of soil to the sample in the cup, reform the soil and repeat the groove. If the soil slides on the surface of the cup, repeat the test with a higher water content. If after several attempts at higher water contents, the soil continues to slide in the cup or the number of blows to close the groove is always below 25, the liquid limit cannot be determined. When the liquid limit can not be determined record 0 for Liquid Limits and Plastic Limits in the Laboratory Information Management System (TALS) worksheet and create a non conformance memo (NCM).

Record the number of blows that it took to close the groove in the TALS worksheet.

Label a small aluminum pan for each sample. Place the pan on a tared balance and upload the weight measurement into the TALS worksheet.

Remove a section of sample approximately the width of the spatula, crossing the closure of the groove, and place it into the pre-weighed aluminum pan. Upload the weight measurement of pan + sample into the TALS worksheet.

Transfer the soil that remains in the cup back to the 250 mL beaker then wash and dry the cup, grooving tool and spatula.

Remix the sample and repeat the analysis at three different water contents. The trials should be set such that closure is achieved with 15 to 25 blows (1 Trial), 20 to 30 blows (2nd Trial) and 25 to 35 (3rd Trial).

When the trials are complete, determine the water content of the soil. To do so, place the aluminum pans + sample in the oven and dry for at least 16 hours at a temperature of 105ºC. Reweigh each pan and upload the weight measurements into the TALS worksheet.

Calculate the liquid limit using the equation given in Section 11.0.

10.3 Plastic Limit – Hand Method

Select ~20 g from the sample material that was prepared for the liquid limit test. Reduce the water content of the sample so it can be rolled without sticking to the hands by spreading the sample aliquot onto a frosted glass plate.

Take a 1.5 – 2.0 g portion of sample and form into an ellipsoidal mass. Using your fingertips and the glass plate quickly roll the mass into a thread of uniform diameter then continue rolling to reduce the diameter to 3.2mm (1/8”) taking no more than two minutes to do so.

Break the thread into several smaller pieces, reform the pieces into ellipsoidal masses, and re-roll into 3.2mm threads. Continue forming and rolling until the thread crumbles under the pressure for rolling and the soil can no longer be formed into a 3.2mm thread.

Label an aluminum pan with its close-fitting lid for each sample. Place the pan on the balance and upload the weight measurement to the TALS worksheet.

Gather the portions of the crumbled thread together and place it in the pan then immediately cover the pan.

Select another 1.5-2.0 g portion of the sample and repeat the previous steps until the covered aluminum pan contains at least 6 grams. Upload the final weight into the TALS worksheet.

Repeat the above steps to generate a second covered pan containing at least 6 g of soil.

Place both pans into the oven and dry for at least 16 hours. Once dry, re-weigh each pan and upload the weight measurements into the TALS worksheet.

If Plasticity Limits can not be determined record Non-Plastic in the TALS worksheet.

Calculate the plastic limit and plasticity index using the equations given in Section 11.0.

11.0 Calculations

- Liquid Limit (LL)

  $LL = W^n(N/25)^{0.121}$

  Plot the relationship between the water content (Wn) and the corresponding number of drops (N) on a semi-logarithmic scale. The water content (Wn) is plotted on the X-axis with an arithmetical scale, and the number of blows (N) is plotted on the Y-axis with a logarithmic scale. Draw the best straight line through three or more points. Take the water content that corresponds with 25 drops as the liquid limit.

- Plastic Limit (PL)

  Compute the average of the two water contents.

  $PL = (Wc_1+Wc_2)/2$

  Where:

  PL = plastic limit
  Wc_1 = water content of first trial
  Wc_2 = water content of second trial

- Plasticity Index (PI):

  $PI = LL – PL$

  If the liquid limit or plastic limits could not be determined, or the plastic limit is equal to or greater than the liquid limit, report the soil as non-plastic, NP.

12.0 Data Review

Refer to laboratory SOP BR-QA-019 for additional instruction on the requirements for data review. The following sections summarize the general procedure as described in the data review SOP.

12.1 Primary Review

Verify that the batch editor is complete and all observations have been recorded in the TALS Batch Worksheet. Review the results against acceptance criteria. If acceptance criteria are not met, perform corrective action or make arrangements for corrective action with another analyst.

Set results to primary or rejected as appropriate. Record all instances where acceptance criteria are not met with a nonconformance memo (NCM).

Verify project requirements or program specific requirements (PRS) specified for the job(s) included in the batch were followed and met. If not, immediately notify the project manager (PM) to determine an appropriate course of action. Record decisions made in the data review checklist.

Set the batch to 1st level review.

12.2 Secondary Review

Record the review using the data review checklist.

Review project requirements or program specific requirements (PRS) specified for the job(s) included in the batch and verify these requirements were followed and met. If not, consult with the primary analyst to determine cause. Any decisions made should be recorded on the data review checklist and retained as part of the analytical record.

Review the TALS batch editor to verify ancillary information for the work performed is filled in.

Verify that that the procedures in this SOP were followed. If a discrepancy between the SOP and the analytical record is found, consult with the primary analyst to determine the source of the discrepancy. Resolve the discrepancy and verify any modifications to the SOP are properly documented and were approved by laboratory management.

Spot-check ~15% of samples in the batch to verify data.

Verify acceptance criteria were met. If not, verity that corrective actions were performed and the nonconformance was documented with an NCM. Review the NCM to verify the form is filled out and the requisite information has been included in the internal comments tab. If corrective action was not performed and the failure not documented, consult with the primary analyst to determine the cause. Consult with the primary analyst and department management to determine what actions should be taken, then follow-through with the decision made.

Run and review the deliverable. Fix any problems found.

When review is complete set the method chain to lab complete. Forward any necessary paperwork to report/project management.

13.0 Method Performance

13.1 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.

14.0 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."

15.0 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.

16.0 References / Cross-References

- ASTM Standard D 4318-05 "Standard Test Methods for Liquid Limit, Plastic Limit and Plasticity Index of Soils". ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org
- Corporate Environmental Health and Safety Manual (CW-E-M-001)

17.0 Method Modifications

#	Method Reference	Modification	Technical Justification
1	ASTM Method D4318-05 Section 10.1	Method states to use the wet preparation procedure unless dry preparation is specified. The laboratory's practice is to use dry preparation for samples containing particles retained on the #40 sieve.	Both preparation methods are approved in the method.

18.0 Attachments

None

19.0 Revision History

BR-GT-011, Revision 8:
- Title Page: Updated approval signatures.
- All Sections: Replaced LIMS with TALS
- Added section 12.0, Data Review, and renumbered following sections accordingly.

BR-GT-011, Revision 7:
- Title Page: Updated approval signatures.
- Section 5.2: Updated MSDS to SDS
- Section 10.0: Updated calibration procedure
- Section 10.2.3: Addition of process to report results when the test is not amendable for the method
- Section 10.3: Addition of process to report results when the test is not amendable for the method
- Attachments: Removed Figure 1.

BR-GT-011, Revision 6:
- Title Page: Updated approval signatures.
- All Sections: changed DI water to reagent water.
- Section 1.0: Distinguished the difference when the laboratory will use wet or dry preparation.
- Section 2.0: Addition of dry preparation summary.
- Section 6.0: Added missing equipment
- Section 10.2: Changed procedure to reflect lab practice
- Section 16.0: Addition of modification table

Title: Water (Moisture) Content of Soil and Rock by Mass (ASTM D2216- 05, Method B)

Approval Signatures:

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Approval Date: 23 February, 2016

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 smaller 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

There are no materials with a health rating of 3 or 4 used in this procedure. If a chemical material is listed, employees must review the information in the SDS (Safety Data Sheet) 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

All data is 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 8:
- Title Page: Updated Approval Signatures
- Section 5.2: Updated language to reflect that no hazardous materials are used in the method.

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

Title: Density in Soils by Drive Cylinder Method (ASTM D2937-04)

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Approval Date: July 14, 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 standard operating procedure (SOP) describes the laboratory procedure for the determination of in-place density of natural, inorganic soil by the drive cylinder method.

This procedure is not suitable for organic soils that can compress upon sampling, very hard natural soils, heavily compacted soils, soils with low plasticity or soils with large amounts of gravel. The procedure is not recommended for friable soils or soft, highly plastic, non-cohesive, saturated or other soils which are not easily deformed.

2.0 Summary of Method

A representative portion of sample is removed from the sample collection tube and dried in an oven maintained at a temperature of 110°C for 16 hours. The moisture content of the sample is determined and expressed as a percent of the oven-dried mass. Density is subsequently calculated by dividing the value obtained for oven-dried mass by the determined volume of the drive cylinder.

This procedure is based on the following reference method:

- ASTM Standard D D2937-04 "Standard Test Method for Density of Soil in Place by the Drive-Cylinder Method. ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

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

This method is not appropriate for samples that can be "altered" during sampling, shipping and/or processing.

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.

- Oven, 110°C (+/-5°C), Barnstead LC Oven Model# 3513 or equivalent.
- Top loading balance, Mettler Model# PB3002 or equivalent.
- Aluminum measuring pans, Fisher Scientific or equivalent.
- Stainless steel spatulas and spoons, Fisher Scientific or equivalent.
- Ruler/meter stick with millimeter increments
- 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. Sample collection procedures are provided in this SOP for guidance only. The laboratory recommends that all samples be collected in accordance with a client field and sampling plan. Immediately after collection the sample(s) should be cooled and stabilized with packing material or wax to prevent shifting during transport.

Holding times are not applicable. Unless otherwise specified by client or regulatory program, after analysis samples are held for a minimum of 30 days and then disposed of in accordance with applicable regulations.

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 Sample Preparation/Analysis

Clean the outside of the sample collection tube then remove the end caps, wax any other protective material from each end of the sample collection tube. Remove any loose material from the collection tube. If the sample extends beyond the tube, trim the end of the sample so that it is

equal to the length of the tube.

Note: If a sample is received in a container other than a collection tube, the lab must create an NCM. The lab will then pack a clean, empty, and appropriately sized collection tube with the sample and proceed with the test method.

Measure the diameter of the sample tube and enter this value into the LIMS worksheet.

If sample fills the entire tube, measure the length of the tube and enter this value into the LIMS worksheet. If sample does not fill the entire tube, measure the length of the tube and measure the length of empty space in the tube, then subtract the length of empty space. Enter this value into the LIMS worksheet.

Weigh the tube and sample and enter this value into the LIMS worksheet.

Empty the sample into a large pan then clean the tube with a spatula to ensure all sample is taken into account. Weigh the clean tube and enter the weight measurement into the LIMS worksheet.

Label a clean aluminum pan with the sample ID and weigh the pan and enter this weight measurement into the LIMS worksheet.

Thoroughly mix the sample to homogenize with a spatula or spoon. Measure at least 100 g of the sample into the preweighed pan, or if practical, use the entire sample. Enter this weight measurement into the LIMS worksheet.

Place the sample into an oven maintained at 110°C and allow the sample to dry for a minimum of 16 hours. After this time period has elapsed, remove the pan from the oven and re-weigh. Enter this weight measurement into the LIMS worksheet.

The LIMS method calculate the moisture content, sample length, sample volume and in-place density using the equations give in Section 11.0.

11.0 Calculations / Data Reduction

11.1 Calculations

Percent Moisture Content

Moisture Content, % = [(A-B) * 100]/B

Where:
A = pan + wet sample, g
B = pan + dry sample, g

Sample length:

$L=L_1-(L_2+L_3)$ mm

Where:
L = sample length
L_1 = length of sample tube
L_2 = average recovery, top
L_3 = average recovery, bottom

Sample volume:

$V = [(\pi(D/2)^2)L]$

Where:
V = sample volume (calculated)
D = sample tube diameter
L = sample length

In-place Density:
$= m_1/V$ g/cm^3 (dry)

$= m_2/V$ g/cm^3 (wet)

Where:
= calculated dry density
m_1 = mass of sample, dry
m_2 = mass of sample, wet
m_3 = mass of sample tube
V = sample volume

11.2 Data Review

Primary 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.

Enter the batch information into LIMS and complete the batch editor and worksheet for each extraction and cleanup batch performed. Initiate NCMs for any anomalies observed during the process. Set the status of each 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 each batch to second level review.

Run the QC Checker, review the deliverable and set the job to lab complete.

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 D2937-04 "Standard Test Method for Density of Soil in Place by the Drive-Cylinder Method. ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

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

16.0 Method Modifications

None

17.0 Attachments

None

18.0 Revision History

BR-GT-018, Revision 6
- Title Page: Updated Approval signatures and copyright date
- Section 5.2: Reference to Table 1 replaced with 'not applicable' as hazardous materials are not used in this method.
- Section 10.2: Updated procedure section.
- Appendix B: This appendix was added.

- Updated MSDS to SDS

BR-GT-018, Revision 5:

- Title Page: Updated approval signatures.
- Section 4.0: Inserted a statement saying this method is not appropriate for all soil samples.
- Section 10.2: changed minimum weight for water content from 50 g to 100 g.

Appendix B: Porosity Calculation

Porosity is calculated using the sample's determined Specific Gravity and In Place Density. The calculation is as follows:

n = 100 [1-(pb/pd)]

Where:

n = porosity in %
pb = bulk density of the sediment in g/cm^3
pd = particle density in g/cm^3

Fetter, C.W. 2001. Applied Hydrogeology. Prentice Hall, Upper Saddle River, NJ. on p. 70. Book has 598 p.

Title: TOC in Soil

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Approval Date: September 30, 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 total organic carbon (TOC) and black carbon in soils, sediments and other solids.

The procedure for TOC in soils and sediments is provided in the main body of this SOP. The procedure for the determination of TOC in marine sediment high in inorganic carbon is provided in Appendix B and the procedure for black carbon is provided in Appendix D.

1.1 Analytes, Matrix(s), and Reporting Limits

This procedure may be used to determine percent dry weight in soil and solid materials. Oily matrices may not be amenable to this procedure.

The routine reporting limit is 1000 mg/kg based on an initial sample weight of 10 mg.

2.0 Summary of Method

10 mg of dried sample is transferred to a tin capsule, treated with phosphoric acid and dried in an oven at a temperature of 105℃ for 30 minutes to one hour in order to separate the organic carbon from inorganic carbonates and bicarbonates. The sample is analyzed on an instrument where it is pyrolyzed in an inductive type furnace. The carbon is converted to carbon dioxide and measured by a differential thermal conductivity detector.

This procedure is based on the following reference documents:

- EPA Region II Document Determination of Total Organic Carbon in Sediment, July 27, 1998, authored by Lloyd Kahn, Quality Assurance Specialist.

- Dixon, Wilfrid J., and Massey, Frank J. Jr.: Introduction to Statistical Analysis (fourth edition). Edited by Wilfrid J. Dixon. McGraw-Hill Book Company, New York, 1983. P377 and P548.

The procedure in this SOP for total organic carbon is modified from the above reference method. The procedures for black carbon and marine sediment are not based on a method and should be considered laboratory derived methods.

3.0 Definitions

A list of general laboratory terms and definitions are provided in Appendix A.

4.0 Interferences

Volatile organics in the sediments may be lost in the decarbonation step resulting in a low bias.

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. The table does not include all materials used in the procedure**.** A complete list of materials used can be found in section 7.0. 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. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 Equipment and Supplies

- Drying Oven: Capable of maintaining a temperature of 105 ±2℃.
- Carlo Erba Elemental Analyzer Model EA1108 and Model NA 1500 or equivalent.
- Costech Elemental Analyzer: Model 4010 or equivalent.
- Analytical Balance: Capable of weighing to the nearest 0.0001g.
- Aluminum Weigh Boats.
- Tweezers
- 5mm X 9mm tin capsules
- Quartz Columns: Costech Analytical or equivalent.
- Quartz wool: for segregating and containing column materials
- Copper Wire, Reduced: Costech Analytical or equivalent.
- Tungsten on Alumina: Costech Analytical or equivalent.
- High Temperature Gloves
- Clear Plastic Sample Trays: Costech Analytical or equivalent.

7.0 Reagents and Standards

7.1 Reagents

- Reagent water

- Phosphoric Acid, Concentrated: Reagent Grade, J.T. Baker recommended.

Phosphoric Acid Solution (1:19): Add approximately 100 mL of reagent water to a 200 mL volumetric flask. Add 18.34 g of concentrated phosphoric acid to the volumetric flask then adjust to volume with reagent water. Mix the solution well then transfer the solution to a 250 mL polyethylene bottle. Assign an expiration date of six months from date made and store the solution at room temperature.

7.2 Standards

- Potassium Hydrogen Phthalate (KHP) (Primary Standard Grade) Used to calibrate the instrument. 47.05% Carbon by weight

1% Carbon KHP Solution (10,000 mg Carbon/L): Add 50 mL of reagent water to a 100 mL volumetric flask. Add 2.128 g of KHP and dissolve completely. Adjust to final volume with reagent water. To mix the solution, cap the flask and invert. Allow the air bubble to reach the top of the flask. Repeat 9 times. Assign an expiration of 6 months from the date prepared and store at room temperature.

0.1% Carbon KHP Solution (1000mg Carbon/L): Add approximately 25 mL of reagent water to a 50 mL volumetric flask. Add 5 mL of 1 % Carbon KHP solution to the flask and adjust to final volume with reagent water. To mix the solution, cap the flask and invert. Allow the air bubble to reach the top of the flask. Repeat 9 times. Assign an expiration date of 6 months from the date prepared so long as the parent solution does not expire sooner, in which case use the earliest expiration date. Store the solution at room temperature.

0.01% Carbon KHP Solution (100mg Carbon/L): Add approximately 25 mL of reagent water to a 50 mL volumetric flask. Add 0.5 mL of 1% Carbon KHP Solution and adjust to final volume with reagent water. To mix the solution, cap the flask and invert. Allow the air bubble to reach the top of the flask. Repeat 9 times. Assign an expiration date of 6 months from the date prepared so long as the parent solution does not expire sooner, in which case use the earliest expiration date. Store the solution at room temperature.

Note: Alternatively a 10,000mg/L TOC standard may be purchased from a reputable vendor (Spex Certiprep, SCP Science or ERA) and diluted appropriately to prepare the intermediate solutions above.

- Laboratory Control Samples (LCS) Material, Organic Material of known Carbon percentage: Purchased from LECO Corporation.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so sampling procedures are not included in this SOP. Sampling requirements may be found in the published reference method.

Listed below are the laboratory recommended minimum sample size, preservation and holding time requirements:

Parameter	Sample Container	Minimum Sample Size	Preservation	Holding Time[1]	Reference
Total Organic Carbon	Amber glass	10 g	Chilled to ≤ 4℃	14 Days	TOC by Lloyd Kahn
Black Carbon	Amber glass	10 g	Chilled to ≤ 4℃	None	None

[1] Holding time is determined from date of collection.

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

9.1 Sample QC

The laboratory prepares the following quality control samples with each batch of samples.

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 in 20 or fewer samples	< RL
Laboratory Control Sample (LCS)	1 in 20 or fewer samples	%R (75-125)
Sample Duplicate (DP)	Client Request	RPD (≤ 20)
Matrix Spikes (MS)	Client Request	%R (75-125)

If a sample quadruplicate is not designated by the PM analyze the LCS in quadruplicate as a measure of method precision.

9.2 Instrument QC

The laboratory analyzes the following instrument check standards:

QC Item	Frequency	Acceptance Criteria
Initial Calibration (ICAL)	Initial Method Set-Up, after combustion chamber is changed (approx. every 200 drops)	Correlation coefficient must be >0.995
Initial Calibration Verification (ICV)	After initial calibration	%R(75-125)
Calibration Verification (CCV)	Every 20 drops and at the end of the analytical sequence	%R (75-125)
Calibration Blank (CCB)	After every CCV	<RL

10.0 Procedure

10.1 Calibration

Analyze a calibration curve each time the combustion column is changed. Change the column after 200 drops or when you experience result issues or odd peak shapes or baseline issues. The column change procedure is provided in Appendix C.

The recommended formulations for each calibration level are provided in the following table:

Calibration Standards	1.0% C KHP uL	0.1% C KHP uL	0.01%C KHP uL	% Carbon KHP	KHP (mg)	Carbon (mg)	mg/Kg of Carbon (10mg sample)
Level 1	0	0	0	47.05	0	0	0
Level 2	0	0	100	47.05	0.0213	0.010	1000
Level 3	0	40	0	47.05	0.0850	0.040	4000
Level 4	25	0	0	47.05	0.5313	0.25	25000
Level 5	50	0	0	47.05	1.0627	0.500	50000
Level 6	75	0	0	47.05	1.5940	0.750	75000

Measure a single drop for each calibration point. The instrument software system plots peak area against mg of Carbon and calculates a correlation coefficient using standard linear regression. The correlation coefficient (r) must be $\geq$ 0.995 for the calibration to be considered acceptable. If it is not, repeat the calibration prior to further analysis.

10.2 Troubleshooting

- Calibration passes at > 0.995 correlation, but LCS fails abnormally low: Re-calibrate.
- Large peak before Carbon peak; Indicates leak in system, perform leak test, isolate and repair leak.
- Carbon peak “maxes out” at instrument 1200mv (peak has flat top): Reanalyze sample at lower weight.
- No peaks on any chromatograms, no results: Gases to instrument may be off. Turn on all gasses at valve manifold.
- Autosampler will not work at all: Gasses to instrument may be off. Turn on all gasses at valve manifold.
- Carry over; Clean autosampler slide, if persists reduce sample mass. Note sample carryover in NCM. Oily samples may not be amenable to this test.
- Single chromatogram shows results at bottom of page, but no peak or baseline in chromatogram window: Re-print single chromatogram.
- Some or all chromatograms show carbon peak at same retention time as CCV, but peak is not identified as carbon, or is identified as another element: Retention time shifted. Adjust retention time in calibration window, and reprint chromatograms.
- Upon recalibration, peaks are not being identified as carbon: In calibration window, general tab, adjust retention time to match peaks. Starting at level 1, “Open Standard”, open level1 curve pt. in calibration directory, click “Add Peak” button, click on peak itself. Increase level #, opening standard for each curve pt and add each peak. Carbon Tab should have all five calibration points on curve, if done correctly.

- Peaks in chromatograms identified as carbon, but all results in summary table below chromatogram are zero: Current calibration not associated with run when started. Open current calibration, copy first two columns for all points (5 rows) in small table in general tab. Then, open calibration that was associated with run (should be empty) and paste into table in calibration tab. Reprint all chromatograms on run.
- Software crashes during analysis: Boot up software normally. Chromatograms already printed/analyzed are ok, but, sample that was analyzing during shutdown is lost. Restart table at next sample by un-checking "run" box for samples already run and sample that was lost.
- Autosampler error causes few samples to remain in autosampler tray after run has finished: Identify samples that got stuck. Create a new run and analyze stuck samples (with initial weights) with bracketing QC. No PBS/LCS needed.
- Autosampler error causes many sequential samples to remain in autosampler tray after run has finished (usually end of run): Add rows onto existing table. Identify samples that did not get analyzed and repeat Ids and weights into added rows. Restart table. All analyzed samples' status should be blue (analyzed), added rows should be green (not analyzed yet).
- Various result issues or odd peak shapes or baseline issues: Column may be leaking or cracked. Change column, recalibrate.

10.3 Sample Preparation

Dry 5-10 g of sample in at 105 ^{o}C for 12-24 hrs. (The sample from the moisture fraction may be used for this step.) Disaggregate the sample to break up clumps to ensure exposure to acidification in next step. Do not grind the sample.

For each field sample prepare two tins for analysis. Using tweezers, and working directly from the box, place a tin capsule on the analytical balance and tare the balance. Using the small sample scoop, add approximately 10 mg (or the project specified sample weight) of sample to a tin capsule. Record the actual sample weight used on sample preparation log. Remove the capsule from the balance and place into one of the aluminum holding trays.

To prepare the method blank, set two empty tin capsules into an aluminum holding tray.

To prepare the LCS, weigh 9 to 11 mg of the LECO LCS material into two tin capsules and set them in sequence in an aluminum holding tray.

For the matrix spike, weigh out an additional sample aliquot and record its weight. Add 35 uL of 1% KHP calibration stock.

For the sample duplicate, weigh out an additional sample aliquot. Prepare two aliquots for both the matrix spike and the sample duplicate.

Add two drops of 1:19 phosphoric acid to each tin capsule. Place the aluminum trays into a drying oven set to a temperature of 105 ±2 ºC for 30-60 minutes or until all samples appear dry.

Using tweezers pinch the top of each tin capsule closed and compress the capsule around the material inside. Work carefully so as not to tear the capsule, but crush it down to the smallest size. Set the prepared samples in line in a clear plastic sample tray for storage, or place directly

into an autosampler tray for analysis. For the latter, leave positions open for the CCV check standards and associated calibration blanks.

Prepare the ICV, CCV standards and blanks as follows:

Prepare an ICV for each sequence. To prepare the ICV, weigh 9 to11 mg of the LECO LCS material into a tin capsule.

For each CCV, transfer 35uL of 1% KHP solution into a tin capsule. Dry the capsules in a drying oven set to a temperature of 105 ±2 ºC for 30-60 minutes or until all samples appear dry. Fold the capsule up and compress down to the smallest size possible. Prepare enough CCVs to ensure a frequency of every 20 drops and the end of the analytical sequence. For each associated calibration blank, leave an empty position in the autosampler tray.

10.4 Preparation of the ICV, CCV and Blanks

If the column has been changed generate a new calibration curve. If not, use the existing calibration curve for analysis. Each column will analyze approximately 200 individual sample drops. When the counter on the instrument approaches 200, watch the instrument data for signs that the column is deteriorating; poor peak resolution, trailing baselines, extraneous peaks. If a column change is necessary, refer to Appendix C for the procedure. After changing the column, generate a new calibration curve.

Select the appropriate channel: Channel 1 is the NA 1500, Channel 2 is the EA 1108, and Channel 3 is the Costech instrument, which has its own PC. At the main screen select the sample table icon. The last sample table that was run will be shown on the screen.

Open a new sample table, and select the appropriate number of sample positions for the analysis, then name the table with the date and a unique alpha designator (i.e. 061505a). In front of the %3r in the file name column of the sample table, add the sample table name to ensure that each individual chromatogram generated from this sample table has a unique filename associated with it.

If the combustion column has been changed and instrument needs to be calibrated, follow the procedure below:

Prepare a “bypass” drop to determine the retention time for carbon with the new column. The bypass is an aliquot of CCV. Enter 10 mg for the weight. Drop the bypass into the instrument and initiate a singular analysis. Set the retention time for carbon in the software to match that of the bypass drop.

Identify the first five sample lines with the names Std1 through Std 5. Enter their respective weights in the weight column, assign them a level # in the level column (Std1 is level 1, Std2 is level 2, etc.) to alert the software the order in which to place the calibration standards. In the sample type column, use the drop down and select “standard” for each. Finally, use the drop down in the Standard name column and select “KHP” for each. Enter the KHP weights from the calibration table. Add the standards to the autosampler tray and hit “start”

10.5 Software Set-up and Analysis of a Curve

Open a new sample tray and create a unique file name. When the instrument was last calibrated, the software creates a calibration file with the same name as the sample table in which it was run. Open this file and save it with the same name as the sample table about to be run to ensure that the analysis is calculated from the most recent calibration. To do this, click on the calibration icon (looks like a little calibration curve) and use the file option to open the calibration file last performed. Save this file with the same name as your sample table. Click on the sample table icon (looks like a little sample table) to get back to your sample table.

Enter each sample ID and their respective weights and save the sample table. Enter a weight of 10 mg for the Method Blank (PBS) and instrument blanks.

An example analytical sequence follows:

Initial Calibration (calibration blank and 5 calibration standards)

ICV	(1 drop)
ICB	(1 drop)
CCV	(1 drop)
CCB	(1 drop)
PBS	(2 individual drops)
LCS	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
CCV	(1 drop)
CCB	(1 drop)

Turn the autosampler carriage until the number 1 position is behind the post, in front of the autosampler. Add the CCV, blanks and samples to the autosampler tray starting at position 2. Place the tray on the autosampler carriage. Place the ICV directly into position 1. Ensure the tin has dropped to the loaded position. The tray is now set to run.

Click the “start” icon to begin the analysis.

After analysis review the analytical results against the acceptance criteria given in Table 2, Section 18.0, and perform corrective action as necessary. Report results in mg/kg Carbon.

11.0 Calculations / Data Reduction

11.1 Calculations

11.1.1 Percent Carbon to mg/kg Carbon Conversion

% Carbon × 10,000 = mg/kg Carbon

11.1.2 LCS Percent Recovery (%R)

$$\%R = \frac{\text{LCS Result}}{\text{LCS True Value}} \times 100$$

11.1.3 MS Percent Recovery (%R)

$$\text{mg/Kg wet SA} = \frac{\text{Spike TV} \times \text{weight of MS added}}{\text{sample weight}} \times 1\text{million}$$

$$\text{mg/Kg dry SA} = \frac{\text{mg/Kg wet SA}}{\%\text{ solid}} \times 100$$

$$\text{mg/Kg dry Carbon} = \frac{\text{mg/Kg wet Carbon (from instrument)}}{\%\text{ solid}} \times 100$$

$$\%R = \frac{A - B}{C} \times 100$$

Where:
A= Average of two drops of MS sample result: mg/Kg dry carbon
B= Average of two drops of parent sample: mg/Kg dry carbon
C= Average of two drops of mg/Kg dry SA
SA= spike added (mg/Kg)
Spike TV= 0.7686 (mg/Kg)

11.1.4 Relative Percent Difference (RPD)

$$RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} \times 100$$

Where:

D_1 = First Sample Value

D_2 = Second Sample Value (duplicate)

11.1.5 Dixon Test (Use 3-7 results)

1. Sort all the results in ascending order (low values to high).
2. Calculate the tau statistic for the low and high values.
3. Compare the calculated tau statistics (low and high) to critical values listed below.
4. If either calculated tau is higher than the critical value, reject that value and repeat the test.

Tau statistic for lowest value = $\tau_L = (X_2 - X_1) / (X_k - X_1)$
Tau statistic for highest value = $\tau_H = (X_k - X_{k-1}) / (X_k - X_1)$

Where:
X_2 = Second lowest value in sorted list.
X_1 = Lowest value in sorted list.
X_k = Highest value in sorted list.
X_{k-1} = Second highest value in sorted list.

Number of observations, k	Critical Values
3	0.941
4	0.765
5	0.642
6	0.560
7	0.507

11.2 Data Review

11.2.1 Primary Data Review

Evaluate the results of the field and QC samples against the established acceptance criteria. If criteria are not met, perform corrective action. If any data is reported outside criteria, initiate a nonconformance memo (NCM).

The instrument method is configured to flush between each sample and/or standard. Flush times are based upon the time required for instrument response to return to baseline following a standard at the LDR. However, it is impossible to predict the memory characteristics of every sample. Therefore carefully monitor samples analyzed immediately after high concentration samples for signs of carry-over. Reanalyze the sample at a lower mass or with blanks following injection if carry over is suspected.

Narrative note samples whose results exceed the concentration of the established linear range.

Upload the data into TALS. Enter the batch information in the TALS batch. Set results to primary or acceptable as appropriate, check QC linkages then set the TALS batch to first level review. Complete the data review checklist designed for this task.

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 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.

Verify that the acceptance criteria for the calibration and QC items listed in Table 2 were met. If the results do not fall within the established limits verify the recommended corrective actions were performed. If not, initiate corrective actions and/or verify an NCM was created to document the criteria exception. Verify analytical results are qualified accordingly and the TALS batch information is complete. Set samples to 2nd level review.

Run the LIMS QC Checker, investigate and correct any problems found. Run and review the deliverable. Fix any problems found then set the method chain to lab complete. Complete the data review checklist designated for this task.

11.2.3 Data Reporting

The report format, application of data qualifiers and creation of the data deliverable is performed by the LIMS using the formatter set by the project manager during log-in.

Records of electronic and hardcopy data are maintained as described in laboratory SOP BR-QA-014.

12.0 Method Performance MDL

Determine a method detection limit (MDL) on each instrument used for analysis for each matrix and non-prepared analyses prior to initial use of the method and annually thereafter.

Refer to laboratory SOP BR-QA-005 for the laboratory's procedure for method detection limit 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 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 *Hazardous Waste*.

The following waste streams are produced when this method is carried out.

- Caustic waste – 2.5 L glass satellite container.
- Acidic Waste - 2.5L glass satellite container
- Non-Hazardous waste- 2.5L glass satellite container

The satellite containers are labeled "Hazardous Waste" along with the type of waste category generated. Authorized personnel routinely transfer the contents of the satellite containers to the hazardous waste storage room for future disposal in accordance with Federal, State and Local regulations.

15.0 References / Cross-References

- EPA Region II Document Determination of Total Organic Carbon in Sediment, July 27, 1998, authored by Lloyd Kahn, Quality Assurance Specialist.

- Dixon, Wilfrid J., and Massey, Frank J. Jr.: Introduction to Statistical Analysis (fourth edition). Edited by Wilfrid J. Dixon. McGraw-Hill Book Company, New York, 1983. P377 and P548.
- Corporate SOP CW-E-M-001 Corporate Environmental Health and Safety Manual
- Laboratory SOP BR-QA-005, Procedures for the Determination of Limits of Detection (LOD), Limits of Quantitation (LOQ) and Reporting Limits (RL).
- Laboratory SOP BR-QA-011 Employee Training
- Laboratory SOP BR-EH-011 Hazardous Waste
- Laboratory SOP BR-QA-014 Laboratory Records
- Laboratory Quality Assurance Manual (QAM)

16.0 Method Modifications

The laboratory procedure is modified from the reference method as follows:

Modification Number	Method Reference	Modification
1	TOC by Lloyd Kahn	The laboratory analyzes two drops per sample and if the RPD is greater than 40% the Dixon test is utilized.
2	TOC Lloyd Kahn	Due to the small sample size the laboratory dries and disaggregates the sample prior to analysis. This step improves precision associated with high moisture or clay type matrices.
3	TOC by Lloyd Kahn	The Laboratory uses 1:19 (w/w) phosphoric acid to decarbonize the sample and dries the sample in an oven at 105^{o}C

17.0 Attachments

- Table 1: Primary Materials Used
- Table 2: QC Summary & Recommended Corrective Action
- Appendix A: Terms and Definitions
- Appendix B: TOC Procedure for High Concentration Marine Sediments (CITHON)
- Appendix C: Column change procedure
- Appendix D: Determination of Black Carbon in Sediment Procedure

18.0 Revision History

BR-WC-0024, Revision 2:

- Section 1.1: Removed last sentence of paragraph.
- Section 2.0: Added drying of sample prior to preparation
- Section 9.2 and Table 2: Updated ICV criteria.
- Section 10.5: Removed reference to moisture correction

BR-WC-0024, Revision 1:

- Title Page: Updated approval signatures and copyright date.
- Updated MSDS to SDS
- Section 1: Added note that procedure may not be amenable to oily matrices.

- Section 7.2: Added CIPA (05/10/11) information to body of SOP. Added option to purchase calibration stock material.
- Section 9.1: Added CIPA (05/10/11) information to body of SOP
- Section 9.2 & Table 2: Added ICV criteria, and update CCV criteria
- Section 10.3: Added drying and disaggregation step to improve precision. Update CCV, ICV, and MS spiking to match laboratory practice. Updated sequence to match laboratory practice.
- Section 12: Added Data Review procedures
- Section 13: Added Method Performance procedure.
- Section 16.0: Added dry and disaggregation procedure.
- Table 2: Added ICV criteria

BR-WC-0024, Revision 0:

This is the first version of this SOP.

Table 1: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Phosphoric Acid	Corrosive	1 Mg/M3 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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 2: QC Summary, Frequency, Acceptance Criteria and Recommended Corrective Action (TOC Lloyd Kahn)

QC Item	Frequency	Acceptance Criteria	Recommended Corrective Action[1]
ICAL	Following each column change	correlation coefficient ≥ 0.995	Standards check, re-calibration
ICV	Following Calibration	75-125 %R	Reanalyze, If still fails recalibrate and reanalyze all samples associated with failing ICV.
CCV	Every 20 drops and at the end of the analytical run	%R (75-125)	Re-prepare and reanalyze samples not bracketed by passing standard.
Blank (paired with CCV)	Following each CCV	< RL	Re-prepare and reanalyze batch.
Method Blank (MB)	Once per batch of 20 samples	< RL DoD: ½ RL	Re-prepare and reanalyze batch.
LCS	Once per batch of 20 samples	%R (75-125)	Re-prepare and reanalyze batch.
Sample Duplicate (DP)	One per batch of 20 or less samples	RPD (≤ 20)	Discuss outlier in project narrative
MS/MSD	One per batch of 20 or less samples	%R (75-125)	Discuss outlier in project narrative
Sample precision	Each sample is run in duplicate	%RPD<40%	Analyze 2 more replicates and perform Dixon test for high and low outliers. Include Dixon spreadsheet in the data package and narrative note results.

[1]*The recommended corrective action may include some or all of the items listed in this column. The corrective action taken may be dependent on project data quality objectives and/or analyst judgment but must be sufficient to ensure that results will be valid. If corrective action is not taken or is not successful, data must be flagged with appropriate qualifiers.*

Appendix A: Terms and Definitions

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria.

Calibration: the establishment of an analytical curve based on the absorbance, emission intensity or other measured characteristic of known standard.

Calibration Standards: a series of known standard solutions used to calibrate the instrument response with respect to analyte concentration. A standard containing the analyte in question (KHP) is prepared at varying concentrations and analyzed. This standard is a separate source from the LCS. The KHP is used to calibrate the instrument response with respect to analyte concentration.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Duplicate (DP): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate.

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Appendix B: Marine Sediments High in Inorganic Carbon

Sample Preparation

Transfer approximately 10 g of a thoroughly mixed sample to an aluminum weigh dish, and dry in the 105℃ oven. Grind the sample with the pink mor tar and pestle to a fine powder. Record the weight of a 250 mL Teflon beaker then transfer ~ 5 g of the ground sample to this beaker.

If the sample is to be spiked, weigh the beaker to the nearest 0.1mg and record the weight. Likewise determine and record the weight of the added sample. Add 0.1g of NIST 1632b Trace Elements in Coal (80.11% Carbon) to the sample. Record the weight added. Evenly distribute the spike over the sample and use a glass stir rod to mix the spike with the sample. Do not use that stir rod with any other sample.

Use Talc-free latex gloves from this point on to minimize the risk of acid burns. Add several drops of 1:1 HCL to each sample and stir each sample with its own glass stir rod. Carefully rinse the stir rod and beaker walls with DI water using a fine-tipped squirt bottle. Use only what is needed to bring the entire sample to the bottom of the beaker. ***When adding water to acid use necessary precautions to avoid splashing!*** Samples with high concentrations of inorganic carbon may effervesce to the point of overflowing the beaker, so take care to add the acid in small aliquots and stir vigorously. If the sample "boils over" it must be re-prepared. Continue to add 1:1 HCL in small aliquots until there is no further reaction, taking sample to dryness after each addition of acid in a 105-degree oven.

Dry the treated samples in the oven after each acid/water addition. Do not add more than a total of 200 mL of 1:1 HCL to any sample.

NOTE*: Samples are hygroscopic and will absorb water if they are exposed to air for too long.*

Weigh beaker with residue and record the residue weight measurement. After the sample is thoroughly dry, scrape the sample residue from the beaker and grind to a powder using the pink mortar and pestle. Transfer the ground sample to a clean, dry 40-mL vial reserved for this analysis.

NOTE: *Depending on the nature of the sample, it may be difficult to completely remove the dried residue from the beaker or to grind it to a homogenous powder. Where difficulties are encountered, make a note on the preparation worksheet.*

Analysis

Perform TOC analysis on processed sample material as outlined in section 10.0 of this SOP.

Appendix C: Column Change Procedure

Turn off the helium and oxygen supplies to the instrument.

Dial the left furnace temperature to a reading of 052 (this equates to 520˚C). Wait until the temperature drops below 600˚C to remove the column.

Remove the panel covering the furnace and unscrew the autosampler connection from the top of the column.

Unscrew the fitting at the bottom of the column and remove.

Lift the column up and out of the furnace using high temperature gloves.

CAUTION: The column will still be 500-600˚C. Do not touch the center portion of the column. Place the spent column in the metal can designated for this purpose.

Lay a new quartz column on the bench top, measure and mark off for the following:

- One inch up from the bottom and add a ½ inch plug of quartz wool. Note: pack the quartz wool tightly enough for it to stay in place.
- Pour in 2 ½ inches of copper wire
- Pack another ½ inch quartz wool plug on top of the copper
- Pour in 3 inches of tungsten
- Pack a final ½ inch quartz wool plug on top of the tungsten

Place the new column into the furnace and reconnect the top and bottom fittings. Snug these up, but don't over tighten.

Replace the panel covering the furnace, dial the furnace temperature back to 102 (this equates to

1020˚C), and turn the helium and oxygen supplies back on.

When the instrument comes up to operating temperature, it is ready to calibrate.

Appendix D: Determination of Black Carbon in Sediment Procedure

1. Obtain a representative subsample of the sediment. Weight 10 grams of sample into a clean pre-tared aluminum drying pan or equivalent.

2. Dry the sample at 105^{o}C for at least 12 hours.

3. Grind the sample using a mortar and pestle.

4. Sieve the sample using a number 35 sieve (500 um).

5. Treat the sample with phosphoric acid. Add acid drop wise until effervescence is no longer observed.

6. Dry the sample at 105^{o}C for 1 hour.

7. Set aside an aliquot of the sample at this stage for direct TOC analysis, reported without correction for the IN623 percent solids. Continue with the sample for Black Carbon.

8. Place the dried sample into a clean crucible and cover the sample.

9. Bake the samples at 375^{o}C in a muffle for 24 hours or until the LCS is +/- 50% of the true value.

10. Allow the samples to cool and transfer approximately 10.0 mg into each of two tin capsules.

11. Transfer the sample (in the tin capsules) to the TOC analyzer for analysis by the Lloyd Kahn Method.

12. The sample is pyrolyzed in an inductive type furnace, where the carbon is converted to carbon dioxide, which is measured using a differential thermal conductivity detector.

13. The results will be reported as mg/Kg Black Carbon.

Note: Black carbon LCS material: NIST Standard Reference Material 1944 New York-New Jersey Waterways Sediment.

References:

Orjan Gustafsson, Thomas D. Bucherli, Zofia Kukulska, Mette Andersson, Claude Largeau, Jean-Noel Rouzaud, Christopher M. Reddy and Timothy I. Eglinton (December 2001) Evaluation of a Protocol for the Quantification of Black Carbon in Sediments, Global Biogeochemical Cycles, Volume 15, pages 881-890.

Orjan Gustafsson, Farnaz Haghseta, Charmaine Chan, John MacFarlane & Philip M. Gschwend (1997) Quantification of the Dilute Sedimentary Soot Phase: Implications for PAH Speciation and Bioavailability, Environmental Science & Technology, Volume 31, pages 203-209.

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Title: Polynuclear Aromatic Hydrocarbons by GC/MS Selected Ion Monitoring (SIM) [SW 846 Method 8270C and 8270D]

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1.0 Scope and Application

1.1 This procedure is a Gas Chromatography/Mass Spectrometry (GC/MS) technique for the analysis of polynuclear aromatic hydrocarbons (PAH) and heterocyclic compounds at the part per trillion (ng/L or ng/kg) level in waters or solids. This procedure follows the general guidelines of EPA Methods 8270C and 8270D for Selected Ion Monitoring (SIM) analysis.

1.2 The SIM technique optimizes quantitative information at the expense of qualitative information gained from other methods of analysis. It is important to note that this procedure is intended for the analysis of samples previously characterized by another method such as open-scan 8270C/D. The initial characterization is necessary to avoid misidentification of the parent compounds producing the ions used for this analysis.

1.3 In addition, this procedure is appropriate only for sample analytes of interest at less than 10,000 ng/L or 330,000 ng/kg. Samples containing semivolatile organics at concentrations greater than 10,000 ng/L and 330,000 ng/kg should be analyzed by a method designed to detect at higher (part per billion) levels. Samples at these levels may still be analyzed by this procedure, however, extra measurement uncertainty would be introduced because of the sample dilutions that would be required.

1.4 This procedure is applicable to water and soil samples. For water samples, 1 liter of water is extracted. It is also possible to extract 250 mL of water and analyze by an LVI (large volume injection) method designed to maintain reporting limits while reducing the initial volume of sample required for extraction. For soil samples, a sample aliquot of 30 g is extracted.

1.5 Analytes, Matrix(s), and Reporting Limits

The standard list of compounds that can be analyzed by this procedure is shown in Table IV. Typical reporting limits are 100 ng/L for aqueous samples and 5.0 μg/kg for soil samples for the PAH compounds.

2.0 Summary of Method

2.1 Sample Preparation

2.1.1 Aqueous Samples

Analytes of interest are extracted from water samples using separatory funnel extraction (EPA 3510C or 3510C_LVI) described in SOP DV-OP-0006. The PAH compounds are extracted from the sample without any adjustment to pH. The concentration of organic extracts is covered in SOP DV-OP-0007.

2.1.2 Solid Samples

Solid samples are extracted by sonication (EPA 3550C), which is

covered in SOP DV-OP-0016 or by microwave extraction (EPA 3546) described in SOP DV-OP-0015. The extraction solvent is a 1:1 mixture of methylene chloride and acetone. The concentration of organic extracts is covered in SOP DV-OP-0007.

2.2 Instrumental Analysis

2.2.1 Quantitation of the extracted compounds is performed by gas chromatography - mass spectrometry (GC/MS) in the selected ion monitoring mode (SIM). Routine instrument conditions and the ions used for analysis are shown in Tables I and IV, respectively.

2.2.2 Development of a successful SIM method requires identifying the ions to be monitored, the ion dwell times, the ions in each group, and the timing for switching between groups. A quantitation ion is selected with a confirmation ion being monitored for identification purposes (see Table IV). Switching times are set where there is adequate resolution (a gap of 1-2 minutes) between peaks. If there is inadequate time between eluting peaks, small retention time shifts may cause peaks to partially or completely disappear as there are changes in the ions monitored. Dwell times will be set by default once the ions per group and the switching times are identified in the data acquisition method. These can be adjusted manually in order to optimize sensitivity as needed.

3.0 Definitions

3.1 Refer to TestAmerica Denver's Quality Assurance Manual (QAM) and SOP DV-QA-003P for definitions of the quality control terms used in this document.

3.2 Selected Ion Monitoring - A mass spectrometry technique that provides lower detection level capability by monitoring fewer mass scans for longer periods of time than is done in open-scan methods.

3.3 Primary Ion Area - The signal chosen for quantitation purposes.

3.4 Secondary Ion Area - The signal chosen for identification and confirmation purposes.

3.5 LVI – Large Volume Injection – An analysis method designed to maintain reporting limits while reducing the initial volume of sample required for extraction by increasing the volume of sample extract introduced onto the GC column.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. The use of high purity reagents and solvents helps to minimize interference problems.

4.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the environment being sampled.

4.3 An interference that is unique to selected ion monitoring techniques can arise from the presence of an interfering compound which produces the same ion used for quantitation of one of the PAHs. This event results in a positive interference to the reported value for the compound of interest. This interference is controlled to some degree by acquiring data for a confirmation ion. If the ion ratios between the quantitation ion and the confirmation ion are not within the specified limits, then interferences may be present. Open scan analysis to identify compounds throughout the mass range is the most reliable assurance against reporting false positives.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

5.2 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, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately. Latex and vinyl gloves provide no protection against the organic solvents used in this method. Nitrile or similar gloves must be used.

5.3.2 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 must cool them to room temperature prior to working on them.

5.3.3 The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.3.4 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 the instrument from its source of power.

5.4 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. 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.

Materials with Serious or Significant Hazard Rating

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.
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.
PAH standards can contain all or some of the following:			Standards contain low concentrations of compounds known to be or suspected to be carcinogens. All PAH compounds are considered to be hazardous, toxic, and irritants. Some or all are reported human carcinogens, mutagens, and/or teratogens.
benzo(a)anthracene	Carcinogen		
benzo(b)fluoranthene	Carcinogen		
benzo(k)fluoranthene	Carcinogen		
benzo(a)pyrene	Carcinogen		
chrysene	Carcinogen	0.2 mg/m^3 - PEL	
dibenz(a,h)anthracene	Carcinogen		
indeno(1,2,3-cd)pyrene	Carcinogen		
naphthalene		10 ppm - PEL	

(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

6.1.1 Gas Chromatograph (See Table I for operating conditions)

The analytical system includes a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port is designed for on-column injection when using packed columns and for split or splitless injection when using capillary columns.

6.1.2 Mass Spectrometer (See Table I for operating conditions)

A mass spectrometer operating at 70 eV (nominal) electron energy in the electron impact ionization mode and tuned to maximize the sensitivity of the instrument to the compounds being analyzed. The GC capillary column is fed directly into the ion source of the mass spectrometer.

6.1.3 A computer system interfaced to the mass spectrometer 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 any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. The computer allows acquisition at pre-selected mass windows for selected ion monitoring.

6.1.4 Please refer to the Master List of Documents, Software, and Hardware (or current revision) located on R:\QA\Read\Master List of Documents for the current software and hardware to be used for data processing.

6.2 Supplies

6.2.1 All glassware used, both within the scope of this SOP and for the initial sample extraction (see SOPs DV-OP-0006, DV-OP-0008, DV-OP-0007, DV-OP-0015, and DV-OP-0016) must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water, and rinses with tap water, reagent water, and finally with acetone.

6.2.2 Glassware should not be oven dried or heated in a muffle furnace. Successive solvent rinses of the CLLE, separatory funnel, sonication, and Kuderna-Danish glassware are required to minimize low level contamination of samples.

6.2.3 Store glassware inverted or in sealed containers capped with aluminum foil.

6.2.4 Gas-tight syringes, various sizes, and SMI pipettors.

6.2.5 Serological pipettes are used for final extract volume measurement.

6.2.6 Micro reaction vessels, 1.8 mL vials with Teflon caps, for storing concentrated extracts.

6.2.7 Column – A Varian VF-5MS 30-meter fused silica capillary column, 0.5 μm film thickness, 0.25mm ID, plus 10-meter EZguard, or equivalent.

7.0 Reagents and Standards

7.1 Reagents

All solvents are reagent grade or higher unless specified otherwise. See SOPs CA-Q-S-001 and CA-Q-S-001 DV-1 for a description of the program for testing solvents prior to use.

7.1.1 Methanol, reagent grade.

7.1.2 Methylene chloride, reagent grade.

7.1.3 Helium gas, 99% + purity.

7.2 Standards

Commercial standards are received in flame-sealed ampoules or as neat, 100% concentration solutions. Standards are verified before use. Details concerning verification of standards are given in SOP DV-QA-0015. Stock standards are stored refrigerated at ≤ 6 °C. All stock standards must be protected from light. Stock standards are monitored for signs of degradation or evaporation. The standards must be replaced annually from the date of opening or earlier, if the vendor indicates an earlier date.

7.2.1 GC/MS Tuning Standard

A methylene chloride solution containing decafluorotriphenylphosphine (DFTPP) at a concentration of 50 μg/mL (25 μg/mL for LVI) is prepared.

7.2.2 Calibration Standards

Calibration standards for the initial calibration (ICAL) are prepared at 7 concentrations to cover the calibration range by diluting vendor stock standard solutions using methylene chloride. The standards are prepared directly in autosampler vials by using syringes to deliver the appropriate volumes of stock standard solution, internal standard solution, and methylene chloride. The following tables summarize a typical set of calibration standards:

Standard Method: Prepared using a PAH SIM stock standard with a concentration of 20 µg/mL for levels 4 through 7. A secondary PAH SIM stock standard with a concentration of 2 µg/mL is used to prepare levels 1 through 3:

Vol Stock (µL)	Methylene Chloride (µL)	Internal Standard (µL)	Final Volume (µL)	Conc PAH (µg/mL)
5	495	50	500	0.02
25	475	50	500	0.1
75	425	50	500	0.3
15	485	50	500	0.6
30	470	50	500	1.2
62.5	437.5	50	500	2.5
125	375	50	500	5.0

LVI Method: Prepared using a PAH SIM stock standard with a concentration of 20 µg/mL for levels 6 and 7. A secondary PAH SIM stock standard with a concentration of 2 µg/mL is used to prepare levels 1 through 5:

Vol Stock (µL)	Methylene Chloride (µL)	Internal Standard (µL)	Final Volume (µL)	Conc PAH (µg/mL)
1	499	50	500	0.004
5	495	50	500	0.02
15	485	50	500	0.06
30	470	50	500	0.12
60	440	50	500	0.24
12.5	487.5	50	500	0.5
25	475	50	500	1.0

7.2.3 Initial Calibration Verification (ICV) Standard

A second source initial calibration verification (ICV) standard is prepared using a standard solution that is obtained from a source independent from the source that supplies the standard used for the initial calibration. The final PAH SIM concentration for this ICV standard is 1.2 µg/mL (0.24 µg/mL for LVI).

7.2.4 Continuing Calibration Verification (CCV) Standard

A standard with the same analytes and concentrations as the 600 ng/mL (120 ng/mL for LVI) calibration standard. The standard may be from the same preparation as the initial calibration or prepared at a later date.

7.2.5 Surrogate Spiking Solutions

The surrogate spike solution contains neutral surrogates at

concentrations of 500 ng/mL in methanol. Table II lists the surrogate compounds for the standard list of PAHs.

- o 1.0-liter water extractions, add 1.0 mL of the surrogate spike solution
- o 250-mL LVI water extractions, add 0.250 mL of the surrogate spike solution
- o 30-gram soil sample extractions, add 1.0 mL of the surrogate spike solution

7.2.6 Internal Standard (IS) Solutions

A 6000 ng/mL solution of the internal standards is prepared in methylene chloride from vendor stocks. Table III lists the IS compounds.

To each sample extract, 20 μL of the respective IS solution is added to a 200 μL aliquot of the sample extract for both standard (1 L sample) and LVI extracts.

7.2.7 LCS, MS, and MSD Spike Solution

A methanol solution containing the requested spike compounds at a concentration of 900 ng/mL each is prepared from vendor stock solutions. Following are the final sample concentrations of the spiked compounds for the water and solid extractions:

- o 1.0-liter water extractions, add 1.0 mL of the spike solution, [PAH] = 900 ng/L
- o 250-mL LVI water extractions, add 0.250 mL of the spike solution, [PAH] = 900 ng/L
- o 30-gram soil sample extractions, add 1.0 mL of the spike solution, [PAH] = 30 μg/kg

7.3 All stock and working standards are stored according to the manufacturer's instructions. Dilutions from stocks may not be assigned expiration dates that exceed the stock standard expiration date set by the manufacturer.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample Amounts

8.1.1 Water samples are collected in pre-cleaned amber glass bottles fitted with a Teflon-lined cap. To guarantee the ability to meet routine reporting limits, two full bottles of sample should be provided. Additional bottles are needed to satisfy the requirements for matrix spikes and duplicate matrix spikes. For the standard method, each bottle should be 1.0 L; for the LVI method, each bottle should be 250 mL.

8.1.2 Soil samples are collected in an 8-ounce, pre-cleaned, wide-mouth jar with a Teflon-lined lid.

8.2 Samples are chilled to a temperature between 0 and 6 °C immediately after collection and shipped via overnight carrier to the laboratory.

8.3 Samples and excess sample volume must be stored refrigerated at ≤ 6 °C from when the log-in process is completed (see SOP DV-QA-0003) to storage after analysis.

8.4 Water samples must be extracted within 7 days of the time of sample collection, while solid samples must be extracted within 14 days of sampling. Extracts must be analyzed within 40 days from sample extraction.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS Method Comments to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Assurance Program.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy SOP DV-QA-024P, Requirements for Federal Programs. Table 8 details the components of the DoD QSM 5.0 and DoE QSAS 3.0 that are different from TestAmerica Denver's standard procedures, for further details, see SOP DV-QA-024P. Also listed are the variances that TestAmerica is requesting for this analysis; these alternate criteria are only used with project-specific approval.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in the LIMS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Method Blank (MB)

A method blank is processed and analyzed with each analytical batch, not to exceed 20 samples. For aqueous samples, the method blank consists of reagent

water spiked with surrogates. For soil samples, the method blank is Ottawa sand spiked with surrogates. This sand is mixed with sodium sulfate for extraction by ultrasonication. Method blanks are used to assess whether the laboratory has contributed contamination to the sample analysis process that adversely affects the accuracy of the determination of target analytes. The goal is to have no detectable contaminants in the method blank. However, due to the sensitivity of this analysis, it is not uncommon to detect target analytes at levels above the method detection limit (MDL).

Acceptance Criteria: MB results must be less than ½ the reporting limit.

Corrective Action: If the MB exceeds ½ the RL for any target analyte, then one of the following must apply for acceptance of the batch:

The blank contamination is less than $^{1}/_{10}$ of the measured concentration of any sample in the associated preparation batch, or

The blank contamination is less than the concentration present in the samples and is less than $^{1}/_{10}$ of the regulatory limit, or

The same contaminants are not found in the associated samples.

NOTE: Positive method blank results below the reporting limit should be evaluated by the analyst for potential impact on sample results at or near the reporting limit.

9.3 Laboratory Control Samples (LCS)

A Laboratory Control Sample (LCS) is processed and analyzed with each analytical batch not to exceed 20 samples. For aqueous samples, the LCS consists of reagent water spiked with the analytes of interest and surrogates. For soil samples, the LCS is Ottawa sand spiked with analytes of interest and surrogates. For ultrasonic extraction, sodium sulfate is added to the reagent sand. The LCS spiking solution is described in Section 7.2.7. LCS results are used to determine whether the analytical system is in control. Depending on project requirements, a duplicate LCS (LCSD) may be required to assess the precision of the analytical system.

Acceptance Criteria: The percent recovery for each requested target analyte in the LCS must fall within the established control limits (found in the LIMS system).

Corrective Action: If the percent recovery for any requested analyte in the LCS exceeds the upper control limit and the analyte is not detected in any of the associated samples, then no further action is required, and data are reported with an NCM.

If the percent recovery for any analyte in the LCS exceeds the upper control limit and the analyte is detected in any of the associated samples, then reanalyze the LCS. If similar results are obtained on the second attempt, then investigate and correct any problems. Re-extract and reanalyze the preparation batch.

If the percent recovery for any analyte in the LCS is below the lower control limit, reanalyze the LCS. If similar results are obtained on the second attempt, then investigate and correct any problems. Re-extract and reanalyze the preparation batch.

If re-extraction of samples is not possible, qualify data and explain in a NCM.

9.4 Matrix Spike and Spike Duplicate (MS/MSD)

One matrix spike (MS) sample and one matrix spike duplicate (MSD) sample are prepared and analyzed for each preparation batch. An MS sample is a field sample to which known amounts of the target analytes, as well as the surrogates, have been added. An MSD is a second aliquot of the same sample that is spiked the same as the MS. The MS/MSD spiking solution is described in Section 7.2.7. MS results are used to assess the effects of the sample matrix on the accuracy of the analytical system. The MSD results are used to assess the effects of the sample matrix on the precision of the analytical system. Given the expected variability in sample matrix, the MS/MSD results are applicable to only the sample used to prepare the MS and MSD. MS/MSD results should not be extrapolated to other samples without extensive investigation and characterization to demonstrate similarity between samples.

Acceptance Criteria: The percent recovery for each requested target analyte in the MS and MSD must fall within the established control limits (found in the LIMS system). The relative percent difference (RPD) between the MS and MSD must be less than or equal to the established control limit.

Corrective Action: The information obtained from MS data is sample/matrix specific and is not normally used to determine the validity of the entire batch. If the MS and/or MSD recovery falls outside of the established control limits, the CCV and batch LCS recoveries must be within control limits in order to accept results for the associated samples. The following corrective actions are required for MS/MSD recovery failures to rule out lab error:

- Check calculation and instrument performance;
- Verify, if possible, that the MS and MSD were spiked correctly (especially if recoveries are very low or very high);

- Consider objective evidence of matrix interference (e.g., heterogeneous sample, interfering peaks seen on chromatograms, or interference demonstrated by prior analyses);

- Flag the data for any results outside of acceptance limits and note it on the final report.

- For any single RPD failure, check calculations; verify, if possible, that the MS and MSD were spiked correctly; check instrument performance; consider objective evidence of matrix interference or sample inhomogeneity; and flag the data.

- When the MS/MSD concentration is above the linear range; the MS/MSD and parent sample **MUST** be re-analyzed at a dilution.

NOTE: Some client programs require reanalysis to confirm matrix interferences. Check special project requirements for this corrective action.

9.5 Internal Standards

The internal standards listed in Table III and described in Section 7.2.6 are spiked at the same level in all field sample extracts, QC sample extracts, instrument blanks, and calibration standards.

Acceptance Criteria: The peak area for each internal standard in each field sample and QC sample extract should be between 50% and 200% of the peak area for the same internal standard in the midlevel standard of the initial calibration.

Corrective Action: If the internal standard fails acceptance criteria, then perform the following corrective actions:

- o Inspect system for malfunction and correct as needed.

- o Reanalyze the affected samples.

- o If the interference cannot be corrected for field samples, the earlier analysis is reported with discussion in an NCM.

- o If QC samples have internal standard failures that are confirmed by re-analysis, the cause of the failures must be investigated.

9.6 Surrogate Compound Analysis

Surrogate compounds listed in Table II and described in Section 7.2.4 are added to all field and QC samples prior to extraction. Surrogate recoveries are used to assess individual sample matrix effects on sample preparation and analysis.

Acceptance Criteria: Surrogate recoveries must fall within established control limits. QC sample results are not acceptable unless the surrogate recoveries for those samples are in control.

Corrective Action: Corrective action must be considered for any surrogate failure and may depend on project-specific instructions. Lacking instructions to the contrary the following actions shall be taken:

- Evaluate sample chromatogram and other QC.
- If the surrogate(s) fail in the LCS and/or method blank, then re-prepare and reanalyze all associated samples.
- For surrogate failures in field samples, re-prepare and reanalyze the samples, unless matrix interference is evident from earlier analysis or from chromatograms in which case the samples are reported with an NCM.

9.7 Instrument QC

9.7.1 Instrument Optimization

9.7.1.1 The GC/MS system must be tuned to meet manufacturer's specifications, using a suitable calibration such as perfluorotri-n-butylamine (FC-43). This is performed through the auto-tune feature in the software. The mass calibration and resolution of the GCMS system is then verified by the analysis of DFTPP prior to the analysis of any standards or samples. In some instances the laboratory will opt to omit the DFTPP. The DFTPP tune check is less useful for SIM analysis than it is for full scan analysis because the DFTPP analysis must necessarily be done in full scan mode. When this check is omitted, the FC-43 check will be performed daily.

9.7.1.2 The instrument is tuned for DFTPP (decafluorotriphenylphosphine), calibrated initially with a seven-point calibration curve, and verified each 12-hour shift that samples are to be run with one or more continuing calibration verification (CCV) standard(s).

9.7.2 Instrument Tuning

At the beginning of every 12-hour shift when analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria (Table VI) are achieved for DFTPP.

9.7.2.1 Inject 1 μL of the 50 μg/mL GC/MS tuning standard (see Section 7.2.1) into the GC/MS system.

9.7.2.2 The mass spectrum of the DFTPP must be obtained in the

following manner: three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is also required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of the DFTPP. Do not subtract part of the DFTPP peak. A procedure compliant with these requirements is programmed into a Macro used to evaluate the DFTPP spectrum. Confirm that all the key m/z criteria in Table VI are achieved.

9.7.2.3 If all the criteria are not achieved, the analyst must adjust or retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

9.7.3 Initial Calibration (ICAL)

9.7.3.1 A new calibration curve must be generated initially, after major changes to the system, or when continuing calibration criteria cannot be met. Major changes include installation of new columns and source maintenance.

9.7.3.2 A minimum five-point initial calibration curve must be established for linear fit calibrations (weighted or unweighted). Six points or more are required for second order curve fits. See Section 9.7.4 for Calibration Acceptance Criteria.

- The concentrations of standards commonly used to construct the PAH calibration curve are 20,100, 300, 600 (often analyzed before the rest of the standards and called the ICIS), 1200, 2500, and 5000 ng/mL.

- For the LVI method, the concentrations of standards commonly used to construct the PAH calibration curve are 4, 20, 60, 120 (often analyzed before the rest of the standards and called the ICIS), 240, 500, and 1000 ng/mL.

9.7.3.3 If the concentration of any target compound in a sample exceeds the calibration range, the extract must be diluted so that the concentrations of all target compounds fall within the range of the calibration curve, and be reanalyzed. Any samples analyzed immediately following the sample that exceeded the linear range may require reanalysis due to possible carryover from the high-level sample.

9.7.3.4 Generally, it is NOT acceptable to remove points from a calibration for the purposes of meeting calibration criteria,

unless the points are the highest or lowest on the curve AND the reporting limit and/or the linear range is adjusted accordingly. The only exception is that a level may be removed from the calibration if the reason can be clearly documented, for example a broken vial. A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration. All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 12 hours.

9.7.3.5 Calculate the response factor (RF) for each analyte for each calibration standard level as described in Section 10.2. Calculate the mean RF and relative standard deviation (RSD) for each analyte as described in Section 11.3, respectively.

9.7.4 Calibration Acceptance Criteria and Corrective Action:

Acceptance Criteria 8270C:

The RSD of the initial calibration for each analyte of interest must be ≤ 35%.

Acceptance Criteria 8270D:

Refer to Table VII for the acceptance criteria for minimum response factor and RSD. Two target compounds and surrogates may fail to meet the minimum RRF criteria listed in Table VII but must still meet the minimum RRF criteria of 0.010 (excluding compounds with a minimum RRF requirement of 0.010). In addition, two target compounds and surrogates may fail to meet the RSD criteria listed in Table VII but must still meet the maximum RSD requirement of 40%. (excluding compounds with a maximum RSD requirement of 40%). Refer to SOP DV-QA-024P for requirements for federal programs.

Acceptance Criteria for DoD5:

The RSD of the initial calibration for each analyte of interest must be < 15%. See SOP DV-QA-024P for further details for QSM 4.2 requirements.

Corrective Actions:

If these criteria cannot be met, least-squares weighted or unweighted linear regression may be used to establish a calibration function as described in Section 11.4. In this case, the correlation coefficient (r) must be greater than 0.995 (equivalent to $r^2 \geq 0.99$) or a second-order regression fit with coefficient of determination (COD, r^2) greater than 0.99

may be used. If these linearity criteria are not achieved, verify the standard preparation and instrument conditions, and then recalibrate the instrument. If technical acceptance criteria are not met, it may be necessary to clean the ion source, perform injector maintenance, change the column, or take other corrective actions.

9.7.5 In the event that a least-squares regression is used, the analyst should evaluate the bias at the lower portion of the curve. This can be accomplished by re-fitting the low point standard back into the curve. The recalculated concentration should be within ±50% of the standard's true concentration. If these criteria are not met, the analyst may have to evaluate the concentration range of the standards, or the lower limit of quantitation.

9.8 Initial Calibration Verification (ICV)

The Initial Calibration Verification (ICV) is a second-source, mid-level standard that is analyzed immediately following the initial calibration standards.

Acceptance Criteria: The absolute value of the difference between the measured PAH analyte concentration and the true value must be ≤ 30 % or be ≤ 20 % for DoD QSM 4.2 or 5.0.

Corrective Action: If the ICV recovery fails, then take the following actions:

- Verify standard preparation, and if incorrect, re-prepare the ICV standard solution.
- If preparation of the ICV standard was correct, then re-prepare the initial calibration standards and recalibrate.

9.9 Continuing Calibration Verification (CCV)

Every 12 hours, the mass spectrometer response for each PAH relative to the internal standard is determined by analyzing a 600 ng/mL calibration standard (120 ng/mL for the LVI method). The RF for each compound in the continuing calibration verification (CCV) analysis is compared to the RF for that compound in the ICAL.

9.9.1 Acceptance Criteria 8270C

The absolute value of the difference between the CCV RF for each PAH analyte and the corresponding ICAL value must be ≤ 35 %.

9.9.2 Acceptance Criteria 8270D

The absolute value of the difference between the CCV RF for each PAH analyte and the corresponding ICAL value must meet the criteria in Table VII. The compounds must also meet the minimum response factor criteria listed in Table VII. Two target compounds and surrogates may fail to meet the minimum RRF criteria in Table VII (excluding compounds with a

minimum RRF requirement of 0.010) but must still meet the minimum RRF criteria of 0.010. In addition, two target compounds and surrogates may fail to meet the difference criteria in Table VII (excluding compounds with a maximum percent difference requirement of ±40%) but must still meet the maximum difference requirement of ±40%. (Refer to SOP DV-QA-024P for requirements for federal programs).

9.9.3 Acceptance Criteria for DoD QSM 4.2 or 5.0

The absolute value of the difference between the CCV RF for each PAH analyte and the corresponding ICAL value must be ≤ 20 % for DoD QSM 4.2 or 5.0.

9.9.4 Acceptance Criteria 8270C & 8270D

9.9.4.1 The internal standard response of the CCV must be within 50-200% of the internal standard response in the mid-level (ICIS) of the most recent ICAL sequence.

9.9.4.2 The internal standard retention time must be within ± 30 seconds of the internal standard retention time in the corresponding level of the most recent ICAL sequence.

9.9.5 Corrective Action:

9.9.5.1 If, for any analyte, the CCV RF does not meet the stipulated acceptance criteria, a five-point calibration curve must be repeated for that analyte prior to the analysis of samples.

9.9.5.2 If any internal standard retention time in the CCV changes by more than 30 seconds from that of the corresponding level of the most recent ICAL sequence, the chromatographic system must be inspected for malfunctions and corrections made, as required.

9.10 Closing CCV (DoD QSM 5.0 only)

DoD QSM 5.0 requires a closing CCV, injected within 12 hours of the DFTPP injection.

9.10.1 Acceptance Criteria

All reported analytes and surrogates must be within ±50%.

9.10.2 Corrective Action

Recalibrate and reanalyze all affected samples since the last acceptable CCV

Or

Immediately analyze two additional consecutive CCVs. If both pass,

samples may be reported without reanalysis. If either fails perform column maintenance and recalibrate; tehn reanalyze all affected samples sine the last acceptable CCV.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP # DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 Sample Preparation

10.3.1 Aqueous Sample Extraction and Concentration

10.3.1.1 Instructions for the extraction of aqueous samples may be found in SOP DV-OP-0006.

10.3.1.2 Instructions for the concentration of extracts may be found in SOP DV-OP-0007.

10.3.2 Soil Sample Extraction and Concentration

10.3.2.1 Instructions for the ultrasonic extraction of soil samples may be found in SOP DV-OP-0016.

10.3.2.2 Instructions for the microwave extraction of soil samples may be found in SOP DV-OP-0015.

10.3.2.3 Instructions for the concentration of extracts may be found in SOP DV-OP-0007.

10.4 Sample Analysis

10.4.1 All aliquotting, extract dilutions, and spike additions must be performed in the trace fume hood using equipment dedicated to PAH-SIM analysis. An aliquot of each sample extract is placed into a two-milliliter GC/MS autosampler vial. Sufficient volume of extract remains should reanalysis be necessary.

10.4.2 Prior to analysis, internal standard is added to the sample vial giving a final internal standard concentration of 600 ng/mL (150 ng/mL for LVI) in the extract.

10.4.3 Representative aliquots are injected into the gas chromatograph/mass spectrometer using similar conditions to those summarized in Table I. The injection volume is 1 μL (5 μL for LVI).

10.4.4 Whenever an unusually concentrated sample is encountered, it may be necessary to reanalyze the subsequent sample extracts after analyzing an instrument blank to demonstrate that there is no cross contamination.

10.4.5 The following is a typical analytical sequence:

- Solvent rinses, as needed
- MS tune
- ICAL plus ICV or CCV
- Instrument blank
- MB, LCS
- LCSD (if requested by client)
- Sample extracts
- MS and MSD are interspersed with sample extracts, and usually run after the sample from which they are produced.
- The last sample extract must be injected within 12 hours of the tune.

10.4.6 The sequence may be altered to accommodate reanalysis or additional instrument blank and calibration evaluations. At a minimum, an instrument blank or a method blank shall be included in the sequence. Refer to QC policy DV-QA-003P for additional details.

10.4.7 The effluent from the GC capillary column is fed directly into the ion source of the mass spectrometer. The MS is operated in the selected ion monitoring (SIM) mode using appropriate windows to include the quantitation and confirmation masses for each analyte as shown in Table IV.

10.4.8 All compounds detected at concentrations above the method MDL are checked to ensure that the confirmation ion is present at the appropriate ratio.

10.4.9 All compounds detected at concentrations above the highest calibration standard require dilution and reanalysis. In addition, any samples that were analyzed immediately following a high-level sample should be reanalyzed to rule out carryover from the high-level sample, unless they are preceded by an acceptable instrument blank or the high compound(s) were not detected in the subsequent samples.

10.4.10 Manual Integrations

10.4.10.1 Upon completion of the analytical sequence, transfer the raw instrument data to Chrom for further processing. Review the chromatograms to ensure correct assigning of peaks and correct integration of each peak.

10.4.10.2 Note that certain compounds (e.g., benzo(b)fluoranthene and benzo(k)fluoranthene) may require frequent manual integrations. Special attention must be exercised by the analyst and secondary reviewer for compounds that are commonly mis-integrated in automated software or are manually integrated. If manual data manipulations are necessary, they must be justified and documented. See DV-QA-011P requirements for manual integration.

10.5 Troubleshooting and Maintenance

10.5.1 Daily Instrument Maintenance

In addition to the checks listed in Appendix B, the following daily maintenance should be performed.

- Clip column as necessary.
- Install new or cleaned injection port liner as necessary.
- Install new septum as necessary.
- Install new or cleaned gold seal and washer as necessary.
- Perform mass calibration as necessary.

10.5.2 Major Maintenance

A new initial calibration is necessary following certain maintenance procedures. These maintenance procedures include changing the column, cleaning the repeller, cleaning the source, replacing the multiplier, and replacing the “topboard” or RF-related electronics. Refer to the manufacturer's manual for specific guidance.

11.0 Calculations / Data Reduction

11.1 Qualitative Identification

Obtain electronic ion current profiles (EICP) for the primary mass ion and the confirmatory ion for detected compounds. The following criteria must be met to make a qualitative identification:

11.1.1 The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

11.1.2 The retention time (RT) of unknown peaks must fall within ± 0.2 minute of the RT for the compound in the daily calibration standard (mid-point ICAL or daily CCV).

11.1.3 The relative peak areas of the primary ion compared to the confirmation or secondary ion masses in the EICPs must fall within ± 20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library. A compound that does

not meet secondary ion confirmation criteria may still be determined to be present in a sample after close inspection of the data by the mass spectroscopist. Supportive information includes correct relative retention time (RRT) and the presence of the secondary ion, but the ratio falls outside of ± 20% of the primary ion, which may be caused by an interference of the secondary ion.

11.1.4 Structural isomers that have very similar mass spectra and less than a 30-second difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if there is a definitive inflection between the two peaks, according to the analyst's judgment. Otherwise, structural isomers are identified as isomeric pairs.

11.2 Detailed information regarding calibration models and calculations can be found in Corporate SOP CA-Q-P-003, *Calibration Curves and the Selection of Calibration Points* and the public folder *Arizona Calibration Training*.

11.3 Average Response Factor Calibration

The following formula is used to calculate the response factor for each analyte of interest relative to the applicable internal standard for each of the calibration standards:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:

A_s	=	Area of the characteristic ion for the target analyte in the calibration standard
A_{is}	=	Area of the characteristic ion for the internal standard
C_{is}	=	Concentration of the internal standard, (ng/mL)
C_s	=	Concentration of the target analyte in the calibration standard (ng/mL)

The calibration uses the average response factor for each target analyte, which is calculated as follows:

$$\text{average (mean) RF} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where:

RF_i	=	Response factor for the i^{th} calibration level
n	=	Number of calibration levels

The standard deviation for the mean RF for each target analyte is calculated as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_i - \overline{RF}\right)^2}{n-1}}$$

The relative standard deviation (RSD) for the average response factor for each target analyte is calculated as follows:

$$RSD = \frac{SD}{\overline{RF}} \times 100\%$$

The concentration of each target analyte in the sample extract is calculated using the average response factor that was calculated in Section 0 as follows:

$$C_e = \frac{A_e \times C_{is}}{A_{is} \times \overline{RF}}$$

Where:

C_e	=	Concentration of target analyte in the sample extract, ng/mL
A_e	=	Area of the characteristic ion for the target analyte in the sample extract.
A_{is}	=	Area of the characteristic ion for the internal standard
C_{is}	=	Concentration of the internal standard, (ng/mL)
$\overline{RF}$	=	Average response factor for the target analyte as determined by calibration

11.4 Linear Least-Squares Regression Calibration (Unweighted)

A linear least-squares regression is performed using the concentration of the target analyte in the calibration standard as the independent variable (x) and the instrument response as the dependent variable (y). The regression produces the slope and intercept terms for a linear equation in the following form:

$$y = mx + b$$

Where:

y	=	instrument response (e.g., peak area)
x	=	concentration of target analyte in calibration standard
m	=	slope of the line
b	=	intercept of the line

For the internal standard calibration, the regression equation is rewritten as follows:

$$\frac{A_s C_{is}}{A_{is}} = mC_s + b$$

Where:

A_s	=	Area of the characteristic ion for the target analyte in the calibration standard

A_{is}	=	Area of the characteristic ion for the internal standard
C_s	=	Concentration of the target analyte in the calibration standard, (ng/mL)
C_{is}	=	Concentration of the internal standard, (ng/mL)
m	=	slope of the line
b	=	intercept of the line

The concentration in an unknown extract is then calculated by rearranging the calibration equation as follows:

$$C_e = \frac{\left[\frac{A_s C_{is}}{A_{is}} - b\right]}{m}$$

Where C_e is the concentration of the target analyte in the sample extract, and A_e is the area of the characteristic ion for the target analyte in the sample extract.

The actual sample concentration (C) for each compound is calculated as follows:

$$C = C_e \times \left(\frac{V_e}{V_o}\right) \times DF$$

Where:

C	=	Concentration of the target analyte in the original sample, ng/L (water sample) or ng/kg (solid sample)
C_e	=	Concentration of the target analyte in the sample extract, ng/mL
V_e	=	Final extract volume, mL.
V_o	=	The original volume or weight of the sample that was extracted, L (aqueous sample) or kg (solid sample).
DF	=	Dilution factor, if appropriate.

11.5 Additional Regression Calibration Models

As needed, weighted linear least-squares or second order regressions may be utilized for this analysis. See Corporate SOP CA-Q-P-003, *Calibration Curves and the Selection of Calibration Points* (Attachment 1) and the public folder *Arizona Calibration Training* for calculations and further explanations.

11.6 A second-level technical review of the organic data is performed prior to data reporting. This review is performed by a peer or supervisor using the guidelines and checklists detailed in SOP DV-QA-0020.

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 policy in DV-QA-005P. 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 or program requirements require a greater frequency.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

12.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.

12.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. TNI 2009 requires consecutive passing results. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.2.4 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

12.3 Training Requirements

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. Training and qualification requirements are detailed in SOP DV-QA-0024.

12.4 Retention Time Study

12.4.1 Expected absolute retention times (RTs) are initially determined by analyzing all target analytes in the open-scan mode. Example RTs are listed in Table V.

12.4.2 Relative retention times (RRTs) are then calculated for samples in each analytical run based on the RTs found in the continuing calibration verification standard (CCV).

12.4.3 RTs are re-established after any significant instrument maintenance, including source cleaning and changing columns, or whenever compounds are not adequately detected in CCVs or LCSs.

13.0 Pollution Control

Standards and reagents are prepared in volumes consistent with laboratory use to

minimize the volume of expired standards and reagents requiring disposal.

14.0 Waste Management

14.1 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 procedure, the policies in Section 13, "Waste Management and Pollution Prevention", of the Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

14.2 The following waste streams are produced when this method is carried out:

14.2.1 Expired Chemicals/Reagents/Standards – Contact Waste Coordinator

14.2.2 Methylene chloride solvent rinse waste – Waste Stream B

14.2.3 Expired extract vial waste – Waste Stream A

14.2.4 Radioactive and potentially radioactive waste must be segregated from non-radioactive and mixed waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Soil Waste Physical/Chemical Methods (SW-846), Third Edition, September 1986, Final update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final update IIB, January 1995; Final Update III, December 1996, Final Update IV January 2008.

15.1.1 Method 8000B, Determinative Chromatographic Separations, Revision 2, December 1996.

15.1.2 Method 8270C, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 3, December 1996.

15.1.3 Method 8000C, Determinative Chromatographic Separations, Revision 2, February 2007.

15.1.4 Method 8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, February 2007.

15.1.5 Method 3510C, Separatory funnel Liquid-Liquid Extraction, Revision 3, December 1996.

15.1.6 Method 3520C, Continuous Liquid-Liquid Extraction, Revision 3, December 1996.

15.1.7 Method 3550B, Ultrasonic Extraction, Revision 2, December 1996.

15.1.8 Method 3546, Microwave Extraction, Revision 0, February 2006.

15.2 CLP Statement of work for Multi-Media, Multi-Concentration Organics Analysis, SOM01.2. June 2007.

16.0 Method Modifications

16.1 The CLP SOW referenced in 8270D does not require the analysis of DFTPP prior to the analysis of samples. The method relies on the successful analysis of calibration standards to verify acceptable function of the mass spectrometer. TestAmerica Denver utilizes the DFTPP check to identify any operational issues with the mass spectrometer prior to the analysis of the calibration standards. This allows the analyst to identify possible problems independent of the GC. As a result, the laboratory will start the 12 hour clock with the injection of the DFTPP, not the calibration standard as required in the method.

16.2 Method 8270C serves as the basis for this SOP, but the method has been modified extensively for low-level analysis using selected ion monitoring (SIM) and optimizing instrument conditions for the low-level analysis. Consequently the sensitivity of the method has been enhanced and it is not uncommon to detect low-level contamination in the method blank at levels well below the limits of detection for the less sensitive GC/MS method. For example, Method 8270C states that the RSD of the initial and continuing calibration must be less than or equal to 15% and 20% respectively. Due to the low-level nature of the analysis, this SIM procedure allows both of these criteria to be less than or equal to 35%.

16.3 Method 8270C stipulates qualitative identification based on relative retention time (RRT), which is calculated by dividing the retention time (RT) of the target analyte by the RT of the internal standard. The RRT of the suspected target analyte in the sample extract must be within ± 0.06 RRT units of the RRT for that analyte in the calibration standard. This SOP stipulates qualitative identification based on an absolute RT. Namely the RT of the suspected target analyte in the sample extract must be within ± 0.2 minute of the RT for that analyte in the calibration standard. Additionally, the RT for the internal standard in the sample extract must also be within ± 0.2 minute of the RT for the internal standard in the calibration standard. The criteria used in this SOP are more restrictive than those imposed by the referenced method. For the earliest eluting compounds, the RT for the internal standard is typically 8 minutes. The earliest eluting target analyte must be at a RRT of at least 0.8, which translates to a RT of 6.4 minutes. Assuming a worst-case scenario where the RT of the internal standard is 0.2 minute higher (i.e., 8.2 minutes) and the RT of the target analyte is 0.2 minute lower (i.e., 6.2 minutes), the calculated RRT is 0.76. The total deviation from the expected RRT is 0.04 RRT units, which is smaller than what is allowed by Method 8270C.

17.0 Attachments

Table I: Routine Instrument Operating Conditions
Table II: Surrogates for Standard List Analysis
Table III: Internal Standards for Standard List Analysis
Table IV: PAH Compounds and Ions Used for Analysis
Table V: Example Retention Times, IS and Surrogate Associations
Table VI: DFTPP Key Ions and Ion Abundance Criteria for 8270C and 8270D

Table VII: 8270D Relative Response Factor Criteria for Initial and Continuing Calibration
Table VIII: Specific DoD QSM 5.0 and DoE QSAS 3.0 Requirements for 8270D
Appendix I: Extended List PAHs
Appendix II: Suggested Instrument Maintenance Schedule – Mass Spectrometer & Gas Chromatograph
Appendix III: Mass Spectrometer Settings for Single Ion Monitoring

18.0 Revision History

- Revision 10: 2 September 2015
  - Formatting and editorial changes throughout
  - Updated Section 9.4 on corrective action for MS/MSD to reflect current practice
  - Added requirement for Initial Calibration to be %RSD = $\pm$15%, or Linear regression or 2nd order to be $r^2 \geq 0.99$; CCV and ICV to be $\pm$ 20% to meet DOD 5 criteria in appropriate sections per DOD requirement that these must be explicitly stated in the SOP.
  - Added new Section 9.10 to address closing CCV required by DoD QSM 5.0.
  - Updated references to corporate SOP on Calibration Curves in Section 11.2 and 11.5.
  - Updated Sections 12.1-12.3 to reflect current practice.
  - Updated Table IV analytes and ions used for analysis
  - Added Appendix III to identify MS Settings for SIM for each compound
- Revision 9: 31 August 2014
  - Added Table 8, Specific DoD QSM 5.0 and DoE QSAS 3.0 Requirements for 8270 C or D
  - Added reference to DoD QSM 5.0
  - Modified the large volume injection (LVI) internal standard concentration to 600ng/mL
  - Added Appendix II, Suggested Instrument Maintenance Schedules
- Revision 8: 31 August 2013
  - Annual Technical Review
  - Added references to analysis by LVI
  - Updated Appendix I to reflect current practice
- Revision 7: 31 July 2012
  - Annual Technical Review
  - Grammatical and formatting changes throughout
  - Updated the quant ion for surrogate terphenyl-d14 to IS#2 in Table V
  - Updated Table 1 to match current GC conditions
- Revision 6.2: 31 August 2011
  - Inserted Section 7.2.4.
  - Revised QC section (Section 9)
  - Inserted paragraph 10.2.10. regarding manual integration
  - Added Section 11.5
  - Revised Section 16.2 regarding calibration criteria
  - Updated prep methods used and inserted prep methods in reference section
  - Annual Technical Review

- Grammatical and formatting changes throughout

Earlier revision histories have been archived and are available upon request.

Table I: Routine Instrument Operating Conditions

GC Conditions[1]	
Inlet	Split or Pulsed Split at 275 °C Split ratio - 3.1 : 1 Split Flow – 10.4 mL / min
Capillary Column	Varian Vf-5MS, 30 m length, 0.25 mm diam ID, 0.5 μm thickness
Column Mode	Constant flow, 3.4 mL/min
Temperature Program	Initial temp = 55 °C 30 °C/min ramp to 256 °C 4 °C/min ramp to 296 °C 30 °C/min ramp to 340 °C and hold for at least 1 minute past the elution time of the last compound.
Run Time	About 20 minutes with a new column.
Carrier Gas	Helium Purge flow = 25.0 mL/min, 3.00 min Total flow ≈ 31 mL/min
Injection Volume	1.0 μL (5.0 μL for LVI)
Transfer Line	290 °C or 300 °C
Mass Spectrometer Conditions[1,2]	
MS Source	230 °C or 240 °C
MS Quadrupole	200 °C
Dwell Time per Ion	Ranges from 30 to 100 milliseconds
Ions	See following tables

1 The conditions listed above are subject to final fine adjustments to maximize instrument sensitivity. Changes to the above conditions are acceptable as long as method criteria are met.

2 Details on the mass assignments in each window along with start and dwell times are given in Appendix III.

Table II: Surrogates for Standard List Analysis

PAH Surrogates	Mass Ion	Confirmation Ion
Nitrobenzene-d_5	82	128
2-Fluorobiphenyl	172	171
Terphenyl-d_{14}	244	122

Table III: Internal Standards for Standard List Analysis

Compound	Mass Ion	Confirmation Ion
Acenaphthene-d_{10}	164	162
Phenanthrene-d_{10}	188	94
Chrysene-d_{12}	240	120

Table IV: PAH Compounds and Ions Used for Analysis

Compound	Mass Ion	Confirmation Ion
Acenaphthene	153	152
Acenaphthylene	152	151
Anthracene	178	179
Benzo(a)anthracene	228	226
Benzo(a)pyrene	252	253
Benzo(b)fluoranthene	252	253
Benzo(g,h,i)perylene	276	138
Benzo(k)fluoranthene	252	253
Chrysene	228	226
Dibenzo(a,h)anthracene	278	139
Dibenzofuran	168	139
Fluoranthene	202	101
Fluorene	166	165
Indeno(1,2,3,cd)pyrene	276	138
1-Methylnaphthalene	142	141
2-Methylnaphthalene	142	141
Naphthalene	128	129
Phenanthrene	178	179
Pyrene	202	101
Morpholine	57	87

Table V: Example Retention Times, IS and Surrogate Associations

Compound	RT[1] (min.)	IS #	Surrogate #
Morpholine	4.001	1	1
Naphthalene	5.921	1	1
2-Methylnaphthalene	6.595	1	1
1-Methylnaphthalene	6.700	1	1
Acenaphthylene	7.512	1	2
Acenaphthene	7.686	1	2
Dibenzofuran	7.861	1	2
Fluorene	8.210	1	2
Phenanthrene	9.194	2	2
Anthracene	9.255	2	2
Fluoranthene	10.768	2	2
Pyrene	11.166	2	2
Benzo(a)anthracene	13.827	3	3
Chrysene	13.924	3	3
Benzo(b)fluoranthene	17.004	3	3
Benzo(k)fluoranthene	17.089	3	3
Benzo(a)pyrene	18.034	3	3
Indeno(1,2,3,cd)pyrene	21.509	3	3
Dibenz(a,h)anthracene	21.583	3	3
Benzo(g,h,i)perylene	22.306	3	3
Acenaphthene-d_{10} (IS)	7.657	1	-
Phenanthrene-d_{10} (IS)	9.177	2	-
Chrysene-d_{12} (IS)	13.856	3	-
Nitrobenzene-d_5 (Surr)	5.201	1	1
2-Fluorobiphenyl (Surr)	6.945	1	2
Terphenyl-d_{14} (Surr)	11.38	2	3

[1]Retention times may vary depending upon chromatographic conditions.

Table VI: DFTPP Key Ions and Ion Abundance Criteria
8270C

Mass	Ion Abundance Criteria
51	30-60 % of mass 198
68	< 2 % of mass 69
69	Mass 69 relative abundance
70	< 2 % of mass 69
127	40-60 % of mass 198
197	< 1 % of mass 198
198	Base peak, 100 % relative abundance
199	5-9 % of mass ion 198
275	10-30 % of mass 198
365	> 1 % of mass 198
441	Present, but less than mass 443
442	40-100 % of mass 198
443	17-23 % of mass 442

With the exception of mass 442, the tune criteria for SW846 method 8270D are less stringent for the criteria required in SW846 method 8270C. For 8270D, the 442 mass must be greater than 50% of mass 198 to meet the tune criteria. By using the 8270C criteria, the rest of the data will be within the 8270D criteria.

Table VII: 8270D Relative Response Factor Criteria for Initial and Continuing Calibration

Compound	Minimum RRF	Maximum %RSD	Maximum %Diff
Acenaphthene	0.900	20	25
Acenaphthylene	0.900	20	25
Anthracene	0.700	20	25
Benzo(a)anthracene	0.800	20	25
Benzo(a)pyrene	0.700	20	25
Benzo(b)fluoranthene	0.700	20	25
Benzo(g,h,i)perylene	0.500	20	25
Benzo(k)fluoranthene	0.700	20	25
Chrysene	0.700	20	25
Dibenzo(a,h)anthracene	0.400	20	25
Dibenzofuran	0.800	20	25
Fluoranthene	0.600	20	25
Fluorene	0.900	20	25
Indeno(1,2,3,cd)pyrene	0.500	20	25
1-Methylnaphthalene	0.400	20	25
2-Methylnaphthalene	0.400	20	25
Naphthalene	0.700	20	25
Phenanthrene	0.700	20	25
Pyrene	0.600	20	25

Table VIII
Specific DoD QSM 5.0 and DOE QSAS 3.0 Requirements for 8270D

This table includes components of the DoD QSM 5.0 and DoE QSAS 3.0 that are different from TestAmerica's standard procedures. For a complete description of the requirements, see DV-QA-024P. Also listed are the variances that TestAmerica is requesting for this analysis; these alternate criteria are only used with project-specific approval

Requirement	Variance (if allowed)	DoD QSM 5.0 and DoE QSAS 3.0
Initial Calibration Verification (ICV)	--	All analytes must be within ± 20% of the true value.
	4PP	Allow ± 30% of true value for known poor performers only if these compounds are not identified as critical compounds of concern by the client for the project under consideration.
Continuing calibration Verification (CCV)	--	Run before sample and at the end of the analytical batch (end of 12 hours). Acceptance limits for all analytes is ± 20% of true value for CCV at start of 12 hours.
	4PP	Allow ±30% of true value for known poor performers only if these compounds are not identified as critical compounds of concern by the client
	3HR	If the CCV is above the project acceptance limits and there are no detections in the samples, TestAmerica will report the non-detect results with a case narrative comment in addition to applying any data qualifier flags required by the project
	7MS	Allow ± 50% for end of analytical batch excluding poor performing compounds. Reanalysis performed due to failed closing CCV only for the analytes identified by the client as critical compounds of concern for the project, and to report qualified results for other analytes.
		If any analytes fail in a CCV, recalibrate and re-analyze all affected samples or immediately (within one hour) analyze two consecutive CCVs and if both pass for the analytes that failed, the CCV is acceptable.
Internal Standards (IS)	--	RT must be ± 10 seconds from RT of the midpoint standard in the ICAL
	8ISRT	RT must be ± 30 seconds from RT of the midpoint standard in the ICAL. Daily routine column maintenance often results in larger RT changes than 10 sec. within a short time.
LCS	--	Include all analyte(s) in LCS that are required to be reported, including surrogates, except those compounds listed as "Additional Analytes" by TestAmerica. These compounds are rarely requested and historical limits may not accurately reflect current performance.
	4PP	If the LCS recovery is above the project acceptance limits and there are no detections in the samples, TestAmerica will report the non-detect results with a case narrative comment in addition to applying any data qualifier flags required by the project
	3HR	Otherwise, correct any problems then re-prep and reanalyze the LCS and all associated samples for failed analytes. If insufficient sample, then apply Q-flag to specific analyte(s) in all samples in the associated prep batch. Flagging is only appropriate when samples cannot be reanalyzed unless 3HR is accepted by the client.
	1SME	Marginal exceedances are not allowed for critical chemicals of concern (risk drivers). Client must notify TestAmerica of these targets or if marginal exceedances will not be allowed.
Surrogates	--	For QC and field samples, correct any problems, then re-prep and reanalyze all failed samples for failed surrogates in the associated prep batch. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.
	4PP	If surrogate recoveries are above the project acceptance limits and there are no detections in the samples, TestAmerica will report the non-detect results with a case narrative comment in addition to applying any data qualifier flags required by the project.

Appendix I: Extended List PAH Analysis by GC/MS

Summary of Method

This is the extended list for the SIM analysis that some clients require. All of the compounds listed in this appendix are analyzed for in addition to the standard compounds discussed throughout this SOP.

Modifications from the SIM analysis are as follows:

- The DFTPP tune has tailing factors that are calculated for Pentachlorophenol and Benzidine and a DDT breakdown check is performed.
- The instrument is calibrated at eight concentration levels. The calibration levels are made by diluting two stock standards with concentrations of 20 μg/mL [PAHXSIM stock (#1)] and 2μg/mL [PAHXSIM 2º stock (#2)] down to the concentrations listed below, in methylene chloride. All phthalate compounds and 2-methylnaphthalane are at a ratio of 2:1 in the stock standards. Therefore, if the concentration is 0.02 μg/mL for the target analytes, the phthalates are at 0.04 μg/mL.

Level (μg/mL)	Stock ID	Stock Amt (μL)	Solvent amount (μL)	IS amount (μL)	Final Volume (μL)
0.02 μg/mL	#2	5	495	50	500
0.1 μg/mL	#2	25	475	50	500
0.3 μg/mL	#2	75	425	50	500
0.6 μg/mL	#1	15	485	50	500
1.2 μg/mL	#1	30	470	50	500
2.5 μg/mL	#1	62.5	437.5	50	500
5.0 μg/mL	#1	125	375	50	500
10.0 μg/mL	#1	250	250	50	500

Response factors for each compound must be ≤ 20% RSD. If any compound is > 20% RSD, must use the best curve fit.

Initial Calibration Verification

- The second source calibration stock is also at 20 μg/mL (PAHSIM SSV stock).
- The second source verification (SSV or ICV) is analyzed at 1.2 μg/mL.

- The acceptance criterion for the ICV is ± 25%D.

Continuing Calibration Verification

- The CCV is run at 0.6 μg/mL
- The criterion: The Average %D for all compounds must be <20%D, with no single compound exceeding 30%D.

Sample extraction: See DV-OP-0008 (aqueous) and DV-OP-0009 (soil).

Sample concentration: See DV-OP-0007.

Sample analysis:

- Internal Standard final concentration is 6 μg/mL in standards and extracts. The stock is at 400 μg/mL
- For the MS/MSD, the recovery for the spike pair must be within the control limits stored in the LIMS system. The MS/MSD pair is generally aliquotted and run two times on the instrument, to confirm the results. If the results to be reported are from the first analysis, it is not required that the second analysis be within the 12 hour tune clock.

Instrument Configuration:

The GCMS instrumentation is configured the same as in the SIM analysis.

Extended List Compounds, Reporting Limits and Ions Used for Analysis:

Compound	Water Reporting Limit (ng/L)	Soil Reporting Limit (µg/kg)	Mass Ion	Confirmation Ion
1,4-Dioxane	NA	20	88	58
N-Nitrosodiphenylamine	1000	20	169	168
N-Nitrosodimethylamine	400	18	74	42
N-Nitrosodiethylamine (LVI)	100	--	102	44
N-Nitrosodi-n-propylamine (LVI)	100	--	70	42
Butyl Benzyl Phthalate	1000	20	149	91
Dimethyl Phthalate	1000	20	163	164
Diethyl Phthalate	1000	20	149	177
Bis(2-Ethylhexyl) Phthalate	1000	20	149	167
Di-n-octyl Phthalate	1000	20	149	150
Di-n-butyl Phthalate	1000	20	149	150

Extended List Compounds Example Retention Times, IS and Surrogate Associations:

Compound	RT[1] (min.)	IS #	Surrogate #
1,4-Dioxane	1.60	1	2
N-Nitrosodiphenylamine	6.75	2	2
N-Nitrosodimethylamine	2.16	1	2
N-Nitrosodiethylamine (LVI)	2.72	1	1
N-Nitrosodi-n-propylamine (LVI)	3.69	1	1
Butyl Benzyl Phthalate	10.33	2	2
Dimethyl Phthalate	5.92	1	2
Diethyl Phthalate	6.51	1	2
Bis(2-Ethylhexyl) Phthalate	11.67	2	2
Di-n-octyl Phthalate	13.69	3	2
Di-n-butyl Phthalate	7.95	2	2
Acenaphthene-d_{10} (IS)	7.657	1	-
Phenanthrene-d_{10} (IS)	9.177	2	-
Chrysene-d_{12} (IS)	13.856	3	-
Nitrobenzene-d_5 (Surr)	5.201	1	1
2-Fluorobiphenyl (Surr)	6.945	1	2
Terphenyl-d_{14} (Surr)	11.38	2	3

[1]Retention times may vary depending upon chromatographic conditions.

APPENDIX II

Instrument Maintenance Schedules
Mass Spectrometer & Gas Chromatograph

MASS SPECTROMETER Instrument Maintenance Schedule				
Daily	**Weekly**	**As Needed**	**Quarterly**	**Annually**
Check for sufficient gas supply. Check for correct column flow and/or inlet pressure.	Check mass calibration (PFTBA or FC-43).	Check level of oil in mechanical pumps and diffusion pump if vacuum is insufficient. Add oil if needed between service contract maintenance.	Check vacuum, relays, gas pressures, and flows.	Replace the exhaust filters on the mechanical rough pump every 1 to 2 years.
Check temperatures of injector, detector. Verify temperature programs.		Replace electron multiplier when the tuning voltage approaches the maximum and/or when sensitivity falls below required levels.		Change the oil in the mechanical rough pump.
Check inlets, septa.		Clean source, including all ceramics and lenses. Source cleaning is indicated by a variety of symptoms, including inability of the analyst to tune the instrument to specifications, poor response, and high background contamination.		Relubricate the turbomolecular pump-bearing wick.
Check baseline level.		Repair/replace jet separator.		
Check values of lens voltages, electron multiplier, and relative abundance and mass assignments of the calibration compounds.		Replace filaments when both filaments burn out or performance indicates the need for replacement.		

APPENDIX II (continued)

Instrument Maintenance Schedules
Mass Spectrometer & Gas Chromatograph

GAS CHROMATOGRAPH Instrument Maintenance Schedule (For GC/MS only.)	
Daily	***As Needed***
Check for sufficient supply of carrier and detector gases. Check for correct column flow and/or inlet pressures.	Replace front portion of column packing or guard column or break off front portion of capillary columns. Replace column if this fails to restore column performance or when column performance indicates it is required (e.g., peak tailing, poor resolution, high backgrounds, etc.).
Check temperatures of injectors and detectors. Verify temperature programs.	Change glass wool plug in injection port and/or replace injection port liner when front portion of column packing is changed or front portion of capillary column is removed.
Check inlets, septa. Clean injector port.	Replace septa.
Check baseline level.	Perform gas purity check (if high baseline indicates that impure carrier gas may be in use).
Inspect chromatogram to verify symmetrical peak shape and adequate resolution between closely eluting peaks.	Repair or replace flow controller if constant gas flow cannot be maintained.
	Reactivate flow controller filter dryers when the presence of moisture is suspected.
	Autosampler: Replace syringe, fill wash bottle, dispose of waste bottle contents.

APPENDIX III
Mass Spectrometer Settings for Single Ion Monitoring

Group ID	Group Start Time[1] (min)	Analyte	Masses	Dwell Times
1	1.45	N-Nitrosodimethylamine	74, 42	50, 50
		1,4-Dioxane	88, 58	50, 50
		Morpholine[2]	57, 87	50, 50
		N-Nitrosodiethylamine (LVI)[3]	102, 44	50, 50
2	2.60	Nitrobenzene-d_5	82, 128	50, 50
		Naphthalene	128, 129	50, 50
		N-Nitrosodiethylamine (LVI)[3]	102, 44	50, 50
		N-Nitrosodi-n-propylamine (LVI)	70, 42	50, 50
3	4.79	2-Fluorobiphenyl	172, 171	50, 50
		2-Methylnaphthalene	142, 141	50, 50
		1-Methylnaphthalene	142, 141	50, 50
4	5.46	Dimethyl Phthalate	163, 164	50, 50
		Acenaphthene- d_5	164, 162	50, 50
		Acenaphthene	153, 152	50, 50
		Acenaphthylene	152, 151	50, 50
		Dibenzofuran[4]	168, 139	50, 50
5	6.06	Diethyl Phthalate	149, 177	50, 50
		N-Nitrosodiphenylamine	169, 168	50, 50
		Fluorene	166, 165	50, 50
		Dibenzofuran[4]	168, 139	50, 50
6	6.78	Phenanthrene-d_{10}	188, 94	50, 50
		Phenanthrene	178, 179	50, 50
		Di-n-butyl Phthalate	149, 150	50, 50
		Anthracene	178, 179	50, 50
7	8.05	Butyl Benzyl Phthalate	149, 91	50, 50
		Terphenyl-d_{14}	244, 122	50, 50
		Fluoranthene	202, 101	50, 50
		Pyrene	202, 101	50, 50
8	10.48	Chrysene- d_{12}	240, 120	50, 100
		Bis(2-Ethylhexyl) Phthalate	149, 167	100, 100
		Chrysene	228, 226	50, 50
		Benzo(a)anthracene	228, 226	50, 50
9	12.33	Di-n-octyl Phthalate	149, 150	50, 50
		Benzo(a)pyrene	252, 253	50, 50
		Benzo(b)fluoranthene	252, 253	50, 50
		Benzo(k)fluoranthene	252, 253	50, 50
10	16.48	Dibenzo(a,h)anthracene	278, 139	50, 50
		Indeno(1,2,3-cd)pyrene	276, 138	50, 50
		Benzo(g,h,i)perylene	276, 138	50, 50

[1]Group start times may vary due to chromatographic conditions.
[2]Morpholine method detection limit verifications not kept current. Laboratory does not stock standards.
[3]N-Nitrosodiethylamine (LVI) elutes between windows 1 and 2 and was therefore included in both.
[4]Dibenzofuran elutes between windows 4 and 5 and was therefore included in both.

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Title: Extraction of Aqueous Samples by Separatory Funnel, SW846 3510C and EPA 600 Series

Approvals (Signature/Date):

Cheyana Cokley 6/27/16
Cheyana Cokley Date
Technical Specialist

Adam Alban 28 June 16
Adam Alban Date
Health & Safety Manager / Coordinator

Margaret S. Sleevi 6/28/16
Margaret S. Sleevi Date
Quality Assurance Manager

6/28/16
William S. Cicero Date
Laboratory Director

Facility Distribution No. _____ **Distributed To: _____**

1.0 Scope and Application

1.1 This Standard Operating Procedure (SOP) is applicable to the solvent extraction of organic compounds from water samples, TCLP leachates, and SPLP leachates, using a separatory funnel. This SOP based on SW-846 Method 3510C, EPA 608, EPA 610, EPA 614, AK102, NWTPH-Dx, and Oklahoma DRO method.

1.2 The determinative methods used in conjunction with this procedure are listed in Table 1. This extraction procedure may be used for additional methods when appropriate pH and spiking mixtures are used.

1.3 This procedure does not include the concentration and cleanup steps. See SOP DV-OP-0007, "Concentration of Organic Extracts", for details concerning the concentration and cleanup of extracts.

2.0 Summary of Method

A measured volume of sample, is placed in a separatory funnel. The pH is adjusted as required for the efficient extraction of specific compounds. The organic compounds are extracted with three portions of methylene chloride. The water phase is discarded. The organic phase is dried using sodium sulfate.

3.0 Definitions

3.1 **Extraction Holding Time**: The elapsed time expressed in days from the date of sample collection to the date the extraction starts. The holding time is tracked in the laboratory LIMS system, and is the primary basis of prioritizing work.

3.2 **Preparation Batch**: A group of up to 20 samples that are of the same matrix and are processed together in the same extraction event using the same procedure and lots of reagents and standards

3.3 **Method Comments:** The Method Comments are used to communicate to the bench level chemists special requirements and instructions from the client. Please reference WI-DV-0032 for details on Method Comments.

3.4 **Quality Assurance Summary (QAS)**: Certain clients may require extensive specific project instructions or program QC, which are too lengthy to fit conveniently in the Method Comments field in LIMS. In these situations, laboratory Project Managers describe the special requirements in a written QAS to address these requirements. QASs are posted on a public drive for easy accessibility by all lab employees. Normally, QASs are introduced to analysts in an initial project kick-off meeting to be sure that the requirements are understood.

3.5 **Aliquot**: A part that is a definite fraction of a whole; as in "take an aliquot of a sample for testing or analysis." In the context of this SOP, "aliquot" is also used as a verb, meaning to take all or part of a sample for preparation, extraction, and/or analysis.

3.6 **Reagent Water** (aka ELGA water – water generated from ELGA water polishing units): Water with a resistivity of 1 Megohm-cm or greater. The TestAmerica Denver deionized water supply meets this requirement with a resistivity of at least 10 Megohm-cm.

4.0 Interferences

4.1 Chemical and physical interferences may be encountered when analyzing samples using this method.

4.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.3 Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented in an NCM.

4.4 The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them. Especially take note of the possibility of phthalate contamination from gloves. Gloves should be changed out frequently and whenever they come in contact with solvent. Glassware should be handled in a fashion that keeps gloves away from the interior and mouth of the glassware.

4.5 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenol may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510C. Method 3510C is preferred over Method 3520C for the analysis of these classes of compounds. However, the recovery of phenols is optimized by using Method 3520C and performing the initial extraction at the acid pH.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

5.2 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, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 The use of separatory funnels to extract samples using methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the separatory funnel has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity. Either a face shield must be worn over safety glasses or goggles must be worn when it is performed.

5.3.2 Glass centrifuge tubes can break in the centrifuge if proper care is not taken. This can lead to a hazardous material spill and endanger employees. Do not exceed the manufacturer's recommended maximum RPM for glass containers. Normally speeds greater than 2700 rpm are not advisable.

5.3.3 The procedure calls for the use of an electric rotator. The rotator is equipped with a safety latch that does not allow the rotator to rotate even if the power switch is turned on. The separatory funnels are secured to the rotator using straps. During the procedure it will be necessary to loosen the straps in order to un-stopper the separatory funnels. Whenever the straps are loose, the safety latch must be fastened to prevent the rotator from rotating.

5.3.4 Glasswool is a carcinogen and therefore should be handled in a hood to avoid inhalation of dust.

5.4 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.

Materials with Serious or Significant Hazard Rating

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
Sodium Hydroxide	Corrosive Poison	2 mg/m3	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, and runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes and can cause burns that may result in permanent impairment of vision, even blindness with greater exposures.
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.
Sulfuric Acid	Corrosive Carcinogen	1 mg/m3	Inhalation may cause irritation of the respiratory tract with burning pain the nose and throat, coughing, wheezing, shortness of breath, and pulmonary edema. Causes chemical burns to the respiratory tract. Inhalation may be fatal as a result of spasm, inflammation, edema of the larynx and bronchi, chemical pneumonitis, and pulmonary edema. Causes skin burns. Causes severe eye burns. May cause irreversible eye injury, blindness, permanent corneal opacification.
(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

NOTE: All glassware used in this procedure is cleaned following SOP DV-OP-0004. In addition, the glassware is rinsed with methylene chloride immediately prior to use.

6.1 Supplies

- Separatory funnel, 2-liter with polytetrafluoroethylene (PTFE) stopcock and stopper.
- Separatory funnel, 500-mL with polytetrafluoroethylene (PTFE) stopcock and stopper.
- Separatory funnel rack and mechanical rotator.

- Balance, ≥ 1400 g capacity, accurate to ± 1 g, calibration checked daily per SOP DV-QA-0014.
- pH indicator paper, wide range.
- Class A Graduated Cylinder, sizes ranging from 50 mL to 1 L.
- Media bottles, 300 mL with Teflon-lined caps or capped with aluminum foil.
- Media bottles, 100 mL with Teflon-lined caps or capped with aluminum foil.
- Disposable pipettes, various volumes.
- Stemless glass funnel.
- Glass wool, baked at 400 °C for four hours.
- Mechanical pipette, 1 mL, positive displacement, with disposable tips, calibrated per SOP DV-QA-0008.
- Aluminum foil.
- Paper towels.

6.2 Computer Software and Hardware

Please refer to the master list of documents, software and hardware located on G:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

7.0 Reagents and Standards

Reagent grade chemicals shall be 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.

7.1 Reagent Water

TestAmerica Denver has two ELGA water purification systems. The water coming from the ELGA system should be 18-18.2 Mohm-cm. The performance of the water polishing system is checked daily and recorded per SOP DV-QA-0026.

7.2 Methylene Chloride

Each lot of solvent is tested following SOP CA-Q-S-001 DV-1 before it is put into use. QA personnel post the list of approved lots at solvent storage areas.

7.3 Acids and Bases

7.3.1 1:1 Sulfuric Acid (H2SO4), *TALS Reagent ID "1:1 H2SO4"*

Place an ice water bath on a stir plate. Place a container with a magnetic stir bar in the bath. While stirring, slowly add 1 part concentrated reagent grade sulfuric acid (36N) to 1 part water from the ELGA purification system. Assign a 1 year expiration date from the date made or the vender expiration date, whichever is shorter.

7.3.2 10N Sodium Hydroxide (NaOH), *TALS Reagent ID "10N_NaOH"*

Purchased at ready-to-use concentration from commercial vendors. Assign a 1 year expiration date from the date opened or the vender expiration date, whichever is shorter.

7.3.3 1N Hydrochloric Acid (HCl), *TALS Reagent ID "1N_HCl"*

Dilute 100 mL of stock reagent grade, concentrated HCl to 1000 mL with reagent water.

7.4 Baked Sodium Sulfate, 12-60 mesh

Heat sodium sulfate in a 400 °C oven for at least four hours. Store in tightly closed container.

7.5 Baked Sodium Chloride

Bake in 400 °C oven for at least 4 hours.

7.6 Standards

Please reference SOP DV-OP-00020 and WI-DV-009 for information regarding the surrogate and spike standards used in this procedure.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix and Method	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Water	Amber Glass	1000 mL	Cool, ≤ 6°C	7 Days	40 CFR Part 136.3
Water for Method AK 102	Amber Glass	1000 mL	Cool, ≤ 6°C and pH ≤ 2 with HCl	14 Days if properly preserved. 7 Days if un-preserved.	Method AK 102
Water for Method Oklahoma DRO	Amber Glass	1000 mL	Cool, ≤ 6°C and pH ≤ 2 with HCl	7 Days	Oklahoma Dept. of Environmental Quality
Water for Method NWTPH-DX	Amber Glass	1000 mL	Cool, ≤ 6°C and pH ≤ 2 with HCl	7 Days	NWTPH-Dx
Water for Method 8082 or 8082A	Amber Glass	1000 mL	Cool, ≤ 6°C	None [2]	SW-846 Chapter 4, Revision 4, Feb 2007
Water for Method 8081 or 8082 by Large Volume Injection	Amber Glass	250 mL	Cool, ≤ 6°C	7 Days	40 CFR Part 136.3
Water for Method 8270SIM by Large Volume Injection	Amber Glass	250 mL	Cool, ≤ 6°C	7 Days	40 CFR Part 136.3
TCLP Leachates	Glass	200 mL for 8270 100 mL for 8081 100mL for 8141	Cool, ≤ 6°C	7 Days from the start of the leach	SW-846 1311
SPLP Leachates	Glass	1000 mL	Cool, ≤ 6°C	7 Days from the start of the leach	SW-846 1312

[1] Exclusive of analysis.

[2] Some regulatory agencies do not accept SW-846 Revision 4 of Chapter 4 and will require a 1 week hold time for method 8082 and 8082A. The states of California, South Carolina, Pennsylvania, and Connecticut require a 1 week hold time.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS Method Comments to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Assurance Program.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs. This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in the LIMS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Initial Performance Studies

Before analyzing samples, the laboratory must establish a method detection limit (MDL). In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument he/she will be using. On-going proficiency must be demonstrated by each analyst on an annual basis. See Section 13 for more details on detection limit studies, initial demonstrations of capability, and analyst training and qualification.

9.3 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. The method blank must be run on each instrument that is used to analyze samples from the same preparation batch. See QC Policy DV-QA-003P for further details.

9.4 Method Blank (MB)

9.4.1 At least one method blank must be processed with each preparation batch. The method blank is processed and analyzed just as if it were a field sample.

9.4.2 The method blank for batches of aqueous samples for Large Volume Injection (prep method 3510C_LVI) consists of 250mL of reagent water free of any of the analyte(s) of interest.

9.4.3 The method blank for batches of aqueous samples for all other methods consists of 1 L of reagent water free of any of the analyte(s) of interest.

9.4.4 The method blank for batches of TCLP leachates for methods 8081 and 8141 consists of 100 mL of leach fluid.

9.4.5 The method blank for batches of TCLP leachates for method 8270 consists of 200 mL of leach fluid.

9.4.6 The method blank for batches of SPLP leachates consists of 1 L of leach fluid.

9.5 Laboratory Control Sample / Laboratory Control Sample Duplicate (LCS/LCSD)

9.5.1 At least one LCS must be processed with each preparation batch. The LCS is carried through the entire analytical procedure just as if it were a sample.

9.5.2 The LCS for batches of aqueous samples for Large Volume Injection (prep method 3510C_LVI) consists of 250mL of reagent water to which the analyte(s) of interest are added at known concentrations.

9.5.3 For aqueous sample batches for all other methods, the LCS consists of 1 L of reagent water to which the analyte(s) of interest are added at known concentration.

9.5.4 For methods 8081 and 8141 TCLP leachates, the LCS consists of 100 mL of leach fluid to which the analyte(s) of interest are added at known concentration.

9.5.5 For method 8270 TCLP leachates, the LCS consists of 200 mL of leach fluid to which the analyte(s) of interest are added at known concentration.

9.5.6 For SPLP leachates, the LCS consists of 1 L of leach fluid to which the analyte(s) of interest are added at known concentration.

9.5.7 Method 608, 614, 610 requires a LCS at a 10% frequency. In other words one LCS is required for a batch of 10 or less samples. A LCSD is required for a batch of 11 or more samples.

9.5.8 Method AK102 requires LCS and a LCSD for every batch for every spike compound.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1 One MS/MSD pair must be processed with each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. It is prepared in a manner similar to the LCS, but uses a real sample matrix in place of the blank matrix. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked exactly as the MS) that is prepared and analyzed along with the sample and matrix spike. Some programs allow spikes to be reported for project-related samples only. Samples identified as field blanks cannot be used for the MS/MSD analysis.

9.6.2 If insufficient sample volume is available for MS/MSD, an NCM must be written and a LCSD must be prepared unless Method Comments indicate otherwise.

9.6.3 Method 608, 610, and 614 requires one matrix spike for every 10 samples. If the batch has more than 10 samples, then two matrix spikes must be performed. The two matrix spikes are to be performed on two different samples. If there is insufficient sample volume for matrix spikes, then a LCSD must be performed.

9.6.4 Method NWTPH-Dx requires a matrix spike and a matrix spike duplicate for every 10 samples. If insufficient sample volume is available for MS/MSD, a NCM must be written and a LCS and LCSD must be performed for every 10 samples.

9.7 Surrogate Spikes

Every calibration standard, field sample, and QC sample (i.e. method blank, LCS, LCSD, MS, and MSD) is spiked with surrogate compounds.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP # DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative. Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.2 All equipment IDs for any support equipment (pipettes, thermometers, etc.) must be recorded in the batch record.

10.3 Critical Procedural Considerations

10.3.1 As stated throughout this SOP, analysts must review the Method Comments and any applicable QASs before starting work. This review is also documented on the Organic Extraction Checklist (see WI-DV-0009).

10.3.2 Analyst must focus on using clean technique throughout this procedure. Any parts or pipettes that come into direct contact with dirty surfaces or any other separatory funnel than the designated one should be cleaned or disposed of before coming into contact with the sample.

10.4 Assemble and clean the glassware immediately before use.

NOTE: Rotate glassware; do **not** use specific glassware or positions for the MB and LCS/LCSD.

10.4.1 Place a stopcock in each separatory funnel. For 1-liter extractions use a 2000 mL sepfunnel. For 250 mL, 200 mL and 100 mL extractions, use a 500 mL sepfunnel. Place a stopper for each separatory funnel on a clean sheet of aluminum foil that is marked with individual positions for each stopper. This is done to prevent cross-contamination.

NOTE: Samples logged with method 3510_LVI are for Large Volume Injection methods and require 250 mL initial volumes. Samples logged for 8270 with a TCLP pre-prep require 200mL initial volumes. Samples logged for 8081 and 8141 with a TCLP pre-prep require 100 mL initial volumes.

10.4.2 For each separatory funnel, plug a glass funnel with baked glass wool and add baked sodium sulfate. Place the funnel on a media bottle and place the media bottle below the separatory funnel.

10.4.3 Rinse each separatory funnel once with methylene chloride. Be sure that all surfaces come into contact with the solvent. Drain the methylene chloride into the media bottle through the sodium sulfate.

10.4.4 Rinse the sodium sulfate with additional methylene chloride if the first rinse did not completely saturate the sodium sulfate.

10.4.5 Allow the methylene chloride to drain completely into the media bottle. Swirl the media bottle to ensure all surfaces come into contact with the solvent. Add additional methylene chloride to the rinse if necessary.

10.4.6 Discard the methylene chloride.

10.4.7 Label each media bottle with the sample ID or batch QC ID.

10.5 Prepare LCS and Method Blank Samples

NOTE: For SW-846 methods if there is not a MS/MSD pair in the batch then perform a LCS/LCSD. Methods 608, 610, and 614 require a LCS and LCSD in batches of 11 samples or more or if there are no Matrix Spikes in batches of 10 or less.

10.5.1 For aqueous sample batches logged for Large Volume Injection, (3510_LVI), pour 250 mL of reagent water into the separatory funnels marked for the LCSs and the MB.

10.5.2 For all other aqueous sample batches, pour 1 liter of reagent water into the separatory funnels marked for the LCSs and the MB.

10.5.3 For 8270 TCLP leachates, use a 250 mL or 500 mL Class A graduated cylinder to measure out 200 mL of the appropriate leach fluid for each MB and LCS and LCSD. Record the volume to the nearest mL. Place the leachate bottle beside the separatory funnel so a second analyst can check that the correct leach fluid was used.

10.5.4 For 8081 and 8141 TCLP leachates, use a 100 mL or 250 mL Class A graduated cylinder to measure out 100 mL of the appropriate leach fluid for each MB and LCS and LCSD. Record the volume to the nearest mL. Place the leachate bottle beside the separatory funnel so a second analyst can check that the correct leach fluid was used.

10.5.5 For SPLP leachates, use a 1000 mL Class A graduated cylinder to measure out 1000 mL of the appropriate leach fluid for each MB and LCS and LCSD. Record the volume to the nearest 10 mL. Place the leachate bottle beside the separatory funnel so a second analyst can check that the correct leach fluid was used.

10.6 Measure the initial sample pH of the samples.

10.6.1 Measure the initial sample pH with wide-range pH paper and record the pH on the extraction bench sheet.

10.6.2 If the sample is logged for AK102_103, Okla_DRO, or NWTPH_Dx the samples should have been field preserved. See Section 8. If the samples are not preserved, an NCM should be written.

10.7 Aliquot the samples

10.7.1 For 8270 TCLP leachates, use a 250 mL or 500 mL Class A graduated cylinder to measure out 200 mL of the leachate. Record the volume to the nearest mL. Place the leachate bottle beside the separatory funnel so a second analyst can check that the correct leach fluid was used.

10.7.2 For 8081 and 8141 TCLP leachates, use a 100 mL or 250 mL Class A graduated cylinder to measure out 100 mL of the leachate. Record the volume to the nearest mL. Place the leachate bottle beside the separatory funnel so a second analyst can check that the correct leach fluid was used.

10.7.3 For SPLP leachates, use a 1 Liter Class A graduated cylinder to measure out 1000 mL of the leachate. Record the volume to the nearest 10 mL. Place the leachate bottle beside the separatory funnel so a second analyst can check that the correct leach fluid was used.

10.7.4 For water samples, it should be noted that TestAmerica Denver routinely aliquots gravimetrically. This is done to prevent cross-contamination due to volumetric glassware and to provide a more accurate initial volume measurement. However, some clients and regulatory programs require the laboratory to aliquot samples volumetrically. The Method Comments and QASs must be read before samples are aliquotted to check for this requirement. If samples are to be aliquotted

volumetrically, use Class A volumetric glassware only and proceed to Section 10.7.6

10.7.5 Weigh the bottle (250 mL amber bottles for 3510C_LVI or 1000 mL amber bottles for all other aqueous samples) and record the gross weight to the nearest gram. If there is any indication that the sample's density is not 1 g = 1 mL, then measure the density of the sample using a calibrated pipette and an analytical balance. The weight of the sample extraction will be corrected for the density later. See Section 11 for the calculation. For example, normally a 1 liter bottle weighs 500 g when empty and when filled completely can only hold 1060 mL, therefore a full bottle weighing more than 1560 g is an indication that either the sample density is greater than 1g or the sample bottle contains a lot of sediment. Document any sample with a density greater than 1 g in an NCM.

10.7.6 Inspect the samples for large amounts of sediment that may interfere with the extraction of the sample by causing excessive emulsions or clogging the stop-cock.

10.7.6.1 If the sample contains so much sediment that the entire sample volume cannot be extracted, decant the sample into the separatory funnel (or a 1 L graduated cylinder if volumetric aliquotting is required), careful not to transfer the sediment. Write a NCM to document the sediment and that it prevented the entire sample volume from being extracted and the sample container from being solvent rinsed.

10.7.6.2 If the sample does not contain a significant amount of sediment, then the entire sample volume will be used in the extraction. Do not pour the sample into the separatory funnel (or into the graduated cylinder if volumetric aliquotting is required) until after the surrogates and any necessary spikes have been added to the samples.

10.7.6.3 For the 600 method series: if there is no more than an inch of sediment in the bottom of the sample bottle, shake the sample well and determine if the sediment resettles in approximately 1 minute. If not, the density of the sediment is likely to be low enough to stay suspended and not block the sidearm.

10.7.6.4 For the 600 method series: if the density of the sediment is high and likely to cause a problem in the extraction or if there is more than an inch of sediment contact the PM so that the client's input can be obtained. Not extracting the entire sample and rinsing the bottle with the extraction solvent is a method deviation. If the client concurs that the sample can be decanted write an NCM to describe the deviation from the procedure.

10.7.7 Place the sample containers in front of the separatory funnel labeled for that sample. A second analyst should then check the labels to make sure the correct sample is being extracted. This check is documented in the Organic Extraction Checklist (WI-DV-0009)

10.8 Add Surrogates to All Field Samples and QC Samples

10.8.1 The standards should be allowed to come to room temperature before spiking the samples. Record the ID of the standard used on the benchsheet.

NOTE: The addition of spikes and surrogates to samples must be done only immediately after a second analyst has reviewed the batch. Reference work instruction WI-DV-009.

10.8.2 Only one batch should be surrogated at a time to ensure the correct standards are used.

10.8.3 Add the appropriate volume of the appropriate working surrogate standard to the sample container for each sample and MS/MSD. Add the surrogate standard to the MB and the LCS's in the separatory funnels. Record the ID of the standard used on the bench sheet. Reference work instruction WI-DV-009 to determine the appropriate standard and the appropriate volume.

NOTE: If the sample contains an amount of sediment that has been deemed to interfere with the extraction process then the surrogate standard is added to the sample in the separatory funnel or in the graduated cylinder. This is considered a deviation and must be documented in a NCM.

10.9 Add Spikes to all LCS's and MS/MSDs

10.9.1 Add the appropriate volume of the appropriate working spike standard to the MS/MSD sample containers and the separatory funnels for the LCS and/or LCSD samples. Record the ID of the standard used on the bench sheet. Reference work instruction WI-DV-009 to determine the appropriate standard and the appropriate volume.

10.10 Add approximately 6g (1 teaspoon) of NaCl to all samples and all QC samples. This is done to give the reagent water used in the MBs and LCSs some ionic strength to more closely mimic the matrix of actual water samples and to aide in the extraction of the more polar target compounds. Record the lot number of the sodium chloride on the bench sheet.

10.11 If volumetric aliquotting is required, transfer the entire sample into a Class A graduated cylinder and record the volume on the benchsheet. If the sample bottle contains more than 1000 mL, a 100 mL Class A graduated cylinder can be used to complete the measurement. The entire sample volume must be used. Record the volume to the nearest 10 mL. Then pour the sample into the labeled separatory funnel. Place the used graduated cylinder in front of the appropriate separatory funnel so it can be solvent rinsed later.

NOTE: A 1000 mL Class A graduated cylinder is not accurate enough to measure to the nearest 1 mL. Therefore all samples that are aliquoted using a 1000 mL Class A

graduated cylinder will have the initial volume recorded to the nearest 10 mL. This accuracy is sufficient.

10.12 If volumetric aliquotting is not required, pour the sample directly into the separatory funnel. Place the empty sample container in front of the appropriate separatory funnel so it can be solvent rinsed.

10.13 Adjust pH of Field Samples and QC Samples

Adjust the sample pH as indicated in the chart below using a minimum amount of 1:1 sulfuric acid (or 1 M hydrochloric acid for Methods AK102, Okla_DRO and NWTPH_Dx) or 10 N sodium hydroxide, as necessary. Record the adjusted pH and the lot number of the acid or base on the bench sheet. For TCLP leachates by method 8270, usually 1 mL of 1:1 sulfuric acid is sufficient.

NOTE: TCLP Leachates may have pH of < 5. In those cases, the pH should be adjusted per the table below.

Method	Initial Extraction pH	Secondary Extraction pH
All 8270 methods *except* SIM.	1 – 2	If samples are TCLP leachates extract at 14. If samples are water extract at 11 - 12
All 8270 SIM methods	As Received	None
All 8081, 8082 and 608 methods.	5 - 9	None
All 8141 and 614 methods	5-8	None
All 8015 methods	As Received	None
All 8310 and 610 methods	As Received	None
AK102_103 Okla_DRO NWTPH_Dx	If samples are preserved between pH 1 – 2, then acidify the MB and LCS. Otherwise extract as received and document insufficient preservation in an NCM.	None

10.14 For 1 Liter samples, add 60 mL of methylene chloride to each empty sample container, unless the entire sample volume was not used. For 250 mL or smaller samples, add 30 mL of methylene chloride to each empty sample container, unless the entire sample volume was not used. Cap the container and shake gently to rinse all internal surfaces of the bottle. Pour the methylene chloride from the sample container into the appropriate separatory funnel. If a graduated cylinder was used to aliquot volumetrically, rinse the cylinder and add that rinse to the separatory funnel as well. Record the lot number of the methylene chloride on the bench sheet. If the sample contained significant sediment and the entire sample contents could not be extracted, do not rinse the empty sample

container, but instead add the solvent directly to the separatory funnel. If the solvent rinse of the sample container cannot be performed, prepare a NCM.

10.15 For water samples that were aliquotted gravimetrically, reweigh the bottle and calculate the initial sample volume by subtracting the empty bottles weight from the full bottles weight, assuming a density of 1 g = 1 mL. If there is any indication that the samples density is not 1 g = 1 mL then measure the density of the sample and correct the calculated initial volume accordingly using the formula in Section 11. Document abnormal sample density in an NCM. For example, normally a 1 liter bottle when filled completely can only hold 1060 mL, therefore an initial volume greater than 1060mL is an indication that the density is not 1 g. Document any sample with a density greater than 1 g in an NCM.

10.16 If the initial volume is less than 80% of the nominal volume, the sample reporting limits and method detection limits will be elevated substantially. Document this in a NCM.

10.17 Stopper and rotate the separatory funnel for 3 minutes with periodic venting to release excess pressure. Document the extraction date and time on the benchsheet.

WARNING: Methylene chloride creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken a few seconds. Vent into hood away from people and other samples. A face shield or goggles must be worn during venting.

10.18 Allow the organic layer to separate from the water phase for at least 5 minutes or until complete visible separation has been achieved. This can take up to 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, use mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, pouring the solvent layer and emulsion back through the top of the separatory funnel (pour-back), or centrifugation. The emulsion could also be filtered through the glass funnel by adding additional sodium sulfate to remove all water in the emulsion. This technique should only be used after other techniques have failed to make complete phase separation and only after the last shake.

NOTE 1: If an emulsion forms, the analyst does not have to wait a complete 5 minutes before attempting to break the emulsion with pour-backs and centrifuge. Start employing the mechanical techniques right away to achieve phase separation.

NOTE 2: As much as 15 to 20 mL of methylene chloride is expected to dissolve in 1 L of water. Thus, solvent recovery could be as low as 35 mL from the first shake and still be acceptable. Subsequent shakes should recover at least 50 mL of solvent.

10.19 Drain the lower methylene chloride layer into the sodium sulfate filled glass funnel. Allow the methylene chloride to drain completely into the media bottle. Rinse the sodium sulfate with a small amount of methylene chloride to ensure that all compounds of interest are collected in the media bottle. Record the lot number of the sodium sulfate on the bench

sheet. If the sodium sulfate becomes saturated with water, add more to the funnel or replace the existing sodium sulfate with fresh drying agent.

10.20 Repeat the extraction two more times for a total of 3 extractions. Collect all three methylene chloride extracts in the same media bottle. For the 2nd and 3rd extractions it is not necessary to wait 5 minutes to allow the solvent to separate from the water; a 3 minute wait time should be sufficient.

10.21 For the base/neutral and acid extractable method 8270, adjust the pH of the samples according to chart in Section 10.12. For 8270 TCLP leachates an excess of base is required to effectively extract pyridine, therefore at least 7 mL of base should be used to ensure the pH is 14. Then extract the sample 3 more times. For these extractions, it is not necessary to wait 5 minutes to allow the solvent to separate from the water; a 3 minute wait time should be sufficient.

10.22 Cap the media bottle with a Teflon-lined cap or aluminum foil and submit for concentration and possible clean-up steps.

10.23 Dispose of the solvent-saturated water remaining in the separatory funnel in the appropriate waste container. See Section 14.

10.24 Initial weights and volumes of samples are entered into LIMS, and the transcribed data must be verified by a second person. This verification is documented on the Organic Extraction Checklists (see WI-DV-009).

10.25 Troubleshooting

10.25.1 If the sample appears very dark or viscous or in any way un-like water, stop and test the sample's miscibility before attempting to extract the sample by this procedure. Place a few milliliters of sample in a vial with methylene chloride. Cap and shake. If the sample is miscible in methylene chloride, the sample should be re-logged as a waste matrix with a prep method of 3580A.

10.26 Maintenance

10.26.1 Approximately every 6 months, the centrifuge should be lubricated.

10.26.2 Contact the Facilities Manager immediately if the rotator is observed to be making un-familiar noises or rotating in a "jerking" manner.

11.0 Data Analysis and Calculations

$$InitialVolume(mL) = \frac{FullBottle(g) - EmptyBottle(g)}{Density(g/mL)}$$

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 policy in DV-QA-005P. 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 or program requirements require a greater frequency.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

12.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.

12.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. TNI 2009 requires consecutive passing results. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.2.4 Until the IDOC is approved by the QA Manager (or designee); the trainer and trainee must be identified in the batch record.

12.2.5 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

12.3 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. A new analyst must be working under documented supervision prior to approval of the IDOC. Documentation that a new analyst is performing under supervision must be entered into the batch record (View Batch Information) until that analyst's IDOC has been approved by the QA Manager (or designee). See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

13.0 Pollution Control

The volume of spike solutions prepared is minimized to reduce the volume of expired standard solutions requiring hazardous waste disposal.

14.0 Waste Management

14.1 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 procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

14.2 The following waste streams are produced when this method is carried out:

14.2.1 Methylene chloride – Waste Stream B

14.2.2 Solid waste/sodium sulfate – Waste Stream D

14.2.3 Basic aqueous sample waste saturated with methylene chloride – Waste Stream X.

14.2.4 Acidic aqueous sample waste saturated with methylene chloride – Waste Stream Y.

14.2.5 Neutral aqueous sample waste saturated with methylene chloride – Waste Stream X or Waste Stream Y.

14.2.6 Expired Standards/Reagents – Contact Waste Coordinator for guidance

NOTE: Radioactive waste, mixed waste, and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of these materials.

15.0 References / Cross-References

15.1 SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005, Method 3510C, Separatory Funnel Liquid-Liquid Extraction, Revision 3, December 1996.

15.2 Code of Federal Regulations, Title 40 – Protection of the Environment, Part 136 – Guidelines Establishing Test Procedures for the Analysis of Pollutants, Appendix A – Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Method 608, Organochlorine Pesticides and PCBs.

15.3 Code of Federal Regulations, Title 40 – Protection of the Environment, Part 136 – Guidelines Establishing Test Procedures for the Analysis of Pollutants, Appendix A – Methods for

Organic Chemical Analysis of Municipal and Industrial Wastewater, Method 610, Polynuclear Aromatic Hydrocarbons.

15.4 Code of Federal Regulations, Title 40 – Protection of the Environment, Part 136 – Guidelines Establishing Test Procedures for the Analysis of Pollutants, Appendix A – Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Method 614, Organophosphorous Pesticides.

15.5 Alaska Method AK102, "For the Determination of Diesel Range Organics", Version 04/08/02.

15.6 Alaska Method AK103, "For the Determination of Residual Range Organics", Version 04/08/02.

15.7 NWTPH-Dx "Semi-Volatile Petroleum Products Method for Soil and Water.

15.8 Oklahoma Department of Environmental Quality Methods 8000/8100 (Modified) Diesel Range Organics (DRO) Revision 4.1 Date 10/22/97

16.0 Modifications:

16.1 Modifications from SW-846 Method 3510C

16.1.1 Section 7.1 of the method calls for initial sample volume to be determined volumetrically either by measuring out exactly 1 liter or marking the meniscus on the sample container and later determining the volume of water required to fill the bottle back up to the mark. This SOP allows the initial sample volume to be determined by weight in order to achieve a more accurate initial volume and to avoid cross-contamination via glassware.

16.1.2 Section 7.5 of the method calls for shaking the separatory funnel 1-2 minutes. This SOP calls for shaking the separatory funnel for 3 minutes.

16.1.3 Section 7.6 of the method calls for allowing the organic layer to separate from the water phase for a minimum of 10 minutes. This SOP calls for allowing the organic layer to separate from the water phase for a minimum of 5 minutes after the first extraction and a minimum of 3 minutes for subsequent extractions, up to 10 minutes if the separation is not complete.

16.1.4 The source method does not call for the use of sodium chloride. This procedure calls for the addition of approximately 6g of sodium chloride to all samples and all QC samples in order to help the extraction efficiency.

16.1.5 The source method calls for samples to be extracted for method 8141 at the pH they are received. This procedure calls for the extraction to be performed at a pH between 5 and 8. This is done per guidelines found in Section 2 and Section 8 of SW-846 8141B.

16.2 Modifications from 40 CFR Method 608 and 610

16.2.1 Section 10.1 of the method calls for initial sample volume to be determined volumetrically. This SOP allows the initial sample volume to be determined by weight.

16.2.2 Section 10.2 of the method calls for shaking the separatory funnel 1-2 minutes. This SOP calls for shaking the separatory funnel for 3 minutes.

16.2.3 Section 10.2 of the method calls for allowing the organic layer to separate from the water phase for a minimum of 10 minutes. This SOP calls for allowing the organic layer to separate from the water phase for a minimum of 5 minutes after the first extraction and a minimum of 3 minutes for subsequent extractions, up to 10 minutes if the separation is not complete.

16.2.4 Section 10.3 of the method calls for rinsing the sample collection bottle with the 60 mL methylene chloride aliquot for the second and third extraction as well as the first extraction. This SOP calls for rinsing the sample collection bottle with only the first 60-mL methylene chloride aliquot.

16.2.5 The source method does not call for the use of sodium chloride. This procedure calls for the addition of approximately 6g of sodium chloride to all samples and all QC samples in order to help the extraction efficiency.

16.3 Modifications from 40 CFR Method 614

16.3.1 Section 10.1 of the method calls for initial sample volume to be determined volumetrically. This SOP allows the initial sample volume to be determined by weight.

16.3.2 Section 10.2 of the method calls for the extraction to be performed with at 15% v/v methylene chloride in hexane solvent. This procedure uses methylene chloride for the extraction. SOP DV-OP-0007 calls for the methylene chloride extract to be concentrated and exchanged to hexane.

16.3.3 Section 10.2 of the method calls for shaking the separatory funnel 1-2 minutes. This SOP calls for shaking the separatory funnel for 3 minutes.

16.3.4 Section 10.2 of the method calls for allowing the organic layer to separate from the water phase for a minimum of 10 minutes. This SOP calls for allowing the organic layer to separate from the water phase for a minimum of 5 minutes after the first extraction and a minimum of 3 minutes for subsequent extractions, up to 10 minutes if the separation is not complete.

16.3.5 Section 10.3 of the method calls for rinsing the sample collection bottle with the 60 mL solvent aliquot for the second and third extraction as well as the first extraction. This SOP calls for rinsing the sample collection bottle with only the first 60-mL methylene chloride aliquot.

16.3.6 The source method does not call for the use of sodium chloride. This procedure calls for the addition of approximately 6g of sodium chloride to all samples and all QC samples in order to help the extraction efficiency.

16.4 Modifications from Method AK 102

16.4.1 Section 9.1.1.1 of the method calls for using no more than 1 liter of sample and to determine the volume either by measuring out exactly 1 liter or marking the meniscus on the sample container and later determining the volume of water required to fill the bottle back up to the mark. This SOP allows the initial sample volume to be determined by weight in order to achieve a more accurate initial volume and to avoid cross-contamination via glassware. This SOP allows for the extraction of more than 1 L as it calls for the use of the entire sample volume.

16.4.2 Section 9.1.1.6 of the method says to allow the water and solvent layers to separate for approximately 10 minutes. This SOP calls for the allowing the organic layer to separate from the water phase for a minimum of 5 minutes after the first extraction and a minimum of 3 minutes for subsequent extractions, up to 10 minutes if the separation is not complete.

16.4.3 The source method does not call for the use of sodium chloride. This procedure calls for the addition of approximately 6g of sodium chloride to all samples and all QC samples in order to help the extraction efficiency.

16.5 Modifications from Method NWTPH-Dx

16.5.1 The method calls for determining the initial volume of the sample my marking the meniscus on the bottle and later determining the volume of tap water required to fill the bottle back up to the mark. This SOP allows the initial sample volume to be determined by weight in order to achieve a more accurate initial volume and to avoid cross-contamination via glassware.

16.5.2 The method calls for shaking the separatory funnel for one minute. This SOP calls for the separatory funnel to be shaken for at least three minutes.

16.5.3 The source method does not call for the use of sodium chloride. This procedure calls for the addition of approximately 6g of sodium chloride to all samples and all QC samples in order to help the extraction efficiency.

16.6 Modifications from Oklahoma DRO

16.6.1 The method calls for aliquotting 800 mL to 900 mL of the sample volumetrically. This SOP calls for the initial sample volume to be determined by weight in order to achieve a more accurate initial volume and to avoid cross-contamination via glassware. This SOP allows for the extraction of more than 1 L as it calls for the use of the entire sample volume.

16.6.2 The method calls for extracting using 50 mL of solvent. This SOP calls for the extraction to be done using at least 60 mL of solvent.

16.6.3 The method calls for shaking the separatory funnel for two minutes. This SOP calls for the separatory funnel to be shaken for at least three minutes.

16.6.4 The method calls for a method blank and LCS to be analyzed every 10 samples. This SOP calls for a method blank and LCS to be analyzed every batch of 20 samples.

16.6.5 The source method does not call for the use of sodium chloride. This procedure calls for the addition of approximately 6g of sodium chloride to all samples and all QC samples in order to help the extraction efficiency.

17.0 Attachments

Table 1. Determinative Methods Using Separatory Funnel Extractions

18.0 Revision History

- **Revision 14.0, June 30, 2016**
  - Added Section 3.6 – definition of reagent water
  - Revised the table in Section 8 to reflect the nominal leachate volume for method 8141.
  - Updated sections 9.4.4, 9.5.4, 10.4.1, and 10.5.4 to include 8141 TCLP.
  - Added Section 10.2 - recording of support equipment IDs
  - Added note to Section 10.4 regarding the rotation of glassware
  - Added reference to method 8141 TCLP leachates to Section 10.7.2
  - Removed references to preparation of Wyoming Leachates throughout. Lab no longer performs Wyoming Leach method
  - Added Sections 10.7.6.3 and 10.7.6.4 to provide guidance for 600 method series in relation to sediment and decanting issues.
  - Updated Section 12 to be consistent with other SOPs
  - Renumbered paragraphs throughout due to the removal of the WY Leachate prep

- **Revision 13, August 31, 2015**
  - Annual Technical Review.
  - Removed the Notes from Section 2 and Section 10.9 regarding South Carolina. The laboratory no longer holds South Carolina certification for this method.
  - Added detail to Section 10.12 and 10.20 on how much acid and base is normally required to adjust the pH of leachates for method 8270.

- **Revision 12.0, August 31, 2014**
  - Revised Section 2 to remove references to initial volume. The procedure is used on waters and leachates with a variety of initial volumes. That detail is documented later in the procedure and was therefore removed from the summary found in Section 2.
  - Added a comment to Section 9.1.2 that states: “This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated.”
  - Section 9 was revised to remove Acceptance Criteria and Corrective Action details. This information is found in the analytical procedures.

- Removed the Note following Section 10.4.2 that instructs the analyst to check the samples for sodium thiosulfate preservation. TestAmerica Denver does not analyze drinking water samples by this procedure and therefore this preservation is not needed.
- All references to 8270 by LVI were removed. TestAmerica Denver does not extract samples by this procedure for 8270 by LVI. Instead the samples are extracted by 3520C under DV-OP-0008.
- The table in Section 10.12 was revised to make it easier to read and locate the correct Method.
- Troubleshooting and Maintenance sections were added per DoD QSM 5.0 requirements.

- **Revision 11.0, August 19, 2013**
  - Added statement to Section 2.0 that LVI must not be used on SC samples

- **Revision 10.0, May 14, 2013**
  - The procedure was revised to instruct the analyst to allow the organic and aqueous phases to separate for a minimum of 5 minutes after the first extraction and 3 minutes after subsequent extractions.
  - The procedure was revised to increase the amount of sodium chloride added to samples and QC from 3g to 6g.
  - Section 5 was revised to include the hazards of glasswool and to instruct the analysts to handle it only in a fumehood.
  - Section 8 was revised to change the hold-time calculation for leachates from the start of the leaching procedure instead of the completion of the leaching procedure. This was done to ensure the holding times are contiguous.
  - Section 10.13 was revised to instruct the analyst to extract 250 mL to 100 mL samples with 30 mL of solvent instead of 15 mL of solvent. This was done to increase extraction efficiency while still reducing solvent usage.
  - Sections 2.0, 9.1 and 10.1 were updated to reflect current practice.

- **Revision 9.0, January 15, 2013**
  - Section 10.9 was updated to include note to eliminate use of salt in South Carolina samples.

- **Revision 8.0, September 25, 2012**
  - This procedure was updated to include instructions on how to extract 8270 water samples for Large Volume Injection.

- **Revision 7.0, January 31, 2012**
  - Annual Technical Review
  - Updated Section 6.2 to describe the requirements for computer software and hardware

- Updated Section 7.0 to describe requirements for Reagents and Standards.
- Updated Section 8.0 to state PCBs by method 8082 have no holding time as per SW-846 Update 4 and that samples for analysis by NW-TPH have a 7 day hold time, even if acid preserved.
- Updated Section 9.1.4 and Section 10.1 to accurately describe the NCM notification system.
- Updated Section 10.4 and 10.6 to state the appropriate size of the graduated cylinders to be used to measure out 100 mL and 200 mL of leachate.
- Updated Sections 10.6.6 and 10.14 to give guidance to the analyst when a density check of a sample is required.
- Updated Section 10.9 to give more detail on how much sodium chloride should be added to the samples.
- Updated Section 16 to include the method modification of the sodium chloride addition.
- Updated Table 1 to reflect the current analytical SOPs.
- Corrected grammatical and formatting errors

- **Revision 6.0 dated 01/10/11**
  - Added note to Section 6 that sodium sulfate should be stored in tightly closed container.
  - Revised Section 7 to reference DV-OP-00020 for information about surrogate and spike standards.
  - Corrected Section 7.1 to indicate that the reagent water should be 18 to 18.2 Mohm/cm.
  - Revised procedure to include details on the extraction of Wyoming Leachates.
  - Added references to methods NWTPH-Dx, and Oklahoma DRO.
  - Added Section 6.2 computer software and hardware.
  - Section 8 was revised to give more detail on the preservation and hold times for methods AK102, AK103, NWTPH-Dx, and Oklahoma DRO.
  - Revised Section 9 to include more detail on QC requirements for methods AK102_103, NWTPH-Dx, and Oklahoma DRO.
  - Revised Section 10 to clarify that when 1 liter graduated cylinders are used to measure the initial volume of the water samples, that the volume should be recorded to the nearest 10 mL.
  - Revised Section 10 to instruct that if samples for methods AK102_103, NWTPH-Dx, and Oklahoma DRO are received preserved, then the MB and the LCS samples should also be acidified with HCl. Otherwise the samples are extracted as received.
  - Revised Section 16 to include more detail on modification from methods AK102_103, NWTPH-Dx, and Oklahoma DRO

- Revised the procedure to call for the 2nd fraction of 8270 TCLP leachates to be extracted at a pH of 14 instead of the pH 11 to 12 used in water samples. This was done to help the recovery of pyridine.

Earlier revision histories have been archived and are available upon request.

TABLE 1.

Determinative Methods Using Separatory Funnel Extractions

Method Description	*Determinative Method*	*SOP*
Diesel Range Organics & Jet Fuels	SW-846 8015, California LUFT Method, Alaska Methods AK102 & AK103 SW-846 8015C	DV-GC-0027
Chlorinated Pesticides	SW-846 8081A SW-846 8081B EPA Method 608	DV-GC-0020 DV-GC-0016
Polychlorinated Biphenyls	SW-846 8082 SW-846 8082A EPA Method 608	DV-GC-0021 DV-GC-0016
Organophosphorus Pesticides	SW-846 8141A, & EPA Method 614	DV-GC-0017
Polynuclear Aromatic Hydrocarbons (PAH)	SW-846 8310 & EPA Method 610	DV-LC-0009
Semi-volatiles by GC/MS	SW-846 8270 SW-846 8270D	DV-MS-0011 DV-MS-0012
PAH by GC/MS SIM	SW-846 8270	DV-MS-0002

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Title: Concentration and Clean-up of Organic Extracts [SW-846, 3510C, 3520C, 3540C, 3546, 3550B, 3550C, 3620C, 3660B, 3665A, ASTM Method D7065-11, and EPA 600 Series Methods]

Approvals (Signature/Date):

Brittany Scoles 12/17/15 Date Technical Specialist	Adam Alban 17 Dec 15 Date Health & Safety Manager / Coordinator
Margaret S. Sleevi 12/21/15 Date Quality Assurance Manager	William S. Cicero 12/31/15 Date Laboratory Director

Facility Distribution No. _____ **Distributed To:_____**

1.0 Scope and Application

1.1 This standard operating procedure (SOP) provides instructions for the concentration, and if necessary, cleanup, of solvent extracts of organic compounds from water samples, soil samples, TCLP leachates, and SPLP leachates. This SOP is based on SW-846 Methods 3510C, 3520C, 3540C, 3546, 3550B, 3550C, 3620C, 3630C, 3660B, 3665A, ASTM Method D7065-11, and EPA 600 Series methods.

1.2 The determinative methods and extraction methods used in conjunction with this procedure are listed in Attachment 1.

1.3 This procedure does not include the extraction steps. See the following SOPs for the applicable extraction procedures:

DV-OP-0006: Extraction of Aqueous Samples by Separatory Funnel, SW-846 3510C and EPA 600 Series

DV-OP-0008: Extraction of Aqueous Samples by Continuous Liquid/Liquid Extraction (CLLE) by Method SW-846 3520C, and Method 625 and ASTM Method D7065-11

DV-OP-0010: Soxhlet Extraction of Solid Samples, SW-846 3540C

DV-OP-0015: Microwave Extraction of Solid Samples, SW-846 3546

DV-OP-0016: Ultrasonic Extraction of Solid Samples, SW-846 3550B and 3550C

DV-OP-0021: Extraction of Aqueous Samples by Continuous Liquid/Liquid Extraction (CLLE) by Method SW-846 3520C for Low-Level NDMA by GC/CI/MS/MS

NOTE: This SOP does not include the concentration steps of extracts for Herbicides by method 8151A. See DV-OP-0011 instead.

2.0 Summary of Method

Sample extracts are concentrated to a specific final volume using an S-EVAP, N-EVAP, or Turbo-Vap. Some methods require a solvent exchange. If necessary, various clean-up techniques are performed before the extract is sent for analysis.

3.0 Definitions

3.1 **Extraction Holding Time:** The elapsed time expressed in days from the date of sample collection to the date the extraction starts. The holding time is tracked in the laboratory LIMS system, and is the primary basis of prioritizing work.

3.2 **Preparation Batch:** A group of up to 20 samples that are of the same matrix and are processed together in the same extraction event using the same procedure and lots of reagents and standards.

3.3 **Method Comments:** The Method Comments are used to communicate to the bench level chemists special requirements and instructions from the client. See WI-DV-0032

3.4 **Quality Assurance Summary (QAS):** Certain clients may require extensive specific project instructions or program QC, which are too lengthy to fit conveniently in the special instructions/Method Comments field in LIMS. In those situations, laboratory Project Managers describe the special requirements in a written QAS to address these requirements. QASs are posted on a public drive for easy accessibility by all lab employees. Normally QASs are introduced to analysts in an initial project kick-off meeting to be sure that the requirements are understood.

4.0 Interferences

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2 Visual interferences or anomalies (such as foaming, emulsions, odor, more than one layer of extract, etc.) must be documented.

4.3 The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.4 Due to the low reporting limits and the potential for contamination, the extracts that are to be analyzed for NDMA by 8270D_SIM_LL must be concentrated in glassware designated for that method. K-D flasks, concentrator tubes, stem-less glass funnels, and Snyder columns will be clearly marked and segregated for this purpose.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual 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, nitrile gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 In order to limit the emission of methylene chloride, TestAmerica Denver uses a solvent recovery system. The system condenses and collects methylene chloride that has been evaporated off the sample extracts while on the S-EVAP.

5.1.1.1 Each analyst must inspect the system before using it to ensure the collection tubes are in good condition, the in-process tanks are not full, and the chiller is operating correctly.

5.1.1.2 While concentrating methylene chloride or methylene chloride / acetone extracts on the S-Evap, the analyst must check the level of the solvent collected in the in-process tanks at a frequency to ensure the tank will not be overfilled. A tank will not be filled more than 90%. The analyst may use a timer set at 30 minute intervals to help remind the analyst to check the level of the solvent collected in the in-process tanks.

5.1.1.3 The solvent recovery system will never be used for the collection of ether due to the potential danger to analysts if the system were to fail during operation.

5.1.2 Glasswool is a carcinogen and therefore should be handled in a hood to avoid inhalation of dust.

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
Acetonitrile	Flammable Irritant Poison	40 ppm TWA	Exposure may cause cyanide poisoning resulting in reddening of the skin and eyes and pupil dilation. Effects of overexposure are often delayed due to the slow formation of cyanide ions in the body. May cause nose and throat irritation, flushing of the face, tightening of the chest. Also may cause headache, nausea, abdominal pain, convulsions, shock.
Hexane	Flammable Irritant	50 ppm TWA	Causes irritation to eyes, skin and respiratory tract. Aspiration hazard if swallowed. Can enter lungs and cause damage. May cause nervous system effects. Breathing vapors may cause drowsiness and dizziness. Causes redness and pain to the skin and eyes.

Material	Hazards	Exposure Limit (1)	Signs and Symptoms of Exposure
Methanol	Flammable Irritant Poison	200 ppm TWA	Methanol evaporates at room temperature. Inhalation, ingestion and/or eye and skin contact can all possibly cause light-headedness, nausea, headache, and drowsiness. Prolonged exposure can lead to permanent blindness.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Mercury	Corrosive Irritant Highly Toxic	0.05 mg/m^3 TWA	May be fatal if inhaled. May cause respiratory tract irritation. May be harmful if absorbed through skin. May cause skin irritation.
Methylene Chloride	Irritant Carcinogen	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.
(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

NOTE 1: All glassware used in this procedure is cleaned following SOP# DV-OP-0004. In addition, the glassware is rinsed with methylene chloride immediately prior to use.

NOTE 2: Due to the low reporting limits and the potential for contamination, the extracts that are to be analyzed for NDMA method 8270D_SIM_LL and PAHs by method 8270C_SIM_LL must be concentrated in glassware designated for that method. K-D flasks, glass funnels, concentrator tubes, and snyder columns will be clearly marked and segregated for this purpose.

6.1 Kuderna-Danish (K-D) flasks.

6.2 Concentrator tubes for K-D flasks, un-graduated, approximately 10 mL.

6.3 Concentrator tubes for K-D flasks, graduated at 1mL, calibration checked before use following the steps detailed in DV-QA-0008.

6.4 Snyder columns, 3-ball with ground glass joints at top and bottom

6.5 Manual, adjustable positive-displacement pipette and bottle-top re-pipettor, used to

dispense 1 to 20 mL. Calibration is checked following the steps detailed in DV-QA-0008.

6.6 Extract Storage Vials – variety of sizes, clear and amber

6.7 Pasteur pipettes – 6 inch and 9 inch in length.

6.8 Stem-less glass funnels

6.9 Glass wool, baked at 400℃ for four hours.

6.10 Boiling Chips – contaminant free, approximately 10/40 mesh Teflon®, PTFE. For concentrating extracts to a final volume greater than 1mL.

6.11 Boiling Chips – contaminant free, carborundum #12 granules, for concentrating extracts to a 1mL final volume. These boiling chips are sufficiently small as to not add any error to the 1mL final volume.

6.12 Solvent Recovery System – includes re-circulating chiller, set at 5℃, cooling condensers, Teflon® PTFE tubing and In-Process Tanks with quick-connect attachments

6.13 S-Evap, thermostat controlled water bath

6.14 N-Evap, thermostat controlled water bath with regulated nitrogen supply

6.15 Computer Software and Hardware

Please refer to the master list of documents, software and hardware located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

7.0 Reagents and Standards

Reagent grade chemicals shall be 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.

7.1 Methylene Chloride

Each lot of solvent is tested following CA-Q-S-001 or before it is put into use. QA personnel post the list of approved lots at solvent storage areas. For solvents packaged in CYCLETAINERS, that have not been previously tested per CA-Q-S-001, the first batch of samples prepared with a new lot of solvent is monitored and reported to the QA group per the instructions in CA-Q-S-001 DV-1. If any problems are identified, use of the solvent is suspended until further testing can be done and determines the solvent is acceptable.

7.2 Hexane

For solvents packaged in bottles, each lot of solvent is tested following CA-Q-S-001 before it is put into use. QA personnel post the list of approved lots at solvent storage areas. For solvents packaged in CYCLETAINERS, the first batch of samples prepared with a new lot of solvent is monitored and reported to the QA group per the instructions in CA-Q-S-001 DV-1. If any problems are identified, use of the solvent is suspended until further testing can be done and determines the solvent is acceptable.

7.3 Methanol, HPLC Grade

Each lot of solvent is tested following CA-Q-S-001 before it is put into use. QA personnel post the list of approved lots at solvent storage areas.

7.4 Acetone

Each lot of solvent is tested following CA-Q-S-001 before it is put into use. QA personnel post the list of approved lots at solvent storage areas.

7.5 Acetonitrile

Each lot of solvent is tested following CA-Q-S-001 DV-1 before it is put into use. QA personnel post the list of approved lots at solvent storage areas.

7.6 Baked Sodium Sulfate, 12-60 mesh

Heat sodium sulfate in a 400℃ oven for at least fo ur hours.

7.7 Sulfuric Acid, Concentrated

For use in PCB extract clean-up.

7.8 Florisil Solution, (FlorisilSol)

Add 900mL of hexane to a Class A graduated cylinder. Add 100 mL of Acetone to the same graduated cylinder for a final volume of 1000 mL. Pour the mixture into a 1 L amber bottle.

7.9 Florisil Cartridges,

Purchased ready to use. 1000 mg in 6 mL tube. Stored in a desiccator after opening. Restek part number 24034 or equivalent.

7.10 Anhydrous Silica Gel, 60-100 mesh, (SiGel60-100UA)

Sigma Aldrich part number 23799-1KG or equivalent

7.11 Activated Anhydrous Silica Gel, 60-100 mesh, (Active SilGel)

Bake Silica Gel from Section 7.10 above at 400°C for at least 4 hours. Store in a desiccator.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample extracts waiting to be concentrated are stored refrigerated at 0°C - 6°C in glass bottles or flasks and capped with Teflon-lined lids or aluminum foil. Final sample extracts are stored in glass vials with Teflon-lined lids. See Table 3 for details on storage vial types. Final concentrated extracts are stored refrigerated at 0°C - 6°C. Extracts have a holding time of 40 days from the date of extraction to the date of analysis.

8.2 All sample extracts, before or after concentration, are stored separately from standards.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS Method Comments to determine specific QC requirements that apply. For SOPs that address only preparation, QC acceptance limits on the analytical results are not included. Refer to the appropriate SOP that describes the determinative method.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs. This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated. Any deviation or exceptions from QSM 5.0 requirements must have prior approval in the project requirements.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in the LIMS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Initial Performance Studies

Before analyzing samples, the laboratory must establish a method detection limit (MDL). In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument he/she will be using. On-going proficiency must be demonstrated by each analyst on an annual basis. See Section 12.0 for more details on detection limit studies, initial demonstrations of capability, and analyst training and qualification.

9.3 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. The method blank must be run on each instrument that is used to analyze samples from the same preparation batch. See QC Policy DV-QA-003P for further details.

9.4 Method Blank (MB)

At least one method blank must be processed with each preparation batch. The method blank for batches of aqueous samples consists of reagent water, and for batches of soil samples, consists of Ottawa sand, both of which are free of any of the analyte(s) of interest. The method blank for batches of TCLP and SPLP leachates consists of leach fluid. The method blank is processed and analyzed just as if it were a field sample.

9.5 Laboratory Control Sample (LCS)

9.5.1 At least one LCS must be processed with each preparation batch. For aqueous sample batches, the LCS consists of reagent water to which the analyte(s) of interest are added at known concentration. For soil sample batches, the LCS consists of Ottawa sand to which the analyte(s) of interest are added at a known concentration. For TCLP and SPLP leachates, the LCS consists of leach fluid to which the analyte(s) of interest are added at known concentration. The LCS is carried through the entire analytical procedure just as if it were a sample.

9.5.2 EPA Methods 608, 610, 614, and 625 require a LCS at a 10% frequency. In other words, one LCS is required for a batch of 10 or less samples. A LCSD is required for a batch of 11 or more samples.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1 One MS/MSD pair must be processed with each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. It is prepared in a manner similar to the LCS, but uses a real sample matrix in place of the blank matrix. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked exactly as the MS) that is prepared and analyzed along with the sample and matrix spike. Some programs allow spikes to be reported for project-related samples only. Samples identified as field blanks cannot be used for the MS/MSD analysis.

9.6.2 EPA Methods 608, 610, 614, and 625 require one matrix spike for every 10 samples. If the batch has more than 10 samples, then two matrix spikes must be performed. The two matrix spikes are to be performed on two different samples.

9.6.3 If insufficient sample volume is available for MS/MSD, an NCM must be written and a LCSD must be prepared.

9.7 Surrogate Spikes

Every calibration standard, field sample, and QC sample (i.e. method blank, LCS, LCSD, MS, and MSD) is spiked with surrogate compounds.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 Critical Procedural Considerations

NOTE: Rotate glassware; do **not** use specific glassware or positions for the MB and LCS/LCSD.

10.3.1 As stated throughout this SOP, analysts must review Method Comments and any applicable QASs before starting work. This review is also documented on the Organic Extraction Checklist (see WI-DV-0009).

10.3.2 Analyst must focus on using clean technique throughout this procedure. Any parts or pipettes that come into direct contact with dirty surfaces should be cleaned or disposed of before coming into contact with the sample.

10.3.3 According to the type of sample and any cleanup procedures needed, different final solvents and volumes will be required. Refer to WI-DV-0009 for the appropriate final solvents and final volumes.

10.4 Refer to WI-DV-0009 to determine if the extract is to be concentrated by the Kuderna-Danish / N-Evap method described in Section 10.5 and 10.6, or the Turbo-Vap method described in Section 10.6.6

10.5 Concentration by the Kuderna-Danish Method

10.5.1 Refer to WI-DV-0009. If the extract is to be concentrated to a 1 mL final volume, use a 1 mL graduated concentrator tube. For extracts that are to be concentrated to any other final volume, use an un-graduated concentrator tube.

10.5.2 Assemble the Kuderna-Danish concentrator by attaching the appropriate concentrator tube to the 500 mL K-D flask with a clip. Make sure the attachment is firm at the joint. While wearing cut-resistant gloves, tighten the joint with your fingertips and thumb. Do NOT over-tighten. Refer to Attachment 3 for configuration of the Kuderna-Danish concentrator.

NOTE: Due to the low reporting limits and the potential for contamination, the extracts that are to be analyzed for NDMA by method 8270D_SIM_LL and PAHs by method 8270C_SIM_LL must be concentrated in glassware designated for those methods. K-D flasks, concentrator tubes, and Snyder columns will be clearly marked and segregated for this purpose.

10.5.3 Rinse the apparatus with methylene chloride. Discard the rinse solvent into the appropriate waste container. Care should be taken to ensure all surfaces of the glass are coated with solvent.

10.5.4 If the extract is to be concentrated to a 1 mL final volume, add 2-3 carborundum granules to the K-D concentrator. If the extract is to be concentrated to a final volume greater than 1 mL, add 1-2 Teflon® boiling chips to each K-D concentrator.

10.5.5 If the sample extracts have not been filtered through sodium sulfate at the time of extraction, or if the sample extract have visible water, then the extracts must be dried at this point. Plug a glass funnel with baked glass wool and add approximately 1 teaspoon of baked sodium sulfate. Rinse the funnel and the sodium sulfate with methylene chloride and place it on top of the K-D. During the quantitative transfer in section 10.5.6 the extract will be filtered through the sodium sulfate.

NOTE 1: Glass wool dust is a carcinogen and therefore glass wool should only be handled in a hood to avoid inhaling any glass particles. Once covered with sodium sulfate, it can be removed from the hood.

NOTE 2: If the extract contains more water than can be easily removed by filtering through 1 teaspoon of sodium sulfate, either more sodium sulfate can be used or a solvent-rinsed separatory funnel can be used to separate the water out of the extract. A NCM should be prepared if this is necessary.

10.5.6 Quantitatively transfer the sample extract to the K-D flask. Transfer the sample label to the K-D flask. Perform a quantitative transfer of the extract by rinsing the sample extract container with methylene chloride and adding the rinse solvent to

the K-D. If the extract is being filtered through sodium sulfate, be sure to rinse the sodium sulfate well to ensure no target compounds are left on the sodium sulfate. Allow the solvent to drain from the sodium sulfate into the K-D flask then discard the sodium sulfate.

10.5.7 Turn a three-ball Snyder column upside down and rinse with methylene chloride, then rinse the bottom joint with methylene chloride. Attach the Snyder column to the top of the K-D concentrator as shown in Attachment 3.

10.5.8 Place the K-D concentrator on a water bath so that the tip of the receiver tube is submerged. The water level should not reach the joint between the concentrator tube and the K-D flask. Refer to WI-DV-0009 for the correct water bath temperature. Record both the observed and the corrected temperature on the benchsheet.

10.5.9 For extracts that are methylene chloride or 50/50 methylene chloride/acetone, attach the solvent recovery system tube to the top of the Snyder column. At the appropriate rate of distillation, the balls will actively chatter but the chambers should not flood.

NOTE 1: For extracts for analysis for low-level NDMA by method 8270D_SIM_LL and PAHs by 8270C_SIM_LL, the solvent recovery system will not be used to avoid possible contamination.

NOTE 2: At this time, a timer may be set for no longer than 30 minutes as a reminder to check the in-process solvent tanks.

10.5.10 If the method does not require a solvent exchange, skip to Section 10.5.12. If the method requires a solvent exchange, continue on to Section 10.5.11.

10.5.11 If the method requires a solvent exchange at this time, detach the solvent recovery system tube from the top of the Snyder column and add the appropriate exchange solvent through the top of the Snyder column. The exchange solvent should be added when the extract has concentrated to a level that it forms a quarter-sized pool of solvent in the bottom of the K-D. Refer to WI-DV-0009 for details of exchange solvents and volumes. Mark the K-D flask and sample label to indicate the exchange has been performed. There is no need to re-attach the solvent recovery system at this time as the majority of the methylene chloride has already been evaporated and collected.

10.5.12 Continue to concentrate the sample on the water bath back down to 10-15 mL, or just below the K-D and concentrator tube joint. At this point the boiling sample is just barely splashing above the top of the receiver tube.

NOTE: It is very important not to concentrate to dryness as analytes will be lost. Some of the analyses, especially for 8270 and 8015, are especially temperature sensitive and the sample should be taken off the water bath as soon as possible to avoid losing analytes. The 8081 surrogate TCMX is fairly volatile and can be lost if the extract is allowed

to concentrate too low either before or after hexane exchange. If the analyst has concerns that the extract might have concentrated too low, they should notify their supervisor and/or write a NCM.

10.5.13 Remove the K-D concentrator from the water bath. Rinse the Snyder column down with a minimal amount of solvent. If the extract was exchanged, use the exchange solvent to perform the rinse, otherwise use methylene chloride.

10.5.14 Allow the extract to cool to room temperature, about 10 minutes.

10.5.15 After the extract is allowed to cool, if the level of the extract is above the level of the concentrator tube joint, add a fresh boiling chip and return the K-D concentrator to the water bath.

10.5.16 After the extract is cool, remove the snyder column. Remove the clip holding the K-D flask and concentrator tube together. Use a Kim-wipe to dry the water off of the joint area so that water does not get into the extract. Remove the concentrator tube from the K-D flask and rinse the lower K-D flask joint into the concentrator tube with methylene chloride or the appropriate exchange solvent.

10.6 Nitrogen Evaporation (N-Evap) to Final Concentration.

10.6.1 N-evap needles should be cleaned weekly by soaking overnight in methylene chloride. This is documented in the N-evap needle log-book.

10.6.2 At the beginning of each shift, the N-evap needles should be wiped clean with a Kim-wipe soaked in methylene chloride to remove any potential contamination. If a needle comes in contact with an extract, then it needs to be cleaned before being used on the next extract.

10.6.3 Place the concentrator tube on the nitrogen evaporator. The temperature of the water bath should be at least 5℃ below the boiling temperature of the solvent being evaporated (See Attachment 2). Lower the needle down to the sample so that a small dimple forms on the surface of the solvent. The stream of nitrogen should be gentle enough that it does not cause the extract to splash.

10.6.4 During the course of the evaporation, rinse the sides of the concentrator tube with approximately 1 mL of clean solvent. The rinse should occur when the solvent gets close to the final volume. Concentrate the solvent to just below the final volume and remove from the nitrogen evaporator.

10.6.5 Transfer the extract into the appropriate vial. Refer to WI-DV-0009 for the appropriate final volume and correct vial.

10.6.5.1 If the extracts are to have a final volume of 1 mL, they should be in 1 mL graduated concentrator tubes. Using a Pasteur pipette, or a solvent wash bottle, add the appropriate solvent to the tube until the extract meniscus reaches the 1 mL gradation. Then using the Pasteur pipette transfer the extract to a labeled 2 mL amber glass vial.

10.6.5.2 For extracts with a final volume greater than 1mL, the vials should be calibrated using the manual, adjustable positive-displacement pipette or bottle-top re-pipettor. Pipette the correct volume of clean solvent into the vial and mark the bottom of the meniscus with a thin marker. Discard the solvent. Transfer the extract into the vial using a Pasteur pipette and rinse the concentrator tube with solvent. Transfer the rinse to the vial. Bring the meniscus of the solvent up to the marked line. Cap with a Teflon-lined cap.

NOTE 1: The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

NOTE 2: Some extracts might not concentrate down to the required final volume. If the extract is very dark and viscous, or an oil layer or precipitate starts to form, a higher final volume can be used. This should be documented in an NCM.

10.6.6 After the extract has been transferred to the appropriate vial, rinse the concentrator tube with methylene chloride before washing per DV-OP-0004. This is important to remove any residual contamination.

10.7 TurboVap Method

10.7.1 Turn on the TurboVap and adjust the water temperature to 40℃. Turn the nitrogen supply on. Record both the observed and the actual temperature on the benchsheet.

10.7.2 Switch the endpoint sensor to “Manual”.

10.7.3 Adjust the water bath level. The water level should be at least 1 inch above the extract level.

10.7.4 Turn on the nitrogen gas and adjust the gas pressure to approximately 12 psi. Lower pressure may be used if needed to prevent samples from splashing out of the TurboVap tubes.

10.7.5 Rinse the TurboVap tube with methylene chloride or the solvent the extract is in. Discard the waste.

10.7.6 Transfer the sample to the TurboVap tube. For 8141 soils extracted by soxhlet, dry the extract first by filtering through a funnel with baked sodium sulfate. Rinse the sample extract container with clean solvent and transfer to the TurboVap tube. Do not fill the TurboVap tubes over the fill line or approximately ¾ full.

10.7.7 Place the TurboVap tube into the TurboVap and turn on nitrogen to the position the tube is in.

10.7.8 Close the lid. You should be able to see the sample extracts swirling in the

tubes.

NOTE: If the extract splashes when the nitrogen flow starts, transfer a portion of the extract back into the original extract container, or lower the gas pressure.

10.7.9 As the extract concentrates, transfer the remainder of the extract in to the appropriate Turbovap tube. Rinse the sample container with a few milliliters of methylene chloride or appropriate solvent and transfer to the Turbovap tube.

10.7.10 During the concentration rinse the Turbovap tube walls with a few milliliters of solvent 1 or 2 times.

10.7.11 If a solvent exchange is required, concentrate to about 5 mL and add the exchange solvent. After the exchange solvent is added, swirl the extract to make sure the extract is well mixed. Concentrate back down to slightly less than the appropriate volume. Refer to Attachment 3 for details of exchange solvents and final volumes.

10.7.12 Transfer the extract into the appropriate vial.

10.7.12.1 Currently, the TurboVap is only used to concentrate extracts with final volumes greater than 1 mL. Ask the supervisor for guidance if a project requires a 1 mL final volume by TurboVap.

10.7.12.2 For extracts with a final volume greater than 1 mL, the vials should be calibrated using the manual, adjustable pipette or bottle-top re-pipettor. Pipette the correct volume of clean solvent into the vial and mark the bottom of the meniscus with a thin marker. Discard the solvent. Transfer the extract to the vial using a Pasteur pipette and rinse the concentrator tube with solvent. Transfer the rinse to the vial. Bring the meniscus of the solvent up to the marked line. Cap with a Teflon-lined cap.

10.7.12.3 Rinse the Turbovap tube with methylene chloride 2-3 times before washing. Turbovap tubes are not baked. They are cleaned in accordance with DV-OP-0004. If the Turbovap tubes need to be used again before they are dry, rinse with acetone to dry the Turbovap tube.

10.8 Cleanup Techniques

NOTE: If any sample in a batch requires a clean-up, the batch QC must also undergo the same clean-up technique.

10.8.1 Florisil Cartridge Cleanup

Florisil can be used to remove low-medium molecular weight polar hydrocarbon interfering compounds from pesticide extracts. The laboratory will use Florisil

cleanups whenever water extracts have any color, whenever soil extracts have any color darker than a Post-It® Note, or whenever there is clear evidence of interferences, such as significant interfering peaks in the RT range for the target pesticide compounds or failing sample surrogate recoveries. Extracts that are to be analyzed for kepone will not be florisil cleaned, because florisil will remove kepone from the extract.

NOTE: Florisil cartridge performance checks are conducted for every lot of Florisil before use. Add 1.0 mL of the Florisil check solution described in Attachment 4 to a pre-rinsed Florisil cartridge. Following the procedure described below, load and elute the 1mL of check solution through the Florisil cartridge. Bring the final volume back down to 1.0 mL in hexane. The test sample must show 80-115 % recovery of the controlled analytes with < 5% trichlorophenol recovery, and no peaks interfering with target compounds can be detected. The non-controlled analytes will be monitored for problems, but do not have to pass the 80-115% limits. If the check fails, repeat the test. If the re-check fails, contact QA for guidance.

10.8.1.1 Clean the manifold and ports

Prior to each use, the top and underside of the manifold lid must be wiped down with hexane and a Kim-wipe to prevent any cross-contamination. The manifold ports must be left open and placed in a jar with fresh acetonitrile, in a sonication bath for a minimum of 30 minutes. The jar used in the soak and sonication of the ports must be replaced weekly to ensure it does not spread contamination. This is documented in the Organic Extraction Weekly Cleaning Logbook.

10.8.1.2 Place one Florisil cartridge into the vacuum manifold for each sample extract. Make sure all valves are closed.

10.8.1.3 Add approximately 6 mL of hexane to each cartridge by filling the tube.

10.8.1.4 Slowly open the valves to allow a few drops of hexane to pass through, then close the valve and allow the hexane to soak the cartridge for at least 5 minutes.

10.8.1.5 Slowly open the valves again and allow the hexane to drain through the cartridge but close the valve when the solvent level is right above the glass frit. Do not allow the cartridges to go dry. If cartridges go dry, repeat the conditioning step.

10.8.1.6 Remove the manifold top and place one clean, labeled 16 x 125 mm disposable glass test tube in each position for each of the samples. Replace the manifold top. Make sure that the solvent line from each cartridge is placed inside the appropriate tube.

10.8.1.7 Add exactly 2.0 mL of the concentrated extract to the appropriate

Florisil cartridge. Turn the valve to the on position.

10.8.1.8 Allow the extract to gravity drip through the cartridge. The flow through the cartridges should be drop-wise, not streaming.

10.8.1.9 Just before the extract level drops below the glass frit, fill the cartridge with (90:10) Florisil solution. Allow this to pass through the cartridge, then just before it falls below the glass frit again, fill the cartridge again with (90:10) Florisil solution.

10.8.1.10 Allow all of the 90:10 solution to drip through the cartridges.

NOTE: Do not use the vacuum to recover solvent from the cartridge. If the vacuum is used and the cartridge goes dry under vacuum, then the interfering compounds that should be retained in the packing might come through into the cleaned extract.

10.8.1.11 Remove the tubes from the vacuum manifold and concentrate them back down to just below 2.0 mL on the nitrogen evaporator. Quantitatively transfer the extract to a 4mL vial that has been calibrated to hold 2.0 mL and bring the extracts up to the 2.0 mL calibration mark with hexane.

10.8.1.12 Discard the used cartridges.

10.8.2 Sulfur Removal

Sulfur can be removed by one of three methods: mercury, copper, or tetrabutylammonium sulfite (TBA), according to laboratory preference. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipette, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

10.8.2.1 Sulfur Removal with Elemental Mercury

NOTE: Use Mercury in a hood and sparingly in order to minimize exposure and disposal costs.

10.8.2.1.1 Transfer approximately 2 mL of sample extract into a clean Teflon-sealed vial.

10.8.2.1.2 Add one to three drops of mercury to the extract vial and seal.

10.8.2.1.3 Shake well for 15-30 seconds. If prolonged shaking is

required, use a mechanical shaker.

10.8.2.1.4 Remove the extract from the mercury using a disposable pipette and transfer to a clean vial.

10.8.2.1.5 If the mercury turns black, sulfur was present. Decant or pipette off the extract to a clean vial and repeat the procedure by adding one to three drops of fresh mercury. Do this until the mercury does not turn black.

10.8.2.1.6 If the extract is cloudy, filter the extract through a 1um disposable syringe filter.

10.8.2.1.7 Properly dispose of the mercury waste.

10.8.2.2 Sulfur Removal with Copper Powder

NOTE: This technique requires the copper powder to be very reactive, as demonstrated by a bright and shiny appearance. A pre-cleaned, activated copper may be purchased from a valid vendor. If manual preparation of reactive copper is performed, take care to remove all traces of acid in order to prevent degradation of some analytes.

10.8.2.2.1 Weigh out copper into a 20 mL VOA VIAL assuming two grams of copper needed per sample.

10.8.2.2.2 Remove oxides by treating with 10% nitric acid.

10.8.2.2.3 Rinse the copper with DI organic-free water three times to remove all traces of acid.

10.8.2.2.4 Rinse the copper with acetone and dry under a stream of nitrogen.

10.8.2.2.5 Add approximately 2 grams of the copper powder to a 2 mL vial with approximately 1ml of sample extract and shake vigorously on a mechanical shaker for at least one minute.

10.8.2.2.6 After phase separate, draw off extract and transfer to a clean vial.

10.8.3 Sulfuric Acid Cleanup

10.8.3.1 Add 1 mL of concentrated sulfuric acid to approximately 2 mL of sample extract in a Teflon capped vial.

CAUTION: There must be no water or acetone present in the extract or the reaction may shatter the sample container.

10.8.3.2 Vortex for about 5 seconds and allow to settle. (Centrifuge if necessary)

10.8.3.3 Remove the sample extract (top layer) from the acid using a Pasteur pipette and transfer to a clean vial.

CAUTION: It is not necessary to remove all the extract since the final volume is already determined. Transferring any amount of sulfuric acid along with the extract will result in extremely rapid degradation of the chromatographic column

10.8.3.4 If the sulfuric acid layer becomes highly colored after shaking with the sample extract, transfer the hexane extract to a clean vial and repeat the cleanup procedure until color is no longer being removed by the acid, or a maximum of 5 acid cleanups.

10.8.3.5 Properly dispose of the acid waste.

10.8.4 Silica Gel Clean-up for DRO extracts

10.8.4.1 Concentrate the DRO to slightly below 1 mL on the N-Evap. Add 100uL of the “SilicaGelSurr” standard to the extract and then bring the sample to a 1 mL final volume with methylene chloride.

10.8.4.2 While the extract is still in the concentrator tube, add approximately 0.05 g of activated silica gel to the extract and mix with a Pasteur pipette.

10.8.4.3 Transfer the extract to a new vial, leaving the silica gel behind. Then add a second aliquot of activated silica gel to the extract and mix by capping and shaking.

10.8.4.4 Allow the silica gel to settle out again and then transfer the extract to an empty vial and send on for analysis.

10.9 Documentation

All observations are recorded either directly into LIMS or on the hard-copy benchsheets. Any hand-written data recorded on the hard-copy benchsheets are transferred into LIMS before extracts are delivered to the analytical group. The hard-copy benchsheets are then saved and scanned into pdf files and sent to QA for archiving.

10.10 Maintenance

10.10.1 The chiller that operates the solvent recovery system should be checked periodically to ensure the water level is sufficient.

10.10.2 The SPE ports and valves used in the florisil are open and placed in a jar with fresh acetonitrile, in a sonication bath for a minimum of 30 minutes. The jar used in the soak and sonication of the ports must be replaced weekly to ensure it does not spread contamination. This is documented in the Organic Extraction Weekly Cleaning Logbook.

10.10.3 The N-Evap needles are removed once a week and soaked overnight in a jar of methylene chloride. This is documented in the Organic Extraction Weekly Cleaning Logbook.

10.10.4 The water bath used in the concentration of extracts has a thermostat that occasionally needs auto-tuned to keep the bath temperature within a narrow range.

To start autotuning:

1. **Press the ◉Advance key** until the [AUE] prompt appears in the data display.

2. **Select a thermal response value using the ▲Up-arrow/▼Down-arrow keys:** 1 for a slow response, 2 for an average response and 3 for a system that responds quickly. A thermal response value of 2 satisfactorily tunes most thermal systems.

3. **Press the ◉Advance key.** While the controller is in the tuning mode, the lower display alternately displays the normal information and the prompt [AUE], at one-second intervals.

10.11 Troubleshooting

Unusual sample matrix may cause problems. If the extracts do not behave normally, contact a supervisor or senior analyst if you are unsure how to proceed. Document all observations and anomalies in a NCM.

11.0 Calibration

Not applicable to this procedure. See the determinative methods for calibration of the analytical instrumentation.

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 policy in DV-QA-005P. 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 or program requirements require a greater frequency.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

12.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.

12.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. TNI 2009 requires consecutive passing results. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.2.4 Until the IDOC is approved by the QA Manager (or designee); the trainer and trainee must be identified in the batch record.

12.2.5 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

12.3 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. A new analyst must be working under documented supervision prior to approval of the IDOC. Documentation that a new analyst is performing under supervision must be entered into the batch record (View Batch Information) until that analyst's IDOC has been approved by the QA Manager (or designee). See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

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

14.1 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 procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Environmental Health & Safety Manual, and DV-HS-001P, "Waste Management Plan."

14.2 The following waste streams are produced when this method is carried out:

14.2.1 Methylene chloride – Waste Stream B

14.2.2 Flammable Solvents – Waste Stream C

14.2.3 1:1 MeCl2:Acetone – Waste Stream CA

14.2.4 Solid waste/sodium sulfate – Waste Stream D

14.3 Radioactive waste, mixed waste, and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Waste Coordinator for proper management of these materials.

NOTE: Radioactive, mixed waste and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, January 2005.

15.1.1 Method 3510C, Separatory Funnel Liquid-Liquid Extraction, Revision 3, December 1996.

15.1.2 Method 3520C, Continuous Liquid-Liquid Extraction, Revision 3, December 1996.

15.1.3 Method 3550B, Ultrasonic Extraction, Revision 2, December 1996.

15.1.4 Method 3550C, Ultrasonic Extraction, Revision 3, February 2007.

15.1.5 Method 3540C, Soxhlet Extraction, Revision 3, December 1996.

15.1.6 Method 3546, Microwave Extraction, Revision 0, February 2006.

15.1.7 Method 3620C, Florisil Cleanup, Revision 3, February 2007.

15.1.8 Method 3660B, Sulfur Cleanup, Revision 2, December 1996.

15.1.9 Method 3660A, Sulfur Cleanup, Revision 1, July 1992.

15.1.10 Method 3665A, Sulfuric Acid/Permagante Cleanup, Revision 1, December 1996.

15.1.11 Method 3630C, Silica Gel Cleanup, Revision 3, December 1996.

15.2 Code of Federal Regulations, Title 40 – Protection of the Environment, Part 136 – Guidelines Establishing Test Procedures for the Analysis of Pollutants, Appendix A – Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater

15.2.1 Method 608, Organochlorine Pesticides and PCBs.

15.2.2 Method 610, Polynuclear Aromatic Hydrocarbons.

15.2.3 Method 614, The Determination of Organophosphorus Pesticides in Municipal and Industrial Wastewater

15.2.4 Method 625, Base/Neutrals and Acids.

15.3 ASTM D7065-11, Standard Test Method for Determination of Nonylphenols, Bisphenol A, p-tert-Octylphenol, Nonylphenol Monoethoxylate, and Nonylphenol Diethoxylate in Environmental Waters by Gas Chromatography Mass SpectrometryMethod Modifications:

16.0 Modifications

16.1 Method SW-846 3665A calls for the clean-up to be performed using 1:1 Sulfuric Acid:H_2O. This procedure calls for the clean-up to be performed using concentrated sulfuric acid.

16.2 ASTM D7065-11 calls for the samples to be concentrated to a 0.5 mL final volume. This procedure calls for a 1 mL final volume.

16.3 Method SW-846 3620C calls for the florisil lot check to be performed using a standard containing the some pesticides at various concentrations from 5 ug/L to 50 ug/L. Per the source method, 1 mL of the standard is diluted to 2 mL (for concentrations between 2.5 ug/L and 25 ug/L) and the cleanup is then carried out and the cleaned extract concentrated to 1 mL for a final concentration of 5 ug/L to 50 ug/L. This procedure calls for the lot check to be performed using a standard containing all the pesticides at the same concentration of 50 ug/L. 1 mL of this standard is cleaned up without prior dilution and then concentrated back down to 1 mL.

16.4 Method SW-846 3620C states that the florisil lot check passes if the pesticide recoveries are between 80% and 110% recovery. This procedure says the lot check passes if the pesticide recoveries are between 80% and 115%. This is done to match the CCV control limits.

16.5 Method SW-846 3620C states that the florisil lot check is to be performed using a standard containing the 2,4,5-Trichlorophenol at 0.1 ug/L. Per the source method, 0.5 mL of this standard is diluted to 2 mL (for a concentration of 0.025 ug/L) and the cleanup is then carried out and the cleaned extract concentrated to 1 mL for a concentration of 0.05 ug/L. This procedure calls for the lot check to be performed using a standard containing 2,4,5-trichlorophenol at 100 ug/L. 1 mL of this standard is cleaned up without prior dilution and then concentrated back down to 1 mL.

16.6 Method SW-846 3620C Section 11.1.3 states to condition the florisil cartridge with 4 mL of hexane. This procedure calls for 5 mL of hexane to be used. This is done for convenience.

16.7 Method SW-846 3630C calls for the silica gel clean-up to be performed with a column or SPE cartridge. This procedure calls for the silica gel to be added directly to the extract and mixed. The reverse surrogate used indicates if the clean-up is effective.

17.0 Attachments

Attachment 1: Determinative and Extraction Methods Used in Conjunction with this SOP.
Attachment 2: Boiling Points of Solvents
Attachment 3: Kuderna-Danish Concentrator
Attachment 4: Florisil Check Solution

18.0 Revision History

- Revision 10 dated 31 December 2015
  - Updated formatting and numbering throughout the document
  - Revised method code references to reflect current practice
  - Numbered NOTES where there were multiples (Sections 6.0, 10.4.5, 10.4.9, 10.5.5.2)
  - Updated drive reference in Section 6.1
  - Updated “Reagent Grade Chemicals” definition in Section 7.0 to be consistent with other SOPs
  - Added statement in Section 8 to specify that extracts are stored separately from standards
  - Updated Section 9.1 to be consistent with other SOPs
  - Added new section 10.2 for consistency with other SOPs
  - Added NOTE to Section 10.3
  - Added a requirement to Section 10.6.6 to rinse all concentrator tubes with methylene chloride before washing
  - Removed the reference to South Carolina in Section 10.8.2. The laboratory no longer holds certification for South Carolina by this method
  - Updated Section 12 to be consistent with other SOPs
  - Added NOTE to Section 14.3
  - Revised the concentration of 2,4,5-Trichlorophenol in the Florisil Check Solution described in Attachment 4.
    - The compound used to be at a concentration of 0.1 ug/mL in the standard
    - It is now at a concentration of 0.5 ug/mL
    - One mL of the standard is used in the Florisil check procedure, resulting in 0.5 µg of the compound loaded onto the 6 g of Florisil

  - Removed references to DV-MS-0005 in Section 1 and Attachment 1, the laboratory no longer performs this procedure
- Revision 9 dated 31 December 2014
  - Section 5.1.1.2 and Section 10.4.9 were revised to match current practice on the use of the solvent recovery system.
  - Section 6.1 Computer Software and Hardware was added.
  - Section 7.6 Baked Sodium Sulfate was revised to match current practice and the latest revision of CA-Q-S-001 DV-1.
  - Section 7.11 was revised to correct the TAL Reagent ID.
  - Section 9.1 was revised to include the statement "This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated".
  - Section 9.4, 9.5, 9.6, and 9.7 were revised to remove information on Acceptance Criteria and Corrective Action. This information can be found in the analytical and QA SOPs.
  - Section 10.4.5 was revised to instruct the analyst to use approximately 1 teaspoon of sodium sulfate to dry extracts. This was done to limit the extract's exposure to sodium sulfate which can cause low recoveries for some acid compounds. A note was also added to this section to instruct the analyst to use more sodium sulfate or a separatory funnel to remove water if a teaspoon of sodium sulfate is not sufficient.
  - The Note in Section 10.4.12 was revised to instruct the analyst to write an NCM and/or notify their supervisor if they have a concern that an extract concentrated too low.
  - Section 10.7.1 Florisil Clean-up was revised to give guidance on what to do if the florisil check fails.
  - Section 10.7.1 was revised to instruct the analyst to not use the vacuum to pull all of the solvent from the cartridge. This was done to prevent interfering compounds and 2,4,5-TCP from eluting off of the cartridge.
  - Section 10.7.1 and Attachment 4 Florisil Check Solution were revised to indicate which compounds are controlled and which compounds are monitored. In addition, surrogate compounds were added to the solution.
  - Section 10.7.1 and 10.9 were revised to instruct the analyst to soak the SPE ports in a jar with the valves open instead of disassembling the valves.
  - Section 10.7.3 was revised to instruct the analyst to perform the clean-up on approximately 2mL of extract. This was done to match current practice.
  - Section 10.7.4 Silica Gel Clean-up and Sections 15.1 and 16.0 were revised to match current practice.
  - Section 10.9 Maintenance was revised to include instructions on how to tune the water bath thermostat.
  - Attachment 3 – Concentration Summary was removed and replaced with WI-DV-0009. All other Attachments were re-numbered.
- Revision 8 dated 13 December 2013
  - The procedure was revised to include ASTM D7065-11.
  - The procedure was revised to include steps for silica gel clean-up for DRO extracts.
  - Section 7 was revised to include details on the Florisil Solution and Florisil cartridges. These details were lacking in previous revisions.
  - Section 10.4.2 was revised to give more detail on how to safely tighten the ground glass joint between the KD and concentrator tube.
  - Section 10.6.3 was revised to give more detail about the required water level in the Turbo-Vap.

  - Maintenance and Troubleshooting sections were added as Sections 10.8 and 10.9.
  - Section 16 was revised to include method modifications from SW-846 3620C.
  - Attachment 1 was updated to reflect the current SOPs in use in the laboratory.
  - Attachment 3 was updated.
- Revision 7 dated 5 December 2012
  - Section 5 and Section 10.4.5 were revised to instruct the analysts to handle glass wool in a hood to avoid breathing in the dust.
  - Revised Section 10.4.8 to instruct the analysts to document both the observed and corrected temperatures.
  - Section 10.7.1.11 was revised to describe in more detail how the florisiled extracts are taken to the 2 mL final volume.
  - Section 14.2 was revised to include the waste stream for 1:1 MeCl2:Acetone – Waste Stream CA.
  - Attachment 1 was revised to include DV-OP-0015 as an acceptable extraction for Diesel Range Organics.
  - Attachment 3 was revised to include details on 8081/3510_LL concentration steps.
- Revision 6.0 dated 14 October 2011
  - The procedure was revised to remove instructions on how to concentrate and clean up extract for method 8070 and 607. TestAmerica Denver no longer supports these methods.
  - Section 1.3 was corrected to give the correct SOP number to Extraction of Aqueous Samples by Continuous Liquid/Liquid Extraction (CLLE) by Method SW-846 3520C for Low-Level NDMA by GC/CI/MS/MS.
  - Section 7.5 was revised to state acetonitrile is tested before use. Previously this solvent was not tested before use.
  - The procedure was revised to include instructions that all extracts for analysis by method 8081, 8082, or 608 to be hexane exchanged only after concentration on the S-Evap. Previously the SOP instructed analysts to add the hexane exchange before the S-Evap for extracts that were concentrated by microwave extraction. This resulted in poor hexane exchanges, therefore the extracts are now concentrated before the exchange.
  - The procedure was revised to instruct analysts not to use the solvent recovery system when concentrating samples for analysis of low-level NDMA by GC/CI/MS/MS. This was done to eliminate a possible source of contamination in this ppt level analysis.
  - The procedure was revised to instruct analysts to use concentrated sulfuric acid in the acid clean up of PCB extracts.
  - The procedure was revised to clarify the exact steps used in the sulfur removal with mercury.

Earlier revision histories have been archived and are available upon request.

Attachment 1.

Determinative and Extraction Methods Used in Conjunction with this SOP

Method Description	Determinative Method	Determinative Method SOP	Extraction Method	Extraction Method SOP
Diesel Range Organics & Jet Fuels	SW-846 8015B, 8015C, 8015D, California LUFT Method, & AK102 & AK103, NW-TPH, OK DRO	DV-GC-0027	WATER: SW-846 3510C, AK102 AK103 NW-TPH OK DRO SOIL: SW-846 3550B/C SW-846 3546 AK102, AK103 NW-TPH OK DRO	WATER: DV-OP-0006 SOIL: DV-OP-0016 or DV-OP-0015
Chlorinated Pesticides	SW-846 8081A, 8081B & EPA Method 608	DV-GC-0020 DV-GC-0016	WATER: SW-846 3510C SOIL: SW-846 3550B/C SW-846 3546	WATER: DV-OP-0006 SOIL: DV-OP-0016 or DV-OP-0015
Polychlorinated Biphenyls	SW-846 8082, 8082A EPA Method 608	DV-GC-0021 DV-GC-0016	WATER: SW-846 3510C SOIL: SW-846 3550B/C SW-846 3546	WATER: DV-OP-0006 SOIL: DV-OP-0016 or DV-OP-0015
Organo-phosphorus Pesticides	SW-846 8141A, 8141B, & EPA Method 614	DV-GC-0017	WATER: SW-846 3510C SOIL: SW-846 3540C	WATER: DV-OP-0006 SOIL: DV-OP-0010
Polynuclear Aromatic Hydrocarbons	SW-846 8310 & EPA Method 610	DV-LC-0009	WATER: SW-846 3510C SOIL: SW-846 3550B/C	WATER: DV-OP-0006 SOIL: DV-OP-0016
Semi-volatiles by GC/MS	SW-846 8270C, 8270D & EPA 625	DV-MS-0011 DV-MS-0012	WATER: SW-846 3510C SW-846 3520C SOIL: SW-846 3550B/C	WATER: DV-OP-0006 or DV-OP-0008 SOIL: DV-OP-0016
Low-Level Semi-Volatiles by GC/MS	SW-846 8270C	DV-MS-0011	WATER: SW-846 3520C	WATER: DV-OP-0008
Polynuclear Aromatic Hydrocarbons by GC/MS SIM	SW-846 8270C SIM	DV-MS-0002	WATER: SW-846 3510C SOIL: SW-846 3550B/C SW-846 3546	WATER: DV-OP-0008 SOIL: DV-OP-0016 or DV-OP-0015
Isotope Dilution Analysis of n-Nitrosodimethylamine by GCMS SIM using LVI	SOP	DV-MS-0015	WATER: SW-846 3520C SOIL: SW-846 3550B/C	WATER: DV-OP-0021 SOIL: DV-OP-0016

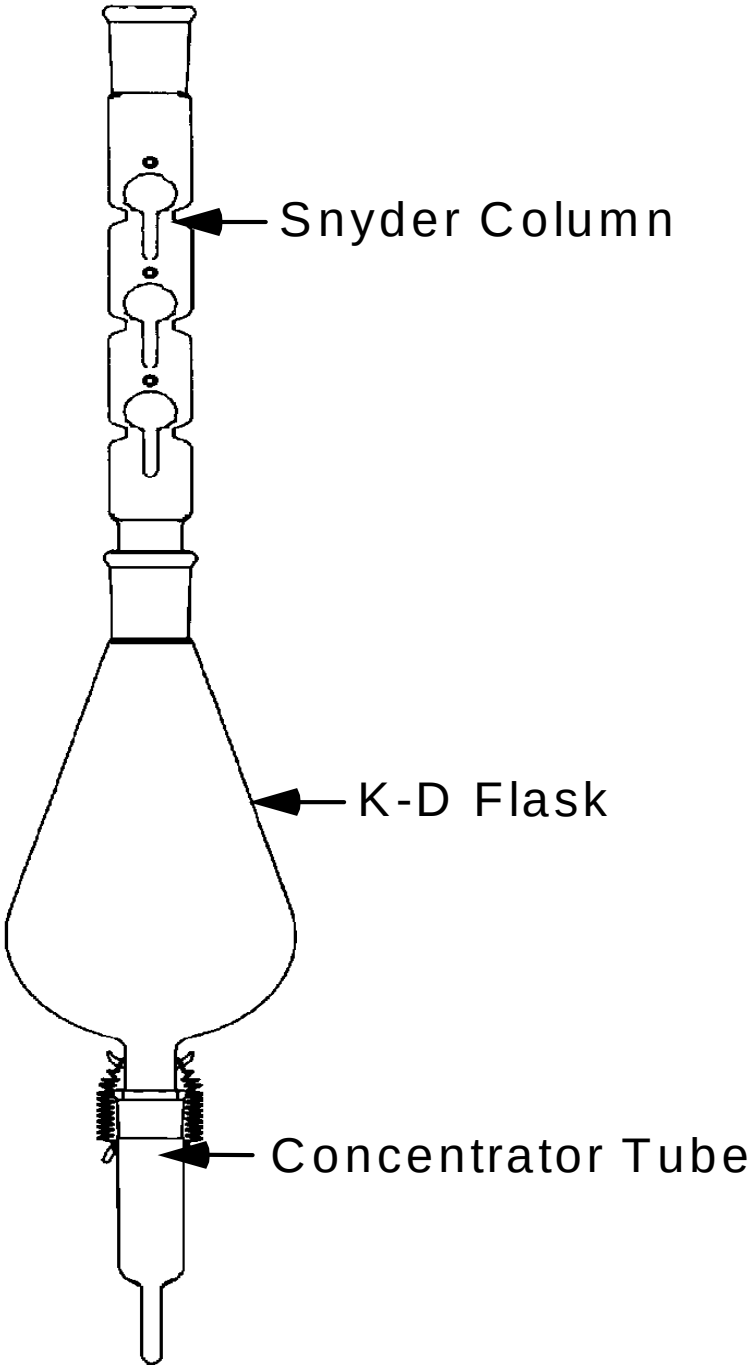
Attachment 2.

Boiling Points of Solvents

Solvent	Boiling Point (°C)
Methylene chloride	40
Acetone	56
Hexane	69
Methanol	65
Acetonitrile	82

Attachment 3.

Kuderna-Danish Concentrator



Attachment 4.

Florisil Check Solution
Prepared in Hexane

Compound	Concentration	Control
2,4,5-Trichlorophenol	0.05ug/mL	Y
Alpha-BHC	0.05ug/mL	Y
Alpha-Chlordane	0.05ug/mL	N
Aldrin	0.05ug/mL	N
Beta-BHC	0.05ug/mL	N
Dieldrin	0.05ug/mL	Y
Endosulfan I	0.05ug/mL	Y
Endosulfan II	0.05ug/mL	N
Endosulfan sulfate	0.05ug/mL	N
Endrin	0.05ug/mL	Y
Endrin Aldehyde	0.05ug/mL	N
Endrin Ketone	0.05ug/mL	N
Gamma-BHC	0.05ug/mL	Y
Gamma-Chlordane	0.05ug/mL	N
Heptachlor	0.05ug/mL	Y
Heptachlor expoxide	0.05ug/mL	N
Methoxychlor	0.05ug/mL	Y
4,4-DDD	0.05ug/mL	Y
4,4-DDE	0.05ug/mL	N
4,4-DDT	0.05ug/mL	Y
Tetrachloro-m-xylene	0.02ug/mL	Y
Decachlorobiphenyl	0.02ug/mL	Y

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Isotope Dilution Analysis of Selected Semivolatile Organic Compounds and Alkylated PAHs by Gas Chromatography/Mass Spectrometry - Selected Ion Monitoring (GC/MS-SIM)

(SUPERSEDES: KNOX-ID-0016, Rev. 10)

Prepared By: _____

Reviewed By: _____ 2/25/15
Technical Specialist

Approved By: _____ 2/25/15
Quality Assurance Manager

Approved By: _____ 2-25-15
Environmental, Health and Safety Coordinator

Approved By: _____ 02/25/15
Laboratory Director

1. Scope and Application

1.1. This procedure is used for the determination of selected semivolatile organic compounds and alkylated polynuclear aromatic hydrocarbons (PAHs) in water, soil, sediment, sludge, tissue, emissions from stationary sources and other sample matrices.

1.2. This procedure reflects an enhanced GCMS analytical technique utilizing the Selective Ion Monitoring approach permitted by SW-846 8270C modified to also include the use of isotope dilution internal standards providing additional specificity and recovery corrected results.

1.3. The individual compounds and homologue groups listed in Table 1 may be determined by this procedure.

1.3.1. Additional compounds requested by this method are outside the scope of this SOP. This SOP was written for PAH's in Table 1, with similarly labeled internal standards to reference for quantitation; thus the concentration of the analytes are 'recovery corrected' (section 9.2.2). Additional analytes requested (especially non-PAH analytes) may not behave similarly to the PAH internal standards in this method; therefore the calibration and recovery criteria for these analytes may not meet the limits assigned by this method. Additional analytes should not be assigned the same criteria as the PAH analytes listed in Table 1, unless a deuterated analog of that analyte can be used in the analysis. Therefore, additional compounds outside the limits assigned by this method are not considered a non-conformance, but will be narrated. Also see section 9.7 for QAS guidance, and 17.1 for deviations from the reference methods.

1.4. The standard reporting limits for this method are approximately 10 ng/L for aqueous samples, 1 ng/g for soil/sediment/tissue samples, and 10 ng/g for air (XAD & filter) samples. Some analytes have higher reporting limits (refer to Table 1). Reporting limits will be proportionately higher for samples and extracts that require dilution.

1.5. This procedure is written for use by analysts who are experienced with residue analysis and skilled in GC/MS SIM.

1.6. Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PAHs and other target compounds. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2. Summary of Method

2.1. This procedure uses capillary column gas chromatography/mass spectrometry (GC/MS) techniques. The mass spectrometer is operated in the selected ion monitoring (SIM) mode.

2.2. Samples are spiked with a solution of known amounts of the isotopically labeled internal standards listed in Table 4. The samples are then extracted using matrix specific extraction and cleanup techniques. The final extract is prepared by adding a known amount of the labeled recovery standard and concentrating to the final volume.

2.3. An aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a mass spectrometer.

2.4. The identification of the target compounds is based on their retention time relative to the labeled internal standards as established during routine calibration and the simultaneous detection of a quantitation and confirmation ion.

2.5. Quantitation of the target compounds is based on their relative response to the internal standards. A multipoint calibration is performed to establish mean response factors for the target analytes. Alkylated homologues are quantitated on the basis of response factors of the parent PAH. The instrument performance is routinely checked by the analysis of continuing calibration standards. Method performance is demonstrated by the analysis of method blanks and laboratory control samples (LCS), as well as an initial demonstration of capability.

3. Definitions

3.1. Alternate Surrogate Standard - A labeled compound which is used in 2 cases: (1) It is added to source air impinger contents prior to extraction to estimate the extraction efficiency for PAHs and other target compounds in the impinger sample. It is only used when the impinger extract is to be combined with the XAD sample extract prior to analysis. (2) It is added to the second liter of aqueous sample when the extracts from two separatory funnel extractions are to be combined for analysis.

3.2. Continuing Windowing Standard (Win) – A dilute mixture of coal tar and crude oils, selected for light, medium and heavy molecular weight distributions. This standard is used to verify and update the retention times of the characteristic peaks of PAH homologue groups (e.g., C2 Alkylnaphthalenes and C3 Alkylnaphthalenes). The solution is analyzed at the beginning of each shift during which homologue data is to be acquired.

3.3. Data Acquisition Parameters – Parameters affecting the scanning operation and conversion of the analytical signal to digitized data files. These include the configuration of the ADC circuitry, the ion dwell time, the MID cycle time, and acquisition modes set up for the method. Examples of acquisition modes for the MS include SIM mode, and Low Mass Resolution mode.

3.4. Labeled Internal Standards - Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the sample before extraction and are used to calculate the concentration of the target analytes.

3.5. Recovery Standard - Labeled compounds which are added to every sample, blank, and quality control spike sample extract prior to analysis. They are used to measure

the recovery of the internal standards and the alternate surrogate standard.

3.6. Sampling Surrogate Standard - A labeled compound added in a known amount to the XAD-2 resin of the sampling train, and allowed to equilibrate with the matrix before sampling is performed. The sampling surrogate standard has to be a component that can be completely resolved, is not present in the sample, and does not have any interference effects. Its measured concentration in the extract is an indication of how effectively the sampling train retains the target compounds collected on the XAD-2 resin. The recovery of the sampling surrogate standards in the field blanks can be used to determine whether there are any matrix effects caused by time or conditions under which the sample is transported and stored prior to analysis.

3.7. Additional definitions can be found in the TestAmerica Knoxville QAM glossary.

4. Interferences

4.1. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of analysis by performing laboratory method blanks. Analysts should avoid using PVC gloves, powdered gloves, or gloves with measurable levels of phthalates.

4.2. The use of high purity reagents and solvents helps minimize interference problems.

4.3. Transformation of PAHs and the formation of artifacts can occur in the sampling train. PAH degradation and transformation on sampling train filters have been demonstrated. Certain reactive PAHs such as benzo(a)pyrene, benz(a)anthracene, and fluoranthene when trapped on filters can readily react in corrosive matrices. These PAHs are transformed by reaction with low levels of nitric acid and higher levels of nitrogen oxides, ozone, and sulfur oxides.

4.4. Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for carry-over.

4.5. Non-target interferences may cause peaks on selected ion current profiles (SICPs) intended for PAHs and their alkylated homologues. Pattern recognition must be employed for identifying interfering peaks that should not be considered for the homologue or target PAH under consideration. Analysts should be intimately familiar with both parent and alkyl PAH analyses in complex environmental samples. This procedure is particularly important for newer operators. See Figure 3 for chromatograms for identifying alkyl PAHs.

4.6. Sulfur will be evident in chromatograms, depending on concentration. Sulfur ions may interfere with compounds sharing the same quantitation ion, specifically 1-methylphenanthrene, C3-dibenzothiophenes, and C1-phenanthrene/anthracene. Sulfur interferences may inhibit proper peak integration or detection. A simple

copper clean-up procedure can reduce or eliminate the sulfur interferences. Sulfur clean-up is discussed in section 11.3.6.

4.7. Atmospheric contamination can cause significant background peaks, especially for lower molecular weight parent and alkyl PAHs. The source of contamination can be significant in areas containing atmospheric PAHs (e.g., from diesel exhaust). Quality control requirements for the blank and appropriately qualifying the data are discussed in section 9.3.

5. Safety

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. Safety Concerns or Requirements.

5.2.1. The preparation of all standards and reagents, and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.2.2. The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or pass through an appropriate filter.

5.2.3. Training: Workers must complete the new employee Corporate Safety Manual safety orientation prior to working in the laboratory.

5.2.4. Personal Hygiene: Thoroughly washing of hands and forearms is recommended after each manipulation and before breaks.

5.2.5. Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

5.2.6. Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

5.3. 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

Hexane	Flammable, Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause light-headedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
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.
Isooctane	Flammable, Toxic Irritant	None Established	Inhalation of vapors may cause respiratory tract irritation. Overexposure may cause drowsiness and dizziness. Toxic if absorbed through skin. May cause skin irritation. May cause eye irritation. May be harmful if swallowed.
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.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3.1. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include the following PAHs: benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

5.4. Exposure to chemicals will be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. All work must be stopped in the event of a known or potential compromise to the health or safety laboratory personnel. The situation must be reported immediately to a laboratory supervisor.

5.6. The autosampler, gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.7. The mass spectrometer is under high vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.8. 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.

6. Equipment and Supplies

6.1. Gas Chromatograph/Mass Spectrometer (GC/MS) System – Analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, autosampler, analytical columns, and gases. The GC capillary column is directly coupled to the MS source.

6.2. GC column - 30m x 0.25mm ID x 25µm film thickness. RTI-5SILMS with Integra-guard fused silica capillary column, or equivalent.

6.3. Mass Spectrometer - Electron impact ionization with the filament eVs optimized for best instrument sensitivity, stability and signal to noise ratio, shall be capable of repetitively selectively monitoring 20 exact masses minimum during a period of approximately 1 second.

6.4. Data System - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. Target™ software is used and 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 the Extracted Ion Current Profile (EICP). This software allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended

6.5. Carrier gas - Ultra high purity helium.

6.6. Volumetric flask (class A) of appropriate sizes with ground-glass stoppers.

6.7. Balance capable of weighing 0.0001g.

6.8. Syringe: various sizes, Hamilton Laboratory grade syringes or equivalent.

6.9. Glass bottles with PTFE-lined screw caps or crimp tops.

7. Reagents and Standards

7.1. Methanol, pesticide quality, or equivalent.

7.2. Methylene chloride, pesticide quality, or equivalent.

7.3. Hexane, pesticide quality, or equivalent.

7.4. Isooctane, pesticide quality, or equivalent

7.5. Copper. Granulated Activated, 30 mesh, Restek catalog 26136 or equivalent

7.6. Perfluorotributylamine (FC-43) is used in neat form to tune and calibrate the mass spectrometer. Scientific Instruments Services Catalog No. FC-43-100, or equivalent.

7.7. Standards and Calibration Solutions: Obtained as individual solutions and prepared

solutions from Cambridge Isotope Laboratories (CIL), Cerilliant, Accustandard, Supelco or equivalent. Refer to Table 4 for details.

7.7.1. Refer to SOP KNOX-QA-0001, "Standard/Reagent Labeling and Documentation", current revision, for guidance on standard documentation and labeling.

7.7.2. Initial Calibration Standards: CS1-CS7. See Table 3 for a complete list of compounds and their concentrations. Solutions are prepared with hexane as the solvent.

7.7.3. Initial Calibration Verification Standard (ICV): A second source calibration standard different from that used to prepare the initial calibration. A 0.5 µg/mL solution is prepared and combined with internal standard stock solutions in order to prepare a second source standard (the same concentration as a CS4 standard; see Table 3).

7.7.4. Continuing Windowing Standard:

7.7.4.1. The Crude Oil Intermediate solution is prepared by weighing 2.5 g of stock crude oil into 100 mL of hexane (final conc. = 25,000 µg/mL).

7.7.4.2. The Coal Tar Intermediate solution (stock solution = 20% coal tar in 83% alcohol/5%Polysorbate-80) is prepared by taking a known amount of solution and concentrating on a water bath/nitrogen stream to remove as much alcohol as possible, then bringing back to volume with isooctane. A 2 % solution (20,000 µg/mL) is then prepared by diluting a portion with isooctane.

7.7.4.3. 10 mL of each of these are put through a silica gel clean-up and brought back to volume with hexane.

7.7.4.4. The Alkyl Window Spiking solution is prepared by combining 100 µL of the 25,000 µg/mL crude oil stock and 100 µL of the 20,000 µg/mL coal tar stock into 1 mL of hexane. The final concentration of the crude oil and the coal tar is 2,500 µg/mL and 2,000 µg/mL, respectively.

7.7.5. LCS Spiking Solutions: See Table 4 for a complete list of compounds and their concentrations. Solutions are prepared with methanol as the solvent.

7.7.6. Internal Standard Spiking Solutions: See Table 4 for a complete list of compounds and their concentrations. Solutions are prepared with methanol as the solvent.

7.7.7. Recovery Standard Spiking Solution: See Table 4 for a complete list of compounds and their concentrations. Solution is prepared with hexane as the solvent.

7.7.8. Alternate Surrogate Standard Spiking Solution: See Table 4 for a complete list of compounds and their concentrations. Solution is prepared with methanol as the solvent.

7.7.9. Sampling Surrogate Standard Spiking Solution: See Table 4 for a complete list of compounds and their concentrations. Solution is prepared with hexane as the solvent.

7.7.10. Stability of Solutions: Sealed standard solutions used for quantitative purposes expire 2 years from the date received or on the manufacturer's expiration date, unless otherwise specified by program requirements. Lab prepared stock solutions expire 2 years after preparation; lab prepared spiking or working calibration solutions expire 1 year after preparation. No daughter solution expiration date can exceed the parent expiration date. Standards are stored at 6^{o}C or less, or per manufacturer's recommendation.

7.7.11. Since the alkyl window standard is used for qualitative purposes only, the coal tar and crude oil stock materials and intermediate solutions have no expiration date. The daily alkyl window solution expires 1 year after preparation. If degradation of any alkyl window pattern is observed, a new daily solution is to be prepared. If degradation is still observed, a new intermediate solution is to be prepared.

8. Sample Collection, Preservation and Storage

8.1. Sampling is not performed for this method by TestAmerica Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, "Sample Receipt and Log In", current revision.

8.2. All extracts must be analyzed within 40 days from the start of extraction.

8.3. Store extracts in the dark at less than 6°C in sealed vials (e.g. screw-capped or crimp-capped) equipped with unpierced PTFE-lined septa.

8.4. Sample holding times:

8.4.1. Solid samples have a 14 day holding time from collection to extraction. Water samples have a 7 day holding time from extraction to extraction. Tissue samples have a 1 year holding time from collection to extraction. Air samples collected using method CARB 429 have a 21 day holding time from collection to extraction, whereas, air samples collected using SW-846 method 0010 have a 14 day holding time from collection to extraction.

9. Quality Control

9.1. Initial Demonstration of Capability and Method Detection Limit Studies: For the standard analyte list (Table 1), the initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples

may begin. Refer to Table 7 for the initial demonstration of capability acceptance criteria.

9.2. Internal standards are spiked into all samples, blanks, and LCS (LCSD and MS/MSD, if requested) to assess method performance on the sample matrix.

9.2.1. See Table 7 for the acceptance criteria for the recoveries of the internal standards and spiked compounds in field samples, method blanks, and other QC samples.

9.2.2. The isotope dilution technique assumes that results are independent of internal standard recovery (i.e., the target analyte is expected to behave similarly to the internal standard, thus the quantitation of the target analyte should not be impacted by the recovery of the internal standard).

9.2.3. If the recovery of any internal standard is not within the specified limits, one or more of the following steps may be useful in diagnosing the problem and determining the impact to the data:

9.2.3.1. Determine if the outlying recoveries are associated with a pattern, such as 1) an association of the outliers with a specific recovery standard or 2) a trend of low bias early in the chromatogram.

9.2.3.2. Verify that the selection and integration of the recovery standard and the internal standard is appropriate.

9.2.3.3. Verify that the calculations are correct.

9.2.3.4. Inspect the extract volume for discrepancies. Inspect the extraction notes for problems encountered during extraction.

9.2.3.5. Verify that the instrument sensitivity and retention time has not been compromised. Inspect the area counts of the recovery standards for diagnosis. An acceptable bracketing analysis may be used to determine that the instrument was in control and only that specific analysis is suspect.

9.2.3.6. If matrix interference is suspected, a dilution to reduce the matrix effect may be warranted.

9.2.3.7. High internal standard recovery may indicate matrix interferences on the internal standard or a suppression of the recovery standard.

9.2.3.8. Low internal standard recovery may also indicate matrix interferences on the internal standard, or a high recovery of the recovery standard. If a low internal standard recovery is determined to be due to a loss of instrument sensitivity, the impact on the ability to support the reporting limit should be considered.

9.2.3.9. If the poor internal standard recovery is judged to be a result of sample matrix interferences, a reduced portion of the sample may be re-extracted or additional cleanups may be employed.

9.2.4. If it has been determined that the data has been impacted due to the recovery of the internal standard being outside limits, reanalysis at a dilution or a re-extraction of the sample should be performed

9.2.5. If it has been determined that the data has not been impacted, generate a nonconformance memo and discuss the situation in the case narrative. This should be done in consultation with the client.

9.3. Method Blank: A method blank must be extracted with each extraction batch of 20 or fewer samples. The method blank (or an instrument blank) must be analyzed before the samples and must not contain any of the compounds of interest at a concentration above the reporting limit or 10 percent of the analyte concentration in the field samples.

9.3.1. Samples associated with a contaminated method blank must be re-extracted and reanalyzed with an acceptable method blank. The project manager may consult the client to determine project needs. If the client prefers that the original data be reported, the associated data may be reported in lieu of reanalysis. A nonconformance memo and narrative addressing the analytical issues must be generated.

9.3.2. If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.4. A laboratory control sample (LCS) is extracted and analyzed along with each extraction batch of 20 or fewer samples. LCS spike components, and control limits are listed in Table 7.

9.4.1. If any LCS compounds of interest are calculated outside the control limits, the associated samples must be re-extracted and reanalyzed with a compliant LCS. (Refer to QA-003 for additional guidance.) The project manager may consult the client to determine project needs. If the client prefers that the original data be reported, the associated data may be reported in lieu of reanalysis. A nonconformance memo and narrative addressing the analytical issues must be generated.

9.5. Client-specified matrix spike / matrix spike duplicate samples may be analyzed to provide additional precision and accuracy data.

9.6. Nonconformance and Corrective Action: Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the QA Manager.

9.7. Quality Assurance Summaries: Certain clients or regulatory programs may require specific project or program QC that may supersede these method requirements.

Quality Assurance Summaries are developed to address these requirements.

10. Calibration and Standardization

10.1. Refer to CA-Q-S-002, current revision, Acceptable Manual Integration Practices and the TestAmerica Knoxville attachment for information on manual integration practices and documentation requirements.

10.2. Setup the autosampler, GC/MS, and establish the instrument operating conditions. Example GC/MS instrument conditions are shown in Figure 1.

10.3. Tune the mass spectrometer as needed using perfluorotributylamine (PFTBA) and the instrument data system autotune program. Select the DFTPP tune optimization profile for the autotune program.

10.4. Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by the results of continuing calibration procedures described below. The other type, continuing calibration, consists of analyzing the calibration solution (CS4). No samples are to be analyzed until acceptable initial and continuing calibrations are demonstrated and documented.

10.5. Setup the MS to acquire data in MID mode. Setup MID descriptors using the masses listed in Table 6.

10.5.1. Prior to analyzing initial calibration standards for the first time and afterwards as needed, analyze the Continuing Alkyl Window standard and CS4 standard in full scan mode to determine the elution retention time window of the target alkyl PAH groups and target parent analytes.

10.5.2. Use the retention times from the full scan analyses to set the MID switchpoints so that the target analytes and alkyl PAH retention time windows fall within their respective MID groups.

10.6. Initial Calibration

10.6.1. Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 3.

10.6.2. The 12-hour time period begins at the moment of injection of the first calibration analysis that is used to demonstrate the linearity. The time period ends when 12 hours has elapsed according to the system clock. Analysis may proceed until 12 hours from the injection of the calibration have passed.

10.6.3. Analyze 1µL of each of the seven calibration standards and calculate the relative response factor (RRF) of each analyte vs. the appropriate internal standard and each internal standard vs. the appropriate recovery standard listed in Table 5 using the following equation:

$$RRF = \frac{As \times Cis}{Ais \times Cs}$$

Where:

As = area of the quantitation ion of the compound of interest.
Ais = area of the quantitation ion of the appropriate reference standard.
Cis = concentration of the appropriate reference standard.
Cs = concentration of the compound of interest.

NOTE: Alkylated PAH homologues are assigned the RRF calculated for the parent PAH. See table 8 for parent response factor assignment for the alkylated homologues.

10.6.4. Calculate the mean relative response factor and the standard deviation of the relative response factors for each calibration standard solution using the following equations:

$$\overline{RRF} = \frac{1}{n}\sum_{i=1}^{n}(RRF)_i$$

Where:

RRF_i = RRF calculated for calibration solution "i" using the equation in section 10.6.3.
n = The number of calibration points in the curve.

$$\%RSD = \frac{SD}{\overline{RRF}} \times 100$$

Where:

$\overline{RRF}$ = Mean relative response factor calculated above.
SD = the sample standard deviation of the relative response factors used to calculate the mean RRF.

$$SD = \sqrt{\sum_{i=1}^{N}\frac{\left(RFi - \overline{RF}\right)^2}{N-1}}$$

Where:

RFi = RF for each of the calibration levels.
N = Number of RF values.

10.6.5. Criteria for Acceptable Calibration - The percent relative standard deviation (%RSD) for the mean relative response factors for both the target analytes and the internal standards must not exceed 30 percent.

10.6.5.1. If acceptable initial calibration is not achieved, identify the root cause, perform corrective action, and repeat the initial calibration. If the root cause can be traced to an abnormal disruption of an individual acquisition (e.g., low injection volume or the instrument inadvertently loses communication

during elution), repeat the individual analysis and recalculate the percent relative standard deviation. (See the current revision of CA-T-P-002, "Selection of Calibration Points".) If the calibration is acceptable, document the problem and proceed; otherwise repeat the initial calibration.

10.6.6. Initial Calibration Verification Standard (2^{nd} source standard)

Prepare the ICV as described in section 7.6.3. The ICV must contain all the target analytes analyzed in the initial calibration. Analyze 1µL of the ICV standard under the same conditions as the initial calibration. Calculate the concentration of the ICV using the average RRFs from the initial calibration. Calculate the percent recovery (%R) between the expected and the calculated ICV concentration. The %R must not exceed $\pm$ 30% (see Table 7).

10.6.7. If time remains in the 12 hour period initiated by the first calibration injection for the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.7. Continuing Calibration

10.7.1. Continuing calibration is performed at the beginning of a 12-hour period. The 12-hour time period begins at the moment of injection of the continuing calibration standard (CCAL). The time period ends when 12 hours has elapsed according to the system clock. Analyses may proceed until 12 hours from the injection of the CCAL have passed. A sample injected less than 12 hours after the CCAL is acceptable.

10.7.2. Analyze 1µL of the CS4 continuing calibration standard (see Table 3). Use the same data acquisition parameters as those used during the initial calibration. Check for GC resolution and peak shape.

10.7.3. If total homologues are to be acquired during the analytical shift, analyze 1µL of the Continuing Alkyl Windowing Standard Solution (section 7.6.4). Use the same data acquisition parameters as those used during the continuing calibration.

Examine and identify the presence of first and last peaks for the isomers of any total homologues to be quantified during the shift. Representative selected ion chromatograms for alkyl PAH windows are shown in Figure 3.

10.7.4. Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met at the beginning of each 12 hour period during which samples are analyzed. If continuing calibration criteria are not met, identify the root cause, perform corrective action and repeat the continuing calibration. If the second consecutive continuing calibration does not meet acceptance criteria, additional corrective action must be

performed. Acceptable performance must be demonstrated after two consecutive failing continuing calibrations by the analysis of two consecutive acceptable continuing calibrations or by analysis of a new initial calibration.

10.7.4.1. The measured RRFs of all target analytes and internal standards must be within 30 percent difference or drift of the mean values established during the initial calibration. If this criterion is not satisfied, a new initial calibration curve must be established before sample extracts can be analyzed.

$$\%\text{Drift} = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100$$

Where:

C_{actual} = Known concentration in standard
C_{found} = Measured concentration

$$\%\text{Difference} = \frac{\overline{RF} - RF}{\overline{RF}} \times 100$$

Where:

$\overline{RF}$ = Average analyte response factor from initial calibration
RF = Measured analyte response factor from calibration verification

10.7.4.2. The recovery standard response must be within 50-200% of the response in the corresponding CS4 calibration level of the initial calibration.

11. Procedure

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure, except those specified by project specific instructions, shall be completely documented using a nonconformance memo and approved by a Technical Specialist, Project Manager, and QA Manager. If contractually required, the client shall be notified.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. GC/MS Analysis

11.3.1. Calibrate the instrument as described in Section 10.

11.3.2. Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 1 µL into the

GC/MS and acquire data until benzo(ghi)perylene has eluted from the column.

11.3.3. Record analysis information in the instrument logbook. The following information is required:

- Date of analysis
- Time of analysis
- Instrument data system filename
- Analyst
- Lab sample identification
- Bench dilution factor

Additional information may be recorded in the logbook if necessary.

11.3.4. Generate ion chromatograms for the masses listed in Table 6 that encompass the expected retention windows of the target analytes. Integrate the selected ion current profiles of the quantitation ions shown in the table. Representative selected ion chromatograms for alkyl PAH windows are shown in Figure 3.

11.3.5. Dilutions: If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range

11.3.5.1. The maximum dilution of extracts allowed is 50 X before internal standards are considered “diluted out”. If further dilution is warranted, then the extract may further diluted via a Post-Dilution-Spike technique or re-extract the sample using a smaller volume. Consultation with the client should occur before proceeding. See section 12.3.4.

11.3.6. Sulfur Clean-up: If sulfur is present in chromatograms that causes difficult integration or detection of analytes, a copper clean-up technique may be employed to reduce or eliminate the sulfur interference. A small amount of activated copper is mixed with a portion of the extract and shaken for at least 1 minute. The same treatment must be performed on the batch method blank and LCS to show cleanliness and precision/recovery.

12. Data Analysis and Calculations

12.1. Qualitative identification criteria for individual analytes: For a gas chromatographic peak to be identified as a target analyte, it must meet all of the following criteria:

12.1.1. The quantitation ion must be present.

12.1.2. The internal standard quantitation ions must be present.

12.1.3. The relative intensities of confirmation ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%). The absence of confirmation ions should be considered carefully when making decisions regarding qualitative identification. Confirmation ions may have lower response than quantitation ions and may not always be present at lower concentrations. Their absence in this case may not be cause for determining that the analyte is not present. The absence of confirmation ions at higher levels where they should have been detectable may be cause for determination that an analyte is not present.

12.1.4. The sample component retention time must compare to within ± 0.2 min. of the retention time of the internal standard component. For reference, the standard must be run within the same 12 hour period as the sample.

12.1.5. If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

12.2. Qualitative identification criteria for total homologue groups (e.g., total C2 or C3 alkylnaphthalenes) - For gas chromatographic peaks to be identified as a member of the homologue, it must meet all of the following criteria:

12.2.1. The retention time (RT) of the analyte must be no more than 5 seconds before and no more than 5 seconds after the expected RT of the first and last isomer in the homologue, based on the continuing windowing solution analysis. If retention time shifting is observed due to matrix, then the homologue window is adjusted appropriately based on the retention time shifts of the internal standards and parent compounds.

12.2.2. Manual integration of the alkyl PAH homologues (e.g., total C2 or C3 alkylnaphthalenes) by an experienced analyst is required. Proper identification of the alkyl clusters is critical, as is the proper identification and elimination of non-target compounds that occur at the same nominal mass. Retention time window criterion alone is insufficient for correctly identifying alkyl PAH clusters and non-target compounds. Pattern recognition must be used to avoid including non-target species that may occur at the same mass and within the retention time window as the target alkyl PAHs. All alkyl clusters should be integrated baseline to baseline to sum the total area of the cluster (adjusting the baseline for detector drift), but not valley to valley. Manual control and adjustment of the integration parameters is required for proper integration

12.2.3. Whenever a significantly altered alkyl homologue pattern is encountered, which may be due to interferences from non-alkylated compounds

containing the same quantitative mass, and/or different relative concentrations of alkylated isomers, the affected alkyl group is flagged with "AP".

12.3. Quantitation for Target Analytes.

12.3.1. Calculate the internal standard recoveries (Ris) relative to the recovery standard according to the following equation:

$$\text{Ris} = \frac{\text{Ais} \times \text{Qrs} \times \text{S}}{\text{Ars} \times \text{RRFis} \times \text{Qis}} \times 100\%$$

Where:

Ais = area of the quantitation ion of the appropriate internal standard
Ars = area of the quantitation ion of the recovery standard
Qrs = ng of recovery standard added to the extract
Qis = ng of internal standard added to the sample
RRFis = mean relative response factor of internal standard obtained during initial calibration
S = Prep split factor, i.e., the inverse of the proportion of extract used after the addition of internal standards and before the addition of recovery standard.

Example:

Ais = 104067
Ars = 63273
Qrs = 10,000 ng/mL x 0.025 mL = 250 ng
Qis = 250 ng/mL x 3 mL = 750 ng/mL
RRFis = 2.12963
S = 3 (i.e., 1/3 of extract was taken through cleanup after the addition of internal standards)

$$\text{Ris} = \frac{104067 \times 250\,\text{ng} \times 3}{63273 \times 2.12963 \times 750\,\text{ng/mL}} \times 100\% = 77.2\%$$

12.3.2. See Table 7 for the acceptance criteria for recoveries of the internal standards and spiked compounds in field samples, method blanks, and other QC samples. See section 9.2 for guidance for corrective action when internal standards are outside control limits.

12.3.3. Calculate the concentration of individual target analytes according to the following equation:

$$\text{Concentration} = \frac{\text{As} \times \text{Qis}}{\text{Ais} \times \text{RRF} \times \text{W} \times \%\text{S}}$$

Where:

As = area of the quantitation ion of the compound of interest. In the case of total homologues, As = the sum of areas of all

peaks which meet the qualitative criteria listed in Section 12.2.

Ais = area of the quantitation ion of the appropriate internal standard

Qis = ng of internal standard added to the sample

RRF = mean relative response factor of compound obtained during initial calibration

W = amount of sample extracted (grams or mL)

%S = % solids decimal fraction (i.e., % solids/100)

Example:

As = 2082058

Ais = 104067

Qis = 250 ng/mL x 3 mL = 750 ng

RRF = 0.92745

W = 30 g

%S = 0.750

$$\text{Concentration} = \frac{2082058 \times 750\text{ng}}{104067 \times 0.92745 \times 30\text{g} \times 0.750} = 719\ \text{ng/g}$$

NOTE: Alkylated PAH homologues are assigned the RRF calculated for the parent PAH. See table 8 for parent response factor assignment for the alkylated homologues.

12.3.4. If the concentration in the final extract of any target analyte exceeds the upper method calibration level, a dilution of the extract or a re-extraction of a smaller portion of the sample must be performed. Dilutions of up to 50 X may be performed on the extract. Since the internal standards are diluted in the extracts, the internal standards that are used for calculation should be inspected to ensure that they are not diluted below a 10 to 1 signal to noise ratio. If the compounds which exceed the calibration range cannot be brought within the calibration range by a 50x dilution, extraction of a smaller aliquot of sample may be performed or the sample may be analyzed by a more appropriate analytical technique such as full scan GC/MS. Consultation with the client should occur before any re-extraction is performed

12.3.4.1. Alternately, a non-isotope dilution, post-dilution spiking technique is available to quantitate analytes over the calibration range over a 50 x dilution. Consultation with the client should occur before a post-dilution spike is performed.

12.3.4.1.1. Determine the dilution necessary to bring the compound(s) within calibration range. Spike the final diluted extract with stock-concentration internal and recovery standards such that the concentrations in the diluted extract are 0.5 *u*g/mL.

12.3.5. The isotope dilution technique accounts for the dilution factor in the extract. If a sample extract is diluted, the internal standard and recovery standard are also diluted, so a dilution factor is not used in the equation (except for post-dilution spiking technique in 12.3.4.1). However, the analyst must apply the dilution factor in QuantIMS to adjust the RL and MDL appropriately.

12.4. Flag all compound results in the sample which were detected in the method blank with a "B" qualifier.

12.5. Flag all compound results in the sample which are below the reporting limit and above the MDL with a "J" qualifier. See Table 1.

12.6. Flag all compound results in the sample which are above the upper calibration limit with an "E" qualifier.

12.7. Total alkyl homologue concentrations are considered estimated and are qualified with the "EST" flag. The qualitative criteria for these homologues are not as rigorous as they are for individual targets (i.e., the retention times of all the compounds are not known). The compounds are identified as eluting within a retention time window established by examining a variety of coal tar and crude oil standards.

12.8. Data Review

12.8.1. The analyst who performs the initial data calculations must initial and date the QuantIMS data review form.

12.8.2. Refer to Figure 2 for an example data review checklist used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data. The analyst who performs the initial data calculations must initial and date the data review checklist.

12.8.3. All qualitative peak identifications must be verified by a second analyst. If discrepancies are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.8.4. All hand calculations and data entries into calculation programs, databases, or spreadsheets must be checked by a second analyst at a frequency of 100 percent. If discrepancies are found, the data must be returned to the analyst who performed the initial calculation for resolution.

12.8.5. The analyst that performed the second level review must fill out, initial and date the data review checklist.

13. Method Performance

13.1. Method Detection Limit (MDL): An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples (this does not apply to alkyl homologues). Method detection limits are determined and verified as specified in the

current revision of SOP CA-Q-S-006 (and attachment) based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit.

13.2. Initial Demonstration of Capability: Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in TestAmerica Knoxville SOP KNOX-QA-0009. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample is listed in Table 7.

13.2.2. Calculate the average recovery and relative standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in Table 7. Historical matrix specific laboratory control sample acceptance criteria may also be used for evaluation of method demonstrations.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification: The group/team leader has the responsibility to ensure that 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. All attempts will be made to minimize the use of solvents and standard materials.

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 Safety Manual for "Waste Management and Pollution Prevention."

15.2. The following waste streams are produced when this procedure is carried out.

- Solvent waste shall be placed in the flammable waste stream, contained in a steel satellite accumulation container type or flammable solvent container.
- Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials shall be placed in the incinerable laboratory waste stream, contained in a steel or poly satellite accumulation container type.

16. References

16.1. TestAmerica Knoxville Quality Assurance Manual (QAM), current revision.

16.2. Method 429 - Determination of Polycyclic Aromatic Hydrocarbon (PAH) emissions from Stationary Sources, California Environmental Protection Agency Air Resources Board, Adopted: September 12, 1989, Amended: July 28, 1997.

16.3. SW-846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, October 1996, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique, Method 8270C.

16.4. NOAA Technical Memorandum NOS ORCA 130, National Status and Trends Program for Marine Environmental Quality, Sampling and Analytical Methods of the National Status and Trends Program Mussel Watch Project: 1993-1996 Update, March 1998.

16.5. SW-846 Method 3660B – Sulfur Cleanup.

17. Miscellaneous

17.1. Deviations from reference methods: Not applicable. This TestAmerica Knoxville laboratory SOP was developed using information from various sources, including the reference methods listed in section 16. This stand alone procedure is not intended to be compliant with all requirements of the reference methods.

17.2. The NOAA Technical Memorandum NOS ORCA 130 document is used to reference the alkyl groups only and not used for calibration, etc.

17.3. List of appendices, tables and figures referenced in the body of the SOP.

17.3.1. Table 1 – Target Analytes and Reporting Limits

17.3.2. Table 1A – Additional Analytes and Reporting Limits

17.3.3. Table 2 – Matrix, Sample Size, IS Spiking Level, and Final Volume

17.3.4. Table 3 – Concentration of Target Analytes in Calibration Solutions

17.3.5. Table 4 – Concentration of Stock Standards and Spiking Solutions

17.3.6. Table 5 – Quantitation References

17.3.7. Table 6 – Selected Ion Monitored and SIM Groups

17.3.8. Table 7 – Acceptance Criteria for Performance Tests and QC Samples

17.3.9. Table 8 – Response Factor Assignment for the Alkylated Homologues

17.3.10. Figure 1 – Recommended GC and GC/MS Conditions

17.3.11. Figure 2 – Example Data Review Checklist

17.3.12. Figure 3 – C1-C4 Alkyl Homologue Peak Patterns

Table 1 - Standard Target Analytes and Reporting Limits

Analyte	CAS No.	Aqueous (ng/L)	Solid/Sediment and Tissue (ng/g)	Air (Filter) (ng/sample)	Air (XAD) (ng/sample)	Air (Combined) (ng/sample)
Naphthalene	91-20-3	50	20	50	400	400
2-Methylnaphthalene	91-57-6	20	10	20	50	50
1-Methylnaphthalene	90-12-0	10	5	20	50	50
Acenaphthylene	208-96-8	10	1	20	20	20
Acenaphthene	83-32-9	10	1	20	20	20
Fluorene	86-73-7	10	1	10	10	10
Phenanthrene	85-01-8	20	2	20	30	30
Anthracene	120-12-7	10	1	10	10	10
Fluoranthene	206-44-0	10	1	10	10	10
Pyrene	129-00-0	10	2	60	20	60
Benz(a)anthracene	56-55-3	10	1	10	10	10
Chrysene	218-01-9	10	1	10	10	10
Benzo(b)fluoranthene	205-99-2	10	1	10	100	100
Benzo(k)fluoranthene	207-08-9	10	1	10	100	100
Benzo(e)pyrene	192-97-2	10	1	10	10	10
Benzo(a)pyrene	50-32-8	10	1	10	10	10
Perylene	198-55-0	10	1	10	10	10
Indeno(1,2,3-c,d)-pyrene	193-39-5	10	1	10	10	10
Dibenz(ah)anthracene	53-70-3	10	1	10	10	10
Benzo(ghi)perylene	191-24-2	10	1	10	10	10
C2 Naphthalenes	NA	10	2	NA	NA	NA
C3 Naphthalenes	NA	10	2	NA	NA	NA
C4 Naphthalenes	NA	10	1	NA	NA	NA
C1 Fluorenes	NA	10	1	NA	NA	NA
C2 Fluorenes	NA	10	1	NA	NA	NA
C3 Fluorenes	NA	10	1	NA	NA	NA
C1 Phenanthrenes & Anthracenes	NA	10	1	NA	NA	NA
C2 Phenanthrenes & Anthracenes	NA	10	1	NA	NA	NA
C3 Phenanthrenes & Anthracenes	NA	10	1	NA	NA	NA
C4 Phenanthrenes & Anthracenes	NA	10	1	NA	NA	NA
C1 Fluoranthenes & Pyrenes	NA	10	1	NA	NA	NA
C1 Benz(a)anthracenes & Chrysenes	NA	10	1	NA	NA	NA
C2 Benz(a)anthracenes & Chrysenes	NA	10	1	NA	NA	NA
C3 Benz(a)anthracenes & Chrysenes	NA	10	1	NA	NA	NA
C4 Benz(a)anthracenes & Chrysenes	NA	10	1	NA	NA	NA

Table 1A - Additional Analytes and Reporting Limits

Analyte	CAS No.	Aqueous (ng/L)	Solid/Sediment and Tissue (ng/g)	Air (Filter) (ng/sample)	Air (XAD) (ng/sample)	Air (Combined (ng/sample)
Biphenyl	92-52-4	10	1	20	50	50
1-Methylphenanthrene	832-69-9	10	1	10	10	10
2,6-Dimethylnaphthalene	581-42-0	10	2	20	30	30
2,3,5-Trimethylnaphthalene	2245-38-7	10	2	10	10	10
Dibenzothiophene	132-65-0	10	1	10	10	10
C1 Dibenzothiophenes	NA	10	1	NA	NA	NA
C2 Dibenzothiophenes	NA	10	1	NA	NA	NA
C3 Dibenzothiophenes	NA	10	1	NA	NA	NA
C4 Dibenzothiophenes	NA	10	1	NA	NA	NA

Note: For project specific analytes not listed in Table 1 or Table 1A, the quality control criteria of this SOP may not be applicable. For the additional analytes, the performance will be assessed against the quality control criteria in the SOP and described in the project narrative; however non-conformance memoranda are not required.

Table 2 - Matrix, Sample Size, IS Spiking Level and Final Volume

	Water	**Soil/ Sediment**	**Tissue**	**Wipe**	**Air**	**Waste**
Weight/volume/ sample amount	1 L	10 g	10 g	Entire Sample	Entire Sample	1 g
IS Spiking Levels	250 ng/L	25 ng/g	25 ng/g	250 ng	250 ng	250 ng
Final Extract Vol. (mL)	0.5	0.5	0.5	0.5	0.5	0.5

Table 3 - Concentration of Target Analytes in Calibration Solutions

Analyte	CS1 (µg/mL)	CS2 (µg/mL)	CS3 (µg/mL)	CS4 (µg/mL)	CS5 (µg/mL)	CS6 (µg/mL)	CS7 (µg/mL)
Naphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Biphenyl	0.02	0.10	0.25	0.50	1.0	2.5	5.0
2-Methylnaphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
1-Methylnaphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Acenaphthylene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Acenaphthene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Fluorene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Phenanthrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
1-Methylphenanthrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
2,3,5-Trimethylnaphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Anthracene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
2,6-Dimethylnaphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Fluoranthene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Pyrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benz(a)anthracene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Chrysene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(b)fluoranthene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(k)fluoranthene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(e)pyrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(a)pyrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Perylene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Indeno(1,2,3-cd)pyrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Dibenz(ah)anthracene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(ghi)perylene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Dibenzothiophene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Sampling Surrogates							
$^{13}C_6$-Naphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Internal Standards							
d_{10}-Anthracene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_8 Naphthalene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-2-Methylnaphthalene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-1-Methylnaphthalene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_8-Acenaphthylene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-Phenanthrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-Fluorene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-2,6-Dimethylnaphthalene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-Fluoranthene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benz(a)anthracene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Chrysene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(b)fluoranthene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(k)fluoranthene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(a)pyrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Perylene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Indeno(1,2,3-cd)pyrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{14}-Dibenz(ah)anthracene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(ghi)perylene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_8-Dibenzothiophene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Recovery Standards							
d_{10}-Acenaphthene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-Pyrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(e)Pyrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Alternate Surrogate							
d_{14}-p-Terphenyl	0.02	0.10	0.25	0.50	1.0	2.5	5.0

Table 4 - Concentration of Stock Standards and Spiking Solutions

Compound	Recommended Sources*	Catalog Number	Vendor Conc (µg/mL)	Stock Solution (µg/mL)	Spiking Solution (µg/mL)
Native Analytes					
Naphthalene	Restek	31995	2000	20	0.25
Biphenyl	Restek	567839	2000	20	0.25
2-Methyl naphthalene	Restek	31995	2000	20	0.25
1-Methyl naphthalene	Restek	31995	2000	20	0.25
Acenaphthylene	Restek	31995	2000	20	0.25
Acenaphthene	Restek	31995	2000	20	0.25
Fluorene	Restek	31995	2000	20	0.25
Phenanthrene	Restek	31995	2000	20	0.25
1-Methylphenanthrene	Restek	568613-FL	2000	20	0.25
2,3,5-Trimethylnaphthalene	Restek	568613-FL	2000	20	0.25
Anthracene	Restek	31995	2000	20	0.25
2,6-Dimethylnaphthalene	Restek	568613-FL	2000	20	0.25
Fluoranthene	Restek	31995	2000	20	0.25
Pyrene	Restek	31995	2000	20	0.25
Benz(a)anthracene	Restek	31995	2000	20	0.25
Chrysene	Restek	31995	2000	20	0.25
Benzo(b)fluoranthene	Restek	31995	2000	20	0.25
Benzo(k)fluoranthene	Restek	31995	2000	20	0.25
Benzo(e)pyrene	Restek	568613-FL	2000	20	0.25
Benzo(a)pyrene	Restek	31995	2000	20	0.25
Perylene	Restek	568613-FL	2000	20	0.25
Indeno(1,2,3-cd)pyrene	Restek	31995	2000	20	0.25
Dibenz(a,h)anthracene	Restek	31995	2000	20	0.25
Benzo(ghi)perylene	Restek	31995	2000	20	0.25
Dibenzothiophene	Restek	568613-FL	2000	20	0.25
Internal Standards					
d_8-Naphthalene	Accustandard	S-18004	200	20	0.25
d_{10}-2-Methyl naphthalene	Accustandard	S-18004	200	20	0.25
d_{10}-1-Methyl naphthalene	Accustandard	S-18004	200	20	0.25
d_8-Acenaphthylene	Accustandard	S-18004	200	20	0.25
d_{10}-Fluorene	CIL	DLM-1123-1.2	200	20	0.25
d_{10}-Phenanthrene	Accustandard	S-18004	200	20	0.25
d_{12}- 2,6-Dimethylnaphthalene	Accustandard	S-18004	200	20	0.25
d_{10}-Fluoranthene	Accustandard	S-18004	200	20	0.25
d_{12}-Benz(a)anthracene	Accustandard	S-18004	200	20	0.25
d_{12}-Chrysene	Accustandard	S-18004	200	20	0.25
d_{12}-Benzo(b)fluoranthene	Accustandard	S-18004	200	20	0.25
d_{12}-Benzo(k)fluoranthene	Accustandard	S-18004	200	20	0.25
d_{12}-Benzo(a)pyrene	Accustandard	S-18004	200	20	0.25
d_{12}-Perylene	Accustandard	S-18004	200	20	0.25
d_{12}-Indeno(1,2,3-cd)pyrene	Accustandard	S-18004	200	20	0.25
d_{14}-Dibenz(a,h)anthracene	Accustandard	S-18004	200	20	0.25
d_{12}-Benzo(ghi)perylene	Accustandard	S-18004	200	20	0.25
d_8-Dibenzothiophene	Accustandard	S-18004	200	20	0.25
d_{10}-Anthracene	Accustandard	S-18004	200	20	0.25
Recovery Standards					
d_{10}-Acenaphthene	CIL	DLM-108-1.2	200	NA	10
d_{10}-Pyrene	CIL	DLM-155-1.2	200	NA	10
d_{12}-Benzo(e)pyrene	CIL	DLM-257-1.2	200	NA	10
Alternate Surrogate					
d_{14}-p-Terphenyl	CIL	DLM-382-1.2	200	NA	0.25
Sampling Surrogates					
$^{13}C_6$-Naphthalene	CIL	DLM-365	neat	1000	0.25

* Other sources of standards may be used.

Table 5 – Quantitation References

Analyte	Analyte Type	Quantitation Standard (QS)	QS Type
Naphthalene	Native Analyte	d_8-Naphthalene	IS
Biphenyl	Native Analyte	d_{12}-2,6-Dimethylnaphthalene	IS
2-Methylnaphthalene	Native Analyte	d_{10}-2-Methylnaphthalene	IS
1-Methylnaphthalene	Native Analyte	d_{10}-1-Methylnaphthalene	IS
Acenaphthylene	Native Analyte	d_8-Acenaphthylene	IS
Acenaphthene	Native Analyte	d_8-Acenaphthylene	IS
Fluorene	Native Analyte	d_{10}-Fluorene	IS
Dibenzothiophene	Native Analyte	d_8-Dibenzothiophene	IS
Phenanthrene	Native Analyte	d_{10}-Phenanthrene	IS
1-Methylphenanthrene	Native Analyte	d_{10}-Phenanthrene	IS
2,3,5-Trimethylnaphthalene	Native Analyte	d_{12}-2,6-Dimethylnaphthalene	IS
Anthracene	Native Analyte	d_{10}-Anthracene	IS
2,6-Dimethylnaphthalene	Native Analyte	d_{12}-2,6-Dimethylnaphthalene	IS
Fluoranthene	Native Analyte	d_{10}-Fluoranthene	IS
Pyrene	Native Analyte	d_{10}-Fluoranthene	IS
Benz(a)anthracene	Native Analyte	d_{12}-Benz(a)anthracene[1]	IS
Chrysene	Native Analyte	d_{12}-Chrysene	IS
Benzo(b)fluoranthene	Native Analyte	d_{12}-Benzo(b)fluoranthene	IS
Benzo(k)fluoranthene	Native Analyte	d_{12}-Benzo(k)fluoranthene	IS
Benzo(e)pyrene	Native Analyte	d_{12}-Benzo(a)pyrene	IS
Benzo(a)pyrene	Native Analyte	d_{12}-Benzo(a)pyrene	IS
Perylene	Native Analyte	d_{12}-Perylene	IS
Indeno(1,2,3-cd)pyrene	Native Analyte	d_{12}-Indeno(1,2,3-cd)pyrene	IS
Dibenz(ah)anthracene	Native Analyte	d_{14}-Dibenz(ah)anthracene	IS
Benzo(ghi)perylene	Native Analyte	d_{12}-Benzo(ghi)perylene	IS
C2 Naphthalenes	Alkyl Group	d_8-Naphthalene*	IS
C3 Naphthalenes	Alkyl Group	d_8-Naphthalene*	IS
C4 Naphthalenes	Alkyl Group	d_8-Naphthalene*	IS
C1 Fluorenes	Alkyl Group	d_{10}-Fluorene*	IS
C2 Fluorenes	Alkyl Group	d_{10}-Fluorene*	IS
C3 Fluorenes	Alkyl Group	d_{10}-Fluorene*	IS
C1 Dibenzothiophene	Alkyl Group	d_8-Dibenzothiophene*	IS
C2 Dibenzothiophene	Alkyl Group	d_8-Dibenzothiophene*	IS
C3 Dibenzothiophene	Alkyl Group	d_8-Dibenzothiophene*	IS
C4 Dibenzothiophene	Alkyl Group	d_8-Dibenzothiophene*	IS
C1 Phenanthrenes & Anthracenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C2 Phenanthrenes & Anthracenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C3 Phenanthrenes & Anthracenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C4 Phenanthrenes & Anthracenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C1Fluoranthenes & Pyrenes	Alkyl Group	d_{10}-Fluoranthene*	IS
C1 Benz(a)anthracenes & Chrysenes	Alkyl Group	d_{12}-Chrysene *	IS
C2 Benz(a)anthracenes & Chrysenes	Alkyl Group	d_{12}-Chrysene *	IS
C3 Benz(a)anthracenes & Chrysenes	Alkyl Group	d_{12}-Chrysene *	IS
C4 Benz(a)anthracenes & Chrysenes	Alkyl Group	d_{12}-Chrysene *	IS
d_{14}-p-Terphenyl	Alternate Surrogate	d_{10}-Pyrene	RS
$^{13}C_6$-Naphthalene	Sampling Surrogate	d_8-Naphthalene	IS

[1] chrysene-d12 may be used in lieu of benzo(a)anthracene-d12

* Response factor for alkyls taken from parent PAH. See Table 8.

Table 5 – Quantitation References (continued)

Analyte	Analyte Type	Quantitation Standard (QS)	QS Type
d_{-8}-Naphthalene	IS	d_{10}-Acenaphthene	RS
d_{10}-2-Methylnaphthalene	IS	d_{10}-Acenaphthene	RS
d_{10}-1-Methylnaphthalene	IS	d_{10}-Acenaphthene	RS
d_{12}-2,6-Dimethylnaphthalene	IS	d_{10}-Acenaphthene	RS
d_{8}-Acenaphthylene	IS	d_{10}-Acenaphthene	RS
d_{10}-Fluorene	IS	d_{10}- Acenaphthene	RS
d-8 dibenzothiophene	IS	d_{10}-Pyrene	RS
d_{10}-Phenanthrene	IS	d_{10}-Pyrene	RS
d_{10}-Anthracene	IS	d_{10}-Pyrene	RS
d_{10}-Fluoranthene	IS	d_{10}-Pyrene	RS
d_{12}-Benz(a)anthracene	IS	d_{10}-Pyrene	RS
d_{12}-Chrysene	IS	d_{10}-Pyrene	RS
d_{12}-Benzo(b)fluoranthene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Benzo(k)fluoranthene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Benzo(a)pyrene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Perylene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Indeno(1,2,3-cd)pyrene	IS	d_{12}-Benzo(e)pyrene	RS
d_{14}-Dibenz(ah)anthracene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Benzo(ghi)perylene	IS	d_{12}-Benzo(e)pyrene	RS

IS = Labeled Internal Standard
RS = Recovery Standard

Table 6 - Selected Ions Monitored and SIM Groups

Analyte	Classification	Quantitation	Confirmation	SIM Group
d_8-Naphthalene	Internal Standard	136	134	2
Naphthalene	Native Analyte	128	102	2
$^{13}C_6$-Naphthalene	Sampling Surrogate	134	133	2
d_{10}-2-Methylnaphthalene	Internal Standard	152	151	3
2-Methylnaphthalene	Native Analyte	142	141	3
d_{10}-1-Methylnaphthalene	Internal Standard	152	151	3
1-Methylnaphthalene	Native Analyte	142	141	3
Biphenyl	Native Analyte	154	152	4
C2-naphthalenes	Alkyl Group	156	141	4,5
d_{12}-2,6-Dimethylnaphthalene	Internal Standard	168	167	4
2,6-Dimethylnaphthalene	Native Analyte	156	155	4
C3-naphthalenes	Alkyl Group	170	155	5,6
d_8-Acenaphthylene	Internal Standard	160	158	5
Acenaphthylene	Native Analyte	152	151	5
d_{10}-Acenaphthene	Recovery Standard	164	163	5
Acenaphthene	Native Analyte	154	153	5
C4-Naphthalenes	Alkyl Group	184	169	5,6,7
2,3,5-Trimethylnaphthalene	Native Analyte	170	169	6
d_{10}-Fluorene	Internal Standard	176	174	6
Fluorene	Native Analyte	166	165	6
C1-Fluorenes	Alkyl Group	180	165	6,7
Dibenzothiophene	Native Analyte	184	139	7
d_8-Dibenzothiophene	Internal Standard	192	191	7
d_{10}-Phenanthrene	Internal Standard	188	184	7
Phenanthrene	Native Analyte	178	176	7
C2-Fluorenes	Alkyl Group	194	179	7
d_{10}-Anthracene	Internal Standard	188	184	7
Anthracene	Native Analyte	178	176	7
C1-Dibenzothiophenes	Alkyl Group	198	197	7,8
C3-Fluorenes	Alkyl Group	208	193	7,8,9
C1-Phenanthrenes_Anthracenes	Alkyl Group	191	192	7,8
1-Methylphenanthrene	Native Analyte	191	192	8
C2-Dibenzothiophenes	Alkyl Group	212	211	8,9
C2-Phenanthrenes_Anthracenes	Alkyl Group	206	191	8,9
C3-Dibenzothiophenes	Alkyl Group	226	211	8,9
d_{10}-Fluoranthene	Internal Standard	212	208	9
Fluoranthene	Native Analyte	202	200	9
C3-Phenanthrenes_Anthracenes	Alkyl Group	220	205	9
C4-Dibenzothiophenes	Alkyl Group	240	225	8,9
d_{10}-Pyrene	Recovery Standard	212	208	9
Pyrene	Native Analyte	202	200	9
C4-Phenanthrenes_Anthracenes	Alkyl Group	234	219	9

Table 6 - Selected Ions Monitored and SIM Groups (continued)

Analyte	Classification	Quantitation	Confirmation	SIM Group
d_{14}-Terphenyl	Alternate Surrogate	244	242	9
C1-Fluoranthenes_Pyrenes	Alkyl Group	216	215	9
d_{12}-Benz(a)anthracene	Internal Standard	240	236	10
Benz(a)anthracene	Native Analyte	228	226	10
d_{12}-Chrysene	Internal Standard	240	236	10
Chrysene	Native Analyte	228	226	10
C1-Benz(a)anthracenes_Chrysenes	Alkyl Group	242	241	10,11
C2-Benz(a)anthracenes_Chrysenes	Alkyl Group	256	241	10,11
C3-Benz(a)anthracenes_Chrysenes	Alkyl Group	270	255	10,11
d_{12}-Benzo(b)fluoranthene	Internal Standard	264	260	11
Benzo(b)fluoranthene	Native Analyte	252	253	11
d_{12}-Benzo(k)fluoranthene	Internal Standard	264	260	11
Benzo(k)fluoranthene	Native Analyte	252	253	11
C4-Benz(a)anthracenes_Chrysenes	Alkyl Group	284	269	11
d_{12}-Benzo(e)pyrene	Recovery Standard	264	260	11
Benzo(e)pyrene	Native Analyte	252	253	11
d_{12}-Benzo(a)pyrene	Internal Standard	264	260	11
Benzo(a)pyrene	Native Analyte	252	253	11
d_{12}-Perylene	Internal Standard	264	260	11
Perylene	Native Analyte	252	253	11
d_{14}-Dibenz(ah)anthracene	Internal Standard	292	288	12
Dibenz(ah)anthracene	Native Analyte	278	139	12
d_{12}-Indeno(1,2,3-cd)pyrene	Internal Standard	288	284	12
Indeno(1,2,3-cd)pyrene	Native Analyte	276	138	12
d_{12}-Benzo(ghi)perylene	Internal Standard	288	284	12
Benzo(ghi)perylene	Native Analyte	276	138	12

Table 7 - Acceptance Criteria for Performance Tests and QC Samples

Analyte	IDOC Test Conc[1] (ng/µL)	IDOC %RSD	IDOC %R	ICV %R	LCS %R	Method Blank %R	Sample %R
Naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
2-Methyl naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
1-Methyl naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
Biphenyl	0.5	30	60-140	70-130	60-140	NA	NA
2,6-Dimethyl naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
Acenaphthylene	0.5	30	60-140	70-130	60-140	NA	NA
Acenaphthene	0.5	30	60-140	70-130	60-140	NA	NA
2,3,5-Trimethyl naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
Fluorene	0.5	30	60-140	70-130	60-140	NA	NA
Phenanthrene	0.5	30	60-140	70-130	60-140	NA	NA
Anthracene	0.5	30	60-140	70-130	60-140	NA	NA
1-Methyl phenanthrene	0.5	30	60-140	70-130	60-140	NA	NA
Fluoranthene	0.5	30	60-140	70-130	60-140	NA	NA
Pyrene	0.5	30	60-140	70-130	60-140	NA	NA
Benz(a)anthracene	0.5	30	60-140	70-130	60-140	NA	NA
Chrysene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(b)fluoranthene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(k)fluoranthene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(e)pyrene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(a)pyrene	0.5	30	60-140	70-130	60-140	NA	NA
Perylene	0.5	30	60-140	70-130	60-140	NA	NA
Indeno(1,2,3-cd)pyrene	0.5	30	60-140	70-130	60-140	NA	NA
Dibenz(ah)anthracene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(ghi)perylene	0.5	30	60-140	70-130	60-140	NA	NA
Dibenzothiophene	0.5	30	60-140	70-130	60-140	NA	NA
Internal Standards							
d_8-Naphthalene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-2-Methyl naphthalene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-1-Methyl naphthalene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-2,6-Dimethyl naphthalene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_8-Acenaphthylene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-Fluorene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-Phenanthrene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-Fluoranthene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benz(a)anthracene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Chrysene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benzo(b)fluoranthene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benzo(k)fluoranthene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benzo(a)pyrene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Perylene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Indeno(1,2,3-cd)pyrene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{14}-Dibenz(a,h)anthracene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benzo(ghi)perylene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-Anthracene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_8-Dibenzothiophene	0.5	30	60-140	70-130	60-140	60-140	30-120
Alternate Surrogate							
d_{14}-Terphenyl	NA	NA	NA	NA	NA	NA	50-150
Sampling Surrogate							
$^{13}C_6$-Naphthalene	NA	NA	NA	NA	NA	NA	50-150

[1]Test concentration in the final extract, assuming a 0.5 mL volume.

Table 8 – Response Factor Assignment for the Alkylated Homologues

Alkyl Group	Parent to reference for RF
C2 Naphthalenes	Naphthalene
C3 Naphthalenes	Naphthalene
C4 Naphthalenes	Naphthalene
C1 Fluorenes	Fluorene
C2 Fluorenes	Fluorene
C3 Fluorenes	Fluorene
C1 Dibenzothiophene	Dibenzothiophene
C2 Dibenzothiophene	Dibenzothiophene
C3 Dibenzothiophene	Dibenzothiophene
C4 Dibenzothiophene	Dibenzothiophene
C1 Phenanthrenes & Anthracenes	Phenanthrene
C2 Phenanthrenes & Anthracenes	Phenanthrene
C3 Phenanthrenes & Anthracenes	Phenanthrene
C4 Phenanthrenes & Anthracenes	Phenanthrene
C1Fluoranthenes & Pyrenes	Pyrene
C1 Benz(a)anthracenes & Chrysenes	Chrysene
C2 Benz(a)anthracenes & Chrysenes	Chrysene
C3 Benz(a)anthracenes & Chrysenes	Chrysene
C4 Benz(a)anthracenes & Chrysenes	Chrysene

Figure 1 Recommended GC & GC/MS Conditions

```
                              INSTRUMENT CONTROL PARAMETERS:    MP
                              -----------------------------------

   C:\MSDCHEM\1\METHODS\KNX_00171.M
      Fri Nov 21 11:42:22 2014

Control Information
------- -----------

Sample Inlet      :  GC
Injection Source  :  GC ALS
Mass Spectrometer :  Enabled

================================================================================
                                  6890 GC METHOD
================================================================================


OVEN
   Initial temp:  40 'C (On)                  Maximum temp:  375 'C
   Initial time:  0.50 min                    Equilibration time:  0.50 min
   Ramps:
      #  Rate  Final temp  Final time
      1 30.00      240        0.00
      2 21.00      310        0.00
      3  4.00      320        0.10
      4 35.00      345        2.50
      5   0.0(Off)
   Post temp:  0 'C
   Post time:  0.00 min
   Run time:  16.31 min


FRONT INLET (SPLIT/SPLITLESS)              BACK INLET (UNKNOWN)
   Mode:  Pulsed Splitless
   Initial temp:  300 'C (On)
   Pressure:  13.40 psi (On)
   Pulse pressure:  25.0 psi
   Pulse time:  0.50 min
   Purge flow:  10.0 mL/min
   Purge time:  1.25 min
   Total flow:  14.0 mL/min
   Gas saver:  Off
   Gas type:  Helium


COLUMN 1                                   COLUMN 2
   Capillary Column                           (not installed)
   Model Number:  Restek 13623-124
   Rxi-5Sil MS w/ Integra-Guard
   Max temperature:  350 'C
   Nominal length:  28.4 m
   Nominal diameter:  250.00 um
   Nominal film thickness:  0.25 um
   Mode:  constant flow
   Initial flow:  1.0 mL/min
   Nominal init pressure:  13.41 psi
   Average velocity:  22 cm/sec
   Inlet:  Front Inlet
   Outlet:  MSD
   Outlet pressure:  3.80 psi


FRONT DETECTOR (NO DET)                    BACK DETECTOR (NO DET)


SIGNAL 1                                   SIGNAL 2

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```

```
   Data rate:  20 Hz                    Data rate:  20 Hz
   Type:  test plot                     Type:  test plot
   Save Data:  Off                      Save Data:  Off
   Zero:  0.0 (Off)                     Zero:  0.0 (Off)
   Range:  0                            Range:  0
   Fast Peaks:  Off                     Fast Peaks:  Off
   Attenuation:  0                      Attenuation:  0

COLUMN COMP 1                        COLUMN COMP 2
   (No Detectors Installed)             (No Detectors Installed)

THERMAL AUX 2                        AUX PRESSURE 3
   Use:  MSD Transfer Line Heater       Description:  Quick Swap
   Description:                         Gas Type:  Helium
   Initial temp:  300 'C (On)           Initial pressure:  0.00 psi (Off)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)

AUX PRESSURE 4                       AUX PRESSURE 5
   Description:                         Description:
   Gas Type:  Helium                    Gas Type:  Helium
   Initial pressure:  0.00 psi (Off)    Initial pressure:  0.00 psi (Off)

                                     POST RUN
                                        Post Time: 0.00 min

TIME TABLE
   Time       Specifier                  Parameter & Setpoint


                              GC Injector


     Front Injector:
        Sample Washes                 0
        Sample Pumps                  6
        Injection Volume           1.00 microliters
        Syringe Size               10.0 microliters
        PreInj Solvent A Washes       0
        PreInj Solvent B Washes       0
        PostInj Solvent A Washes      3
        PostInj Solvent B Washes      3
        Viscosity Delay               1 seconds
        Plunger Speed              Fast
        PreInjection Dwell         0.00 minutes
        PostInjection Dwell        0.00 minutes


     Back Injector:
No parameters specified

 Column 1 Inventory Number : 1199398
 Column 2 Inventory Number :

                            MS ACQUISITION PARAMETERS


General Information
------- -----------

Tune File               : dftpp.u

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```
Acquistion Mode          : SIM


MS Information
-- -----------

Solvent Delay            : 3.25 min

EMV Mode                 : Relative
Relative Voltage         : 0
Resulting EM Voltage     : 1600

[Sim Parameters]

GROUP 1
Group ID                 : 1
Resolution               : Low
Plot 1 Ion               : 146.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         ( 65.00,     40) ( 75.00,     40) ( 77.00,     40)
                         ( 81.00,     40) ( 94.00,     40) ( 95.00,     40)
                         (105.00,     40) (111.00,     40) (115.00,     40)
                         (119.00,     40) (146.00,     40) (148.00,     40)
                         (150.00,     40) (152.00,     40)

GROUP 2
Group ID                 : 2
Resolution               : Low
Group Start Time         : 4.60
Plot 1 Ion               : 102.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         ( 81.00,     40) (102.00,     40) (110.00,     40)
                         (128.00,     40) (133.00,     40) (134.00,     40)
                         (136.00,     40) (180.00,     40) (182.00,     40)
                         (223.00,     40) (225.00,     40)

GROUP 3
Group ID                 : 3
Resolution               : Low
Group Start Time         : 5.30
Plot 1 Ion               : 141.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         ( 81.00,     35) (110.00,     35) (141.00,     35)
                         (142.00,     35) (151.00,     35) (152.00,     35)
                         (156.00,     35)

GROUP 4
Group ID                 : 4
Resolution               : Low
Group Start Time         : 5.67
Plot 1 Ion               : 152.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         ( 81.00,     15) (110.00,     15) (127.00,     15)
                         (141.00,     15) (152.00,     15) (154.00,     15)
                         (155.00,     15) (156.00,     15) (162.00,     15)
                         (167.00,     15) (168.00,     15) (169.00,     15)

GROUP 5
Group ID                 : 5
Resolution               : Low
Group Start Time         : 6.00
Plot 1 Ion               : 151.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         ( 63.00,     10) (139.00,     10) (141.00,     10)
                         (151.00,     10) (152.00,     10) (153.00,     10)
                         (154.00,     10) (155.00,     10) (156.00,     10)
                         (158.00,     10) (160.00,     10) (163.00,     10)
                         (164.00,     10) (167.00,     10) (168.00,     10)
                         (169.00,     10) (170.00,     10) (184.00,     10)
```

GROUP 6

Group ID	: 6							
Resolution	: Low							
Group Start Time	: 6.70							
Plot 1 Ion	: 165.00							
Ions/Dwell In Group	(Mass,	Dwell)	(Mass,	Dwell)	(Mass,	Dwell)		
	(63.00,	10)	(139.00,	10)	(155.00,	10)		
	(165.00,	10)	(166.00,	10)	(168.00,	10)		
	(169.00,	10)	(170.00,	10)	(171.00,	10)		
	(172.00,	10)	(174.00,	10)	(176.00,	10)		
	(180.00,	10)	(184.00,	10)				

GROUP 7

Group ID	: 7							
Resolution	: Low							
Group Start Time	: 7.30							
Plot 1 Ion	: 139.00							
Ions/Dwell In Group	(Mass,	Dwell)	(Mass,	Dwell)	(Mass,	Dwell)		
	(139.00,	5)	(142.00,	5)	(165.00,	5)		
	(169.00,	5)	(176.00,	5)	(178.00,	5)		
	(179.00,	5)	(180.00,	5)	(182.00,	5)		
	(184.00,	5)	(186.00,	5)	(188.00,	5)		
	(191.00,	5)	(192.00,	5)	(193.00,	5)		
	(194.00,	5)	(197.00,	5)	(198.00,	5)		
	(208.00,	5)	(284.00,	5)				

GROUP 8

Group ID	: 8							
Resolution	: Low							
Group Start Time	: 7.95							
Plot 1 Ion	: 191.00							
Ions/Dwell In Group	(Mass,	Dwell)	(Mass,	Dwell)	(Mass,	Dwell)		
	(179.00,	10)	(191.00,	10)	(192.00,	10)		
	(193.00,	10)	(194.00,	10)	(197.00,	10)		
	(198.00,	10)	(206.00,	10)	(208.00,	10)		
	(211.00,	10)	(212.00,	10)	(225.00,	10)		
	(226.00,	10)	(240.00,	10)				

GROUP 9

Group ID	: 9							
Resolution	: Low							
Group Start Time	: 8.50							
Plot 1 Ion	: 200.00							
Ions/Dwell In Group	(Mass,	Dwell)	(Mass,	Dwell)	(Mass,	Dwell)		
	(149.00,	5)	(167.00,	5)	(191.00,	5)		
	(193.00,	5)	(200.00,	5)	(202.00,	5)		
	(205.00,	5)	(206.00,	5)	(208.00,	5)		
	(211.00,	5)	(212.00,	5)	(215.00,	5)		
	(216.00,	5)	(219.00,	5)	(220.00,	5)		
	(225.00,	5)	(226.00,	5)	(234.00,	5)		
	(240.00,	5)	(242.00,	5)	(244.00,	5)		

GROUP 10

Group ID	: 10							
Resolution	: Low							
Group Start Time	: 9.90							
Plot 1 Ion	: 226.00							
Ions/Dwell In Group	(Mass,	Dwell)	(Mass,	Dwell)	(Mass,	Dwell)		
	(115.00,	25)	(149.00,	25)	(167.00,	25)		
	(226.00,	25)	(228.00,	25)	(232.00,	25)		
	(234.00,	25)	(236.00,	25)	(240.00,	25)		
	(241.00,	25)	(242.00,	25)	(255.00,	25)		
	(256.00,	25)	(270.00,	25)				

GROUP 11

Group ID	: 11
Resolution	: Low
Group Start Time	: 11.00

```
Plot 1 Ion                : 252.00
Ions/Dwell In Group       (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                          (241.00,     30) (242.00,     30) (252.00,     30)
                          (253.00,     30) (255.00,     30) (256.00,     30)
                          (260.00,     30) (264.00,     30) (269.00,     30)
                          (270.00,     30) (284.00,     30)

GROUP 12
Group ID                  : 12
Resolution                : Low
Group Start Time          : 12.60
Plot 1 Ion                : 292.00
Ions/Dwell In Group       (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                          (138.00,     25) (139.00,     25) (150.00,     25)
                          (151.00,     25) (156.00,     25) (276.00,     25)
                          (278.00,     25) (284.00,     25) (288.00,     25)
                          (292.00,     25) (300.00,     25) (302.00,     25)
                          (312.00,     25)

[MSZones]

MS Source                 : 230 C   maximum 250 C
MS Quad                   : 150 C   maximum 200 C

                              END OF MS ACQUISITION PARAMETERS


                               TUNE PARAMETERS for SN: US81839504
                            ------------------------------

 Trace Ion Detection is OFF.

 EMISSION     :       34.610
 ENERGY       :       69.922
 REPELLER     :       25.767
 IONFOCUS     :       73.075
 ENTRANCE_LE  :        0.000
 EMVOLTS      :     1600.000
                                 Actual EMV  :     1600
                                 GAIN FACTOR :        1.15
 AMUGAIN      :     1909.000
 AMUOFFSET    :      124.813
 FILAMENT     :        1.000
 DCPOLARITY   :        0.000
 ENTLENSOFFS  :      17.820@  3    17.820@ 50    15.812@ 69    16.314@131    16.565@219    16.81
6@414    17.318@502    17.318@1049
 MASSGAIN     :     -664.000
 MASSOFFSET   :      -42.000

                               END OF TUNE PARAMETERS
                            -----------------------------------


PostRun InstCntl macro(s) exist: msacq2.mac

                              END OF INSTRUMENT CONTROL PARAMETERS
                              -----------------------------------
```

Figure 2 – Example Data Review Checklist

TestAmerica Knoxville GC/MS-SIM Initial Calibration Data Review / Narrative Checklist
Method: PAHs and Selected SVOCs - KNOX-ID-0016, Revision 11

Analysis Date:		Instrument::		ICAL Batch/Scan Name:		Scanned ☐

A. Review Items	N/A	Yes	No	Why is data reportable?	2nd √
1. Were all injections in sequence within 12 hr of first calibration standard?					
2. Was date/time of analysis verified between header and logbook?					
3. Are peak integrations appropriate?					
4. Were ≥ 5 levels of each analyte/IS analyzed?					
5. Was the high point standard checked for saturation?					
6. Was low level standard at or below RL?					
7. Are all %RSD ≤30% ?					
8. Are the MID descriptors properly set?					
9. Are correct RFs listed in ICAL summary?					
10. Was ICAL summary form processed using the correct method?					
11. Are the ICAL start and end dates/times correct on ICAL summary?					
12. Elution order checked on isomeric pairs?					
• 1,4 dichlorobenzene before 1,2 dichlorobenzene (& d4 isomers)					
• 2-methylnaphthalene before 1-methylnaphthalene (& d10 isomers)					
• acenaphthylene before acenaphthene (& d10 isomers)					
• dibenzothiophene before anthracene					
• phenanthrene before anthracene (& d10 isomers)					
• fluoranthene before pyrene (& d10 isomers)					
• benzo(a)anthracene before chrysene (& d12 isomers)					
• benzo(b)fluoranthene before benzo(k)fluoranthene (& d12 isomers)					
• benzo(e)pyrene before benzo(a)pyrene benzo(a)pyrene before perylene (& d12 isomers)					
• Indeno(1,2,3-cd)pyrene before benzo(g,h,I)perylene (& d12 isomers)					
13. Is the 2nd source ICV with +/- 30% of the expected value?					
14. Are the Alkyl RFs correct (i.e., same as the parent RF)?					
15. If criteria were not met, was a NCM generated and approved by supervisor?					
16. Does the ICAL folder contain **complete** data in the following order? ICAL data review checklist, runlog, Target Initial Calibration Report, followed by the quan report and chromatograms for all calibration and 2nd source standards.					

1st Level Reviewer:	Date:
Comments:	
2nd Level Reviewer:	Date:
Comments:	

TestAmerica Knoxville GC/MS-SIM Continuing Calibration Review / Narrative Checklist
Method: LRPAH PAHs and Selected SVOCs - KNOX-ID-0016, Revision 11

Analysis Date:		CCAL Batch/ Scan Name:		Instrument:		ICAL Batch/ Scan Name:		Scanned ☐

A. Review Items	N/A	Yes	No	Why is data reportable?	2nd √
1. Were all injections in sequence within 12 hr of CCAL?					
2. Was date/time of analysis verified between header and logbook?					
3. Are peak integrations appropriate?					
4. Is the %D or drift <30% for all analytes					
5. Are the recovery standards within 50-200% of the ICAL CS4 level?					
6. Are the MID descriptors properly set?					
7. Are correct RFs listed in CCAL summary?					
8. Was the correct ICAL used for quantitation? (Verify 1 RF.)					
9. Elution order checked on isomeric pairs/coeluters?					
• 1,4 dichlorobenzene before 1,2 dichlorobenzene (& d4 isomers)					
• 2-methylnaphthalene before 1-methylnaphthalene (& d10 isomers)					
• acenaphthylene before acenaphthene (& d10 isomers)					
• dibenzothiophene before anthracene					
• phenanthrene before anthracene (& d10 isomers)					
• fluoranthene before pyrene (& d10 isomers)					
• benzo(a)anthracene before chrysene (& d12 isomers)					
• benzo(b)fluoranthene before benzo(k)fluoranthene (& d12 isomers)					
• benzo(e)pyrene before benzo(a)pyrene benzo(a)pyrene before perylene (& d12 isomers)					
• Indeno(1,2,3-cd)pyrene before benzo(g,h,i)perylene (& d12 isomers)					
10. Were the first/last RTs for each alkyl PAH homologue group properly identified and indicated on the chromatogram?					
11. If criteria were not met, was a NCM generated and approved by supervisor?					
12. Does the CCAL folder contain **complete** data in the following order? CCAL data review checklist, runlog, Target Continuing Calibration Report, followed by the quan report and chromatograms for the CCAL and window standard.					

1st Level Reviewer:	Date:
Comments:	
2nd Level Reviewer:	**Date:**
Comments:	

TestAmerica Knoxville GC/MS-SIM Data Review / Narrative Checklist
Method: LRPAH PAHs and Selected SVOCs - KNOX-ID-0016, Revision 11
Page 1 of 3

Lot Number:			Instrument:		
Scanned Filenames:					

A. Calibration	N/A	Yes	No	Why is data reportable?	2nd √
1. Were all samples injected within 12 hr of CCAL?					
2. Was the correct ICAL used for quantitation? (Check 1 RF per processing batch.)					
B. Sample Results	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd √**
1. Were all special project requirements met?					
2. Were sample preparation and analytical HTs met? If no, list NCM#_____				☐ [ht1] HT expired upon receipt. ☐ [ht2] Client requested analysis after HT expired.* ☐ **Re-extraction done after HT expired.**	
3. Was prep info (sample amount, final vol, split factors, units, prep dates/times) verified?					
4. For sediment samples, were the RLs and MDLs adjusted for % moisture using QuantIMS DF?					
5. Was date/time of analysis verified between header and logbook?					
6. Was header information (WO#, data file, initial wt/vol, extract vol, DF) verified?					
7. Were peaks properly identified?					
8. Are peak integrations appropriate?					
9. Were alkyl group start/end times and patterns verified?				☐ [AP] ☐ [AP 2]	
10. Are internal standards & alternate standards (30-120% R), sampling surrogates (50-150% R) within QC limits for samples and matrix spikes? Sample Reason Sample Reason _____				☐ **[is1] IS above QC limits.** ☐ **[is2] IS below QC limts.** ☐ **[sur1] Surrogates outside QC limits.**	
11. If amount extracted was <80% of nominal amount, were the RLs/MDLs adjusted? List samples:_____				☐ [elev6] Elevated RLs for all analytes due to insufficient sample amount received.	
12. For initial analysis that's a dilution, was the largest analyte >20% of calibration range? List diluted samples and reason (e.g elev1) Sample Reason Sample Reason _____				☐ [elev1] Elevated RL for (ANALYTE) due to sample matrix interferences. ☐ [elev2] Elevated RL for (ANALYTE) due to interfering analyte. ☐ [elev3] Elevated RLs for all analytes due to difficult sample matrix. ☐ [elev4] Diluted based on screening results. ☐ [elev5] Elevated RLs for all analytes due to presence of non-target compounds.	

TestAmerica Knoxville GC/MS-SIM Data Review / Narrative Checklist
Method: LRPAH PAHs and Selected SVOCs - KNOX-ID-0016, Revision 11
Page 2 of 3

Lot Number:	N/A	Yes	No	Why is data reportable?	2nd √
13. If bench dilutions were required, were results within calibration range at maximum dilution? Sample Reason Sample Reason _____				☐ [E1] 1 g reprep performed. ☐ [E2] 1 g multi-spike reprep performed. ☐ [E3] Post-extraction spike performed. ☐ [E4] E values reported per client.	
14. For secondary diluted analyses to bring compounds in calibration range, was the largest analyte targeted to be above 50% of calibration range? List diluted samples and reason (e.g., dil1): Sample Reason Sample Reason _____				☐ [dil1] Conc. of (ANALYTE) > calibration range. RLs adjusted accordingly. ☐ [dil2] Conc. of several compounds > calibration range. RLs adjusted accordingly. ☐ [dil3] Conc. of (ANALYTE) > calibration range. Both analyses reported to provide lowest RLs. ☐ [dil4] Conc. of several compounds > calibration range. Both analyses reported to provide lowest RLs.	
15. Was the upper calibration range (UCL) calculated correctly and were hits >UCL flagged with "E"?					
16. If manual integrations were performed, are they clearly identified, initialed, dated and reason given?				Reasons: 1) Corrected split peak; 2) Unresolved peak; 3) Tailing; 4) RT shift; 5) Wrong peak selected; 6) Other	
17. Have alternate hits and manual integrations been verified as correct?					
C. Preparation/Matrix QC Results	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd √**
1. LCS native analyte %R within QC limits (60-140%)? If no, list NCM#:: _____				☐ **[lcs1] Insufficient sample for reanalysis.** ☐ **[lcs2] Samples consumed during prep.** ☐ **[lcs3] LCS %R high but analyte <RL in associated samples.**	
2. LCS IS %R within QC limits (60-140%)?				☐ **[is3] IS above QC limits.** ☐ **[is4] IS below QC limts.**	
3. Method blank done per prep batch and method blank or instrument blank analyzed with each sequence?					
4. Method blank IS %R within QC limits (60-140%)?.				☐ **[is5] IS above QC limits.** ☐ **[is6] IS below QC limts.**	
5. Are all analytes present in the method blank ≤ RL?				☐ **[mb1] Reported blank after client consultation.** ☐ **[mb3] Analyte < RL in associated samples.** ☐ **[mb4] Sample results >10x blank.** ☐ **[mb5] Insufficient sample for reanalysis.** ☐ **[mb7] Samples consumed during prep.**	
6. Were MS run #'s assigned correctly?					
7. Are MS/MSD or sample duplicate recoveries and RPDs within QC limits?				☐ [ms1] LCS acceptable. High native analyte concentration relative to spike level and/or lack of sample homogeneity.	
D. Final Report	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd √**
1. Final report acceptable? (Results correct, RLs calculated correctly, units correct, IS %R correct, appropriate flags used, dilution factor correct, and extraction/ analysis dates correct.)					

TestAmerica Knoxville GC/MS-SIM Data Review / Narrative Checklist
Method: LRPAH PAHs and Selected SVOCs - KNOX-ID-0016, Revision 11
Page 3 of 3

Lot Number:	N/A	Yes	No	Why is data reportable?	2nd √
2. If samples were split, are the dilution factors & prep factors applied properly & MDL/RLs adjusted				☐ [elev7] Elevated RLs for all analytes due to split; list samples: _____ _____	
3. For alkyl PAHs, are hits fagged with EST?					
4. Were all non-associated internal standards turned to 'NA'?					
5. Was a narrative prepared and all deviations noted?					
6. Are all non-conformances documented appropriately and copy included with deliverable?					
7. Are the correct scanned file names listed?					
8. Were all CCALs and window standards scanned?					
1st Level Reviewer:		**Date:**			
Comments:					
2nd Level Reviewer:		**Date:**			
Comments:					

Figure 3: C1-C4 Alkyl Homologue Peak Patterns

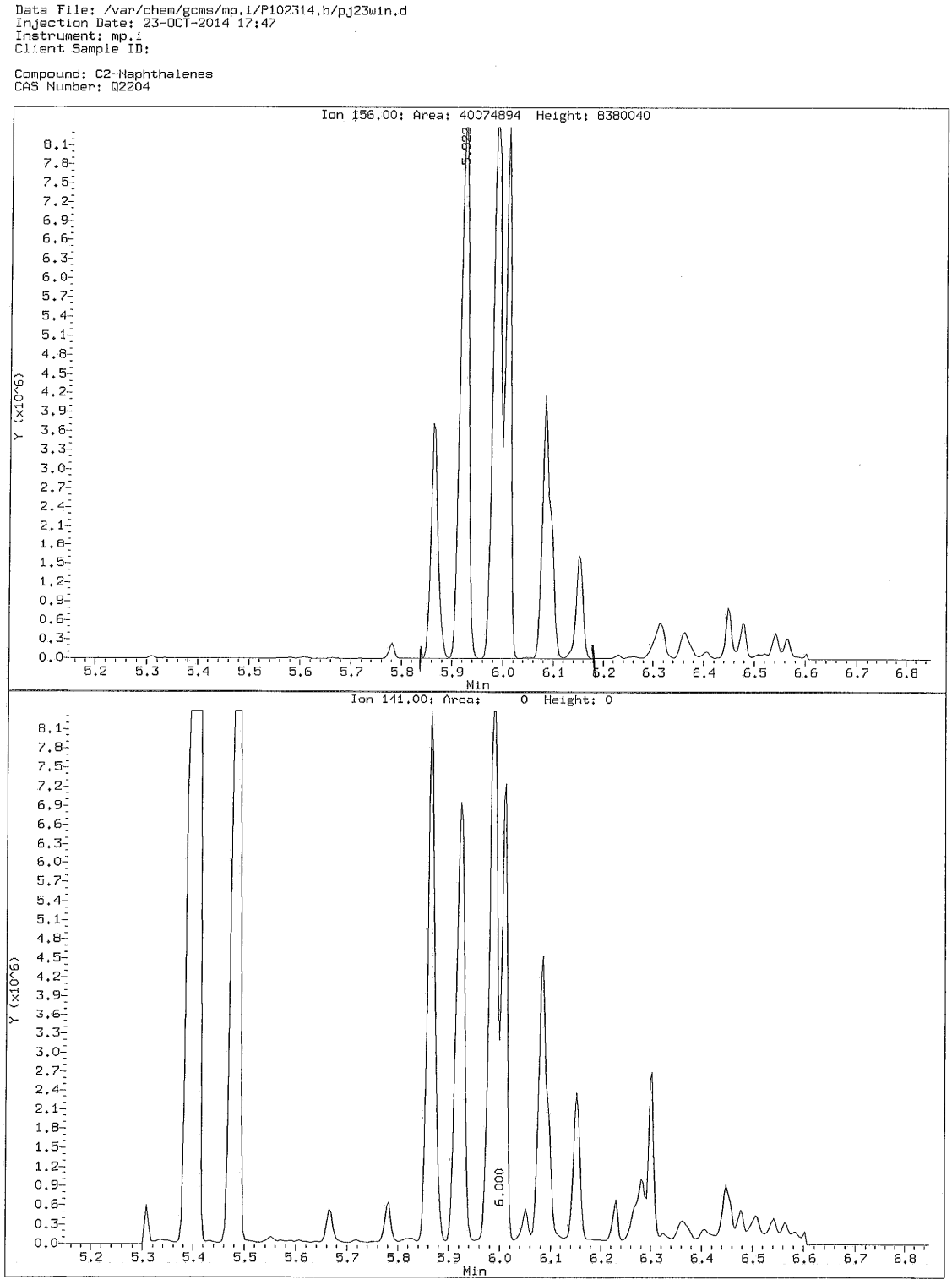


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

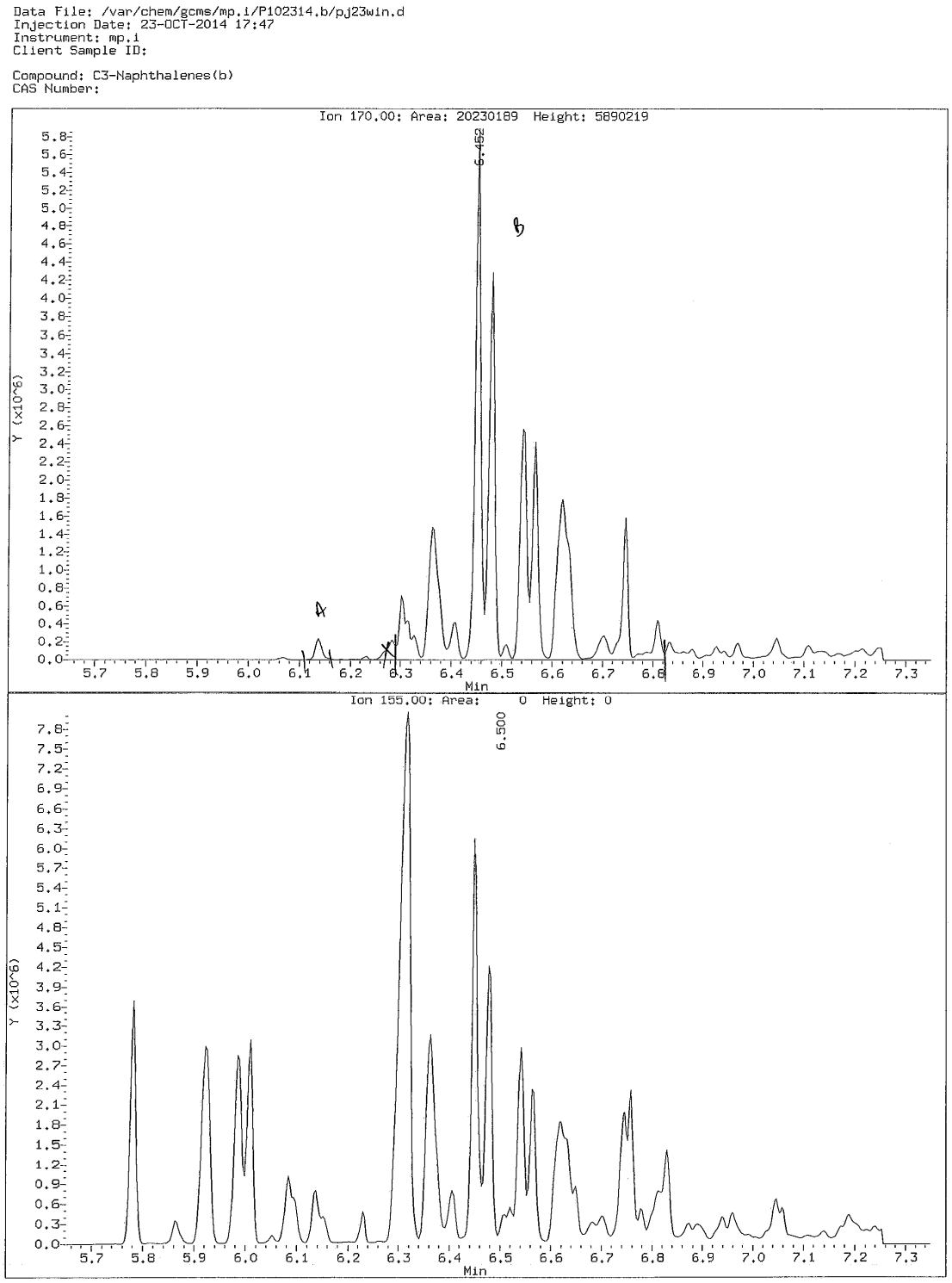


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

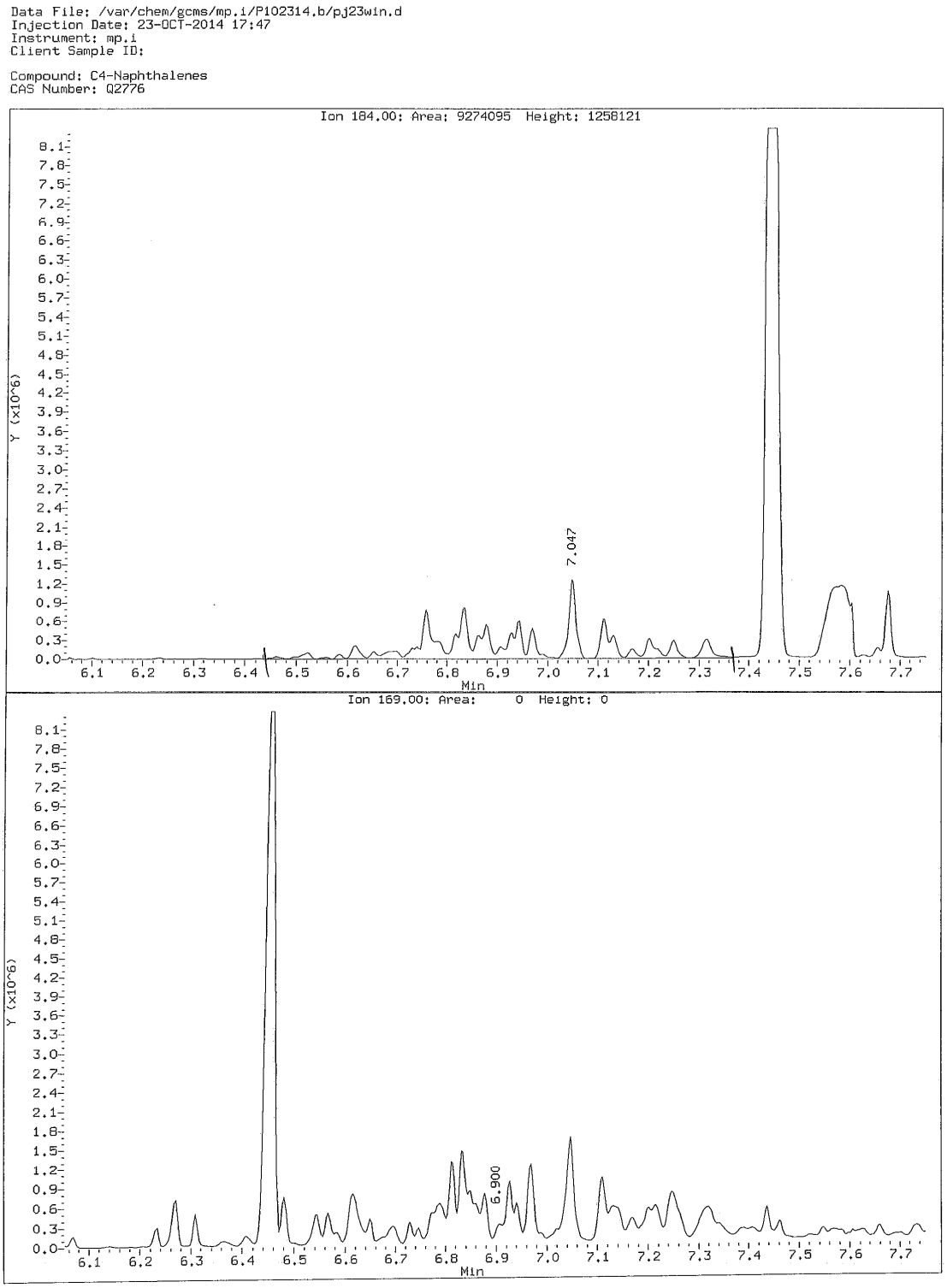


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

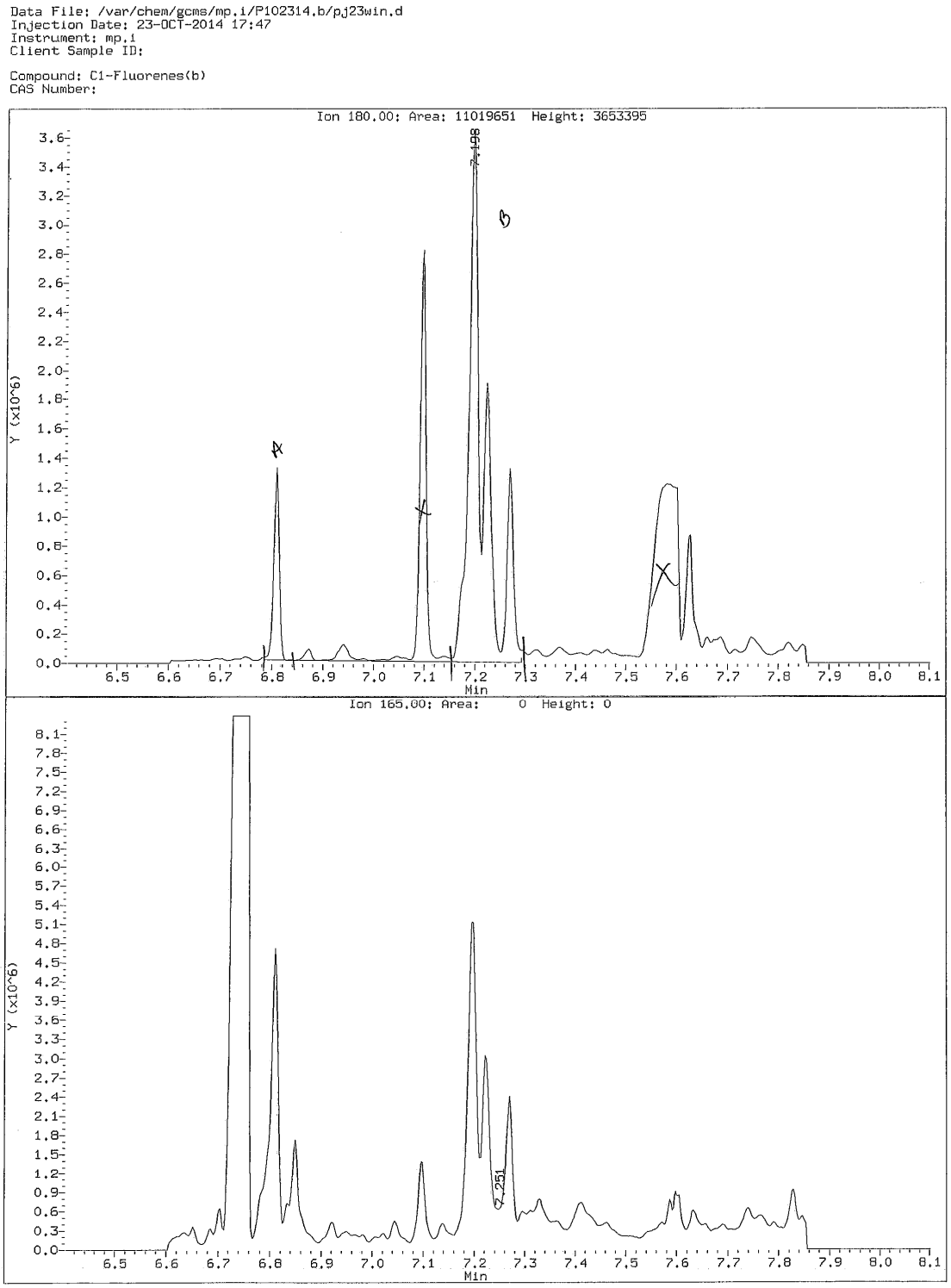


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

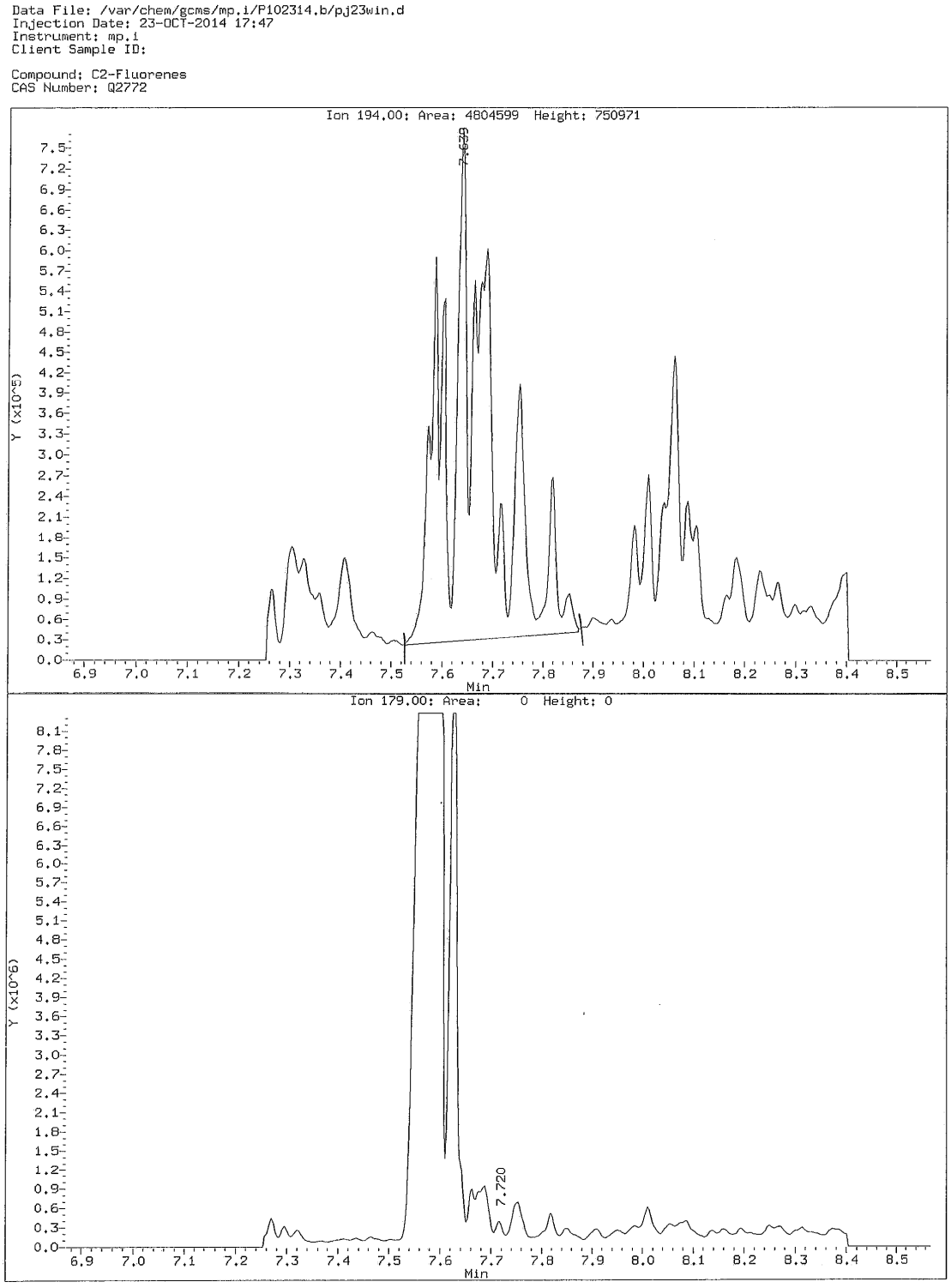


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

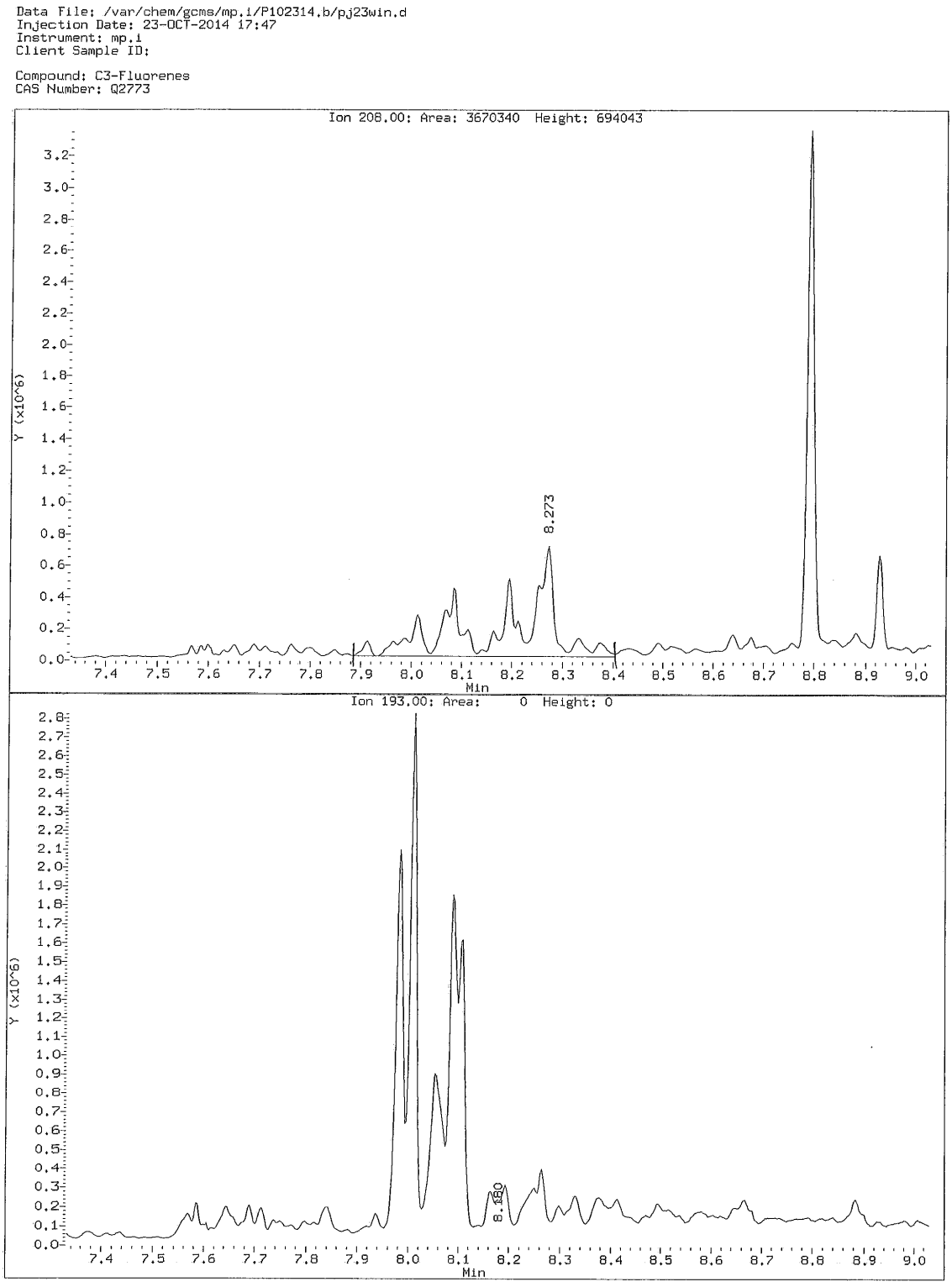


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

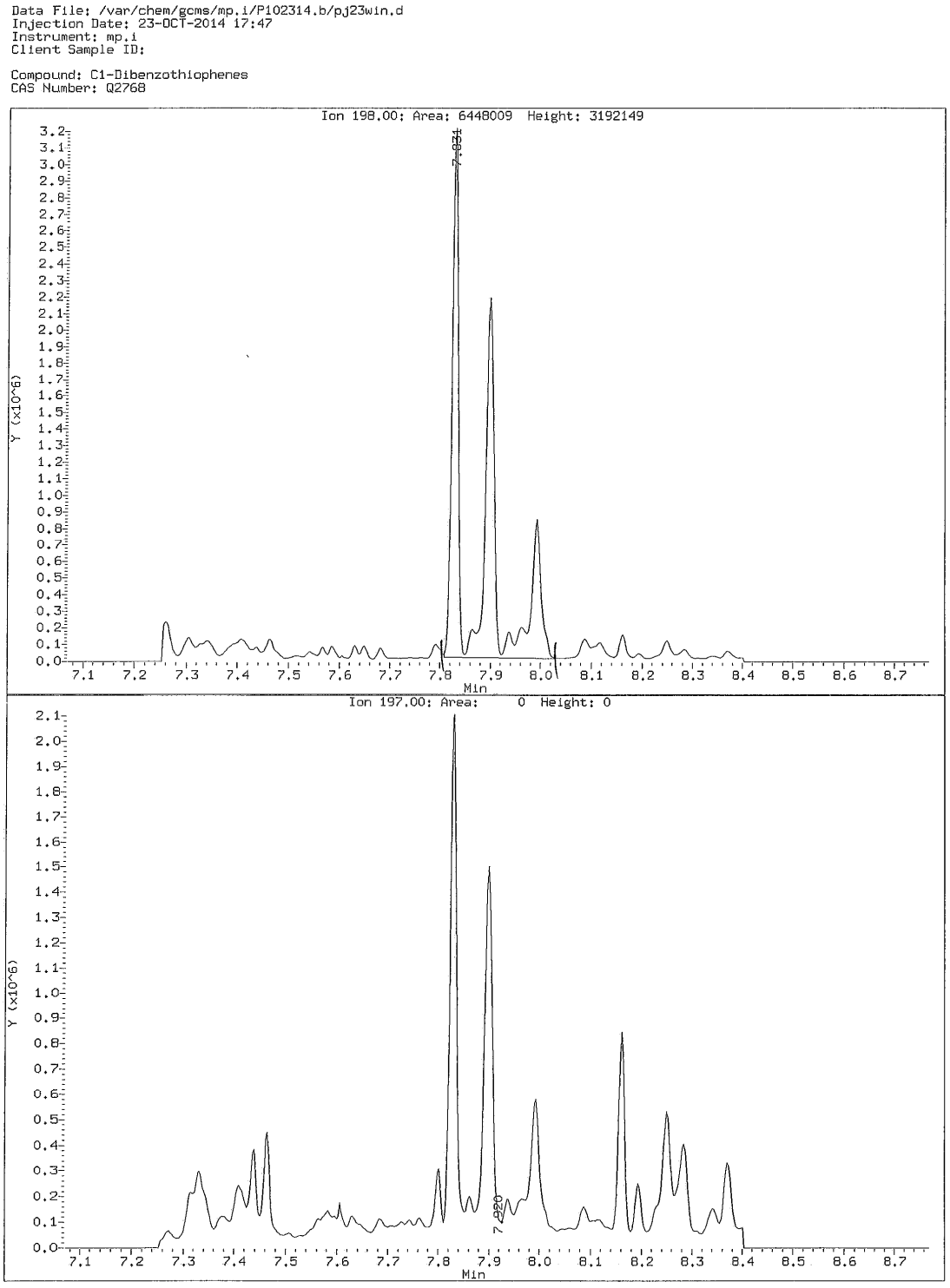


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

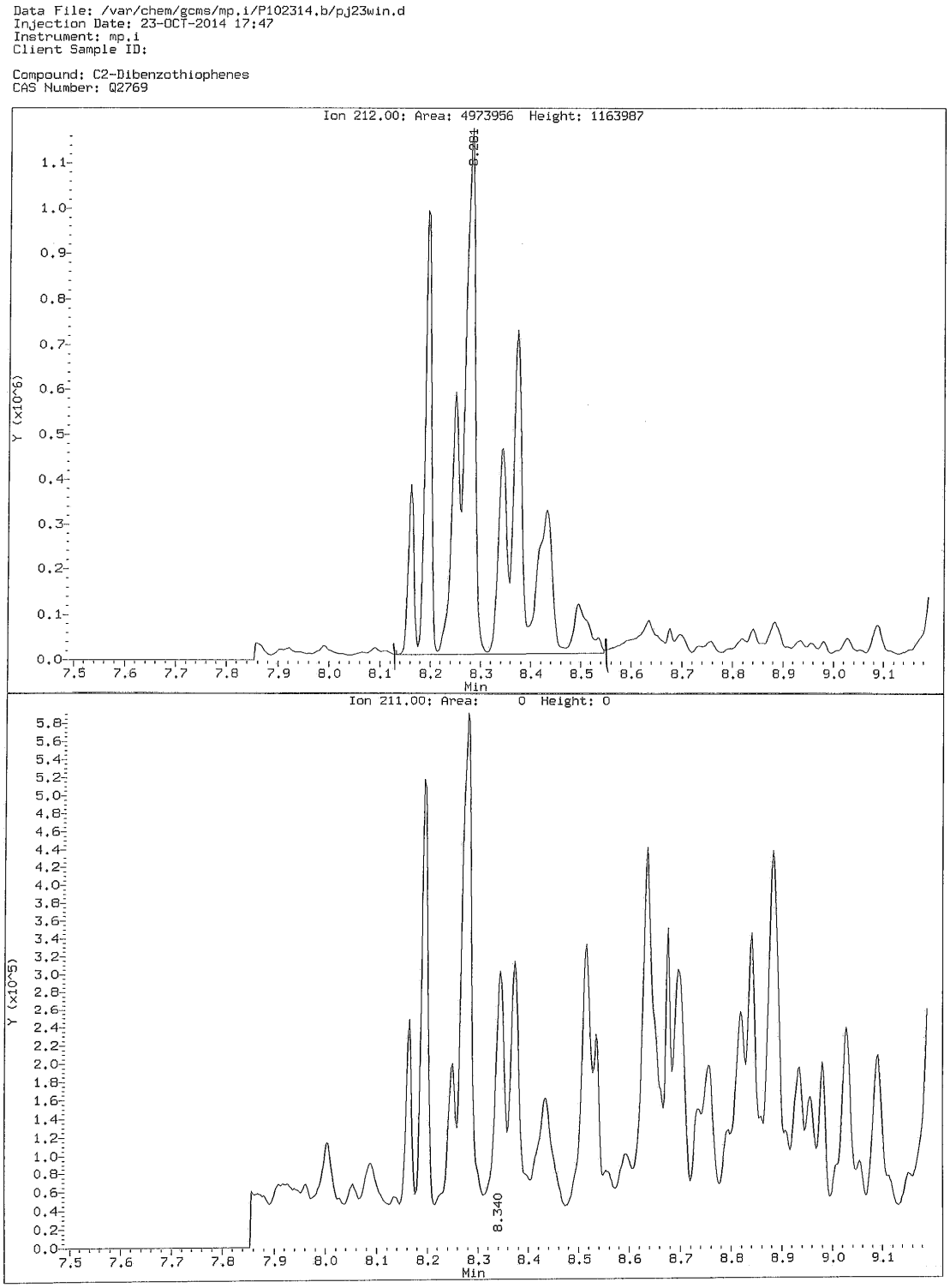


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

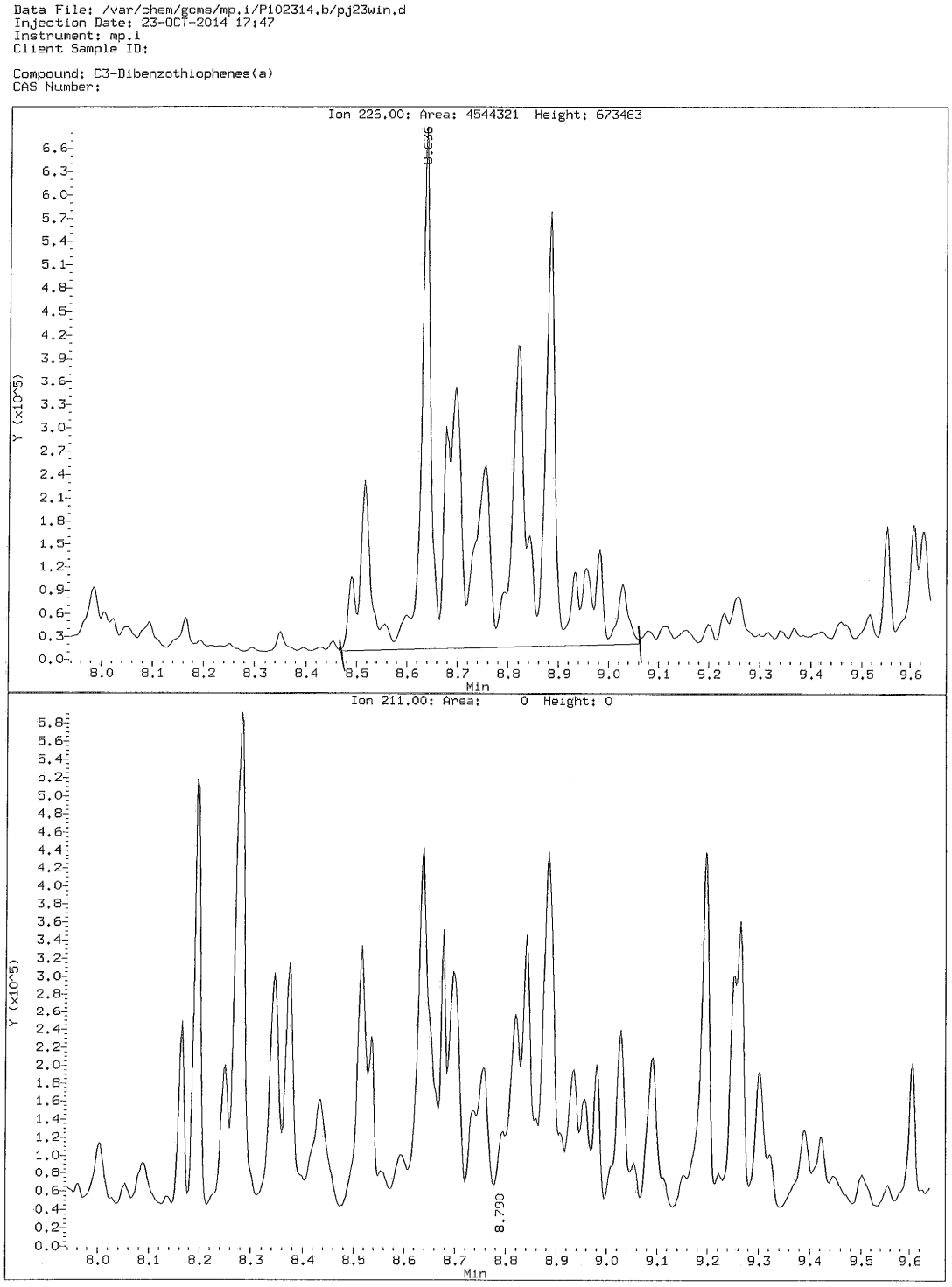


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

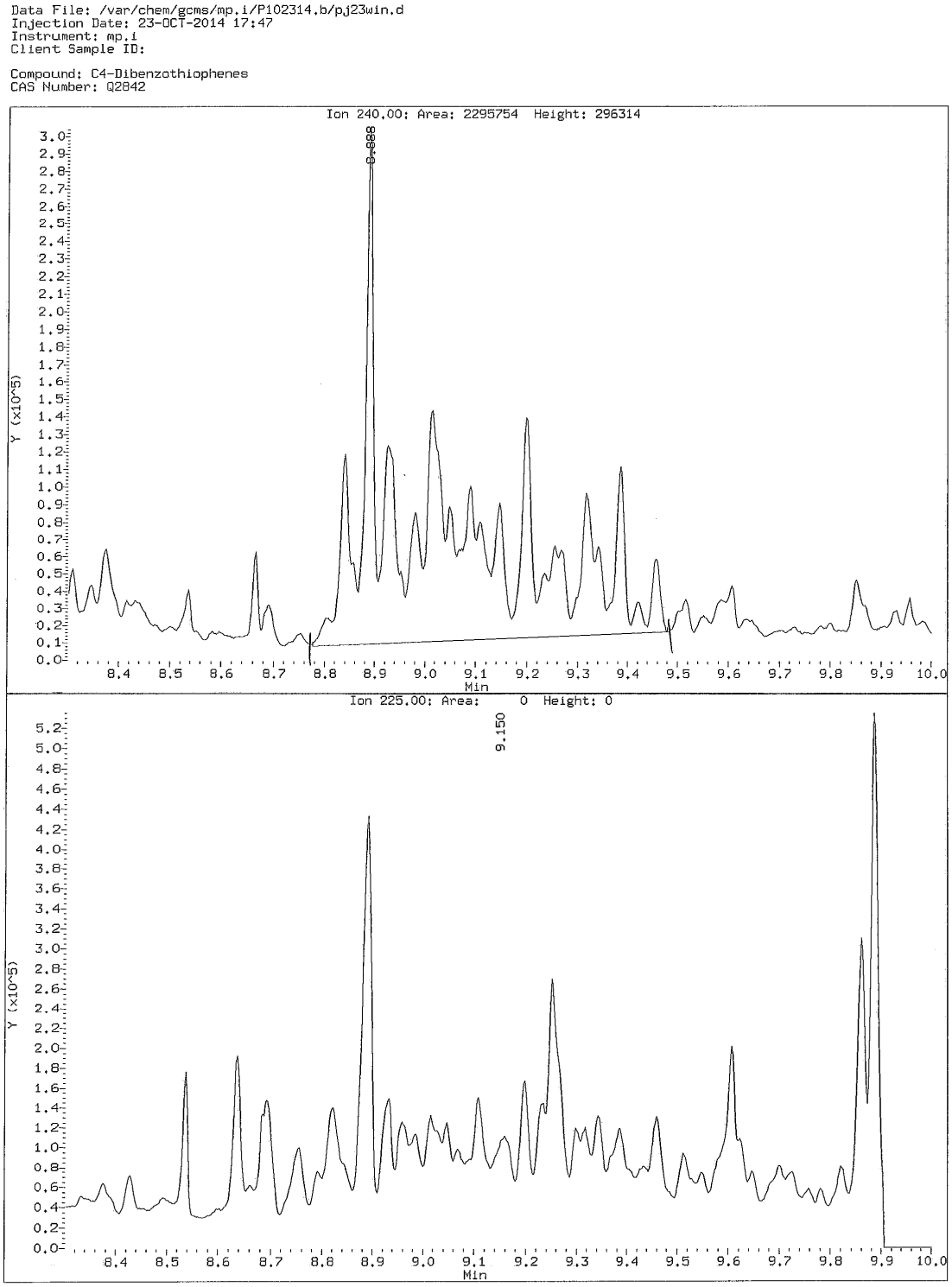


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

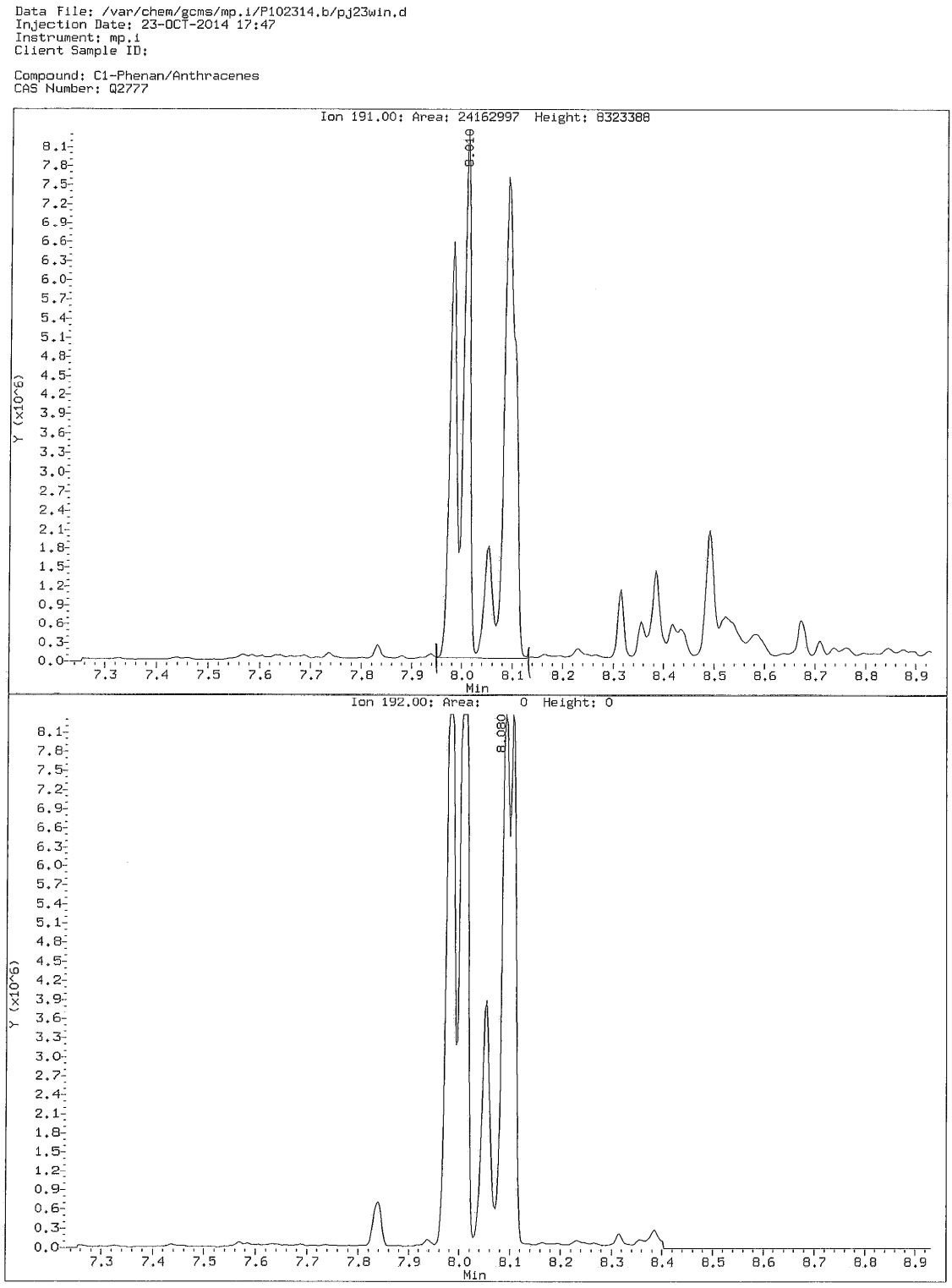


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

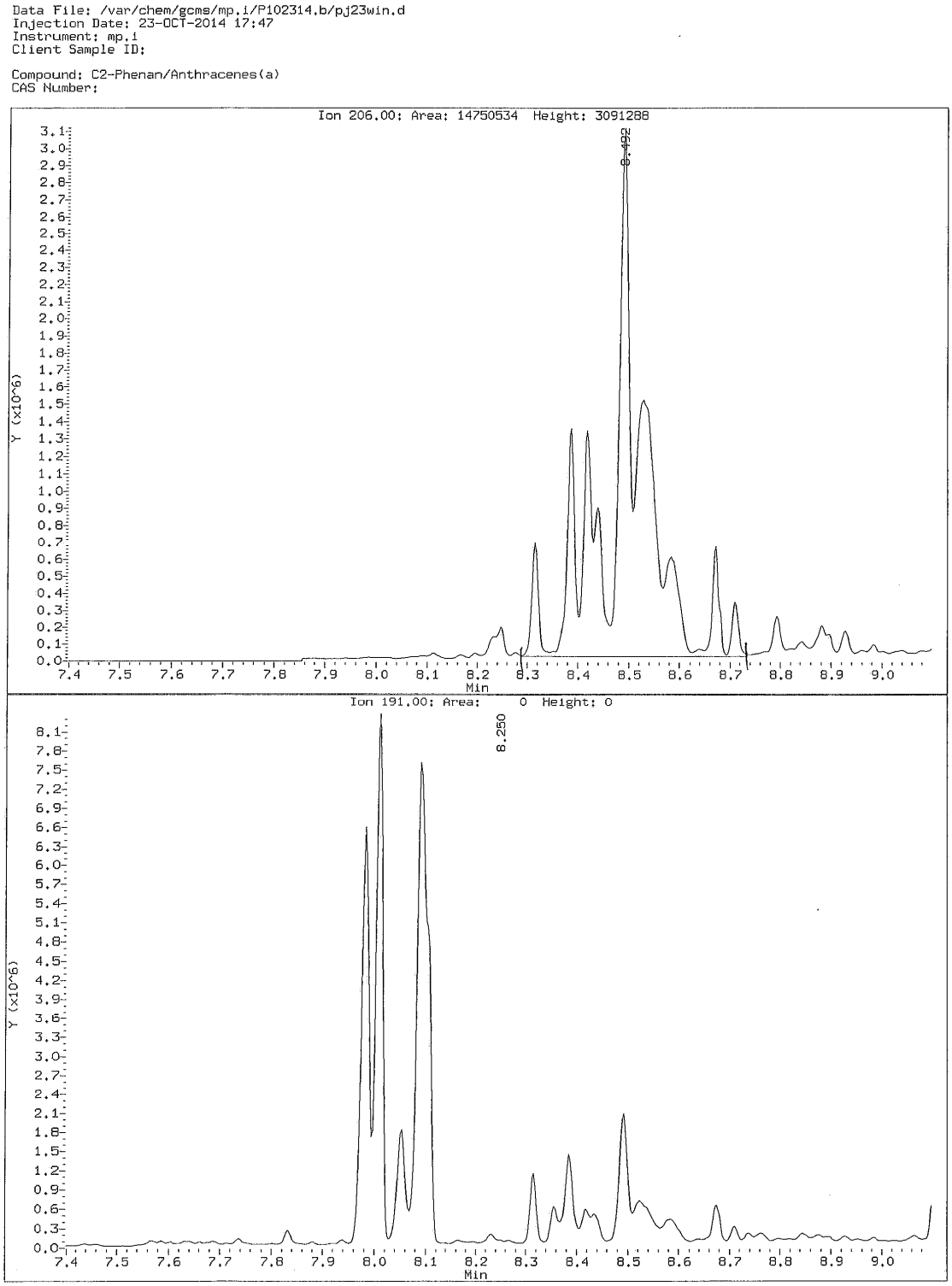


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

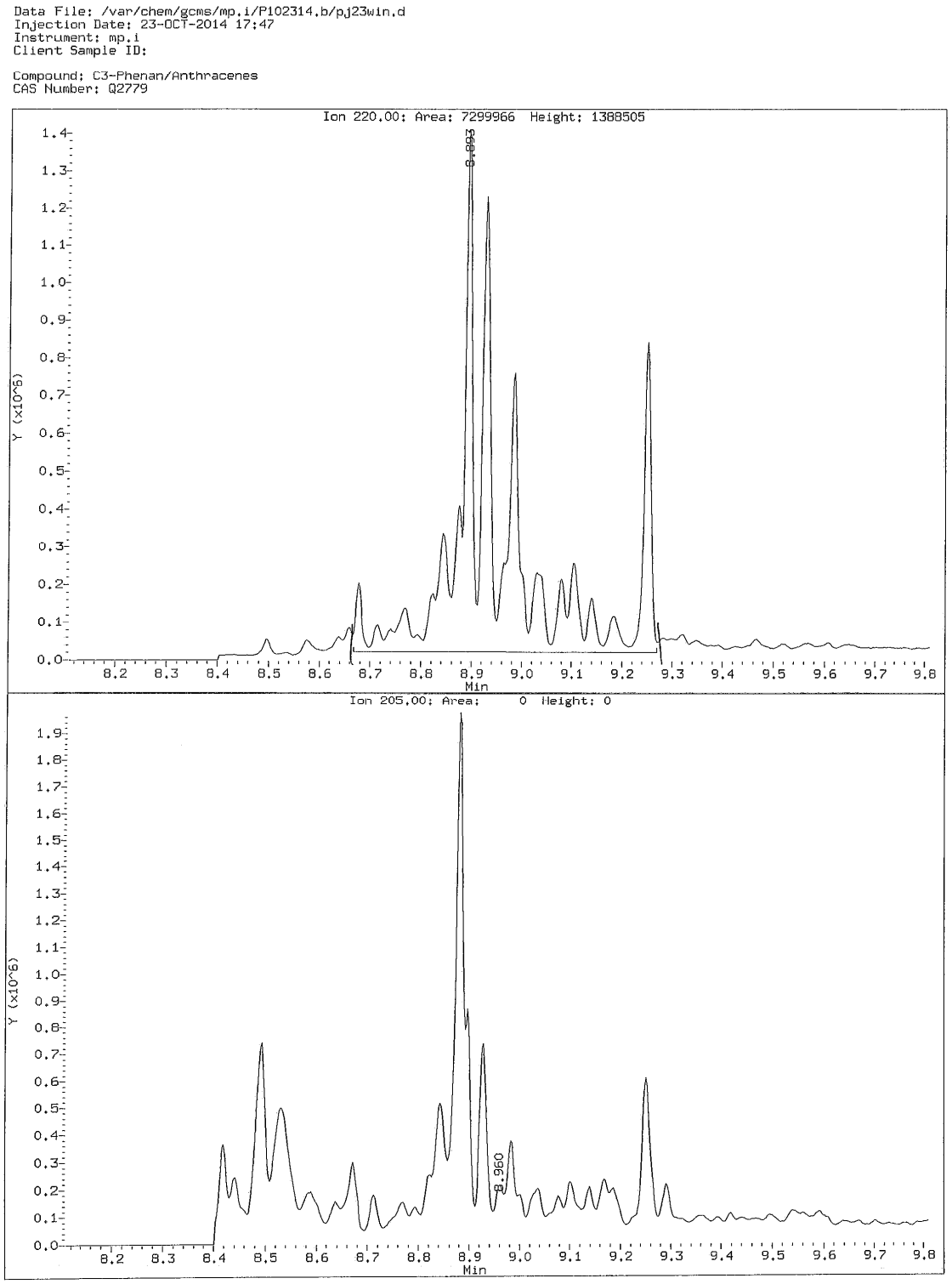


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

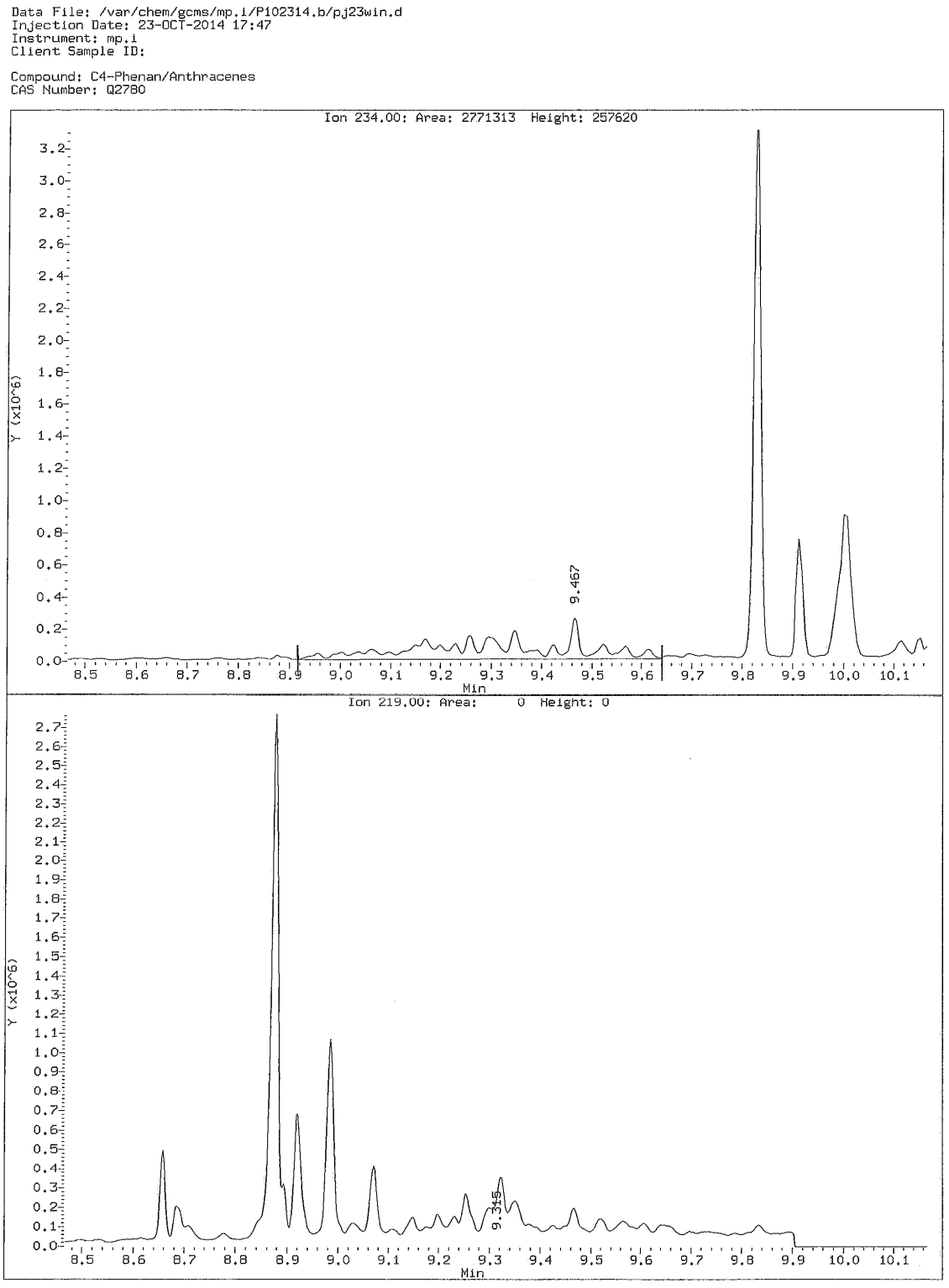


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

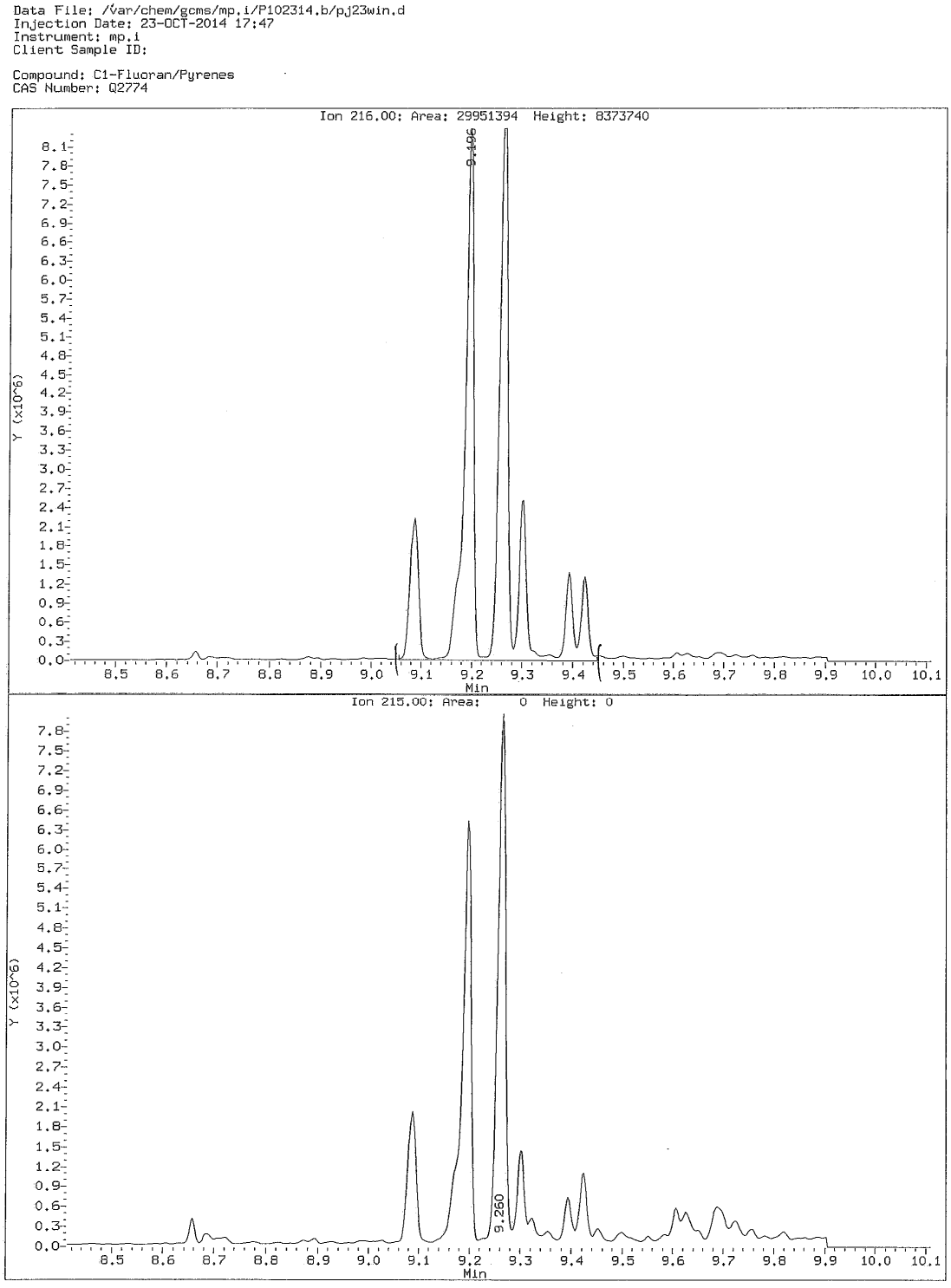


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

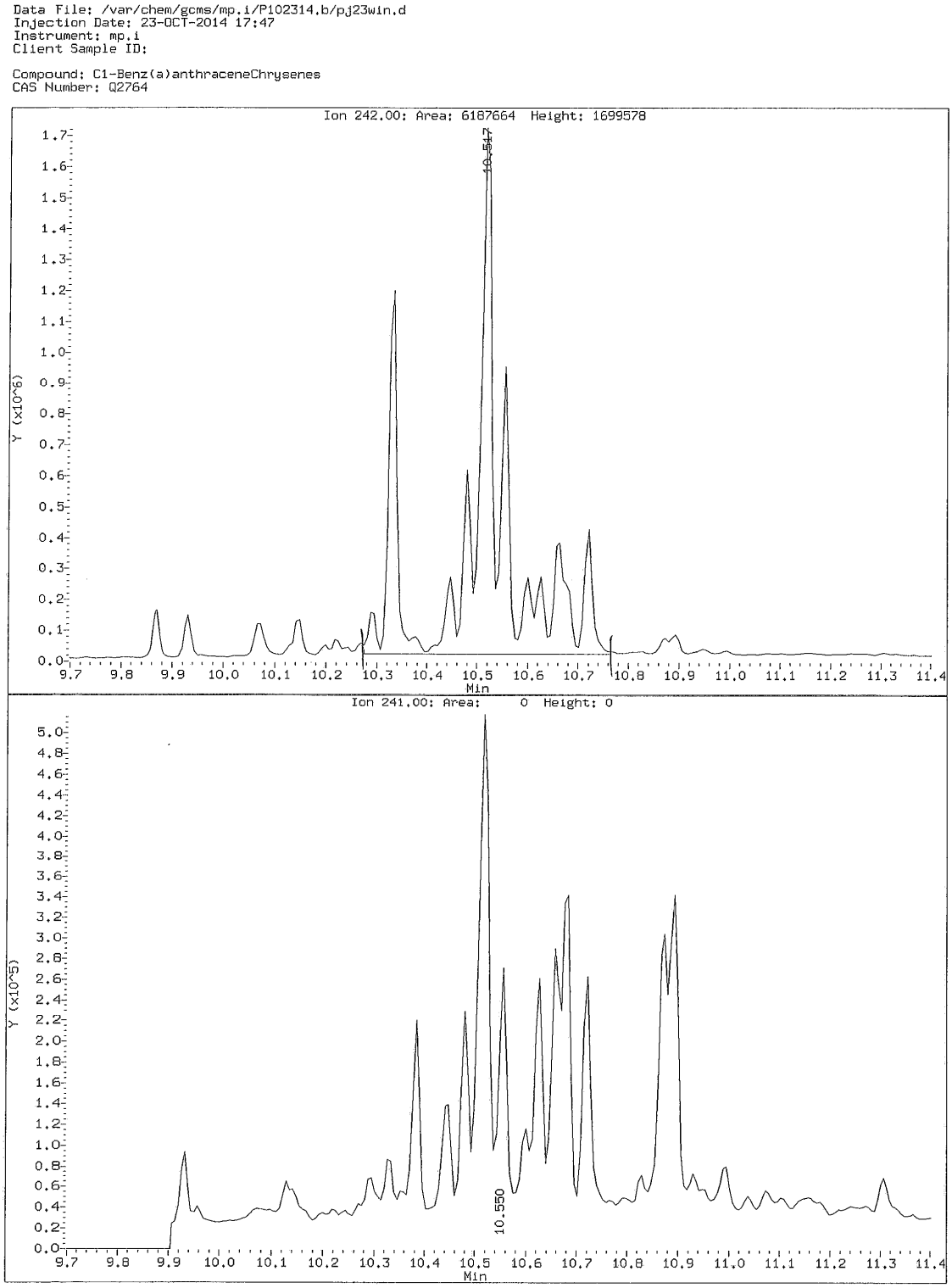


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

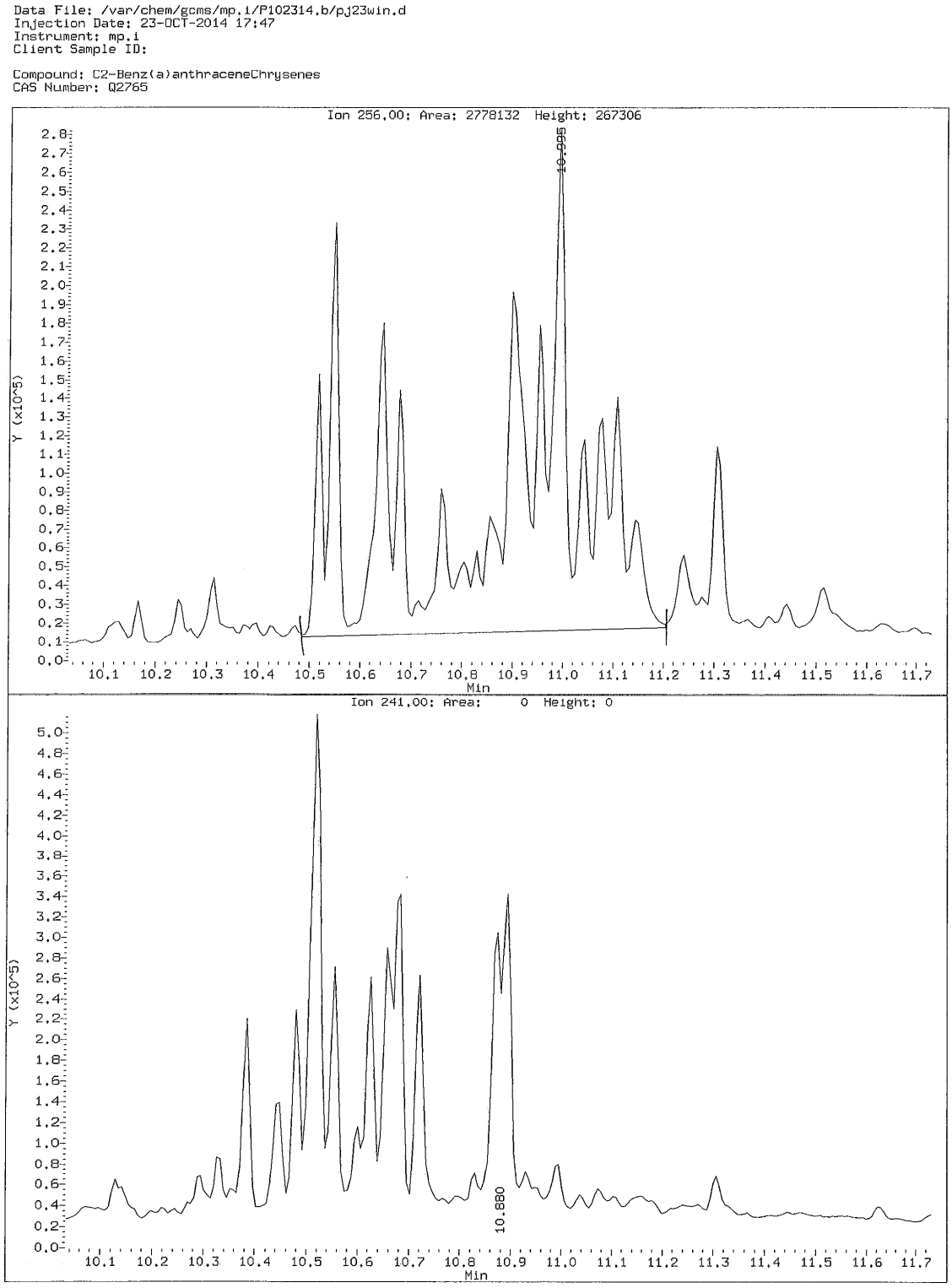


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

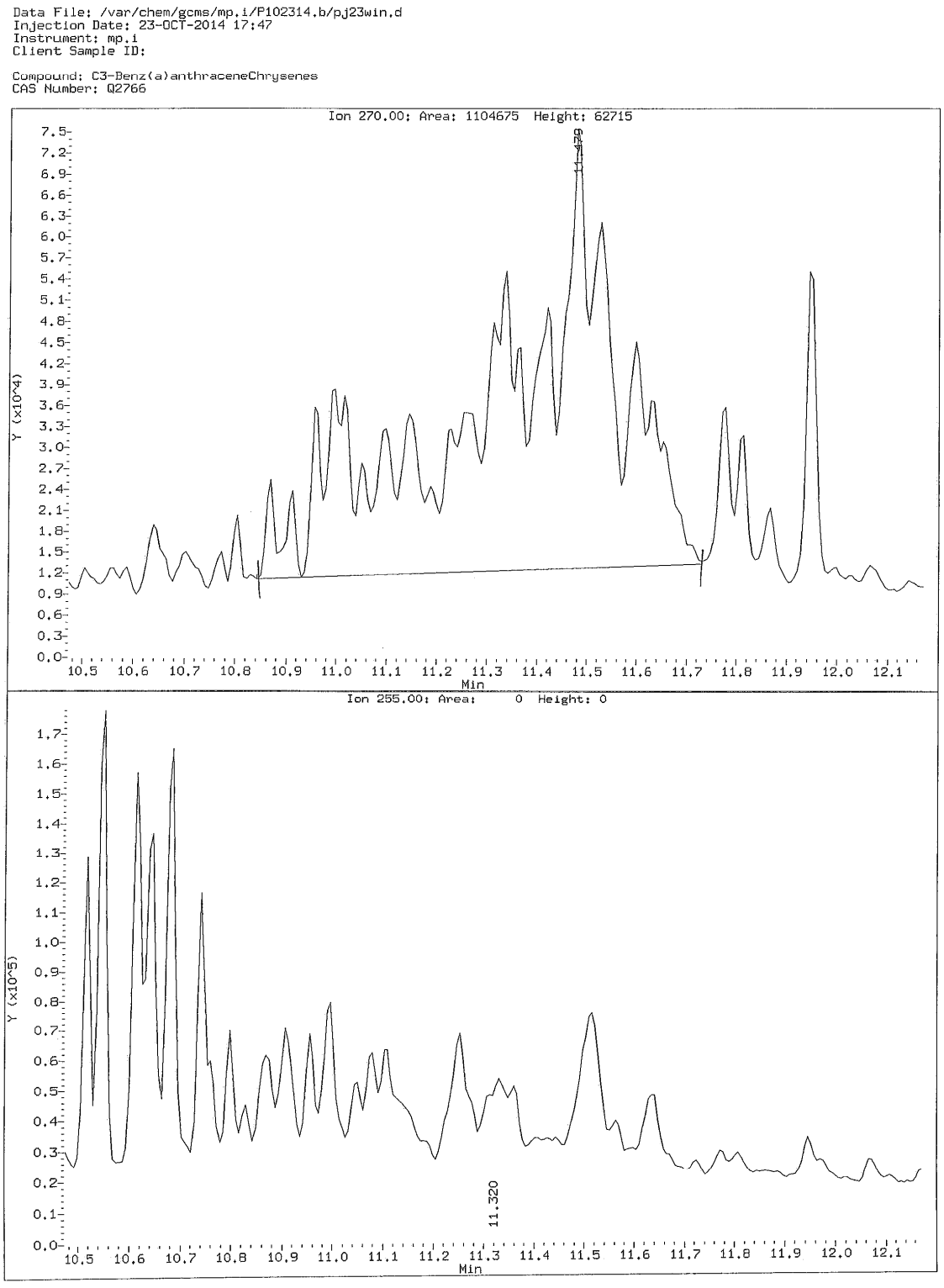
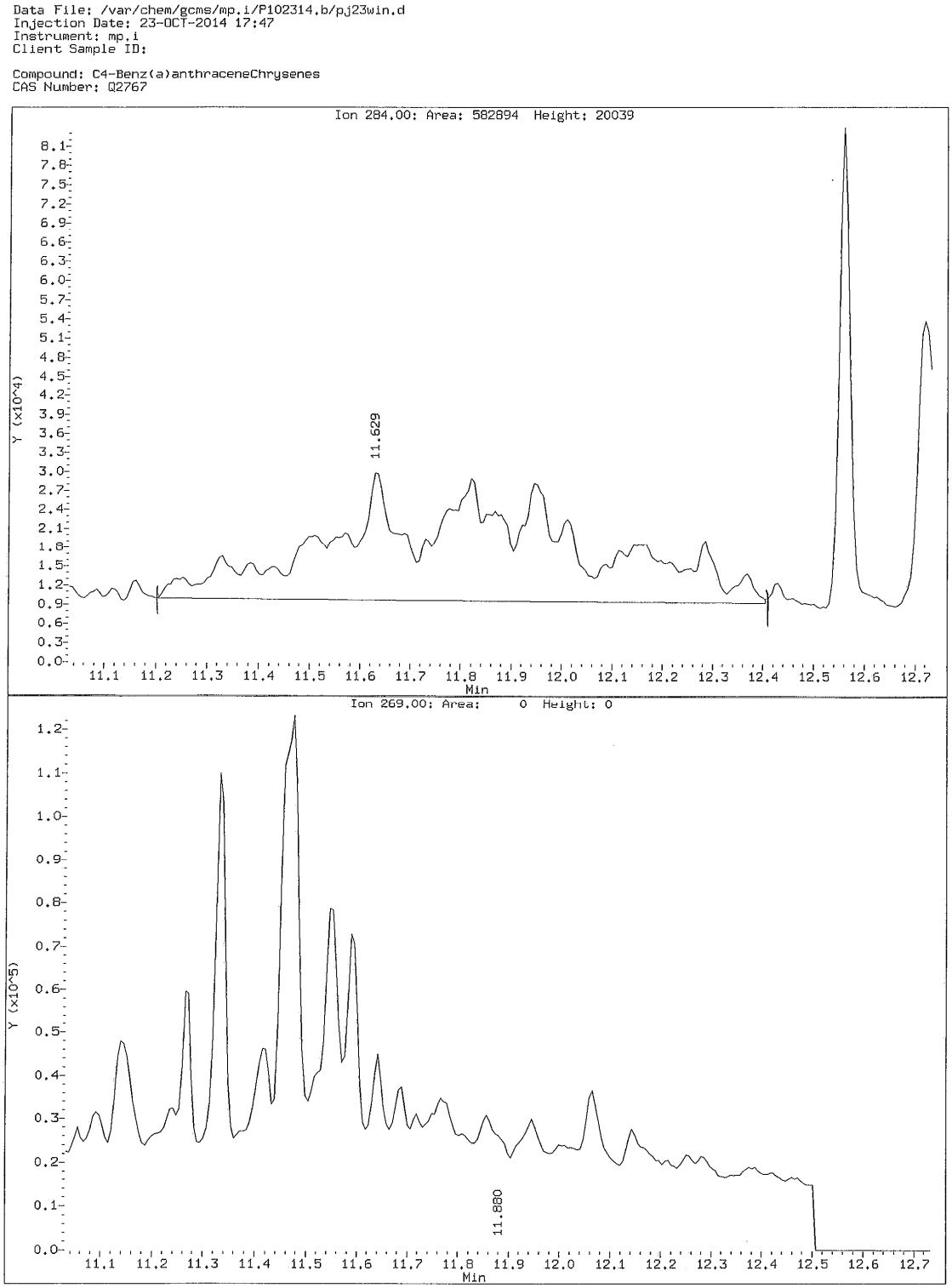


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)



TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Extraction of Selected Semivolatile Organic Compounds and Alkylated PAHs for Analysis by GC/MS-SIM

(SUPERSEDES: KNOX-OP-0023, Rev. 2)

Prepared By: David Mathiel

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Technical Specialist

Approved By: Kevin McGee 2/27/15
Quality Assurance Manager

Approved By: Barbara Clay 2-28-15
Environmental, Health and Safety Coordinator

Approved By: Christopher Russell 03/02/15
Laboratory Director

1. Scope and Application

1.1. This procedure is used by TestAmerica Knoxville for the extraction of selected semivolatile organic compounds and alkylated polynuclear aromatic hydrocarbons (PAHs) from a variety of environmental matrices (including water, soil, sediment, tissue and waste) for analysis by gas chromatography/mass spectrometry with selected ion monitoring (GC/MS-SIM). This procedure is designed to meet analytical program requirements where TestAmerica SOP KNOX-ID-0016 is specified.

1.2. Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PAHs and other target compounds. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2. Summary of Method

2.1. Screening and protocol assignment

2.1.1. Soil, sediment, tissue and waste samples may be screened by GC/FID prior to extraction. Variations to sample size, spiking levels and/or final volume are established based on the screening result.

2.2. Extraction

2.2.1. Aqueous samples: Stable isotopically labeled analogs of the PAHs (i.e., internal standards) are spiked into a 1 L sample and the sample is extracted with methylene chloride using continuous liquid/liquid extraction (CLLE).

2.2.2. Solid and sediment samples: Internal standards are spiked into a sample containing 10 g of solids. The sample is extracted for at least 16 hours with methylene chloride using a Soxhlet extractor. The extract is concentrated for cleanup.

NOTE: Sample sizes may be adjusted for dry weight or processed as received. The laboratory default for soil samples is to process as received. The laboratory default for sediment samples is to adjust the sample amount extracted to 10 g dry weight.

2.2.3. Tissue samples: A 10 g aliquot of homogenized tissue is blended with sodium sulfate, spiked with the internal standards, and extracted for at least 16 hours in a Soxhlet extractor using methylene chloride. If required, a portion of the extract is used to determine the lipids content. (Refer to SOP KNOX-OP-0020, “Gravimetric Percent Lipids Determination”, current revision.) The remaining extract is concentrated for cleanup.

2.2.4. Waste samples: Non-aqueous liquids such as oils and organic solvents are spiked with internal standards and diluted in methylene chloride.

2.2.5. Multi-phase samples: Samples containing multiple phases are separated and the phases are extracted following the procedures for the appropriate matrix. The extracts may be combined for cleanup and analysis or processed separately. Specific handling of multi-phase samples should be discussed and documented with the project manager prior to extraction of samples.

2.3. After extraction, samples may be cleaned up using gel-permeation chromatography and/or silica gel column chromatography.

2.4. After cleanup, recovery standards are added and the extracts are concentrated to 0.5 mL. Extracts are delivered to the GC/MS lab for analysis. Refer to SOP KNOX-ID-0016, "Isotope Dilution Analysis of Selected Semivolatile Organic Compounds and Alkylated PAHs by Gas Chromatography/Mass Spectrometry - Selected Ion Monitoring (GC/MS-SIM)", current revision.

3. Definitions

3.1. Labeled Internal Standards - Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample and calibration solution. They are added to the sample before extraction and are used to calculate the concentration of the target analytes.

3.2. Recovery Standard - Labeled compounds which are added to every sample, blank and quality control spike sample extract prior to analysis. They are used to measure the recovery of the internal standards.

3.3. Additional definitions can be found in the TestAmerica Knoxville Quality Assurance Manual (QAM).

4. Interferences

4.1. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of analysis by performing laboratory method blanks. Analysts should avoid using PVC gloves, powdered gloves or gloves with measurable levels of phthalates.

4.2. The use of high purity reagents and solvents helps minimize interference problems.

5. Safety

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Corporate Safety Manual),

laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. For the operations described herein, Nitrile gloves are to be worn. For operations using solvents that may splash, SilverShield® gloves are recommended. SilverShield® gloves protect against breakthrough for most of the solvents used in this procedure.

5.4. When using a scalpel, wear cut-resistant gloves and cut away from your hand.

5.5. All procedures that involve solvents such as acetone, methylene chloride, toluene and hexane (e.g., glassware cleaning and the preparation of standards and reagents) must be conducted in a fume hood with the sash closed as far as the operations permit.

5.6. Safety glasses or a face shield must be used when employees are using solvents to rinse or clean glassware.

5.7. Personal Hygiene: Thorough washing of hands and forearms is recommended after each manipulation and before breaks.

5.8. Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

5.9. The following is a list of the 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 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.
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.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Toluene	Flammable, Poison, Irritant	200 ppm-TWA, 300 ppm-Ceiling	Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.9.1. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include the following PAHs: benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

5.10. Exposure to chemicals must be maintained **as low as reasonably achievable**; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers must be kept closed unless transfers are being made.

5.11. All work must be stopped in the event of a known or potential compromise to the health or safety laboratory personnel. The situation must be reported **immediately** to a laboratory supervisor.

6. Equipment and Supplies

NOTE: All glassware used in extraction and cleanup procedures is precleaned as described in SOP KNOX-QA-0002, "Glassware Cleaning", current revision.

NOTE: When extracting PAH samples, all of the reusable glassware used in the extraction and concentration process is identified with a "L" or "LL" etch mark. Do not use any glassware that does not have an "L" or "LL" etching.

6.1. Miscellaneous Laboratory Equipment

6.1.1. Laboratory fume hood of sufficient size to contain the equipment used

for sample preparation

6.1.2. Oven, capable of maintaining a temperature of 105 ± 5°C and 125 to 135°C

6.1.3. Balance, >100 g capacity, accurate to ± 0.01 g

6.1.4. Syringes, various sizes

6.1.5. Borosilicate 5.75 inch and 9.0 inch disposable pipettes with rubber bulbs

6.1.6. Class A 1 mL pipettes

6.1.7. Round or flat bottom boiling flasks, 250 or 500 mL

6.1.8. Ultra-Pure PTFE boiling stones

6.1.9. Graduated cylinders, 100 mL, 1000 mL (other sizes may be used)

6.1.10. Glass wool, solvent rinsed

6.1.11. Heating mantles with temperature control

6.1.12. Bottle top solvent dispensers

6.1.13. PTFE squirt bottles, 500 mL

6.2. Tissue Homogenization Equipment:

6.2.1. Laboratory blender with glass body and stainless steel blades

6.2.2. Industrial meat grinder, Intedge Industries, Model C2H, or equivalent

6.2.3. Laboratory homogenizer, OMNI GLH-01, Model LR060902, or equivalent

6.2.4. Scalpels or knives

6.2.5. Cut-resistant gloves

6.3. Continuous Liquid/Liquid Extraction Equipment

6.3.1. Continuous liquid/liquid extractors (CLLE)

6.3.2. Glass condensers, capable of fitting on top of CLLE

6.4. Solid/Tissue Sample Extraction Equipment

6.4.1. Soxhlet extractor, 50-mm ID, 200-mL capacity with 500 mL flat bottom flask

6.4.2. Glass condensers, capable of fitting on top of Soxhlet apparatus

6.4.3. Whatman high purity glass fiber extraction thimbles

6.4.4. Beakers, 500 mL

6.4.5. Spatulas, stainless steel or wood

6.5. Filtration Equipment

6.5.1. Glass or stainless steel funnels

6.5.2. Filter Paper, Whatman 41 or equivalent

6.5.3. Buchner funnel, 15 cm

6.5.4. Glass-fiber filter paper for Buchner funnel

6.6. Cleanup Equipment

6.6.1. GPC Cleanup System, J2 Scientific Prep line, Accuprep or equivalent

6.6.2. Disposable pipets, 150 mm long x 5 mm ID

6.6.3. Disposable pipets, 230 mm long x 5 mm ID

6.6.4. 20 mm x 240 mm glass columns with support ring and tapered tip, for silica gel cleanup

6.6.5. Vortex mixer

6.7. Concentration Equipment

6.7.1. Nitrogen blowdown apparatus, N-EVAP (Organomation Associates, Inc., South Berlin, MA), installed in a fume hood

6.7.2. Kuderna-Danish (KD) Apparatus, 500 mL

6.7.3. Concentrator tubes, 10 mL, attached to KD with clips

6.7.4. Snyder columns, three-ball macro

6.7.5. Water bath, heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.

6.8. Sample Vials

6.8.1. Borosilicate glass, 12 mL and 40 mL disposable with PTFE cap

6.8.2. Mini vials, 2 mL capacity with 0.5 mL calibrated markings, with PTFE-faced, rubber septa and screw caps

6.8.3. Amber glass vials with PTFE-lined screw caps

6.9. Screening Equipment

6.9.1. Shaker table or ultrasonic bath

6.9.2. An analytical system complete with a gas chromatograph with a flame ionization detector (FID) and a data system capable of measuring peak response

7. Reagents and Standards

7.1. Reagent water must be produced by a Millipore DI system, or equivalent, that is capable of producing water with ≥18 megohm-cm (MΩ-cm) resistivity. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Acetone, methylene chloride, toluene and hexane, pesticide quality, or equivalent

7.3. Sodium sulfate, reagent grade, anhydrous, J.T Baker 3375, or equivalent

7.3.1. Sodium sulfate may be cleaned by putting approximately 600 g of sodium sulfate in large amber-colored glass jars and completely covering with methylene chloride, stirring the mixture with a glass stirring rod and letting the sodium sulfate soak for 5 minutes. The methylene chloride is drained and this step is repeated. After the methylene chloride is drained, the sodium sulfate is transferred to a Buchner funnel fitted onto a vacuum flask and rinsed 2 times with methylene chloride while a vacuum is being applied. The sodium sulfate is then placed into shallow borosilicate glass dishes where it is allowed to dry. It is placed in an oven at 125-130°C for 1 hour to complete the drying process. After drying, the sodium sulfate is transferred into pre-cleaned glass jars with PTFE lined screw caps.

7.4. Silica gel, S679-212, Fisher Chromatographic Silica Gel, 100-200 mesh or equivalent: Prepare by Soxhlet extraction with methylene chloride for at least 6 hours. Transfer to a shallow, borosilicate glass dish and air dry. After drying, cover with aluminum foil and activate in an oven at approximately 130°C for a minimum of four (4) hours. Store in labeled glass jars in a desiccator until use.

7.5. Standard Solutions: Obtained as individual solutions and prepared solutions from Cambridge Isotope Laboratories, Radian, Cerilliant, Ultra Scientific and Supelco. Refer to Table 1 for details.

7.5.1. Refer to SOP KNOX-QA-0001, “Standard/Reagent Labeling and Documentation”, current revision, for guidance on standard documentation and labeling.

7.5.2. LCS Spiking Solution: See Table 1 for a complete list of compounds and concentrations. The solution is prepared with acetone as the solvent.

7.5.3. Internal Standard Spiking Solution: See Table 1 for a complete list of compounds and concentrations. The solution is prepared with acetone as the solvent.

7.5.4. Recovery Standard Spiking Solution: See Table 1 for a complete list of compounds and concentrations. The solution is prepared with hexane as the solvent.

7.5.5. Stability of Solutions: Sealed standard solutions used for quantitative purposes expire 3 years from the date received or on the manufacturer's expiration date, unless otherwise specified by program requirements. Lab prepared stock solutions expire 2 years after preparation; lab prepared spiking solutions expire 1 year after preparation. No daughter solution expiration date can exceed the parent expiration date. Standards are stored at 6^{o}C or less, or per manufacturer's recommendation.

8. Sample Collection, Preservation and Storage

8.1. Sampling is not performed for this method by TestAmerica Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, "Sample Receipt and Log In", current revision.

8.2. Aqueous samples should be collected in amber glass jars with PTFE lined lids.

8.3. Solid samples should be collected in 4 oz amber glass jars with PTFE lined lids.

8.4. Sample Storage

8.4.1. Store tissue samples in the dark at <-10°C.

8.4.2. Store aqueous samples and extracts in the dark at ≤6°C.

8.4.3. Store solid and semisolid samples and extracts in the dark at ≤6°C.

8.5. Holding Times:

8.5.1. Solid samples have a 14 day holding time from collection to extraction.

8.5.2. Water samples have a 7 day holding time from collection to extraction.

8.5.3. Tissue samples have a 1 year holding time from collection to extraction.

9. Quality Control

9.1. Initial Demonstration of Capability and Method Detection Limit Studies: The initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin. Refer to Table 2 for the initial demonstration of capability acceptance criteria.

9.2. Internal Standards: Every sample, blank, and QC sample is spiked with isotopically labeled internal standards prior to extraction. Internal standards in samples, blanks, and QC samples are used to calculate the concentration of the target analytes.

9.3. Recovery Standards: Every sample, blank, and QC sample extract is spiked with

labeled recovery standards prior to analysis. They are used to measure the recovery of the internal standards.

9.4. Method Blank: A laboratory method blank must be run along with each batch of 20 or fewer samples. The method blank is processed in the same manner and at the same time as the associated samples. The method blank is used to identify any background interference or contamination of the analytical system that may lead to the reporting of elevated concentration levels or false positive data. Refer to the table below for a cross-reference between the sample matrix and method blank matrix.

Sample Matrix	Method Blank Matrix
Aqueous	Reagent water
Solid	Sodium sulfate
Tissue	Sodium sulfate
Waste	Methylene chloride

9.4.1. Samples associated with a contaminated method blank must be re-extracted and reanalyzed with an acceptable method blank. The project manager may consult the client to determine project needs. If the client prefers that the original data be reported, the associated data may be reported in lieu of reanalysis. A nonconformance memo and narrative addressing the analytical issues must be generated.

9.4.2. If the method blank contains any compounds of interest above the reporting limit, check solvents, reagents, standard solutions apparatus and glassware to locate and eliminate the source of contamination before any more samples are processed.

9.5. Laboratory Control Sample: A laboratory control sample (LCS) is prepared and analyzed with every batch of 20 or fewer samples. The LCS extract must be subject to the same cleanup procedures as the associated sample extracts. LCS spike components and concentrations are listed in Table 1. Refer to the table below for a cross-reference between the sample matrix and LCS matrix.

Sample Matrix	LCS Matrix
Aqueous	Reagent water
Solid	Sodium sulfate
Tissue	Sodium sulfate
Waste	Methylene chloride

9.6. Client-specified matrix spike / matrix spike duplicate samples may be analyzed to provide additional precision and accuracy data.

9.7. Quality Assurance Summaries: Certain clients or regulatory programs may require specific project or program QC that may supersede these method requirements. Quality Assurance Summaries are developed to address these requirements.

10. Calibration and Standardization

10.1. Not applicable.

11. Procedure

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure, except those specified by project specific instructions, shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager, and QA Manager. If contractually required, the client shall be notified.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Samples are extracted by the following procedures depending upon sample matrix. Aqueous samples are prepared by continuous liquid/liquid extraction. Solid samples including soils, sediments, tissues and solid waste materials are prepared by Soxhlet extraction. Non-aqueous liquid wastes and organic solvents are prepared by waste dilution techniques.

NOTE: Samples should be removed from the refrigerator several hours before extraction and allowed to come to room temperature before measuring the volume or performing the extraction.

11.4. Aqueous Sample Extraction

11.4.1. Add several PTFE boiling stones to a flat-bottom boiling flask. Assemble the CLLE apparatus, making sure all the joints are seated properly. Add approximately 300-500 mL of methylene chloride to the extractor body.

11.4.2. Remove the internal standard and LCS spiking solutions from the refrigerator and allow them to warm to room temperature.

11.4.3. If <1% solids are observed in the sample, weigh the sample container on a balance (± 1 g); tare the sample and container. Transfer the sample to the CLLE. Rinse the sample bottle with approximately 60 mL methylene chloride and transfer to the extractor. Reweigh the container. Assume a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter.

11.4.3.1. If >1% solids are present in the water sample, the sample volume is measured volumetrically.

11.4.3.2. For brackish water or salt water, weigh 1.0 mL of the sample. If the weight is <0.98 or >1.02, adjust the sample volume based on the sample density.

11.4.4. Rinse the sample bottle with methylene chloride and add the rinsate to the CLLE.

NOTE: If the sample appears to have a solid content of >1%, the

project manager must be notified and consultation with the client should take place. In cases where the client wants the whole sample analyzed, the sample is filtered through a 0.45 μm glass fiber filter. The particulate on the filter and the filter itself are extracted by Soxhlet extraction following the procedure in this SOP. The resulting extract is combined with the extract of the aqueous portion during the concentration step.

11.4.5. Less than one liter of sample may be used for highly contaminated samples or if the reporting limit can be achieved with less than one liter of sample. In this event, dilute the sample to about 1 L with reagent water.

11.4.6. Use 1000 mL of reagent water for the method blank and the LCS.

11.4.7. Add 1.0 mL of the 0.25 μg/mL internal standard spiking solution to each sample, method blank and LCS. Additionally, add 1.0 mL of the 0.25 μg/mL LCS spiking solution to the LCS (and LCSD, MS/MSD, if required). Record the amount of spike used and the spike standard number on the extraction benchsheet.

NOTE: Rinse the walls of the CLLE with methylene chloride after the addition of the internal standard and LCS spike.

NOTE: Each time the samples are spiked, the spiking process should be witnessed by another analyst. Refer to Appendix I for the steps that must be taken.

11.4.8. If necessary, add reagent water to the extractor body until approximately 350 mL of methylene chloride is pushed over into the boiling flask to ensure proper operation and solvent cycling. Attach a cold condenser (about 10^{o}C). Turn on the heating mantle. Inspect joints for leaks once the solvent has begun cycling. Extract for at least 16 hours.

NOTE: Ensure that no air bubbles are present in the lines to the condensers. There should be a steady drip from the condensers (i.e., a drip rate of approximately 10 to 15 mL per minute).

NOTE: Wrap the boiling flask with aluminum foil during extraction to protect the extract from light.

11.4.9. Turn off the heating mantle and allow the extractor to cool.

11.4.10. If the samples will not be concentrated immediately, cover the boiling flask with aluminum foil. When the samples are ready to be concentrated, filter as described below:

- Place a funnel containing 30-60 g of anhydrous sodium sulfate on the Kuderna-Danish (K-D) flask or other glass container. The funnel can be plugged with glass wool enabling it to hold the

granular anhydrous sodium sulfate or filter paper may be used.

- Dry the extract in the boiling flask by filtering it through the sodium sulfate filled funnel. Note that it is not necessary or advisable to attempt to add the solvent remaining in the continuous extractor body to the extract.
- Rinse the boiling flask that contained the sample extract with 20 to 30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer. Dispose of solvent and water remaining in the extractor in the appropriate waste container.

11.4.11. Concentrate the extract to approximately 3-5 mL using low-level KD glassware. Solvent exchange the extract with hexane and concentrate to approximately 8 mL.

CAUTION: When extracting or concentrating a sample with hexane, toluene or any mixture containing these solvents, the analyst **must** add the boiling chips within 5 minutes of placing the flask on the heat source in order to prevent bumping of the solvent.

11.4.12. If the extract is colored or appears dirty, silica gel cleanup should be performed. Otherwise, place the extract in the N-EVAP concentration apparatus and reduce solvent volume to approximately 0.5 mL to 1.0 mL. Proceed to final concentration beginning with section 11.11.2.

11.5. Solid/Tissue/Waste Sample Screening (Optional)

11.5.1. Weigh out a 1g aliquot of the wet sample in a 40 mL vial and mix with a small amount of sodium sulfate. Add 10 mL hexane.

11.5.2. Cap tightly and extract in a cooled ultrasonic bath or on a shaker table for 1 hour.

11.5.3. Concentrate to 1 mL.

11.5.4. The screening results may be used as needed to adjust the amount of sample extracted, spiking volume, split ratio and/or final volume during sample preparation. Document this information with the screen data. Contact a technical director for details.

11.6. Sample Pretreatment for Tissue Samples

11.6.1. If the sample matrix is tissue and has not been homogenized prior to sample receipt, the entire sample is homogenized prior to extraction using an industrial meat grinder, a laboratory blender, or a laboratory homogenizer. Select the equipment that is most appropriate for the size and type of tissue received.

11.7. Solid Sample Extraction

11.7.1. Prepare and label the required number of Soxhlet systems. Refer to Knoxville SOP KNOX-QA-0002, current revision, for information on glassware cleaning procedures for extraction glassware. Visually inspect all glassware prior to use for scratches or cracks. Retire, repair or replace any glassware found to be damaged.

11.7.2. For soil samples, transfer a well-mixed 10 g aliquot (± 0.5 g) of the sample into a beaker or extraction thimble. Mix thoroughly with 20 g of sodium sulfate. Record the sample weight on the extraction benchsheet.

11.7.3. For sediment samples, adjust the amount weighed to achieve 10 to 10.5 g dry weight, if possible, using a maximum of 20 g sample. Determine the amount of sediment sample to extract using the "Sediment Extraction Amounts" spreadsheet on the local area network in the MSOffice\template\Knx OrgPrep directory. Transfer a well-mixed aliquot of the sample into a beaker or extraction thimble. Mix thoroughly with 20 g of sodium sulfate. Record the sample weight on the extraction benchsheet.

11.7.4. For tissue samples, weigh out 10 g (± 0.5 g) of homogenized tissue into a beaker or extraction thimble. Mix thoroughly with 20 g of sodium sulfate. Record the sample weight on the extraction benchsheet.

NOTE: If gravimetric lipids are to be determined using the tissue extracts, split the extract prior to the initiation of any cleanup steps and use 1 mL of the 10 mL extract for lipids determination. Refer to SOP KNOX-OP-0020, "Gravimetric Percent Lipids Determination", current revision.

11.7.5. Sodium sulfate is used for the blank and LCS.

11.7.6. Spike each sample with 1 mL of the 0.25 µg/mL internal standard spiking solution.

11.7.7. Spike the LCS (and LCSD, MS/MSD, if required) with 1 mL of the 0.25 µg/mL LCS spiking solution.

NOTE: Each time the samples are spiked, the spiking process should be witnessed by another analyst. Refer to Appendix I for the steps that must be taken.

11.7.8. If needed to keep the sample in the extraction thimble, add a small amount of glass wool to the top of the thimble.

11.7.9. Pour approximately 350 mL of methylene chloride into a 500 mL flat bottom flask. Place the flask in the heating mantle. Add several PTFE boiling stones.

11.7.10. Assemble the Soxhlet system and secure to the lab supports.

11.7.11. Place the extraction thimble in the glass Soxhlet extractor.

11.7.12. Adjust the temperature of the heating mantle to bring the solvent in the flat bottom flask to a rolling boil. There should be a steady drip from the condensers so that the solvent should completely cycle at least 5 times an hour.

11.7.13. Soxhlet extract the sample in the above manner for at least 16 hours.

11.7.14. Turn off the heating mantle and allow the Soxhlet apparatus to cool.

11.7.15. Remove the condensers and allow the Soxhlet extractor chamber to empty. Remove the Soxhlet extractor from the 500 mL flat bottom flask.

NOTE: If the samples appear to have a water layer or moisture, dry the extract by filtering it through a sodium sulfate filled funnel.

11.7.16. Concentrate the extract to approximately 6 to 8 mL using low-level KD glassware.

11.7.17. If needed perform GPC cleanup (Section 11.9) followed by silica gel column cleanup (Section 11.10).

11.8. Waste Sample Extraction

11.8.1. Organic wastes, oil, solids that will dissolve in solvent and non-aqueous sludge samples may be prepared by the waste dilution technique.

11.8.2. Carefully weigh out 1.0g (± 0.1 g) of well mixed sample or add an appropriate amount of sample (based on screen results) to a solvent-rinsed 40 mL vial. Record the sample weight on the extraction benchsheet.

11.8.3. Methylene chloride is used for the blank and LCS.

11.8.4. Spike each sample with 1 mL of the 0.25 µg/mL internal standard spiking solution.

11.8.5. Spike the LCS (and LCSD, MS/MSD, if required) with 1 mL of the 0.25 µg/mL LCS spiking solution.

NOTE: Each time the samples are spiked, the spiking process should be witnessed by another analyst. Refer to Appendix I for the steps that must be taken.

11.8.6. Add methylene chloride to bring the volume to approximately 6 to 8 mL. Perform GPC cleanup as needed (Section 11.9) followed by silica gel column cleanup (Section 11.10).

11.9. GPC Cleanup

11.9.1. Gel permeation chromatography (GPC) removes high molecular weight

interferences that cause GC column performance to degrade. It should be used for soil, sediment, tissue and waste sample extracts. It may be used for water sample extracts that are expected to contain high molecular weight organic compounds (e.g., polymeric materials, humic acids).

11.9.2. Refer to SOP KNOX-OP-0022, current revision for detailed instructions regarding GPC cleanup.

11.9.3. After GPC cleanup, concentrate the extract and solvent exchange to ~4 mL hexane using low-level KD glassware. Proceed to section 11.10, Silica Gel Column Cleanup.

CAUTION: When extracting or concentrating a sample with hexane, toluene or any mixture containing these solvents, the analyst **must** add the boiling chips within 5 minutes of placing the flask on the heat source in order to prevent bumping of the solvent.

11.10. Silica Gel Column Cleanup

11.10.1. Prepare 20 mm columns for each extract by placing a small amount of glass wool in the bottom of each column and then solvent rinsing with hexane. Shake out the excess hexane.

11.10.2. Add 4 cm of activated silica gel. Tap the column to settle the silica gel, and then add a ~1 cm layer of anhydrous sodium sulfate.

11.10.3. Elute the column with 30 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the sample extract onto the column using two additional 2 mL rinses of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, begin elution of the column with 25 mL of hexane followed by 25 mL of methylene chloride/hexane (2:3) (v/v). Collect the entire eluate in a 250 mL flat bottom flask.

11.10.4. When the column stops dripping, add 3 to 5 PTFE boiling stones and a solvent-rinsed Snyder column to the flask and concentrate the extract to > 10 mL on a heating mantle.

NOTE: Over-concentration of heated extracts is known to cause the more volatile PAHs to vaporize and be lost. Therefore, do not concentrate to less than 10 mL.

CAUTION: When extracting or concentrating a sample with hexane, toluene or any mixture containing these solvents, the analyst **must** add the boiling chips within 5 minutes of placing the flask on the heat source in order to prevent bumping of the solvent.

11.10.5. Transfer the extract to a 40 mL vial, rinsing the flask with a small

amount of hexane and add the rinse to the 40 mL vial. Repeat the rinse 2 more times.

11.10.6. Proceed to Section 11.11, Final Concentration.

11.11. Final Concentration

11.11.1. Place the 40 mL vial containing the extract in the N-EVAP concentration apparatus and reduce the solvent volume to approximately 0.5 to 1.0 mL.

Caution: At no time should the extract volume drop below 0.5 mL. If the volume drops below 0.5 mL, **loss of analytes could occur**.

11.11.2. Label a 2.0 mL mini-vial marked at 0.5 mL increments with the sample ID. Assure that the vial and cap fit together properly before use.

11.11.3. Add 25 µL of the 10 µg/mL recovery standard spiking solution to the mini-vial. Transfer the concentrated extract into the mini-vial, rinsing 2 times with small amounts of hexane. Then reduce the extract volume back down to 500 µL. Deliver the mini-vial to the GC/MS lab for analysis.

12. Data Analysis and Calculations

12.1. Not applicable

13. Method Performance

13.1. Method Detection Limit (MDL): An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples (this does not apply to alkyl homologues). Method detection limits are determined and verified as specified in the current revision of SOP CA-Q-S-006 (and attachment) based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit.

13.2. Initial Demonstration of Capability: Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently (this does not apply to alkyl homologues). The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in TestAmerica Knoxville SOP KNOX-QA-0009. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample is listed in Table 2.

13.2.2. Calculate the average recovery and relative standard deviation of the recovery for each analyte of interest. Compare these results with the

acceptance criteria given in Table 2. Historical matrix specific laboratory control sample acceptance criteria may also be used for evaluation of method demonstrations.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification: The group/team leader has the responsibility to ensure that 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. All attempts will be made to minimize the use of solvents and standard materials.

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 Safety Manual for "Waste Management and Pollution Prevention."

15.2. The following waste streams are produced when this procedure is carried out:

15.2.1. Waste methylene chloride, acetone, toluene and hexane shall be placed in the flammable waste stream, contained in a steel satellite accumulation container or flammable solvent container.

15.2.2. Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials shall be placed in the incinerable laboratory waste stream, contained in a steel or HDPE satellite accumulation container.

15.2.3. Extracted solid/tissue samples, paper funnel filters, glass wool, etc., contaminated with solvents shall be placed in the incinerable laboratory waste stream, contained in a steel or HDPE satellite accumulation container.

15.2.4. Extracted aqueous samples, contaminated with methylene chloride shall be placed in the organic water waste stream, contained in a HDPE satellite accumulation container.

16. References

16.1. TestAmerica Knoxville SOP KNOX-ID-0016, "Isotope Dilution Analysis of Selected Semivolatile Organic Compounds and Alkylated PAHs by Gas

Chromatography/Mass Spectrometry - Selected Ion Monitoring (GC/MS-SIM)", current revision

16.2. Method 429 - Determination of Polycyclic Aromatic Hydrocarbon (PAH) emissions from Stationary Sources, California Environmental Protection Agency Air Resources Board, Adopted: September 12, 1989, Amended: July 28, 1997.

16.3. NOAA Technical Memorandum NOS ORCA 130, National Status and Trends Program for Marine Environmental Quality, Sampling and Analytical Methods of the National Status and Trends Program Mussel Watch Project: 1993-1996 Update, March 1998.

16.4. TestAmerica Knoxville SOP KNOX-OP-0020, "Gravimetric Percent Lipids Determination" current revision

16.5. TestAmerica Knoxville SOP KNOX-OP-0022, "GPC Cleanup", current revision

16.6. TestAmerica Knoxville SOP KNOX-QA-0001, "Standard/Reagent Labeling and Documentation", current revision

16.7. TestAmerica Knoxville SOP KNOX-QA-0002, "Glassware Cleaning", current revision

16.8. TestAmerica Knoxville SOP KNOX-QA-0009, "Personnel Orientation and Training", current revision

16.9. TestAmerica Knoxville Quality Assurance Manual (QAM), current revision.

17. Miscellaneous

17.1. Deviations from reference methods: Not applicable. This TestAmerica Knoxville laboratory SOP was developed using information from various sources, including the reference methods listed in section 16. This stand alone procedure is not intended to be compliant with all of the requirements of the reference methods.

17.2. List of appendices, tables and figures referenced in the body of the SOP

17.2.1. Table 1 – Concentration of Stock Standards and Spiking Solutions

17.2.2. Figure 1 – Example Extraction Benchsheet

17.2.3. Appendix I – Guidelines for the Spike Witnessing Process

Table 1 - Concentration of Stock Standards and Spiking Solutions

Compound	Recommended Sources*	Catalog Number	Vendor Conc (µg/mL)	Stock Solution (µg/mL)	Spiking Solution (µg/mL)
Native Analytes					
Naphthalene	Restek	31995	2000	20	0.25
Biphenyl	Restek	567839	2000	20	0.25
2-Methyl naphthalene	Restek	31995	2000	20	0.25
1-Methyl naphthalene	Restek	31995	2000	20	0.25
Acenaphthylene	Restek	31995	2000	20	0.25
Acenaphthene	Restek	31995	2000	20	0.25
Fluorene	Restek	31995	2000	20	0.25
Phenanthrene	Restek	31995	2000	20	0.25
1-Methylphenanthrene	Restek	568613-FL	2000	20	0.25
2,3,5-Trimethylnaphthalene	Restek	568613-FL	2000	20	0.25
Anthracene	Restek	31995	2000	20	0.25
2,6-Dimethylnaphthalene	Restek	568613-FL	2000	20	0.25
Fluoranthene	Restek	31995	2000	20	0.25
Pyrene	Restek	31995	2000	20	0.25
Benz(a)anthracene	Restek	31995	2000	20	0.25
Chrysene	Restek	31995	2000	20	0.25
Benzo(b)fluoranthene	Restek	31995	2000	20	0.25
Benzo(k)fluoranthene	Restek	31995	2000	20	0.25
Benzo(e)pyrene	Restek	568613-FL	2000	20	0.25
Benzo(a)pyrene	Restek	31995	2000	20	0.25
Perylene	Restek	568613-FL	2000	20	0.25
Indeno(1,2,3-cd)pyrene	Restek	31995	2000	20	0.25
Dibenz(a,h)anthracene	Restek	31995	2000	20	0.25
Benzo(ghi)perylene	Restek	31995	2000	20	0.25
Dibenzothiophene	Restek	568613-FL	2000	20	0.25
Internal Standards					
d_8-Naphthalene	Accustandard	S-18004	200	20	0.25
d_{10}-2-Methyl naphthalene	Accustandard	S-18004	200	20	0.25
d_{10}-1-Methyl naphthalene	Accustandard	S-18004	200	20	0.25
d_8-Acenaphthylene	Accustandard	S-18004	200	20	0.25
d_{10}-Fluorene	CIL	DLM-1123-1.2	200	20	0.25
d_{10}-Phenanthrene	Accustandard	S-18004	200	20	0.25
d_{12}- 2,6-Dimethylnaphthalene	Accustandard	S-18004	200	20	0.25
d_{10}-Fluoranthene	Accustandard	S-18004	200	20	0.25
d_{12}-Benz(a)anthracene	Accustandard	S-18004	200	20	0.25
d_{12}-Chrysene	Accustandard	S-18004	200	20	0.25
d_{12}-Benzo(b)fluoranthene	Accustandard	S-18004	200	20	0.25
d_{12}-Benzo(k)fluoranthene	Accustandard	S-18004	200	20	0.25
d_{12}-Benzo(a)pyrene	Accustandard	S-18004	200	20	0.25
d_{12}-Perylene	Accustandard	S-18004	200	20	0.25
d_{12}-Indeno(1,2,3-cd)pyrene	Accustandard	S-18004	200	20	0.25
d_{14}-Dibenz(a,h)anthracene	Accustandard	S-18004	200	20	0.25
d_{12}-Benzo(ghi)perylene	Accustandard	S-18004	200	20	0.25
d_8-Dibenzothiophene	Accustandard	S-18004	200	20	0.25
d_{10}-Anthracene	Accustandard	S-18004	200	20	0.25
Recovery Standards					
d_{10}-Acenaphthene	CIL	DLM-108-1.2	200	NA	10
d_{10}-Pyrene	CIL	DLM-155-1.2	200	NA	10
d_{12}-Benzo(e)pyrene	CIL	DLM-257-1.2	200	NA	10
Alternate Surrogate					
d_{14}-p-Terphenyl	CIL	DLM-382-1.2	200	NA	0.25
Sampling Surrogates					
$^{13}C_6$-Naphthalene	CIL	DLM-365	neat	1000	0.25

* Other sources of standards may be used.

Figure 1: **Example Extraction Benchsheets**

TestAmerica Knoxville Extraction Sheet
SIM PAH Solids by Soxhlet - KNOX-OP-0023

Batch Number: _____ Native Spike ID: _____ $MeCl_2$ Lot #: _____ Recovery Std ID: _____ Delivered: _____ Initials/Date/Time
Start Date/Time: _____ Internal Std ID: _____ Na_2SO_4 ID: _____ Spiker: _____
Compl Date/Time: _____ Spiker: _____ Hexane Lot #: _____ Witness: _____ Received: _____ Initials/Date/Time
Witness:

Lot Sample Number	Work Order Number	Suffix	SAC	Water layer decanted? (Y,N,NA)	Record sample aliquot weight in g. Mix sample with Na_2SO_4 and add to Soxhlet thimble.	Add 1.0 mL (250 ng/mL) PAH IS mix to all samples and QC.	Add 1.0 mL (250 ng/mL) native spike to LCS, LCSD, MS, MSD.	Extract 16 hr with $MeCl_2$.	Conc to appropriate volume in KD.	Record the percentage of extract taken through GPC cleanup.	Concentrate/solvent exchange to hexane by KD to appropriate volume.	Perform silica gel column cleanup.	Conc to >10 mL on heating mantle. Conc to 0.5 to 1 mL by N-EVAP.	Add 25 µL recovery std (10 µg/mL) to 2 mL vial. Transfer sample extract to vial.	Conc to 500 µL hexane by N-EVAP.

Balance ID: _____ Comments: _____

SG Col Reagents	Hexane Lot #: _____	Silic Gel ID: _____
	2:3 $MeCl_2$/Hexane ID:	Na_2SO_4 ID:

OP122r0, 12/11/13 OP122r0 SIM PAH Solid Soxhlet.xls Printed: 2/27/2015 2:21 PM

Figure 1: **Example Extraction Benchsheets (continued)**

TestAmerica Knoxville Extraction Sheet
SIM PAH by Continuous Liquid/Liquid Extraction - KNOX-OP-0023

Batch Number: _____ Spiker: _____ Native Spike ID: _____ $MeCl_2$ Lot #: _____ Delivered: _____ Initials/Date/Time
Start Date/Time: _____ Witness: _____ Internal Std ID: _____ Hexane Lot #: _____
Compl Date/Time: _____ Recovery Std ID: _____ Na_2SO_4 ID: _____ Received: _____ Initials/Date/Time
Balance ID: _____

Lot Sample Number	Work Order Number	Suffix	SAC	Measure sample volume (mL).	Add 1.0 mL (250 ng/mL) PAH IS mix to all samples and QC.	Add 1.0 mL (250 ng/mL) native spike to LCS, LCSD, MS, MSD.	Extract 16 hr with $MeCl_2$.	Filter extract thru Na_2SO_4 / Whatman 41 filter paper into 500 mL KD.	Concentrate/solvent exchange to hexane by KD to appropriate volume.	Perform Silica gel cleanup.	Conc to >10 mL on heating mantle. Conc to 0.5 to 1 mL by N-EVAP.	Add 25 µL recovery std (10 µg/mL) to 2 mL vial. Transfer sample extract to vial.	Conc to 500 µL hexane by N-EVAP.

Comments: _____

SG Col Reagents: Hexane Lot #: _____ Silic Gel ID: _____
2:3 $MeCl_2$/Hexane ID: _____ Na_2SO_4 ID: _____

Appendix I - Guidelines for the Spike Witnessing Process

- Make sure there are no distractions, for example, phone calls, checking samples on water bath, people coming in to ask questions.
- The person spiking must tell the person who is witnessing what is being spiked and how much. Make sure the paperwork shows the spike amounts and spike IDs.
- The person witnessing should make sure they know and understand what is to be spiked and how much. Check the paperwork to verify.
- Check the syringe for air bubbles and also check the spike volume.
- It is a good idea to also check for cracks in the glassware.
- If client service requires spiking to occur when another analyst is not available, a witness is not required. In this case, the analyst will serve as his/her own witness, and must carefully double check the spike solutions and spike amounts added to the client samples and associated quality control samples. The analyst enters his/her initials as both the analyst and witness.

Title: PREPARATION AND ANALYSIS OF METHYL MERCURY BY GAS CHROMATOGRAPHY WITH COLD VAPOR ATOMIC FLUORESCENCE DETECTION

[Method: EPA Method 1630]

Approvals (Signature/Date):

Technology Specialist	12/07/15 Date	Health & Safety Coordinator	12/07/15 Date
Quality Assurance Officer	12/08/15 Date	Technical Director	12/11/15 Date

This SOP was previously identified as SOP No. NC-SA-001, Rev 3, 03/04/13

Facility Distribution No. _____ Distributed To:_____

The controlled copies of this SOP are the copy that is posted to the laboratory's SOP Directory and, where applicable, the printed copy that is placed in the General Chemistry SOP binder. Printed or electronic copies of this SOP that are distributed outside of the facility are considered uncontrolled.

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LIST OF APPENDICES

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of methyl mercury (CAS # 22967-92-6) using Method 1630.

1.2. This method is for the determination of methyl mercury in water samples including surface water, rainwater, and ground water. Alternative prep methods have been developed to make this analytical method applicable to solid matrices including sediment, soil, and tissue. Most natural waters contain trace levels of methyl mercury of a few hundred pg/L or less. There is a need to monitor methyl mercury at these levels due to its high toxicity, bioaccumulation and biomagnification in the environment. The Method Detection Limit (MDL) listed in Method 1630 is 0.02 ng/L of methyl mercury in water samples, where minimal background or matrix interference is present. The Reporting Limit (RL) for water samples is 0.05 ng/L of methyl mercury. The reporting limit for highly impacted waters analyzed by the alternate USGS water prep is 0.3 ng/L. The reporting limit for solid samples ranges from 0.01 µg/kg to 0.5 µg/kg depending on the matrix and preparation option selected. Detection limits, sensitivity, and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation, and volume of sample used.

1.3. The Florida Department of Environmental Protection (FDEP), Bureau of Laboratories, developed a direct-ethylation sample preparation and automated analysis technique for the determination of methyl mercury, based on modifications to the EPA draft Method 1630. The modified method incorporates the following steps: direct aqueous ethylation, purge and trap concentration, gas chromatography separation, pyrolysis, and cold-vapor fluorescence spectrometry (CVAFS) detection. Addition of the surrogate compound, n-propyl mercury, is another modification from the original method, that provides enhanced monitoring and assessment of the analytical process.

1.4. FDEP developed a prep procedure for solid matrices, but TestAmerica Canton only uses this prep procedure for tissue analysis.

1.5. United States Geological Survey (USGS) developed a prep procedure for the analysis of soil, sediment, and other solids. TestAmerica Canton uses this procedure for solids and has modified this procedure for use with highly impacted aqueous samples.

2. SUMMARY OF METHOD

2.1. The analytical procedures used in this SOP are based on EPA Method 1630. The FDEP has made significant modifications in the sample preparation to simplify the process and enhance performance of the method. These modifications have been incorporated into the TestAmerica Canton SOP.

2.2. The modified method consists of three major steps for water samples and aqueous extracts of solid samples—1) matrix modification, 2) derivatization, and 3) analysis.

Most surface waters contain small quantities of dissolved organic matter, also referred to as Dissolved Organic Carbon (DOC) . This organic matter primarily consists of humic and fulvic acids and it often imparts color to the water. The DOC constitutes a serious interferant in the determination of methyl mercury because of inhibition during the derivatization step and foaming caused by DOC during the sample purge procedure. The interference can either be inhibited by matrix modification or eliminated by sample cleanup. The matrix modification is achieved by adding citrate buffer and antifoaming reagents. This modification greatly reduces the chances of destroying (adding low bias) or creating methyl mercury (adding high bias) during sample preparation.

2.3. Following matrix modification, the sample is analyzed using a combination of chemical derivatization, sample concentration, chromatographic separation, pyrolysis, and atomic fluorescence detection.

2.3.1. The derivatization step transforms the methyl mercury into a volatile compound, methylethyl mercury, which may be easily purged from the sample and concentrated on a Tenax ™ trap. The derivatization also converts the inorganic mercury species Hg^{+2} and the surrogate compound n-propyl mercury chloride into the volatile derivatives diethyl mercury and n-propylethyl mercury, respectively. Small amounts of atomic mercury (Hg^0) and dimethyl mercury may also be present and will be concentrated in the trap.

2.3.2. In the analysis step, the volatile mercury components are collectively desorbed from the Tenax ™ trap, separated by gas chromatography, and detected using a fluorescence detector. As the separated components emerge from the gas chromatograph, they pass through a pyrolysis furnace at 700°C to convert the organomercury compounds to atomic mercury prior to detection. The atomic mercury is detected with great sensitivity and selectivity using a fluorescence detector.

2.4. The USGS preparation is used for sediment and soil. It has also been modified for use with aqueous samples that present a challenging matrix. Samples are extracted with acidic potassium bromide, copper sulfate solution, and dichloromethane. The dichloromethane extract is then exchanged back to reagent water and analyzed as a water sample.

2.5. The FDEP preparation is used for tissue. Samples are digested/extracted with methanolic potassium hydroxide at elevated temperature. A dilution of this digestate solution is then prepared and analyzed as a water sample.

3. DEFINITIONS

3.1. Dissolved methyl mercury: The methyl mercury that passes through a 0.45 μm membrane. (Sample is preserved after filtration.)

3.2. Total methyl mercury: The concentration determined on an unfiltered water sample or solid sample.

3.3. ICV (Initial Calibration Verification) is equivalent to the Method 1630 term QCS (Quality Control Standard).

3.4. CCV (Continuing Calibration Verification) is equivalent to the Method 1630 term OPR (Ongoing Precision and Recovery).

3.5. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version for additional definitions.

4. INTERFERENCES

4.1. Chemical and physical interferences may be encountered when analyzing samples using this method.

4.2. Environmental Mercury: Methyl mercury is not a common contaminant. However, other species of mercury are common at part per trillion concentrations. Precautions should be made to reduce exposure to dust and gaseous mercury during the sample preparation process.

4.3. Laboratory Contamination: 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 must be kept as clean as possible Samples, standards, and blanks must only be opened in a clean area. Gloves must be powder free, and must be checked for mercury contamination. Do not use powdered nitrile gloves as they have been shown to contain either low-level mercury contamination or interferences. Only clean gloves must touch the instrument and other equipment used to process blanks, standards, and samples.

4.4. Fluorescence Quenching: One form of negative interference may be caused by impurities that decrease or “quench” atomic fluorescence. These include traces of oxygen and water vapor in the carrier gas stream. Using UHP grade Argon as the carrier and makeup gases minimize the problem of negative interference. Inline oxygen and hydrocarbon traps can also be used if carrier gas purity is insufficient.

4.5. Dissolved Organic Carbon (DOC): Elevated levels of DOC can interfere with the derivatization step. The presence of elevated levels of DOC in the sample matrix may be visually apparent as color, typically yellow or brown, in the water sample. This interference may require sample dilution.

4.6. Suspended Solids: Unfiltered suspended solids may interfere with the derivatization step. The presence of particulates is normally apparent by the sample appearance. Filtering or diluting the sample may remove the interference.

4.7. Sulfides: Elevated levels of sulfide in the sample matrix may interfere with the derivatization step. Purging of the acidic extract prior to ethylation can reduce this interference in some instances.

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 Safety Data Sheet (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.
Sulfuric Acid	Corrosive Poison	1/mg/m3	Irritation of nose and throat. Labored breathing, redness and pain of skin, causes burns.
Potassium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3 2 mg/m^3-Ceiling	This material will cause burns if comes into contact with the skin or eyes. 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.
Potassium Bromide	Irritant	None listed	Eye, skin and upper respiratory tract irritant. Exposure can cause rashes especially to the face resembling acne and boils.
Copper Sulfate Penta Hydrate	Poison	None listed	Causes eye and skin irritation. May be irritating to the mucus membranes and the upper respiratory tract.
Potassium Permanganate	Oxidizer	5 mg/m^3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may 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.
Hydroxylamine Hydrochloride	Poison Corrosive	None listed	Burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting may occur. Irritation to the eyes and 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.

Dichloromethane	Poison	25 ppm PEL 125 ppm STEL	Has a strong narcotic effect. Causes mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Irritating to the skin causes a burning sensation, redness and pain. Irritating to the eyes.
Sodium Tetraethyl Borate	Flammable Poison	None listed	May cause eye and skin irritation. May cause irritation to digestive tract if swallowed. May be harmful if swallowed. May cause respiratory tract irritation.
Methyl Mercury Chloride	Poison	0.1 mg/m^3 ceiling	Metallic taste in the mouth. Tingling of the digits and face, tremors, headache, fatigue, difficulty thinking, loss of coordination, slurred speech, hearing loss, constriction of visual capacity. Irritant to eyes, skin, and respiratory tract.
Propyl Mercury Chloride	Poison	0.1 mg/m^3 ceiling	Metallic taste in the mouth. Tingling of the digits and face, tremors, headache, fatigue, difficulty thinking, loss of coordination, slurred speech, hearing loss, constriction of visual capacity. Irritant to eyes, skin, and respiratory tract.
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 clean up 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 must 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 must be removed and discarded; other gloves must be cleaned immediately.

5.5. Full face shield must be worn during the preparation of the Sodium Tetraethyl Borate standard.

5.6. It is recommended that analysts break up work tasks to avoid repetitive motion tasks, such as opening a large number of vials or containers in one time period.

5.7. 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 must be kept closed unless transfers are being made.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported immediately to the EH&S Coordinator and to a laboratory supervisor.

5.9. Do not look directly into the beam of the Hg lamp. Do not look directly into the UV light source used for sterilization of the citrate buffer solution discussed in Section 7.11. The UV light these lamps radiate is harmful to the eyes.

5.10. 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.

5.11. The CVAFS apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. EST Centurion VOC autosampler or equivalent: 100 sample capacity

6.2. Tekmar Stratum Purge and Trap Concentrator equipped with Tenax™ trap and TekLink software or equivalent

6.3. Agilent 7890 gas chromatograph equipped with DB-1, 15 m length, 0.53 mm ID column or equivalent

6.4. Chemstation or equivalent for data collection

6.5. PS Analytical Atomic Fluorescence Detector connected to pyrolysis oven with ~1.2 m deactivated fused silica 0.53 mm ID column (protected in an FEP tube) or equivalent.

6.6. Sample vials, 43-mL amber and clear borosilicate glass VOC vials with Teflon™-faced silicone rubber septa, QEC or equivalent, <0.05 ng/L methyl mercury contamination when used for Method 1630. In actual practice, sample vials generally contribute less than 0.01 ng/L in order to facilitate meeting method blank criteria. Unless tested by the manufacturer for cleanliness and accuracy, 12 vials from each lot must be tested to ensure the entire lot meets the blank acceptance criteria. Start by adding reagent water to the vials. Store the test vials under refrigeration for at least 12 hours and analyze as samples. All vial blank results must be less than the reporting limit.

6.6.1. Pre-preserved amber vials: 0.2 mL of 6M HCl, used for all water samples and USGS solid sample water exchanged extracts

6.6.2. Unpreserved amber vials: used for solid FDEP digestions

6.6.3. Unpreserved clear vials: used during USGS extraction process (tested for Low Level Mercury)

6.7. Calibrated mechanical pipettes: 0.1-1 mL variable, 0.5-5 mL variable, 1-10 mL variable, 2-20 mL variable, 0.05-0.25 mL positive displacement, 0.1-1 mL positive displacement

6.8. Repeater Pipette: 50 mL variable

6.9. Glass Volumetric Flasks: various volumes

6.10. Microsyringes: various volumes

6.11. Dry heater block

6.12. Tissue homogenizer, chopper, blender

6.13. Wide-mouth glass jars: 2 or 4 oz.

6.14. PFTE boiling chips

6.15. Glass Pasteur-type pipettes (5-¾ inch)

6.16. Bottle top dispenser (10 mL), dichloromethane compatible components

6.17. Gas distribution manifold, 10 positions for Pasteur pipettes

6.18. Laboratory shaker: 43 mL vials

6.19. Centrifuge: 43 mL vial capacity with rubber stopper in bottom of centrifuge tubes to prevent breakage.

6.20. 0.95 L bottle: A one-liter bottle with a mark at 950 mL. The 950 mL mark is determined gravimetrically. The bottle is used for making the Citrate Buffer (section 7.11).

7. REAGENTS AND STANDARDS

7.1. HPLC grade reagent water is used. Reagent water may be produced by a US Filter PureLab Plus deionized water system or equivalent, to meet 18 MΩ-cm specific resistance. Reagent water mercury content and interferences must be less than the reporting limit as demonstrated through the analysis of reagent and method blanks.

7.2. Methanol: (CH_3OH) - Purge and trap grade methanol

7.3. Dichloromethane (CH_2Cl_2): pesticide grade

7.4. Hydrochloric acid (HCl): concentrated, trace metal grade, and ultra-trace mercury grade

7.5. Sulfuric acid (H_2SO_4): concentrated, trace metal grade

7.6. Potassium bromide: reagent grade

7.7. Hydroxylamine hydrochloride ($NH_2OH*HCl$) 30% solution (w/v): reagent grade

7.8. Copper sulfate penta hydrate ($CuSO_4*5H_20$): reagent grade

7.9. Argon: UHP grade

7.10. Helium: UHP grade

7.11. Citrate Buffer: The buffer solution is used to adjust the pH of the samples to a range of 4.0 to 4.5 before ethylation. The solution is prepared by weighing 102.5 g of reagent grade citric acid monohydrate, 139.45 g of reagent grade sodium citrate and 120 µL of Antifoaming Agent-A into a 0.95-L bottle (see section 6.20) and then dissolving this mixture into approximately 700 mL of reagent water. After the solid has dissolved, bring the solution up to the 950 mL mark using reagent water, and mix well. The citrate buffer solution must have a methyl mercury concentration below the reporting limit. Normally, no additional purification is required. The citrate buffer is stored in a Teflon™ bottle. Sterilize the citrate buffer solution by exposing the solution to UV radiation. The buffer may be used on the day it is made prior to UV exposure, but must be placed in a chamber with a UV light source overnight at the end of the working day.

7.11.1. UV radiation can be used to decompose MeHg in the buffer solution. Using UV treatment is very simple and has the added benefit of killing any algae that may be present in the solution. In a sterile Teflon™ bottle, the solution may be stored as long as one year.

7.12. Sodium tetraethyl borate ($NaBEt_4$) solution (2%): Sodium tetraethyl borate (98% purity from Strem or equivalent) is the ethylating reagent used to derivatize the methyl mercury to volatile methylethyl mercury, Hg^{+2} to diethyl mercury, and n-propyl mercury to ethylpropyl mercury. The ethylating reagent is prepared by following the steps outlined below:

7.12.1. Vial Preparation: Fifty (50) 2 mL amber GC vials with Teflon™-lined caps are needed for storing the reagent. The vials (without cap) are first baked overnight. After baking, cool the vials to room temperature. Fill each vial with Argon gas and cap immediately. Place the capped vials in a rack. The rack is then placed in a low temperature freezer (-20°C) for at least 30 minutes or until needed.

7.12.1.1. A 50-vial rack was modified and filled with freezer gel, then sealed. The modified rack is kept frozen and is used to cool the vials as they are filled with ethylating agent. Secure a towel around the barrel of a 50 mL repeater pipette. Wet it and freeze overnight. Attach a tube to the tip of the frozen 50 mL repeater pipette barrel for ease of drawing and dispensing the ethylating agent.

7.12.2. KOH Solution Preparation: One gram of reagent grade KOH pellets is dissolved in 50 mL of reagent water in a glass 120 mL bottle. Add Argon gas to the bottle to exclude air. The KOH solution is then chilled to near freezing (2 – 4°C) by placing the bottle in a low temperature refrigerator or a freezer for a short period of time. The KOH solution is ready to use when it starts to form a slush, but take care not to freeze the solution completely.

7.12.3. Sodium tetraethyl borate ($NaBEt_4$) Solution (2%) Preparation: Face shield must be worn during preparation of this standard. Solid sodium tetraethyl borate ($NaBEt_4$) is purchased in small (1.0 g) quantities. The compound is received in flame sealed ampoules under Argon gas since it is air-sensitive. The original bottle containing the compound is stored in a freezer until

needed. To prepare the reagent, carefully score the neck of the ampoule with a ceramic wafer (column cutter). Place the vial of $NaBEt_4$, frozen repeater pipette, KOH container, and any miscellaneous items required, including paper towels and two pairs of gloves, into an inert atmosphere glove box or equivalent. Crack open the 1.0 g ampoule of $NaBEt_4$ and immediately pour and mix the entire contents of the ampoule into the glass bottle containing 50 mL of chilled KOH. Draw up the entire 50 mL solution and remove from inert atmosphere. Remove the chilled rack of 2 mL vials from the freezer and swiftly fill each of the vials with 1 mL of the $NaBEt_4$ solution. The transfer process into the smaller vials goes faster and gives better results when two people work together. Cap and label the filled vials. Place the vials into the freezer (-20°C) for storage until needed. Notify the EH&S Coordinator if a spill of more than 1 mL of derivatizing agent occurs.

7.12.4. Use of the $NaBEt_4$ Solution: Remove a prepared 2 mL vial of $NaBEt_4$ solution from the freezer as needed, and allow to almost completely thaw. This reagent is very sensitive to any oxidant; therefore, it is imperative to minimize the length of time the reagent is exposed to air. The vial must be capped tightly during use, and returned to the freezer. In the frozen state, the solution may be stored as long as one year.

7.13. Methanolic Potassium Hydroxide: 25 g potassium hydroxide per 100 g methanol.

7.14. DL-Methionine (Sigma 99% purity)

7.14.1. High-level solution (solid samples): 0.5 g is dissolved in 5 mL 25% KOH in MeOH. Then dilute to 50 mL with purge and trap grade methanol.

7.14.2. Low-level solution (water samples): 0.5 mL high-level solution (Section 7.14.1) diluted to 25 mL with purge and trap grade methanol.

7.15. Potassium Permanganate 5% solution (w/v): purchased from a commercial vendor

7.16. Acidic Potassium Bromide extraction solution: Dissolve 180 g KBr in reagent water. Add 50 mL concentrated H_2SO_4. Dilute to 1 L. Add 0.66 mL NH_2OH*HCl solution to stabilize the solution. Store in amber glass bottle and refrigerate. Solution has a one-month expiration.

7.17. Copper sulfate solution: Dissolve 125 g of $CuSO_4$*$5H_20$ in 500 mL of reagent water. The solution must be stored in an amber bottle and expires one year after preparation.

7.18. Alkyl Mercury Standards Preparation

Note: Concentrated solutions of alkyl mercury species (e.g., MeHgCl, n-propylHgCl) are highly toxic. Care must be taken while working with these solutions. If a spill should occur, change your gloves immediately and wash your hands with copious amounts of water. Notify the EH&S Coordinator if the spill is more than 1 mL of stock standard solution.

7.18.1. Care must be taken to ensure manufacturers correctly represent mercury salts. Certificates of analysis are often ambiguous and contacting the manufacturer is recommended to clarify this uncertainty. Using the molar mass of methyl mercury and the confirmed analyte concentration the corrected methyl mercury concentration can be determined.

7.18.1.1. Example 1: Solution reported as 8 ng/L MeHgCl

7.18.1.1.1. 8 ng/L MeHgCl x 215.625 g/mol MeHg / 251.078 g/mol MeHgCl = 8 ng/L x 0.8588 = 6.87 ng/L MeHg

7.18.1.2. Example 2: Solution reported as 4 ng/L Hg from MeHgCl.

7.18.1.2.1. 4 ng/L Hg x 215.625 g/mol MeHg / 200.59 g/mol Hg = 4 ng/L x 1.075 = 4.30 ng/L MeHg.

Compound	Molar Mass (g/mol)
Hg	200.59
MeHg	215.625
MeHgCl	251.078

7.18.2. Methyl Mercury Stock Standard (1000 µg/L MeHg: The methyl mercury primary stock solution is custom prepared by ERA Chemical Corp. in purge and trap grade methanol. Store the standard in a refrigerator at 4 ± 2°C until needed. Opened ampoules may be stored in a VOA vial with a Teflon™ lined septa. The methyl mercury standard has a one-year expiration.

7.18.2.1. The n-Propyl Mercury surrogate stock solution is purchased from the same vendor as the Methyl Mercury stock and is identical to the Methyl Mercury stock in concentration and storage

7.18.3. Intermediate Methyl Mercury Standard (100 µg/L MeHg) in methanol: The standard is prepared by diluting 10 mL of stock standard and diluting to 100 mL in MeOH. Store the standard in a VOA vial with a Teflon™ lined septa, and refrigerated at 4 ± 2°C until needed. The methyl mercury standard has a one-year expiration. This standard is used to prepare solid matrix laboratory control samples and matrix-spiked solid samples.

7.18.3.1. An intermediate n-Propyl Mercury standard is created using the same process as used for the intermediate Methyl Mercury standard.

7.18.4. Working Methyl Mercury Standard (2 µg/L MeHg) in methanol: The standard is prepared by diluting 2 mL of intermediate standard to 100 mL in MeOH. Store the standard in a VOA vial with a Teflon™ lined septa, and refrigerated at 4 ± 2°C until needed. The methyl mercury standard has a one-year expiration. This standard is used to prepare solid matrix laboratory control samples and matrix-spiked solid samples.

7.18.4.1. A working n-Propyl Mercury standard is created using the same process as used for the working Methyl Mercury standard.

7.18.5. Second Source Methyl Mercury Standard is purchased from Alfa Aesar as 1000 mg/L MeHgCl in water, which is equivalent to ≈ 858.8 mg/L as MeHg.

7.18.5.1. Dilute 50 µL of 858.8 mg/L stock solution to 100 mL FV MeOH to make an intermediate solution with a concentration of 429.4 µg/L.

7.18.5.2. Dilute 500 µL of the 429.4 µg/L intermediate solution to 100 mL FV MeOH to yield a working standard with a concentration of 2.147 µg/L.

7.18.5.3. The initial calibration verification standard (ICV) must be made from a different manufacturer or lot than that of the calibration standards.

7.18.6. ICAL Standard (200ng/L MeHg and n-PrHg) [initial calibration]: Dilute 200 µL of the intermediate MeHg and n-PrHg standards to 100 mL in a volumetric flask with purge and trap grade methanol. Store the standard in a VOA vial with a Teflon™ lined septa, and refrigerated at 4 ± 2°C until needed. The ICAL standard has a one-year expiration.

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 1A are maintained.

7.19. Refer to Tables 1A and 1B (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification, and spiking solutions. All standards must be processed with reagents that are used for sample preparation.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Sample Collection

8.1.1. Water samples for total methyl mercury analysis are collected in 43-mL amber borosilicate glass vials that contain HCl for preservation. Water samples for dissolved methyl mercury analysis are collected in 43-mL amber borosilicate glass vials without acid. The vials are filled with sample, placed in polyethylene bags, and shipped to the lab on wet ice. Each sample is collected in an individual bag and must be uniquely identified.

8.1.2. Soil and sediment samples are collected in 2- to 4-ounce amber jars and cooled with wet ice during shipment.

8.1.3. Tissue samples should be frozen and shipped on dry ice.

8.2. Preservation and Holding Time

8.2.1. Sample Preservation

8.2.1.1. Water samples are preserved with ~ 0.2 mL of 6M HCl per 43-mL vial. The pH must be < 2. The samples are then stored in a sample refrigerator at 4.0 ±2°C, and protected from light until analysis.

8.2.1.2. Dissolved water samples must be filtered within 48 hours of sampling. The filtrate is transferred into vials that have been pre-preserved with HCl. Samples are then stored in a sample refrigerator at 4.0 ±2°C, and protected from light until analysis.

8.2.1.3. Soil and sediment samples are stored in a sample refrigerator at 4.0 ±2 °C, and protected from light until analysis.

8.2.1.4. Tissue samples are frozen at ≤ -10°C and protected from light until analysis.

8.2.2. Sample Holding Time - The holding time for preserved water samples is six months. For solid, tissue, or sludge sediment samples, the holding time is 28 days from time of sample collection to analysis.

9. QUALITY CONTROL

9.1. Table 2 (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria, and corrective action.

9.2. Initial Demonstration of Capability

9.2.1. Prior to the analysis of any analyte using Method 1630, the following requirements must be met:

9.2.2. Method Detection Limit (MDL): An MDL must be determined for each analyte/matrix prior to the analysis of any samples. MDLs must be determined in accordance with 40 CFR Part 136 Appendix B requirements. In addition, the MDL for Method 1630 must be ≤ 0.02 ng/L for water analysis. Refer to TestAmerica North Canton SOPs NC-QA-021 and CA-Q-S-006 for details on MDL analysis and criteria.

9.2.3. Initial Demonstration of Capability Study (precision and recovery study): This study requires the analyses of four QC check or laboratory control

samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable (method or laboratory-generated criteria must be met) before analysis of samples may begin. If criteria are not met, additional training, process modification, or other corrective actions must be taken. Only when the IDOC has been successfully completed can sample analyses proceed.

9.3. Preparation Batch: A group of up to 20 samples of the same matrix that are processed together using the same procedures and reagents. The preparation batch must contain a method blank, an LCS and a matrix spike/matrix spike duplicate (two MS/MSD pairs if the batch has more than ten samples). In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain more than two MS/MSD pairs.

9.4. Sample Count: Laboratory-generated QC samples (Method Blanks, LCS, and MS/MSDs) are not included in the sample count for determining the size of a preparation batch.

9.5. Method Blank (MB): One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences, contamination of the analytical system that may lead to the reporting of elevated analyte concentrations, or false positive data. The method blank must not contain any analyte of interest at, or above, the reporting limit.

9.5.1. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. If the amount of blank contamination is not > 5% of the value of the analyte in the sample, the results may be accepted. **Such action must be addressed in the project narrative.**

9.5.2. Re-preparation and re-analysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exceptions noted above).

9.5.3. If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative.

9.6. System / Calibration / Reagent Blank: The reagent blank, consisting of all reagents used to prepare samples and standards, must be used with the initial calibration and as needed for system cleanliness monitoring. At least three reagent blanks are prepared and analyzed with the initial calibration curve (ICal). The average raw response from these calibration blanks must be less than the reporting limit. Subsequent reagent blanks are run as ICB and CCB in conjunction with the ICV and CCV. These IC and CC

blanks are used to monitor the cleanliness of the instrument and are calculated in the same manner as samples; they are NOT used for background subtraction purposes. The absolute value of the calculated MeHg concentration must be less than the reporting limit.

9.7. Surrogate

9.7.1. Surrogate recoveries in samples and QC samples must be assessed to ensure that recoveries are within established limits. Surrogate recoveries must be met in the method blank (MB) and Laboratory Check Samples (LCS or LCS/LCSD) . If any surrogate is outside limits, the following corrective actions must take place (except for dilutions).

9.7.1.1. Check all calculations for error.

9.7.1.2. Ensure instrument performance is acceptable.

9.7.1.3. Recalculate the data and/or re-analyze the extract if either of the above checks reveals a problem.

9.7.1.4. It is only necessary to re-prepare / re-analyze a sample once to demonstrate poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out-of-control results are not due to matrix effect.

9.7.1.5. Aqueous samples exhibiting low surrogate recoveries should be diluted and reanalyzed.

9.7.2. If the surrogate is out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and re-preparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then re-preparation or flagging of the data is required. Re-preparation includes the parent sample and MS/MSD.

9.7.2.1. In the instance where the surrogate recovery is greater than the maximum and the sample results are < RL, the data may be reported; but must have qualifiers. **Such action must be addressed in the case narrative.**

9.8. Laboratory Control Sample (LCS): One LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going 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. If the LCS is outside established control limits the system is out of control and corrective action must occur.

9.8.1. In the instance where the LCS recovery is greater than the maximum and the sample results are < RL, the data may be reported; but must have qualifiers. **Such action must**

be addressed in the case narrative.

9.8.2. Corrective action must be re-preparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.9. Additional information on QC samples can be found in QA Policy QA-003.

9.10. Matrix Spike/Matrix Spike Duplicate (MS/MSD): Method 1630 requires that each matrix be spiked at a 10% frequency. One MS/MSD pair must be processed for each 10 samples in a preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. 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. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Tables 1A and 1B (Appendix A).

9.10.1. If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Method control limits are generated in-house and are listed in Table 2 (Appendix A) .If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action may include re-preparation and re-analysis of the batch. MS/MSD results, which fall outside the control limits, must be addressed in the narrative.

9.10.2. Matrix spike recoveries must be reported unless the dilution is more than 4X (at which point the surrogate has been diluted below the range of detection) .For samples with more than 4X dilution, the recovery is entered into LIMS and flagged with a “4”.

9.11. Initial Calibration Verification (ICV/ICB): Calibration accuracy is verified by analyzing a second source standard (ICV). The control limits for the ICV are given in Table 2 (Appendix A). An ICB is analyzed immediately following the ICV to demonstrate 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 must be terminated, the problem corrected, and the instrument recalibrated (see Section 11.6.3 for required run sequence).

9.12. Continuing Calibration Verification (CCV/CCB): Calibration accuracy and cleanliness is monitored throughout the analytical run through the analysis of a known standard at least every 12 hours. The CCV concentration is given in Table 1A (Appendix A). The control limits are in Table 2 (Appendix A). A CCB is analyzed immediately following each CCV (see Section 11.6.3 for required run sequence). The CCB (system/reagent 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/ICB or CCV/CCB pairs.

9.12.1. In the instance where the CCV is greater than the maximum, or the CCB is greater than the RL, and the sample results are < RL, the data may be reported. **Such action must be addressed in the case narrative.**

9.13. Control Limits

9.13.1. Control limits are specified in Method 1630 and are easily accessible via the LIMS.

9.14. Method Detection Limits (MDLs) and MDL Checks

9.14.1. MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.14.2. Water MDL must be less than or equal to 0.02 ng/L.

9.14.3. MDLs are easily accessible via the LIMS.

9.15. Nonconformance and Corrective Action

9.15.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.

10.2. 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.

10.3. The following calibration models can be used: Average, or weighted linear. Average response factor calibration must have a %RSD ≤ 15%. For linear regression with 1/response weighting, the correlation coefficient must be evaluated for linearity, and be greater than or equal to 0.995.

10.4. Removal or replacement of levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted unless an injection or instrument problem confined to that point can be clearly documented as described below.

10.5. If the analyst can document that a level is not valid because of an injection or instrument problem confined to that run, the level may be excluded if the curve still has sufficient levels, or the run may be repeated once only. The whole level (all compounds) must be

removed or replaced. The curve is evaluated with the level removed or replaced. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve reanalyzed. Corrective action may include, but is not limited to, instrument maintenance and/or re-preparation of standards.

10.6. One of the following conditions must be satisfied to allow removal or replacement of a level:

10.7. The data file is corrupted and unusable or the run is interrupted before completion.

10.8. The analyst observes and documents a problem such as leaking of a purge vessel.

10.9. The reason for replacing the level must be documented in the run log. The fact that the curve passes criteria with the level removed is not alone sufficient evidence to document an injection or instrument problem confined to the level.

10.10. Removal of the highest or lowest levels is permitted, but the calibration range must be adjusted accordingly. If the lowest level is removed then the reporting limit is raised to be equivalent to the lowest level used in the calibration curve. In any event the number of levels remaining in the calibration must be at least that required by the method.

10.11. Removal of the highest or lowest point is permitted on a compound specific basis. This may be necessary when strongly responding and poorly responding analytes are included in the same standard mix at the same level. Each compound must have at least the minimum number of calibration levels required by the method

10.12. Set up the instrument with the operating parameters summarized in Table 3. Allow the instrument to become thermally stable before beginning calibration. The most stable results are obtained if the lamp is left on full time. Refer to the CVAFS detector manual for detailed setup and operation protocols.

10.13. Calibration reagent water blanks are analyzed to ensure that the instrument and reagent solutions are adequately clean.

10.14. Calibrate the instrument according to instrument manufacturer's instructions, using at least six standards and three calibration blanks. One standard must be at, or below, the TestAmerica Canton reporting limit. Analyze standards in ascending order beginning with the blanks. Refer to Section 7.18 and Table 1A for additional information on preparing calibration standards and calibration levels.

10.15. When the calibration blank is less than 25% of the low standard, an average calibration factor may be used. The % RSD of the calibration factors must not be >15%. Otherwise, a weighted linear regression is used.

10.16. The weighted (1/response or $1/response^2$) linear regression correlation coefficient must be ≥0.995; otherwise, the instrument must be recalibrated prior to running samples. Instrument maintenance may be required prior to recalibration. Sample results cannot be reported from a curve with an unacceptable correlation coefficient. Also, the low

standard must calculate back within ± 35% of the true value. When the calibration blank is less than 25% of the low standard, an average calibration factor may be used. The % RSD of the calibration factors must not be >15%.

10.17. Refer to Sections 9.11 and 9.12 for calibration verification procedures, acceptance criteria, and corrective actions.

11. PROCEDURE

11.1. Sample Screening

11.1.1. Screening of samples may be useful in preventing instrument damage. In the absence of historical information for a sample, recommended screening dilutions are as follows:

11.1.1.1. Animal tissue samples: 10x - 20x.

11.1.1.2. Plant tissue samples: Screening not required.

11.1.1.3. Soils and sediments: 5x – 10x

11.1.1.4. Total water: 10x – 100x

11.1.1.5. Dissolved (Filtered) water: Screening not required unless total methyl mercury content indicates high levels of any mercury species.

11.1.2. Other screening dilutions are acceptable, if available information indicates that larger or smaller dilutions are more appropriate.

11.2. Aqueous Sample Preparation

11.2.1. All initial calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed with the reagents used for the field samples.

11.2.2. Remove the cap from a 43 mL vial and remove at least 4 mL of sample water using a pipette. Save this sample aliquot in the vial cap for use in Section 11.2.7.

11.2.2.1. Verify and record the pH of all samples. The pH must be <2.

11.2.2.2. For calibration standards and QC samples, fill the vial with reagent water until the surface forms a slightly convex shape above the vial rim. Remove 4 mL of reagent water from the filled vial and discard that portion.

11.2.2.3. For samples that require dilution, fill the vial with regent water until the surface forms a slightly convex shape above the vial rim. Remove and discard 4 mL reagent water from the filled vial plus sufficient volume to accommodate the sample to be diluted.

11.2.3. Add 25 µl low-level DL-methionine solution (Section 7.14).

11.2.4. Add 9.75 µL of the n-propyl mercury working surrogate solution 2ng/L. See Table 1A for volumes used in initial calibration.

11.2.5. Add the 9.75 µl of 2 ng/L MeHg working standard (see Table 1) to all LCS and matrix spike samples.

11.2.6. Add 4 mL of the citrate buffer solution (Section 7.11). The buffer solution contains the antifoam agent needed to control foaming from samples with high dissolved organic compound (DOC) content.

11.2.7. Add sample water (Section 11.2.2) until a slightly convex shape forms above the vial rim. This step is not necessary for diluted samples, calibration standards, or QC samples.

11.2.8. Add 25 µL of the ethylating reagent solution ($NaBEt_4$) (Section 7.12).

11.2.9. Immediately screw the Teflon™ septum cap on firmly. Flip the vialvial upside down and check for bubbles inside the vial. If there are bubbles in the vial larger than 6 mm in diameter, re-prepare the vial Vials are inverted several times then shaken vigorously by hand for 5 seconds. Mix the capped vial on a vortex mixer for 1 minute to ensure thorough mixing of the vial contents. Allow the sample to sit for 15 minutes to allow the ethylation reaction to reach completion. The ethylation chemistry has a limited reaction time; therefore, it is critical to perform these operations rapidly once the ethylating reagent is added to the sample.

Note: The importance of good mixing immediately upon addition of the ethylating reagent must be stressed. Low recoveries have been observed in cases where the sample was inadequately mixed during the ethylation step.

11.2.10. AFTER ANALYSIS, ETHYLATED SAMPLES MUST BE STORED IN A HOOD UNTIL POTASSIUM PERMANGANATE CAN BE ADDED.

11.3. High-Level Solid sample preparation (FDEP)

11.3.1. Place a 1 g representative sub-sample in an amber 43 mL vial.

11.3.1.1. Thoroughly mix soil and sediment samples and/or withdraw 5-10 small increments to make up the 1 g sample aliquot.

11.3.1.2. This prep method is much more efficient at extracting divalent mercury (Hg^{2+}) than the USGS prep described below. Divalent mercury is an interfering peak in the analysis of methyl mercury; therefore, the USGS method is the preferred analysis for all sediment and soil samples.

11.3.1.3. Tissue samples are processed through an appropriately sized chopping or grinding device then sub-sampled with 5-10 small increments to make up the 1 g sample aliquot. Mixing with dry ice prior to chopping can facilitate homogenization for samples that do not cut or grind well at ambient or freezer temperatures.

11.3.1.4. For solid QC samples, use 1 g of PTFE boiling chips as a solid matrix.

11.3.2. Add 25 µL of high-level methionine solution (Section 7.14).

11.3.3. Add 50 µL of the 100 ppb n-propyl mercury surrogate solution .

11.3.4. Add 50 µL of 100 ppb MeHg standard (Section 7.18.3) to all LCS and matrix spike samples.

11.3.5. Add 10 mL of methanolic potassium hydroxide (Section 7.13)

11.3.6. Cap the 43 mL vial, and heat to 90°C ± 5°C for 1-4 hours. Animal tissue samples should dissolve completely producing a yellow solution with minimal particulates. Plant tissues, soils, and sediments will have more undigested solid residue.

11.3.7. After cooling to room temperature, dilute to a final volume of 20 mL with methanol.

11.3.8. Remove a 78 µL aliquot, and dilute with reagent water to about 35 mL in a 43 mL vial. If the solid sample is expected to contain high concentrations of methyl mercury or interferences, prepare larger dilutions by using initial aliquots less than 78 µL. Most animal tissues have high levels of methyl mercury and should be screened using a 6 µL sample aliquot.

11.3.9. Add 4 mL of the citrate buffer solution (Section 7.11). The buffer solution contains the antifoam agent needed to control foaming from samples with high dissolved organic compound content.

11.3.10. Add reagent water until a slightly convex shape forms above the vial rim.

11.3.11. Add 25 µL of the ethylating reagent solution ($NaBEt_4$) (Section 7.12).

11.3.12. Immediately screw the Teflon™ septum cap on firmly. Flip the vial upside down to check for bubbles inside the vial. If there are bubbles in the vial, larger than 6 mm in diameter, re-prepare the vial vialVials are inverted several times then shaken vigorously by hand for 5 seconds. Mix the capped vial on a vortex mixer to ensure thorough mixing of the vial contents. Allow the sample to sit for 15 minutes to allow the ethylation reaction to reach completion. The ethylation chemistry has a limited reaction time; therefore, it is critical to perform these operations rapidly once the ethylating reagent is added to the sample.

Note: The sensitivity of this sample preparation process can be improved by 5X by increasing the methanolic extract volume from 78 to 390 µL when minimal interferences are present. This can be used as an alternative to the USGS low-level sample preparation process in the absence of interferences.

11.3.13. AFTER ANALYSIS, ETHYLATED SAMPLES MUST BE STORED IN A HOOD UNTIL POTASSIUM PERMANGANATE CAN BE ADDED.

11.4. Low Level Sediment Sample Preparation (USGS)

11.4.1. Place a 1 g representative sub-sample in a clear 43 mL vial.

11.4.1.1. Thoroughly mix soil and sediment samples and withdraw 5-10 small increments to make up the 1 g sample aliquot.

11.4.1.2. For QC samples use 1 g of PTFE boiling chips as a solid matrix.

11.4.2. Add 25 µL of high-level methionine solution (Section 7.14).

11.4.3. Add 10 µL of the 100 ppb n-propyl mercury surrogate solution (Section **Error! Reference source not found.**).

11.4.4. Add 10 µL of 100 ppb MeHg standard (Section 7.18.3) to all LCS and matrix spike samples.

11.4.5. Add 5 mL of acidic potassium bromide solution (Section 7.16), 1 mL of copper sulfate solution (Section 7.17), and 10 mL of dichloromethane (DCM).

11.4.6. Allow sample vials to sit at room temperature for one hour, then place on laboratory shaker for one hour at high setting.

11.4.7. Refrigerate the DCM water extract until cool. Allowing the extract to sit overnight may help break up any emulsion that may have formed. If necessary, centrifuge to separate aqueous and organic phases.

11.4.8. Prepare aqueous solvent exchange vials by adding about 10 mL of reagent water to an HCl preserved amber 43 mL vial.

11.4.9. Using a calibrated positive displacement pipette, transfer 2 mL of DCM extract from the sample extraction vial to the corresponding aqueous solvent exchange sample vial. Do not transfer any of the aqueous layer or emulsion. Heat the solvent exchange vial at 50°C ± 5°C, while bubbling argon through the liquid in the vial. Continue bubbling until all solvent is gone.

11.4.10. Remove a 4.2 mL aliquot and dilute with reagent water to about 35 mL in an unpreserved 43 mL vial. If the solid sample has high concentrations of methyl mercury or interferences, prepare larger dilutions by using initial aliquots less than 4.2 mL.

11.4.11. Add 4 mL of the citrate buffer solution (Section 7.11). The buffer solution contains the antifoam agent needed to control foaming from samples with high dissolved organic compound content.

11.4.12. Add reagent water until a slightly convex shape forms above the vial rim.

11.4.13. Add 25 µL of the ethylating reagent solution ($NaBEt_4$) (Section 7.12).

11.4.14. Immediately screw the Teflon™ septum cap on firmly. Flip the vial upside down to check for bubbles inside the vial. If there are bubbles in the vial, larger than 6 mm in diameter, re-prepare the vial vialVials are inverted several times then shaken vigorously by hand for 5 seconds. Mix the capped vialvial on a vortex mixer to ensure thorough mixing of the vial contents. Allow the sample to sit for 15 minutes to allow the ethylation reaction to reach completion. The ethylation chemistry has a limited reaction time; therefore, it is critical to perform these operations rapidly once the ethylating reagent is added to the sample.

11.4.15. AFTER ANALYSIS, ETHYLATED SAMPLES MUST BE STORED IN A HOOD UNTIL POTASSIUM PERMANGANATE CAN BE ADDED..

11.5. Preparation of aqueous samples with challenging matrix (USGS)

11.5.1. Place 19.5 mL of sample in a clear 43 mL vial.

11.5.1.1. For QC samples use 19.5 mL reagent water. Add 25 µL of low-level methionine solution (Section 7.14).

11.5.2. Add 19.5 µL of the 2 ppb n-propyl mercury surrogate solution (Section 7.17.6).

11.5.3. Add 19.5 µL of 2 ppb MeHg standard (Section 17.7.2) to all LCS and matrix spike samples.

11.5.4. Add 5 mL of acidic potassium bromide solution (Section 7.16), 1 mL of copper sulfate solution (Section 7.17), and 10 mL of DCM.

11.5.5. Secure vials on their sides in a box to allow for proper mixing, then place on laboratory shaker for one hour at high setting.

11.5.6. Refrigerate the DCM/water extract until cool. Allowing the extract to sit overnight may help break up any emulsion that may have formed. If necessary, centrifuge to separate aqueous and organic phases.

11.5.7. Prepare aqueous solvent exchange vials by adding about 10 mL of reagent water to an amber 43 mL vial.

11.5.8. Remove approximately 20 mL of the aqueous layer from the sample extract vial and discard.

11.5.9. Using a calibrated positive displacement pipette, transfer 5 mL of the DCM extract from the sample extraction vial to the corresponding aqueous solvent exchange sample vial. Do not transfer any of the aqueous layer or emulsion.

11.5.10. Heat the solvent exchange vial at 50°C ± 5°C while bubbling argon through the liquid in the vial. Continue bubbling until all solvent is gone.

11.5.11. Allow to cool and then add 4 mL of the citrate buffer solution (Section 7.11). The buffer solution contains the antifoam agent needed to control foaming from samples with high dissolved organic compound content.

11.5.12. Add reagent water until a slightly convex shape forms above the vial rim.

11.5.13. Add 25 µL of the ethylating reagent solution ($NaBEt_4$) (Section 7.12).

11.5.14. Immediately screw the Teflon™ septum cap on firmly. Flip the vialvial upside down to check for bubbles inside the vial. If there are bubbles in the vial, larger than 6 mm in diameter, re-prepare the vialvial. Vials are inverted several times then shaken vigorously by hand for 5 seconds. Mix the capped vial on a vortex mixer to ensure thorough mixing of the vial contents. Allow the sample to sit for 15 minutes to allow the ethylation reaction to reach completion. The ethylation chemistry has a limited reaction time; therefore, it is critical to perform these operations rapidly once the ethylating reagent is added to the sample.

11.5.15. AFTER ANALYSIS, ETHYLATED SAMPLES MUST BE STORED IN A HOOD UNTIL POTASSIUM PERMANGANATE CAN BE ADDED..

11.6. Sample Analysis

11.6.1. The instrument parameters are summarized in Table 3.

11.6.2. All measurements must fall within the defined calibration range in order to be valid. Dilute and reanalyze all samples that exceed the highest calibration standard.

11.6.3. The following analytical sequence must be used.
Rinse Blanks should be analyzed at the beginning of each day.
Instrument Calibration
ICV
ICB
Maximum 12 hr. sequence (client and QC samples)
CCV
CCB
Maximum 12 hr. sequence (client and QC samples)
CCV
CCB

Refer to Quality Control Section 3 and Table 2 (Appendix A) for the appropriate quality control criteria.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples, and sample dilutions.

Note: Initial calibration need not be performed if the opening CCV/CCB pair indicates that the system is in control.

11.7. 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 must be completely documented using a Nonconformance Memo.

11.8. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.9. Analytical Documentation

11.9.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.9.2. Standards and reagents are recorded in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

11.9.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.9.4. Record all sample results and associated QC in the LIMS. Level I and Level II data reviews are performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if J flags are required. Second column confirmation is not performed at this time. Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented automatically by the data system. Chromatograms are automatically recorded before and after manual integration. Additional information on manual integration can be found in SOP CA-QS-002.

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 matrix spike sample concentration
MSD = Determined matrix spike duplicate sample 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 x D

Where:
C = Concentration (ng/L) from instrument readout
D = Instrument dilution factor

12.8. The final concentration for a solid sample (FDEP Prep) is calculated as follows.

$$C_{Sample}\left(\frac{\mu g}{kg}\right) =$$

$$\frac{C_{Instr}\left(\frac{ng}{L}\right) x \frac{1\ \mu\ g}{1000\ ng} x \frac{1\ L}{1000\ mL} x V_{f\ Dilution}\ mL}{V_{Aliquot}\ \mu\ L\ x \frac{1\ mL}{1000\ \mu\ L}} x \frac{V_{f\ Digestate}\ mL}{W_{Sample}\ g} x \frac{1000\ g}{1\ kg}$$

Where:

C_{Instr} = Concentration (ng/L) from instrument readout
$V_{f\ Dilution}$ = (e.g., 39 mL) Final volume in 43 mL vial
$V_{f\ Digestate}$ = (e.g., 20 mL) Final volume of digestate
$V_{Aliquot}$ = (e.g., 390 µL) Volume of digestate diluted for analysis
W_{Sample} = (e.g., 1 g) Weight of solid sample (tissue)

12.9. The final concentration for a solid sample (USGS Prep) is calculated as follows.

$$C_{Sample}\left(\frac{\mu g}{kg}\right) =$$

$$\frac{C_{Instr}\left(\frac{ng}{L}\right) x \frac{1\ \mu g}{1000\ ng} x \frac{1\ L}{1000\ mL} x V_{f\ Dilution}\ mL}{V_{Aliq\ Aq\ Extract}\ mL} x \frac{V_{f\ Aq\ Extract}\ mL}{V_{Aliq\ DCM\ Extract}\ mL} x \frac{V_{f\ DCM\ Extract}\ mL}{W_{Sample}\ g} x \frac{1000\ g}{1\ kg}$$

Where:

C_{Instr} = Concentration (ng/L) from instrument readout
$V_{f\ Dilution}$ = (e.g., 39 mL) final volume in 43 mL vial
$V_{f\ Aq\ Extract}$ = (e.g., 43 mL) final volume of aqueous extract
$V_{Aliq\ Aq\ Extract}$ = (e.g., 4.2 mL) volume of aqueous extract diluted for analysis
$V_{f\ DCM\ Extract}$ = (e.g., 10 mL) final volume of methylene chloride (DCM) extract
$V_{Aliq\ DCM\ Extract}$ = (e.g., 2 mL) volume of methylene chloride (DCM) extract exchanged to water
W_{Sample} = (e.g. , 1 g) Weight of solid sample (tissue)

12.10. The final concentration for an aqueous sample prepared by the modified USGS prep is calculated as follows.

$$C_{sample}\left(\frac{ng}{L}\right) = C_{Instr}\left(\frac{ng}{L}\right) \times \frac{V_{f\ Aq\ Extract}\ mL}{V_{Aliq\ DCM\ Extract}\ mL} \times \frac{V_{f\ DCM\ Extract}\ mL}{V_{sample}\ mL}$$

Where:

C_{Instr} = Concentration (ng/L) from instrument readout
$V_{f\ Aq\ Extract}$ = (e.g., 39 mL) final volume of aqueous extract
$V_{f\ DCM\ Extract}$ = (e.g., 10 mL) final volume of methylene chloride (DCM) extract
$V_{Aliq\ DCM\ Extract}$ = (e.g., 5 mL) volume of methylene chloride (DCM) extract exchanged to water
V_{Sample} = (e.g., 19.5 mL) Initial sample volume extracted.

12.11. If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and re-analyzed. It may also be necessary to dilute samples due to matrix.

13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of performance data on file as described in Section 9.2.

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 9.5.

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 must 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 must 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. Ethylated aqueous waste: The waste from the autosampler and the residual sample in the autosampler vials might contain dialkyl mercury species. **These must be destroyed by adding potassium permanganate to oxidize the dialkyl mercury species to Hg^{2+}.** Then the waste is added to the aqueous metals waste stream "Acid Waste". Do not add to the mercury analysis waste stream that has stannous chloride, since this might produce elemental mercury vapor.

15.2.2. Acidic aqueous waste from preserved water samples: 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.

15.2.3. Methanol extracts from solid samples are collected in a 30-gallon flammable drum called "Digested Tissue and Soil Samples".

15.2.4. The "USGS extract" waste that contains methylene chloride is collected in the 55-gallon drum located in GC prep called "Vial Waste"

15.2.5. Vials that contained ethylating agent are collected in a container labeled hazardous waste when they emptied or deemed unfit for use.

16. REFERENCES

16.1. References

16.1.1. EPA Method 1630, "Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS", USEPA Office of Water, January, 2001

16.1.2. Florida DEP SOP HG-005-2.6, Analysis Of Ultra-Trace Level Methyl Mercury In Water By Aqueous Phase Ethylation, February 5, 2008

16.1.3. Florida DEP SOP HG-003-2.7, Analysis Of Methyl Mercury In Sediment and Tissue, July 30, 2007

16.1.4. US Geological Survey, Methods for the Preparation and Analysis of Solids and Suspended Solids for Methyl Mercury, Chapter 7 of Book 5, Laboratory Analysis Section A, Water Analysis, 2004

16.1.5. Corporate Quality Management Plan (CQMP), current version

16.1.6. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.7. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.8. Revision History

Historical File:		Revision 0: 03/06/09 (NC-GC-039)		Revision 2: Does not exist
		Revision 1: 04/09/09 (NC-GC-039)		Revision 3: 03/04/13
		Revision 2: 10/27/09 (NC-GC-039)		
		Revision 0: 04/13/11 (NC-SA-001)		
		Revision 1: 05/03/11		

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

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference method.

17.1.1. 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 LCS replicates (see Section 9.2 of this SOP).

17.1.2. Conventional MS/MSD techniques and criteria have been maintained in contrast to the variable matrix spike concentration in Section 9.3.1 of the Method 1630 (January 2001).

17.1.3. Section 9.4.3.1 of the Method 1630 (January 2001) recommends field blank analysis be performed 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. The analytical procedures used in this SOP are based on EPA Method 1630, but incorporate significant modifications in the sample preparation to simplify the process and enhance method performance developed by the FDEP and USGS. Side-by-side comparisons between this method and Method 1630 have been performed by the FDEP. The primary modifications from the original method include:

17.1.4.1. Full automation of the sample purge and trap and GC analysis

17.1.4.2. Direct sample ethylation without distillation

17.1.4.3. Use of a citrate buffer instead of an acetate buffer

17.1.4.4. Use of a silicone-based anti-foaming agent

17.1.4.5. Inclusion of a surrogate compound

17.1.4.6. Use of a Tenax™ trapping media instead of a Carbotrap™

APPENDIX A – TABLES

TABLE 1A
Methyl Mercury Reporting Limits, Calibration Standards, Qc Standards, And Spiking Levels (Ng/L) (Aqueous Matrices)

	MeHg ng/L	µL 2 ppb MeHg Std. (Sec.7.18.2)	µL 0.2 ppb ICAL Std. (Sec. 7.18.6	µL 2 ppb PrHg Std. (Sec.7.18)	
Water RL	0.05				
Cal Blank (x3)	0		0	9.75	
Std 1	0.05		9.75		
Std 2	0.1		19.5		
Std 3	0.2		39		

Std 4	0.5		97.5		
Std 5	1.0		195		
Std 6	2.0		390		
Std 7	4.0		780		
ICV (Second source MeHg)	0.5	9.75 (Sec. 7.18.5)		9.75	
CCV	0.5	9.75		9.75	
LCS	0.5	9.75		9.75	
MS/MSD	0.5	9.75		9.75	
Sample for USGS waters LCS and MS/MSD	2	19.5		19.5	

TABLE 1B

Methyl Mercury Reporting Limits, Calibration Standards, Qc Standards, And Spiking Levels (µg/Kg) (Solid Matrices)

	MeHg µg/kg	**µL 100 ppb MeHg Std. (Sec.7.18.3)**	**µL 100 ppb PrHg Std. (Sec.**Error! Reference source not found.**)**
Low Solid RL (USGS)	0.10		
LCS (USGS)	1.0	10	10
MS/MSD (USGS)	1.0	10	10
Sample (USGS)			10
High Solid RL (FDEP)	0.50		
LCS (FDEP)	5.0	50	50
MS/MSD (FDEP)	5.0	50	50
Sample (FDEP)			50

TABLE 2
Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY*	ACCEPTANCE CRITERIA 1630	CORRECTIVE ACTION
ICV	Immediately following every calibration	69-131 % recovery	Terminate analysis, correct the problem, recalibrate or re-prepare with calibration curve (see Section 9.11)
ICB	Immediately following the ICV, after every calibration.	The result must be within ± RL (0.05 ng/L for aqueous)	Terminate analysis, correct the problem, recalibrate or re-prepare with calibration curve (see Section 9.11)
Low standard in ICal	Every ICAL	65-135%	Terminate analysis, correct the problem, recalibrate (see Section 9.11)
CCV	Every 12 hrs. and at the end of the run	67-133 % recovery	Terminate analysis, correct the problem, recalibrate and rerun all samples not bracketed by acceptable CCV or re-prepare with calibration curve (note exceptions in Section 9.12)
CCB	Immediately following each CCV	The result must be within ± RL (0.05 ng/L for aqueous)	Terminate analysis, correct the problem, recalibrate and rerun all samples not bracketed by acceptable CCB or re-prep with calibration curve (note exceptions in Section 9.11)
Method Blank	One per sample preparation batch of up to 20 samples	The result must be within ± RL. Sample results greater than 20x the blank concentration are acceptable.	Re-prepare and re-analyze samples. Note exceptions under criteria section. See Section 9.5 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples	In house generated.	Terminate analysis, correct the problem, re-prepare and re-analyze all samples associated with the LCS (Note: exception under Section 9.8)
Matrix Spike	Ten percent frequency per preparation batch, rounding up.	In house generated	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added (see Section 9.10)
Matrix Spike Duplicate	See matrix spike	In house generated	See corrective action for matrix spike
Surrogate	All samples	In house generated.	Check calculations for error. Check instrument performance. Flag or re-prepare / re-analyze a sample. See Section 9.7.

*See Section 11.6.3 for exact run sequence to be followed.

TABLE 3
Recommended Instrument Parameters

Instrument Parameter	Setting
Detector	
Psaserv gain setting	100
Argon regulator	40 psi
Sheath gas flow	75 ml/min
Make-up gas flow	150ml/min
Pyrolizer	700°C
GC	
Argon regulator to GC	75 psi
Oven equilibration time	0.5 min
Temperature Program	40°C for 2.5 min, then ramp at 35°C/min to 200°C for 1 min
Total run time	8.0714 min
GC inlet	Bypassed with direct connection from P&T concentrator to GC column
Column pressure	5.5 psi
Concentrator	
Valve oven temp	150°C
Transfer line temp	150°C
Sample mount temp	90°C
Purge ready temp	35°C
Standby flow	5 ml/min
Pre-purge time	0.5 min
Pre-purge flow	40 ml/min
Sample heater	off
Sample preheat time	1.00 min
Sample temp	40°C
Purge time	11.00 min
Purge temp	Room temperature (set 0)
Purge flow	40 mL/min
Condenser ready temp	40°C
Condenser purge temp	20°C
GC start	Start of desorb
Desorb preheat temp	175°C
Desorb drain	on
Desorb time	2.00 min
Desorb temp	180°C
Desorb flow	300 ml/min
Bake time	5.00 min
Bake temp	180°C
Bake flow	100 ml/min
Condenser bake temp	175°C
Autosampler	
Sample loop fill	29
Loop equilibration	5
Sample transfer	30
Needle rinse	15
Needle sweep	15
Sample loop rinse	30
Sample loop sweep	40
Sample drain	120
Sparge rinse	70
Sparge rinse transfer	40

TestAmerica Canton

SOP Amendment Form

SOP NUMBER: NC-GC-045 Rev. 1

SOP TITLE: Gas Chromatographic Analysis Based on Methods 8082 and 8082A

REASON FOR ADDITION OR CHANGE: Adding Retention Time wording from Corporate, adding “of PCBs" to the title

CHANGE EFFECTIVE FROM: (DATE): 6/22/16

Change(s) Made:

Title changed to read: GAS CHROMATOGRAPHIC ANALYSIS of PCBs BASED ON METHODS 8082 and 8082A

Added section 10.20 Retention Time Windows

EDITED BY/DATE: Melissa Fuller-Gustavel 6/22/16

TestAmerica Canton

SOP Amendment Form

SOP NUMBER: NC-WC-045 Rev. 1
SOP TITLE: Gas Chromatographic Analysis Based on Methods 8082 and 8082A
REASON FOR ADDITION OR CHANGE: Removal of references to DoD
CHANGE EFFECTIVE FROM: (DATE): 6/14/16
Change(s) Made: All references to DoD and/or QSM have been removed.
EDITED BY/DATE: 6/14/16

Title: GAS CHROMATOGRAPHIC ANALYSIS BASED ON METHODS 8082 and 8082A

Approvals (Signature/Date):

Technology Specialist	01/13/16 Date	Health & Safety Coordinator	01/14/16 Date
Quality Assurance Manager	01/13/16 Date	Technical Director	01/14/16 Date

This SOP was formerly known as NC-GC-045 Rev. 0, dated 03/17/14

Facility Distribution No. _____ Distributed To:_____

The controlled copies of this SOP are the PDF copy that is posted to the laboratory's SOP Directory and, where applicable, the copy of the SOP that is printed and placed in the General Chemistry SOP binder. Printed or electronic copies of the SOP distributed outside of the facility are considered uncontrolled.

TABLE OF CONTENTS

1. SCOPE AND APPLICATION

1.1. This SOP describes procedures to be used when SW-846 Method 8082 or 8082A are applied to the analysis of polychlorinated biphenyls (PCB) by GC/ECD. This SOP is applicable to extracts derived from any matrices which are prepared according to the appropriate sample extraction SOPs. PCBs are determined and quantitated as Aroclor mixes.

1.2. Tables 1 and 5 list compounds, which are routinely determined by this method and the Reporting Limits (RL) for each matrix. Matrix interferences and/or high concentrations of PCB compounds may result in higher RLs than those listed.

2. SUMMARY OF METHOD

2.1. PCBs in aqueous samples are prepared for analysis using continuous liquid/liquid or separatory funnel extraction (SOP NC-OP-037 and NC-OP-038). Solid samples are prepared using sonication or soxhlet extraction (SOP NC-OP-039 and NC-OP-040). After the initial preparation step, the sample is introduced into the GC and the concentration of each target analyte is measured by the detector response within a defined retention time (RT) window, relative to the response of the reference standards.

3. DEFINITIONS

3.1. Refer to the Test America Canton Quality Assurance Manual (QAM), current version, for definitions of terms and acronyms used in this document.

4. INTERFERENCES

4.1. Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results. All glassware is cleaned per SOP NC-QA-014.

4.2. Interferences in the GC analysis can arise from many compounds which are amenable to gas chromatography and give a measurable response on the electron capture detector (ECD). Phthalate esters, which are common contaminants found in plastics, can pose a major problem in the determinations. Avoiding contact with any plastic materials minimizes interferences from phthalates.

4.3. Compounds extracted from the sample matrix to which the detector will respond, such as single-component chlorinated pesticides, including the DDT analogs (DDT, DDE, and DDD) will cause interference. A standard of the DDT analogs should be injected to determine which of the PCB or Aroclor peaks may be subject to interferences on the analytical columns used. There may be substantial DDT interference with the last major Aroclor 1254 peak in some soil and sediment samples.

4.4. Sulfur will interfere and can be removed using procedures described in SOP NC-OP-025.

4.5. Interferences co-extracted from samples will vary considerably. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts. These cleanup procedures are included in SOP NC-OP-025.

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. Eye protection that prevents splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Refer to the TestAmerica Canton Corporate Environmental Health and Safety Manual for a complete description of personal protection equipment.

5.2. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated must be removed and discarded; other gloves must be cleaned immediately. Nitrile gloves provide adequate protection against the solvents used in this method.

5.3. 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 Safety Data Sheet (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	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-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.
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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.5. All ^{63}Ni sources (ECD) must be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.6. All ^{63}Ni sources must be inventoried every six months. If a detector is missing, the EH&S Director must be immediately notified and a letter sent to the NRC or local state agency.

5.7. Exposure to chemicals must be limited as much 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 must be kept closed unless transfers are being made.

5.8. Opened containers of neat standards must be handled in a fume hood.

5.9. Sample extracts and standards, which are in a flammable solvent, must be stored in an explosion-proof refrigerator.

5.10. When using hydrogen gas as a carrier, all precautions listed in the CSM must be observed.

5.11. Standard preparation and dilution must be performed inside an operating fume hood.

5.12. The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.13. There are areas of high voltage in 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.

5.14. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported immediately to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Gas Chromatograph (GC) equipped with Electron Capture Detectors (ECDs)

6.2. Software: ChemStation or equivalent

6.3. Refer to Table 2- for analytical columns and run conditions

6.4. Microsyringes and syringes: various sizes, for standards preparation, sample injection, and extract dilution

6.5. Autosampler vials, inserts, and caps

6.6. Class A volumetric flasks: various sizes

6.7. Transfer pipettes: disposable

6.8. VOA vials

6.9. Carrier gas: Hydrogen

6.10. Makeup gas: Nitrogen

7. REAGENTS AND STANDARDS

7.1. Stock Standards: Stock standards are purchased as certified solutions or prepared from pure solutions.

7.1.1. Other stock standard solutions are stored as recommended by the manufacturer. All stock standards must be protected from light. Stock standard solutions must be brought to room temperature before using.

7.1.2. Stock standard solutions must be replaced after one year.

7.1.3. Expiration times for all standards are measured from the time the standard is prepared or from the time that the standard ampoule is opened, if the standard is supplied in a sealed ampoule. If vendor-supplied standard has an earlier expiration date then the vendor's expiration date is used. Refer to SOP NC-QA-017, Standards and Reagents, for additional information. The standard preparation information is detailed in the LIMS standards and reagents module.

7.2. Calibration Standards

7.2.1. PCB Calibration Standards

7.2.1.1. PCB calibration standards are prepared as dilutions of the stock standards. Surrogates and internal standards are used as specified in the method. PCB calibration solutions must be refrigerated at 4° C ± 2° C and protected from light. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

7.2.1.2. Refer to Table 3 for details of calibration standards. See the TALS Reagent module for details on sample preparation.

7.3. Surrogate Standards

7.3.1. Tetrachloro-m-xylene (TMX) and decachlorobiphenyl (DCB) are the surrogate standards. Refer to Table 4 for details of surrogate standards.

7.4. Internal Standard

7.4.1. The internal standard used for PCB analysis is 1-Bromo-2-nitrobenzene (BNB)

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Unless otherwise specified by regulatory or client programs, holding time for PCB samples (regardless of matrix) is 1 year.

8.2. Sample extracts are stored at 4 ± 2°C. The holding time for PCB sample extracts is 40 days.

9. QUALITY CONTROL

9.1. Batch definition

9.1.1. The batch is a set of up to 20 samples of the same matrix processed at the same time using the same procedures and reagents. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank (MB). Laboratory generated QC samples (Method Blank, LCS and MS/MSD do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count. In some cases, at client request, the MS/MSD may be replaced with an MS and an unspiked sample duplicate (DU).

9.2. Method Blank (MB)

9.2.1. For each batch of samples, analyze a MB. The MB consists of reagent water for aqueous PCB samples and sodium sulfate for PCB soils tests and all surrogates required for the analysis. Refer to SOPs NC-OP-037, NC-OP-038, NC-OP-039, and NC-OP-040 for details.

9.2.2. The MB must not contain any analyte of interest at, or above, the reporting limit or at, or above, 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

Note: Some programs such as Wisconsin require that the MB be clean to ½ the RL. Method notes should inform the analyst if the samples are part of a special program. Analysts are responsible for checking the program requirements.

9.2.3. Corrective action

9.2.3.1. Re-extraction and re-analysis of samples associated with an unacceptable MB is required when reportable concentrations are determined in the samples.

9.2.3.2. If there is no target analyte greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers.

Note: For Ohio VAP projects, the MB result must be below the reporting limit or samples must be re-extracted, unless the samples are non-detect.

9.3. Laboratory Control Samples (LCS)

9.3.1. For each batch of samples, analyze an LCS. The LCS contains a representative subset of the analytes of interest and all surrogates required for the analysis, and must contain the same analytes as the matrix spike. If any

LCS analyte is outside the laboratory established historical control limits, corrective action must occur.

9.3.2. Corrective Action

9.3.2.1. Corrective action may include re-analysis of the LCS. If the re-analysis fails to meet criteria, re-extraction and re-analysis of the batch may be needed. If the LCS is biased high, samples that are non-detect for the failing analyte can be reported with proper narration.

Note: For Ohio VAP samples, re-analyze an aliquot of the LCS to verify the outlier; if the LCS exhibits the same anomaly upon re-analysis, the sample batch must be re-extracted and re-analyzed. The exceptions are as follows: (a) insufficient sample for re-extraction, (b) expired holding times, or (c) the LCS is biased high and the samples are non-detect for those analytes. Under the above circumstances, results may be reported with proper narration.

9.3.3. LCS compound lists and surrogates are included in table 4.

9.4. Matrix Spikes/Spike Duplicates (MS/MSD)

9.4.1. For each QC batch, analyze an MS/MSD. Spiking compounds and surrogates and levels are given in Table 4. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory-specific historically generated limits.

9.4.2. If any individual recovery or RPD falls outside the acceptable range, corrective action must occur unless samples for this compound are ND. The initial corrective action must be to check the recovery of that analyte in the LCS. Generally, if the recovery of the analyte in the LCS is within limits, adverse matrix effect is indicated, the laboratory operation is in control and analysis may proceed.

9.4.3. If the recovery for any component is outside QC limits for both the MS/MSD and the LCS, the laboratory process is out of control and corrective action must be taken.

9.4.4. The MS/MSD must be analyzed at the same dilution as the un-spiked sample, unless the matrix spike components would then be above the calibration range.

9.5. Surrogates

9.5.1. Surrogates are added to all samples, MB, and LCS during the preparation procedure. Surrogates are added to instrument QC for the 1016/1260 Aroclor mix, which includes the calibration standards, the ICV, and the CCVs. Surrogate recoveries in samples and QC samples must be assessed to ensure that recoveries are within established limits.

9.5.2. Method Blank

9.5.2.1. Surrogates are added to the MB and the MB is carried through the entire analytical procedure. The MB must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the MB and affected samples will normally be required. If surrogate recoveries are high, and the samples are non-detect, the data can be reported with proper narration.

Note: For Ohio VAP samples, all MB surrogates must meet criteria or the samples must be re-extracted if sufficient volume of sample remains. The exceptions are as follows: (a) insufficient sample for re-extraction (b) expired holding times, or (c) the surrogates are biased high and the samples are non-detect.

9.5.3. LCS

9.5.3.1. The LCS must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the LCS has served the purpose of demonstrating effectiveness of the extraction process. If surrogate recoveries are low, re-extraction of the LCS and affected samples will normally be required. None of the surrogate recoveries can fall below 10% in the LCS. If surrogate recoveries are high, and the samples are non-detect, the data can be reported with proper narration.

Note: For Ohio VAP samples, all LCS surrogates must meet criteria or the samples must be re-extracted if sufficient volume of sample remains. The exceptions are as follows: (a) insufficient sample for re-extraction (b) expired holding times, or (c) the surrogates are biased high and the samples are non-detect.

9.5.4. Instrument QC

9.5.4.1. Surrogates in the 1016/1260 calibration standards must meet the same criteria as the ICAL. See section 10 for ICAL criteria.

9.5.4.2. Surrogates in the ICV, Daily/12-hour calibration verification, and CCVs must have a %Drift/%Difference of < 20%.

9.5.4.3. Corrective action for failing surrogates in the instrument QC are discussed in section 10.

9.5.5. Samples

9.5.5.1. If either surrogate is outside limits, the following corrective actions must take place (except for dilutions greater than 5X):

9.5.5.1.1. Check all calculations for error.

9.5.5.1.2. Ensure instrument performance is acceptable.

9.5.5.1.3. Recalculate the data and/or re-analyze the extract if either of the above checks reveals a problem.

9.5.5.2. It is only necessary to re-prepare / re-analyze a sample once to demonstrate poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out-of-control results are not due to matrix effect.

Note: For Ohio VAP Projects, all surrogates must meet criteria unless the samples are ND and the surrogates are out high. Otherwise, the analyst should re-analyze the sample, re-prep and re-analyze the sample, or a dilution may be performed if the analyst believes it will solve the issue. When there is an obvious interference causing the surrogate outlier that the analyst knows a corrective action would not resolve, it is permissible to flag the data with a qualifier indicating matrix interference.

9.5.5.3. If the surrogates are out of control for the sample and MS/MSD, then matrix effect has been demonstrated for that sample and re-preparation is not necessary. If the sample is out of control and the MS/MSD is in control, then re-preparation or flagging of the data is required. Re-preparation includes the parent sample and the MS/MSD.

9.5.6. For some jobs, depending on the program, one surrogate may be outside of acceptance criteria, but neither may be below 10% regardless of program, or the sample will need re-extracted.

Note: Use of such data requires data quality objective (DQO) driven review, professional judgment of an experienced analyst, QA personnel, and/or approval of the group leader or designee.

Note: This is not applicable to OVAP projects under any circumstance. Both surrogates must meet criteria for OVAP projects.

9.5.7. Refer to TestAmerica North Canton QC Program document (Policy QA-003) for further details of the corrective actions.

9.6. Internal Standard (IS)

9.6.1. This procedure is an IS procedure. 1-Bromo-2-nitrobenzene (BNB) is the internal standard used.

9.6.2. Prior to analysis, this IS must be added to all standards, field samples, and QC samples. The concentration of the IS must be the same in all calibration samples, field samples and QC samples. A concentration of 0.05 ug/mL is used.

9.6.3. The response of the IS in the ICV/CCV must be within 50-200% of the response of the IS in the CCV-level standard in the initial calibration sequence. If the response is outside of this range, the analysis of the CCV must be repeated and any samples associated with the CCV must also be re-analyzed. Repeated failure of the IS response will require recalibration.

9.6.4. The response of the IS in the samples and batch QC items must be within 50-200% of the response of the previous CCV. If the response is outside of the range, corrective action must be taken which can include re-analysis of the extract, re-spiking the extract with IS and re-analysis, or re-calibration of the analytical system. Obvious matrix interferences are qualified and noted in an NCM.

9.6.5. For OVAP samples, samples with failing internal standards must be re-analyzed unless matrix interference is apparent. In cases where matrix interference is not obvious, spike a fresh aliquot of sample with IS solution and re-analyze. If the IS fails to meet criteria again, and the IS meets criteria in batch and instrument QC, the re-analysis serves to confirm matrix interference and the sample will be re-analyzed at a dilution as described below. If matrix interference is apparent, dilute the sample with hexane for re-analysis. When, in the analyst's professional judgment, there is obvious interference causing the IS failure that corrective action will not remedy, data must be flagged with a qualifier to indicate the effect of matrix interference. If the batch QC (MB and/or LCS) has failing internal standards, re-spike a fresh aliquot of the applicable QC sample with internal standard solution and re-analyze. If there is continuing failure, the batch may require re-preparation of the IS solution, and/or recalibration. If the ICV and/or CCV have failing internal standards, the batch must be re-analyzed. Continued failure may necessitate re-preparation of the IS solution and/or recalibration.

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via LIMs.

10. CALIBRATION AND STANDARDIZATION

10.1. Internal or external calibration may be used. Prepare standards containing each analyte of interest at a minimum of five concentration levels. The low-level standard must be at, or below, the reporting limit. The other standards define the working range of the detector. .

10.2. The initial calibration block for PCB must include at least one level with 1016 analyzed separately for pattern recognition purposes. This run does not have to be part of the

calibration.

10.3. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns or replacing the ECD detector. A new calibration is not required after clipping the column, replacing the septum or syringe, or other minor maintenance, unless CCV criteria cannot be met.

10.4. With the exception of section 10.5 below, it is not acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve and the reporting limit and/or linear range is adjusted accordingly. In any event, at least five points must be included in the calibration curve. Quadratic (second order) calibrations require at least six points.

Note: Quadratic calibrations are not acceptable for PCB analysis for OVAP projects.

10.5. A level may be removed from the calibration if the reason can be clearly documented (for example, a broken vial or no purge run). A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be re-analyzed and the re-analysis used for the calibration. All initial calibration points in a single calibration curve must be analyzed without any changes to instrument conditions, and all points in a single calibration curve must be analyzed within 24 hours.

10.6. Internal Standard Calibration

10.6.1. Internal standard calibration involves the comparison of instrument responses from the target compounds in the sample to the responses of specific standards added to the sample or sample extract prior to injection. The ratio of the peak area (or height) of the target compound in the sample or sample extract is compared to a similar ratio derived for each calibration standard. The ratio is termed the response factor (RF), and may also be known as a relative response factor.

10.6.2. When preparing calibration standards for use with internal standard calibration, add the same amount of internal standard solution to each calibration standard, such that the concentration of each internal standard is constant across all of the calibration standards, whereas the concentrations of the target analytes will vary. The mass of the internal standard added to each sample extract immediately prior to injection into the instrument must be the same as the mass of the internal standard in each calibration standard. The volume of the solution spiked into sample extracts should be such that minimal dilution of the extract occurs.

10.6.3. Prepare calibration standards at a minimum of five concentration levels for each parameter of interest and each surrogate. Six standards must be used for a quadratic least squares calibration. Add the appropriate amount of the IS mixture to result in a 0.05 ug/mL concentration. The low standard must be at or below the reporting limit

10.6.4. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound and surrogate using the equations in Section 12.

10.7. External standard calibration

10.7.1. Quantitation by the external standard method assumes a proportional relationship between the analyte or surrogate response and the concentration that is the same in all of the calibration standards and the samples. To use this approach, introduce each calibration standard into the GC using the technique that will be used for samples. The ratio of the peak height or area response to the mass or concentration injected is used to prepare a calibration curve.

10.8. Calibration Curve Fits

10.8.1. The calculations for all calibration curve fits are found in section 12.

10.8.2. Weighted linear regression, average calibration factor, non-weighted linear regression, or quadratic curves may be used to fit the data. Weighted linear regression is the preferred calibration model used for PCB.

10.9. Average calibration factor (CF) / response factor (RF)

10.9.1. The average CF (external calibration) or RF (internal standard) may be used if the average percent relative standard deviation (% RSD) of all the CFs / RFs taken together is $\leq$ 20%. The average % RSD is calculated by summing the RSD value for each peak and dividing by the total number of peaks.

10.10. Linear Regression / Weighted Linear Regression

10.10.1. Linear / weighted linear regressions must have a minimum of 5 calibration levels with the lowest being at or below the reporting limit. The correlation coefficient (r) must be >0.990. The ICV % Drift (%D) must be <20%, and the CCV %D must be <15% for Method 8082. For Method 8082A, the criteria for both ICV and CCV are < 20% % Drift/ Difference.

10.11. Quadratic Curve

10.11.1. A quadratic calibration curve must only be used if the analyst has reason to believe that a linear or average model does not fit the normal concentration-to-response behavior of the detector. A quadratic curve fit may be used only if the compounds have historically exhibited a non-linear response and cannot be used to extend the calibration range for compounds that normally exhibit a linear response, but within a narrower calibration range.

10.11.2. A quadratic calibration curve must have a minimum of 6 calibration levels with the lowest being at or below the reporting limit. The coefficient of determination (r^2) must be > 0.990.

10.12. Evaluation of Calibration Curves

10.12.1. The percent relative standard error (% RSE) from the calibration curve is used to evaluate the initial calibration. This provides a measure of how much error is associated with using the calibration curve for quantitation.

10.12.2. The least squares regression line is calculated and used to calculate the predicted concentration for each level.

Note: When average calibration factors are used, %RSE is equivalent to %RSD.

10.13. The following requirements must be met for any calibration to be used.

10.13.1. Response must increase with increasing concentration.

10.13.2. If a curve is used, the calculated intercept of the curve at zero response must be less than ± the reporting limit for the analyte.

10.13.3. The average Relative Standard Error (RSD for average response factors) of the calibration points from the curve used must be ≤ 20%.

10.13.4. Some data systems will not measure the %RSE from a linear or quadratic fit. For the linear case, the correlation coefficient may be used as an alternative to the %RSE, and must be greater than or equal to 0.990. For the quadratic case the Coefficient of Determination (COD) may be used, and must be greater or equal to 0.990.

Note: The Relative Standard Error (RSE) is superior to the Correlation Coefficient (*r*) and Coefficient of Determination (r^2) for testing the fit of a set of calibration points to a line. The lower points on a curve have little effect on *r.* As a result, a curve may have a very good correlation coefficient (>0.990) while also having > 100% error at the low point.

Note: The surrogates must be judged against this same criteria.

10.14. Weighting of Data Points

10.14.1. In linear and quadratic calibration fits, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason, it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and must be used if the data system has this capability.

10.15. Non-standard analytes are sometimes requested. For these analytes, it may be acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five-point initial calibration. This action must be with client approval. If the analyte is detected in any of the samples, a five-point initial calibration must be generated, and the sample(s) re-analyzed for quantitation.

10.16. Initial Calibration

10.16.1. Refer to Table 6 for the initial calibration analytical sequence.

10.16.2. A minimum five-point calibration of all Aroclors is generated. The low-level standard must be at or below the reporting limit. The other standards define the working range of the detector.

10.16.3. If any Aroclor is determined above the calibration range, the extract must be diluted and re-analyzed. See Table 3 for calibration levels.

10.16.4. The surrogate calibration curve is included in the calibration from the Aroclor 1016/1260 mix.

10.17. Initial Calibration Verification (ICV)

10.17.1. The ICVs are analyzed immediately after an initial calibration. The acceptance criterion is ± 20%. If this is not met, a new initial calibration curve is analyzed.

Note: An ICV is run for all Aroclors, however only 1016 and 1260 are reported unless others are required by client program such as OVAP.

10.18. Daily 12-Hour Continuing Calibration

10.18.1. The 12-hour calibration verification must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration standard must be analyzed and criteria met before proceeding with the sequence. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12-hour calibration. For Method 8082A, the CCV acceptance criterion is ± 20%. For Method 8082, the CCV acceptance criterion is ±15%.

10.18.2. At a minimum, the 12-hour calibration includes analysis of the Aroclor 1016/1260 mix.

10.18.3. Other Aroclors may be included in the daily calibration check at client or project request.

10.18.4. The retention time windows for any analytes included in the daily calibration and CCVs are updated from the beginning CCVs.

10.18.5. Evaluate the resolution requirements. For PCB, the minimum resolution requirement for the triplet towards the end of the1260 chromatogram is 25% on one of the two columns used.

10.19. Continuing Calibration Verification (CCV)

10.19.1. Mid-level standards covering all Aroclors of interest are used for the calibration verifications.

Note: only the 1016/1260 Aroclor CCV will be reported unless others are required per client request.

10.19.2. It may be appropriate to analyze a mid-point standard more frequently than every 12 hours. If these calibration verification standards are analyzed, requirements are the same as the 12-hour calibration with the exception that retention times are not updated.

10.19.3. For external calibration models, the Aroclor 1016/1260 calibration mid-point working standard solution is analyzed after every 20 samples, including matrix spikes, LCSs, and MBs (Depending on the type of samples and at analyst discretion, it may be advisable to analyze verifications more frequently in order to minimize reruns.) Samples quantitated by external standard must be bracketed by calibration verification standards that meet the criteria listed in 10.14.4. Bracketing CCVs are not required for IS calibrations.

Note: Various programs require a CCV every 10 samples. Analysts are responsible for checking the program requirements.

10.19.4. Any individual compounds with %D <15% (for 8082) or %D <20% (for 8082A) meet the calibration criteria. If the CCV fails high, only sample results that are below the reporting limit can be reported with narration. Samples bracketed by a CCV that fails low require re-analysis (external calibration models only).

10.19.5. It is not necessary to run a calibration verification standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.19.6. If the CCV is biased high, and the associated samples are non-detect for those analytes, the sample results are reported. Appropriate comments must be made in the narrative to provide further documentation in these cases.

10.19.7. If highly contaminated samples are expected, it is acceptable to analyze solvent blanks or primers at any point in the run.

10.19.8. Corrective Actions for Continuing Calibration

10.19.8.1. If the overall average percent drift of all analytes is greater than ±15% (±20% for method 8082A), corrective action must be taken. This may include clipping the column, changing the liner, or other minor instrument adjustments, followed by re-analyzing the standard. If the overall average percent drift still varies by more than ± 15% (±20% for method 8082A), a new calibration curve may be required.

10.19.9. Corrective Action for Samples

10.19.9.1. Any samples injected after the last good continuing calibration standard must be re-injected. This applies to external calibration only.

Note: The laboratory performs Update IV's recommended analysis of DDT and analogs DDD and DDE daily to assure there is no interference with major 1254 peaks.

10.20. Retention Time Windows

10.20.1. Retention time (RT) windows must be determined for all analytes.

10.20.2. Initial determination of Retention time windows

10.20.2.1. The center of the retention time (RT) window shall be updated based on the middle level in the initial calibration or the first CCV in the daily analytical sequence, whichever is more recent.

10.20.2.2. Evaluate the deviation from expected retention time for each analyte in at least three CCV and/or LCS samples spread over at least 72 hours.

10.20.2.3. If three days of analytical data are not available, use a default RT window of 0.01 minutes. At the end of the batch evaluate all CCVs and LCS in the batch. If necessary, widen the window such that all analytes fall within the RT window. Reprocess the batch using the new RT windows.

10.20.2.4. Multiply the standard deviation by 3. This is the retention time window, unless the result is less than 0.01 min, in which case the window is set at 0.01 min.

10.20.2.5. An alternative method to determine the retention time window is to multiply the maximum deviation of all points by 1.5. The minimum retention time window is 0.01 minutes. For example, if the maximum RT deviation for a specific analyte is 0.008 min, then the RT window is set at +/- 0.012 min.

Note: For the multi-component analytes, for example Aroclors, Toxaphene and Technical Chlordane, the maximum deviation must be evaluated for each of the 3 to 6 major peaks used for sample calculations.

10.20.2.6. If the retention time windows for analytes of interest overlap, the analyte must be confirmed on a dissimilar column.

10.20.3. Ongoing evaluation of retention time windows

10.20.3.1. Evaluate the retention time windows on an ongoing basis. The center of the RT window is updated on the first CCV of the day and verified every 12 hours. All analytes for all subsequent CCVs, LCS and matrix

spikes must fall within the retention time window (except as discussed below).

10.20.3.2. Matrix spike analytes may fall outside the retention time window if there is a large non-target peak coeluting with the analyte in the matrix spike.

10.20.3.3. If any analytes fall outside the retention time window in CCVs, LCS or matrix spikes (except as discussed above for matrix spikes) then the RT windows for those analytes shall be widened to the minimum degree required for the analyte to fall within the RT window. All samples in the batch shall be reprocessed with the new RT window, and the wider RT window shall remain in place for subsequent batches.

10.20.3.4. Retention time windows should be reliably narrower than +/- 0.03 min. If RT windows wider than this are necessary, the instrument should be evaluated and maintenance performed as needed. Subsequent to maintenance, RT windows shall be narrowed to the extent that is consistent with the data obtained.

11. PROCEDURE

11.1. 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 must be completely documented using a Nonconformance Memo. The Nonconformance Memo must be filed in the project file. The nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. Procedural deviations are not allowed for Ohio VAP Projects.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3. Extraction

11.3.1. Extraction procedures are referenced in the SOPs NC-OP-037, NC-OP-038, NC-OP-039, and NC-OP-040, current revisions.

11.4. Suggested gas chromatographic conditions are given in Table 2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table 6

11.7. Sample Analysis

11.7.1. For samples analyzed by IS calibration models, transfer 100 uL of the extract to an autosampler vial and add 5 uL of the IS solution or equivalent volumes to

give an IS concentration of 0.05 ug/mL. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples. LVI (Low Volume Initiative) samples will require a more dilute working IS standard. See LIMS reagents module for details.

11.7.2. For samples analyzed by external calibration models, transfer an adequate amount of extract into an autosampler vial and load the vials onto the instrument.

11.7.3. The sample extract must be injected using the same injection volume used for the calibration standards.

11.8. Identification of Aroclors

11.8.1. Retention time windows are used for identification of Aroclors, but the "fingerprint" produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

11.8.2. A clearly identifiable Aroclor pattern serves as confirmation for single column GC analysis.

11.9. Quantitation of Aroclors

11.9.1. For PCB analysis, the preferred reporting approach is the primary column approach. Dependent upon client program, the best column approach may be used for quantitation.

11.9.2. Use 3-10 major peaks or total area for quantitation

11.9.3. If the analyst believes that a combination of Aroclor 1254 and 1260 or a combination of 1242, 1248 and 1232 is present, then only the predominant Aroclor is quantitated and reported; but the suspicion of multiple Aroclors is discussed in the narrative. If well-separated Aroclor patterns are present, then multiple Aroclors may be quantitated and reported.

11.9.4. Every sample undergoes dual column analysis, however, reporting the second column results will only be performed when requested by the client or regulatory program. The appearance of the multiple characteristic peaks in the sample usually serves as a confirmation of Aroclor presence.

11.10. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX). Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits, however, neither may be <10%.

Note: For Ohio VAP samples all surrogates must meet acceptance limits, unless the

surrogate is biased high and the sample is ND.

11.11. Calibration Range

11.11.1. If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and re-analyzed. Dilutions must target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

11.12. Dilutions

11.12.1. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample may be re-analyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.13. Guidance for Dilutions Due to Matrix

11.13.1. If the sample is initially run at a dilution and only minor matrix peaks are detected, then the sample may be re-analyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination.

11.14. Reporting Dilutions

11.14.1. The most concentrated dilution with no target compounds above the calibration range should be reported. Other dilutions may be reported at client request if the lower dilutions will not cause detector saturation, column overload, or carryover. Analyst judgment and client site history will be factors in the reporting of dual dilutions.

11.15. Interferences

11.15.1. If peak detection is prevented by interferences, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

11.16. Analytical Documentation

11.16.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.16.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

Note: When making new standards, it is required that all information entered into TALS is reviewed by another analyst.

11.16.3. Record sample and associated QC information in the LIMs. Level I and Level II technical reviews are performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calibration Calculations

12.1.1. Calibration Factor (CF) for external calibration and Response Factor (RF) internal standard calibration

$$CF = \frac{A_S}{M_S}$$

Where A_s = Peak area (or height) in standard

M_s = Total mass of standard injected

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where: A_x = Peak Area (or height) of the analyte or surrogate

A_{is} = Peak Area (or height) of the internal standard

C_x = Concentration of the analyte or surrogate (µg/L)

C_{is} = Concentration of the internal standard (µg/L)

12.1.2. Evaluating the linearity of the initial calibration using an Average Calibration fit:

Mean CF = $\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$ (external calibration)

Mean RF = $\overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$ (internal standard calibration)

Where n = the number of calibration standards

Standard Deviation (SD) = $\sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n-1}}$ (external calibration)

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - \overline{RF})^2}{n-1}}$$ (internal standard calibration)

Where n = the number of calibration standards

$$\%RSD = \frac{SD}{\overline{CF}} \times 100$$ (external)

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$ (internal standard)

Note: If the RSD of the calibration or response factors is less than or equal to 20%, the average calibration or response factor may be used to determine sample concentrations.

12.1.3. Percent Difference (%D)

$$\%D = \frac{CF_c - \overline{CF}}{\overline{CF}} \times 100$$

Where CF_c = The calibration factor from the CCV or ICV

$\overline{CF}$ = The average calibration factors from the initial calibration

$$\%D = \frac{RF_c - \overline{RF}}{\overline{RF}} \times 100$$

Where RF_c = The response factor from the CCV or ICV

$\overline{RF}$ = The average response factors from the initial calibration

12.2. Linear and weighted linear regressions

y = ax + b

or for weighted linear:

$$y = \frac{1}{SD^2} \times (ax + b)$$

Where y = Instrument response

a = Slope of the line

x = Concentration of the calibration standard

b = The intercept

SD = Standard deviation from 12.1.2

12.2.1. For internal standard the equation for weighted or non-weighted linear regression is:

$$C_s = \frac{\left(\frac{A_s C_{is}}{A_{is}} - b\right)}{a}$$

Where A_s = Area (or height) of the peak for the target analyte in the sample

A_{is} = Area (or height) of the peak for the internal standard

C_s = Concentration of the target analyte in the calibration standard

C_{is} = Concentration of the internal standard

a = Slope of the line

b = The intercept

12.2.2. Correlation Coefficient

$$r = \frac{\sum d_x d_y}{\sqrt{\sum d_x^2 \sum d_y^2}}$$

Where:

d_x = deviation of x from the mean

d_y = deviation of y from the mean

12.2.3. Relative Standard Error (%RSE)

$$\%\,RSE = 100\% \times \sqrt{\frac{\sum_{i=1}^{N}\left[\frac{C_i - PC_i}{C_i}\right]^2}{(N-P)}}$$

Where: N = Number of points in the curve
P = Number of parameters in the curve (= 1 for average response factor, 2 for linear, 3 for quadratic)
C_I = True concentration for level i
PC_i = Predicted concentration for level i

12.2.4. Percent Drift for CCV and ICV

$$\%\,Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

C_{actual} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.3. Quadratic calibration fit (only to be used if applicable)

$y = ax^2 + bx + c$

Where: y = Response

x = Concentration

a = Slope

b = Intercept

c = Curvature

12.3.1. Coefficient of Determination (COD)

$$COD = \frac{\sum_{i=1}^{n}(y_{obs} - \bar{y})^2 - \left(\frac{n-1}{n-p}\right)\sum_{i=1}^{n}(y_{obs} - y_i)^2}{\sum_{i=1}^{n}(y_{obs} - \bar{y})^2}$$

Where: y_{obs} = Observed response (area) for each concentration from each initial calibration standard

$\bar{y}$ = Mean observed response from the initial calibration

y_i = Calculated response at each concentration from the initial calibration

n = Total number of calibration points

p = Number of adjustable parameters in the polynomial equation (2 for second order polynomial)

12.4. Concentration

12.4.1. Aqueous

Concentration, ug/L = $\frac{C_{ex} V_t}{V_o}$

Where C_{ex} = Concentration in ng/uL on column

V_t = Volume of total extract in uL

V_o = Volume of water extracted in mL

12.4.2. Non-aqueous

Concentration, ug/Kg = $\frac{C_{ex}V_t}{W_sD}$

Where C_{ex} = Concentration in ng/uL on column

V_t = Volume of total extract in uL

W_s = Weight of sample extracted or diluted in g

D = (100-%moisture in sample) / 100 for dry weight basis

or

D = 1 for a wet weight basis

13. METHOD PERFORMANCE

13.1. Method Detection Limit

13.1.1. Each laboratory analyst must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in SOPs NC-QA-021 and CA-Q-S-006.

13.2. Training Qualification

13.2.1. The Group/Team Leader has the responsibility to ensure an analyst who has been properly trained in its use and has the required experience performs this procedure.

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 must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must 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. Vials containing sample extracts. These vials are placed in the vial waste located in the GC/MS laboratory.

15.2.1.2. **Tubes containing sample extracts, for PCBs:** these are capped and placed in the PCB/flammable waste located the GC prep laboratory.

15.2.1.3. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCB's must be segregated into their own waste stream. PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB and PCB vial waste. PCB containing samples are located through a LIMS query and disposed of as PCB containing.

15.2.1.4. **Extracted solid samples contaminated with methylene chloride/acetone or acetone/hexane:** These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.

15.2.1.5. **Discarded samples:** These samples are collected in the solid debris drum.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, and Section 8000B

16.2. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.3. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.4. Corporate Quality Management Plan (CQMP), current versions

16.5. SW846, Update III, December 1996, Method 8082

16.6. SW846, Update IV, Revision 1, February 2007, Method 8082A

16.7. Revision History

Historical File:				
Revision 0: 03/17/14				

16.8. Associated SOPs and Policies, current version

16.8.1. QA Policy, QA-003

16.8.2. Glassware Washing, NC-QA-014

16.8.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.8.4. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.8.5. Standards and Reagents, NC-QA-017

16.8.6. Cleanup Procedures for Organic Extractable Samples, NC-OP-025

16.8.7. Acceptable Manual Integration Practices, CA-Q-S-002

16.8.8. Calibration Curves (General), CA-Q-S-005

16.8.9. Section of Calibration Points, CA-T-P-002

16.8.10. Continuous Liquid / Liquid Extraction of Organic Compounds from Waters Based on Methods SW846 3520C and 600 Series and Waste Dilution Based on Method 3580A, NC-OP-037

16.8.11. Separatory Funnel Extraction of Organic Compounds from Waters Based on Methods SW846 3510C and 600 Series and Waste Dilution Based on Method, NC-OP-038

16.8.12. Sonication Extraction of Organic Compounds from Soils Based on Method SW846 3550C and Waste Dilution Based on Method 3580A, NC-OP-039

16.8.13. Soxhlet (Traditional) Extraction of Organic Compounds from Soils Based on Method SW846 3540C and Waste Dilution Based on Method 3580A, NC-OP-040

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Chapter 1 of SW-846 states the method blank must not contain any analyte of interest at, or above, the Method Detection Limit. This SOP states the Method Blank must not contain any analyte of interest at, or above, the reporting limit.

17.1.2. SW-846 method 8082 and 8082A provides incomplete guidance for determination of individual PCB congeners. This SOP does not include directions for congener specific analysis.

17.1.3. The extended hold time for PCBs can be applied to 8082 as per SW846 Update IV. State requirements should be consulted as applicable.

17.2. Tables

TABLE 1
Standard Analyte list and Reporting Limits for Methods 8082 and 8082A

	Reporting Limit, µg/L or µg/kg		
Compound	**Water**	**Soil**	**Waste**
Aroclor-1016	0.5	33	500
Aroclor-1221	0.5	33	500
Aroclor-1232	0.5	33	500
Aroclor 1242	0.5	33	500
Aroclor-1248	0.5	33	500
Aroclor-1254	0.5	33	500
Aroclor-1260	0.5	33	500

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	*Final Vol.*
Ground water	*1000 mL*	*5 mL (or *2 mL)*
Low-level Soil	*30g*	*10 mL*
High-level soil / waste	*1g*	*10 mL*
LVI	*250 mL*	*2 mL*

**a 0.1 ug/L can also be reached with an initial volume of 1000 mL to a final volume of 2 mL.*

TABLE 2
Suggested Instrumental Conditions for Methods 8082 and 8082A

Parameter	Recommended Conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	70°C for 0.5min, 30°C/min to 190°C, 2.5°C/min to 225, 18°C/min to 280°C, 3 min hold

Column 1	CLPesticide I, 30m, 0.53mm id, 0.5um
Column 2	CLPesticide II, 30m, 0.53 mm id, 0.5um
Injection	1µL, 2uL, or 4 uL (for LVI)
Carrier gas	Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

TABLE 3
Calibration Levels for Methods 8082 and 8082A in ug/mL

	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Aroclors 1016/1260	0.05	0.1	0.2	0.5	1.0	2.0
Aroclors 1242/1268	0.05	0.1	0.2	0.5	1.0	2.0
Aroclors 1221 +1254	0.05	0.1	0.2	0.5	1.0	2.0
Aroclors 1232/1262	0.05	0.1	0.2	0.5	1.0	2.0
Aroclor 1248	0.05	0.1	0.2	0.5	1.0	2.0
1-Bromo-2-nitrobenzene (IS)	0.05	0.05	0.05	0.05	0.05	0.05
Surrogate is included in the 1016/1260 calibration mix at the following levels:						
Tetrachloro-m-xylene	0.0025	0.005	0.01	0.025	0.05	0.1
Decachlorobiphenyl	0.0025	0.005	0.01	0.025	0.05	0.1

TABLE 4
Laboratory Control Sample (LCS) / Matrix Spike/Spike Duplicate (MS/MSD) and Surrogate Spike levels for Aroclor analysis µg/L or µg/kg for Methods 8082 and 8082A

	Aqueous	Soil	Waste
Aroclor 1016/1260	2.5, 5	333	10,000
Tetrachloro-m-xylene (Surrogate)	0.20	6.67	200
Decachlorobiphenyl (Surrogate)	0.20	6.67	200

TABLE 5
Michigan Analyte List and Reporting Limits for Methods 8082 and 8082A*

	Reporting Limit		
Compound	**water (µg/L)**	**soil (µg/Kg)**	
Aroclor-1016	0.1	330	
Aroclor-1221	0.1	330	
Aroclor-1232	0.1	330	
Aroclor 1242	0.1	330	

TABLE 5 Michigan Analyte List and Reporting Limits for Methods 8082 and 8082A*			
	Reporting Limit		
Compound	**water (µg/L)**	**soil (µg/Kg)**	
Aroclor-1248	0.1	330	
Aroclor-1254	0.1	330	
Aroclor-1260	0.1	330	

**Reporting limits only for samples performed under the Michigan program.*

Table 6
Suggested Analytical Sequence for Methods 8082 and 8082A

Initial Calibration

Solvent blank (optional)
Aroclors 1016/1260 Level 1
Aroclors 1016/1260 Level 2
Aroclors 1016/1260 Level 3
Aroclors 1016/1260 Level 4
Aroclors 1016/1260 Level 5
Aroclors 1016/1260 Level 6
Aroclors 1232/1262 An Initial Calibration includes Levels 1-6. A midpoint is used as CCV.
Aroclors 1242/1268 An Initial Calibration includes Levels 1-6. A midpoint is used as CCV.
Aroclor 1248 An Initial Calibration includes Levels 1-6. A midpoint is used as CCV.
Aroclors 1221/1254 An Initial Calibration includes Levels 1-6. A midpoint is used as CCV.

ICVs

Sample 1-20

Aroclor 1016/1260 Level 3

Note: A solvent blank or primer may be analyzed at any time during the sequence when highly contaminated samples are expected. A solvent blank or primer may not be analyzed as routine immediately prior to standards.

Note: All Aroclors are reported in the ICV when required for OVAP.

TestAmerica Canton

SOP Amendment Form

SOP NUMBER: NC-IP-010 Rev. 6

SOP TITLE: Acid Digestion for Solid Samples

REASON FOR ADDITION OR CHANGE: Added prep procedure for ISM samples

CHANGE EFFECTIVE FROM (DATE): 3/18/16

Change(s) Made:

Added Section 11.9 *Incremental Sampling Method (ISM) Solid Preparation Procedure for Analysis by ICP and ICPMS.*

EDITED BY/DATE: Melissa Fuller-Gustavel 18 March 2016

TestAmerica Canton

SOP Amendment Form

SOP NUMBER: NC-IP-010 Rev. 6

SOP TITLE: Acid Digestion for Solid Samples

REASON FOR ADDITION OR CHANGE: Fixing some of the ISM wording

CHANGE EFFECTIVE FROM: (DATE): NA

Change(s) Made:

Section 11.9.6: Samples heated for 10 minutes vs 15 minutes

11.9.15 – 11-9-17 was:

11.9.15. *Rinse a Whatman #41 filter paper (or equivalent) with reagent water into the 500mL plastic bottle.*
11.9.16. *Filter both 5g sub-samples through the rinsed filter into the 500mL plastic bottle, rinsing the digestion tube, cover, and filter paper with reagent water to ensure quantitative transfer of all of the digestion solution.*
11.9.17. *Dilute to the 500 mL mark on the plastic bottle with reagent water, cap, and shake. The sample is now ready for analysis.*

Now reads:

11.9.15. *Take each sample (2 digestate bottles per one sample) and pour the digestates into the appropriate labeled 500 mL plastic bottle. Rinse each digestion bottle twice with DI.*
11.9.16. *Using Ultra Pure water, bring the final volume up to the calibrated 500 mL mark and shake the sample vigorously to mix.*
11.9.17. *Filter approximately 50 mL to 60 mL of the sample from 11.9.16 through a Whatman #4 filter into a 4 oz. snap seal container. The sample is now ready for analysis.*

EDITED BY/DATE: Melissa Fuller-Gustavel 4/25/16

Title: ACID DIGESTION FOR SOLID SAMPLES

[Method: SW846 Method 3050B]

Approvals (Signature/Date):

Technology Specialist	02/18/16 Date	Health & Safety Coordinator	02/19/16 Date
Quality Assurance Manager	03/01/16 Date	Technical Director	02/22/16 Date

This SOP was previously identified as SOP No. NC-IP-010, Rev 5, dated 9/30/14

Facility Distribution No. _____ Distributed To:_____

The controlled copies of this SOP are the PDF copy of thie 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 of soil samples for the analysis of certain metals by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) and Inductively Coupled Plasma-Mass Spectrometry (ICPMS) as specified in SW846 Method 3050B.

1.2. Samples prepared by the protocols detailed in this SOP may be analyzed by ICP or ICPMS for the elements listed in Table 1 (Appendix A). Other elements and matrices may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This method is not a total digestion, but will dissolve almost all metals that could become “environmentally available”. By design, metals bound in silicate structures are not dissolved by this procedure, as they are not usually mobile in the environment. This SOP can be applied to metals in solids, sludges, wastes, sediments, biological samples, and wipes.

1.4. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. A representative 1 gram (wet weight) portion of sample is digested in nitric acid and hydrogen peroxide. The digestate is refluxed with hydrochloric acid for ICP and ICPMS analysis. The digestates are then filtered and diluted to 100 mL for subsequent analysis.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), latest version.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include metallic or metal-containing lab-ware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination, and take appropriate measures to minimize or avoid them. All glassware is cleaned per SOP NC-QA-014.

4.2. The entire work area, including the bench top and fume hood, must be thoroughly

cleaned on a routine schedule in order to minimize the potential for environmental contamination.

4.3. Boron from the glassware may leach into the sample solution during and following, sample processing. For critical low-level determinations of boron, only quartz and/or plastic lab-ware are recommended.

4.4. Visual interferences or anomalies, such as foaming, emulsions, precipitates, etc., must be documented.

4.5. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs, the sample must be re-prepared. Antimony is easily lost by volatilization from hydrochloric media.

4.6. Specific analytical interferences are discussed in each of the determinative methods.

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. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. 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 Safety Data Sheet (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.
Hydrogen Peroxide	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.

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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

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 must be removed and discarded; other gloves must be cleaned immediately.

5.5 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 analyst must also be aware of the potential for a vigorous reaction.

5.6 Exposure to 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 must be kept closed unless transfers are being made.

5.7 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.8 Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.9 Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.

5.10 Discard chipped or broken glassware to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

6. EQUIPMENT AND SUPPLIES

6.1. Hot plate, digestion block, steam bath, or other heating source capable of maintaining

a temperature of 91-99°C

6.2. Calibrated thermometer that covers a temperature range of 0-110°C

6.3. Vapor recovery device (Watch glasses, ribbed or other device)

6.4. Whatman No. 41 filter paper or equivalent

6.5. Funnels or equivalent filtration apparatus

6.6. Analytical balance capable of accurately weighing to the nearest 0.01 grams

6.7. Repeaters or suitable reagent dispensers

6.8. Calibrated automatic pipettes with corresponding pipette tips: 100uL, 500uL, 1mL-5mL

6.9. Class A volumetric flasks

6.10. Plastic digestate storage bottles, such as Corning Snap Seals™ (may be used if their accuracy is documented and is better than 2%)

6.11. Boiling Stones: Ultra Pure Polytetrafluoroethylene (PTFE) or equivalent

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a DI water purification system that produces DI water approved for use in metals analysis. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks (MB) as defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom solutions. All standards must be stored in fluorinated ethylene propylene (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. Additional information can be found in SOP NC-QA-017.

7.3. Working ICP LCS/ MS solution: Prepare the ICP LCS/ MS working spike solutions from custom stock standards to the final concentration listed in Table 2. The working spike must be prepared in a matrix of 5% HNO_3. This acid (5 mL of concentrated HNO_3 per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working ICP LCS/MS solution must be made fresh every six months. Refer to the reagent module in LIMS for details on standard preparation.

7.4. ICPMS LCS/MS solution: LCS/MS solutions are custom made so the final concentrations after spiking equals the concentrations listed in Table3.

7.4.1. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.5. Nitric acid (HNO_3), concentrated, trace metal grade or better

7.6. Nitric acid, 1:1 - dilute concentrated HNO_3 with an equal volume of reagent water

Note: When preparing diluted acids, always add acid to water. If the water is added to the acid a violent reaction may occur.

7.7. Hydrochloric acid (HCl), concentrated, trace metal grade or better

7.8. 30% Hydrogen peroxide (H_2O_2), Ultrapure grade

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Solid samples are collected and stored in wide-mouth glass jars with PTFE-lined lids. A minimum of 10 g must be collected.

8.2. Sample holding time for metals included under the scope of this SOP is 180 days from the date of sample collection to the date of analysis.

8.3. Soil samples do not require preservation.

9. QUALITY CONTROL

9.1. Preparation Batch

9.1.1. A preparation batch consists of a group of up to 20 client samples (not counting the batch QC) that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain an MB, an LCS, and an MS/MSD. In some cases, at client request, it may be appropriate to process a matrix spike and 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. Criteria for the acceptance of MB are contained within the individual analytical method SOPs. If the MB does not meet the criteria contained within the analytical method SOPs, the blank and all associated samples in the batch must be re-digested.

9.2.2. The MB is prepared by weighing a 1g aliquot of PTFE boiling chips. The MB is then processed as described in Section 11.9.

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is 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. Criteria for the acceptance of LCS results are contained within the individual analytical method SOPs. Corrective action when LCS results fail to meet control limits must be repreparation and reanalysis of the batch. Table 2 provides the details regarding the stock, working standards, and final spike concentrations for ICP and ICPMS. Refer to Section 7 for instructions on preparation of the LCS.

9.3.2. The ICP LCS is prepared by spiking a 1g aliquot of PTFE boiling chips with 2 mL of the working LCS/ MS spike solution (Section 7.4). The ICPMS LCS is prepared by spiking a 1g aliquot of boiling chips with 1 mL of the LCS/MS solution (Section 7.4). The LCS is then processed as described in Section 11.9.

9.4. Additional information on QC samples can be found in QA Policy QA-003. Ohio VAP projects must reference this SOP instead of policy QA-003 for information on QC samples.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1. One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have 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 matrix spike. Some client specific data quality objectives (DQOs) may require the use of 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. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.5.1.1. If any analyte recovery or Relative Percent Difference (RPD) falls outside the control limits, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside of control limits, corrective action must be taken. Corrective action must include re-preparation and reanalysis of the batch.

9.5.1.2. Corrective action when the MS results fail to meet control limits does not include re-preparation of samples unless the results indicate that a spiking error may have occurred. Client specific samples may require corrective action. Such action is noted in the project narrative.

9.5.2. Tables 2 and 3 provide the details regarding the stock, working standards and final matrix spike concentrations for ICP and ICPMS. Refer to Section 7 or the LIMS reagent module for instructions on preparation of the working matrix spike solutions.

9.5.3. The ICP MS/MSD is prepared by spiking a 1g aliquot of sample with 2 mL of the working LCS/MS spike solution (Section 7). The ICPMS MS/MSD is prepared by spiking a 1g aliquot of sample with 1 mL of the LCS/MS solution (Section 7.4). The MS/MSD is then processed as described in Section 11.9.

9.6. Control Limits

9.6.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.6.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs.

9.7. Method Detection Limits (MDLs) and MDL Checks

9.7.1. MDLs and MDL Checks are established by the laboratory as described in SOPs CA-Q-S-006 and NC-QA-021.

9.7.2. MDLs are accessible via LIMs.

9.8. Nonconformance and Corrective Action

9.8.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Hot block temperature must be verified daily for each unit used, and must be recorded in a hot block temperature log.

10.2. Laboratory support equipment is calibrated per SOPs NC-QA-004 and NC-QA-015.

11. PROCEDURE

11.1. 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 must be completely documented using a Nonconformance Memo (NCM).

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. Deviations are not allowed for Ohio VAP projects.

11.3. The heating procedures are carried out in a properly functioning hood.

11.4. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample. LIMS provides sample labels to reduce transcription errors.

11.5. Samples are typically logged in as soils. Wastes, such as organic liquids or sludges and tissues (animal/vegetable), are usually logged in as solids. When initiating prep, examine the sample to see if the sample matches the matrix designation.

11.6. If possible, prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab.

11.7. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards. Refer to Appendix B for details.

11.8. Preparation of Soils, Sediments, and Sludges for Analysis by ICP and ICPMS

11.8.1. If sample can be mixed easily in the sample jar, mix thoroughly by stirring with a clean plastic or wooden spoon or spatula. If the sample cannot be easily mixed (i.e., clay samples or samples of various and very different particle sizes), use the spoon or spatula to select enough separate portions from locations within the jar to produce a representative sample. Analyst judgment is important in determining how many portions and which locations are used to produce a representative aliquot. If the sample is uniform clay, at least 3 portions should be selected from different locations in the sample jar, if particle sizes or materials indicate a very non-homogenous sample, selection should be made carefully to collect an aliquot that represents the relative percentages of the various particle sizes and types in the sample jar.

11.8.2. For each digestion procedure required (i.e., ICP or ICPMS), weigh a 1g portion of solid and record the exact weight to the nearest 0.01g. A 2g sample size may also be used if needed to meet the reporting limits.

Note: Wipe samples are not weighed. The entire wipe is used.

11.8.3. Measure additional aliquots of the designated sample(s) for the MS/ MSD analyses. MS/MSD samples must be weighed to the exact nominal weight due to a limitation of the LIMS system.

11.8.4. Add 10 mL of 1:1 HNO_3 and mix the sample.

11.8.5. Heat sample to $95^{o} \pm 4°$ C and reflux for 10 minutes without boiling, using a vapor recovery device.

Note: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY during any part of the digestion. Doing so will result in the loss of analyte and the sample must be re-prepared.

11.8.6. Add 5 mL of concentrated HNO_3.

11.8.7. Reflux at $95^{o} \pm 4°$ C for 30 minutes. (Add reagent water, as needed, to ensure that the volume of solution is not reduced to less than 5 mL.)

11.8.8. Add approximately 2 mL of reagent water and 1 mL of 30 % H_2O_2. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

11.8.9. Continue adding 30% H_2O_2 in 1 mL aliquots until effervescence is minimal or sample appearance is unchanged. Make sure effervescence subsides before each addition of H_2O_2.

Note: Do not add more than a total of 10 mL of 30 % H_2O_2.

11.8.10. Continue heating at $95^{o} \pm 4°$ C until the volume is reduced by cooking two hours or to approximately 5-10 mL.

11.8.11. Add 10 mL of concentrated HCL and reflux for an additional 15 minutes without boiling.

11.8.12. Allow the sample to cool.

11.8.13. Filter sample through Whatman 41 filter paper or equivalent, that has been rinsed with deionized water, into a measuring bottle (for example, Corning Snap Seals™). These may be used if their accuracy is documented and is better than $\pm$ 2%. Rinse sample container and filter paper with reagent water to ensure complete sample transfer.

11.8.14. Dilute sample to 100 mL with reagent water into a 120 mL graduated Snap Seal. The sample is now ready for analysis.

11.9. Incremental Sampling Method (ISM) Solid Preparation Procedure for Analysis by ICP and ICPMS

11.9.1. The laboratory will receive a single sample aliquot containing approximately 10 g from the Solids Lab. The Metals Prep department will divide this aliquot into two separate aliquots for the digestion procedure.

11.9.2. Two approximately 5 g aliquots of a sample are each digested in two separate 130 mL Environment Express tubes (or equivalent) and then combined and diluted to a final volume of 500mL. Because of this, reagents will be entered into TALS at 5X the usual amount, but only 2.5X of each reagent will be added to each tube since one sample is divided between two tubes.

11.9.3. To the two MB tubes, add exactly 5 g of Teflon® boiling chips each and 12.5 mL of reagent water each.

11.9.4. To the two LCS standard tubes, add exactly 5 g of Teflon® boiling chips each, 12.5 mL of reagent water each and the appropriate amount of the working mercury standard (see Table 1).

11.9.5. To each sample and batch QC bottle carefully add 25 mL of concentrated HNO3 in no more than 5 mL increments.

11.9.6. Cover the sample containers with a watch glass or similar device. Heat the samples to 95° ±4° C and reflux for 10 minutes without boiling.

Note: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY during any part of the digestion. Doing so will result in the loss of analyte and the sample must be re-prepared.

11.9.7. Add 12.5 mL of concentrated HNO3 to each sample and batch QC digestion tube and replace the cover.

11.9.8. Continue heating at 95° ±4° C and reflux for 30 minutes.

11.9.9. Add approximately 5 mL of reagent water and add 30% H2O2 in 1mL increments to each tube letting the effervescence subside between each addition until a total of 25mL has been added. It important to do this step carefully as the effervescence can be high.

11.9.10. Continue heating at 95° ±4° C and reflux for 2 hours.

11.9.11. Add 25mL of concentrated HCl to each tube. It is important to do this step carefully as the reaction of the hot sample with HCl can be high.

11.9.12. Continue heating at 95° ±4° C and reflux for 15 minutes.

11.9.13. Remove each sample and batch QC tube from the hotblock and allow the samples to cool.

11.9.14. Transfer one of the sample ID labels to a 500mL plastic bottle that has been marked by pouring out 500mL of water from a graduated cylinder into each empty 500mL plastic bottle.

11.9.15. Take each sample (2 digestate bottles per one sample) and pour the digestates into the appropriate labeled 500 mL plastic bottle. Rinse each digestion bottle twice with DI.

11.9.16. Using Ultra Pure water, bring the final volume up to the calibrated 500 mL mark and shake the sample vigorously to mix.

11.9.17. Filter approximately 50 mL to 60 mL of the sample from 11.9.16 through a Whatman #4 filter into a 4 oz. snap seal container. The sample is now ready for analysis.

11.10. Analytical Documentation

11.9.1 Record all analytical information in LIMS including the analytical data from standards, blanks, LCSs, and MS/MSDs, Any corrective actions or modifications to the method must be noted in an NCM.

11.9.2 Record all standards and reagents in the LIMS Reagents module. All standards are assigned a unique number for identification.

12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

13.1. Method performance is determined by the analysis of MS/MSD samples as well as MBs and LCSs. Acceptance criteria are given in LIMS.

13.2. Initial Demonstration

13.2.1. Each analyst must make a one-time initial demonstration of capability (IDOC) for each individual method and matrix. This requires analysis of QC check samples containing all of the target analytes for the method and each matrix type. For some tests, it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.2. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample must be equivalent to a mid-level calibration.

13.2.3. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria in LIMS.

13.2.4. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification

13.3.1. The Group/Team Leader has the responsibility to ensure that 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 must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must 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. Acidic waste containing nitric acid generated by the extraction. This waste is disposed of in a designated container labeled "Acid Waste".

15.2.1.2. Contaminated disposable materials utilized for the analysis. This waste is disposed of in a designated container labeled "Solid Waste".

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, December 1996, Method 3050B

16.1.2. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.3. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.4. Corporate Quality Management Plan (CQMP), current version

16.1.5. Revision History

Historical File:		Revision 2.1: 02/11/00		Revision 0: 07/18/08 (NC-IP-010)
(formerly CORP-IP0002NC)		Revision 2.2: 09/25/01		Revision 1: 01/07/09
		Revision 2.3: 01/18/02		Revision 2: 08/12/10
		Revision 2.4: 02/19/03		Revision 3: 11/23/12
		Revision 2.5: 12/02/04		Revision 4: 09/04/13
		Revision 2.6: 07/29/07		Revision 5: 09/30/14

16.2. Associated SOPs and Policies, current version

16.2.1. Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Methods 6010B and 200.7, NC-MT-012

16.2.2. Inductively Coupled Plasma-Mass Spectrometry, EPA Methods 6020 and 200.8, NC-MT-002

16.2.3. TestAmerica North Canton Quality Control Program, QA-003

16.2.4. Glassware Washing, NC-QA-014

16.2.5. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.6. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.7. Standards and Reagents, NC-QA-017

16.2.8. Subsampling, NC-IP-001

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Method Deviations

17.1.1. The laboratory uses the same preparation procedure for ICP and ICPMS. Hydrochloric acid can be used for ICPMS due to the collision cell technology on newer instruments. Due to the potential chloride interferences, and possible inability to analyze for arsenic and tin, the laboratory must follow the instrument manufacturer guidelines pertaining to the use of HCL and ICP/MS analyses.

APPENDIX A: TABLES

TABLE1

Method 3050B Analyte List

Element	Symbol	CAS Number
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	Li	7439-93-2
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
Thallium	Tl	7440-28-0
Tin	Sn	7440-31-5
Titanium	Ti	7440-32-6
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

TABLE 2

ICP Soil Matrix Spike (MS) and Laboratory Control Sample (LCS) Levels

Element	Working LCS/MS Standard (mg/L)	Soil MS/LCS Level * (mg/kg)
Aluminum	100	200
Antimony	25	50
Arsenic	100	200
Barium	100	200
Beryllium	2.5	5
Cadmium	2.5	5
Calcium	2500	5000
Chromium	10	20
Cobalt	25	50
Copper	12.5	25
Iron	50	100
Lead	25	50
Magnesium	2500	5000
Manganese	25	50
Molybdenum	50	100
Nickel	25	50
Potassium	2500	5000
Selenium	100	200
Silver	2.5	5
Sodium	2500	5000
Thallium	100	200
Vanadium	25	50
Zinc	25	50
Boron	50	100
Tin	100	200
Titanium	50	100
Silicon	50	100
Silica	107	214

** Final soil spike concentration based on the addition of 2.0 mL working spike (Section 7.3) to 1.0 g of sample/100 mL final volume (assumes 100% solids).*

TABLE 3

ICPMS Soil Matrix Spike (MS) and Laboratory Control Sample (LCS) Levels

Element	Working LCS/MS Standard (mg/kg)	Soil MS/LCS Level * (mg/kg)
Aluminum	1000	1000
Antimony	10	10
Arsenic	10	10
Barium	10	10
Beryllium	10	10
Cadmium	10	10
Calcium	1000	1000
Chromium	10	10
Cobalt	10	10
Copper	10	10
Iron	1000	1000
Lead	10	10
Lithium	10	10
Magnesium	1000	1000
Manganese	10	10
Molybdenum	10	10
Nickel	10	10
Potassium	1000	1000
Selenium	10	10
Silver	10	10
Sodium	1000	1000
Strontium	10	10
Thallium	10	10
Vanadium	10	10
Zinc	10	10
Boron	10	10
Tin	10	10
Titanium	10	10

** Final soil spike concentration based on the addition of 1.0 mL working spike (Section 7.4) to 1.0 g of sample/100 mL final volume (assumes 100% solids).*

APPENDIX B. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All glassware must be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the Metals Lab. All work areas must be kept scrupulously clean.

Powdered gloves must not be used in the Metals Lab since the powder contains zinc, as well as other metallic analytes.

Glassware must be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

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 soak with sulfuric acid prior to routine cleaning.

Title: ACID DIGESTION FOR AQUEOUS SAMPLES

[Methods: SW846 3005A, 3010A, and MCAWW 200 Series]

Approvals (Signature/Date):

Technology Specialist	02/18/16 Date	Health & Safety Coordinator	02/19/16 Date
Quality Assurance Manager	02/26/16 Date	Technical Director	02/22/16 Date

This SOP was previously identified as SOP No. NC-IP-011, Rev 5, dated 8/6/14

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 of aqueous samples for the analysis of certain metals by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP), and Inductively Coupled Plasma-Mass Spectrometry (ICPMS) using the MCAWW 200 series methods (NPDES) and SW846 Methods 3005A, and 3010A.

1.2. The applicability of each of these preparation protocols to specific analytes is detailed in Tables 1 and 2(Appendix A). Additional elements may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This SOP provides procedures applicable to the preparation of dissolved suspended, total recoverable and total elements in ground water, aqueous samples, certain aqueous sludges, and leachates/extracts.

1.4. SW846 Method 3005A / MCAWW Method 200.8 are used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by ICP and ICPMS.

1.5. MCAWW Method 200.7 is used to prepare surface water, domestic and industrial waste samples for total, total recoverable and dissolved metals determination by ICP.

1.6. SW846 Method 3010A is used to prepare aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for total metals analysis by ICP.

2. SUMMARY OF METHOD

2.1. Method 3005A / Method 200.7 / Method 200.8 - Preparation for Total Recoverable or Dissolved Metals Analysis by ICP and ICPMS

2.1.1 A representative aliquot of sample is heated with nitric and hydrochloric acids and reduced to a low volume. The digestate is filtered (if necessary) and diluted to volume.

2.2. Method 3010A / Method 200.7 / - Preparation for Total Metals Analysis by ICP

2.2.1 A representative aliquot of sample is refluxed with nitric acid. After the digestate has been reduced to a low volume, it is refluxed with 1:1 hydrochloric acid, filtered (if necessary), and diluted to volume.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include metallic or metal-containing lab ware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them. All glassware is cleaned per SOP NC-QA-014.

4.2. The entire work area, including the bench top and fume hood, must be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix B for additional contamination control guidelines.

4.3. Boron from the glassware will migrate into the sample solution during and following sample processing. For critical low-level determinations of boron, it is recommended quartz or plastic lab ware be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents, and other matrices may not be digested using these methods if they are not soluble with acids.

4.5. Visual interferences or anomalies (such as dilution due to oily matrix) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be re-prepared. Antimony is easily lost by volatilization from hydrochloric acid media.

4.7. Precipitation of silver chloride (AgCl) may occur when chloride ions and high concentrations of silver (i.e., greater than 1 mg/L) are present in the sample.

4.8. Specific analytical interferences are discussed in each of the determinative methods.

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. Samples that contain high concentrations of carbonates, or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. 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**

Safety Data Sheet (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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

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 must be removed and discarded; other gloves must be cleaned immediately.

5.5. 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 analyst should also be aware of the potential for a vigorous reaction.

5.6. Exposure to 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 must be kept closed unless transfers are being made.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.8. Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.9. Acid spills must be neutralized immediately, flushed with water, and cleaned up using appropriate spill kits.

5.10. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire-polished as an alternative to disposal.

6. EQUIPMENT AND SUPPLIES

EQUIPMENT AND SUPPLIES
Hot plate/digestion block: capable of maintaining a temperature of 90-95º C
Calibrated thermometer: range 0-110º C
Beakers, assorted sizes: Griffen, calibrated digestion beakers, or equivalent
Ribbed watch glasses, or equivalent
Whatman #41 filters, or equivalent
Funnels
Graduated cylinder: 50 mL
Analytical balance capable of weighing to ± 0.01 g
Repeaters or suitable reagent dispensers
Pipettes and disposable tips: various volumes
Volumetric flasks: Class A
pH indicator strips: range 0-6
Plastic digestate storage bottles: Corning snap seals, or equivalent

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks (MB) as defined in the determinative SOPs.

7.2. Reagents

Reagents
Nitric Acid (HNO_3): Concentrated, trace metal grade or better
Hydrochloric Acid (HCl): Concentrated, trace metal grade or better
1:1 Hydrochloric Acid: dilute concentrated HCl with an equal volume of reagent water

Note: When preparing diluted acids, always add acid to water. If the water is added to the acid, a violent reaction may occur.

7.3. Standards

7.3.1. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom solutions. 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. Additional information can be found in SOP NC-QA-017.

7.3.2. Working ICP laboratory control sample (LCS)/matrix spike (MS) spike solution: Prepare the ICP LCS/MS working spike solution from custom stock standards to the final concentration listed in Table 3. The working spike must be prepared in a matrix of 5% HNO_3. This acid (5 mL of concentrated HNO_3 per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working ICP LCS solution must be made fresh every six months.

7.3.3. The ICPMS LCS/MS solution is provided directly by the vendor. No further standard preparation is necessary.

7.3.4. The TCLP MS working spike solution is provided directly by the vendor, no further standard preparation is necessary. Refer to Table 5 for final digestate spike concentrations.

7.3.5. The LCS/MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.3.6. Aqueous LCS and MS samples are prepared as described in Sections 9.4 and 9.6. Refer to Tables 3 and 4 (Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP and ICPMS LCS and MS preparations.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and must be stored in either plastic or glass. If boron is to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. Metals samples that are preserved at the laboratory must be held for 24 hours before digestion. For metals samples that require preservation, the Sample Receiving Department must note the time of acid addition.

Note: If the samples are preserved the same day of collection, the 24-hour waiting period is not required

8.4. For dissolved metals analysis, the samples must be filtered through a 0.45 um filter prior to preservation. Filtration must be done in the field. In the event that samples are not field filtered, filtration occurs in the laboratory prior to preparation.

9. QUALITY CONTROL

9.1. Quality Control Batch

9.1.1. The batch is a set of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank (MB), a laboratory control sample (LCS), and a matrix spike / matrix spike duplicate (MS/MSD) If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs. See Policy QA-003 for further definition of the batch. Laboratory generated QC (MB, LCS, MS/MSD) are not included in the sample count.

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.

9.2.2. Aqueous and TCLP MBs are prepared by taking 50 mL of reagent water through the appropriate procedure as described in Section 11.

9.2.3. TCLP Leachate Blanks (LBs) are prepared by taking 50 mL of leachate fluid through the appropriate procedure as described in Section 11.

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is 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. Criteria for the acceptance of LCS results are contained

within the individual analytical method SOPs. Refer to Sections 7.3 and 7.4 for instructions on preparation of the aqueous LCS spike solution.

9.3.2. The aqueous LCS is prepared by spiking a 50 mL aliquot of reagent water with 1.0 mL for ICP and 0.5 mL for ICPMS of the working LCS/MS spike solution (Sections 7.3 or 7.4). The LCS is then processed through the appropriate procedure as described in Section 11.

Note: TCLP LCS is prepared by spiking 50 mL of leachate fluid with 1.0 mL for ICP and 0.5 mL for ICPMS of the working LCS/MS solution and taking it through the appropriate procedure as described in Section 11.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the matrix spike) prepared and analyzed along with the sample and MS. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates (DU) 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. Samples identified as field blanks cannot be used for MS/MSD analysis.

Note: For Method 200.7, an MS/MSD pair is required for every 10 samples. 2 MS/MSD pairs must be analyzed if the batch contains more than 10 samples for 200.7 analysis.

9.4.2. The aqueous MS sample is prepared by spiking a 50 mL aliquot of a sample with 1.0 mL for ICP and 0.5 mL for ICPMS of the working LCS/MS spike solution (Sections 7.3 or 7.4). The MS sample is then processed as described in Section 11.

9.4.3. The ICP TCLP MS/MSD sample is prepared by spiking a 50 mL aliquot of a leachate with 0.5 mL of the working TCLP spike solution (Section 7.5). For ICPMS analysis, the MS/MSD is spiked the same as a water sample. The MS/MSD sample is then processed as described in Section 11.

Note: The TCLP matrix spike standard must be added prior to preservation of the leachate.

Note: If analytes outside of the RCRA list are requested, l mL of additional spiking solution(s) is added.

9.6 Additional information on QC samples can be found in QA Policy QA-003.

9.7 Control Limits

9.7.1 Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2 Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via LIMS.

9.8 Method Detection Limits (MDLs) and MDL Checks

9.8.1 MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.8.2 MDLs are easily accessible via LIMS.

9.9 Nonconformance and Corrective Action

9.9.1 Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action. Procedural deviations are not allowed for Ohio VAP projects.

10. CALIBRATION AND STANDARDIZATION

10.1. The hot plate/hot block temperature must be verified daily for each hotplate used, and must be recorded on a hotplate/hot block temperature log

10.2. Support equipment used for this procedure will be checked for calibration as per SOP NC-QA-015, current version. .

11. PROCEDURE

11.1. 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 must be completely documented using a Nonconformance Memo. The Nonconformance Memo must be filed in the project file. Procedural deviations are not allowed for Ohio VAP projects.

11.2. All digestion procedures must be carried out in a properly functioning hood.

11.3. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample.

11.4. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test

codes. When initiating prep, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment, etc.), contact the lab supervisor or project manager for further instructions. In some cases, it may be more appropriate to process these samples as solids.

11.5. If possible, prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab.

11.6. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

11.7. The following procedure must be followed for all aqueous sample preparations.

11.7.1. Mix sample by shaking the container.

11.7.2. Measure 50 mL of the sample into a calibrated digestion tube. (Beakers may be used for oil matrices.)

Note: For samples with particulate matter, the aliquot may be taken through a repeated series of shake and pour steps.

11.7.3. Measure two extra aliquots of sample selected for the MS/MSD analysis. Spike each aliquot with the appropriate spiking solutions (Sections 7.3 to 7.5 and 9.6).

11.7.4. Measure 50 mL of reagent water into a calibrated digestion tube for the MB.

11.7.5. Measure 50 mL of reagent water into a calibrated digestion tube for the LCS and add the appropriate spiking solutions (Sections 7.3 to 7.5 and 9.6).

11.8. Method 3005A / Method 200.7 / Method 200.8 - Preparation for Total Recoverable or Dissolved Metals Analysis by ICP / ICPMS

11.8.1. To the sample container, add 1 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl.

11.8.2. Cover with ribbed watch glass.

11.8.3. Heat at 90-95°C until volume is reduced to less than or equal to 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be re-prepared.

11.8.4. Cool the beaker in a fume hood.

11.8.5. If insoluble materials are present, filter the sample through Whatman 41 filter paper into a plastic storage container, such as a Corning Snap Seal™

Note: If any samples in a preparation batch are filtered, the MB and LCS associated with that batch must also be filtered.

11.8.6. Rinse container and filter paper with reagent water to ensure complete sample transfer.

11.8.7. Adjust the final volume to 50 mL with reagent water in the Snap Seal™ container if the digestate was filtered or in the hot block digestion tube if filtering was not necessary. The sample is now ready for analysis.

11.9. Method 3010A / Method 200.7 - Preparation for Total Metals Analysis by ICP Spectroscopy

11.9.1. To the sample container, add 3.0 mL of concentrated HNO_3.

11.9.2. Cover with ribbed watch glass.

Place container on hot block 90-95°C, and reflux until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing) and the volume is less than or equal to 20 mL. **NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY.** Doing so will result in the loss of analyte and the sample must be re-prepared.

11.9.3. Add 5 mL of 1:1 HCl.

11.9.4. Cover and reflux for an additional 15 minutes to dissolve precipitate or residue. Cool in a fume hood.

11.9.5. Filter sample, if insoluble materials are present, through Whatman 41 filter paper into a plastic storage container, such as a Corning Snap Seal™.

Note: If any samples in the QC batch are filtered, the MB and LCS associated with that batch must also be filtered.

11.9.6. Rinse container and filter paper with reagent water to ensure complete sample transfer.

11.9.7. Adjust final volume to 50 mL with reagent water in the Snap Seal™ container if the digestate was filtered, or in the hot block digestion tube if filtering was not necessary. The sample is now ready for analysis.

11.10. Analytical Documentation

11.10.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.10.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification

11.10.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.10.4. Record all sample results and associated QC into LIMS. Level I and Level II review is performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

13.1. Initial Demonstration

13.1.1. Each analyst must make an initial demonstration of capability and yearly continuing demonstrations of capability for each individual analyte. This requires analysis of four QC Check samples.

13.1.2. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.1.3. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs.

13.2. Training Qualification

13.2.1 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.

13.2.2 Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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 must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must 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. Acidic waste containing nitric acid generated by the extraction: This waste is disposed of in the designated container labeled "Acid Waste".

15.2.1.2. Contaminated disposable materials utilized for the analysis. This waste is disposed of in a designated container identified as "Solid Waste".

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update I, Revision 1, July 1992. Methods 3005A and 3010A

16.1.2 Methods for the Chemical Analysis of Water and Waste (MCAWW), 1983

16.1.3 TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.4 TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.5 Corporate Quality Management Plan (CQMP), current version

16.1.6 Revision History

Historical File:		Revision 1.2: 03/20/00		Revision 0: 01/07/09 (NC-IP-011)
(formerly CORP-IP-0003NC)		Revision 1.3: 09/25/01		Revision 1: 01/28/10 (NC-IP-011)
		Revision 1.4: 02/19/03		Revision 2: 05/17/11
		Revision 1.5: 12/07/04		Revision 3-A: 06/28/12
		Revision 1.6: 02/07/07		Revision 4: 06/28/14
				Revision 5: 08/06/14

16.2. Associated SOPs and Policies, current version

16.2.1 TestAmerica QC Program, 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

16.2.7 Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analyses, SW846 Methods 6010B, 6010C, and 200.7, NC-MT-012

16.2.8 Inductively Coupled Plasma – Mass Spectrometry, NC-MT-002

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference methods

17.1.1 Modifications applicable to SW-846 reference methods

17.1.1.1. The referenced methods as well as Table 3-1 of SW-846 refer to the use of a 100 mL aliquot for digestion. This SOP requires the use of a 50 mL sample size to reduce waste generation. The use of reduced sample volumes are supported in EPA's document "Response to Public Comments Background Document, Promulgation of the Second Update to SW-846, Third Edition" dated November 3, 1994. This document stated "flexibility to alter digestion volumes is addressed and "allowed" by Table 3-1 and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples. EMSL-Ci has also taken the stance that "reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology." Additionally, in written correspondence from the Office of Solid Waste, Oliver Fordham stated "As a "representative sample" can be assured, scaling causes no loss of precision and accuracy in the analysis."

17.1.1.2. Modifications Specific to Method 3010A

17.1.1.2.1. Section 11.8.3 of this SOP requires the sample be reduced to a volume –less than or equal to 20 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL, but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.1.3. Modifications Specific to MCAWW Methods

17.1.1.3.1. It was determined by technical review that several of the MCAWW methods were equivalent to the SW-846 methods and therefore were combined under the scope of this SOP as described in Section 11.0. The nature of the differences were deemed insignificant in regards to the amount of acid added and the evaporative volume based on the flexibility allowed by the methods (i.e., add additional acid as required) and the subjective wording of the methods (i.e., evaporate to near dryness vs. an exact volume).

APPENDIX A - TABLES

TABLE 1: Approved Preparation Method Analytes - SW846

ELEMENT	Symbol	CAS Number	3005A	3010A
Aluminum	Al	7429-90-5	X	X
Antimony	Sb	7440-36-0	X	
Arsenic	As	7440-38-2	X	X
Barium	Ba	7440-39-3	X	X
Beryllium	Be	7440-41-7	X	X
Cadmium	Cd	7440-43-9	X	X
Calcium	Ca	7440-70-2	X	X
Chromium	Cr	7440-47-3	X	X
Cobalt	Co	7440-48-4	X	X
Copper	Cu	7440-50-8	X	X
Iron	Fe	7439-89-6	X	X
Lead	Pb	7439-92-1	X	X
Magnesium	Mg	7439-95-4	X	X
Manganese	Mn	7439-96-5	X	X
Molybdenum	Mo	7439-98-7	X	X
Nickel	Ni	7440-02-0	X	X
Potassium	K	7440-09-7	X	X
Selenium	Se	7782-49-2	X	X
Silver	Ag	7440-22-4	X	X
Sodium	Na	7440-23-5	X	X
Thallium	Tl	7440-28-0	X	X
Vanadium	V	7440-62-2	X	X
Zinc	Zn	7440-66-6	X	X

X - Designates that the preparation method is approved for an element.

Note: *Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.*

TABLE 2: Approved Preparation Method Analytes – NPDES

ELEMENT	Symbol	CAS Number	200.7 (9.4)	200.7 (9.3)
Aluminum	Al	7429-90-5	X	X
Antimony	Sb	7440-36-0	X	X
Arsenic	As	7440-38-2	X	X
Boron	B	7440-42-8	X	X
Barium	Ba	7440-39-3	X	X
Beryllium	Be	7440-41-7	X	X
Cadmium	Cd	7440-43-9	X	X
Calcium	Ca	7440-70-2	X	X
Chromium	Cr	7440-47-3	X	X
Cobalt	Co	7440-48-4	X	X
Copper	Cu	7440-50-8	X	X
Iron	Fe	7439-89-6	X	X
Lead	Pb	7439-92-1	X	X
Magnesium	Mg	7439-95-4	X	X
Manganese	Mn	7439-96-5	X	X
Molybdenum	Mo	7439-98-7	X	X
Nickel	Ni	7440-02-0	X	X
Potassium	K	7440-09-7	X	X
Selenium	Se	7782-49-2	X	X
Silicon	Si	7631-86-9	X	X
Silver	Ag	7440-22-4	X	X
Sodium	Na	7440-23-5	X	X
Thallium	Tl	7440-28-0	X	X
Vanadium	V	7440-62-2	X	X
Zinc	Zn	7440-66-6	X	X

X - Designates that the preparation method is approved for an element

Note: *Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.*

TABLE 3: ICP Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	Working Laboratory Control Sample (LCS)/Matrix Spike (MS) Standard (mg/L)	Aqueous Laboratory Control Sample (LCS)/ Matrix Spike (MS) Level * (ug/l)
Aluminum	100	2000
Antimony	25	500
Arsenic	100	2000
Barium	100	2000
Beryllium	2.5	50
Cadmium	2.5	50
Calcium	2500	50000
Chromium	10	200
Cobalt	25	500
Copper	12.5	250
Iron	50	1000
Lead	25	500
Magnesium	2500	50000
Manganese	25	500
Molybdenum	50	1000
Nickel	25	500
Potassium	2500	50000
Selenium	100	2000
Silver	2.5	50
Sodium	2500	50000
Thallium	100	2000
Vanadium	25	500
Zinc	25	500
Boron	50	1000
Tin	100	2000
Titanium	50	1000
Lithium	50	1000
Silicon	50	1000
Strontium	50	1000

* *Levels shown indicate the spike concentration in the final digestate of the aqueous laboratory control sample (LCS) or matrix spike (MS) based on the addition of 1.0 mL working spike (7.3) to 50 mL of sample.*

TABLE 4: ICPMS Aqueous Laboratory Control Sample (LCS) and Matrix Spike/Matrix Spike Duplicate (MS/MSD) Levels

ELEMENT	Working Laboratory Control Sample (LCS)/Matrix Spike (MS) Standard (mg/L)	Aqueous Laboratory Control Sample (LCS)/Matrix Spike (MS) Level* (ug/L)
Aluminum	1000	10000
Antimony	10	100
Arsenic	100	1000
Barium	100	1000
Beryllium	100	1000
Cadmium	100	1000
Calcium	1000	10000
Chromium	100	1000
Cobalt	100	1000
Copper	100	1000
Iron	1000	10000
Lead	100	1000
Lithium	10	100
Magnesium	1000	10000
Manganese	100	1000
Molybdenum	10	100
Nickel	100	1000
Potassium	1000	10000
Selenium	100	1000
Silver	10	100
Sodium	1000	10000
Strontium	100	1000
Thallium	25	250
Vanadium	100	1000
Zinc	100	1000
Boron	10	100
Tin	100	1000
Titanium	10	100
Tungsten	10	100

* *Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or MS based on the addition of 0.5 mL working spike (Section 7.4) to 50 mL of sample.*

Note: *Spiking levels may be adjusted as long as the concentrations are documented.*

TABLE 5: TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels for ICP

ELEMENT	RL (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)*
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

* *Levels shown indicate the spike concentration in the final digestate of the aqueous MS based on the addition of 0.5 mL working spike (Section 7.5) to 50 mL of sample.*

APPENDIX B

CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All glassware must be washed with detergent and tap water and rinsed with 1:1 nitric 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 Latex Gloves must not be used in the metals laboratory since the powder contains zinc, as well as other metallic analytes. Only unpowdered latex or nitrile gloves must be used in the metals laboratory.

Glassware must be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

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 soak with sulfuric acid prior to routine cleaning.

Title: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS AND SOLID SAMPLES BY COLD VAPOR ATOMIC FLUORESCENCE

[Method: 1631E]

Approvals (Signature/Date):

Technology Specialist	04/28/16 Date	Health & Safety Coordinator	03/18/16 Date
Quality Assurance Manager	04/28/16 Date	Technical Director	03/18/16 Date

This SOP was previously identified as SOP No. NC-MT-001, Rev 7, dated 1/9/15

Facility Distribution No. _____ Distributed To:_____

The controlled copy 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.

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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 (BrCl), 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. The reporting limit for mercury 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 BrCl. For solid or biological samples, 1 gram of sample is digested with cold aqua regia (HCL/HNO_3), diluted, and further oxidized with BrCl (except as detailed in work instruction WI-NC-0165 Sample Preparation Guidelines for Digestion of Micro Volume Tissues). 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 ($SnCl_2 \bullet 2H_2O$) and purged from solution with argon in a gas / liquid separator. 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 Safety Data Sheet (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	Hazards	Exposure Limit (1)	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.
Note: Always add acid to water to prevent violent reactions.			
1 – 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

6.1.8. Gold traps (2): Quartz tube containing gold-coated sand

6.1.9. 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. Class A glass volumetric flasks: various volumes

6.4. Starch Paper Test Strips

6.5. 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 glass volumetric flasks or glass 40 mL VOC vials. 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 µg/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 µg/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. 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. The ICV standard solution is also used for spiking the LCS.

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 the same reagents that are used for sample preparation.

7.8. Stannous Chloride ($SnCl_2 \cdot 2H_2O$): ACS Reagent grade suitable for mercury determination (< 1 ppb) is recommended.

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade.

Note: Ultra trace mercury HCl should be used to prepare the BrCl solution Trace metal grade HCl may be used to prepare the $SnCl_2$ and 2% HCl rinse solutions provided that these solutions are purged with argon prior to use.

7.10. 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.

7.11. $SnCl_2 \bullet 2H_2O$ Solution Concentrate: Add 500 g of $SnCl_2 \bullet 2H_2O$ to 2.4 L trace metals concentrated HCl. Allow the $SnCl_2 \bullet 2H_2O$ to completely dissolve.

7.12. $SnCl_2 \bullet 2H_2O$ 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% $SnCl_2 \bullet 2H_2O$. 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).

7.13. Hydroxylamine Hydrochloride Solution: Purchased

7.14. Bromine monochloride, intermediate solution: Purchased 10 mL tubes

7.15. BrCl, 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.

7.16. Nitric acid, concentrated, trace metal grade

7.17. 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 2 mL BrCl may be added to digest the sample. 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 kept 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

9.1.1. Carry-Over Determination: The carry-over determination is to be analyzed once on every instrument. The results from the determination must be kept on file.

9.1.1.1. 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.

9.2. Preparation Batch

9.2.1. 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 MSand 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.

9.3. Method Blank (MB)

9.3.1. 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.

Note: For Wisconsin projects, three MBs are required.

9.3.2. 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.**

9.3.3. 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).

9.3.4. 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.

9.4. 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. The 0.2 mL blank is met by the analysis of the method blank. It is not necessary to prepare a preparation blank with a 2 mL volume of BrCl. See the note in section 11.1.7 for details.

9.4.1. 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

9.5. System / Subtraction Blank

9.5.1. 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.

9.6. Reagent Blank

9.6.1. 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.

9.6.2. 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.

9.7. Laboratory Control Sample (LCS).

9.7.1. 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.

9.7.2. 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.**

9.7.3. Corrective action will be re-preparation and re-analysis of the batch unless other corrective action is agreed upon with the client.

9.8. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.8.1. 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).

9.8.2. If mercury recovery or RPD falls outside the acceptance range, corrective action will include:

9.8.2.1. 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.

9.8.3. MS/MSD results which again fall outside the control limits must be addressed in the case narrative.

9.9. Additional information on QC samples can be found in QA Policy QA-003.

9.10. Control Limits

9.10.1. Control limits are prescribed in method 1631E. Control limits are easily accessible via the LIMS.

9.11. Method Detection Limits (MDLs) and MDL Checks (MDL Verifications or MDLVs)

9.11.1. MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.11.2. MDLs are easily accessible via the LIMS

9.12. Nonconformance and Corrective Action

9.12.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.2, except they do not need a minimum of 12 hours of oxidation time and can be used immediately since the mercury is already in an oxidized state in the standard.

10.2. 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.

10.3. 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.

10.4. 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 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.

10.5. 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 a correlation coefficient < 0.995. Also,

the low standard must calculate back against the curve within ±25% of the true value.

10.6. Initial Calibration Verification/Initial Calibration Blank (ICV/ICB)

10.6.1. 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.

10.7. Continuing Calibration Verification/Continuing Calibration Blank (CCV/CCB) (

10.7.1. 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.

10.7.2. 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, CCB) and laboratory QC samples (LCS, MB, MS, 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. The MB consists of 40 mL of DI water with 0.2 mL of BrCl. Mix and store the vial at room temperature for at least 12 hours. Proceed to section 11.5 sample screening and treat the MB the same as the samples for analysis.

Note: The MB also serves as the 0.2 mL BrCl preparation blank.

11.1.4. To prepare the LCS, add 40 mL of DI water to a VOA vial. With a pipette, carefully remove 0.2 mL of the DI water. Spike the LCS with 0.2 mL of the ICV working standard. Add 0.2 mL of BrCl. Mix and store the vial at room temperature for at least 12 hours. Proceed to section 11.5 sample screening and treat the LCS the same as the MB and the samples for analysis.

11.1.5. 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.

11.1.6. 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.

11.1.7. 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. This process can be repeated by 0.2 mL increments of BrCl up to 1 mL, and then directly to the 2 mL maximum.

Note: If 2 mL of BrCl is used, a 2x dilution must be performed on the sample prior to analysis. Studies have demonstrated that additions of BrCl in excess of 1 mL suppresses mercury recovery.

11.1.8. 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.

11.1.9. If 2 mL of BrCl is consumed, a 10x dilution from the original digestion vial is created and digestion is continued with 0.2 mL BrCl additions as above, noting that the equivalent of 0.2 mL BrCl is already present in the 10x dilution.

Note: Samples completing successful digestion at 2 mL of BrCl must be diluted a minimum of 2x for matrix impact created by the suppressive effect documented in internal studies.

11.1.10. Preparation blanks must be prepared with the samples. See section 9.4 for details.

11.1.11. If there is a positive detection in any of these preparation 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. Any necessary preparation blanks must have an equivalent amount of BrCl added and also be reheated with the samples..

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 ± 0.05 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. For the MB, add approximately 1 g of Teflon boiling chips.

11.2.4. For the LCS, add 1.0 mL of the 10 ug/L ICV intermediate mercury standard (Section 7.3) to1g of Teflon boiling chips.

11.2.5. 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. 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.

11.2.7. After digesting at room temperature, place the digestion vessel in a hotblock in the hood and slowly bring to 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.

11.2.8. 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.

11.2.9. Proceed to Section 11.4.4.

11.2.10. For LL Hg digestion for micro volumes of tissues, see work instruction WI-NC-0171.

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.

11.3.1.1.1. 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.

11.3.1.1.2. 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.

11.3.1.2. Following the above guidelines, homogenize the sample then weigh 1.0 ± 0.05 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).

11.3.1.2.1. For the MB, add approximately 1g of Teflon boiling chips.

11.3.1.2.2. For the LCS, add 1.0 mL of the 10 ug/L ICV intermediate mercury standard (Section 7.3) to1g of boiling chips.

11.3.1.2.3. 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.

11.3.1.3. 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.

11.3.1.4. 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.

11.3.1.5. 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.

11.3.2. For LL Hg wipe digestion, see work instruction WI-NC-0172.

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 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.) or any failed MS/MSD pairs

11.5.9.4. Field-generated blanks with concentrations of mercury above the reporting limit.

11.5.9.5. Serial dilutions that don't show reasonable 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 laboratory 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 9.3.

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		Revision 7: 01/09/15

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. WI-NC-0171 LL Hg Digestion for Micro Volume Tissues

16.2.4. WI-NC-0172 LL Hg Wipe Digestion

16.2.5. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.6. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.7. Standards and Reagents, NC-QA-017

16.2.8. 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 C

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 D

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 E

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 F

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.

TestAmerica Canton

SOP Amendment Form

SOP NUMBER: NC-MT-002 Rev. 7

SOP TITLE: Inductively Coupled Plasma – Mass Spectrometry

REASON FOR ADDITION OR CHANGE: Fixing limit in section 10.9

CHANGE EFFECTIVE FROM: (DATE): 8/29/16

Change(s) Made:

Section 10.9.1

Internal standard intensity of the calibration blank for method 6020 was changed from 50-150% to 30-150%.

EDITED BY/DATE: Melissa Fuller-Gustavel 8/29/16

TestAmerica Canton

SOP Amendment Form

SOP NUMBER: NC-MT-002 Rev. 7

SOP TITLE: Inductively Coupled Plasma – Mass Spectrometry

REASON FOR ADDITION OR CHANGE: Wording changes requested by Laboratory

CHANGE EFFECTIVE FROM: (DATE): 6/13/16

Change(s) Made:

7.5 change Rinse to 2% nitric 1% HCL

9.1.1.1 / 9.1.1.2 and 9.1.1.3 Reword :

The IDL for each for each analyte must be determined for each instrument. The IDL must be determined annually.
The IDL will be determined by multiplying the standard deviation obtained from the analysis of seven consecutive measurements of a blank solution, by three. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse at minimum).

IDLs should be determined at least once using new equipment and/or
after major instrument maintenance such as changing the detector.
IDLs may be run more frequently dependent upon requirements of state
programs or client needs.

9.4.1 Added at end of paragraph: The LCS limits for solid samples are statistically derived from historical laboratory data. Water samples have criterion of 80% - 120%. For Method 200.8, LCS limits are 85% - 115%.

10.4.1 Note: The only exception is if the ICV/CCV recoveries are biased high and the associated sample is ND…

10.7.1 Note: The only exceptions are if the ICB/CCB recoveries are biased high and …

EDITED BY/DATE: Melissa A. Fuller-Gustavel for Karen Counts 6/13/16

Title: INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY

[Method: EPA Method 200.8, SW846 Methods 6020 and 6020A]

Approvals (Signature/Date):

Technology Specialist	04/18/16 Date	Health & Safety Coordinator	04/18/16 Date
Quality Assurance Manager	05/31/16 Date	Technical Director	05/16/16 Date

This SOP was previously identified as SOP No. NC-MT-002, Rev 6, dated 4/2/14

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 copy of the SOP that is printed and placed in the General Chemistry SOP binder. Printed or electronic copies of the SOP that are distributed outside of the facility are considered uncontrolled.

TABLE OF CONTENTS

Tables

1. SCOPE AND APPLICATION

1.1. This procedure describes multi-elemental analysis by inductively coupled plasma-mass spectrometry (ICP-MS) based on SW-846 protocol as described in EPA Methods 6020, 6020A, and 200.8. The source method lists the following elements approved for analysis by ICP/MS (Al, Sb, As, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Li, Mg. Mn, Ni, K, Ag, Tl, Se, Na, V, and Zn). Additional elements may be included provided that the method performance criteria presented in Section 9 is met. However, project approval may be required from the controlling agencies for compliance testing beyond the elements included in the method.

1.2. The procedure is applicable to the analysis of waters (groundwaters and surface waters), soils, and wastes. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, biological matrices, and other solid wastes for which total (acid-leachable) elements are requested. See SOPs NC-IP-010 and NC-IP-011 for preparation details.

1.3. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. Aqueous samples, digestates, or leachates are nebulized into a spray chamber where a stream of argon carries the sample aerosol through the quartz torch and injects it into a radio frequency inductively coupled plasma. There the sample is decomposed and desolvated. The ions produced are entrained in the plasma gas, and by means of a water-cooled differentially-pumped interface, introduced into a high-vacuum chamber that houses a quadrapole mass spectrometer capable of providing a resolution less than, or equal to, 0.9 AMU full width at 10% of the peak height. For analysis by Method 200.8, the resolution requirement is 1.0 amu at 5% peak height. The ions are sorted according to their mass-to-charge ratio and measured with a channel electron multiplier. Interference must be assessed and valid corrections applied, or the data flagged, to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents and the constituents of the sample matrix. Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Isobaric Interferences: Isobaric interferences in the ICPMS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). Most interferences of this type are corrected for by the instrument software.

4.2. Isobaric Molecular and Doubly Charged Ion Interferences: Isobaric molecular interferences are caused by ions consisting of more than one atom or charge. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections must be applied; and the data flagged to indicate the presence of interferences. Using Collision Cell Technology (CCT) can reduce these interferences. Collision Cell Technology is accomplished by adding an auxiliary gas into the lens chamber. A Hydrogen/Helium (Thermo XSeries 2) or Helium (Agilent 7700) gas mixture is used. This gas mixture is used to knock polyatomic ions out of the path as they collide with the cell gas. The ions are dissociated into their component atoms/ions or converted into non-interfering species. The transmission of analyte ions is minimally affected. This process is called Kinetic Energy Displacement (KED).

4.3. Physical Interferences: Physical interferences are associated with the transport and nebulization process. Internal standards are used to compensate for these types of interferences.

4.3.1. Generally, the mass of the internal standard should be no more than 50 AMU (Atomic Mass Unit) of the mass of the measured analyte.

4.3.2. Matrix effects will be monitored by comparing the internal standard intensity in the sample to the internal standard intensity of the calibration blank.

4.3.3. Memory effects are dependent on the relative concentration differences between samples and/or standards, which are analyzed sequentially. The rinse period between samples must be long enough to eliminate significant memory interference.

4.3.4. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be demonstrated routinely to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. All glassware is cleaned per SOP NC-QA-014.Specific selection of reagents may be required to avoid introduction of contaminants.

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. 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 must be removed and discarded; other gloves must be cleaned immediately.

5.3. 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 Safety Data Sheet (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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. The RF Generator produces strong radio frequency waves--most of which are unshielded. People with pacemakers must not go near the instrument while in operation.

5.5. Exposure to 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 must be kept closed unless transfers are being made.

5.6. The ICPMS plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor and the EH&S Coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Argon gas: High purity grade (99.99%)

6.2. Inductively Coupled Plasma Mass Spectrometer capable of providing resolution less than, or equal to, 1.0 AMU at 10% peak height from a mass range of at least 6-240 and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass flow controller for the nebulizer argon and a peristaltic pump for the sample solution is recommended.

6.3. A three channel peristaltic pump

6.4. Appropriate water-cooling device

6.5. Calibrated adjustable pipettes

6.6. Autosampler with autosampler tubes

6.7. Hydrogen/helium gas mixture with approximate ratio of 7% hydrogen and 93% helium used for CCT mode on the Thermo X Series II, and helium only on the Agilent.7700

7. REAGENTS AND STANDARDS

7.1. Calibration standards are purchased as custom multi-element mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Additional information can be found in SOP NC-QA-017.

7.2. Check Calibration Standard (ICV) - A quality control standard similar to the calibration standards and prepared in the same acid matrix. This solution must be made at a concentration near the midpoint of the calibration curve. This standard is composed of analytes from a different source from those used in the calibration of the instrument. See Table 5. Refer to the LIMS standards and reagents module for details on preparation.

7.3. The tuning solution is purchased as custom multi-element mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. The solution must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year.

7.4. Reagent water - ASTM Type I, or equivalent for the elements of interest, generated using an ion-exchange water polishing system.

7.5. Rinse Solution – 2% HNO3 and 1% HCL in reagent grade water.

7.6. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.7 Concentrated hydrochloric acid (HCl), trace metal grade or better

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Aqueous samples are preserved with nitric acid to a pH of < 2, and may be stored in plastic or glass. Preservation must be verified prior to analysis.

8.2. Soil samples do not require preservation, but must be stored at 4° ± 2°C until the time of preparation.

8.3. The analytical holding times for metals are six months from the time of collection to analysis.

8.4. Solid and aqueous samples must be digested prior to analysis by the appropriate method.

8.5. Samples preserved in the laboratory must be held for 24 hours before digestion.

Note: If the samples are preserved the same day of collection, the 24-hour waiting period is not required.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. Instrument Detection Limit (IDL)

9.1.1.1. The IDL for each analyte must be determined for each instrument. The IDL must be determined annually.

9.1.1.2. The IDL will be determined by multiplying the standard deviation obtained from the analysis of seven consecutive measurements of a blank solution by three. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse at minimum).

9.1.1.3. IDLs should be determined at least once using new equipment and/or after major instrument maintenance such as changing the detector. IDLs may be run more frequently dependent upon requirements of state programs or client needs.

9.1.2. Linear Calibration Ranges

9.1.2.1. Linear calibration ranges are primarily detector limited. The linear range must be determined at instrument setup, and the upper limit must be verified annually or whenever a change in instrument hardware or operating conditions occurs. In the judgment of the analyst, linear ranges may be lowered based on results obtained during the verification process. Standards used to determine or verify linear ranges must be analyzed during a routine analytical run. The linear range is the concentration above which sample results cannot be reported. The linear range must be verified every six months for Method 6020A.

9.1.2.2. For initial determination of the upper limit of the linear range, determine the signal responses from three different concentration standards across the estimated range. One standard must be at the upper limit of the estimated range. Results must recover within 10% of the expected value for the three standards. The linear range is then set at the concentration of the high standard.

9.1.2.3. For verification of the upper limit of the linear range, the high standard must recover within 10% of its expected value

9.2. Batch Definition

9.2.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD), which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.3. Method Blank (MB)

9.3.1. 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 must not contain any analyte of interest at, or above, the reporting limit (exception: common laboratory contaminants see below) or at, or above, 10% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 10x higher than the blank contamination level).

Note: For Ohio VAP samples, all analytes must be less than the reporting limit unless the samples are non-detect.

9.3.2. Corrective Action for MBs

9.3.2.1. If the analyte is a common laboratory contaminant (copper, iron, lead, barium, chromium, manganese, calcium, potassium, magnesium, sodium, or zinc), the data may be reported with qualifiers if the concentration of the analyte in the MB is less than two times the RL. **This is not applicable for Ohio VAP samples.**

9.3.2.2. Re-preparation and re-analysis of all samples associated with an unacceptable MB is required when reportable concentrations are determined in the samples (see exception noted above).

9.3.2.3. If there is no analyte 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.

9.3.2.4. If the above criteria are not met and re-analysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative.

9.4. Laboratory Control Sample (LCS)

9.4.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is 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 historical limits for the LCS for each analyte are in the LIMS system. If the LCS exceeds these limits for any analyte, that analyte is judged to be out of control and must be corrected before the analysis can be reported. The LCS limits for solid samples are statistically derived from historical laboratory data. Water samples have criterion of 80% - 120%. For Method 200.8, LCS limits are 85-115%.

9.4.2. Corrective Action for LCS

9.4.2.1. If any analyte is outside established control limits, the system is out of control and corrective action must occur.

9.4.2.2. The only exception is if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest. **This must be addressed in the project narrative.**

9.4.2.3. Corrective action will be repreparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.

Note: For Ohio VAP samples, the batch must be re-digested if the exception in Section 9.4.2.2 is not applicable.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of 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. Samples identified as field blanks cannot be used for MS/MSD analysis. The historical spike recovery acceptance limits for each analyte are in the LIMS system. If they are not in control, and all other quality control criteria have been met, then matrix interference is suspected.

9.5.2. Corrective action for MS/MSDs

9.5.2.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control; and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include re-preparation and re-analysis of the sample and MS/MSD.

9.5.2.2. If the native analyte concentration in the MS/MSD exceeds four times the spike level for that analyte, the recovery data is flagged with a “4” in LIMS.

9.5.2.3. If client program requirements specify to confirm matrix interferences, re-preparation and re-analysis of the MS/MSD may be necessary.

9.5.2.4. For Method 6020A, a post digestion spike will be run on a sample if the MS/MSD for the sample falls outside of the percent recovery criteria. A post digestion spike is a matrix spike on the same sample from which the MS/MSD aliquots were prepared, where the spike is added after the sample preparation is completed. The post digestion spike recovery for Method 6020A should be within 80-120%. If this spike fails, then the dilution test should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed. A post digestion spike is not required for Method 200.8 nor Method 6020.

9.6. Sample Duplicate (DU)

9.6.1. A DU is a second aliquot of an environmental sample taken from the same sample container, when possible, that is processed with the first aliquot of that sample. That is, DUs are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the

MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.6.2. DUs may be performed in lieu of, or in addition to, MSDs.

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via LIMs.

9.8. Method Detection Limits (MDLs) and MDL Checks

9.8.1. MDLs and MDL Checks are established by the laboratory as described in SOPs CA-Q-S-006 and NC-QA-021.

9.8.2. MDLs are easily accessible via LIMs.

9.9. General Corrective Action Requirements: The general requirements for evaluation of QC results and corrective action for failures is described in TestAmerica Policy QA-003. Ohio VAP projects must reference this SOP instead of Policy QA-003 for information on QC Samples.

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. Procedural deviations are not allowed for Ohio VAP Projects.

10. CALIBRATION AND STANDARDIZATION

10.1. Instrument Startup: Set up the instrument according to manufacturer's operating instructions. Allow the instrument to become thermally stable for at least 30 minutes before tuning.

10.2. Instrument Tuning / Mass Calibration / Daily Performance

10.2.1. Daily Performance

10.2.1.1. Verify instrument performance daily with a solution containing elements representing all of the mass regions of interest. The relative standard deviations must be less than 5% after running the tuning solution a minimum of four times. Tuning criteria are listed in Table 4.

10.2.2. Check mass calibration and resolution daily.

10.2.2.1. Mass Calibration Check

10.2.2.1.1. The mass calibration results must be within 0.1 amu from the true value. If this criterion is not met, the mass calibration must be adjusted before running samples.

10.2.2.2. Mass Resolution Check

10.2.2.2.1. The resolution must be verified to be less than, or equal to, 0.9 amu full width at 10% peak height.

10.3. Initial Calibration

10.3.1. Calibrate the instrument for the analytes of interest according to manufacturer's instructions. Routine calibration and calibration verification levels are shown in Table 5. The calibration should include a minimum of a blank and one standard. For a linear multi-point calibration curve, the correlation coefficient must be >/= 0.995 for Method 200.8 and Method 6020. The correlation coefficient must be >/= 0.998 for Method 6020A. Report the average of at least three integrations for both calibration and sample analysis. A calibration must be performed daily and each time the instrument is set up. Instrument analytical runs may be continued over periods exceeding 24 hours as long as calibration verification, interference check, and internal standard QC criteria are met. Calibration standard concentrations and/or vendors are subject to change.

10.4. Initial and Continuing Calibration Verification

10.4.1. ICV/CCV. Calibration accuracy is verified at the beginning of each analytical run by analyzing a second-source initial calibration verification (ICV) standard. A continuing calibration verification (CCV) standard is analyzed at a 10% frequency throughout the run. The ICV must be within 10% of the expected value, or the analysis is terminated. The CCV must be within 10% of the expected value... Sample results may only be reported when bracketed by valid CCVs.

Note: The only exception is if the ICV/CCV recoveries are biased high and the associated sample is ND for the parameter(s) of interest. **This must be addressed in the project narrative.**

10.5. Low Level CCV (CRI/LLCCV)

10.5.1. The CRI/LLCCV for Method 6020A must be within the 70 – 130% recovery range and analyzed at the beginning and end of the analytical sequence. .In addition a LLCCV can be analyzed on a more frequent basis. If any analyte is outside the range indicated, the CRI/LLCCV may be re-analyzed once. If the results fall within the required values upon re-analysis, no further corrective action needs to be taken. If still outside the acceptable range, then samples

containing the affected analytes at similar concentrations cannot be reported and must be re-analyzed.

Note: The only exception is if the CRI/LLCCV recoveries are biased high and the associated sample is ND for the parameter(s) of interest. **This must be addressed in the project narrative.**

10.6. RL Verification Standard (CRI) Method 6020

10.6.1. An independent standard is analyzed after the ICB to monitor the lab's ability to produce reliable results at RL-level concentrations. There is no set acceptance criteria established for this standard, but generally results should be within 50% of the expected value. Individual program requirements may vary.

10.7. ICB/CCB

10.7.1. The ICB/CCB solution is prepared with reagent water (ASTM Type I or equivalent) using the same acid matrix as the calibration standards. The Initial Calibration Blank (ICB) must be analyzed immediately following the ICV. The Continuing Calibration Blank (CCB) must be analyzed at a minimum frequency of 10% throughout the remainder of the analytical run. The ICB/CCB must fall within +/- the reporting limit from zero.

Note: The only exceptions are if the ICB/CCB recoveries are biased high and the associated sample is ND for the parameter(s) of interest or at, or above, 10 % of the measured concentration of that analyte in associated samples, (sample result must be a minimum of ten times higher than the ICB/CCB contamination level).
This must be addressed in the project narrative.

10.8. Interference Check Solutions (ICSA/ICSAB), ***Methods 6020 and 6020A only***

10.8.1. The interference check solution is prepared with known concentrations of interfering elements so a determination may be made as to the magnitude of the interference on analytes of interest as well as a test of any software corrections. The required elements and their concentrations are listed in Table 2. The interference check solutions must be analyzed at the beginning of every analytical run and every 12 hours thereafter. The results of solution "A" and solution "AB" must be monitored for possible interferences.

10.8.1.1. Control limits of spiked analytes in the ICSA/ICSAB solution are ± 50% of true value. Some projects may require control limits of ± 20% of true value. Control limits of non-spiked analytes are +/- the reporting limit when the reporting limit is greater than 10 ug/L, ± two times the reporting limit when the reporting limit is 1 ug/L to 10 ug/L or less than 1 ug/L when the reporting limit is less than 1 ug/L..

Note: It may not be possible to obtain absolutely clean ICSA/ICSAB

standards. If contamination can be confirmed by another method (ICP/GFAA), acceptance criteria will be applied at that level and the data accepted.

10.9. Internal Standards

10.9.1. The intensities of all internal standards must be monitored throughout the run. The internal standard in the samples must be between 30% and 120% of the intensity of the calibration blank for Method 6020, 30-150% for Method 6020A, and between 60% and 125% for Method 200.8. If the sample falls outside of these criteria, perform the following procedures. First, evaluate nearby CCVs and CCBs. If sample internal standard recoveries appear to be related to instrument drift, then rerun affected samples undiluted. If the internal standard recoveries fall outside acceptance criteria and appear to be due to matrix effects, a five fold dilution is performed on the sample to correct for matrix effects and the sample re-analyzed. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal standard intensities are within acceptance criteria. In no case may sample results be reported with internal standard recoveries greater than 40% higher than recoveries in surrounding CCVs/CCBs. Alternately, the run may be reprocessed with an alternative internal standard that is not in the samples and at an appropriate mass for the masses being reported. See Table1 for a list of Internal Standard analytes. See Table 7 for the Internal Standard assignments.

10.10. Serial Dilution, Methods 6020 and 6020A only

10.10.1. One serial five-fold dilution must be analyzed per batch for each matrix. If the analyte concentration is within linear range of the instrument and sufficiently high (generally, a factor of 100 times above the reporting limit), the serial dilution must agree within 10% of the original analysis. If not, an interference effect must be suspected; the result is flagged, and included in the final report narrative. Samples identified as blanks cannot be used for serial dilution.

10.11. Post-Digestion Spike Addition (PDS), ***Method 6020*** **(*performed when required by client or project)***

10.11.1. If the serial dilution fails to meet the acceptance criteria, a re-analysis of the serial dilution can be performed on a diluted sample provided that the concentration of the original sample after the dilution is above the requested reporting limit. If the serial dilution is still outside acceptance limits then a post digestion spike must be performed. An analytical spike added to a portion of a prepared sample, or its dilution, should be recovered within 75 - 125% of the known value. If the PDS fails to meet this criterion, matrix interference is suspected.

11. PROCEDURE

11.1. 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 must be completely documented using a Nonconformance Memo. The Nonconformance Memo must be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. Procedural deviations are not allowed for Ohio VAP projects.

11.3. Sample Preparation

11.3.1. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are requested. See SOPs NC-IP-010 and NC-IP-011 for preparation details.

11.4. Sample Analysis

11.4.1. Flush the system with the rinse blank for at least 30 seconds between samples and standards during the analytical run.

11.4.2. Dilute and re-analyze samples that are more concentrated than the linear range for an analyte or specific isotope of interest. The sample should be diluted to the approximate midrange of the linear range unless the dilution is for internal standard recoveries. To reduce the levels of Total Dissolved Solids (TDS), a two-fold dilution will be performed before analysis on solid digestates including batch QC.

11.4.3. The analytical run sequence must be performed as follows to meet all quality control criteria:

Warm-up
Verify instrument performance
Calibration blank
Calibration standards
ICV
ICB
RL verification standard (CRI/LLCCV)
ICSA (6020 and 6020A only)
ICSAB (6020 and 6020A only)
CCV
CCB
10 Samples
CCV
CCB
RL verification standard (CRI/LLCCV) for 6020A if applicable

11.5. Analytical Documentation

11.5.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Record all sample results and associated QC in the LIMS. Level I and Level II reviews are performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

Note: The mean of three exposures is used to derive the sample concentrations used in the calculations in this section.

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = \mathbf{100\ x}\left(\frac{\mathbf{Found\ (ICV)}}{\mathbf{True\ (ICV)}}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = \mathbf{100\ x}\left(\frac{\mathbf{Found\ (CCV)}}{\mathbf{True\ (CCV)}}\right)$$

12.3. Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = \mathbf{100\ x}\left(\frac{\mathbf{SSR\ -\ SR}}{\mathbf{SA}}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

Note: When sample concentration is less than the method detection limit, use SR = 0 for purposes of calculating % Recovery.

12.4. The relative percent difference (RPD) of sample duplicates are calculated according to the following equation:

$$RPD = \mathbf{100\ x}\left[\frac{\mathbf{(DU1\ -\ DU2)}}{\mathbf{(DU1\ +\ DU2)\ /\ 2}}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration for an aqueous sample is calculated as follows:

$$\text{Result (ug/L)} = \frac{\mathbf{(C\ x\ V1\ x\ D)}}{\mathbf{V2}}$$

Where:
C = Concentration from instrument readout, ppb (mean of three exposures)
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6. The concentration determined in digested solid samples when reported on a wet weight basis is as follows:

$$\text{Result (mg/kg)} = \frac{\mathbf{(C\ x\ V\ x\ D)}}{\mathbf{W}}$$

Where:
C = Concentration from instrument readout, ppb (mean of three exposures)
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight, in g, of wet sample digested

12.7. Calculation for Hardness

Total Hardness, mg equivalent $CaCO_3$/L, = 2.497 (Ca, mg/L) + 4.118 (Mg, mg/L)

12.8. Calculation for Trivalent Chromium ($Cr^{=3}$)

Cr^{+3} mg/L = Total Chromium mg/L – Hexavalent Chromium (Cr^{+6}) mg/L

12.9. Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002.

13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of performance data on file. Each laboratory must have corresponding method detection limit files.

13.2. Refer to Table 5 for the list of analytes that may be analyzed using this SOP for Methods 6020, 6020A, and 200.8. Additional analytes may be analyzed if all method-required QC is acceptable.

13.3. Training Qualifications

13.3.1. The Group/Team Leader has the responsibility to ensure that 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 must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must 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. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

15.4. Waste Streams Produced by the Method

15.4.1. Acid waste consisting of sample and rinse solution is generated by this method.

15.4.1.1. Any sample waste generated must be collected and disposed of in the acid waste drum located in the Metals Lab.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, EPA SW-846, 3rd Edition, Final Update III, Method 6020: Inductively Coupled Argon Plasma - Mass Spectrometry, Revision 0, September 1994

16.1.2. Test Methods for Evaluating Solid Waste, EPA SW-846, Method 6020A Inductively Coupled Argon Plasma - Mass Spectrometry, Revision 1, February 2007

16.1.3. Test Methods for Evaluating Solid Waste EPA SW-846 Method 6020B, Inductively Coupled Plasma – Mass Spectrometry, Revision 2 July 2014

16.1.4. Environmental Monitoring Systems Laboratory, EPA Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, EMMC version

16.1.5. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.6. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.7. Corporate Quality Management Plan (CQMP), current version

16.1.8. Revision History

Historical File:		Revision 0: 08/01/95		Revision 4.5: 07/30/08
		Revision 1: 06/06/01		Revision 4.6: 02/15/11
		Revision 3: 03/26/02		Revision 4.7-A: 04/27/12
		Revision 4: 03/06/03		Revision 5: 04/24/13
		Revision 4.1: 10/01/03		Revision 6: 04/02/14
		Revision 4.2: 01/08/04		
		Revision 4.3: 07/28/07		
		Revision 4.4: 07/30/08		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Acid Digestion of Soils, SW846 Method 3050B, NC-IP-010

16.2.3. Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods, NC-IP-011

16.2.4. Glassware Washing, NC-QA-014

16.2.5. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.6. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.7. Standards and Reagents, NC-QA-017

16.2.8. Selection of Calibration Points, CA-T-P-002

16.2.9. Calibration Curves (General), CA-Q-S-005

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. Reporting limits for solids and waters are easily accessible via the LIMS.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method Deviations

17.2.1. Deviations from Method 6020

17.2.1.1. Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.

17.2.1.2. The results of the calibration blank as well as all other blanks must be less than the reporting limit--not three times the instrument IDL.

17.2.1.3. Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by the analysis of blanks.

17.2.1.4. Internal standard recoveries may be less than 80% in CCVs and CCBs as long as QC criteria are met. Sample internal standard recoveries may never be greater than 40% higher than recoveries in associated CCVs/CCBs.

17.2.1.5. The method requires 1% nitric acid for the calibration blank, initial calibration standards, CCVs, ICV, and CRI. The laboratory uses 2% nitric acid and 5% hydrochloric acid.

17.2.1.6. The method states that the ICV should be prepared near the midpoint of the linear range. The laboratory prepares the standard near the midpoint of the calibration curve.

17.2.1.7. The method states in Section 8.5 that the dilution test sample result must be at least 100 times the concentration in the reagent blank. The laboratory uses 100 times the reporting limit as the criteria.

17.2.1.8. The ICSA/ICSAB solution is prepared at least every six months, or if expired.

17.2.1.9. The laboratory references the criteria found in SW-846 method 6020B for the frequency at which IDLs are determined.

17.2.2. Deviations from Method 200.8

17.2.2.1. Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.

17.2.2.2. The results of the calibration blank as well as all other blanks must be less than the reporting limit--not three times the instrument IDL.

17.2.2.3. Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by the analysis of blanks.

17.2.2.4. Resolution criteria of the mass calibration are met if the resolution criteria for Method 6020 are satisfied.

17.2.2.5. The concentration of most analytes in the LCS is 1000 µg/L. This is made from a commercially available stock solution and has all analytes at the same level. Verification records for this solution are kept in the laboratory.

17.2.2.6. The method requires 1% nitric acid for the calibration blank, initial calibration standards, CCVs, ICV, and CRI. The laboratory uses 2% nitric acid and 5% hydrochloric acid.

17.2.2.7. The tuning solution and internal standard solution are prepared with 2% nitric acid. The method states 1% nitric acid.

17.2.2.8. The method requires a dilution prior to analysis to adjust the chloride concentration in the sample. Due to newer instrument technology, this dilution is no longer needed.

17.3. Tables and Appendices

Table1: Recommended Internal Standards
Li
Sc
Y
Rh
In
Tb
Ho
Bi
Ge

Table 2: Interference Check Sample Components and Recommended Concentrations

Interference Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Ag	0.0	0.1
Al	50	50
As	0.0	0.1
B	0.0	0.1
Ba	0.0	0.1
Be	0.0	0.1
C	100	100
Ca	50	50
Cd	0.0	0.1
Cl	500	500
Co	0.0	0.1
Cr	0.0	0.1
Cu	0.0	0.1
Fe	50	50
K	50	50
Li (Agilent only)	0.0	0.1
Mg	50	50
Mn	0.0	0.1
Mo	1.0	1.1
Na	50	50
Ni	0.0	0.1
P	50	50
Pb	0.0	0.1
S	50	50
Sb	0.0	0.1
Se	0.0	0.1
Sn	0.0	0.1
Sr	0.0	0.1
Ti	1.0	1.1
Tl	0.0	0.1
V	0.0	0.1
W	0.0	0.1
Zn	0.0	0.1

TABLE 3: Tuning Solution

A tuning solution containing elements representing all of the mass regions of interest must be analyzed. Below are two groups of suggested solutions which cover a typical mass calibration range.

Table 3 A: Thermo XSeries II

Element	Concentration (µg/L)
Mg	10
Rh	10
Pb	10
Li	10
Co	10
In	10
Tl	10

Element	Concentration (µg/L)
Be	10
Mg	10
Co	10
In	10
Pb	10
Ba	10
Ce	10

Table 3 B: Agilent 7700

Element	Concentration (ug/L)
Ce	1
Co	1
Li	1
Mg	1
Tl	1
Y	1

TABLE 4: Suggested Tuning and Response Factor Criteria / Minimum Response from Tuning Solution

Minimum Response from Tuning Solution (Standard Mode)
With a Peristaltic Pump Speed of 18 RPM on the Thermo XSeries II

Be	> 8,000
In	> 300,000
Pb	> 100,000
Co	> 100,000
Mg	> 10,000

Minimum Response from Tuning Solution (CCT Mode)
With a Peristaltic Pump Speed of 18 RPM on the Thermo XSeries II

In > 75,000
Se < 20

Suggested Mass Calibration for Thermo XSeries II

Be	9.0122
Mg	23.98
Rh	102.91
Pb	207.98
Li	7.016
Co	58.9332
In	114.904
Tl	204.9744

Suggested Response From Tuning Solution (No He Gas) for the Agilent 7700

6 >1000
89 >3000
205 > 2000
156/140 (Oxides) <1.0

Suggested Minimum Response From Tuning Solution (He Gas) for the Agilent 7700

59 >1000 with <5%RSD
51 <200
52 <200
51/59 <10%

TABLE 5: ICP/MS Calibration and Calibration Verification Checklist
Suggested Levels in µg/L

Element	Calibration 1A (Agilent only)	Calibration		ICV	CCV
		1	2		
Aluminum	50	250	500	200	250
Antimony	10	50	100	40	50
Arsenic	10	50	100	40	50
Barium	10	50	100	40	50
Beryllium	10	50	100	40	50
Boron	10	50	100	40	50
Cadmium	10	50	100	40	50
Calcium	5000	25000	50000	20000	25000
Chromium	10	50	100	40	50
Cobalt	10	50	100	40	50
Copper	10	50	100	40	50
Iron	2500	12500	25000	10000	12500
Lead	10	50	100	40	50
Lithium	10	50	100	40	50
Manganese	50	250	500	200	250
Magnesium	5000	25000	50000	20000	25000
Molybdenum	10	50	100	40	50
Nickel	10	50	100	40	50
Potassium	5000	25000	50000	20000	25000
Selenium	10	500	200	40	500
Sodium	5000	25000	50000	20000	25000
Silver	10	50	100	40	50
Strontium	10	50	100	40	50
Thallium	10	50	100	40	50
Tin	10	50	100	40	50
Titanium	10	50	100	40	50
Tungsten	10	50	100	40	50
Vanadium	10	50	100	40	50
Zinc	10	50	100	40	50

This procedure has been developed for additional elements. Additional elements may be included in the calibration solution at the appropriate levels. Levels may be adjusted to meet specific regulatory or client programs.

Table 6 A: Internal Standard Assignments for Thermo XSeries II		
Standard Mode Internal Standards: 6Li and 45Sc		
CCT Mode Internal Standards: 45Sc, 72Ge, 115In, 159Tb*, 165Ho, 209Bi*		
*Not used on a daily basis but may be used as an alternative or additional internal standard		
Mass - Element	**Associated Internal Standards**	**Possible Alternatives**
9Be	6Li	45Sc Standard
10B	6Li	45Sc Standard
23Na	45Sc CCT	72Ge Only
25Mg	45Sc CCT	72Ge Only
27Al	45Sc CCT	72Ge Only
39K	45Sc Standard	6Li
43Ca	45Sc Standard	6Li
47Ti	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
51V	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
52Cr	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
55Mn	45Sc Standard	6Li
56Fe	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
59Co	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
60Ni	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
65Cu	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
66Zn	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
75As	72Ge and 115In	72Ge Only or 115In Only

78Se	72Ge and 115In	72Ge Only or 115In Only
88Sr	72Ge and 115In	72Ge Only or 115In Only
95Mo	72Ge and 115In	72Ge Only or 115In Only
107Ag	72Ge and 115In	72Ge Only or 115In Only
111Cd	72Ge and 115In	72Ge Only or 115In Only
118Sn	115In and 165Ho	115In Only, 159Tb Only, or 165Ho only
121Sb	115In and 165Ho	1115In Only, 159Tb Only, or165 Ho only
137Ba	115In and 165Ho	115In Only, 159Tb Only, or 165Ho only
159 Tb		
165Ho		
182W	115In and 165Ho	159Tb only, 165Ho only, or 209Bi
205Tl	115In and 165Ho	159Tb only, 165Ho only, or 209Bi only
208Pb	115In and 165Ho	159Tb only, 165Ho only, or 209Bi
The analyst has the option to associate an alternative Internal Standard with an element if acceptance criteria are not met.		
Generally, the mass of the internal standard should be no more than 50 amu of the mass of the measured analyte, however,		

Table 6 A: Internal Standard Assignments for Agilent 7700		
Mass-Element	**Associated Internal Standards**	**Possible Alternatives**
7Li	45Sc No Gas	
9Be	6Li	45Sc No Gas
11B	6Li	45Sc No Gas
23Na	45Sc He	
25Mg	45Sc He	
27Al	45Sc He	
39K	45Sc He	
44Ca	45Sc He	
47Ti	45Sc He	
51V	45Sc He	
52Cr	45Sc He	
55Mn	45Sc He	103Rh
56Fe	45Sc He	103Rh
59Co	45Sc He	103Rh
60Ni	45Sc He	103Rh
63Cu	45Sc He	103Rh
66Zn	45Sc He	103Rh
75As	115In	103Rh
78Se	115In	103Rh
88Sr	45Sc He	103Rh, 115In
95Mo	103Rh	45Sc He, or 115In
107Ag	103Rh	115In
111Cd	115In	103Rh or 159Tb
118Sn	115In	103Rh, 159Tb, or 165Ho
123Sb	115In	103Rh, 159Tb, or 165Ho
137Ba	115In	103Rh or 159Tb

182W	159Tb	165Ho or 209Bi
205Tl	165Ho	165Ho or 209Bi
208Pb	165Ho	165Ho or 209Bi
i		
The analyst has the option to associate an alternative Internal Standard with an element if acceptance criteria are not met.		
Generally, the mass of the Internal Standard should be no more than 50 amu of the mass of the measured analyte.		

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TestAmerica Canton

SOP Amendment Form

SOP NUMBER: NC-MT-002 Rev. 7

SOP TITLE: Inductively Coupled Plasma – Mass Spectrometry

REASON FOR ADDITION OR CHANGE: Wording changes requested by Laboratory

CHANGE EFFECTIVE FROM: (DATE): 6/13/16

Change(s) Made:

7.5 change Rinse to 2% nitric 1% HCL

9.1.1.1 / 9.1.1.2 and 9.1.1.3 Reword :

The IDL for each for each analyte must be determined for each instrument. The IDL must be determined annually.
The IDL will be determined by multiplying the standard deviation obtained from the analysis of seven consecutive measurements of a blank solution, by three. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse at minimum).

IDLs should be determined at least once using new equipment and/or
after major instrument maintenance such as changing the detector.
IDLs may be run more frequently dependent upon requirements of state
programs or client needs.

9.4.1 Added at end of paragraph: The LCS limits for solid samples are statistically derived from historical laboratory data. Water samples have criterion of 80% - 120%. For Method 200.8, LCS limits are 85% - 115%.

10.4.1 Note: The only exception is if the ICV/CCV recoveries are biased high and the associated sample is ND…

10.7.1 Note: The only exceptions are if the ICB/CCB recoveries are biased high and …

EDITED BY/DATE: Melissa A. Fuller-Gustavel for Karen Counts 6/13/16

Title: INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY

[Method: EPA Method 200.8, SW846 Methods 6020 and 6020A]

Approvals (Signature/Date):

Technology Specialist	04/18/16 Date	Health & Safety Coordinator	04/18/16 Date
Quality Assurance Manager	05/31/16 Date	Technical Director	05/16/16 Date

This SOP was previously identified as SOP No. NC-MT-002, Rev 6, dated 4/2/14

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 copy of the SOP that is printed and placed in the General Chemistry SOP binder. Printed or electronic copies of the SOP that are distributed outside of the facility are considered uncontrolled.

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Tables

1. SCOPE AND APPLICATION

1.1. This procedure describes multi-elemental analysis by inductively coupled plasma-mass spectrometry (ICP-MS) based on SW-846 protocol as described in EPA Methods 6020, 6020A, and 200.8. The source method lists the following elements approved for analysis by ICP/MS (Al, Sb, As, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Li, Mg. Mn, Ni, K, Ag, Tl, Se, Na, V, and Zn). Additional elements may be included provided that the method performance criteria presented in Section 9 is met. However, project approval may be required from the controlling agencies for compliance testing beyond the elements included in the method.

1.2. The procedure is applicable to the analysis of waters (groundwaters and surface waters), soils, and wastes. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, biological matrices, and other solid wastes for which total (acid-leachable) elements are requested. See SOPs NC-IP-010 and NC-IP-011 for preparation details.

1.3. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. Aqueous samples, digestates, or leachates are nebulized into a spray chamber where a stream of argon carries the sample aerosol through the quartz torch and injects it into a radio frequency inductively coupled plasma. There the sample is decomposed and desolvated. The ions produced are entrained in the plasma gas, and by means of a water-cooled differentially-pumped interface, introduced into a high-vacuum chamber that houses a quadrapole mass spectrometer capable of providing a resolution less than, or equal to, 0.9 AMU full width at 10% of the peak height. For analysis by Method 200.8, the resolution requirement is 1.0 amu at 5% peak height. The ions are sorted according to their mass-to-charge ratio and measured with a channel electron multiplier. Interference must be assessed and valid corrections applied, or the data flagged, to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents and the constituents of the sample matrix. Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Isobaric Interferences: Isobaric interferences in the ICPMS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). Most interferences of this type are corrected for by the instrument software.

4.2. Isobaric Molecular and Doubly Charged Ion Interferences: Isobaric molecular interferences are caused by ions consisting of more than one atom or charge. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections must be applied; and the data flagged to indicate the presence of interferences. Using Collision Cell Technology (CCT) can reduce these interferences. Collision Cell Technology is accomplished by adding an auxiliary gas into the lens chamber. A Hydrogen/Helium (Thermo XSeries 2) or Helium (Agilent 7700) gas mixture is used. This gas mixture is used to knock polyatomic ions out of the path as they collide with the cell gas. The ions are dissociated into their component atoms/ions or converted into non-interfering species. The transmission of analyte ions is minimally affected. This process is called Kinetic Energy Displacement (KED).

4.3. Physical Interferences: Physical interferences are associated with the transport and nebulization process. Internal standards are used to compensate for these types of interferences.

4.3.1. Generally, the mass of the internal standard should be no more than 50 AMU (Atomic Mass Unit) of the mass of the measured analyte.

4.3.2. Matrix effects will be monitored by comparing the internal standard intensity in the sample to the internal standard intensity of the calibration blank.

4.3.3. Memory effects are dependent on the relative concentration differences between samples and/or standards, which are analyzed sequentially. The rinse period between samples must be long enough to eliminate significant memory interference.

4.3.4. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be demonstrated routinely to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. All glassware is cleaned per SOP NC-QA-014.Specific selection of reagents may be required to avoid introduction of contaminants.

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. 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 must be removed and discarded; other gloves must be cleaned immediately.

5.3. 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 Safety Data Sheet (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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. The RF Generator produces strong radio frequency waves--most of which are unshielded. People with pacemakers must not go near the instrument while in operation.

5.5. Exposure to 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 must be kept closed unless transfers are being made.

5.6. The ICPMS plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor and the EH&S Coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Argon gas: High purity grade (99.99%)

6.2. Inductively Coupled Plasma Mass Spectrometer capable of providing resolution less than, or equal to, 1.0 AMU at 10% peak height from a mass range of at least 6-240 and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass flow controller for the nebulizer argon and a peristaltic pump for the sample solution is recommended.

6.3. A three channel peristaltic pump

6.4. Appropriate water-cooling device

6.5. Calibrated adjustable pipettes

6.6. Autosampler with autosampler tubes

6.7. Hydrogen/helium gas mixture with approximate ratio of 7% hydrogen and 93% helium used for CCT mode on the Thermo X Series II, and helium only on the Agilent.7700

7. REAGENTS AND STANDARDS

7.1. Calibration standards are purchased as custom multi-element mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Additional information can be found in SOP NC-QA-017.

7.2. Check Calibration Standard (ICV) - A quality control standard similar to the calibration standards and prepared in the same acid matrix. This solution must be made at a concentration near the midpoint of the calibration curve. This standard is composed of analytes from a different source from those used in the calibration of the instrument. See Table 5. Refer to the LIMS standards and reagents module for details on preparation.

7.3. The tuning solution is purchased as custom multi-element mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. The solution must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year.

7.4. Reagent water - ASTM Type I, or equivalent for the elements of interest, generated using an ion-exchange water polishing system.

7.5. Rinse Solution – 2% HNO3 and 1% HCL in reagent grade water.

7.6. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.7 Concentrated hydrochloric acid (HCl), trace metal grade or better

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Aqueous samples are preserved with nitric acid to a pH of < 2, and may be stored in plastic or glass. Preservation must be verified prior to analysis.

8.2. Soil samples do not require preservation, but must be stored at 4° ± 2°C until the time of preparation.

8.3. The analytical holding times for metals are six months from the time of collection to analysis.

8.4. Solid and aqueous samples must be digested prior to analysis by the appropriate method.

8.5. Samples preserved in the laboratory must be held for 24 hours before digestion.

Note: If the samples are preserved the same day of collection, the 24-hour waiting period is not required.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. Instrument Detection Limit (IDL)

9.1.1.1. The IDL for each analyte must be determined for each instrument. The IDL must be determined annually.

9.1.1.2. The IDL will be determined by multiplying the standard deviation obtained from the analysis of seven consecutive measurements of a blank solution by three. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse at minimum).

9.1.1.3. IDLs should be determined at least once using new equipment and/or after major instrument maintenance such as changing the detector. IDLs may be run more frequently dependent upon requirements of state programs or client needs.

9.1.2. Linear Calibration Ranges

9.1.2.1. Linear calibration ranges are primarily detector limited. The linear range must be determined at instrument setup, and the upper limit must be verified annually or whenever a change in instrument hardware or operating conditions occurs. In the judgment of the analyst, linear ranges may be lowered based on results obtained during the verification process. Standards used to determine or verify linear ranges must be analyzed during a routine analytical run. The linear range is the concentration above which sample results cannot be reported. The linear range must be verified every six months for Method 6020A.

9.1.2.2. For initial determination of the upper limit of the linear range, determine the signal responses from three different concentration standards across the estimated range. One standard must be at the upper limit of the estimated range. Results must recover within 10% of the expected value for the three standards. The linear range is then set at the concentration of the high standard.

9.1.2.3. For verification of the upper limit of the linear range, the high standard must recover within 10% of its expected value

9.2. Batch Definition

9.2.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD), which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.3. Method Blank (MB)

9.3.1. 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 must not contain any analyte of interest at, or above, the reporting limit (exception: common laboratory contaminants see below) or at, or above, 10% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 10x higher than the blank contamination level).

Note: For Ohio VAP samples, all analytes must be less than the reporting limit unless the samples are non-detect.

9.3.2. Corrective Action for MBs

9.3.2.1. If the analyte is a common laboratory contaminant (copper, iron, lead, barium, chromium, manganese, calcium, potassium, magnesium, sodium, or zinc), the data may be reported with qualifiers if the concentration of the analyte in the MB is less than two times the RL. **This is not applicable for Ohio VAP samples.**

9.3.2.2. Re-preparation and re-analysis of all samples associated with an unacceptable MB is required when reportable concentrations are determined in the samples (see exception noted above).

9.3.2.3. If there is no analyte 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.

9.3.2.4. If the above criteria are not met and re-analysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative.

9.4. Laboratory Control Sample (LCS)

9.4.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is 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 historical limits for the LCS for each analyte are in the LIMS system. If the LCS exceeds these limits for any analyte, that analyte is judged to be out of control and must be corrected before the analysis can be reported. The LCS limits for solid samples are statistically derived from historical laboratory data. Water samples have criterion of 80% - 120%. For Method 200.8, LCS limits are 85-115%.

9.4.2. Corrective Action for LCS

9.4.2.1. If any analyte is outside established control limits, the system is out of control and corrective action must occur.

9.4.2.2. The only exception is if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest. **This must be addressed in the project narrative.**

9.4.2.3. Corrective action will be repreparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.

Note: For Ohio VAP samples, the batch must be re-digested if the exception in Section 9.4.2.2 is not applicable.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of 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. Samples identified as field blanks cannot be used for MS/MSD analysis. The historical spike recovery acceptance limits for each analyte are in the LIMS system. If they are not in control, and all other quality control criteria have been met, then matrix interference is suspected.

9.5.2. Corrective action for MS/MSDs

9.5.2.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control; and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include re-preparation and re-analysis of the sample and MS/MSD.

9.5.2.2. If the native analyte concentration in the MS/MSD exceeds four times the spike level for that analyte, the recovery data is flagged with a “4” in LIMS.

9.5.2.3. If client program requirements specify to confirm matrix interferences, re-preparation and re-analysis of the MS/MSD may be necessary.

9.5.2.4. For Method 6020A, a post digestion spike will be run on a sample if the MS/MSD for the sample falls outside of the percent recovery criteria. A post digestion spike is a matrix spike on the same sample from which the MS/MSD aliquots were prepared, where the spike is added after the sample preparation is completed. The post digestion spike recovery for Method 6020A should be within 80-120%. If this spike fails, then the dilution test should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed. A post digestion spike is not required for Method 200.8 nor Method 6020.

9.6. Sample Duplicate (DU)

9.6.1. A DU is a second aliquot of an environmental sample taken from the same sample container, when possible, that is processed with the first aliquot of that sample. That is, DUs are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the

MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.6.2. DUs may be performed in lieu of, or in addition to, MSDs.

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via LIMs.

9.8. Method Detection Limits (MDLs) and MDL Checks

9.8.1. MDLs and MDL Checks are established by the laboratory as described in SOPs CA-Q-S-006 and NC-QA-021.

9.8.2. MDLs are easily accessible via LIMs.

9.9. General Corrective Action Requirements: The general requirements for evaluation of QC results and corrective action for failures is described in TestAmerica Policy QA-003. Ohio VAP projects must reference this SOP instead of Policy QA-003 for information on QC Samples.

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. Procedural deviations are not allowed for Ohio VAP Projects.

10. CALIBRATION AND STANDARDIZATION

10.1. Instrument Startup: Set up the instrument according to manufacturer's operating instructions. Allow the instrument to become thermally stable for at least 30 minutes before tuning.

10.2. Instrument Tuning / Mass Calibration / Daily Performance

10.2.1. Daily Performance

10.2.1.1. Verify instrument performance daily with a solution containing elements representing all of the mass regions of interest. The relative standard deviations must be less than 5% after running the tuning solution a minimum of four times. Tuning criteria are listed in Table 4.

10.2.2. Check mass calibration and resolution daily.

10.2.2.1. Mass Calibration Check

10.2.2.1.1. The mass calibration results must be within 0.1 amu from the true value. If this criterion is not met, the mass calibration must be adjusted before running samples.

10.2.2.2. Mass Resolution Check

10.2.2.2.1. The resolution must be verified to be less than, or equal to, 0.9 amu full width at 10% peak height.

10.3. Initial Calibration

10.3.1. Calibrate the instrument for the analytes of interest according to manufacturer's instructions. Routine calibration and calibration verification levels are shown in Table 5. The calibration should include a minimum of a blank and one standard. For a linear multi-point calibration curve, the correlation coefficient must be >/= 0.995 for Method 200.8 and Method 6020. The correlation coefficient must be >/= 0.998 for Method 6020A. Report the average of at least three integrations for both calibration and sample analysis. A calibration must be performed daily and each time the instrument is set up. Instrument analytical runs may be continued over periods exceeding 24 hours as long as calibration verification, interference check, and internal standard QC criteria are met. Calibration standard concentrations and/or vendors are subject to change.

10.4. Initial and Continuing Calibration Verification

10.4.1. ICV/CCV. Calibration accuracy is verified at the beginning of each analytical run by analyzing a second-source initial calibration verification (ICV) standard. A continuing calibration verification (CCV) standard is analyzed at a 10% frequency throughout the run. The ICV must be within 10% of the expected value, or the analysis is terminated. The CCV must be within 10% of the expected value... Sample results may only be reported when bracketed by valid CCVs.

Note: The only exception is if the ICV/CCV recoveries are biased high and the associated sample is ND for the parameter(s) of interest. **This must be addressed in the project narrative.**

10.5. Low Level CCV (CRI/LLCCV)

10.5.1. The CRI/LLCCV for Method 6020A must be within the 70 – 130% recovery range and analyzed at the beginning and end of the analytical sequence. .In addition a LLCCV can be analyzed on a more frequent basis. If any analyte is outside the range indicated, the CRI/LLCCV may be re-analyzed once. If the results fall within the required values upon re-analysis, no further corrective action needs to be taken. If still outside the acceptable range, then samples

containing the affected analytes at similar concentrations cannot be reported and must be re-analyzed.

Note: The only exception is if the CRI/LLCCV recoveries are biased high and the associated sample is ND for the parameter(s) of interest. **This must be addressed in the project narrative.**

10.6. RL Verification Standard (CRI) Method 6020

10.6.1. An independent standard is analyzed after the ICB to monitor the lab's ability to produce reliable results at RL-level concentrations. There is no set acceptance criteria established for this standard, but generally results should be within 50% of the expected value. Individual program requirements may vary.

10.7. ICB/CCB

10.7.1. The ICB/CCB solution is prepared with reagent water (ASTM Type I or equivalent) using the same acid matrix as the calibration standards. The Initial Calibration Blank (ICB) must be analyzed immediately following the ICV. The Continuing Calibration Blank (CCB) must be analyzed at a minimum frequency of 10% throughout the remainder of the analytical run. The ICB/CCB must fall within +/- the reporting limit from zero.

Note: The only exceptions are if the ICB/CCB recoveries are biased high and the associated sample is ND for the parameter(s) of interest or at, or above, 10 % of the measured concentration of that analyte in associated samples, (sample result must be a minimum of ten times higher than the ICB/CCB contamination level).
This must be addressed in the project narrative.

10.8. Interference Check Solutions (ICSA/ICSAB), ***Methods 6020 and 6020A only***

10.8.1. The interference check solution is prepared with known concentrations of interfering elements so a determination may be made as to the magnitude of the interference on analytes of interest as well as a test of any software corrections. The required elements and their concentrations are listed in Table 2. The interference check solutions must be analyzed at the beginning of every analytical run and every 12 hours thereafter. The results of solution "A" and solution "AB" must be monitored for possible interferences.

10.8.1.1. Control limits of spiked analytes in the ICSA/ICSAB solution are ± 50% of true value. Some projects may require control limits of ± 20% of true value. Control limits of non-spiked analytes are +/- the reporting limit when the reporting limit is greater than 10 ug/L, ± two times the reporting limit when the reporting limit is 1 ug/L to 10 ug/L or less than 1 ug/L when the reporting limit is less than 1 ug/L..

Note: It may not be possible to obtain absolutely clean ICSA/ICSAB

standards. If contamination can be confirmed by another method (ICP/GFAA), acceptance criteria will be applied at that level and the data accepted.

10.9. Internal Standards

10.9.1. The intensities of all internal standards must be monitored throughout the run. The internal standard in the samples must be between 30% and 120% of the intensity of the calibration blank for Method 6020, 50-150% for Method 6020A, and between 60% and 125% for Method 200.8. If the sample falls outside of these criteria, perform the following procedures. First, evaluate nearby CCVs and CCBs. If sample internal standard recoveries appear to be related to instrument drift, then rerun affected samples undiluted. If the internal standard recoveries fall outside acceptance criteria and appear to be due to matrix effects, a five fold dilution is performed on the sample to correct for matrix effects and the sample re-analyzed. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal standard intensities are within acceptance criteria. In no case may sample results be reported with internal standard recoveries greater than 40% higher than recoveries in surrounding CCVs/CCBs. Alternately, the run may be reprocessed with an alternative internal standard that is not in the samples and at an appropriate mass for the masses being reported. See Table1 for a list of Internal Standard analytes. See Table 7 for the Internal Standard assignments.

10.10. Serial Dilution, Methods 6020 and 6020A only

10.10.1. One serial five-fold dilution must be analyzed per batch for each matrix. If the analyte concentration is within linear range of the instrument and sufficiently high (generally, a factor of 100 times above the reporting limit), the serial dilution must agree within 10% of the original analysis. If not, an interference effect must be suspected; the result is flagged, and included in the final report narrative. Samples identified as blanks cannot be used for serial dilution.

10.11. Post-Digestion Spike Addition (PDS), ***Method 6020*** **(*performed when required by client or project)***

10.11.1. If the serial dilution fails to meet the acceptance criteria, a re-analysis of the serial dilution can be performed on a diluted sample provided that the concentration of the original sample after the dilution is above the requested reporting limit. If the serial dilution is still outside acceptance limits then a post digestion spike must be performed. An analytical spike added to a portion of a prepared sample, or its dilution, should be recovered within 75 - 125% of the known value. If the PDS fails to meet this criterion, matrix interference is suspected.

11. PROCEDURE

11.1. 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 must be completely documented using a Nonconformance Memo. The Nonconformance Memo must be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. Procedural deviations are not allowed for Ohio VAP projects.

11.3. Sample Preparation

11.3.1. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are requested. See SOPs NC-IP-010 and NC-IP-011 for preparation details.

11.4. Sample Analysis

11.4.1. Flush the system with the rinse blank for at least 30 seconds between samples and standards during the analytical run.

11.4.2. Dilute and re-analyze samples that are more concentrated than the linear range for an analyte or specific isotope of interest. The sample should be diluted to the approximate midrange of the linear range unless the dilution is for internal standard recoveries. To reduce the levels of Total Dissolved Solids (TDS), a two-fold dilution will be performed before analysis on solid digestates including batch QC.

11.4.3. The analytical run sequence must be performed as follows to meet all quality control criteria:

Warm-up
Verify instrument performance
Calibration blank
Calibration standards
ICV
ICB
RL verification standard (CRI/LLCCV)
ICSA (6020 and 6020A only)
ICSAB (6020 and 6020A only)
CCV
CCB
10 Samples
CCV
CCB
RL verification standard (CRI/LLCCV) for 6020A if applicable

11.5. Analytical Documentation

11.5.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Record all sample results and associated QC in the LIMS. Level I and Level II reviews are performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

Note: The mean of three exposures is used to derive the sample concentrations used in the calculations in this section.

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = \mathbf{100\ x}\left(\frac{\mathbf{Found\ (ICV)}}{\mathbf{True\ (ICV)}}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = \mathbf{100\ x}\left(\frac{\mathbf{Found\ (CCV)}}{\mathbf{True\ (CCV)}}\right)$$

12.3. Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = \mathbf{100\ x}\left(\frac{\mathbf{SSR\ -\ SR}}{\mathbf{SA}}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

Note: When sample concentration is less than the method detection limit, use SR = 0 for purposes of calculating % Recovery.

12.4. The relative percent difference (RPD) of sample duplicates are calculated according to the following equation:

$$RPD = \mathbf{100\ x}\left[\frac{\mathbf{(DU1\ -\ DU2)}}{\mathbf{(DU1\ +\ DU2)\ /\ 2}}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration for an aqueous sample is calculated as follows:

$$\text{Result (ug/L)} = \frac{\mathbf{(C\ x\ V1\ x\ D)}}{\mathbf{V2}}$$

Where:
C = Concentration from instrument readout, ppb (mean of three exposures)
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6. The concentration determined in digested solid samples when reported on a wet weight basis is as follows:

$$\text{Result (mg/kg)} = \frac{\mathbf{(C\ x\ V\ x\ D)}}{\mathbf{W}}$$

Where:
C = Concentration from instrument readout, ppb (mean of three exposures)
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight, in g, of wet sample digested

12.7. Calculation for Hardness

Total Hardness, mg equivalent $CaCO_3$/L, = 2.497 (Ca, mg/L) + 4.118 (Mg, mg/L)

12.8. Calculation for Trivalent Chromium ($Cr^{=3}$)

Cr^{+3} mg/L = Total Chromium mg/L – Hexavalent Chromium (Cr^{+6}) mg/L

12.9. Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002.

13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of performance data on file. Each laboratory must have corresponding method detection limit files.

13.2. Refer to Table 5 for the list of analytes that may be analyzed using this SOP for Methods 6020, 6020A, and 200.8. Additional analytes may be analyzed if all method-required QC is acceptable.

13.3. Training Qualifications

13.3.1. The Group/Team Leader has the responsibility to ensure that 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 must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must 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. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

15.4. Waste Streams Produced by the Method

15.4.1. Acid waste consisting of sample and rinse solution is generated by this method.

15.4.1.1. Any sample waste generated must be collected and disposed of in the acid waste drum located in the Metals Lab.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, EPA SW-846, 3rd Edition, Final Update III, Method 6020: Inductively Coupled Argon Plasma - Mass Spectrometry, Revision 0, September 1994

16.1.2. Test Methods for Evaluating Solid Waste, EPA SW-846, Method 6020A Inductively Coupled Argon Plasma - Mass Spectrometry, Revision 1, February 2007

16.1.3. Test Methods for Evaluating Solid Waste EPA SW-846 Method 6020B, Inductively Coupled Plasma – Mass Spectrometry, Revision 2 July 2014

16.1.4. Environmental Monitoring Systems Laboratory, EPA Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, EMMC version

16.1.5. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.6. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.7. Corporate Quality Management Plan (CQMP), current version

16.1.8. Revision History

Historical File:		Revision 0: 08/01/95		Revision 4.5: 07/30/08
		Revision 1: 06/06/01		Revision 4.6: 02/15/11
		Revision 3: 03/26/02		Revision 4.7-A: 04/27/12
		Revision 4: 03/06/03		Revision 5: 04/24/13
		Revision 4.1: 10/01/03		Revision 6: 04/02/14
		Revision 4.2: 01/08/04		
		Revision 4.3: 07/28/07		
		Revision 4.4: 07/30/08		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Acid Digestion of Soils, SW846 Method 3050B, NC-IP-010

16.2.3. Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods, NC-IP-011

16.2.4. Glassware Washing, NC-QA-014

16.2.5. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.6. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.7. Standards and Reagents, NC-QA-017

16.2.8. Selection of Calibration Points, CA-T-P-002

16.2.9. Calibration Curves (General), CA-Q-S-005

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. Reporting limits for solids and waters are easily accessible via the LIMS.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method Deviations

17.2.1. Deviations from Method 6020

17.2.1.1. Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.

17.2.1.2. The results of the calibration blank as well as all other blanks must be less than the reporting limit--not three times the instrument IDL.

17.2.1.3. Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by the analysis of blanks.

17.2.1.4. Internal standard recoveries may be less than 80% in CCVs and CCBs as long as QC criteria are met. Sample internal standard recoveries may never be greater than 40% higher than recoveries in associated CCVs/CCBs.

17.2.1.5. The method requires 1% nitric acid for the calibration blank, initial calibration standards, CCVs, ICV, and CRI. The laboratory uses 2% nitric acid and 5% hydrochloric acid.

17.2.1.6. The method states that the ICV should be prepared near the midpoint of the linear range. The laboratory prepares the standard near the midpoint of the calibration curve.

17.2.1.7. The method states in Section 8.5 that the dilution test sample result must be at least 100 times the concentration in the reagent blank. The laboratory uses 100 times the reporting limit as the criteria.

17.2.1.8. The ICSA/ICSAB solution is prepared at least every six months, or if expired.

17.2.1.9. The laboratory references the criteria found in SW-846 method 6020B for the frequency at which IDLs are determined.

17.2.2. Deviations from Method 200.8

17.2.2.1. Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.

17.2.2.2. The results of the calibration blank as well as all other blanks must be less than the reporting limit--not three times the instrument IDL.

17.2.2.3. Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by the analysis of blanks.

17.2.2.4. Resolution criteria of the mass calibration are met if the resolution criteria for Method 6020 are satisfied.

17.2.2.5. The concentration of most analytes in the LCS is 1000 µg/L. This is made from a commercially available stock solution and has all analytes at the same level. Verification records for this solution are kept in the laboratory.

17.2.2.6. The method requires 1% nitric acid for the calibration blank, initial calibration standards, CCVs, ICV, and CRI. The laboratory uses 2% nitric acid and 5% hydrochloric acid.

17.2.2.7. The tuning solution and internal standard solution are prepared with 2% nitric acid. The method states 1% nitric acid.

17.2.2.8. The method requires a dilution prior to analysis to adjust the chloride concentration in the sample. Due to newer instrument technology, this dilution is no longer needed.

17.3. Tables and Appendices

Table1: Recommended Internal Standards
Li
Sc
Y
Rh
In
Tb
Ho
Bi
Ge

Table 2: Interference Check Sample Components and Recommended Concentrations

Interference Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Ag	0.0	0.1
Al	50	50
As	0.0	0.1
B	0.0	0.1
Ba	0.0	0.1
Be	0.0	0.1
C	100	100
Ca	50	50
Cd	0.0	0.1
Cl	500	500
Co	0.0	0.1
Cr	0.0	0.1
Cu	0.0	0.1
Fe	50	50
K	50	50
Li (Agilent only)	0.0	0.1
Mg	50	50
Mn	0.0	0.1
Mo	1.0	1.1
Na	50	50
Ni	0.0	0.1
P	50	50
Pb	0.0	0.1
S	50	50
Sb	0.0	0.1
Se	0.0	0.1
Sn	0.0	0.1
Sr	0.0	0.1
Ti	1.0	1.1
Tl	0.0	0.1
V	0.0	0.1
W	0.0	0.1
Zn	0.0	0.1

TABLE 3: Tuning Solution

A tuning solution containing elements representing all of the mass regions of interest must be analyzed. Below are two groups of suggested solutions which cover a typical mass calibration range.

Table 3 A: Thermo XSeries II

Element	Concentration (µg/L)
Mg	10
Rh	10
Pb	10
Li	10
Co	10
In	10
Tl	10

Element	Concentration (µg/L)
Be	10
Mg	10
Co	10
In	10
Pb	10
Ba	10
Ce	10

Table 3 B: Agilent 7700

Element	Concentration (ug/L)
Ce	1
Co	1
Li	1
Mg	1
Tl	1
Y	1

TABLE 4: Suggested Tuning and Response Factor Criteria / Minimum Response from Tuning Solution

Minimum Response from Tuning Solution (Standard Mode)
With a Peristaltic Pump Speed of 18 RPM on the Thermo XSeries II

Be	> 8,000
In	> 300,000
Pb	> 100,000
Co	> 100,000
Mg	> 10,000

Minimum Response from Tuning Solution (CCT Mode)
With a Peristaltic Pump Speed of 18 RPM on the Thermo XSeries II

In > 75,000
Se < 20

Suggested Mass Calibration for Thermo XSeries II

Be	9.0122
Mg	23.98
Rh	102.91
Pb	207.98
Li	7.016
Co	58.9332
In	114.904
Tl	204.9744

Suggested Response From Tuning Solution (No He Gas) for the Agilent 7700

6 >1000
89 >3000
205 > 2000
156/140 (Oxides) <1.0

Suggested Minimum Response From Tuning Solution (He Gas) for the Agilent 7700

59 >1000 with <5%RSD
51 <200
52 <200
51/59 <10%

TABLE 5: ICP/MS Calibration and Calibration Verification Checklist
Suggested Levels in µg/L

Element	Calibration 1A (Agilent only)	Calibration		ICV	CCV
		1	2		
Aluminum	50	250	500	200	250
Antimony	10	50	100	40	50
Arsenic	10	50	100	40	50
Barium	10	50	100	40	50
Beryllium	10	50	100	40	50
Boron	10	50	100	40	50
Cadmium	10	50	100	40	50
Calcium	5000	25000	50000	20000	25000
Chromium	10	50	100	40	50
Cobalt	10	50	100	40	50
Copper	10	50	100	40	50
Iron	2500	12500	25000	10000	12500
Lead	10	50	100	40	50
Lithium	10	50	100	40	50
Manganese	50	250	500	200	250
Magnesium	5000	25000	50000	20000	25000
Molybdenum	10	50	100	40	50
Nickel	10	50	100	40	50
Potassium	5000	25000	50000	20000	25000
Selenium	10	500	200	40	500
Sodium	5000	25000	50000	20000	25000
Silver	10	50	100	40	50
Strontium	10	50	100	40	50
Thallium	10	50	100	40	50
Tin	10	50	100	40	50
Titanium	10	50	100	40	50
Tungsten	10	50	100	40	50
Vanadium	10	50	100	40	50
Zinc	10	50	100	40	50

This procedure has been developed for additional elements. Additional elements may be included in the calibration solution at the appropriate levels. Levels may be adjusted to meet specific regulatory or client programs.

Table 6 A: Internal Standard Assignments for Thermo XSeries II		
Standard Mode Internal Standards: 6Li and 45Sc		
CCT Mode Internal Standards: 45Sc, 72Ge, 115In, 159Tb*, 165Ho, 209Bi*		
*Not used on a daily basis but may be used as an alternative or additional internal standard		
Mass - Element	**Associated Internal Standards**	**Possible Alternatives**
9Be	6Li	45Sc Standard
10B	6Li	45Sc Standard
23Na	45Sc CCT	72Ge Only
25Mg	45Sc CCT	72Ge Only
27Al	45Sc CCT	72Ge Only
39K	45Sc Standard	6Li
43Ca	45Sc Standard	6Li
47Ti	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
51V	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
52Cr	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
55Mn	45Sc Standard	6Li
56Fe	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
59Co	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
60Ni	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
65Cu	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
66Zn	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
75As	72Ge and 115In	72Ge Only or 115In Only

78Se	72Ge and 115In	72Ge Only or 115In Only
88Sr	72Ge and 115In	72Ge Only or 115In Only
95Mo	72Ge and 115In	72Ge Only or 115In Only
107Ag	72Ge and 115In	72Ge Only or 115In Only
111Cd	72Ge and 115In	72Ge Only or 115In Only
118Sn	115In and 165Ho	115In Only, 159Tb Only, or 165Ho only
121Sb	115In and 165Ho	1115In Only, 159Tb Only, or165 Ho only
137Ba	115In and 165Ho	115In Only, 159Tb Only, or 165Ho only
159 Tb		
165Ho		
182W	115In and 165Ho	159Tb only, 165Ho only, or 209Bi
205Tl	115In and 165Ho	159Tb only, 165Ho only, or 209Bi only
208Pb	115In and 165Ho	159Tb only, 165Ho only, or 209Bi
The analyst has the option to associate an alternative Internal Standard with an element if acceptance criteria are not met.		
Generally, the mass of the internal standard should be no more than 50 amu of the mass of the measured analyte, however,		

Table 6 A: Internal Standard Assignments for Agilent 7700		
Mass-Element	**Associated Internal Standards**	**Possible Alternatives**
7Li	45Sc No Gas	
9Be	6Li	45Sc No Gas
11B	6Li	45Sc No Gas
23Na	45Sc He	
25Mg	45Sc He	
27Al	45Sc He	
39K	45Sc He	
44Ca	45Sc He	
47Ti	45Sc He	
51V	45Sc He	
52Cr	45Sc He	
55Mn	45Sc He	103Rh
56Fe	45Sc He	103Rh
59Co	45Sc He	103Rh
60Ni	45Sc He	103Rh
63Cu	45Sc He	103Rh
66Zn	45Sc He	103Rh
75As	115In	103Rh
78Se	115In	103Rh
88Sr	45Sc He	103Rh, 115In
95Mo	103Rh	45Sc He, or 115In
107Ag	103Rh	115In
111Cd	115In	103Rh or 159Tb
118Sn	115In	103Rh, 159Tb, or 165Ho
123Sb	115In	103Rh, 159Tb, or 165Ho
137Ba	115In	103Rh or 159Tb

182W	159Tb	165Ho or 209Bi
205Tl	165Ho	165Ho or 209Bi
208Pb	165Ho	165Ho or 209Bi
i		
The analyst has the option to associate an alternative Internal Standard with an element if acceptance criteria are not met.		
Generally, the mass of the Internal Standard should be no more than 50 amu of the mass of the measured analyte.		

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Title: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS AND SOLID SAMPLES BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY

[Method: MCAWW Method 245.1, SW846 Method 7470A, SW846 7471A, and 7471B]

Approvals (Signature/Date):

Technology Specialist	06/15/16 Date	Health & Safety Coordinator	06/15/16 Date
Quality Assurance Manager	06/16/16 Date	Technical Director	06/23/16 Date

This SOP was previously identified as SOP No. NC-MT-014, Rev5, dated 9/28/15

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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 Absorption Spectroscopy (CVAA) using SW846 Methods 7470A, 7471A, and 7471B, and MCAWW Method 245.1.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants and potassium permanganate has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity, and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation, and volume of sample used.

1.3. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, TCLP, and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed; however, Method 7471A is usually the method of choice. All matrices require sample preparation prior to analysis.

1.4. Method 245.1 is applicable to the determination of mercury in surface and saline waters, and domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.5. Methods 7471A and 7471B are applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits, wastes, wipes, biological material, and sludge-type materials. All matrices require sample preparation prior to analysis.

1.6. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric (aqueous samples), or hydrochloric and nitric acids (soil samples). Organic mercury compounds are oxidized with potassium permanganate (aqueous and soil samples) and potassium persulfate (aqueous samples), and the mercury reduced to its elemental state with stannous chloride 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. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control (QC) section. All glassware is cleaned per SOP NC-QA-014. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Chemical and physical interferences may be encountered when analyzing samples using this method.

4.3. Potassium permanganate, which is used to break down organic mercury compounds, also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide (as sodium sulfide) do not interfere with the recovery of inorganic mercury from reagent water.

4.4. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.5. Chlorides can cause a positive interference. Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (maximum 25 mL); because during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride

4.6. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.7. Samples containing high concentrations of oxidizable organic materials, as evidenced by high Chemical Oxygen Demand (COD) levels, may not be completely oxidized by this procedure. When this occurs, the recovery of mercury will be low. Reducing the volume of original sample used can eliminate this problem.

4.8. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them. Refer to Appendix B for Contamination Control Guidelines.

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. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. 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 Safety Data Sheet (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	**Hazards**	**Exposure Limit (1)**	**Signs and symptoms of exposure**
Mercury (10PPM in Reagent)	Oxidizer Corrosive Poison	0.1 g/m^3 Ceiling (Mercury Compounds)	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 eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	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.
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.
Hydroxyl-amine Hydro-chloride	Corrosive Poison	None	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. Corrosive to the eyes. Irritant and possible sensitizer. May cause burns to the skin.
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.
Potassium Permanganate	Oxidizer	5 mg/m^3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may 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.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

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 must be removed and discarded; other gloves must be cleaned immediately.

5.5. Exposure to 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 must 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 Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.7. Do not look directly into the beam of the Hg lamp. The Ultra Violet (UV) light that 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 be located outside the laboratory, and the gas led to the instrument through approved lines.

5.9. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature-controlled hot block or equivalent

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption cell with quartz end windows perpendicular to the longitudinal axis: 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.

6.2.2. Mercury-specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL)

6.2.3. Peristaltic pump which can deliver 1 L/min air

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min

6.2.5. Recorder or printer

6.2.6. Drying device to prevent condensation in cell

Note: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. Plastic bottles – capable of holding 100 mL

6.4. Nitrogen or argon gas supply, welding grade or equivalent

6.5. Calibrated automatic pipettes

6.6. Class A volumetric flasks

6.7. Top-loading balance, capable of reading up to two decimal places

6.8. Thermometer (capable of accurate readings at 95 °C)

6.9. Disposable cups or tubes

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore Deionized Water (DI) system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (10 ppm calibration and ICV) mercury standards are purchased as custom solutions. 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. Additional information can be found in SOP NC-QA-017. Refer to the reagent module in the Laboratory Information Management System (LIMS) for details on standard preparation.

7.3. Working mercury standard (0.1 ppm): Take 2 mL of the 10 ppm stock standard (Section 7.2) and dilute to 200 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (300 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot. Refer to the reagent module in LIMS for details on standard preparation.

7.4. Working ICV standard (0.1 ppm): Take 1 mL of the 10 ppm ICV stock standard (Section 7.2) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot. Refer to the reagent module in LIMS for details on standard preparation.

7.5. The calibration standards must be prepared fresh daily from the working standard (Section 7.3) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into sample preparation bottles for solid samples or by transferring 0, 0.1, 0.25, 0.5, 2.5, and 5.0 mL aliquots of the working mercury standard into sample preparation bottles for aqueous samples and proceeding as specified in Section 11.1. The laboratory control sample (LCS) solution is prepared by transferring 5.0 mL (solids) or 2.5 mL (waters) of working standard (Section 7.3) into sample preparation bottles and proceeding as specified in Section 11.1. Refer to the reagent module in LIMS for details on standard preparation.

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 (Appendix A) are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.7. Refer to Table 1 (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade or better

7.10. Sulfuric acid (H_2SO_4), concentrated, traces metal grade or better

7.11. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.12. Stannous chloride solution: Add 50g ± 0.5g of stannous chloride and 25 mL of concentrated HCl, and bring to a final volume of 500 mL with DI water.

Note: Stannous sulfate may be used in place of stannous chloride. Prepare the stannous sulfate solution according to the recommendations provided by the instrument manufacturer.

7.13. Sodium chloride-hydroxylamine hydrochloride solution: Add 240g ± 0.5g of sodium chloride and 240g ± 0.5g of hydroxylamine hydrochloride to every 2000 mL of reagent water.

7.14. Potassium permanganate, 5% solution (w/v): Dissolve 100g of potassium permanganate for every 2000 mL of reagent water.

7.15. Potassium persulfate, 5% solution (w/v): Dissolve 100 g of potassium persulfate for every 2000 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of sample collection to the time of sample analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. Soil samples and biological material do not require preservation, but must be collected in wide-mouth glass jars with PFTE-lined lids and stored at 4° C ± 2° C (and/or freezing for tissues) until the time of analysis.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well-characterized, laboratory-generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.2.1. Four aliquots of the laboratory check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.3. A Preparation Batch is a group of up to 20 samples, excluding QC Samples (Laboratory Control Sample (LCS), Method Blank (MB), Matrix Spike (MS), Matrix Spike Duplicate (MSD)), that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain an MB, an LCS and an MS/MSD. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes. In some cases, at client request, it may be appropriate to process a MS and sample duplicate (DU) in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.4. Method Blank (MB) -

9.4.1. 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 must not contain any analyte of interest at, or above, the reporting or at, or above, 10% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of ten times higher than the MB contamination level).

Note: For Ohio VAP projects, the result must be below the reporting limit or samples must be re-digested and re-analyzed unless the samples are non-detect.

9.4.2. Re-digestion and re-analysis of all samples associated with an unacceptable MB is required when reportable concentrations are determined in the samples (see exception noted above).

9.4.3. If there is no analyte 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.**

9.4.4. 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.**

9.5. Laboratory Control Sample (LCS)

9.5.1. One LCS must be processed with each preparation batch. The LCS is 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. If the LCS is outside established control limits, the system is out of control and corrective action must occur. See Section 12 for the LCS calculation.

9.5.2. In the instance where the LCS recovery is greater than the upper control limit and the sample results are less than RL, the data may be reported. Such action must be addressed in the project narrative. For Method 245.1, the LCS must be 85% - 115%. For Methods 7470A, 7471A, and 7471B, the laboratory control sample recovery must be 80%-120%.

9.5.3. Corrective action must be re-digestion and re-analysis of the batch unless the client agrees that other corrective action is acceptable. For Ohio VAP projects the corrective action must be re-digestion and reanalysis of the batch.

9.6. Additional information on QC samples can be found in QA Policy QA-003. Ohio VAP projects must reference this SOP instead of policy QA-003 for information on QC samples.

9.7. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.7.1. One MS/MSD pair must be processed for each preparation batch. An MS is a field sample to which known concentrations of target analytes have 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 sample duplicates (DU) 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. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table 1 (Appendix I). See Section 12 for the MS/MSD and Relative Percent Difference (RPD) calculation.

9.7.2. If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. A control limit of=, 70 – 130% for Method 245.1, and 20% RPD must be applied to the MS/MSD. A control limit of 80-120% for Methods 7470A, 7471A, and 7471B and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within control limits, then the laboratory operation is in control and the results may be accepted. Client specific MS/MSD samples may require corrective action. Such action must be addressed in the project narrative by means of a non-conformance memo (NCM). If the recovery of the LCS is outside of control limits, corrective action must be taken. Corrective action must include re-digestion and re-analysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

9.7.3. If the native analyte concentration in the MS/MSD exceeds four times the spike level for that analyte, the recovery data are reported with a “4” as a flag. In the event an MS/MSD analysis is not possible, notation in the project narrative is required.

9.8. Control Limits

9.8.1. Control limits are established by the laboratory as described in SOP NC-QA-018

9.8.2. Control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMS

9.9. Method Detection Limits (MDLs) and MDL Checks

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 the LIMS

9.10. Nonconformance and Corrective Action

9.10.1. Any deviations from QC procedures must be documented as a nonconformance. Procedural deviations are not allowed for Ohio VAP Projects.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols, separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily and each time the instrument is set up. 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. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a calibration blank. One standard must be at, or below, the reporting limit. Analyze standards in ascending order beginning with the calibration blank. Refer to Section 7 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥ 0.995, or the instrument must be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient. NOTE: If any digested calibration standard does not meet SW846 criteria, all associated Ohio VAP samples must be re-digested.

10.7. Initial Calibration Verification/Initial Calibration Blank (ICV/ICB)

10.7.1. Calibration accuracy is verified by analyzing a second source standard ICV. The ICV result must fall within 5% (for method 245.1) or 10% (for methods 7470A, 7471A, and 7471B) 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 $\pm$ the reporting limit (RL) from zero. See Section 12 for the ICV calculation. If either the ICV or ICB fail to meet criteria, the analysis must be terminated, the problem corrected, and the instrument recalibrated (see Section 11.6.4.1 for required run sequence). The calibration curve standards are reanalyzed to determine if the failure was instrument related. If the cause of the ICV or ICB failure was not directly instrument-related, the corrective action must include re-digestion of the ICV, ICB, CRA, CCV, and CCB with the calibration curve. For Ohio VAP, the sample batch must be re-digested.

10.8. Continuing Calibration Verification/Continuing Calibration Blank (CCV/CCB)

10.8.1. Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV.

10.8.2. The CCV result for Methods 7470A, 7471A, and 7471B must fall within 20% of the true value for that solution. For Method 245.1, the criterion is $\pm$ 10%. See Section 12 for the CCV calculation.

10.8.3. A CCB is analyzed immediately following each CCV (see Section 11.7.4 for

required run sequence). The CCB result must fall within ± RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. If the CCV/CCB is biased high and the sample results associated with the CCV/CCB are below the requested reporting limit, then the results can be reported. Sample results may be reported when bracketed by valid CCV/CCB pairs. If any digested calibration standard does not meet SW846 criteria, all associated Ohio VAP samples must be re-digested.

10.9. Detection Limit Standard (CRA) -To verify linearity at the reporting limit, a CRA standard is run at the beginning of each sample analysis run after the ICV/ICB. The CRA standard mercury concentration is 0.2 ug/L. It is recommended that the recovery be ± 50% of the true value. If the CRA recovery is outside of the recommended criterion, correct any problem and re-analyze. Re-calibration may be required. The CRA is only required when requested.

11. PROCEDURE

11.1. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. Procedural deviations are not allowed for Ohio VAP projects.

11.2. Standard and Sample Preparation- Solids

11.2.1. All calibration and calibration verification standards (ICV, ICB, CCV, and CCB) are processed through the digestion procedure as well as the field samples.

11.2.2. Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (Section 7.3) into a series of sample digestion bottles. The ICB/CCB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. For the ICV, transfer a 5 mL aliquot of the working ICV standard to the digestion bottle. The ICV standard must be from a source other than that used for the calibration standards. For the CCV, transfer a 5.0 mL aliquot of the working standard into a sample digestion bottle.

Note: Alternate volumes and concentrations of standard may be prepared as long as the accuracy and final standard concentrations support laboratory or project reporting limits.

11.2.3. Add reagent water to each standard bottle for a total volume of 10 mL. Continue preparation as described under Section 11.4 below.

11.2.4. Transfer 0.6g of a well-mixed sample into a clean sample digestion bottle, and add 10mL of reagent water. Continue preparation as described under Section 11.4.

11.3. Sample preparation for incremental sampling method (ISM) solids

11.3.1. Calibration standards and instrument QC are prepped as per section 11.1.1.

11.3.2. The laboratory will receive a single sample aliquot containing approximately 3 g. of sample from the Solids Lab. The Metals Prep department will divide this aliquot into 5 separate aliquots of approximately 0.6 g each for the digestion procedure.

11.3.3. The Method Blank is treated in the same manner, using 0.6 g of Teflon boiling chips in each of the 5 digestion bottles.

11.3.4. The LCS is treated the same as the samples and the method blank, except that each of the 5 digestion bottles will be spiked with 5 mL of the 0.1 ppm mercury working standard.

11.3.5. Each 0.6 g aliquot is then prepared and digested as described in section 11.4 below.

11.3.6. After the digestion process is completed, the 5 individual aliquots are re-combined prior to analysis.

11.4. Hot Block Protocol – Solid Samples

11.4.1. To each LCS standard bottle, add 5 mL of reagent water, 5 mL of Aqua Regia, and 5 mL of the working mercury standard (0.1 ppm) (see Section 7.3).

11.4.2. To each sample and MB bottle, add 5 mL of Aqua Regia.

11.4.3. Heat for two minutes in a hot block at 90 - 95 ° C.

11.4.4. Add 40 mL of distilled water.

11.4.5. Add 15 mL of potassium permanganate solution. Cover containers with digestion bottle lids.

11.4.6. Heat for 30 minutes in the hot block at 90 - 95 °C.

11.4.7. Record the time on and off of the hotblock in the batch info.

11.4.8. Check the temperature when heating is finished and note in batch information whether temperature requirement was met.

11.4.9. Cool

11.4.10. Add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce the excess permanganate.

11.4.11. Bring each standard, quality control sample, and sample up to a final volume of 100 mL with reagent water..

Note: Digestion bottles are calibrated by vendor lot to ensure the consistency and accuracy of final volumes.

11.4.12. Continue with analysis as described under Section. 11.6.

11.5. Standard and Sample Preparation Waters

11.5.1. All calibration and calibration verification standards (ICV, ICB, CCV, and CCB) are processed through the digestion procedure as well as the field samples. Transfer 0, 0.1, 0.25, 0.5, 2.5 and 5.0 mL aliquots of the working standard (Section 7.3) into a series of sample digestion bottles. For the ICV, transfer a 2.5 mL aliquot of the working standard to the digestion bottle. The ICV standard must be from a source other than that used for the calibration standards. For the CCV, transfer a 2.5 mL aliquot of the working standard into a sample digestion bottle. The Method Blank (MB) consists of 50 mL of reagent water.

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations support laboratory or project reporting limits.

11.5.2. Transfer 50 mL of well-mixed sample or standard to a clean sample digestion bottle. Continue preparation as described under Section 11.5.

Note: Reduced sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the same sample to reagent ratio. All samples and standards must be processed similarly.

Note: Spiking is done before the addition of acids or reagents.

11.6. Hot Block Protocol – Water Samples

11.6.1. Add 2.5 mL of concentrated H_2SO_4 and 1.25 mL of concentrated HNO_3.

11.6.2. Add 7.5 mL of potassium permanganate solution. For samples high in organic materials or chlorides, 7.5 mL may be insufficient to fully break down all organic mercury compounds. If the purple color does not persist for at least 15 minutes after the addition of potassium permanganate, the sample must be discarded and re-prepped at a dilution.

11.6.3. Add 4 mL of potassium persulfate solution, cover, and heat for two hours in a hot block at 90 - 95 °C.

11.6.4. Cool samples.

11.6.5. Add 3 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce the excess permanganate.

11.6.6. Bring each standard, quality control sample and sample up to a final volume of 75mL with reagent water.

Note: Digestion bottles are calibrated by vendor lot to ensure the consistency and accuracy of final volumes.

11.7. Sample Analysis

11.7.1. Automated determination: Refer to the instrument manual for details on instrument setup.

11.7.2. Create a calibration curve by plotting response of calibration standards vs. concentrations of mercury. Determine the mercury concentration in the samples from the linear fit of the calibration curve. The calibration acceptance criteria are listed in Section 10.6. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.7.3. 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.

11.7.4. The following analytical sequence is consistent with Methods 7470A, 245.1, 7471A and 7471B.

11.7.4.1. Instrument Calibration

ICV
ICB
CRA if required
CCV

CCB
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete the run
CCV
CCB

11.7.5. Refer to Quality Control Section 9.0 for quality control criteria.

Note: Samples include the MB, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.7.6. To facilitate the early identification of QC failures and samples requiring rerun, it is strongly recommended that sample data be reviewed periodically throughout the run.

11.7.7. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance, and troubleshooting.

11.8. Analytical Documentation

11.8.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.8.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.8.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.8.4. 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. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike (MS) 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

12.4. 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:
Matrix Spike (MS) = determined spiked sample concentration
Matrix Spike Duplicate (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

12.5. The final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

mg/kg, dry weight = (C x V x D)/(W x S)

Where:
C = Concentration (ug/L) from instrument readout
V = Volume of digestate (L)

D = Instrument dilution factor
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor must be omitted from the above equation.

12.6. The final concentration for an aqueous sample is calculated as follows:

$$mg/L = C \times D$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor

12.7. The Laboratory Control Sample (LCS) percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. Appropriate factors must be applied to sample values if dilutions are performed.

12.9. Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.1.

13.2. Training Qualification

13.2.1. 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 must be disposed of in accordance with Federal, State, and Local laws and 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 this Method

15.2.1. The following waste streams are generated by this method.

15.2.1.1. Acid Waste: This waste disposed of in the designated container labeled "Acid Waste".

15.2.1.2. Acid waste/aqueous waste generated by the analysis: Samples are disposed of in the acid waste drum located in the Metals lab. The contents of the drum are neutralized and released to the POTW.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury)

16.1.2. "Methods for the Chemical Analysis of Water and Wastes", Rev. 3.0 (1994)

16.1.3. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A (Mercury)

16.1.4. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Revision 2, February 2007, Method 7471B (Mercury)

16.1.5. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.6. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.7. Corporate Quality Management Plan (CQMP), current version

16.1.8. Revision History

Historical File: (formerly Corp-MT-0007NC, NC-MT-011, and NC-MT-013)				
Revision 1.1: 04/17/97		(NC-MT-011) Rev 0: 12/12/07		Revision 2: 03/20/13
Revision 2.2: 02/06/01		(NC-MT-011) Rev 1: 01/07/09		Revision 3: 06/05/13
Revision 2.3: 05/15/01		(NC-MT-013) Rev 0: 01/07/09		Revision 4: 06/06/15
Revision 2.4: 10/28/02		(NC-MT-014) Rev 0: 09/27/10		Revision 5: 6/15/15
Revision 2.5: 11/24/04		Revision 1-A: 04/17/12		

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. Calibration Curves (General), CA-Q-S-005

16.2.7. Selection Of Calibration Points, CA-T-P-002

16.2.8. Subsampling, NC-IP-001

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from Reference Method

17.1.1. Modifications from Method 7471A

17.1.1.1. Chapter 1 of SW846 specifies the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.1.2. Chapter 1 of SW-846 states that the method blank must not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.1.2. Modifications from both Methods 7470A and 245.1

17.1.2.1. The 200 series methods and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.2.2. This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, “Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology.”

17.1.3. Modifications from Method 7470A

17.1.3.1. Chapter 1 of SW-846 states that the method blank must not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit if the samples associated with the method blank are equal to or above the reporting limit.

17.1.4. Modifications from Method 245.1

17.1.4.1. Method 245.1 states that standards are not heated. TestAmerica North Canton prepares heated standards for this method.

17.1.4.2. Stannous Chloride is prepared in hydrochloric acid, instead of sulfuric acid, per instrument manufacturer recommendations.

17.1.4.3. Section 9.3.4 of the method states that the CCB must be less than the MDL. The laboratory uses the criteria that the CCB result must fall within ± RL from zero.

APPENDIX A - TABLES

TABLE 1. MERCURY REPORTING LIMITS, CALIBRATION STANDARD, QC STANDARD AND SPIKING LEVELS

Soil RL (mg/kg)	0.1
Standard Aqueous RL (mg/L)	0.0002
TCLP RL (mg/L)	0.002
Std 0 (mg/L)	0
Std 1/CRA (mg/L)	0.0002
Std 2 (mg/L)	0.0005
Std 3 (mg/L)	0.001
Std 4 (mg/L)	0.005
Std 5 (mg/L)	0.010
ICV (mg/L)	0.005
CCV/Laboratory Control Sample (LCS) (mg/L)	0.005
LCS (mg/L)	0.005
Matrix Spike (MS) (mg/L)	0.001
TCLP Matrix Spike (MS)	0.005

APPENDIX B - CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by Deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas should be kept scrupulously clean.

Powdered Gloves should not be used in the metals laboratory since the powder contains zinc, as well as other metallic analytes. 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 soak with sulfuric acid prior to routine cleaning.

Title: CONTINUOUS LIQUID / LIQUID EXTRACTION OF ORGANIC COMPOUNDS FROM WATERS BASED ON METHOD SW846 3520C AND 600 SERIES

[Methods: SW846 3520C and 600 Series]

Approvals (Signature/Date):

Technology Specialist	11/06/15 Date	Health & Safety Coordinator	08/26/15 Date
Quality Assurance Manager	09/11/15 Date	Technical Director	11/09/15 Date

This SOP was previously identified as SOP No. NC-OP-037, Rev 4, dated 06/04/14,

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 Tables

1. SCOPE AND APPLICATION

1.1. This SOP describes procedures for preparation (extraction) of semivolatile organic analytes in aqueous, and TCLP leachate, matrices for analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS) using Continuous Liquid/Liquid Extraction. The procedures are based on SW846 and 600 series methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1.1. Extraction procedures for the following determinative methods are covered: 8081A, 8081B, 8082, 8082A, 8270C, 8270D, 8015B, 8015C, 8015D, 608, and 625.

1.1.2. The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

2. SUMMARY OF METHOD

2.1. Continuous Liquid/Liquid Extraction

2.1.1 A measured volume of sample (typically 1 liter, or 250 mL for reduced volume extraction requiring large volume injection) is placed into a continuous liquid/liquid extractor, adjusted if necessary, to a specific pH, and extracted with the appropriate solvent for 18-24 hours.

2.2. Concentration

2.2.1 Procedures are presented for drying and concentration of the extract to final volume for analysis.

3. DEFINITIONS

3.1. Definitions of terms and acronyms used in this SOP may be found in the glossary of the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

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. 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 become contaminated must be removed and discarded, other gloves must be cleaned immediately.

5.3. The following analytes have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'dichlorobenzindine, benzo(a)pyrene, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, dibenz(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyl compounds. Primary standards of these toxic compounds must be prepared in the hood.

5.4. 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 Safety Data Sheet (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
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.

Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3 2 mg/m^3-Ceiling	This material will cause burns if comes into contact with the skin or eyes. 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.
Sulfuric Acid (1)	Corrosive Oxidizer Dehydrator Poison Carcinogen	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. 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.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
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.
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.			

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 must be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride must be conducted in a fume hood with the sash closed as far as the operations will permit. If more than 500 mL of methylene chloride is spilled, evacuate the area until the area has been cleaned by EH&S.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be

reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.8. During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard. The KD apparatus and glass separatory funnels have ground glass joints, which can become stuck. Technicians must use Kevlar or other cut/puncture-resistant gloves when separating stuck joints.

5.9. 3520 Extraction Continuous Liquid/Liquid

5.9.1. All personnel are to ensure liquid-liquid area is clear of unnecessary items. Heating mantles used with liquid-liquid extractions generate temperatures that could ignite some materials that come in contact with the heating mantles.

5.9.2. Ensure all solvents are away from liquid-liquid extractor. Increased temperatures near solvents can cause the pressure in the containers to increase.

5.9.3. Ensure all boiling flasks have cooled to room temperature before disconnecting liquid-liquid bodies from boiling flasks to prevent any burns.

6. EQUIPMENT AND SUPPLIES

6.1. Glassware must be cleaned per Glassware Washing, SOP NC-QA-014.

6.2. Equipment and supplies for extraction procedures:

EQUIPMENT AND SUPPLIES	CLLE	Conc
pH Indicator paper, ranges: 0-14, 7.5-14, 0-6	√	
Graduated cylinder: Class A 1 liter. (other sizes may be used as needed)	√	√
Methylene chloride collection tank	√	
Initial volume template	√	
Solvent dispenser pump or 100 mL Class A graduated cylinder		√
Continuous liquid / liquid extractor	√	
Round or flat bottom: 250	√	
Boiling chips: contaminant-free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent)	√	√
Cooling condensers	√	
Heating mantle: rheostat controlled	√	
Auto-timer for heating mantle	√	
Beakers: 250 & 400 mL, graduated	√	√
Kuderna-Danish (K-D) apparatus: 500 mL		√
Concentrator tube: 10 mL, attached to K-D with clips		√
Snyder column: three-ball macro		√
Water bath: heated, with concentric ring cover, capable of		√

EQUIPMENT AND SUPPLIES	CLLE	Conc
temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.		
Vials: glass, 2 / 2.5/ 40 mL capacity with Teflon®-lined screw-cap		√
Nitrogen blowdown apparatus		√
Nitrogen: reagent grade.		√
Culture tubes: 10 mL, 16 mmx100 mm		√
Microliter pipette, syringe 1 mL	√	
Glass wool	√	
Funnel: 75 X 75 mm	√	√
Disposable pipettes, 5 ¾ in, and 9in.	√	√
Aluminum foil	√	√
Paper towels	√	√

7. REAGENTS AND STANDARDS

7.1. Reagents For Extraction Procedures

7.1.1. All reagents must be ACS reagent grade or better unless otherwise specified.

REAGENTS	CLLE	Conc
Sodium hydroxide (NaOH), pellets: reagent grade	√	
Sodium hydroxide solution, 10 N: dissolve 40 g of NaOH in reagent water and dilute to 100 mL.	√	
Sulfuric acid (H_2SO_4), concentrated: reagent grade	√	
Sulfuric acid (1:1): carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.	√	
Hydrochloric acid (HCl)	√	
Organic-free reagent water	√	
Sodium sulfate (Na_2SO_4), granular, anhydrous: purify by heating at 800°C a minimum of one hour	√	√
Extraction / exchange solvents: methylene chloride, hexane, acetonitrile, acetone, pesticide quality or equivalent	√	√
Acetone, methylene chloride: used for cleaning	√	√
TCLP Fluid #1 : Made fresh daily in the Leachates department, or see SOP NC-OP-033 TCLP-SPLP	√	√
Sodium Chloride (NaCl) crystal	√	

7.2. Standards

7.2.1. Stock Standards

7.2.1.1 Stock standards are purchased as certified solutions. Standards shall be stored according to manufacturer's instructions. All stock standards must be protected from light. Stock standard solutions must be replaced after one year (from the time of preparation, if

prepared in house, or from the time the ampoule is opened if purchased). Standards must be allowed to come to room temperature before use.

7.2.2. Surrogate Spiking Standards

7.2.2.1 Prepare or purchase surrogate spiking standards at the concentrations listed in Table 5. Surrogate spiking standards are purchased or prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light or stored according to manufacturer's instructions. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.2.3. Matrix Spiking and Laboratory Control Spiking Standards

7.2.3.1 The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 6. Spiking standards are purchased or prepared as dilutions of the stock standards.

7.2.3.2 Spiking solutions must be refrigerated and protected from light or stored according to manufacturer's instructions. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.2.4 See SOP NC-QA-017 for additional information on Standards and Reagents.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps.

8.3. Holding Times

8.3.1. The holding time for aqueous samples is seven days from sampling to extraction.

8.3.2. For TCLP leachates, the holding time is 14 days from sampling to the leach process. The extraction holding time seven days from when the TCLP Leach tumbling has been completed, excluding the filtration step, to the extraction step. If the filtration step requires extended times, this time counts as part of the seven-day holding time.

8.3.3. Analysis of the extracts is completed within 40 days of extraction.

9. QUALITY CONTROL

9.1. Quality Control Batch

9.1.1. The batch is a set of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, an LCS, and a matrix spike / matrix spike duplicate. (In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS / MSD). If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD. See Policy QA-003 for further definition of the batch.

9.2. Sample Count

9.2.1. Laboratory-generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count. Field samples are included.

9.3. Method Blank (MB)

9.3.1. A MB consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the MB at the same level as the samples. See Table 3 for the appropriate amount of surrogate to use for each analytical method. The method blank is used to identify any background interference or contamination of the analytical system, which may lead to the reporting of elevated concentration levels or false positive data.

9.3.2. Aqueous MBs use 1000 mL (or 250 mL for reduced volume extraction) of reagent water spiked with the surrogates. The method blank goes through the entire analytical procedure.

9.3.3. TCLP MBs use 250 mL of leachate fluid spiked with the surrogates. SPLP MBs use 1000 mL of leachate fluid spiked with the surrogates. The leachate may optionally be diluted to 1000 mL with reagent water. The MB goes through the entire analytical procedure.

9.4. Laboratory Control Sample (LCS)

9.4.1. LCSs are well-characterized laboratory-generated samples used to monitor the laboratory day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within

accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure.

9.4.2. The LCS is made up in the same way as the method blank (see Sections 9.3.1 through 9.3.3), but spiked with the LCS standard and the surrogates. See Tables 3 and 4 for the appropriate amount of spike to use for each analytical method.

9.5. Surrogates

9.5.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.5.2. Each applicable sample, blank, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. See Table 3 for the appropriate amount of surrogate spike to use for each analytical method.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1. A MS is an environmental sample to which known concentrations of target analytes have been added. A MSD is a second spiked aliquot of the same sample, which is prepared and analyzed along with the sample and MS. See Tables 3 and 4 for the appropriate amount of spike to use for each analytical method.

9.7. QC requirements can be found in the various associated analytical SOPs.

9.8. Initial Demonstration of Capability

9.8.1. The initial demonstration and method detection limit studies described in Section 13 must be acceptable before analysis of samples may begin.

9.9. Control Limits

9.9.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.10. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via LIMs

9.11. Method Detection Limits (MDLs) and MDL Checks

9.11.1. MDLs and MDL Checks are established by the laboratory as described in SOPs

9.11.2. MDLs are accessible via LIMs.

9.12. Nonconformance and Corrective Action

9.12.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. On a weekly basis, measure the appropriate volumes of solvents into the appropriate sized glass culture tubes gravimetrically. The “standard” glass culture tubes are sealed, and the meniscus is noted by marking a line on the bottles. The glass culture tubes containing the sample extracts are then compared against the “standard” glass culture tubes of the appropriate volume and solvent to ensure the volumes are consistent. The bottle top dispenser is calibrated quarterly and must be within ±5% of the target volume with an RSD ≤ 1%.

11. PROCEDURE

11.1. Procedural Variations

11.1.1. 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 must be completely documented using a Nonconformance memo. The Nonconformance memo will be filed in the project file. Procedural variations are not allowed for Ohio VAP projects.

11.2. Continuous Liquid/Liquid Extraction from Water Samples

11.2.1. Remove surrogate and matrix spiking solutions from refrigerator and allow to return to room temperature.

11.2.2. Assemble the apparatus. Add approximately 250 mL of methylene chloride (or approximately 100 mL for reduced volume extractor bodies) to the extractor body. Add three to five boiling chips to the round-bottom distilling flask. Label the flask with a LIMS ID label.

11.2.3. Measure the initial sample pH with wide-range pH by inserting a disposable pipette into the sample, and placing a drop of sample onto the wide range pH paper. Record on the extraction benchsheet. pH will be entered manually into LIMS during level I review.

11.2.4. Measure the initial volume using the volume template. Place the template next to the sample bottle and read the volume marking from the template. Record this volume on the benchsheet. Volumes will be entered manually

into LIMS during level I review. Prepare a MB, LCS, and MS/MSD for each batch as specified in Section 9 of this SOP. See Tables 3 and 4 for the appropriate amount of spike to use for each analytical method. Use 1 L of reagent water for method blanks and LCS. If the sample cannot be prepared using continuous liquid/liquid extraction due to matrix, a waste dilution may be required. Refer to SOP NC-OP-043 for the waste dilution procedure.

11.2.5. For pesticide and PCB samples (method series 8000 and method series 600), add 100 mL of TCLP Buffer Fluid #1.

11.2.6. Use 250mL of leachate for TCLP semivolatiles and TCLP pesticides. Use 1000 mL of leachate for SPLP semivolatiles and SPLP pesticides. Dilute to about 1 liter with reagent water.

11.2.7. For a TCLP method blank and LCS, measure 250 mL of the buffer solution in a beaker and transfer to the continuous liquid/liquid extractor. Dilute to about 1 liter with reagent water. For an SPLP method blank and LCS, measure 1000 mL of the buffer solution using the volume template and transfer to the continuous liquid/liquid extractor. No dilution with reagent water is required.

11.2.8. Less than one liter of sample may be used for highly contaminated samples, or if the reporting limit can be achieved with less than one liter of sample. In this event, dilute the sample to about 1 liter with reagent water. This must be documented with a Non-Conformance Memo.

11.2.9. Add reagent water to the extractor body until approximately 150 mL (approximately 50mL for reduced volume preps) of methylene chloride is pushed over into the round-bottomed flask to ensure proper operation and solvent cycling. Prime the extractor using reagent water.

11.2.10. The MB and samples are spiked with the surrogates, the LCS and matrix spikes with the surrogates, and matrix spiking solutions. All samples are spiked in the original sample bottle.

11.2.11. Pour the sample into the extraction vessel. Use 15 mL of Methylene Chloride to rinse the bottle and pour it directly into the extraction vessel. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH, as necessary. Recheck the sample with pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible. Attach cold condenser (about 10^{o}C). Turn on heating mantle. Inspect joints for leaks once solvent has begun cycling. Extract for 18-24 hours (24 hours required for 600 series).

11.2.12. If extraction at a secondary pH is required (see Table 1), turn off the heating mantle and allow the extractor to cool. Detach the condenser and

adjust the pH of the sample in the extractor body to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure by inserting a disposable pipette into the sample, and placing a drop of sample on the pH paper. Record the adjusted pH on the benchsheet. Re-attach the condenser, and turn on the heating mantle. Extract for 18-24 hours.

11.2.13. Turn off the heating mantle and allow the extractor to cool.

11.2.14. Cover with aluminum foil and refrigerate if the extract is not concentrated immediately. Refer to Section 11.4 for concentration.

11.3. Concentration

11.3.1. According to the type of sample, different solvents and final volumes will be required. Refer to Table 2 for the appropriate final volumes and concentrations.

11.3.2. Kuderna-Danish (KD) Method

11.3.2.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL K-D flask. Label the CT and K-D. Transfer the sample to the labeled K-D flask, filtering Continuous Liquid/Liquid and Soxhlet samples through funnels filled with sodium sulfate. Rinse the funnel with 20-30 mL of methylene chloride to complete the quantitative transfer.

11.3.2.2. Add one or two clean boiling chips to the KD flask and attach a three-ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column. (This is important to ensure that the balls are not stuck, and the column will work properly). Attach to the KD flask.

11.3.2.3. Place the KD apparatus on a water bath (90-98^{o}C) so the tip of the concentrator tube is submerged. The water level must not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter; but the chambers should not flood.

11.3.2.4. Concentrate to 15-20 mL. If the determinative method requires a solvent exchange, add the appropriate exchange solvent to the top of the Snyder Column, and then continue the water bath concentration back down to 5-8 mL. Refer to Table 2 for details of exchange solvents and final volumes. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.3.2.5. Remove the KD apparatus from the water bath and allow to cool for a minimum of 10 minutes. If the level of the extract is above the level of the concentrator tube joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

11.4. Nitrogen Evaporation to Final Concentration

11.4.1. Transfer the CT to the evaporation apparatus.

11.4.2. Place the tube in a warm water bath that is at least 5°C below the boiling temperature of the solvent being evaporated and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but must not create splattering of the extract.

Boiling points of commonly used solvents are:

Methylene chloride	40°C
Acetone	56°C
Hexane	69°C
Acetonitrile	82°C
Toluene	111°C

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.4.3. Refer to Table 1 to determine the final volume needed for a specific test method. Evaporate to slightly less than the required final volume.

11.4.4. Quantitatively transfer the extract to the appropriate final container and dilute to the appropriate final volume using the “standard” glass vial noted in Section 10.1. Cap the sample and affix the appropriate label. The sample is now ready for analysis.

Note: The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

11.5. Analytical Documentation

11.5.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Record all sample and associated QC information in LIMS. Level I and Level II reviews are performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

13. METHOD PERFORMANCE

13.1. Initial Demonstration

13.1.1. Each analyst must make an initial demonstration of capability for each individual method. This requires analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which must contain all the analytes of interest. The spiking level must be equivalent to a mid-level calibration. (For certain tests, more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

13.1.2. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.1.3. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs. See SOPs NC-GC-038, NC-MS-018, NC-MS-003, and NC-GC-007 for detailed information on the determinative methods.

13.2. Training Qualification

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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 laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method 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. The following waste streams are produced when this method is carried out.

15.2.1. Extracted aqueous samples contaminated with methylene chloride. This tank is then periodically rolled to the Tank Room, the pH is verified, contents are neutralized with sodium bicarbonate, pH re-verified, and Dichloromethane waste drained into a waste drum located outside the building. The wastewater is discharged to the POTW.

15.2.2. Used sodium sulfate and glass wool or filter paper contaminated with methylene chloride/acetone or acetone/hexane from the extract drying step. These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.

15.2.3. **Assorted flammable solvent waste from various rinses**. These wastes are put into the halogenated/non-halogenated 25 gallon solvent waste container located under the fume hood in extractions.

15.2.4. **Methylene chloride waste from various rinses:** These wastes are disposed of in the liquid-liquid separation unit.

15.2.5. **Hexane- Hexane waste:** These samples are to be disposed in the flammable waste.

15.2.6. **Waste Hexane in vials.** These vials are placed in the vial waste located in the GC prep laboratory.

15.2.7. **Waste Methylene Chloride sample vials**. These vials are placed in the vial waste located in the GC prep laboratory.

15.2.8. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCBs must be segregated into their own waste stream. PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB, and PCB vial waste.

15.2.9. Solvent Recovery System Waste. Methylene Chloride waste from the Solvent Recovery System is collected and disposed of in the liquid-liquid

separation unit. Acetone/Methylene Chloride waste from this system is disposed of in the flammable waste containers located in the laboratory.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B, 3520C, and 3580A

16.1.2. Federal Register - Environmental Protection Agency, 40 CFR, Part 136, Volume 49, No. 209, October 26, 1984, Method 625

16.1.3. EPA 600, Methods for Chemical Analysis of Water and Wastes, Method 608

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. Corporate Quality Management Plan (CQMP), current version

16.1.7. Revision History

Historical File:		Revision 3.4: 10/16/98		Revision 0: 03/12/08 (NC-OP-032)
(formerly CORP-OP-0001NC)		Revision 3.5: 04/22/99		Revision 1: 01/07/09 (NC-OP-032)
		Revision 3.6: 05/13/99		Revision 0: 03/03/11 (NC-OP-037)
		Revision 3.7: 03/20/01		Revision 1: 04/24/12
		Revision 3.8: 05/23/01		Revision 2: 02/05/13
		Revision 3.9: 04/22/02		Revision 3: 04/05/13
		Revision 4.0: 02/04/03		Revision 4: 06/04/14
		Revision 4.1: 10/07/03		
		Revision 4.2: 01/30/06		

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. GC/MS Analysis based on Method 8270C and 8270D, NC-MS-018

16.2.6. Analysis of Pesticides and PCBs by EPA Method 608, NC-GC-007

16.2.7. GC/MS Semivolatile Organic Compounds Capillary Column Technique Based on EPA Method 625, NC-MS-003

16.2.8. Gas Chromatographic Analysis of Pesticides Based on Methods 8081A and 8081B, NC-GC-042

16.2.9. Gas Chromatographic Analysis of Diesel Range Organics Based on Methods 8015B, 8015C, and 8015D, NC-GC-043

16.2.10. Gas Chromatographic Analysis of PCBs Based on Methods 8082 and 8082A, NC-GC-045

16.2.11. Standards and Reagents, NC-QA-017

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.1.2. Spiking levels for method 608 have been reduced by a factor of ten to bring the levels within the normal calibration range of the instrument.

17.1.3. Sodium Sulfate is heated for 1 hour at 800°C to purify. The reference method lists a minimum of 4 hours at 400°C.

17.2. Tables

TABLE 1
Liquid /Liquid Extraction Conditions

Determinative Method	Initial Ext. pH	Secondary Ext. pH
BNA	Acid ext; 1-2 or Base ext; 11-12	Acid ext; 1-2 or Base ext; 11-12
Pesticide/PCB	5-9	None
TPH	As received	None

[1] If the laboratory has validated acid only 8270 extraction for the target compound list required then the base extraction step may be omitted. The required validation consists of a four-replicate initial demonstration of capability and a method detection limit study (see Section 13). Additionally, either of the base or acid fractions of Method 8270 can be run first.

TABLE 2
Final Volumes and Exchange Solvents

Type	Exchange Solvent for Analysis	Final Volume for Analysis in mL
BNA	N/A	2.0 mL
PCB	Approximately 18 mL hexane – water	5.0 for H2O 2.0 for H2O*
Pesticides	Approximately 18 mL hexane	5.0 for H2O 2.0 for H2O*
Pesticides/TCLP	Approximately 18 mL hexane	3.0 mL
BNA – SIM	N/A	2.0 mL 5.0 mL for reduced volume preps
TPH	N/A	5 mL

* Michigan work requires a final volume of 2 mL.

Note: Different final volumes may be necessary to meet special client reporting limit requirements.

TABLE 3
Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
BNA	20 ppm BNA Surrogate Spike	1.0 mL
PEST	0.2 ppm DCB/TCX	0.25 mL for 2 mL final, 0.5 mL for 5 mL final
TPH	40 ng/uL o-Terphenyl	1.0 mL
PCB	0.2 ppm DCB/TCX	0.25 mL for 2 mL final, 0.5 mL for 5 mL final
BNA – SIM	20 ppm BNA Surrogate Spike	0.1 mL

* Note: surrogate spiking levels are adjusted for reduced volume preps which utilize large volume injection.

TABLE 4
Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
PEST	1.0 ppm Pest NPDES Spike	0.25 mL for 2 mL final, 0.5 mL for 5 mL final
TPH	2500 ppm Diesel Spike	1.0 mL
PCB	10 ppm PCB Spike	0.25 mL for 2 mL final, 0.5 mL for 5 mL final
BNA – SIM	20 ppm BNA List 1	0.1 mL
BNA	20 ppm BNA All-Analyte Spike	1.0 mL

* Note: surrogate spiking levels are adjusted for reduced volume preps which utilize large volume injection.

TABLE 5

Surrogate Spike Components

Analyte Group	Compounds	Conc. (µg/mL)
BNA	2-Fluorobiphenyl	20
	Nitrobenzene-d_5	20
	2-Fluorophenol	20
	Phenol-d_5	20
	2,4,6-Tribromophenol	20
	Terphenyl-d_{14}	20
Pesticides PCB	Decachlorobiphenyl	0.2
	Tetrachloro-m-xylene	0.2
TPH	o-Terphenyl	40.0

TABLE 6
LCS and Matrix Spike Components

Type	Compounds	Conc. (µg/mL)
BNA	1,1'Biphenyl	20
	1,2,4,5-Tetrachlorobenzene	20
	1,2,4-Trichlorobenzene	20
	1,2-Dichlorobenzene	20
	1,2-Diphenylhydrazine	20
	1,3-Dichlorobenzene	20
	1,3-Dinitrobenzene	20
	1,4-Dichlorobenzene	20
	1,4-Dioxane	20
	1-Methylnaphthalene	20
	2,2'-oxybis[1-chloropropane]	20
	2,3,4,6-Tetrachlorophenol	20
	2,4,5-Trichlorophenol	20
	2,4,6-Trichlorophenol	20
	2,4-Dichlorophenol	20
	2,4-Dimethylphenol	20
	2,4-Dinitrophenol	40
	2,4-Dinitrotoluene	20
	2,6-Dichlorophenol	20
	2,6-Dinitrotoluene	20
	2-Chloronaphthalene	20
	2-Chlorophenol	20
	2-Methylnaphthalene	20
	2-Methylphenol	20
	2-Nitroanaline	20
	2-Nitrophenol	20
	3&4-Methylphenol	20
	3,3'-Dichlorobenzidine	40
	3-Methylphenol	10
	3-Nitroanaline	20
	4,6-Dinitro-2-methylphenol	40
	4-Bromophenyl phenyl ether	20
	4-Chloro-3-methylphenol	20
	4-Chloroanaline	20
	4-Chlorophenyl phenyl ether	20
	4-Methylphenol	10
	4-Nitroanaline	20
	4-Nitrophenol	40

TABLE 6
LCS and Matrix Spike Components

Type	Compounds	Conc. (µg/mL)
BNA	Acenaphthene	20
	Acenaphthylene	20
	Acetophenone	20
	Aniline	20
	Anthracene	20
	Azobenzene	20
	Benzidine	40
	Benzo[a]anthracene	20
	Benzo[a]pyrene	20
	Benzo[b]fluoranthene	20
	Benzo[g,h,i]perylene	20
	Benzo[k]fluoranthene	20
	Benzoic acid	40
	Benzyl alcohol	20
	Bis(2-chloroethoxy)methane	20
	Bis(2-chloroethyl)ether	20
	Bis(2-ethylhexyl)phthalate	20
	Butyl benzyl phthalate	20
	Carbazole	20
	Chrysene	20
	Dibenz(a,h)anthracene	20
	Dibenzofuran	20
	Diethyl phthalate	20
	Dimethyl phthalate	20
	Di-n-butyl phthalate	20
	Di-n-octyl phthalate	20
	Fluoranthene	20
	Fluorene	20
	Hexachlorobenzene	20
	Hexachlorobutadiene	20
	Hexachlorocyclopentadiene	20
	Hexachloroethane	20
	hexadecane	20
	Indene	40
	ideno[1,2,3-cd]pyrene	20
	isophorone	20
	Naphthalene	20
	n-Decane	20
	Nitrobenzene	20
	N-Nitrosodimethylamine	20
	N-Nitrosodi-n-propylamine	20
	N-Nitrosodiphenylamine	40

TABLE 6 LCS and Matrix Spike Components		
Type	**Compounds**	**Conc. (µg/mL)**
	n-Octadecane	20
	Pentachlorophenol	40
	Phenanthrene	20
	Phenol	20
	Pyrene	20
	Pyridine	20
Pesticides TCLP	Heptachlor	0.5
	Heptachlor epoxide	0.5
	Lindane	0.5
	Endrin	0.5
	Methoxychlor	1.0
Pesticides NPDES	Aldrin	1.0
	Alpha-BHC	1.0
	beta-BHC	1.0
	delta-BHC	1.0
	gamma-BHC (Lindane)	1.0
	4,4'-DDD	1.0
	4,4'-DDE	1.0
	4,4'-DDT	1.0
	Dieldrin	1.0
	alpha-Endosulfan	1.0
	beta-Endosulfan	1.0
	Endosulfan Sulfate	1.0
	Endrin	1.0
	Heptachlor	1.0
	Heptachlor Epoxide	1.0
TPH	Diesel Fuel	2500 **µg/mL**

TestAmerica Canton

SOP Amendment Form

SOP NUMBER: NC-OP-040 Rev. 4

SOP TITLE: Soxhlet (Traditional) Extraction Of Organic Compounds From Soils Based On Method Sw846 3540c

REASON FOR ADDITION OR CHANGE: Adding information for 10 g PCB prep

CHANGE EFFECTIVE FROM: (DATE): 8/10/16

Change(s) Made:

Section 9.2.2 added:

For PCB, use approximately 10 g ± 0.5 g of sodium sulfate.

Section 11.2.3 added:

For PCB Extraction, weigh approximately 10 g of sample ± 0.5 g.

Note: *Alternate sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the sample to reagent ration. All samples and standards must be processed similarly.*

EDITED BY/DATE: Melissa Fuller-Gustavel 8/10/16

Title: SOXHLET (TRADITIONAL) EXTRACTION OF ORGANIC COMPOUNDS FROM SOILS BASED ON METHOD SW846 3540C

[Method: SW846 3540C]

Approvals (Signature/Date):

Technology Specialist	01/15/16 Date	Health & Safety Coordinator	01/18/16 Date
Quality Assurance Manager	01/15/16 Date	Technical Director	01/15/16 Date

This SOP was previously identified as SOP No. NC-OP-040, Rev 3, dated 8/25/14

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 Tables and Appendices

1. SCOPE AND APPLICATION

1.1. This SOP describes procedures for preparation (extraction) of semivolatile organic analytes in soil, sediment, waste and wipe matrices for analysis by Gas Chromatography (GC) and Gas Chromatography/Mass Spectrometry (GC/MS) using Soxhlet Extraction. The procedures are based on SW846 series methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1.1. Extraction procedures for the following determinative methods are covered: 8081A, 8081B, 8082, 8082A, 8270C, 8270D, 8015B, 8015C, and 8015D.

1.1.2. The extraction procedures herein may be appropriate for other determinative methods when appropriate spiking mixtures are used.

2. SUMMARY OF METHOD

2.1. Soxhlet Extraction (Traditional)

2.1.1 A 30 g sample is mixed with anhydrous sodium sulfate until free flowing, or a 1 wipe sample is placed in an extraction thimble. They are extracted by refluxing with solvent.

2.2. Concentration

2.2.1 Procedures are presented for drying the extract and concentration of the extract to final volume for analysis.

3. DEFINITIONS

3.1. Definitions of terms and acronyms used in this SOP may be found in the glossary of the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

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. 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 become contaminated must be removed and discarded; other gloves must be cleaned immediately.

5.3. The following analytes have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'dichlorobenzindine, benzo(a)pyrene, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, dibenz(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyl compounds. Primary standards of these toxic compounds must be prepared in the hood.

5.4. 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 Safety Data Sheet (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
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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

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 must be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride must be conducted in a fume hood with the sash closed as far as the operations will permit. If more than 500 mL of methylene chloride is spilled, evacuate the area until the area has been cleaned by EH&S.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.8. During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard. The KD apparatus and glass separatory funnels have ground glass joints that can become stuck. Technicians must use Kevlar or other cut/puncture-resistant gloves when separating stuck joints.

6. EQUIPMENT AND SUPPLIES

6.1. Glassware must be cleaned per Glassware Washing, SOP NC-QA-014.

6.2. Equipment and supplies for extraction procedures:

EQUIPMENT AND SUPPLIES	Sox	Conc
Graduated cylinder: 1 liter. (other sizes may be used as needed)		√
Erlenmeyer flask: 250 mL (other sizes optional)		√
Solvent dispenser pump or 100 mL graduated cylinder	√	√
Round or flat bottom: 250 mL	√	
Boiling chips: contaminant free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent)	√	√
Cooling condensers	√	
Heating mantle: rheostat controlled or equivalent	√	
Auto-timer for heating mantle	√	
Soxgriddle or equivalent	√	
Beakers: 450mL wide-mouth glass jars		√
Balance: >100 g capacity, accurate to ±1.00 g	√	√
Soxhlet extractor	√	
Cellulose and glass thimbles	√	
Kuderna-Danish (K-D) apparatus: 500 mL		√

EQUIPMENT AND SUPPLIES	Sox	Conc
Concentrator tube: 10 mL, attached to K-D with clips		√
Snyder column: three-ball macro		√
Water bath: heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.		√
Vials: glass, 2 mL and 40 mL capacity with Teflon®-lined screw-cap		√
Clean wipes for wipe matrix method blanks and laboratory control samples		
Nitrogen blowdown apparatus		√
Nitrogen: reagent grade.		√
Culture Tubes: 10 mL, 16 x100 mm		√
Microliter pipette and/or syringe 1 mL	√	
Glass wool	√	
Glass funnel: 75 X 75 mm	√	√
Disposable pipettes, 5 ¾ in, and 9in.	√	√
Aluminum foil	√	√
Paper towels	√	√

7. REAGENTS AND STANDARDS

7.1. Reagents for Extraction Procedures

7.2. All reagents must be ACS reagent grade or better, unless otherwise specified.

REAGENTS	Sox	Conc
Sodium sulfate (Na_2SO_4), Granular, Anhydrous: Purify by heating at 800°C a minimum of one hour.	√	√
Magnesium sulfate	√	
Extraction Solvents (pesticide quality or equivalent): Methylene chloride, Methylene Chloride/acetone hexane/acetone,	√	√
Hexane/Acetone:, reagent grade: Used for cleaning glassware.	√	√

7.3. Standards

7.3.1. Stock Standards

7.3.1.1. Stock standards are purchased as certified solutions. S tock standards are stored according to manufacturer's instructions. All stock standards must be protected from light. Stock standard solutions must be replaced after one year (from the time of preparation, if prepared in house, or from the time the ampoule is

opened, if purchased). Standards that are cold stored must be allowed to come to room temperature before use.

7.3.2. Surrogate Spiking Standards

7.3.2.1. Prepare or purchase surrogate spiking standards at the concentrations listed in Table 2. Surrogate spiking standards are purchased or prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light, or stored according to manufacturer's instructions. The standards must be replaced every six months at a minimum, or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.3. Matrix Spiking and Laboratory Control Spiking Standards

7.3.3.1. The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 3. Spiking standards are purchased or prepared as dilutions of the stock standards.

7.3.3.2. Spiking solutions must be refrigerated and protected from light, or stored according to manufacturer's instructions. The standards must be replaced every six months at a minimum, or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.4. See SOP NC-QA-017 for additional information on Standards and Reagents.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps.

8.3. Holding Times

8.3.1. The holding time for solid and waste samples is 14 days from sampling to extraction.

8.3.2. Analysis of the extracts is completed within 40 days of extraction.

9. QUALITY CONTROL

9.1. Quality Control Batch

9.1.1. The batch is a set of up to 20 client samples and appropriate QC that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank (MB), an LCS, and a matrix spike/matrix spike duplicate (MS/MSD). (In some cases, at client request, it may be appropriate to process a matrix spike and un-spiked sample duplicate in place of the MS/MSD). If clients designate specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs. See Policy QA-003 for further definition of the batch.

9.2. Method Blank (MB)

9.2.1. An MB consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the MB at the same level as the samples. See Table 2 for the appropriate amount of surrogate to use for each analytical method. The MB is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated concentration levels or false positive data.

9.2.2. For a solid MB, use approximately 30 g of sodium sulfate spiked with the surrogates. For PCB, use approximately 10 g ± 0.5 g of sodium sulfate. See Table 2 for the appropriate amount of surrogate to use for each analytical method. The MB goes through the entire analytical procedure.

9.2.3. For a wipe MB, use 1 clean wipe spiked with the surrogates. See Table 2 for the appropriate amount of surrogate to use for each analytical method. The MB goes through the entire analytical procedure.

9.3. Laboratory Control Sample (LCS)

9.3.1. LCSs are well-characterized laboratory-generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure.

9.3.2. The LCS is made up in the same way as the MB (see Sections 9.2.1 through 9.2.3), but spiked with the LCS standard and the surrogates. See Table 3 for the appropriate amount of spike to use for each analytical method.

9.4. Surrogates

9.4.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.4.2. Each applicable sample, MB, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits of the applicable determinative method. See Table 2 for the appropriate amount of surrogate spike to use for each analytical method.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1. An MS is an environmental sample to which known concentrations of target analytes have been added. An MSD is a second spiked aliquot of the same sample, which is prepared and analyzed along with the sample and MS. See Table 3 for the appropriate amount of spike to use for each analytical method.

9.6. QC requirements can be found in the various associated analytical SOPs.

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2. Laboratory control limits are internally generated and updated periodically, unless method specified. Control limits are easily accessible via the LIMs.

9.8. Method Detection Limits (MDLs) and MDL Checks

9.8.1. MDLs and MDL Checks are established and performed by the laboratory as described in SOPs CA-Q-S-006 and NC-QA-021.

9.8.2. MDLs are easily accessible via the LIMs.

9.9. Nonconformance and Corrective Action

9.9.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. On a weekly basis, measure the appropriate volumes of solvents into the appropriate sized glass culture tubes gravimetrically. The “standard” glass culture tubes are sealed, and the meniscus is noted by marking a line on the tubes. The glass culture tubes containing the sample final extracts are then compared against the “standard” glass culture tubes of the appropriate volume and solvent to ensure the volumes are consistent. (See Table 1 for final volumes)The bottle top dispenser is calibrated quarterly and must be within ±5% of the target volume with an RSD ≤ 1%.

10.2. All labware, pipettes, and balances are calibrated according to SOPs NC-QA-004 and NC-QA-015.

11. PROCEDURE

11.1. Procedural Variations

11.1.1. 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 must be completely documented using a Nonconformance memo and approved by a supervisor. The Nonconformance memo will be filed in the project file. Procedural variations are not allowed for Ohio VAP projects.

11.2. Soxhlet

11.2.1. Remove surrogate and matrix spiking solutions from refrigerator if cold stored, and allow to warm to room temperature.

11.2.2. Do not decant the water layer from sediment samples. The entire sample is used. A higher weight of sample portion must be weighed for sediment samples to account for the dry weight correction (see 11.2.3). Record and document in the LIMS if a water layer was present in the sample. Homogenize the sample by mixing it thoroughly in the container. If this is not possible, place the sample in a clean beaker and homogenize. Upon completion of homogenization in the beaker, return the sample to the original container. Discard foreign objects such as sticks, leaves, and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials, consult with the client (via the Project Manager). If the sample cannot be prepared using a Soxhlet due to matrix issues, a waste dilution may be required. Refer to SOP NC-OP-043 for the waste dilution procedure.

11.2.3. Place approximately 200mL of solvent into a 250 mL flat bottom flask containing one or two clean boiling chips. Weigh 30g ± 0.5 g of sample into a thimble or in a jar, recording the weight to the nearest 0.01g in LIMS. For PCB Extraction, weigh approximately 10 g of sample ± 0.5 g. Sample

weights less than 30g, but over 1g, may be used if the appropriate reporting limits can be met. For sediment samples that contain excessive moisture, weigh 50 g ±0.5 g. For wipe samples, the wipe is placed in an extraction thimble.

Note: Waste samples with difficult matrices (such as caulk) are extracted at 1 g.

Note: Alternate sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the sample to reagent ration. All samples and standards must be processed similarly.

11.2.4. Prepare an MB, LCS, and MS/MSD for each batch as specified in Section 9 of this SOP, using sodium sulfate or a clean wipe as the matrix for the LCS and MB. The parent sample is used for the MS/MSD. The weight of sodium sulfate used must be approximately the weight of soil used for samples.

11.2.5. Add anhydrous sodium sulfate to each solid, sediment or waste sample and mix well. The mixture must have a free-flowing texture. If not, add more sodium sulfate. Add the sample/sodium sulfate mixture to a soxhlet extractor thimble, but do not pack the thimble tightly. The soxhlet extractor or extraction thimble must drain freely for the duration of the extraction period. Thimbles are only used for PCB and Pesticide extraction. A glass wool plug below the sample in the soxhlet extractor is used for other extractions.

Note: For BNA sample prep, clean glass wool is used.

11.2.6. Add the appropriate amount of surrogate and matrix spiking solution as indicated in Tables 2 and 3.

11.2.7. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles per hour. Check the system for leaks at the ground glass joints after it has warmed up.

Note: If a reduced quantity of sample is extracted, it is usually necessary to increase the amount of sodium sulfate added or increase the solvent boiling rate to properly set the cycling rate.

Solvents:

Semivolatile GC/MS and TPH	1:1 v/v Methylene Chloride / Acetone
8270 (MS) Concrete	Methylene Chloride
PCB and Pesticides	1:1 v/v Hexane / Acetone
8082 Concrete	1:1 v/v Methylene

	Chloride/Acetone

11.2.8. Allow the extract to cool after the extraction is complete then disassemble by gently twisting the soxhlet from the flask.

11.2.9. The sample is now ready for the concentration step (Section 11.3).

11.2.10. Cover the extracts with aluminum foil and store at 4°C ± 2°C if the extract will not be concentrated immediately. Refer to Section 11.3 for concentration.

11.3. Concentration: According to the type of sample, different solvents and final volumes will be required. Refer to Table 1 for the appropriate final volumes and concentrations.

11.3.1. Kuderna-Danish (KD) Method:

11.3.1.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube (CT) to the 500 mL KD flask. Label the CT and KD. Transfer the sample to the labeled K-D flask filtering the extracts through funnels filled with sodium sulfate. Rinse the sample flasks from the soxhlet setups with approximately 10 – 20 mL of methylene chloride Transfer the rinsate through the funnel and rinse the funnel with 20-30 mL of methylene chloride to complete the quantitative transfer.

11.3.1.2. Add one or two clean boiling chips to the KD flask and attach a three-ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column. **Note:** It is important to wet with MeCl to ensure that the balls in the Snyder column do not stick, and the column will work properly.

11.3.1.3. Place the KD apparatus on a water bath (90-98^{o}C) so the tip of the concentrator tube is submerged. The water level must not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter; but the chambers should not flood.

11.3.1.4. Concentrate to 15-20 mL. If the determinative method requires a solvent exchange, add the appropriate exchange solvent to the top of the Snyder Column, and then continue the water bath concentration back down to 5-8 mL. Refer to Table 1 for details of exchange solvents and final volumes. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.3.1.5. Remove the KD apparatus from the water bath and allow to cool for a minimum of 10 minutes. If the level of the extract is above the level of the CT joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

11.4. Nitrogen Evaporation to Final Concentration

11.4.1. Transfer the CT to the evaporation apparatus.

11.4.2. Place the tube in a warm water bath that is at least 5°C below the boiling temperature of the solvent being evaporated and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but must not create splattering of the extract.

Boiling points of commonly used solvents are:

Methylene chloride	40°C
Acetone	56°C
Hexane	69°C
Acetonitrile	82°C

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.4.3. Refer to Table 1 to determine the final volume needed for a specific test method. Evaporate to slightly less than the required final volume.

11.4.4. Rinse the CT and quantitatively transfer the extract with the rinsate to the appropriate final container, rinse the CT and transfer the rinsate to the final container and dilute to the appropriate final volume using the “standard” glass vial noted in Section 10.1. Cap the sample and affix the appropriate label. The sample is now ready for analysis.

Note: The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

11.5. Analytical Documentation

11.5.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Record sample and associated QC information into LIMs. Level I and Level II technical reviews are performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

13. METHOD PERFORMANCE

13.1. Initial Demonstration

13.1.1. Each analyst must make an initial demonstration of capability (IDOC) for each individual method. This requires analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which must contain all of the analytes of interest. The spiking level must be equivalent to a mid-level calibration. (For certain tests, more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

13.1.2. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.1.3. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs. See SOPs NC-GC-038, NC-MS-018, NC-MS-003, and NC-GC-007 for detailed information on the determinative methods.

13.1.4. Method validation information (where applicable) in the form of analyst demonstrations of capabilities is maintained for this method in the analyst's training files

13.2. Training Qualification

13.2.1. The Group/Team Leader has the responsibility to ensure that this procedure is performed by an analyst 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 laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method 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. The following waste streams are produced when this method is carried out.

15.2.1. Used sodium sulfate and glass wool or filter paper contaminated with methylene chloride/acetone or acetone/hexane from the extract drying step. These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.

15.2.2. **Assorted flammable solvent waste from various rinses**. These wastes are put into the halogenated/non-halogenated 25 gallon solvent waste container located under the fume hood in extractions.

15.2.3. **Methylene chloride waste from various rinses:** These wastes are disposed of in the liquid-liquid separation unit.

15.2.4. **Hexane-Hexane waste:** These samples are to be disposed in the flammable waste.

15.2.5. **Waste Hexane in vials.** These vials are placed in the vial waste located in the GC prep laboratory.

15.2.6. **Waste Methylene Chloride sample vials**. These vials are placed in the vial waste located in the GC prep laboratory.

15.2.7. **Extracted solid samples contaminated with methylene chloride/acetone or acetone/hexane.** These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.

15.2.8. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCBs must be segregated into their own waste stream. PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB, and PCB vial waste.

15.2.9. Solvent Recovery System Waste. Methylene Chloride waste from the Solvent Recovery System is collected and disposed of in the liquid-liquid separation unit. Acetone/Methylene Chloride waste from this system is disposed of in the flammable waste containers located in the laboratory.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B, 3540C, and 3580A

16.1.2. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.3. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.4. Corporate Quality Management Plan (CQMP), current version16.1.5 Federal Register - Environmental Protection Agency, 40 CFR, Part 136, Volume 49, No. 209, October 26, 1984, Method 625

16.1.5. EPA 600, Methods for Chemical Analysis of Water and Wastes, Method 608

16.1.6. Revision History

Historical File:		Revision 3.4: 10/16/98		Revision 0: 03/12/08 (NC-OP-032)
(formerly CORP-OP-0001NC)		Revision 3.5: 04/22/99		Revision 1: 01/07/09 (NC-OP-032)
		Revision 3.6: 05/13/99		Revision 0: 03/24/11 (NC-OP-040)
		Revision 3.7: 03/20/01		Revision 1-A: 01/24/12
		Revision 3.8: 05/23/01		Revision 2: 08/28/13
		Revision 3.9: 04/22/02		Revision 3: 08/25/14
		Revision 4.0: 02/04/03		
		Revision 4.1: 10/07/03		
		Revision 4.2: 01/30/06		

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. Gas Chromatographic Analysis of Pesticides Based on Methods 8081A and 8081B, NC-GC-042

16.2.6. Gas Chromatographic Analysis of Diesel Range Organics Based on Methods 8015B, 8015C, and 8015D, NC-GC-043

16.2.7. Gas Chromatographic Analysis of PCBs Based on Methods 8082 and 8082A, NC-GC-045

16.2.8. GC/MS Analysis based on Method 8270C and 8270D, NC-MS-018

16.2.9. Analysis of Pesticides and PCBs by EPA Method 608, NC-GC-007

16.2.10. GC/MS Semivolatile Organic Compounds Capillary Column Technique Based on EPA Method 625, NC-MS-003

16.2.11. Standards and Reagents, NC-QA-017

17. MISCELLANEOUS

17.1. Modifications from Reference method

17.1.1. Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.1.2. Sodium sulfate is heated for 1 hour at 800°C to purify. The reference method lists a minimum of 4 hours at 400°C.

17.2. Tables and Appendices

TABLE 1

Final Volumes and Exchange Solvents

Type	Exchange Solvent for Analysis*	Final Volume for Analysis in mL
Semivolatiles	N/A	2.0 mL
PCB	Approximately 36 mL Hexane	10.0
Pesticides	Approximately 18 mL Hexane	10.0
BNA – SIM	N/A	2.0 mL
TPH	N/A	5.0

Note: *PCBs and Pesticides only need the solvent exchange step when they are extracted in methylene chloride / acetone. If they are extracted in hexane / acetone, no solvent exchange is necessary.*
Note: *Different final volumes may be necessary to meet special client reporting limit requirements.*

TABLE 2

Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
BNA	20 ppm BNA	1.0
BNA / SIM	20 ppm BNA	0.1
PEST	0.2 ppm DCB/TCX	1.0

TPH	o-Terphenyl	1.0
PCB	0.2 ppm DCB/TCX	1.0

TABLE 3
Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
BNA	20 ppm BNA All-Analyte Spike	1.0
BNA / SIM	20 ppm BNA All-Analyte Spike	0.1
PEST	Pest NPDES Spike	1.0
PCB	10 ppm PCB Spike	1.0
TPH	Diesel Spike	1.0

Appendix 1

Glass Wool Cleaning Process for BNA Samples

1. PROCEDURE

1.1. A needed amount of glass wool is placed in a Soxhlet setup.

1.2. An appropriate volume of DCM/Acetone is added to the collection flask. This is allowed to cycle at a temperature that will produce 4 – 6 cycles per hour for 16 ± 2 hours.

1.3. At the end of the cycling time, the glass wool is placed in a Pyrex tray in the fume hood to dry.

1.4. Once dry, the cleaned glass wool is placed into a beaker that is marked “BNA only”.

TestAmerica Canton

SOP Amendment Form

SOP NUMBER: NC-WC-024 Rev. 5
SOP TITLE: Chromium, Hexavalent (Colorimetric)
REASON FOR ADDITION OR CHANGE: Remove references to DoD
CHANGE EFFECTIVE FROM: (DATE): 6/14/16
Change(s) Made: All references to DoD and/or QSM have been removed.
EDITED BY/DATE: Melissa Fuller-Gustavel 6/14/16

Title: CHROMIUM, HEXAVALENT (COLORIMETRIC)

[Method: SW846 Method 7196A and SM 3500-CR-B]

Approvals (Signature/Date):

Technology Specialist	06/26/15 Date	Health & Safety Coordinator	06/30/15 Date
Quality Assurance Manager	06/26/15 Date	Technical Director	08/19/15 Date

This SOP was previously identified as SOP NC-WC-024, Rev 4, dated 10/31/13

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

1. SCOPE AND APPLICATION

1.1. This method is used to determine the concentration of Hexavalent Chromium (Cr[VI]) in solids, groundwaters and waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present. It is based on SW846 Methods 7196A and Standard Methods 3500-CR-B. The working linear range is 0.01 - 0.5 mg/L for waters. The working linear range is 0.4 - 40 mg/kg for solid samples. For Michigan DEQ work, the linear range begins at 0.2 mg/kg for solids, and 0.005 mg/L for waters.

1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory.

2. SUMMARY OF METHOD

2.1. Hexavalent chromium in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, is determined colorimetrically by reaction with diphenylcarbazide in acid solution and measurement of the resulting red-violet color at 540 nm.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. All glassware is cleaned per SOP NC-QA-014. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to ten times that of chromium will not cause trouble.

4.3. Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong; and no difficulty is encountered normally if the absorbance is measured photometrically at the appropriate wavelength.

4.4. Interfering amounts of molybdenum, vanadium, iron, and copper can be removed by extraction of the cupferates of these metals into chloroform using cupferron solution.

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. 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 must be removed and discarded; other gloves must be cleaned immediately.

5.3. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.4. 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 Safety Data Sheet (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
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.
Phosphoric Acid	Corrosive	1mg/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.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.

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.			

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable.** Solvent and waste containers must be kept closed unless transfers are being made. 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 must be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents must be conducted in a fume hood with the sash closed as far as the operation will permit.

5.7. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents must be conducted in a fume hood with the sash closed as far as the operations will permit.

5.8. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

5.9. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and a Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Spectrophotometer for use at 540 nm

6.2. 1 cm Spectrophotometer Cell – disposable cuvettes

6.3. Beakers: 150 mL, Class A glass, or calibrated plastic disposable

6.4. Volumetric flasks: 1 L

6.5. Autopipettor with disposable tips

6.6. Funnels: various

6.7. Calibrated SnapSeal® containers

6.8. Glass culture tubes

6.9. Whatman #4 Filter Paper

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sulfuric Acid (H_2SO_4): concentrated

7.1.2. Phosphoric Acid (H_3PO_4): concentrated

7.1.3. Acetone: reagent grade: Avoid material that comes in containers with metal or metal-lined caps.

7.1.4. 1,5-Diphenylcarbazide: Reagent grade

7.1.5. Diphenylcarbazide Solution: Dissolve 0.25 g of 1,5-Diphenylcarbazide in 50 mL of acetone. **The solution must be stored in an amber bottle.** Prepare the solution weekly. If a marked color change is noted, a new solution must be prepared. This solution is commercially available.

7.1.6. Potassium Dichromate ($K_2Cr_2O_7$): Primary standard grade

7.2. Standards

7.2.1. Primary Chromium Stock Solution, 50 mg/L: Dissolve 0.1414 g of dried potassium dichromate in 800 mL of reagent water. Dilute to 1 liter in a volumetric flask with reagent water. Stable for up to six months. Additional information can be found in SOP NC-QA-017.

7.2.1.1. Water Calibration Standards: Add the indicated volume of the appropriate standard and dilute to volume with reagent water. Note: the low standard must be at or below the reporting limit.

Conc., mg/L	MLs	Source, mg/L	Final Vl., mL
0.5	0.5	50	50
0.25	0.25	50	50
0.1	0.10	50	50
0.01	0.01	50	50
0.005	0.005	50	50

7.2.1.2. Secondary Chromium Stock Solution, 50 mg/L: Dissolve 0.1414 g of dried potassium dichromate (secondary source) in 800 mL of reagent

water. Dilute to 1 liter in a volumetric flask with reagent water. Stable for up to six months.

7.2.1.3. Verification Standards: Add the indicated volume of the appropriate standard and dilute to volume with reagent water.

Use	Conc., mg/L	mLs	Source, mg/L	Final Vol., mL
MS/MSD (waters)	0.25	0.25	50	50
CCV	0.25	0.25	50	50
LCS (waters)	0.25	0.25	50	50

7.2.1.4. Solid Calibration Standards: The solid calibration standards are prepared according to SOP NC-WC-086 Alkaline Digestion for Hexavalent Chromium.

Conc.				
mg/L	mg/kg *	mLs	Source, mg/L	Final Vol, mL (after complete sample prep)
1.0	40	2.0	50	100
0.5	20	1.0	50	100
0.25	10	0.5	50	100
0.10	4.0	0.2	50	100
0.02	0.8	0.04	50	100
0.01	0.4	0.02	50	100

*Assuming 2.5 g solid to 100mL final volume

7.2.1.5. Verification Standards: The solid verification standards are prepared according to SOP NC-WC-086 Alkaline Digestion for Hexavalent Chromium.

Use	Conc. mg/kg	mLs	Source, mg/L	Final Vol, mL (after complete sample prep)
CCV/LCS	20	1.0	50	100

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. To retard the chemical activity of hexavalent chromium, the samples and extracts must be stored at 4°C ± 2°C until analyzed.

8.2. For aqueous samples, the maximum holding time prior to analysis of the samples or extracts is 24 hours from sampling to analysis.

8.3. The holding time for solid samples is 30 days from sampling to digestion and 168 hours after digestion to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (Laboratory Control Sample (LCS), Method Blank (MB), Matrix Spike/Matrix Spike Duplicate (MS/ MSD)), which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch. The MB consists of 50mL 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 hexavalent chromium concentrations or false positive data. The MB must not contain any hexavalent chromium at or above the reporting limit. For Ohio VAP projects, the MB must not contain hexavalent chromium above the reporting limit.

9.2.2. Corrective Action for MBs

9.2.2.1. If the hexavalent chromium level in the MB exceeds the reporting limit for the sample, all associated samples are re-prepared and re-analyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.2.2. If there is no hexavalent chromium level 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.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is 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. Acceptance limits are listed in LIMS.

9.3.2. An LCS for waters, consisting of 0.25 mg/L standard, is analyzed with each analytical batch of samples.

9.3.3. For solids, two LCSs must be digested with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is 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.

9.3.3.1. An insoluble LCS for solids is analyzed with each analytical batch of samples. Weigh approximately 0.01g of $PbCrO_4$ (diluted to 50 mL with digestion solution). Record the actual amount added and use in the %R calculation (Section 12.5). Acceptance criterion is 75-125%.

9.3.3.2. A soluble LCS for solids, consisting of 1.0 mL of the 50 mg/L secondary standard diluted to 50 mL with digestion solution is prepared and analyzed with each analytical batch of samples. This LCS is also used as the ICV. Acceptance criterion is 80-120%.

9.3.4. Corrective Action for LCSs

9.3.4.1. If hexavalent chromium recovery is outside established control limits, the system is out of control and corrective action must occur.

9.3.4.2. Corrective action must be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable. For Ohio VAP projects, repreparation of the batch is required unless criteria in Section 9.4.6.3 are met.

9.3.4.3. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for hexavalent chromium, the batch is acceptable. **This must be addressed in the project narrative.**

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD) (Water Samples only)

9.4.1. One MS/MSD pair must be processed for every 10 samples (water matrix). A matrix spike (MS) is a field sample to which known concentrations of hexavalent chromium have been added. A matrix spike duplicate (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 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. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. An MS/MSD consisting of 50 mL of sample and 0.25 mL of 50 mg/L secondary standard must be prepared and analyzed with every batch of samples.

9.4.3. Corrective action for MS/MSDs

9.4.3.1. If the hexavalent chromium recovery or RPD falls outside the acceptance range, the recovery must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action must include re-preparation and re-analysis of the batch.

9.4.3.2. If the native hexavalent chromium concentration in the MS/MSD exceeds four times the spike level for that analyte, the MS/MSD results are flagged with a “4”.

9.4.3.3. If the client program requirements specify to confirm matrix interferences, re-preparation, and re-analysis of the MS/MSD may be necessary.

9.5. Additional information of QC samples can be found in QA Policy QA-003.

9.6. Control Limits

9.6.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.6.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via LIMs

9.7. Method Detection Limits (MDLs) and MDL Checks

9.7.1. MDLs and MDL Checks are established by the laboratory as described in SOP NC-QA-021 and CA-Q-S-006

9.7.2. MDLs are easily accessible via LIMs

9.8. Nonconformance and Corrective Action

9.8.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action. This is not applicable for Ohio VAP.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. A calibration curve is prepared monthly prior to the analysis of water samples, and a calibration curve is digested with each batch of solid samples.

10.2. Initial Calibration

10.2.1. Zero the instrument using a blank. Analyze initial calibration standards for both water and solid matrices as needed and record all absorbances on the analytical logsheet. Derive the correlation coefficient (r), slope (a), and y-intercept (b). The correlation coefficient must be $\geq$ 0.995 to continue. If the criteria are not met, re-analysis or re-calibration is required.

10.2.2. See Section 7.2.1 for preparation of calibration standards.

10.2.2.1. For water samples, add 1mL diphenylcarbazide solution to each container and swirl to mix. For solid samples, add 0.1 mL diphenylcarbazide solution to each container and swirl to mix.

10.2.2.2. Add concentrated sulfuric acid (drop by drop) to each flask until the pH is 2.0 $\pm$ 0.5. Measure the pH by placing a drop of sample or digestate on narrow range pH paper (0 - 3 $\pm$ 0.25). Solid digests may take approximately 1 mL, and all other samples (standards and waters) may take approximately 5 - 10 drops.

NOTE: For samples that may cause color interferences, a second acidified aliquot must be analyzed without the diphenylcarbazide solution. Record the absorbance on the analytical logsheet.

10.2.2.3. Allow five to ten minutes for color development.

10.3. Continuing Calibration Verification/Continuing Calibration Blank (CCV/CCB)

10.3.1. The calibration is verified at the beginning, every ten samples, and at the end of the run using a midrange CCV to verify continued linearity. It cannot vary from the original curve by more than $\pm$ 10%. For aqueous samples, recalibration is required. The previous ten samples must be re-analyzed and bracketed by a

CCV that passes criteria. For solid samples, re-digestion of the sample batch is required.

10.3.2. The system cleanliness is verified at the beginning, every ten samples, and at the end of the run using a CCB. The CCB is 50 mL of reagent water, which is processed through all corresponding preparation and analysis steps like a method blank. It cannot contain the analyte of interest at or above the reporting limit for aqueous samples, or recalibration is required. The previous ten samples must be re-analyzed and bracketed by a CCB that passes criteria. For solid samples, re-digestion of the sample batch is required.

10.4. All supportive laboratory equipment is calibrated as specified in SOPs NC-QA-004 and NC-QA-015.

11. PROCEDURE

11.1. 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 must be completely documented using a Nonconformance Memo. The Nonconformance Memo must be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. This is not applicable for Ohio VAP.

11.3. Recommended Instrument Conditions

11.3.1. Turn on the spectrophotometer and adjust the wavelength to 540 nm. Set the instrument to the absorbance mode. Allow the spectrophotometer to warm up for at least 10 minutes before use.

11.4. Sample Preparation

11.4.1. Water samples require minimal sample preparation. Solid samples require an alkaline digestion procedure after which the sample can be treated as a water sample throughout the remainder of the analysis.

11.4.1.1. Solids: Refer to SOP NC-WC-086, Alkaline Digestion for Hexavalent Chromium.

11.4.1.2. Water Samples

11.4.1.2.1. No preparation is necessary.

11.5. Sample Analysis

11.5.1. Preliminary Evaluation

11.5.1.1. Preliminary evaluation can consist of visual determination by comparison to the standards to determine if dilutions are required.

11.5.1.2. Transfer 50 mL, or aliquot diluted to 50 mL with reagent water, of calibration standards, CCV, CCB, LCS, MBs, and water samples to suitable containers. For solids, pipette 5 mL of filtered sample into a culture tube.

11.5.1.3. Method SM3500 Cr-B(not applicable for solids)

11.5.1.3.1. Add 0.25 mL (approximately 5 drops) of concentrated phosphoric acid to each sample.

11.5.1.3.2. Add concentrated sulfuric acid (drop by drop) to each flask until the pH is 1.0 ± 0.3. Measure the pH by placing a drop of sample on narrow range pH paper (0 - 3 ± 0.25). Standards and waters may take approximately 5 - 10 drops.

NOTE: Samples may cause color interferences, therefore a second acidified aliquot must be analyzed without the diphenylcarbazide solution. Record the absorbances in LIMS.

11.5.1.3.3. For water samples, add 1mL diphenylcarbazide solution to each container and swirl to mix.

11.5.1.4. Method 7196A

11.5.1.4.1. For water samples, add 1mL diphenylcarbazide solution to each container and swirl to mix. For solid samples and MSA standards, add 0.1 mL diphenylcarbazide solution to each container and swirl to mix.

11.5.1.4.2. Add concentrated sulfuric acid (drop by drop) to each container until the pH is 2.0 ± 0.5. Measure the pH by placing a drop of sample or digestate on narrow range pH paper (0 - 3 ± 0.25). Solid digests may take approximately 1 mL, and all other samples (standards and waters) may take approximately 5 - 10 drops.

NOTE: Samples may cause color interferences, therefore a second acidified aliquot must be analyzed without the diphenylcarbazide solution. Record the absorbances in LIMS.

11.5.1.5. Allow five to ten minutes for color development.

11.5.1.6. Analyze each sample and MSA standard for absorbance, and record the value in LIMS.

11.5.1.7. A CCV and CCB are analyzed at the beginning and end of the run and every ten samples to verify linearity. The CCV must be ± 10% or recalibration is required. The CCB must be less than the reporting limit. All samples after the invalid CCV/CCB must be re-analyzed.

11.5.1.8. Any sample with absorbance values greater than the highest calibration standard must be diluted and re-analyzed.

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. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.6.4. Record all sample results and associated QC into LIMS. Level I and Level II review is performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Use linear regression or the following equation to calculate sample results.

$$\frac{\text{Absorbance - a}}{\text{b}} = \text{mg/L } Cr^{6+}$$

Where:

a = y-intercept

b = slope

12.2. **Waters, mg/L Cr^{+6} = (A - B) x C**

Solids, mg/kg Cr^{+6} = (A - B) x C x D

Where:

A = mg/L of sample colorized

B = mg/L of non-colorized sample

C = Dilution Factor = Final Volume / Initial Volume

D = Weight/Volume Factor - = Final Volume / Sample Weight

12.3. ***Water(Laboratory Control Sample) LCS Recovery*** $= \frac{mg/L}{0.25\ (true)} \times 100$

12.4. ***Water CCV Recovery = mg/L x 100***

0.25 (true)

12.5. Water or Solid –Matrix Spike/Matrix Spike Duplicate

(MS/MSD Recovery $= \frac{E - F}{0.25\ (true)} \times 100$

Where:

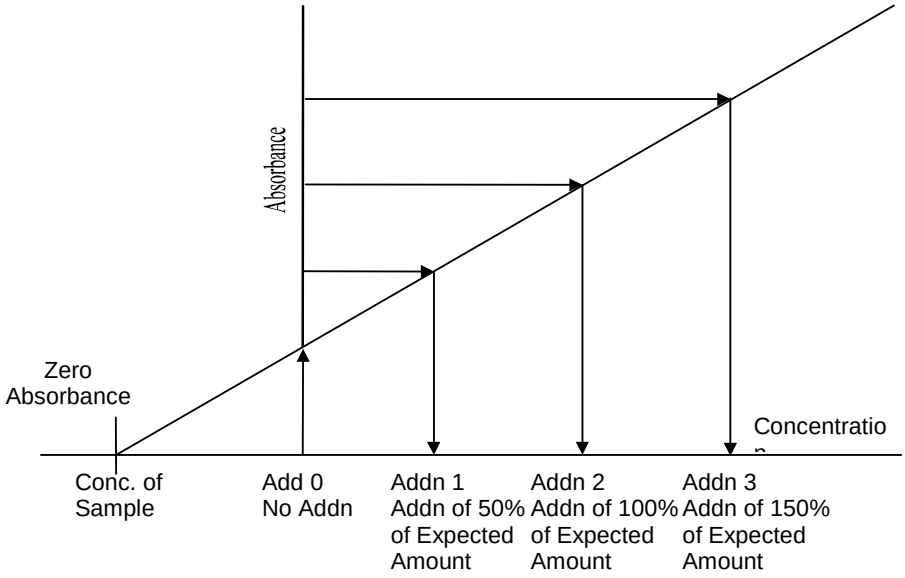
E = Matrix Spike/Matrix Spike Duplicate (MS/MSD), mg/L

F = Sample, mg/L

12.6. Method of Standard Addition – Solid Extracts only

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbency, the point of interception of the horizontal axis is the concentration of the unknown.



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should reflect the aqueous standard curve.
- The correlation coefficient of the MSA curve must be 0.995 or greater. If the criteria is not met, the corrected ABS of the unspiked sample will be calculated against the calibration curve to obtain a more accurate result.

12.7. The correlation coefficient (r) for solids is determined by the Pearson product moment correlation coefficient formula:

$$r = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 \sum (y - \bar{y})^2}}$$

12.8. Solid Laboratory Control Sample (LCS) Recovery = $\frac{\text{mg/kg}}{20(true)} \text{ x } 100 = \%\ \text{Recovery}$

12.9. Solid CCV Recovery = $\frac{\text{mg/kg}}{20\ \text{(true)}} \text{ x } 100 = \%\ \text{Recovery}$

12.10. Solid Soluble Laboratory Control Sample (LCS) Recovery =

$$\frac{\text{mg/kg}}{20\ \text{(true)}} \text{ x } 100 = \%\ \text{Recovery}$$

12.11. Solid Insoluble Laboratory Control Sample (LCS) Recovery =

$$\frac{\text{mg/kg}}{\text{G} \bullet \text{H/I}} \text{ x } 100 = \%\ \text{Recovery}$$

Where:

G = mg of $PbCrO_4$ spiked

H = 0.16 (fraction of Cr in $PbCrO_{4)}$

I = kg of sample spiked

12.12. Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002.

13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of performance data on file. The laboratory must have corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. 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.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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 must be disposed of in accordance with Federal, State, and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must 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

15.3.1 The following waste streams are produced when this method is carried out.

15.3.1.1 Acidic or basic waste generated by the analysis. This waste is disposed of in designated acid waste containers located in the lab.

15.4 Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

16 REFERENCES

16.3 References

16.3.1 SW846 Test Methods for Evaluating Solid Waste, Third Edition, Chromium, Hexavalent (Colorimetric), Method 7196A

16.3.2 Standard Methods For the Examination of Water and Wastewater, Method 3500-CR-B, 2009

16.3.3 TestAmerica Canton Quality Assurance Manual (QAM), current version

16.3.4 SW846 Test Method for Evaluating Solid Waste, Third Edition, Method 7000A, Section 8.7 Method of Standard Additions.

16.3.5 TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.3.6 Corporate Quality Management Plan (CQMP), current version

16.3.7 Revision History

Historical File:		Revision 1.1: 06/03/97		Revision 3.4: 03/07/08

		Revision 3.0: 03/08/99		Revision 3.5: 03/07/08
		Revision 3.1: 10/24/01		Revision 3.6: 07/12/10
		Revision 3.2: 06/12/02		Revision 3.7-A: 04/13/12
		Revision 3.3: 10/08/04		Revision 4: 10/31/13

16.4 Associated SOPs and Policies, current version

16.4.1 QA Policy, QA-003

16.4.2 Glassware Washing, NC-QA-014

16.4.3 Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.4.4 Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.4.5 Standards and Reagents, NC-QA-017

16.4.6 Alkaline Digestion for Hexavalent Chromium, NC-WC-086

16.4.8 Selection of Calibration Points, CA-T-P-002

16.4.9 Calibration Curves (General), CA-Q-S-005

17 MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1 Reporting Limits

17.1.1 The lower reporting limit (RL) is 0.02 mg/L for waters and 0.8 mg/kg for solids.

17.1.2 If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

Title: TOTAL HARDNESS (mg/L $CaCO_3$), TITRIMETRIC

[Method: Standard Method 2340C]

Approvals (Signature/Date):

Technology Specialist	05/25/16 Date	Health & Safety Coordinator	05/26/16 Date
Quality Assurance Manager	06/06/16 Date	Technical Director	06/03/16 Date

This SOP was previously identified as SOP NC-WC-036, Rev 5, dated 6/11/15

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

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Hardness in waters and wastewaters. It is based on Standard Method 2340C. The approximate working range is 2 to 400 mg/L.

1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. Calcium and magnesium ions in the sample are sequestered upon the addition of magnesium ethylenediamine tetraacetate (MgEDTA). The end point of the reaction is detected using Eriochrome Black T indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Some metal ions interfere by causing color fading and indistinct endpoints for the titration. If this is observed, the sample will be analyzed by Method 2340B Hardness by Calculation.

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 Safety Data Sheet (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	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Ammonium Hydroxide	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes.
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.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. 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.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood or under other means of mechanical ventilation where possible. 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.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.

5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Stir plate and stir bars

6.2. Erlenmeyer flasks: various

6.3. Graduated cylinders: various

6.4. Autopipettor and disposable tips

6.5. Class A Microburette: 10 mL

6.6. Volumetric flasks: various

6.7. Plastic bottles: various

6.8. Analytical balance: Capable of accurately weighing ± 0.1 mg

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Ammonium Chloride (NH4Cl): reagent grade

7.1.2. Ammonium Hydroxide (NH_4OH): reagent grade

7.1.3. Magnesium EDTA: reagent grade

7.1.4. EDTA Buffer Solution: Dissolve 16.9 g of NH_4Cl in 143 mL of NH_4OH. Add 1.25 g of magnesium salt of EDTA and dilute to 250 mL with reagent water. Mix well and store in a plastic bottle. This solution is stable for one month. Alternatively, use purchased hardness buffer. Buffer must be kept at room temperature.

7.1.5. Buffer for Water Hardness: Ammonium Chloride-Hydroxide Buffer with Magnesium EDTA. Buffer must be kept at room temperature

7.1.6. Eriochrome Black T Indicator: reagent grade

7.1.7. Sodium Chloride (NaCl): reagent grade

7.1.8. Indicator: Mix together 0.5 g of Eriochrome Black T and 100 g of NaCl. Alternatively, use purchased indicator (such as Calamagite). Indicator must be

kept at room temperature.

7.1.9. 1 N Ammonium Hydroxide: Dilute 7 mL of NH_4OH to 100 mL with reagent water and mix well. This solution must be kept at room temperature.

7.1.10. Disodium EDTA Dihydrate: Primary standard grade

7.1.11. 0.02 N EDTA Titrant: Prepare titrant by dissolving 3.723 g of disodium EDTA dihydrate in about 400 mL of reagent water in a 1000 mL volumetric flash. Dilute to 1 liter with reagent water and mix well. This solution is stable for six months. Calibrate weekly against a standard calcium solution by titration. Store the titrant in polyethylene bottle at room temperature.

Note: Purchased EDTA may also be used. Purchased EDTA does not require weekly standardization.

7.1.11.1. Titrant Standardization Procedure: Place 5.0 mL of 1000 ppm standard calcium solution in a vessel containing about 50 mL of reagent water. Add 1 mL of buffer solution. Add about 0.5 - 1 g of dry indicator. Titrate slowly with continuous stirring until the last reddish tinge disappears, adding the last few drops at 3 - 5 second intervals. At the end point, the color is blue. Repeat the standardization procedure two more times and average the values.

$$\text{N of EDTA} = \frac{0.1}{\text{mL of EDTA}}$$

7.2. Standards

7.2.1. Calcium Carbonate Standard Solution, 1000 mg/L: Purchased standard (Hach or other supplier). Alternately, a standard may be made: Place 1.0 g of anhydrous calcium carbonate (primary standard grade) in a 500 mL Erlenmeyer flask. Slowly add 6 N HCl until all the $CaCO_3$ has dissolved. Add 200 mL of reagent water and boil for five minutes. Cool the solution and add several drops of methyl red indicator. Adjust the solution to an intermediate orange color with 3 N NH_4 OH or 6 N HCl as required. Quantitatively transfer the solution to a 1 liter volumetric flask and dilute to volume with reagent water. This solution is stable for six months.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are preserved to a pH < 2 with concentrated nitric acid.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C.

8.3. The holding time is six months from sampling to the completion of analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD, and Sample Duplicates) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

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 analyte of interest at or above the reporting limit.

9.2.2. A reagent water blank consisting of 50 mL of reagent water and all other reagents added to samples must be analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the MB exceeds the reporting limit for the analytes of interest in the sample, all associated samples are re-prepared and re-analyzed. If this is not possible due to limited sample quantity or holding time considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte 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.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is 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.

9.3.2. A midrange LCS must be analyzed with each analytical batch of samples. The LCS is made of 45 mL reagent water and 5.0 mL 1000 ppm $CaCO_3$ standard.

Alternatively, use 25mL water and 25mL purchased hardness standard.

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.3.2. The only exception is that if the LCS recovery is biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.3.3. Corrective action will be repreparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. 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. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. An MS/MSD must be analyzed per analytical batch. The MS/MSD is composed of 20 mL sample, 25 mL reagent water, and 5 mL 1000ppm $CaCO_3$.

9.4.3. Corrective Action for MS/MSDs

9.4.3.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and re-analysis of the batch.

9.4.3.2. If the native analyte concentration in the parent sample used to prepare the MS/MSD exceeds 4x the spike level, the recovery data is reported and flagged with a "4" in the LIMS.

9.4.3.3. If client program requirements specify to confirm matrix interference's, repreparation and re-analysis of the MS/MSD may be necessary.

9.5 Sample Duplicate (DU)

9.5.1 Sample duplicates are performed at a frequency of 10% and must meet laboratory-specific limits for precision.

9.6 Control Limits

9.6.1 Control limits are established by the laboratory as described in NC-QA-018.

9.6.2 Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs.

9.7 Method Detection Limits (MDLs) and MDL Checks

9.7.1 MDLs and MDL checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.7.2 MDLs are easily accessible via the LIMs.

9.8 Nonconformance and Corrective Action

9.8.1 Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1 See section 7.1.11.1 for EDTA titrant standardization procedure.

11. PROCEDURE

11.1. 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.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Not applicable

11.4. Sample Analysis Procedure

11.4.1. Samples must be at ambient temperature prior to analysis.

11.4.2. Rinse the burette with reagent water once and with EDTA titrant once. Fill with EDTA titrant and be sure all air bubbles are removed.

11.4.3. Place 25 mL of sample and 25 mL of reagent water in an Erlenmeyer flask. Add approximately 1 to 2 mL of 1N NH_4OH, approximately 1 to 2 mL of EDTA buffer (or add 3-4mL of the purchased buffer) and approximately 0.5 to 1 g of Indicator. Titration should be completed within 5 minutes of the addition of the buffer.

11.4.4. While stirring, slowly titrate with EDTA titrant until the last reddish tint disappears. The end point is blue. Record the volume of titrant used and its true normality on the analytical logsheet.

NOTE: Samples requiring more than 10 mL of titrant must be diluted. An aliquot is diluted to 25 mL with reagent water and treated as a sample.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Record all sample results and associated QC in the LIMS. Level I and Level II reviews are performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. **Hardness, mg/L $CaCO_3$** = $\frac{(A- B)xNx50{,}000}{C}xD$

Where:

A = Volume of EDTA titrant used for sample, mL
B = Volume of EDTA titrant used for blank, mL
C = Volume of sample used, mL (not total volume after addition of DI water)

D = Dilution Factor = $\frac{Final\,Dilution\,Volume,mL}{Initial\,Sample\,Volume\,Used\,For\,Dilution,mL}$

N = Normality of EDTA titrant

50,000 = 50 (Equivalent weight of Calcium) x 1000 mg/g

12.1.1. LCS Recovery

$$\textbf{LCS \% Recovery} = \frac{\textbf{mL titrant x N x 50,000}}{\textbf{(25) LCS TV}} \textbf{ x 100}$$

Where:
N = Normality of EDTA titrant
LCS TV = value of purchased hardness standard

12.1.2. MS/MSD Calculation

$$\textbf{MS / MSD \% Recovery} = \frac{\textbf{(A – B)}}{\textbf{200}} \textbf{ x 100}$$

Where:
A = MS/MSD concentration (from 12.1)
B = Sample concentration (from 12.1)

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. 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.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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. **Aqueous waste generated by the analysis.** Aqueous waste can be poured down the drain if the pH is between 5 and 10. Any sample waste generated that is not in this pH range must be collected and disposed of in the acid waste drum labeled as "Acid Waste".

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. Standard Method for EDTA Titrimetric Method, Method 2340C, 1997.

16.1.2. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.3. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.4. Corporate Quality Management Plan (CQMP), current version

16.1.5. Revision History

Historical File:		Revision 2: 12/23/98		Revision 3.4: 11/18/10
		Revision 3: 04/19/99		Revision 4: 12/26/13
		Revision 3.1: 11/06/04		Revision 5: 6/11/15
		Revision 3.2: 03/21/08		
		Revision 3.3: 04/28/10		

16.2. Associated SOPs and Policies, current version

16.2.1. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.2. QA Policy, QA-003

16.2.3. Glassware Washing, NC-QA-014

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting Limits

17.1.1. The lower reporting limit (RL) for undiluted samples is 5 mg/L $CaCO_3$.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Deviation from Standard Method 2340C:

17.2.1. Wastewater samples are not digested.

Title: Polychlorinated Biphenyls (PCBs) and PCBs as Congeners by GC/ECD

Method: SW-846 8082 and 8082A

Approvals (Signature/Date):

7/19/2016		7/18/2016	
Sharon Bacha	Date	Steve Jackson	Date
Technical Manager		Regional Safety Coordinator	
7/18/2016		7/18/2016	
Virginia Zusman	Date	Deborah L. Lowe	Date
Quality Assurance Manager		Laboratory Director	

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedure for the determination of concentrations of polychlorinated biphenyls (PCB) as Aroclors and as individual Congeners (see Appendix A) using the methodology prescribed in EPA SW-846 Methods 8082 and 8082A.

1.2 This procedure is applicable to the analysis of aqueous, solid, sediment, biological, and waste/oil samples. When utilized for the analysis of waste/oils, additional cleanup procedures may be required.

1.3 This SOP does not include the procedures for extracting environmental samples. Refer to TestAmerica SOPs PT-OP-001 for aqueous and PT-OP-026 for solid and waste sample preparation procedures.

1.4 Table 1 at the end of this document lists the specific Aroclors that are determined using this procedure and their associated reporting limits (RLs).

1.5 On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated PT-QA-M-001, Quality Assurance Manual.

2.0 SUMMARY OF METHOD

2.1 Preparation

2.1.1 PCBs are extracted from a one-liter aqueous sample with methylene chloride using a separatory funnel (SW-846 Method 3510). The extract is evaporated to approximately 10 to 20 mL and exchanged to hexane. The final extract volume is 40 mL for normal PCB analysis and 1.0 ml for low-level PCB analysis. The extraction procedure is detailed in SOP PT-OP-001.

2.1.2 PCBs are extracted from soil, sediment and tissue samples using a 50:50 acetone - hexane mixture by the automated Soxtherm (Method 3541). The final extract volume varies depending on the type of “solid” matrix extracted. The extraction procedure is detailed in SOP PT-OP-026.

2.1.3 Oil and liquid waste samples are typically prepared by diluting 1 gram of sample to a final volume of 40 mL with hexane. The extraction procedure is detailed in SOP PT-OP-026.

2.1.4 Wipe Samples are collected using either filter paper or gauze. These samples can then be extracted using the procedure outlined in SOP PT-OP-026.

2.1.5 Cleanup Procedures are discussed in Section 4 below. Instructions for performing various cleanup procedures are detailed in SOP PT-OP-028.

2.2 Analysis

2.2.1 Samples are analyzed using a gas chromatograph with dual electron capture detectors (ECDs). Specific Aroclor mixtures are identified by the pattern of peaks compared to chromatograms of reference standards. The

concentrations of Aroclors in the sample extract are determined using an internal standard calibration.

3.0 DEFINITIONS

3.1 Polychlorinated biphenyls (PCBs): PCBs are a class of organic compounds with 1 to 10 chlorine atoms attached to biphenyl, with a general chemical formula of $C_{12}H_{10-x}Cl_x$. There are 209 possible congeners.

3.2 Aroclor: PCBs were produced as technical mixtures by the chlorination of biphenyl. Production processes were designed to produce mixtures with characteristic chlorine contents. In the United States, most of the PCBs in the environment are in the form of Aroclors, which were produced by Monsanto from the 1930s through 1977. Each Aroclor mixture is identified by a four-digit number, the first two digits of which indicate the number of carbons in the biphenyl ring, i.e., 12, and the second two of which indicate the weight percent of chlorine. For example, Aroclor 1254 has 12 carbons and 54% by weight chlorine. The exception is Aroclor 1016, which has 12 carbons and 41% by weight chlorine.

Each specific Aroclor produces a characteristic gas chromatographic pattern that represents the relative amounts of PCB congeners in the formulation. The formulation of the mixtures from batch to batch was fairly consistent, but never exactly the same. In almost all cases, the gas chromatogram can be used as a fingerprint to identify the specific Aroclor. Exceptions occurred for Aroclors 1254 and 1221. In each case, at least one batch was produced under different conditions, which resulted in an Aroclor mixture with the same approximate chlorine content, but with a significantly different distribution of congeners. These odd batches of 1254 and 1221 produce chromatographic patterns that are very different from the typical formulations. Standards for these odd batch Aroclors can be used to aid in the qualitative identification of Aroclors in environmental samples.

3.3 TALS: TestAmerica Laboratory Information Management System

3.4 NCM: Non-Conformance Memo – a system within TALS for documenting and communicating QC failures or anomalies encountered during sample receipt, preparation or analysis.

3.5 Please see the glossary of the TestAmerica Pittsburgh Quality Assurance Manual (PT-QA-M-001) for additional definitions.

4.0 INTERFERENCES

4.1 Hydrocarbons can co-elute and thereby mask the Aroclor pattern. The laboratory uses acid cleanup with concentrated sulfuric acid to remove hydrocarbons from solid and oil sample extracts, and for water samples when extracts have noticeable color or whenever there is clear evidence of interferences in the initial sample chromatograms. Acid cleanup removes low-to-medium molecular weight polar organic interferences from sample extracts. Detailed instructions for performing acid cleanup are provided in SOP PT-OP-028.

4.2 Sulfur will interfere and can be removed using procedures described in SOP PT-OP-028.

4.3 Carboprep 90 Cleanup – This method may be performed to remove potential interference prior to analysis if the sample extract is colored.

NOTE: When the Carboprep Cartridge Clean-up Method is used, the recovery of the TCMX surrogate is poor.

4.3.1 Cartridge Method

4.3.1.1 Place approximately 2 ml of sample extract into a test tube and mark the sample volume on the tube.

4.3.1.2 Condition the cartridge by adding 2 ml of methylene chloride and allowing it to drip through the cartridge. Do not allow the cartridge packing to go dry in this or any subsequent step, until the final rinse has been completed.

4.3.1.3 Add 2 ml of hexane/methylene chloride (80%/20%) mixture and allow it to drip through the cartridge until almost empty.

4.3.1.4 Add the sample extract to the cartridge and place the test tube under the cartridge to collect the liquid as it drips through.

4.3.1.5 Rinse 3 times with 2 ml aliquots of hexane/methylene chloride (80%/20%) mixture, while not allowing the cartridge to go dry. After the final rinse, use a pipette bulb to force out all of the remaining liquid in the cartridge.

4.3.1.6 Concentrate the sample extract back down to the original volume according to the mark on the test tube. The extract is now ready for analysis.

4.3.2 Quick Method

4.3.2.1 Add a half scoop of Carboprep 90 to approximately 2 ml of sample extract. Swirl for about one minute and allow the extract to settle.

4.3.2.2 Add a half scoop of Copper Granules to 1 mL of sample or a whole scoop to 2 mL of sample, cap the vial and shake vigorously for 2 minutes.

4.3.2.3 Pipette out an aliquot of extract and filter through a 0.45 µm syringe filter. The extract is now ready for analysis.

4.4 Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. Any affected samples are re-analyzed.

4.5 Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate

Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-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.

5.2 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.

5.3 Specific Safety Concerns and Requirements

5.3.1 Eye protection that protects against splash, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.3.2 The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.3.3 There are areas of high voltage in 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.

5.3.4 All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the TestAmerica Denver Radiation Safety Officer and the TestAmerica Corporate EH&S Director shall be immediately notified and a letter sent to the Colorado Department of Public Health and Environment.

5.4 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. 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
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.
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.
Hydrogen Gas	Explosive	None	The main hazard is flammability. Exposure to moderate concentrations may cause dizziness, headache, nausea, and unconsciousness. Exposures to atmospheres less than 8 to 10% oxygen will bring about sudden unconsciousness, leaving individuals unable to protect themselves. Lack of sufficient oxygen may cause serious injury or death.
(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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Instrumentation

6.1.1 A gas chromatographic system with dual columns and dual ECD (^{63}Ni) detectors, and a data system capable of measuring peak area and/or height.

6.2 Supplies

6.2.1 Columns

- Primary Column: RTX-CLP1, 30 m x 0.53 mm id, 0.5 µm coating.
- Secondary Column: RTX-CLP2, 30 m x 0.53 mm id, 0.42 µm coating.
- Additional columns that can be used for confirmation include 30m x 0.53mm id MR1, MR2, RTX5, RTX50 or RTX-1701.

6.3 Autosampler vials, crimp caps with PTFE-faced septa

6.4 Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution

7.0 REAGENTS AND STANDARDS

7.1 The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

7.2 Reagents

7.2.1 Acetone, 99.4% for organic residue analysis

7.2.2 Hexane, pesticide grade.

7.2.3 Carrier Gas: ≥ 99.99999% pure hydrogen

7.2.4 Make-up Gas: ≥ 99.99980% pure nitrogen

7.3 Standards

7.3.1 Stock Standards

7.3.1.1 All standards must be refrigerated at >0.0 ºC but ≤6.0 ºC. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

7.3.1.2 Stock standards are monitored for signs of degradation or evaporation. The standards must be replaced annually from the date of receipt or earlier if the vendor indicates an earlier date.

7.3.1.3 Dilutions from stock standards cannot have a later expiration date than the date assigned to the parent stock solutions. The standards must be replaced at least every six months, or sooner, if comparison with check standards indicates a problem.

7.3.2 PCB, Surrogate and Internal Standard Stock Calibration Standards

7.3.2.1 Stock A

For each of the Aroclors listed in Table 1, a commercially prepared stock standard solution is obtained. Each stock standard contains the specific Aroclor in isooctane at a concentration of 1,000 µg/mL. (Note: At times, specific Aroclor stock standards may also be purchased at various concentration levels, for example 2nd source stock standards are purchased at 200 ug/mL concentration.)

7.3.2.2 Surrogate Stock B

A commercially prepared stock standard solution is obtained that contains the surrogate compounds tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) in acetone, each at a concentration of 200 µg/mL.

7.3.2.3 Internal Standard Stock Standard

A commercially prepared stock standard solution is obtained that contains the internal standard compound, 1-bromo-2-nitrobenzene, at a concentration of 1000 ug/mL.

7.3.3 Intermediate and Working Level Calibration Standard Solutions

7.3.3.1 Stock C (Level 7 Calibration) Standard Solutions

A Stock C standard solution is prepared for the various Aroclors or combination of Aroclors as summarized in the following table. In each case, the Stock C standard solution is also the highest concentration (i.e., Level 7) calibration standard.

Stock C	Recipe	Conc (µg/mL)	Final Volume (mL)	Final Concentrations (µg/mL)	
AR1660	0.1 mL of Aroclor 1016 Stock A 0.1 mL of Aroclor 1260 Stock A	100	10	Aroclor 1016 Aroclor 1260	4.0 4.0
		200	10	TCMX	0.2
	0.2 mL of surrogate Stock B	200	10	DCB	0.2
AR2154	0.125 mL of Aroclor 1221 Stock A	1000	250	Aroclor 1221	0.5
	0.125 mL of Aroclor 1254 Stock A	1000	250	Aroclor 1254	0.5
AR3262	0.125 mL of Aroclor 1232 Stock A	1000	250	Aroclor 1232	0.5
	0.125 mL of Aroclor 1262 Stock A	1000	250	Aroclor 1262	0.5
AR4268	0.125 mL of Aroclor 1242 Stock A	1000	250	Aroclor 1242	0.5
	0.125 mL of Aroclor 1268 Stock A	1000	250	Aroclor 1268	0.5
AR1248	0.125 mL of Aroclor 1248 Stock A	1000	250	Aroclor 1248	0.5

7.3.4 AR1660 Calibration Levels

7.3.4.1 A total of 7 calibration standards are prepared for AR1660 as summarized in the following table. As needed, the following table can be used to prepare calibration standards for any of the Aroclors, but only the AR1660 calibration standards include the surrogates. In all cases, measured volumes of the Stock C standard are diluted using pesticide-grade hexane to the final volume indicated in the following table.

Level	Volume of Stock C Used (mL)	Final Volume (mL)	Final PCB Conc (µg/mL)	Final Surrogate Conc (µg/mL)*
1	0.01	100	0.01	0.0004
2	0.05	100	0.05	0.002
3	0.20	100	0.20	0.008
4 (CCV)	1.0	200	0.50	0.020
5	2.0	200	1.0	0.040
6	2.0	100	2.0	0.080
7	4.0	100	4.0	0.160
*Surrogates are in the AR1660 calibration solutions only. None of the other Aroclor calibration solutions contain the surrogate compounds.				

7.3.5 Working Single-Point PCB Calibration Standards

The Level 4 standard in the table above is used for single-point calibrations of the individual Aroclors. These standards are also used as pattern recognition standards.

7.4 Second-Source Standards for Initial Calibration Verification (ICV)

These standards are purchased from a vendor different from the one that supplied the stock calibration standards.

7.4.1 Second-Source Stock A Aroclor Standard Solutions

Commercially prepared solutions in pesticide-grade hexane (or isooctane) are routinely obtained for Aroclors 1016 and 1260. The Aroclor concentration in each solution is 200 µg/mL. Additionally, a second source standard is obtained for all other Aroclors.

7.4.2 Second-Source Working Level Standards

The working level second-source ICV standard is prepared by combining 0.5 mL of Aroclor 1016 Stock A' and 0.5 mL of Aroclor 1260 Stock A' diluting to a final volume of 200 mL with pesticide-grade hexane. This results in a concentration of 0.5 µg/mL for each of the Aroclors. Note: Surrogates are not added to any 2nd source working level standards.

7.5 Continuing Calibration Verification Standard (CCV), 0.5 µg/mL

The working CCV solution is the same as the Level 4 initial calibration standard, as shown in the table in Section 7.3.4.1.

7.6 Laboratory Control Standard (LCS) Spiking Solution (AR1660)

7.6.1 The LCS/MS spiking solution is prepared and used as part of the scope of the organic preparation SOP PT-OP-001. The following information is provided for reference only.

7.6.2 The working LCS spike solution is prepared in a volumetric flask by combining 1 mL of the Aroclor 1016 Stock standard (10,000 ug/ml) and 1 mL of the Aroclor 1260 Stock standard (10,000 ug/ml), and diluting to a 250 mL final volume with acetone. The final concentration of each Aroclor is 40.0 µg/mL.

7.7 Matrix Spike (MS) Spiking Solution:

The working matrix spike solution is the same as the LCS spike solution. The MS duplicate (MSD) is prepared in the same way using a third aliquot of the selected sample.

Matrix Spike and LCS Solutions		
Analyte Group	Matrix spike Solution ID	Volume added in mL
AR1660	40 ug/mL PCB Spike	1.0 - waters
		0.5 - soils
		0.025 - low-level waters
		0.025 – low-level soils
		1.0 – tissues (40 mL F.V.)
		0.5 – tissues (20 mL F.V.)

7.8 Surrogate Spike Solution

7.8.1 Stock Surrogate Spike Solution: A commercially prepared solution containing 200 µg/mL each of decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX) in acetone is purchased.

7.8.2 Working Surrogate Spike Solution: Samples are spiked with the surrogate compounds during sample preparation, which is described in the organic preparation SOP. The following information is provided for reference only.

7.8.3 The working surrogate spike solution is prepared in a volumetric flask by adding 1.6 mL of the DCB (1000 ug/mL) stock surrogate spike solution, 0.80 mL of the TCMX (2000 ug/mL) stock surrogate spike solution and diluting to a final volume of 2000 mL with acetone. The surrogate compounds are added to all field and QC samples as follows:

Surrogate Spiking Solutions		
Analyte Group	**Surrogate Spike Solution ID**	**Volume added in mL**
PCB Aroclors	0.8 ug/mL DCB/TCMX	1.0 - Waters
		1.0 - Tissues (40 mL F.V.)
		0.5 - Tissues (20 mL F.V.)
		0.5 - Solids
	0.2 ug/mL DCB/TCMX	0.1 - low-level waters
		0.1 - low-level soils

7.9 Internal standard

7.9.1 Stock - A commercially prepared stock standard solution is obtained that contains the internal standard compounds, 1-bromo-2-nitrobenzene and dibutylchlorendate, at concentrations of 1000 ug/ml and 200 ug/ml respectively.

7.9.2 A working standard for the internal standard, 1-bromo-2-nitrobenzene and dibutylchlorendate, is prepared at a concentration of 1 ug/ml. This standard is added to all samples and standards to result in a final concentration of 0.1 ug/ml (20 ul of 1 ug/ml to 200 ul; 10 ul to 100 ul; etc.) after any cleanups or dilutions that may be necessary but before injection.

7.10 Aroclor mixes

The following Aroclors can be analyzed together for calibration and calibration verification: 1016/1260, 1221/1254, 1232/1262, 1242/1268. If standards are mixed together, concentrations need to be taken into account (initial concentrations and final volumes). A calibration curve will be analyzed for 1660 and midpoint standards will be analyzed for all other aroclors.

7.11 RT standard

It is an option to make a multi Aroclor standard for the purposes of the daily RT update.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Water samples are collected in pre-cleaned amber glass bottles fitted with a Teflon-lined caps. To achieve routine reporting limits, a full one liter of sample is required for regular level extraction and 250mL for LVI extraction. Because the entire sample volume is used for extraction, additional bottles are needed to satisfy the requirements for matrix spike and matrix spike duplicate analyses.

8.2 Soil samples are collected in 8-ounce, wide-mouth jars with a Teflon-lined lid.

Matrix	Sample Container	Preservation	Extraction Holding Time	Analysis Holding Time	Reference
Waters	Amber glass	Cool >0.0 but ≤6.0°C	1 year	1 year from extraction	40 CFR Part 136.3
Soils	Glass	Cool >0.0 but ≤6.0°C	14[1] Days	40[1] Days from extraction	N/A
Tissues	Borosilicate glass, PTFE, quartz, aluminum foil	Freeze at < - 10°C can be stored this way for 1 year prior to extraction	14 Days from date of thawing	40 Days from extraction	PSEP [2]

[1] Some states will accept a 1 year holding time from sampling to extraction and from extraction to analysis for Solid samples. Consult the Project Manager or the QA Department for specific project requirements before exceeding 14/40 days.

[2]This maximum holding time is also recommended by the PSEP (1990). The California Department of Fish and Game (1990), and the USGS National Water Quality Assessment Program (Crawford and Luoma, 1993) recommend a more conservative maximum holding time of 1 year at < -10℃ for dioxins/furans. NOAA recommends a maximum holding time of 3 months.

NOTE: LVI is not used for samples from South Carolina. The 1 Liter bottles must be used for sampling.

9.0 QUALITY CONTROL

9.1 Refer to the TestAmerica Pittsburgh QC program document (PT-QA-021) for further details on criteria and corrective actions. Refer to "project checklist" for project specific requirements. More stringent project-specific requirements will supersede the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.

9.2 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP PT-QA-016. This is in addition to the corrective actions described in the following sections.

9.3 If dual column reporting is required, the choice of which column to report the QC from is made in the same manner as for the associated samples.

9.4 The following Quality Controls are required:

Quality Controls	Frequency	Acceptance Limits
Initial Calibration: Minimum 5 points for 1016/1260, One point for all other Aroclors Minimum 6 points for Congeners	Every 6 months, or more often as needed	Average RF: ≤ 20%RSD Linear Regression: Linear Correlation Coefficient ≥0.990 and intercept <1/2 RL
ICV (second source)	After each ICAL	≤ 20%D (80-120% recovery)
CCV[1]	Beginning of run and every 20 samples	8082 ≤ 15%D (85-115% recovery) 8082A ≤ 20%D (80-120% recovery)
RT Windows	With each ICAL (mid-point updated daily with CCVIS)	± 3X SD / ± 0.05 min
Internal Standard (IS)	All standards, samples, and QC	50 – 200% of the response in mid-level ICAL standard
Method Blank (MB)	1 per preparation batch	<RL
Laboratory Control Sample (LCS)	1 per preparation batch	Statistical control limits are maintained in TALS.
Matrix Spike (MS)	1 per preparation batch	Statistical control limits are maintained

Quality Controls	Frequency	Acceptance Limits
		in TALS. MS is not used for batch control.
Matrix Spike Duplicate (MSD)	1 per preparation batch	Statistical control limits are maintained in TALS. MSD is not used for batch control.
Surrogates	All samples and QC	Statistical control limits are maintained in TALS.
Dual column agreement	All positive results	40% RPD (see section 11.4 for reporting instructions)

[1]If the analysis includes the use of internal standards, a closing CCV is not required at the end of the analytical run.

9.5 Method blank

9.5.1 A method blank (MB) is prepared and analyzed with each batch of 20 or fewer samples. The method blank consists of reagent water (for aqueous sample batches) or sodium sulfate (for solid sample batches) to which the surrogate compounds are added (see SOP PT-OP-001 or PT-OP-026). The method blank is subject to the entire extraction, cleanup and analysis process. The method blank must be analyzed daily prior to sample analysis to demonstrate that the chromatographic system is contaminant free.

9.5.2 The method blank must not contain any analyte of interest at or above the reporting. For analytes detected above the MDL, all associated results will be reported with B qualifiers. If the MB is found to be contaminated above the RL, the sample batch must be re-extracted / reanalyzed unless one of the following criteria is met:

- Evaluate the associated sample results. If sample results are non-detect for the Aroclor found in the MB, results may be reported using the “Method Blank – Report, ND” NCM.
- If the associated sample concentrations are >10x the MB concentration, results for these samples may be reported using the “Method Blank – Report, 10X” NCM.
- If neither of the above situations exists, and re-extraction is not possible due to limited sample volume or holding time, the lab must notify the Project Manager. Instructions must be sought from the client on how to proceed with reporting these results. Results that are reported must be properly qualified and an NCM created to document the situation for the case narrative.

9.6 Laboratory Control Sample (LCS)

9.6.1 One LCS is prepared and analyzed with each batch of 20 or fewer samples. The LCS is prepared as described in Section 7.6. The LCS is subject to the entire extraction, cleanup and analysis process.

9.6.2 The LCS recovery must be within the established control limits. The laboratory's standard control limits are set at ± 3 standard deviations around the historical mean, unless project requirements dictate otherwise. Current control limits are maintained in the LIMS. Unless otherwise requested by the client, the PCB LCS contains only Aroclors 1016 and 1260.

9.6.3 For batches that include samples from South Carolina, the LCS control limits are static at 70-130%.

9.6.4 Laboratory generated Control Limits are maintained in TALS and can be provided upon request.

9.6.5 If any analyte is outside the control limits in the LCS, the batch must be re-extracted / reanalyzed unless the following criterion is met:

- If the LCS recovery is above the upper control limit and sample results are non-detect, those associated sample results may be reported with the appropriate qualifier and using the “LCS/LCSD - %R High” NCM.
- If the above situation does not exists, and re-extraction is not possible due to limited sample volume or holding time, the lab must notify the Project Manager. Instructions must be sought from the client on how to proceed with reporting these results. Results that are reported must be properly qualified and an NCM created to document the situation for the case narrative.

9.7 Matrix Spike (MS) and Matrix Spike Duplicate Samples (MSD)

9.7.1 One MS/MSD pair is required with each analytical batch of 20 or fewer samples. Note that some programs (e.g., North Carolina and South Carolina) require preparation and analysis of an MS/MSD pair at a 10% frequency. This shall be noted in the project when required. Preparation of the MS is described in Section 7.7. The MSD is another aliquot of the sample selected for the MS that is spiked in the same manner as the MS.

9.7.2 The MS and MSD recoveries must fall within the established LCS control limits. The relative percent difference (RPD) between the MS and MSD must be less than the established limit, which is based on statistical analysis of past results, unless otherwise dictated by project requirements. Current control limits are maintained in the LIMS.

Laboratory generated Control Limits are maintained in TALS and can be provided upon request.

9.7.3 If analyte recovery or RPD falls outside the acceptance range, but the associated LCS recovery is in control, and all other QC criteria (e.g., continuing calibration verification) are met, then there is no evidence of

analytical problems. This may indicate that the sample matrix itself has an adverse effect on recovering the analyte.

- If a matrix effect is suspected, the parent sample is qualified appropriately, and results are reported using the "MS/MSD - %R, LCS Pass" NCM.
- If the recovery for any component is outside control limits for both the MS and the LCS, the laboratory is out of control and corrective action must be taken. Refer to section 9.6.4.
- If an MS/MSD is not possible due to limited sample, then an LCS duplicate (LCSD) may be analyzed to monitor batch precision.

9.7.4 The MS/MSD must be analyzed at the same dilution level as the parent sample, unless the matrix spike components would then be above the calibration range. In this case, would require a dilution greater than the parent sample to bring the spiked compounds within the calibration range.

9.7.4.1 For PCB analysis, the matrix spike added is diluted to concentrations below the RL at a dilution of 40X. MS/MSD that are diluted above 40X must be reported with a "D" qualifier on the spiked compounds to indicate that recovery is not able to be accurately calculated.

9.7.4.2 If the parent sample concentration is >4X, it may not be possible to accurately calculate %recoveries. Results will be reported with the "MS/MSD – High Targets" NCM.

9.8 Surrogates

9.8.1 Each field sample, QC sample, and calibration standard, is spiked with surrogate compounds decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX). The surrogate spike solution is prepared as described in Section 7.8.

9.8.2 For field samples and batch QC, the surrogate recoveries must be within the established control limits, which are set at ± 3 standard deviations around the historical mean, unless project requirements dictate otherwise. Surrogate recovery limits are maintained in TALS.

9.8.2.1 Surrogate recoveries for both DCB and TCMX in the MB and LCS <u>both must pass</u> on at least one column. If the recovery of the surrogates in MB or LCS's is outside of the control limits, check for calculation or instrument problems.

- Surrogate recoveries (one or both) outside of control limits on both columns for the MB or LCS require re-preparation and reanalysis of the entire preparation batch.

9.8.2.2 For field samples, surrogate recovery is calculated and reported for

both DCB and TCMX. At least one surrogate must pass on the one column from which Aroclors are identified and reported, and that column must have a passing CCV.

9.8.2.3 For CCV standards, Aroclors 1016 and1260 and surrogates must pass on the reporting column, for the data to be considered reportable.

9.8.2.4 If both surrogates fail on both columns for a sample, and matrix interference is not obvious from the initial analysis, it is only necessary to re-prepare and reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effects, as long as the extraction/instrument system is proven to be working properly according to the batch and instrument QC.

9.8.2.5 For PCB analysis, the surrogate spike added is diluted to concentrations below the RL at a dilution of 40X. Samples that are diluted above 40X must be reported with a "D" qualifier on the surrogates to indicate that recovery is not able to be accurately calculated.

9.9 Initial Calibration

9.9.1 See section 10.3 below for initial calibration options and evaluation requirements.

9.9.2 A full calibration (minimum 5 points) is required on both columns for Aroclor 1016 and 1260 and the two surrogates plus internal standards. A single point is used for all other Aroclors.

9.9.3 Each peak in the Aroclor (a minimum of 5 peaks is required for all Aroclors, except 1221, which requires a minimum of 3 peaks) is intergrated using peak height.

9.9.4 The calibration must be verified by the analysis of a second source standard (ICV) near the mid-point of the calibration range. The %Drift/Difference for thei standard must be $\leq$ 20% from the ICAL. (The result for the the average value of peaks chosen to represent the aroclor in the ICV standard must be within ± 20.0% of the expected value. No individual peak can be greater the ±40.0% of the expected value.)

If the ICV response does not meet this limit, repeat the ICV analysis once with a freshly made standard. If failure repeats, the initial calibration and ICV standards must be prepared fresh and calibration repeated.

9.10 Continuing Calibration Verification (CCVIS)

NOTE: It is not necessary to run a CCV standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration and ICV.

9.10.1 A mid-level calibration standard of 1016/1260 is analyzed as the continuing calibration verification (CCVIS) standard at the beginning of the analytical sequence, and after every 20 samples (all injections except solvent blanks count as samples), or every 12 hours, whichever is more frequent, and at the end of the run sequence. Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns. If 12 hours elapsed since the last CCV was analyzed, a new sequence is started with a fresh CCV.

9.10.2 A mid-range CCV standard of each Aroclor must be analyzed at least every 24 hours, for retention time updating.

9.10.3 If Aroclors other than 1016 or 1260 are detected in any sample, a CCV of the associated Aroclor(s) must be analyzed within 12 hours of the sample and pass criteria in order for the sample data to be reported. If a CCV is not run within 12 hours of the sample, or if the CCV does not meet the method CCV criteria, the sample must be re-analyzed along with a passing CCV for that compound. CCV's of other Aroclors may be run every 20 samples/12 hours along with the 1016/1260 CCVs in a routine analysis sequence to meet this requirement. If the analysis includes the use of internal standards, a closing CCV is not required at the end of the analytical run.

9.10.4 Acceptance criteria for CCVs is < 15%D for method 8082 and <20%D for 8082A. The All Aroclors and the surrogates must meet these recovery limits on both columns, unless only reporting from one column. If a CCV does not meet the acceptance criteria explained above, associated samples must be re-analyzed unless one of the following conditions is met:

- If the CCV %D fails high, >15.0% for 8082 or >20.0% for 8082A, and the sample results are ND for that compound, the data may be reported with the appropriate qualifier and the "CCV - %D, High, Samples ND" NCM.
- If the CCV % D fails low, and samples results are ND, then a low level standard can be analyzed to prove that the instrument is sensitive enough to call the sample "Not Detected" and the sample can be reported. This low level standard must be analyzed prior to the samples. Results may be reported with proper qualification and using the "CCV – Low Biased, ND, RL Check Passes" NCM.
- If the CCV fails on the non-reporting, or confirmation, column, and that failure does not exceed 40%D, results may be reported without qualification.
- If the individual %D for one or two peaks, for the Aroclors that require 5

peaks for quantitation, exceeds the control limit, but the average %D is within the limit, results may be reported without qualification and using the "CCV - %D, Multi-component, Avg Acceptable" NCM.

- If a continuing batch CCV fails, and there is evidence that the sample matrix has affected the column performance, samples must be rerun once to confirm this affect. Results may be reported from the first or second analysis, with proper qualification and using the "CCV - %D, Capping, RR Confirms" NCM.

9.11 Retention Time (RT) Windows

9.11.1 Absolute retention times are used for the identification of PCBs as Aroclors. However, in addition to retention times, peak patterns play a large role in the identification of Aroclors.

9.11.2 The center of the retention time (RT) window shall be updated based on the middle level in the initial calibration or the first CCV (CCVIS) in the daily analytical sequence, whichever is more recent,.

9.11.3 Before establishing windows, make sure the GC system is within optimum operating conditions. Evaluate the deviation from expected RT for each analyte in at least three CCV and/or LCS samples spread over at least 72 hours.

- If three days of analytical data are not available, use a default RT window of 0.010 minutes. At the end of the batch, evaluate all CCVs and LCS in the batch. If necessary, widen the window such that all analytes fall within the RT window. Reprocess the batch using the new RT windows.
- Multiply the maximum deviation from the set by 1.5. This is the retention time window, unless the result is less than 0.010 minute, in which case the window is set at 0.010 minute.
- Determine the retention time (RT) windows for the 3-5 major peaks selected for each Aroclor. The AR1016 windows will be used to establish retention time windows for PCBs AR1221, AR1016, AR1232, AR1242, and AR1248. The AR1260 windows will be used to establish retention time windows for PCBs AR1254, AR1260, AR1262, and AR1268.
- Retention time windows for analytes of interest must not overlap.

9.11.4 Evaluate the retention time windows on an ongoing basis. The center of the RT window is updated on the first CCV (CCVIS) of the day. All analytes for all subsequent CCVs, LCS and matrix spikes must fall within the RT window, except as discussed below.

- Matrix spike analytes may fall outside the RT window if there is a large, non-target peak co-eluting, or overlapping, with the analyte in

the matrix.

9.11.5 If any analyte falls outside the RT window in CCV, LCS of matrix spike (except as discussed above for matrix spikes), then the RT window for that analyte shall be widened to the minimum degree required for the analyte to fall within the RT window. All samples in the batch shall be reprocessed with the new RT window, and the wider RT window shall remain in place for subsequent batches.

9.11.6 Retention time windows should be reliably narrower than +/- 0.03 minute. If RT windows wider than this are necessary, the instrument should be evaluated and maintenance performed as needed. Subsequent to maintenance, RT windows shall be narrowed to the extent that is consistent with the data obtained and the foregoing requirements.

9.11.7 The laboratory must calculate retention time windows for each analyte on each GC column and whenever a new type of GC column is installed. The data must be retained by the laboratory and available for review.

9.12 Control Limits: In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be reviewed at least annually. The recovery limits are mean recovery +/- 3 standard deviations, unless that limit is tighter than the calibration criteria, in which case limits may be widened. Refer to policy PT-QA-021 for more details.

9.12.1 Surrogate and matrix spike recoveries will be reported unless the dilution is more than 40X.

9.13 Percent Moisture

9.13.1 Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined on a separate portion of the sample if results will be reported based on dry weight.

9.14 Internal Standard Criteria

9.14.1 If the internal standard response in the continuing calibration is more than 200% or less than 50% of the response in the mid-level of the initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

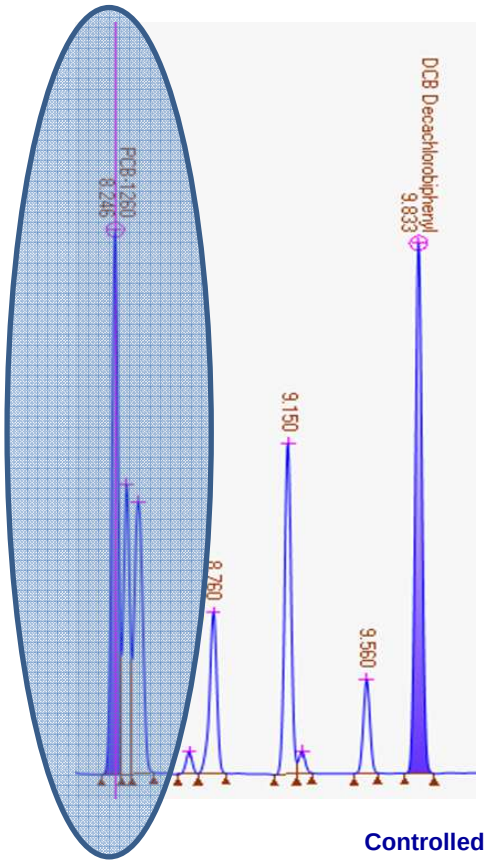
9.14.2 Any samples or standards that do not meet the internal standard criteria of > 50% and <200% of the response when compared back to the continuing calibration must be evaluated for validity. Samples that are reported with internal standard exceedances must have documentation supporting matrix effect. Where the matrix effect is well established it may be reported with narration, otherwise the samples must be reanalyzed to confirm matrix effect is required. If the internal standard exceedance is deemed to be due to an instrumental problem, instrument maintenance will be done and all affected samples must be reanalyzed after the problem is corrected.

9.15 Resolution Check requirement

9.15.1 The circled triplet of peaks in the figure below is observed towards the end of the 1260 pattern on columns such as CLP 1. Minimum resolution (degree of overlap) requirement between peak 1 / 2 and peak 2 / 3 is <75%. This chromatogram shows overlap of about 50% between peak 2 and 3, and 30% between peak 1 and 2.

9.15.2 Resolution (degree of overlap) is calculated as follows:

[Height of the valley / (Sum of the two peak heights / 2)] x 100%



9.16 Procedural Variations

9.16.1 Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a supervisor and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. The nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 Samples are extracted and prepared for analysis as described in SOPs PT-OP-001 and PT-OP-026. Allow extracts to warm to room temperature before injecting.

10.1.2 If needed, extracts are cleaned up using the procedure in section 4.3 of this SOP or one of the clean-up procedures in SOP PT-OP-028. Any clean-up performed is documented either within the method chain or using an NCM.

10.1.3 Internal standard is added to each extract prior to loading the extract on the instrument for analysis. Add 1µL of Internal Standard Spike (7.9) per 100µL of extract or standard.

10.2 Calibration

Chromatographic conditions for this method are presented in Table 2.

10.2.1 Use the ChemStation interface to establish instrument operating conditions for the GC.

10.2.2 Raw data obtained by the ChemStation software is transferred to the CHROM DB(database) for further processing. The data analysis method, including peak processing and integration parameters, calibration, RT windows, and compound identification parameters, is set up in the CHROM DB software.

10.2.3 Transfer calibration standard solutions into autosampler vials and load into the GC autosampler. Use the ChemStation software to set up the analytical sequence.

10.2.4 Unprocessed calibration data are transferred to the CHROM DB database for processing. After processing the calibration data, print the calibration report and review it using the calibration review checklist (GC and HPLC Data Review Checklist - ICAL). Submit the calibration report to a qualified peer or the group leader for final review. The completed calibration reports are scanned and stored as Adobe Acrobat files on the Public Drive.

10.2.5 A new calibration curve must be generated initially, after major changes to the system, or when continuing calibration criteria cannot be met. Major changes include installation of new type of column and replacing the ECD detector. Initial Calibration will be performed at least every 6 months.

10.3 Initial Calibration (ICAL)

10.3.1 An initial standard calibration using seven concentration levels of the AR1660 mixture is routinely performed. (At least five calibration levels are required.) This provides concentration levels for Aroclor 1016, Aroclor 1260, and the surrogate compounds DCB and TCMX.

10.3.2 All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

10.3.3 The calibration curves for Aroclors 1016 and 1260 and the surrogate compounds, relative to the internal standard response, are modeled either as average response factors (RF) or as calibration curves using a systematic approach to selecting the optimum calibration function. PCB's are well established linear responding compounds and an average curve fit should be the norm. If linear regression is utilized, it is acceptable, however the individual points should be evaluated to determine if there has been a change in the instrument sensitivity or if there is a potential issue with the standards.

10.3.4 The calibration for each of the other Aroclors (see Table 1) is initially determined using a single, mid-level calibration standard. As needed, the laboratory may generate a multi-point calibration for other commonly detected Aroclors, such as 1221, 1254, and 1248. When additional multi-point calibrations are developed for the other Aroclors, a second-source ICV standard is also analyzed, see section 9.15.

NOTE: Samples from sites known to be contaminated with specific Aroclors should be analyzed using a multi-point calibration curve for the identified Aroclors. This information is provided to the analyst through special instructions in the LIMS.

NOTE: Generally, it is NOT acceptable to remove points from a calibration for the purposes of meeting calibration criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or the linear range is adjusted accordingly. A minimum of five levels must remain in the calibration for a linear regression. The

documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration.

10.3.5 The high and low standard for the initial calibration of the AR1660 mixture defines the acceptable quantitation range for all of the Aroclors. If a sample extract contains any Aroclor at a concentration that exceeds the upper range of the calibration, then the extract must be diluted and reanalyzed.

10.3.6 Select 5 major peaks (at least 25% peak height of the largest peak in the aroclor) in the analyte pattern (only 3 peaks are usable for Aroclor 1221). The response factors or curves will be generated for each of the major peaks for each Aroclor. The results are based off of an average of the calculated concentrations of these major peaks.

NOTE: A minimum of five accurate peaks must be used to quantify an Aroclor (three peaks for Aroclor 1221).

10.4 Internal Standard Calibration

10.4.1 Internal standard calibration involves the comparison of instrument responses from the samples to the responses from the target compounds in the calibration standards. The area (or height) of a peak and the area (or height) of the internal standard in a sample chromatogram is compared to the area (or height) of the peak and the area (or height) of the internal standard in the standard chromatograms that appears at the same retention time. The ratio of the detector response to the concentration of the target analyte in the calibration standard is defined as the response factor (RF) and is calculated as follows:

$$RF = \frac{Ax \times Cis}{Ais \times Cx}$$

Where:

A_x = Area (or height) of the peak to be measured

A_{is} = Area (or height) of the peak for the internal standard

C_{is} = Concentration of the internal standard

C_x = Concentration of the peak being measured

Note: It is also possible to use the concentration of the standard rather than the mass injected.

10.5 Establishing the Calibration Function

10.5.1 Calibrations are modeled either as average response factors (RF) or as linear regression curves, using a systematic approach to select the optimum calibration function. Start with the simplest model, i.e., a straight line through the origin and progress through the other options until calibration acceptance criteria are met. PCB's are well established linear responding compounds and an average curve fit should be the norm. If linear regression is utilized, it is acceptable, however the individual points should be evaluated to determine if there has been a change in the instrument sensitivity or if there is a potential issue with the standards. Different calibration models can be applied to each of the major peaks chosen to represent the Aroclor.

10.5.2 Linear Calibration Using Average Response Factor (RF)

The response factor is a measure of the slope of the calibration line, assuming that the line passes through the origin. Under ideal conditions, the factors calculated for each calibration level will not vary with the concentration of the standard. In practice, some variation can be expected. When the variation, measured as the relative standard deviation, is relatively small (e.g., ≤ 20%), the use of the straight line through the origin model is generally appropriate.

The average response factor is calculated as follows:

Average RF = $\overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$ Equation 2

Where:

RF_i = The response factor for the i^{th} calibration level.
n = The number of calibration levels.

The relative standard deviation (RSD) is calculated as follows:

$$RSD = \frac{SD}{\overline{RF}} \times 100\%$$ Equation 3

Where SD is the standard deviation of the average RF, which is calculated as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(RF_i - \overline{RF}\right)^2}{n-1}}$$ Equation 4

10.5.3 Evaluation of the Average Response Factor:

Plot the calibration curve using the average RF as the slope of a line that passes through the origin. Examine the residuals, i.e., the difference between the actual calibration points and the plotted line. Particular attention should be paid to the residuals for the highest points, and if the residual values are relatively large, a linear regression should be considered.

Acceptance Criteria: The RSD for each peak chosen to represent the aroclor must be ≤ 20.0% for both 8082 and 8082A. **NOTE:** The laboratory may not use the "grand mean" rule.

NOTE: If the %RSD is <20.0% (8082/8082A), alternative curve fits may still be considered.

Corrective Action: If the RSD exceeds the limit, linearity through the origin cannot be assumed, and alternative curve fits must be considered.

10.5.4 Linear Calibration Using Least-Squares Regression (weighted) - Evaluation of the Linear Least-Squares Regression Calibration Function

With an unweighted linear regression, points at the lower end of the calibration curve have less weight in determining the curve than points at the high concentration end of the curve. For this reason, inverse weighting of the linear function is recommended to optimize the accuracy at low concentrations. Note that the August 7, 1998 EPA memorandum "Clarification Regarding Use of SW-846 Methods", Attachment 2, Page 9, includes the statement "The Agency further recommends the use of this for weighted regression over the use of an unweighted regression."

Acceptance Criteria: To avoid bias in low level results, the absolute value of the y-intercept must be significantly less than reporting limit (RL), and preferably less than the MDL.

Also examine the residuals, but with particular attention to the residuals at the bottom of the curve. If the intercept or the residuals are large, the calibration should be repeated since a higher order regression is not allowed for this method.

If weighted linear regression is used 1/(Amt) or 1/(Amt)2 a minimum of 5 points are required. The coefficient of determination (r2) must be > 0.990. If the correlation of determination falls below the acceptance limit, linear regression cannot be used and a second-order regression should be attempted.

When using Weighted Linear Regression, recalculate the concentration of the low calibration point. Acceptance criteria is ±

30% of true value.

If this readback criteria fails for any analyte, sample detects should be reanalyzed under passing criteria. If reanalysis is not possible, the result must be flagged as estimate, or the situation described in the narrative.

For non-detects, if the readback failed with high recovery, reanalysis is not required, and flagging is not required. If the readback failed low, samples should be reanalyzed. If reanalysis is not possible, the result must be flagged as estimate, or the situation described in the narrative.

Corrective Action: If the correlation coefficient falls below the acceptance limit, the linear regression is unacceptable and the calibration should be repeated since a higher order regression is not allowed for this method.

For non-detects, reanalysis is not required, and flagging is not required.

10.5.5 Other curve types

Due to the stability of the compounds, non-linear calibration curves (quadratic) and unweighted linear regression curves are not applicable for this method.

10.5.6 Removal of calibration points and/or levels

10.5.6.1 Certain analytes that have particularly high or low sensitivity may need to have the high or low calibration points removed in order to optimize the calibration curve. Removal of high or low calibration points is allowed, but the working range of the calibration must be adjusted accordingly. The reporting limit must be supported by the lowest point remaining in the calibration and any samples with concentrations above the highest point in the calibration must be diluted and reanalyzed.

10.5.6.2 Points for individual compounds from the interior levels of the calibration may not be removed. A complete level may be removed if the laboratory can document a clear reason for incorrect response in the standard (for example, analysis of the incorrect level, failure to add internal standards or instrument malfunction).

10.5.6.3 It is acceptable to have different curve fits for the individual peaks chosen to represent the Aroclors.

10.6 Second-Source Initial Calibration Verification (ICV)

10.6.1 Second-source ICV standards are analyzed for all Aroclors. The stock standards are obtained from a source different than that of the standards used for the calibration. The ICV standards are analyzed immediately

following the initial calibration. Refer to section 9.9.4 for acceptance criteria.

10.7 Sample Analysis

10.7.1 An autosampler is used to introduce samples into the chromatographic system by direct injection of 1 or 2 µL of the sample extract.

10.7.2 Samples, standards, and QC samples must be introduced using the same procedure.

10.7.3 All extracts and standards are allowed to warm to room temperature before injection.

10.7.4 Use the ChemStation interface to set up and run the analytical sequence. Sample injection and analysis are automated and may proceed unattended.

10.8 Analytical Sequence

10.8.1 An analytical sequence starts with a minimum five-level initial calibration (ICAL) or a daily calibration verification. The daily run sequence is generated electronically using the ChemStation software.

The following is the typical analytical sequence for routine sample analysis:

Suggested Analytical Sequence		
Initial Calibration	(not required daily)	
Injection No.		
1	Solvent Blank (optional)	
2	Aroclor 2154	Level 4
3	Aroclor 3262	Level 4
4	Aroclor 4268	Level 4
5	Aroclor 1248	Level 4
6	Aroclor 1016/1260	Level 1
7	Aroclor 1016/1260	Level 2
8	Aroclor 1016/1260	Level 3
9	Aroclor 1016/1260	Level 4
10	Aroclor 1016/1260	Level 5
11	Aroclor 1016/1260	Level 6
12	Aroclor 1016/1260	Level 7
13-17	ICV's (2nd source standard of all Aroclors)	
18	Method Blank	
19-38	Sample 1-20 (or 12 hours)	
39	Aroclor 1016/1260	Level 4
At least every 24 hours, counting from the start of the initial calibration or from the start of the last daily calibration, the retention time windows must be updated. CCVs for 1016/1260 must be run every 20 samples or 12 hours, whichever is more frequent. Mid-level standards of any other Aroclors expected to be present in the samples are also injected. For sequences without an initial calibration, start with CCVIS 1660 and CCVs for 1248 and 2154, method blank plus 19 samples, then CCVIS 1660 and CCVs for 3262 and 4268, method blank plus 19 samples. This way all standards are run within 24 hours for RT's and samples with detections other than 1660 have CCVs within 12 hours.		

10.9 When a sample result exceeds the upper calibration range, then that sample extract is diluted to obtain a result in the upper half of the calibration range and reanalyzed. Any samples that were analyzed immediately following the high sample are evaluated for carryover. If the samples had target analyte detections at or above the RL, the samples must be reanalyzed to rule out carryover.

10.10 Upon completion of the analytical sequence, transfer the raw chromatography data to the CHROM DB database for further processing. Review chromatograms online and determine whether manual data manipulations are necessary. All manual integrations must be justified and documented. See CA-Q-S-002 for requirements for manual integration.

10.11 Manual integrations may be processed using an automated macro, which prints the

before and after chromatograms and the reason for the change, and attaches the analyst's electronic signature. Alternatively, the manual integration may be processed manually. In the latter case, print both the both the before and after chromatograms and record the reason for the change and initial and date the after chromatogram. Before and after chromatograms must be of sufficient scale to allow an independent reviewer to evaluate the manual integration.

10.12 Compile the raw data for all the samples and QC samples in a batch. The analytical batch is defined as containing no more than 20 samples, which include field samples and the MS and MSD. Perform a level 1 data review and document the review on the data review checklist (GC Data Review Checklist). Submit the data package and review checklist to a peer analyst for the level 2 review. The data review process is explained in SOP PT-QA-018.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Qualitative Identification of Aroclors

Retention time windows are used for identification of Aroclors, but the “fingerprint” produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst’s judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram. If there are any anomalies in the pattern due to the presence of multiple PCBs or weathering of peaks the analyst should discuss this with another analyst or technical director to come to a consensus about which PCB(s) should be identified. An NCM should be completed indicating the rationale behind the decision made. Sometimes Aroclors 1262 and 1268 are not requested as target analytes. If these patterns are observed, an NCM should be completed informing the project manager of possible PCB detection.

11.2 Quantitation of Aroclors

Quantitation of Aroclors is accomplished using 5 major peaks. The peaks must be within the established retention time windows. If there is an interference that affects the accuracy of results, the analyst must use 5 major peaks (3 peaks for Aroclor 1221). The same peaks that are used for sample quantitation must be used for standards and QC quantitation. The concentrations of each of the major peak are averaged for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be co-eluting with contaminant peaks from the quantitation (i.e. peaks that are significantly larger than would be expected from the rest of the pattern or peaks that have been significantly weathered and are smaller than would be expected). This should be done if there are peaks that differ from the others by a factor of 2 to 5 depending on where the results fall within the calibration curve.

11.3 Second column confirmation of Aroclors is always performed and is reported when requested by the client.

11.4 Dual Column Quantitation

11.4.1 Dual column quantitation is routinely performed for PCB analysis and reported as such when requested by the client.

11.4.2 When reporting the analytical results for field samples of dual column analysis, the higher of the two results is normally reported. The result from the second column confirmation is reported if any of the following is true:

- There is obvious chromatographic interference on the initial quantitation column.
- The difference between the result on the initial quantitation column and the result on the second column is > 40% and chromatographic interference is evident.
- A continuing or bracketing standard fails on the initial quantitation column, but is acceptable on the second column. However, if the difference between the initial quantitation column and second column results is > 40% and the initial quantitation column calibration verification fails, then the sample must be evaluated for reanalysis.

11.4.3 Dual Column Results with > 40% RPD:

- If the relative percent difference (RPD) between the responses on the two columns is greater than 40%, the lower of the two results is reported unless there is obvious interference documented on the chromatogram. If the result is < the RL it will be reported as estimated with a “J” flag.
- If there is visible positive interference, e.g., co-eluting peaks, elevated baseline, etc., for one column and not the other, then

report the results from the column without the interference with the appropriate data qualifier flag, footnote, and/or narrative comment in the final report.

- If there is visible positive interference for both columns, then report the lower of the two results with the appropriate flag, footnote, and/or narrative comment in the final report.
- If the relative percent difference (RPD) between the results on the two columns is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. The RPD is calculated as follows:

$$\%RPD = \frac{|R_1 - R_2|}{1/2(R_1 + R_2)} \times 100\%$$

Where:

R_1 = initial quantitation column result

R_2 = second column result

11.5 Calibration Range and Sample Dilutions

11.5.1 If the concentration of any analyte exceeds the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. Samples that were analyzed immediately following the high sample must be evaluated for carryover. If the samples have results at or above the RL for any analyte, they must be reanalyzed to rule out carryover. It may also be necessary to dilute samples because of matrix interferences.

11.5.2 If the initial diluted run has no hits or hits below 20% of the calibration range, and the matrix allows for analysis at a lesser dilution, then the sample should be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.5.3 Guidance for Dilutions Due to Matrix Interference

If the sample is initially run at a dilution and only minor matrix peaks are present, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination. Ideally, the dilution chosen will make the response of the matrix interferences equal to approximately half the response

of the mid-level calibration standard.

11.5.4 Reporting Dilutions

Some programs (e.g., South Carolina) and some projects require reporting of multiple dilutions (check special requirements in LIMS). In other cases, the most concentrated dilution with no target compounds above the calibration range will be reported. If results are reported from a diluted run, the cause for the dilution should be narrated in an NCM. For dilutions greater than 40X report the surrogates diluted out ("D").

11.6 Interferences in Observed in Samples

11.6.1 Dual column analysis does not entirely eliminate interfering compounds. Complex samples with high background levels of interfering organic compounds can produce false positive and/or false negative results. The analyst must use appropriate judgment to take action as the situation warrants.

11.6.2 Suspected Negative Interferences: If peak detection is prevented by interferences, further cleanup should be attempted. Elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

11.7 Concentration of Analyte in Sample Extract

11.7.1 Depending on the calibration function used, the concentration of the analyte in the sample extract is calculated as follows (see Section 10 for details on establishing the calibration function):

Average Response Factor: $C_{ex} = \frac{R_x C_{is}}{R_{is} RF}$

Linear Regression: $C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$

Where:

Cex = Concentration in the extract, µg/mL

Rx = Response for the analyte

Ris = Response for the internal standard

Cis = Concentration of the internal standard

A = Intercept of linear calibration line

RF = Average response factor

B=Slope of linear calibration line Concentration of Analyte in Original Sample

11.7.2 The concentration of the analyte in the original sample is calculated as follows:

$$C_{sample} = \frac{C_e}{1000\frac{ng}{\mu g}} \times \frac{V_e}{V_s} \times DF$$

Where:

C_{sample} = Concentration of analyte in original sample (µg/L or µg/kg).

C_e = Concentration of analyte in sample extract injected in GC (ng/mL).

$1000\frac{ng}{\mu g}$ = Factor to convert ng/mL to µg/mL.

V_e = Volume of sample extract (mL).

V_s = Volume (or weight) of original sample (L or kg).

DF = Dilution Factor (post extraction dilutions)

11.7.3 Spike Recovery Calculation

$$\%\text{Recovery} = \frac{\text{Measured Concentration}}{\text{Spiked Concentration}} \times 100\%$$

11.7.4 MS/MSD RPD Calculation

$$RPD = \frac{|MS - MSD|}{1/2(MS + MSD)} \times 100\%$$

11.8 All data are subject to two levels of review, which is documented on a checklist, as described in SOP PT-QA-018.

12.0 METHOD PERFORMANCE

12.1 The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 **Demonstration of Capabilities** – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be

performed initially, annually and any time a significant change is made to the analytical system.

12.3 **Method Detection Limit Study** – A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

13.0 POLLUTION CONTROL

13.1 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" and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

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 PT-HS-001. The following waste streams are produced when this method is carried out.

14.2 Methylene Chloride in vials. This waste is placed in waste container identified as "Vials & Extracts", Waste #7.

14.3 Flammable solvents in vials. This waste is placed in waste container identified as "Vials & Extracts", Waste #7.

14.4 Waste flammable solvents. This waste is collected in a waste container identified as "Mixed Flammable Solvent Waste", Waste #3.

14.5 Expired primary and working PCB standards. This waste is placed in a waste container identified as "PCB Standard Waste", Waste #8.

14.6 Samples containing polychlorinated biphenyls (PCB's) at concentrations $\geq$50 ppm are regulated under the Toxic Substance Control Act (TSCA) and must be segregated from all other waste streams. Analysts are responsible for contacting the Group Leader, Sample Control, and the Health and Safety Coordinator immediately if a sample falls into the TSCA category.

15.0 REFERENCES

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 Method 8082, Polychlorinated Biphenyls (PCBs) by Gas Chromatograph, Revision 0, December, 1996

15.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846

Method 8082A, Polychlorinated Biphenyls (PCBs) by Gas Chromatograph, Revision 1, February, 2007

15.3 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 Method 8000B, Determinative Chromatographic Separations, Revision 2, December, 1996

15.4 SOP PT-OP-001, Extraction of Organic Compounds from Waters, SW-846 3500 Series and EPA 600 Series Methods

15.5 SOP PT-OP-026, Extraction of Organic Compounds from Solids, Sediments, Tissues, and Wipes, SW-846 3500 Series Methods

15.6 SOP PT-OP-028, Clean-up of Organic Extracts by SW-846 3600 Series Methods

15.7 SOP PT-QA-001, Employee Orientation and Training

15.8 SOP PT-QA-016, Nonconformance & Corrective Action System

15.9 SOP PT-QA-018, Technical Data Review Requirements

15.10 SOP PT-QA-021, Quality Control Program

15.11 SOP PT-QA-031, Internal Chain of Custody

15.12 PT-QA-M-001, Pittsburgh Laboratory Quality Assurance Manual

15.13 Corporate SOP CA-Q-S-002, Manual Integration

15.14 Corporate Quality Memorandum No. CA-Q-QM-003, Technical Guidance on Reporting of Multicomponent Organochlorine Analytes, September 24, 2009

15.15 Corporate Policy No. CA-T-P-003, Revision 2, Reporting Results for Methods that Require 2nd Column Confirmation, January 2, 2013

15.16 SOP PT-HS-001, Pittsburgh Facility Addendum EH&S Manual, to the Corporate Environmental Health and Safety Manual (CW-E-M-001) for “Waste Management and Pollution Prevention”.

16.0 METHOD MODIFICATIONS:

16.1 Method 8082/8082A references 8000B, which allows the use of third-order calibration curves. This SOP does not allow third-order calibration curves.

17.0 ATTACHMENTS

17.1 Table 1 - Analyte List and Standard Reporting Limits

17.2 Table 2 - Typical Instrument Conditions

17.3 Table 3 - Calibration Levels (µg/mL)

17.4 Table 4 - LCS/Matrix Spike and Surrogate Spike Levels (µg/L)

17.5 Table 5 - Preparation of Calibration Standards

17.6 Appendix A – Analysis of PCB Congeners

18.0 REVISION HISTORY

18.1 Revision 1, 7/27/2009

18.2 Revision 2, 8/5/2011

18.3 Revision 3, 7/24/2011

18.4 Revision 4, 10/16/2012

18.5 Revision 5, 4/25/2014

18.6 Revision 6, 9/28/2015

18.7 Changes to current revision

SOP section	Change from	Change to	Reason
7.9	Internal working standard	Internal working standard	Correction
7.9.1		Added Stock Internal standard text	Update to include IS tock information
7.9.2		Added Internal Standard stock std. of Dibutylchlorendate with concentration of 1000 ug/mL	Update to include 2nd IS
8.2 Table note		Added that South Carolina evaluates holing times to the minute and that South Carolina does not accept LVI extractions	Clarification
9.4 Table and 9.10.3		Added text to note that when IS are added to CCV's no closing CCV is necessary	Clarification
9.9.2		Added "plus internal standard" after "surrogates"	Clarification
9.9.3		Added "peaks" after "3"	Clarification
9.11.6	0.05 min	0.01 min	Correction
9.11.7 through 9.11.12		Added these sections to be in compliance with CA-T-P-005, Policy for Determining RT Windows for GC/ECD Tests	Clarification
9.11.13, 9.11.16 and 9.11.16.1	Removed since this text is now part of section 9.11.9		Correction
9.11.16.2	Moved to section 9.11.9.2		Correction

Table 1				
Standard Analyte List and Reporting Limits				
Compound	**CAS #**	**Reporting Limit, µg/L, µg/wipe or µg/kg**		
		Water/Wipe Regular/ Low Level	**Soil/ Tissue Regular/Low Level**	**Waste**
Aroclor 1016	12674-11-2	0.4/0.01	16.67/0.833	500
Aroclor 1221	11104-28-2	0.4/0.01	16.67/0.833	500
Aroclor 1232	11141-16-5	0.4/0.01	16.67/0.833	500
Aroclor 1242	53469-21-9	0.4/0.01	16.67/0.833	500
Aroclor 1248	12672-29-6	0.4/0.01	16.67/0.833	500
Aroclor 1254	11097-69-1	0.4/0.01	16.67/0.833	500
Aroclor 1260	11096-82-5	0.4/0.01	16.67/0.833	500
Optional Compounds:				
Aroclor 1262	37324-23-5	0.4/0.01	16.67/0.833	500
Aroclor 1268	11100-14-4	0.4/0.01	16.67/0.833	500

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	**Final Vol.**	**Low Level Vol.**
Groundwater	1000 mL	40 mL	1 mL
Wipe	1 wipe	40 mL	NA
Low-Level Soil	30 g / 15 g	40 mL / 20 mL	1 mL
High-Level Soil/Waste	1 g	40 mL	NA
Tissue	6 g	2 mL (1 mL with GPC clean-up)	NA

Table 2	
Typical Instrument Conditions	
Parameter	Recommended Conditions
Injection Port Temperature:	220 °C
Detector Temperature:	325 °C
Temperature Program:	120 °C for 0.75 minute 18 °C/min to 260 °C 1 minute hold 20 °C/min to 300 °C, 1.5 minute hold
Column 1:	RTX-CLP1, 30 m x 0.53 mm id, 0.5 µm
Column 2:	RTX-CLP2, 30 m x 0.53 mm id, 0.42 µm
Injection:	1 or 2 µL
Carrier Gas:	Hydrogen or Helium
Make-up Gas:	Nitrogen

Table 3							
Calibration Levels ng/mL							
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7[1]
AR1660	10	50	200	500	1000	2000	4000
AR1242[2]				500			
AR2154[2]				500			
AR1232[2]				500			
AR1248[2]				500			
Surrogates are included with all the calibration mixes at the following levels:							
TCMX	0.5	2.5	10	25	50	100	200
DCB	0.5	2.5	10	25	50	100	200

[1] Level 7 is optional and should only be used if linearity can be maintained on the instrument to this level.

[2] Aroclors may be quantitated within the range 100 to 2000 ng/mL (4000 ng/mL if the level 6 1016/1260 standard is included). If the Aroclor is more concentrated, it must be reanalyzed at a dilution.

Table 4			
LCS/Matrix Spike and Surrogate Spike Levels for Aroclor Analysis µg/L, µg/wipe or µg/kg			
	Aqueous/Wipe	Soil/Tissue	Waste
Aroclor 1016/1260	10	333	10,000
TCMX (surrogate)	0.20	6.67	200
DCB (surrogate)	0.20	6.67	200

Table 5					
Preparation of Calibration Standards					
Calibration Level	1016/1260 Intermediate (µL)	1221 + 1254 Stock (µL)	1232 Stock (µL)	1242 Stock (µL)	1248 Stock (µL)
Level 1	4				
Level 2	20				
Level 3	80				
Level 4	1000	250	250	250	250
Level 5	400				
Level 6	800				
Level 7	1600				

The surrogate stock is purchased (Decachlorobiphenyl and Tetrachloro-m-xylene) at 200 ug/mL.

The Aroclor 1016 and 1260 stock standards are purchased as certified standards in isooctane at 1000 ug/mL. The other five Aroclor stock standards are purchased at 200 ug/mL.

For Aroclors 1016 and 1260, an intermediate standard is prepared by diluting 1.0 mL of each of the stock standards and 0.25 mL of the surrogate stock standard to 10.0 mL in hexane. The intermediate Aroclor 1016/1260 standard concentrations are 100 ug/mL for each Aroclor and 5 ug/mL for each surrogate.

The Aroclor 1016/1260 calibration standards are prepared by diluting the volumes noted in Table C-6 to a 40.0 mL final volume in hexane except for the Level 3 standard, which is taken to a 200mL final volume in hexane.

The mid-level (Level 3) calibration standards for each of the other five Aroclors (1221, 1232, 1242, 1248, 1254) are prepared by diluting 0.25 mL of the appropriate stock standard to a final volume of 100 mL in hexane. Aroclors 1221 and 1254 are combined into one standard and Aroclors 1232, 1242, and 1248 are prepared individually.

Appendix A

Analysis of PCB Congeners Based on Method 8082A

1.0 SCOPE OF METHOD

1.1 This SOP Appendix describes procedures to be used when SW-846 Method 8000B is applied to the analysis of polychlorinated biphenyls (PCB) congeners by GC/ECD. This Appendix is to be applied when SW-846 Method 8082A is requested, and is applicable to extracts derived from any matrix, which are prepared according to the appropriate TestAmerica sample extraction SOP (PT-OP-001 or PT-OP-026). The PCBs are determined and quantitated as individual PCB congeners.

1.2 Table A-1 lists the congeners, which are routinely determined by this method and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

2.0 SUMMARY OF METHOD

2.1 This method presents conditions for the analysis of prepared extracts for PCB congeners. The PCBs are injected onto the GC column(s) and separated and detected by electron capture detection. Quantitation is by the external standard method.

3.0 DEFINITIONS

3.1 Refer to Section 3 of the main body of this SOP for definitions.

4.0 INTERFERENCES

4.1 Refer to Section 4 of the main body of this SOP for information regarding chromatographic interferences.

5.0 SAFETY

5.1 Refer to Section 5 of the main body of this SOP for general safety requirements.

5.2 PCB congeners have been classified as a potential carcinogen under OSHA. Concentrated solutions of PCB congeners must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

6.0 EQUIPMENT AND SUPPLIES

6.1 Refer to Section 6 of the main body of this SOP for equipment and supplies.

6.2 Refer to Table A-2 for analytical column requirements

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Acetone, 99.4% for organic residue analysis.

7.1.2 Hexane, pesticide grade.

7.1.3 Carrier Gas: ≥ 99.99999% pure hydrogen.

7.1.4 Make-up Gas: ≥ 99.99980% pure nitrogen.

7.2 Standards

7.2.1 Stock Standards

7.2.1.1 All standards must be refrigerated at >0.0˚C but ≤6.0℃. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before use.

7.2.1.2 Stock standards are monitored for signs of degradation or evaporation. The standards must be replaced annually or earlier if the vendor indicates an earlier date.

7.2.1.3 Dilutions from stock standards cannot have a later expiration date than the date assigned to the parent stock solutions. The standards must be replaced at least every six months, or sooner, if comparison with check standards indicates a problem.

7.2.2 PCB Congener and Surrogate Stock Standards

7.2.2.1 PCB Congener Stock Mix 1: For the PCB Congeners listed in Table A-1, except BZ-205 (surrogate), a commercially prepared stock standard solution is obtained. The concentration of the PCB Congeners contained in Mix 1 is 4.0 ug/mL and the concentration of the TCMX (surrogate) is 6.6 ug/mL PCB Congener Stock Add-on Mix: This stock standard is prepared by adding 400 uL of 100 ug/mL of the following individual congener standards brought to a final volume of 10 mL with Hexane and resulting in a final concentration of 4 ug/mL: BZ-205 (surrogate).

7.2.2.2 TCMX (2000 ug/mL) and BZ-205 (100 ug/mL) Surrogate Stock Standards are commercially purchased standards.

7.2.2.3 PCB Congener Matrix Spike Stock Standard is a commercially purchased standard containing BZ-8, BZ-18, BZ-28, BZ-44, BZ-52, BZ-66, BZ-77, BZ-101, BZ-105, BZ-118, BZ-126, BZ-128, BZ-138, BZ-153, BZ-170, BZ-180, BZ-187, BZ-195 and BZ-206 at a concentration of 100 ug/mL. (NOTE: BZ-49, BZ-81, BZ-87, BZ-114, BZ-123, BZ-156, BZ-157, BZ-167, BZ-169, BZ-187 and BZ-189 are also used as needed, however these are separate commercially purchased stock solutions also at a concentration of 100 ug/mL).

7.2.3 Calibration Curve Standard Solutions

The calibration standards are prepared as follows:

Calibration Level	Recipe	Stock Concentration (ug/mL)	Final Volume (ml of Hexane)
1	5 uL of PCB Congener Stock Mix 1 and 5 uL of PCB Congener Stock Add-on Mix	4 ug/mL (TCMX 6.6 ug/mL)	40
2	10 uL of PCB Congener Stock Mix 1 and 10 uL of PCB Congener Stock Add-on Mix	4 ug/mL (TCMX 6.6 ug/mL)	40
3	25 uL of PCB Congener Stock Mix 1 and 25 uL of PCB Congener Stock Add-on Mix	4 ug/mL (TCMX 6.6 ug/mL)	40
4	50 uL of PCB Congener Stock Mix 1 and 50 uL of PCB Congener Stock Add-on Mix	4 ug/mL (TCMX 6.6 ug/mL)	40
5	100 uL of PCB Congener Stock Mix 1 and 100 uL of PCB Congener Stock Add-on Mix	4 ug/mL (TCMX 6.6 ug/mL)	40
6	200 uL of PCB Congener Stock Mix 1 and 200 uL of PCB Congener Stock Add-on Mix	4 ug/mL (TCMX 6.6 ug/mL)	40

7.2.3.1 Refer to Table A-3 for details of calibration standard concentrations.

7.2.4 Surrogate Standards

7.2.4.1 The Working Surrogate Solution is made as follows: 2.5 uL of the 2000 ug/mL commercially purchased TCMX stock and 50 uL of the 100 ug/mL commercially purchased BZ-205 stock brought to a final volume of 20 mL with Acetone (see section 7.2.2.3). The final concentration of the Working Surrogate Solution is 0.025 ug/mL. Refer to Table A-3 for details of surrogate standard concentrations in the calibration standards.

NOTE: The Working Surrogate Solution is prepared and used as part of the scope of the organic preparation SOP PT-OP-001 and PT-OP-026. The preceding information is provided for reference only.

7.2.5 Laboratory Control Standard (LCS) and Matrix Spiking (MS) Solution

The working LCS/MS spiking solution is prepared by combining 1mL of the PCB Congener Matrix Spike Stock Standard and 1 mL each, as needed, of the BZ-49, BZ-81, BZ-87, BZ-114, BZ-123, BZ-156, BZ-157, BZ-167, BZ-169, BZ-187 and BZ-189 stock standards brought to a 100 mL final volume with Acetone. The final concentration of the working LCS/MS spiking solution is 1.0 ug/mL.

NOTE: The LCS/MS spiking solution is prepared and used as part of the scope of the organic preparation SOP SOP PT-OP-001 and PT-OP-026. The following information is provided for reference only.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Refer to Section 8 of the main body of this SOP.

9.0 QUALITY CONTROL

9.1 Refer to Section 9 of the main body of this SOP.

10.0 PROCEDURE

10.1 Calibration and Standardization

10.1.1 PCB Congeners uses an External Standard Calibration as follows:

External standard calibration involves the comparison of instrument responses from the samples to the responses from the target compounds in the calibration standards. The area (or height) of a peak in a sample chromatogram is compared to the area (or height) of the peak in the standard chromatograms that appears at the same retention time. The ratio of the detector response to the concentration of the target analyte in the calibration standard is defined as the calibration factor (CF) and is calculated as follows:

$$CF = \frac{Area\ or\ Height\ of\ Peak}{Mass\ Injected}$$

Note: It is also possible to use the concentration of the standard rather than the mass injected.

10.1.2 Refer to Section 10 of the main body of this SOP for the other general calibration requirements.

10.2 Initial Calibration

10.2.1 Refer to Table A-5 for the initial calibration analytical sequence.

10.2.2 The response for each PCB congener will be calculated by the procedures described in the general method for 8082A analysis, with the following modifications.

10.2.3 A minimum five-point calibration of each of the individual congeners mixes is generated. At least 2 separate mixes are prepared to ensure that there is complete resolution of all congeners in the mixes. Calibration levels are listed in Table A-3. Refer to Table A-6 for preparation of calibration levels.

10.3 Initial Calibration Verification

10.3.1 The ICV will consist of second source standards of all congeners of interest. The ICV is prepared from a second source stock standard of a concentration of 4ppm for all congeners of interest. 25 uL of the ICV stock standard is added to Hexane and brought to a final volume of 40 mL for a concentration of 0.0025 ppm.

10.3.2 Refer to section 9.9.4 in the main body of this SOP for acceptance criteria

and corrective actions for failures.

10.3.3 12 hour Calibration

The 12-hour calibration verification must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12-hour calibration.

The retention time windows for any analytes included in the daily calibration are updated.

For this method, samples must be bracketed with successful calibration verification runs.

10.3.4 Calibration Verification

10.3.4.1 A mid-level calibration mix is analyzed as the calibration verification standard. This is analyzed after every 20 samples or 12 hours, including matrix spikes, LCS, and method blanks. (Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns.).

10.3.4.2 The daily CCV analysis at a concentration other than the mid-level (to meet NELAC requirements) will consist of all of the congeners of interest. All other CCVs will be mid-level calibration standards.

10.3.5 Procedure - Refer to Section 10 of the main body of this SOP for general procedural requirements.

10.3.6 Suggested gas chromatographic conditions are given in Table A-2.

10.3.7 The suggested analytical sequence is given in Table A-5.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Identification of Congeners

Retention time windows are used for identification of PCB congeners. Second column confirmation must be performed.

11.2 Refer to section 11 of the main body of this SOP for calculation details.

12.0 METHOD PERFORMANCE

12.1 Refer to section 12.3 for initial demonstration of capability requirements under Section 12 of the main body of this SOP. The LCS spiking level is used for IDOC.

13.0 POLLUTION CONTROL

13.1 Refer to Section 13 of the main body of this SOP.

14.0 WASTE MANAGEMENT

14.1 Refer to Section 14 of the main body of this SOP.

15.0 REFERENCES

15.1 Refer to Section 15 of the main body of this SOP.

16.0 METHOD MODIFICATIONS

16.1 Refer to Section 16 of the main body of this SOP.

17.0 ATTACHMENTS

17.1 Table A-1: Standard Analyte List and Reporting Limits
17.2 Table A-2: Recommended GC Operating Conditions
17.3 Table A-3: Calibration Levels
17.4 Table A-4: LCS/Matrix Spike and Surrogate Spike Levels
17.5 Table A-5: Suggested Analytical Sequence

18.0 REVISION HISTORY

18.1 See section 18 of the Main Body of this SOP.

Table A-1
Standard Analyte List and Reporting Limits

Reporting Limit					
Compound *	**CAS #**	**Water ng/L**	**Soil/Sediment/Tissue ug/kg**	**Wipe ng/wipe**	**Waste ug/kg**
BZ-8	34883-43-7	1.0	1.0	1.0	10
BZ-18	37680-65-2	1.0	1.0	1.0	10
BZ-28	7012-37-5	1.0	1.0	1.0	10
BZ-44	41464-39-5	1.0	1.0	1.0	10
BZ-49	41464-40-8	1.0	1.0	1.0	10
BZ-52	35693-99-3	1.0	1.0	1.0	10
BZ-66	32598-10-0	1.0	1.0	1.0	10
BZ-77	32598-13-3	1.0	1.0	1.0	10
BZ-81	70362-50-4	1.0	1.0	1.0	10
BZ-87	38380-02-8	1.0	1.0	1.0	10
BZ-101	37680-73-2	1.0	1.0	1.0	10
BZ-105	32598-14-4	1.0	1.0	1.0	10
BZ-114	74472-37-0	1.0	1.0	1.0	10
BZ-118	31508-00-6	1.0	1.0	1.0	10
BZ-123	65510-44-3	1.0	1.0	1.0	10
BZ-126	57465-28-8	1.0	1.0	1.0	10
BZ-128	38380-07-3	1.0	1.0	1.0	10
BZ-138	35065-28-2	1.0	1.0	1.0	10
BZ-153	35065-27-1	1.0	1.0	1.0	10
BZ-156	38380-08-4	1.0	1.0	1.0	10
BZ-157	69782-90-7	1.0	1.0	1.0	10
BZ-167	52663-72-6	1.0	1.0	1.0	10
BZ-169	32774-16-6	1.0	1.0	1.0	10
BZ-170	35065-30-6	1.0	1.0	1.0	10
BZ-180	35065-29-3	1.0	1.0	1.0	10
BZ-183	52663-69-1	1.0	1.0	1.0	10
BZ-184	74472-48-3	1.0	1.0	1.0	10
BZ-187	52663-68-0	1.0	1.0	1.0	10
BZ-189	39635-31-9	1.0	1.0	1.0	10
BZ-195	52663-78-2	1.0	1.0	1.0	10
BZ-206	40186-72-9	1.0	1.0	1.0	10
BZ-209	2051-24-3	1.0	1.0	1.0	10

* The congener identifications are consistent with the short-hand identifications recommended by Ballschmiter and Zell (1980).

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Volume	Dilution Factor
Groundwater	1000 mL	2 mL	1
Soil/Tissue/Sediment	10 g	20 mL	1
Waste	1 g	20 mL	1
Wipe	1 wipe	2 mL	1

Table A-2

Parameter	Recommended Conditions
Injection port temp	225°C
Detector temp	325°C
Temperature program	80°C ramping 30°C/min to 190°C, then 20°C/min to 230°C, then 4°C/min to 270°C and finally 20°C/min to 300°C holding for 5 minutes (22 minute run-time)
Column 1	ZB 50, 30 m, 0.25 mm id, 0.25 µm FT
Column 2	ZB 1701, 30 m, 0.25 mm id, 0.25 µm FT
Injection	1-2µL
Carrier gas	Hydrogen
Make up gas	Nitrogen

Table A-3						
Calibration Levels ug/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
BZ-8	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-18	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-28	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-44	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-49	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-52	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-66	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-77	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-81	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-87	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-101	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-105	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-114	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-118	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-123	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-126	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-128	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-138	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-153	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-156	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-157	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-167	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-169	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-170	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-180	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-183	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-184	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-187	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-189	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-195	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-206	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-209	0.0005	0.001	0.0025	0.0050	0.010	0.020
SURROGATES						
TCMX	0.000825	0.00165	0.004125	0.00825	0.0165	0.033
BZ-205	0.0005	0.001	0.0025	0.0050	0.010	0.020

Table A-4				
LCS/Matrix Spike and Surrogate Spike Levels for Congener Analysis[1]				
ng/L, ng/wipe or ug/kg				
Compound	Aqueous	Soil/Sediment/Tissue	Wipe	Waste
BZ-8	20	20	20	200
BZ-18	20	20	20	200
BZ-28	20	20	20	200
BZ-44	20	20	20	200
BZ-49	20	20	20	200
BZ-52	20	20	20	200
BZ-66	20	20	20	200
BZ-77	20	20	20	200
BZ-81	20	20	20	200
BZ-87	20	20	20	200
BZ-101	20	20	20	200
BZ-105	20	20	20	200
BZ-114	20	20	20	200
BZ-118	20	20	20	200
BZ-126	20	20	20	200
BZ-123	20	20	20	200
BZ-128	20	20	20	200
BZ-138	20	20	20	200
BZ-153	20	20	20	200
BZ-156	20	20	20	200
BZ-157	20	20	20	200
BZ-167	20	20	20	200
BZ-169	20	20	20	200
BZ-170	20	20	20	200
BZ-180	20	20	20	200
BZ-183	20	20	20	200
BZ-184	20	20	20	200
BZ-187	20	20	20	200
BZ-189	20	20	20	200
BZ-195	20	20	20	200
BZ-206	20	20	20	200
BZ-209	20	20	20	200
Surrogates				
TCMX	5	5	5	50
BZ-205	5	5	5	50

[1]Individual Congeners are spiked as needed.

Table A-5		
Suggested Analytical Sequence		
Initial Calibration		
Injection #		
Solvent blank (optional)		
PCB Congener Mix 1	5-point	6-point
ICV (second source standard(s) of all congeners of interest)		
Samples 1-20 (or 12 hours, whichever is more frequent)		
Solvent blank (optional)		
PCB Congener Mix 1		Level 3
After 12 hours:		
PCB Congener Mix 1		Level 3
Samples 1-20 (or 12 hours)		
Solvent blank (optional)		
PCB Congener Mix 1		Level 3
12 hour Calibration		

At least every 24 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Acid Digestion of Soils

Method: SW846 Method 3050B

Approvals (Signature/Date):

10/28/2015	10/20/2015
Roseann Ruyechan Date	Steve Jackson Date
Inorganics Department Manager	Regional Safety Coordinator
10/19/2015	10/29/2015
Virginia Zusman Date	Deborah L. Lowe Date
Quality Assurance Manager	Laboratory Director

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of soil samples for the analysis of certain metals by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) and Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) as specified in SW846 Method 3050B.

1.2. Samples prepared by the protocols detailed in this SOP may be analyzed by ICP or ICP/MS for the elements listed in Table I (Appendix A). Other elements and matrices may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 12.0 of this SOP are met.

1.3. This method is not a total digestion, but will dissolve almost all metals that could become "environmentally available". By design, metals bound in silicate structures are not dissolved by this procedure, as they are not usually mobile in the environment. This SOP can be applied to metals in solids, sludges, wastes, sediments, wipes and tissues.

1.4. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

1.5. On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated in PT-QA-M-001, Quality Assurance Manual.

2. SUMMARY OF METHOD

2.1. A representative 1-2gram (wet weight) portion of sample is digested in nitric acid and hydrogen peroxide. The digestate is refluxed with hydrochloric acid for ICP and ICP/MS analysis. The digestates are then filtered and diluted to 100mL.

3. DEFINITIONS

3.1. TALS – TestAmerica Laboratory Information Management System

3.2. NCM – Non-Conformance Memo – a system within TALS for the lab to communicate to project management and others when there is an anomaly seen with the samples or batch, or a QC failure.

3.3. Please refer to the glossary in the Laboratory Quality Assurance Manual (PT-QA-M-001) for additional definitions.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix C for additional contamination control guidelines.

4.3. Boron and silica from the glassware will leach into the sample solution during and following sample processing. For critical low-level determinations of boron and silica, only plastic, Teflon or quartz labware should be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.

4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric media.

4.7. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-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.

5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. All heating of samples must be carried out in a fume hood.

5.4. 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 analyst should also be aware of the potential for a vigorous reaction.

5.5. 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
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	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.
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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.6. 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 become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.7. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit or under other means of mechanical ventilation.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported immediately to a laboratory supervisor or EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1. Hot block capable of maintaining a temperature of 90-95°C (A hot plate or other heat source may be used if capable of maintaining temperature.)

6.2. Thermometer that covers a temperature range of 50-110°C

6.3. Hot block Disposable Digestion Cup (from Environmental Express)

6.4. Ribbed watch glasses or other equivalent vapor recovery device

6.5. Whatman No. 41 filter paper or equivalent

6.6. Funnels or equivalent filtration apparatus

6.7. Centrifugation equipment (optional)

6.8. Graduated cylinder or equivalent vessel capable of measuring 100 mL within 3% accuracy

6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams

6.10. Repipetor or equivalent reagent dispensers

6.11. Calibrated volumetric pipettes with corresponding pipette tips or Class A glass volumetric pipettes

6.12. Class A volumetric flasks

6.13. pH indicator strips, pH range 0 - 6

6.14. Plastic bottles

6.15. Teflon chips

7. REAGENTS AND STANDARDS

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the SDS prior to the use of any reagent or standard.

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom TestAmerica solutions. All standards must be stored in original manufacturer's container and the standards that contain silver are covered to prevent light degradation. 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. Working ICP LCS/MS spike solution: The ICP LCS/MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

7.3.1. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom TestAmerica solution, a solution must be purchased from a designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.3.2. Refer to Table II (Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for the LCS and matrix spikes.

7.4. Nitric acid (HNO_3), concentrated, trace metal grade or better. For ICPMS analysis, Optima reagents (ultra pure) are used for sample preparation.

7.4.1. Nitric acid, 1:1 - dilute concentrated HNO_3 with an equal volume of reagent water.

Caution: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.5. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.5.1. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

7.6. 30% Hydrogen peroxide (H_2O_2), reagent or ultrex grade.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2. Soil and wipe samples do not require preservation but must be stored at >0.0˚C but ≤6.0 °C until the time of analysis. Tissue samples will be stored frozen.

9. QUALITY CONTROL

9.1. The following Quality Control samples are required to be prepared along with each batch of 20 or fewer samples. Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not counted towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: PT-MT-001 & PT-MT-002	Redigest and reanalyze samples.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: PT-MT-001 & PT-MT-002	Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: PT-MT-001 & PT-MT-002	Reprep not required unless preparation error suspected.
Matrix Spike Duplicate	See Matrix Spike	Refer to determinative SOPs: PT-MT-001 & PT-MT-002	See Corrective Action for Matrix Spike.

9.2. Method Blank (MB) - One method blank must be processed along with each preparation batch. The method blank consists of approximately 1 gram of Teflon chips, to which all reagents specific to the method are added and then carried through the entire analytical procedure along with the samples. The method blank 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. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs, the blank and all associated samples in the batch must be redigested.

9.3. Laboratory Control Sample (LCS) - One LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Table II provides the details regarding the final spike concentrations for the LCS.

9.3.1. The LCS is prepared by spiking a 1g aliquot of Teflon chips with 1mL of the working LCS/MS spike solution (7.3).

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to an MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Refer to the analytical SOPs for control limits and corrective actions. Table II provides the details regarding the final matrix spike concentrations.

9.4.1. The soil matrix spike sample is prepared by spiking a 1g aliquot of a sample with 1mL of the working LCS/MS spike solution (7.3).

10. PROCEDURE

10.1. Hotplate or hot block temperature must be verified daily for each unit used and must be recorded on either the metals preparation log or in a hotplate/hotblock temperature logbook. The hotplate/hotblock temperature should be verified by

measuring the temperature of a beaker of reagent water placed on each hotplate/hotblock. For block digestors, use a tube containing water.

10.2. All preparation procedures must be carried out in a properly functioning hood.

10.3. Proper sample identification is extremely important in any preparation procedure. Labeling of digestion tubes and digestate containers must be done in a manner to ensure connection with the proper sample. Digestion tubes must be labeled in a manner that the labeling will not be damaged by contact with the hot block. The use of automatic label printing programs is recommended to reduce transcription errors.

10.4. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the department manager or designee or project administrator/manager for further instructions. In some cases it may be more appropriate to process these samples as solids.

10.5. Preparation of Soils, Sediments, Sludges, Tissues or Wipes for Analysis by ICP or ICP/MS

10.5.1. Mix sample thoroughly by stirring with a clean plastic or wooden spoon or spatula.

- Refer to SOP PT-QA-024 for subsampling procedures.
- For wipe samples, the entire wipe is used in the digestion.

10.5.2. For each sample, weigh between 1.0 and 2.0 gram portion of solid into the digestion tube. An alternate sample size may also be used if needed to meet the reporting limits. Record the exact weight to the nearest 0.01g.

- For wipe samples, the entire sample is digested and no subsampling is permitted.

10.5.3. Measure 2 additional aliquots of the designated samples for the MS and MSD analyses.

- Due to the unique nature of wipe samples, an MS and MSD are not possible. An LCS/LCSD is used to satisfy precision and accuracy requirements for wipe batches.

10.5.4. Add approximately 1gram of Teflon chips to the digestion tube for the MB and LCS.

- Use 0.5 mL of reagent water, rather than Teflon chips, for the MB, LCS and LCSD associated with wipe samples.

10.5.5. Spike the LCS and each of the MS and MSD aliquots with 1 mL of the working LCS/MS spiking solution (7.3).

10.5.6. Add 10 mL of 1:1 HNO_3 and mix the sample.

- For wipes, add 5 mL of 1:1 HNO_3 and mix the sample.

10.5.7. Cover with a ribbed watch glass (or other vapor recovery device).

10.5.8. Heat sample to 95°C ± 5°C and reflux for 10 minutes without boiling.

Note: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY during any part of the digestion. Doing so will result in the loss of analyte and the sample must be reprepared.

10.5.9. Allow sample to cool.

10.5.10. Add 5 mL of concentrated HNO_3 and replace the watch glass.

- For wipes, add 2.5 mL of concentrated HNO_3 and replace the watch glass.

10.5.11. Reflux at 95°C for 30 minutes. Add reagent water as needed to ensure that the volume of solution is not reduced to less than 5 mL.

10.5.12. If brown fumes are observed, repeat steps 10.5.10 and 10.5.11 until no more fumes are evolved.

10.5.13. Cover the tube with a ribbed watch glass, return the tube to the hot block, and allow the sample to evaporate to 5 - 10 mL while ensuring that no portion of the bottom of the tube is allowed to go dry. Alternatively heat at 95°C ± 5°C for 2 hours.

10.5.14. Allow the samples to cool.

10.5.15. Add 2 mL of reagent water and 3 mL of 30 % H_2O_2. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

- For wipes, add 1 mL of reagent water and 1.5 mL of 30 % H_2O_2. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

10.5.16. Replace the watch glass and heat sample until effervescence subsides.

10.5.17. Allow the sample to cool.

10.5.18. Continue adding 30% H_2O_2 in 1 to 2 mL aliquots and heating covered samples until effervescence is minimal or sample appearance is unchanged.

Note: Do not add more than a total of 10 mL (5 ml for wipe samples) of 30 % H_2O_2.

10.5.19. Continue heating at 95°C ± 5°C until the volume is reduced to approximately 5 mL. Alternatively the sample may be heated for 2 hours.

10.5.20. Add 10 mL of concentrated HCl and reflux for an additional 15 minutes without boiling.

- For wipes, add 5 mL of concentrated HCl and reflux for an additional 15 minutes without boiling.

Note: Antimony and silver have poor solubility in dilute nitric acid solution. Therefore it is strongly recommended that these elements are always determined by the procedure that includes HCl as the final digestion acid.

10.5.21. Allow the sample to cool.

10.5.22. Wash down beaker walls and watch glass with reagent water.

10.5.23. Filter sample through Whatman 41 filter paper, or equivalent, into a volumetric container. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.5.24. Dilute sample to 100 mL with reagent water. The sample is now ready for analysis.

- For wipe samples, dilute sample to 50 mL or 50g with reagent water. The sample is now ready for analysis.

10.6. Documentation and Record Management

10.6.1. The TALS preparation batch should, at a minimum, include the following information:

- Preparation date, analyst ID, matrix, analysis type (ICP or ICP/MS)
- Sample IDs, initial volume and final volume
- Standards Documentation (TALS ID and volume added)
- Reagent lot and volume information
- Balance, hot block and thermometer ID
- Block temperatures
- Reviewer ID

11. CALCULATIONS / DATA REDUCTION

Not Applicable.

12. METHOD PERFORMANCE

12.1. The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilities – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Method Detection Limit Study – A Method Detection Limit (MDL) study, as described in the QA Manual, and SOP PT-QA-007, must be performed initially, annually and any time a significant change is made to the analytical system.

13. POLLUTION CONTROL

13.1. 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" and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

13.2. This method does not contain any specific modifications that serve to minimize or prevent pollution.

WASTE MANAGEMENT

13.3. 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 CW-E-M-001. The following waste streams are produced when this method is carried out.

13.3.1. Contaminated disposable materials utilized for the analysis. These items are placed in trash containers which are emptied in the general trash dumpster located near the shipping/receiving dock.

13.3.2. Acidic waste containing nitric acid generated by the digestion. This waste is collected in a waste container identified as “Acid Waste”, Waste #33. This waste is neutralized to a final pH between 5 and 9 and discharged down into a lab sink.

13.3.3. This waste is collected in a container identified as “Acid Waste”, Waste #6. Acid waste consisting of sample and rinse solution will be collected and placed in the acidic waste stream 55 gallon poly drum. Never use metal containers for acidic waste.

14. REFERENCES

14.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, December 1996. Method 3050B

14.2. SOP PT-MT-001, Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP) for Methods 6010B, 6010C, 6010D, and 200.7

14.3. SOP PT-MT-002, Analysis of Metals by Inductively Coupled Plasma/Mass Spectrometry (ICPMS) for Methods 200.8, 6020, 6020A

14.4. PT-QA-M-001, Pittsburgh Laboratory Quality Assurance Manual

14.5. PT-HS-001, Pittsburgh Facility Addendum EH&S Manual; and CW-E-M-001, Test America Corporate EH&S Manual

14.6. SOP PT-QA-007, Method Detection Limits

14.7. SOP PT-QA-012, Selection and Calibration of Balances and Weights

14.8. SOP PT-QA-016, Nonconformance and Corrective Action System

14.9. SOP PT-QA-017, Aqueous Pipette/Dispenser Calibration – Gravimetric Method

14.10. SOP PT-QA-021, Quality Control Program

14.11. SOP PT-QA-024, Subsampling

14.12. SOP PT-QA-031, Internal Chain of Custody

15. METHOD MODIFICATIONS

15.1. Modifications/Interpretations from reference method.

16.1.1 Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants, as defined in the determinative SOPs, are allowed up to five times the reporting limit in the blank following consultation

with the client. All results associated with a MB that is contaminated above the MDL are reported with appropriate qualifier, but re-digestion is not performed unless the contamination is above the reporting limit.

16. ATTACHMENTS

16.1. Figure 1 – Soil Sample Preparation

16.2. Appendix A – Tables

16.2.1. Table I – Method 3050B Approved Analyte List

16.2.2. Table II – ICP & ICPMS Soil Matrix Spike and LCS Levels

16.3. Appendix B – TALS Metals Prep Worksheet

16.4. Appendix C – Contamination Control Guidelines

17. REVISION HISTORY

17.1. Revision 7, 09/12/07

17.2. Revision 8, 04/28/09

17.3. Revision 9, 02/08/2010

17.4. Revision 10, 01/14/2013

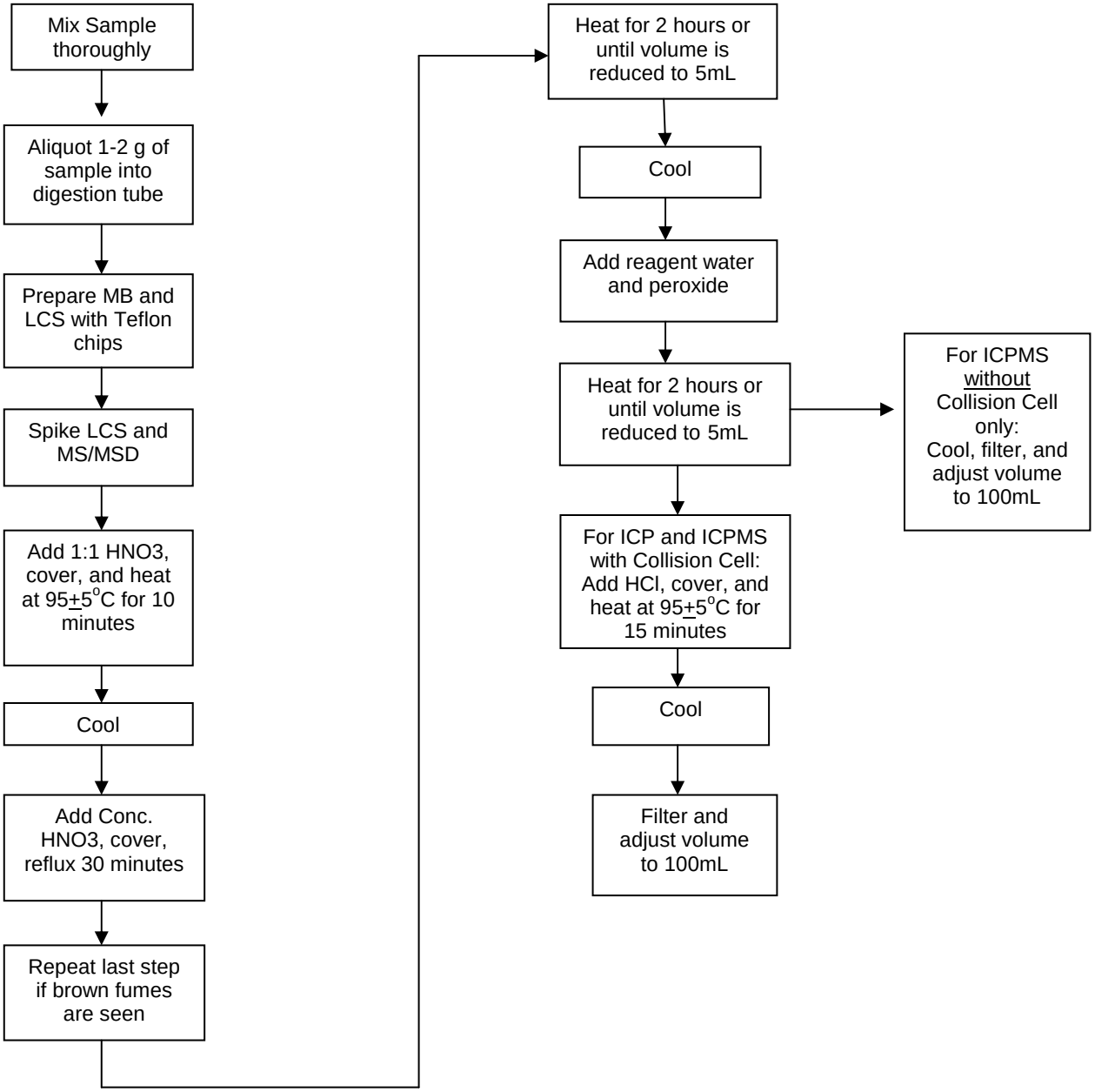
17.5. Revision 11, 09/18/2013

17.6. Revision 12, 09/xx/2015

SOPSECTION	Change from	Change to	Reason
Cover	QAM – Violet Fanning	QAM –Virginia Zusman	Change in personnel
Entire SOP	Removed DoD references throughout the SOP		Correction

Section 10		Added "(ribbed watch glass)" after vapor recovery device throughout section 10	Clarification
1.4 and 1.5	Removed method modification text	Added SOP Checklist text on method modifications as section 1.5	Clarification
5.1, 13.1 and 15.9		Added reference to the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001)	SOP Checklist format
5.4	MSDS	SDS	Compliance with industry standard
8.1	≤6.0˚C	≥0.0˚C but ≤6.0˚C	SOP Review Sheet format
10.8.9, 10.8.14 and 10.8.20	95˚C	95˚C ± 5˚C	Correction
10.8.13	10.10.11 and 10.10.12	10.8.11 and 10.8.12	Correction
10.8.21		Added 'if collision cell technology (CCT) is NOT used for analysis. IF CCT is used in the analysis proceed to section 10.8.2.2	Clarification
10.7		Added 'by CCT' after 'elements' in the sentence	Clarification
10.8	Removed " and reporting group"		Correction
12.2		Added DOC text from SOP Review Checklist	SOP Checklist format
14.1	Removed 'an accepted manner'	Added 'accordance with all federal and state laws and regulations'	SOP Checklist format
15.10 through 15.15		Added Reference to the following SOP's: PT-HS-001, PT-SR-001, PT-QA-009, PT-QA-012, PT-QA-016, PT-QA-017 and PT-QA-031	Correction
Figure 2		Added 'when CCT NOT used' Block	Clarification

Figure 1 - Soil Sample Preparation (Section 10.5)



APPENDIX A

TABLES

TABLE I - Method 3050B Approved Analyte List

ELEMENT	Symbol	CAS Number
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
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
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
Thallium	Tl	7440-28-0
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

TABLE II - ICP & ICPMS Soil Matrix Spike and LCS Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/MS Level* (ug/L)	Soil LCS/MS Level ** (mg/Kg)
Aluminum	200	2000	200
Antimony	50	500	50
Arsenic	200 (ICP); 4 (ICPMS)	2000 (ICP); 40 (ICPMS)	200 (ICP); 4 (ICPMS)
Barium	200	2000	200
Beryllium	5	50	5
Cadmium	5	50	5
Calcium	5000	50000	5000
Chromium	20	200	20
Cobalt	50	500	50
Copper	25	250	25
Iron	100	1000	100
Lead	50 (ICP); 2 (ICPMS)	500 (ICP); 20 (ICPMS)	50 (ICP); 2 (ICPMS)
Lithium	100	1000	100
Magnesium	5000	50000	5000
Manganese	50	500	50
Molybdenum	100	1000	100
Nickel	50	500	50
Phosphorous	1000	10000	1000
Potassium	5000	50000	5000
Selenium	200 (ICP); 1 (ICPMS)	2000 (ICP); 10 (ICPMS)	200 (ICP); 1 (ICPMS)
Silver	5	50	5
Sodium	5000	50000	5000
Strontium	100	1000	100
Thallium	200 (ICP); 5 (ICPMS)	2000 (ICP); 50 (ICPMS)	200 (ICP); 5 (ICPMS)
Vanadium	50	500	50
Zinc	50	500	50
Boron	100	1000	100
Silica	1000	10000	1000
Tin	200	2000	200
Titanium	100	1000	100

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.3) to 100 mL of sample.

** Final soil spike concentration based on the addition of 1.0 mL working spike (7.3) to 1.0 g of sample (or 1.0 g of Teflon chips for the LCS)/100 mL final volume (assumes 100% solids).

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APPENDIX B - EXAMPLE TALS LIMS METALS PREP WORKSHEET

Metals/Inorganics Prep Worksheet

(Used for Collecting Prep Info)

Batch Number: 180-36239
Method Code: 180-3050B-180

Analyst: Shook, Caitlin N

Batch Open: 5/16/2012 3:50:00PM
Batch End: 5/16/2012 7:50:00PM

Preparation, Metals

	Input Sample Lab ID	Input Sample Lab ID (Analytical Method)	SDG	Matrix	Initial Amount	Final Amount	Due Date	Analytical TAT	Dlv Rank	Comments
1	[redacted]	MB~180-36239/1 N/A	N/A		1 mL	100 mL	N/A	N/A	N/A	DI WATER
2	[redacted]	LCS~180-36239/2 N/A	N/A		1 mL	100 mL	N/A	N/A	N/A	DI WATER
3	[redacted]	LCSD~180-36239/3 N/A	N/A		1 mL	100 mL	N/A	N/A	N/A	DI WATER
4	[redacted]	180-10635-A-1-C (6010B)	N/A	TCLP	1 mL	100 mL	5/30/12	13_Days - R	N/A	

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APPENDIX B - EXAMPLE TALS LIMS METALS PREP WORKSHEET (CONT.)

Metals/Inorganics Prep Worksheet

(Used for Collecting Prep Info)

Batch Number: 180-36239 Analyst: Shook, Caitlin N Batch Open: 5/16/2012 3:50:00PM
Method Code: 180-3050B-180 Batch End: 5/16/2012 7:50:00PM

Batch Notes

Perform Calculation (0=No, 1=Yes)	1
Nominal Amount Used	1mL
Digestion Tube/Cup Lot #	1111173
Blank Soil Lot Number	120313
Balance ID	P1856710
Hood ID or number	NA
Hot Block ID number	#9
Lot # of hydrochloric acid	10mL 395624
Lot # of Nitric Acid	5mL 395620
Logbook ID for diluted Nitric	10mL 403550
Hydrogen peroxide lot number	10mL 411714
ID number of the thermometer	IP18 (-1.0)
Temperature	94
Filter Paper Lot Number	4645986A
Acid used for pH adjustment	NA
Pipette ID	03F95602
Analyst	CS
First Start time	15:50
First End time	19:50
Person's name who witnessed reagent drop	CS

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APPENDIX B - EXAMPLE TALS LIMS METALS PREP WORKSHEET (CONT.)

Metals/Inorganics Prep Worksheet

(Used for Collecting Prep Info)

Batch Number: 180-36239 Analyst: Shook, Caitlin N Batch Open: 5/16/2012 3:50:00PM
Method Code: 180-3050B-180 Batch End: 5/16/2012 7:50:00PM

Uncorrected Temperature	95
Oven, Bath or Block Temperature 1	94
Uncorrected Temperature 2	NA
Oven, Bath or Block Temperature 2	NA
Batch Comment	METALS C5

Comments

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APPENDIX B - EXAMPLE TALS LIMS METALS PREP WORKSHEET (CONT.)

Metals/Inorganics Prep Worksheet

(Used for Collecting Prep Info)

Batch Number: 180-36239
Method Code: 180-3050B-180

Analyst: Shook, Caitlin N

Batch Open: 5/16/2012 3:50:00PM
Batch End: 5/16/2012 7:50:00PM

Reagent Additions Worksheet

Lab ID	Reagent Code	Amount Added	Final Amount	By	Witness
LCS 180-36239/2	MTAPITTMSA_00007	1.0 mL	100 mL		
LCS 180-36239/2	MTAPITTMSBREV_00001	1.0 mL	100 mL		
LCS 180-36239/2	MTAPITTMSC_00012	1.0 mL	100 mL		
LCSD 180-36239/3	MTAPITTMSA_00007	1.0 mL	100 mL		
LCSD 180-36239/3	MTAPITTMSBREV_00001	1.0 mL	100 mL		
LCSD 180-36239/3	MTAPITTMSC_00012	1.0 mL	100 mL		

Other Reagents:

Reagent	Amount/Units	Lot#:

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APPENDIX C

CONTAMINATION CONTROL GUIDELINES

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 nitric 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 or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile 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 soak with sulfuric acid prior to routine cleaning.

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: ACID DIGESTION OF AQUEOUS SAMPLES

Method(s): SW846 3005A and 3010A and EPA Methods 200.7 and 200.8

Approvals (Signature/Date):

	7/26/2016		7/22/2016
Roseann Ruyechan Inorganics Department Manager	Date	Steve Jackson Regional Safety Coordinator	Date
	7/21/2016		7/22/2016
Virginia Zusman Quality Assurance Manager	Date	Deborah L. Lowe Laboratory Director	Date

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of aqueous samples for the analysis of certain metals by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) and ICPMS using the MCAWW Method 200.7 (NPDES), EPA Method 200.8 and SW846 Methods 3005A and 3010A (RCRA).

1.2. The applicability of each of these preparation protocols to specific analytes is detailed in Tables I and II in Appendix A. Additional elements may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 12.0 of this SOP are met.

1.3. This SOP provides procedures applicable to the preparation of dissolved, total recoverable and total metals elements in surface water, ground water, aqueous samples, leachates/extracts.

1.4. SW-846 Method 3005A is used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by ICP or ICPMS. TCLP extracts of samples from West Virginia will also use method 3005A for digestion.

1.5. ICP Method 200.7 and ICPMS Method 200.8 are used to prepare surface water, domestic and industrial waste samples for total recoverable and dissolved metals.

1.6. SW-846 Method 3010A is used to prepare TCLP Leachates for total metals analysis by ICP or ICPMS. TCLP extracts of samples from West Virginia will use method 3005A for digestion instead of method 3010A.

1.7. When dissolved metals analysis is requested the samples must be field filtered at the time of collection and prior to preservation.

1.8. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators do require digestion of dissolved samples and this must be clarified before project initiation.

1.9. On occasion clients may request modifications to this SOP. These modifications are handled as indicated in PT-QA-M-001, the Quality Assurance Manual.

2. SUMMARY OF METHOD

2.1. Method 3005A for Method 6010B/C ICP or 6020/6020A ICPMS - Preparation for Total Recoverable or Dissolved Metals Analysis and TCLP Metals for West Virginia.

2.1.1. A representative aliquot of sample is heated with nitric and hydrochloric acids and substantially reduced in volume. The digestate is filtered (if necessary) and diluted to volume.

2.2. Method 3010A - Preparation for Total and TCLP Metals Analysis by Method 6010B/C ICP or 6020/6020A ICPMS.

2.2.1. A representative aliquot of sample is refluxed with nitric acid. This step is repeated until the digestate is light in color or until its color has stabilized. After the digestate has been reduced to a low volume, it is refluxed with hydrochloric acid, filtered (if necessary) and brought up to volume.

2.3. Methods 200.7 and 200.8 have method specific preparations included.

2.3.1. A representative samples, with <1% suspended solids, is refluxed with nitric and hydrochloric acid and substantially reduced in volume. The digestate is filtered (if necessary) and diluted to volume.

2.4. Refer to PT-QA-024 for subsampling procedures.

3. DEFINITIONS

3.1. Dissolved Metals: Those elements that pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

3.5. TALS: TestAmerica Laboratory Information Management System

3.6. NCM: Non-Conformance Memo, an electronic memo from the lab to reviewers and Project Managers, to notify them of a non-conformance, anomaly, or special condition associated with a sample or analytical batch.

3.7. Refer to the glossary in the Laboratory Quality Assurance Manual (PT-QA-M- 001) current version, for additional definitions.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them. Glass and metal labware and powdered gloves are avoided in this area to reduce contamination chances.

4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix C for additional contamination control guidelines.

4.3. Boron and silica from the glassware will migrate into the sample solution during and following sample processing. For critical low-level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they are documented in a sample NCM. Reactions or anomalies such as foaming, emulsions, precipitates, etc., must also be documented.

4.5. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric acid media.

4.6. Precipitation of silver chloride (AgCl) may occur when chloride ions and high concentrations of silver (i.e., greater than 1 mg/L) are present in the sample. If this is suspected, samples may be re-digested at a dilution.

4.7. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-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.

5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. 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 analyst should also be aware of the potential for a vigorous reaction.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. 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
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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5. 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 become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit or under other means of mechanical ventilation.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported immediately to a laboratory supervisor and the EHSC.

6. EQUIPMENT AND SUPPLIES

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1. Hot block, or other adjustable heating source capable of maintaining a temperature of 80 - 95°C

6.2. Thermometer that covers a temperature range of 0-150°C

6.3. Hot Block Disposable Digestion Tubes (from Environmental Express), 50mL, with nominal volume marking certified within Class A tolerance

6.4. Watch glasses, plastic disposable (from Environmental Express)

6.5. Plunger filters, plastic disposable (from Environmental Express)

6.6. Whatman No. 41 filter paper

6.7. Funnels or equivalent plastic filtration apparatus

6.8. Analytical balance capable of accurately weighing to the nearest 0.01 grams

6.9. Repipetors or suitable reagent dispensers

6.10. Calibrated automatic pipettes with corresponding pipet tips

6.11. Class A volumetric flasks

6.12. pH indicator strips (pH range 0 - 6)

6.13. Plastic digestate storage bottles (from Environmental Express)

7. REAGENTS AND STANDARD

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

7.1. Reagent water must be produced by a Millipore DI system. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom TestAmerica solutions. All standards must be stored in the original container or

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 from receipt and must be replaced sooner if verification from an independent source indicates a problem.

7.2.1. Working ICP/ICPMS LCS/MS spike solution: The LCS/MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

7.2.2 The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom TestAmerica solution, a solution must be purchased from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.2.3 Aqueous laboratory control samples and matrix spike samples are prepared as described in Sections 9.5 and 9.6. Refer to Tables III and IV (Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP/ICPMS LCS and matrix spike preparations.

7.3. The TCLP MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

7.4. Nitric acid (HNO_3), concentrated, trace metal grade and Ultrapure

7.4.1. Nitric acid, 1:1 - dilute concentrated HNO_3 with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.5. Hydrochloric acid (HCl), concentrated, trace metal grade and ultra-pure (Omnitrace)

7.6. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.7. All applicable acids and reagents used for ICPMS digestion are ultra-pure reagents.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time	Reference
Water	250 mL Plastic bottle	100 mL	pH <2 preserved with HNO_3	180 days from collection to analysis	40 CFR Part 136
Soil/Wipes	4 oz. clear glass jar	2 grams	>0.0℃ but ≤ 6.0℃	180 days from collection to analysis	40 CFR Part 136
Tissues	4 oz. clear glass jar	2 grams	Frozen until ready to prepare	180 days from collection to analysis	40 CFR Part 136
Sediments	4 oz. clear glass jar	100 grams	>0.0℃ but ≤ 6.0℃	180 days from collection to analysis	40 CFR Part 136

8.1. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica is to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified at the time of receipt by the laboratory.

8.1.1. If the pH of the aqueous is found to be > 2 at the time of receipt, Sample Receiving will add preservative, document the amount of acid added and the time it was added, See Figure 5. The sample will be held for 24 hours from the documented preservation time before proceeding with the sample preparation.

8.2. For dissolved metals analysis, the samples should be filtered through a 0.45 um filter prior to preservation. Filtration should be done in the field within 15 minutes of collection. If the laboratory filters the samples, this process will occur as soon as feasibly possible after receipt, and samples must not be preserved until after filtration.

8.2.1. Dissolved metals samples that are filtered directly into a nitric acid preserved bottle may be digested after filtration is complete.

8.2.2. If a sample being analyzed for dissolved metals is found to contain sediment the analyst should contact their supervisor or group leader. The client should be notified of the problem to decide how to treat the sample.

8.2.3. If samples are received unpreserved and are filtered in the lab for dissolved metals, include the “Filtration – Field Filtration, 15 Minutes” NCM on the filtration batch.

9. QUALITY CONTROL

Table V in Appendix A provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Preparation Batch - A group of up to 20 samples that is of the same matrix and is processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate (SW-846 Methods) or a matrix spike for every 10 or fewer sample (200.7/200.8). In some cases, at client request, it may be appropriate to process a matrix spike and 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. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS, MSD) are not included in the sample count for determining the size of a preparation batch.

9.3. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank 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. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs, the blank and all associated samples in the batch must be redigested.

9.3.1. Aqueous method blanks are prepared by taking 50 mL of reagent water through the appropriate procedure as described in Section 10.

9.3.2. TCLP method blanks are prepared by taking 50 mL of reagent water through the appropriate procedure as described in Section 10.

9.4. Laboratory Control Sample (LCS) - One aqueous LCS (referred to as a Laboratory Fortified Blank in methods 200.7/200.8) must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be repreparation and reanalysis of the batch. Refer to Section 7.2 for instructions on preparation of the aqueous LCS spike solution.

9.4.1. The aqueous LCS is prepared by spiking a 50 mL aliquot of reagent water or TCLP leachate blank with 0.5 mL of the working LCS/MS spike solution (7.2). The LCS is then processed through the appropriate procedure as described in Section 10.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch of up to 20 samples (SW-846 Methods) or one matrix spike is processed for every 10 or fewer samples (200.7/200.8). A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added (referred to as a Laboratory Fortified Matrix in 200.7). A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.5.1. The aqueous matrix spike sample is prepared by spiking a 50 mL aliquot of a sample with 0.5 mL of the working LCS/MS spike solution (7.2). The matrix spike sample is then processed as described in Section 10.

9.5.2. The TCLP matrix spike sample is prepared by spiking a 50 mL aliquot of a leachate with 0.5 mL of the working TCLP spike solution (7.3). The matrix spike sample is then processed as described in Section 10.

NOTE: The TCLP matrix spike must be added prior to preservation of the leachate.

9.5.3. If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria.

10. PROCEDURE

10.1. Hotblock temperature must be verified daily for each hotblock used and must be recorded in the batch information in TALS. The hotblock temperature should be verified by measuring the temperature of a sample container of reagent water placed on each hotblock. The position will be changed daily in order to monitor the temperature of the entire hotblock. This position ID will also be recorded in the TALS batch information and on the Hotblock diagram (see Appendix D).

10.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.3. All preparation procedures must be carried out in a properly functioning hood.

10.4. All samples are to be checked out of sample control with the TALS ICOC.

10.5. Proper sample identification is extremely important in any preparation procedure. Labeling of digestion tubes and bottles must be done in a manner to ensure connection with the proper sample. Do not label digestion tubes below the level where they will be inside the hot block.

10.6. Samples are typically logged in as either waters or wastes. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the project manager for further instructions. In some cases it may be more appropriate to process these samples as solids.

10.7. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab.

10.8. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

10.9. The following procedure must be followed for all aqueous sample preparations:

10.9.1. Measure and record sample pH with pH paper on a separate aliquot of sample. This is typically verified and documented at sample receipt.

Note: If the sample pH is > 2 pH units, the client must be notified of the anomaly.

10.9.2. Mix sample by shaking the container.

10.9.3. Measure and transfer 50 mL of the sample into a digestion tube.

Note: For TCLP samples, a 5 mL sample volume, diluted to 50mL with reagent water, will be digested to minimize matrix interferences for filtered waters and tumbled solids (leachates).

10.9.4. Measure extra aliquots of sample(s) selected for the MS or MS/MSD analysis. Spike each aliquot with 0.5 mL of spiking solution (7.2 or 7.3).

10.9.5. Measure and transfer 50 mL of reagent water into a digestion tube for the method blank.

10.9.6. Measure and transfer 50 mL of reagent water into a digestion tube for the LCS and add 0.5 mL of spiking solution (7.2)

10.10. Proceed to the appropriate Section for the desired method as follows:

Method 3005A	10.11
Method 3010A	10.12
Method 200.7	10.13
Method 200.8	10.14

NOTE: When filtering the final digestates from the processes below, if there is significant suspended matter in the digestate, pre-washed (1% nitric acid) Whatman 41 filter paper in a plastic funnel may be used in place of the Environmental Express plunger filters.

10.11. **Method 3005A - Preparation for Total Recoverable or Dissolved Metals Analysis by ICP/ICPMS (See Figure 1) and TCLP samples from West Virginia**

10.11.1. To the sample in the digestion tube, add 1 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl.

10.11.2. Cover with disposable watch glass.

10.11.3. Heat at 90 - 95°C in the hotblock until volume is reduced to between 15 and 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

10.11.4. Cool the digestion tube in a fume hood.

10.11.5. Wash down digestion tube walls and watch glass with reagent water.

10.11.6. Filter sample, if insoluble materials are present, though a plunger filter into a disposable sample container.

Note: If any samples in a preparation batch are filtered, the method blank and LCS associated with that batch must also be filtered. The LCS will be spiked with the analytes of interest prior to filtering in order to assess the effectiveness of the entire preparation procedure.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.11.7. Rinse digestion tube and plunger filter with reagent water to ensure complete sample transfer.

10.11.8. Adjust the final volume/mass to 50 mL with reagent water. The sample is now ready for analysis

10.12. **Method 3010A - Preparation for Total and TCLP Metals Analysis by ICP/ICPMS Spectroscopy (See Figure 2)**

10.12.1. To the sample digestion tube, add 1.5 mL of concentrated HNO_3.

10.12.2. Cover with disposable watch glass.

10.12.3. Place digestion tube into the hotblock (90-95°C) and evaporate to low volume of 5 - 10 mL while ensuring that no portion of the bottom of the digestion tube is allowed to go dry.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

NOTE: For TCLP samples, a 5 mL sample volume will be digested to minimize matrix interferences for filtered waters and tumbled solids (leachates).

10.12.4. Cool the digestion tube in a fume hood.

10.12.5. Add another 1.5 mL portion of concentrated HNO_3 and re-cover the digestion tube.

10.12.6. Continue refluxing until the digestion is complete.

Note: Digestion is complete when the digestate is light in color or does not change in appearance. For most samples the addition of two nitric acid aliquots is sufficient, additional aliquots of nitric acid may be added if necessary.

10.12.7. Evaporate to low volume of 5 - 10 mL while ensuring that no portion of the bottom of the digestion tube is allowed to go dry.

10.12.8. Cool the digestion tube in a fume hood.

10.12.9. Add 5 mL of 1:1 HCl.

10.12.10. Cover and reflux for an additional 15 minutes to dissolve precipitate or residue.

10.12.11. Wash down digestion tube walls and watch glass with reagent water.

10.12.12. Filter sample, if insoluble materials are present, though a plunger filter into a disposable sample container.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered. The LCS will be spiked with the analytes of interest prior to filtering in order to assess the effectiveness of the prep procedure.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.12.13. Rinse digestion tube and filter paper or plunger filter with reagent water to ensure complete sample transfer.

10.12.14. Adjust final volume/mass to 50 mL with reagent water. The sample is now ready for analysis.

10.13. **Method 200.7 - Preparation for Total Recoverable or Dissolved Metals Analysis by ICP (See Figure 3)**

10.13.1. To the digestion tube containing 50 mL of sample, add 1 mL of 1:1 HNO_3 and 0.5 mL of 1:1 HCl.

Note: If any samples in the QC batch are filtered at the lab prior to digestion, the method blank and LCS associated with that batch must also be filtered. The LCS will be spiked with the analytes of interest prior to filtering in order to assess the effectiveness of the prep procedure.

10.13.2. Heat at 80-85 °C for uncovered digestion tubes, or 90-95℃ for cov ered digestion tubes, until volume is reduced to between 15 and 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be re-prepared.

NOTE: If a sample contains > 1% suspended solid material by visual inspection, add a sample volume containing no more than 1.0 grams of solid to the digestion tube. Increase the acid volume to 4.0 mL of 1:1 HNO_3 and 4.0 mL of 1:1 HCl and proceed with digestion.

10.13.3. Cover with disposable watch glass.

10.13.4. Gently reflux for 30 minutes.

10.13.5. Cool the digestion tube in the fume hood.

10.13.6. Wash down digestion tube walls and watch glass with reagent water.

10.13.7. Filter sample, if insoluble materials are present, though a plunger filter into a disposable sample container.

10.13.8. Rinse digestion tube and plunger filter with reagent water to ensure complete sample transfer.

10.13.9. Adjust the final volume/mass to 50 mL with reagent water. The sample is now ready for analysis.

10.14. **Method 200.8 - Preparation for Total Recoverable or Dissolved Metals Analysis by ICPMS (See Figure 4)**

10.14.1. To the sample digestion tube containing 50 mL of sample, add 1 mL of 1:1 HNO_3 and 0.5 mL of 1:1 HCl.

Note: If any samples in the QC batch are filtered at the lab prior to digestion, the method blank and LCS associated with that batch must also be filtered. The LCS will be spiked with the analytes of interest prior to filtering in order to assess the effectiveness of the prep procedure.

10.14.2. Heat at 80-85 °C for uncovered digestion tubes or 90-95℃ for cove red digestion tubes until volume is reduced to between 15 and 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

NOTE: If a sample contains > 1% suspended solid material by visual inspection, add a sample volume containing no more than 1.0 gram of solid to the digestion tube. Increase the acid volume to 4.0 mL of 1:1 HNO_3 and 4.0 mL of 1:1 HCl and proceed with digestion.

10.14.3. Cover with disposable watch glass.

10.14.4. Gently reflux for 30 minutes.

10.14.5. Cool the digestion tube in the fume hood.

10.14.6. Wash down digestion tube walls and watch glass with reagent water.

10.14.7. Filter sample, if insoluble materials are present, though a plunger filter into a disposable sample container.

10.14.8. Rinse digestion tube and plunger filter with reagent water to ensure complete sample transfer.

10.14.9. Adjust the final volume/mass to 50 mL with reagent water. The sample is now ready for analysis.

10.15. Documentation and Record Management

10.15.1. All information is recorded directly into TALS prep worksheet. Reagent information is documented in the batch information and spiking solutions are documented on the reagent tab in the batch.

11. CALCULATIONS / DATA REDUCTION

11.1. Not Applicable

12. METHOD PERFORMANCE

12.1. The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2. Demonstration of Capabilities – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3. A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially and whenever a significant change is made to the analytical system. The MDL must be verified on at least an annual basis, according to the procedure in QA Manual and SOP PT-QA-007.

13. POLLUTION CONTROL

13.1. 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" and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

13.2. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

14. 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 CW-E-M-001. The following waste streams are produced when this method is carried out.

14.1.1. Acidic waste containing nitric acid generated by the digestion. This waste is collected in a waste container identified as “Acid Waste”, Waste #33. This waste is neutralized to a final pH between 5 and 9 and discharged down into a lab sink.

14.1.2. Contaminated disposable materials utilized for the analysis. These items are placed in trash containers which are emptied in the general trash dumpster located near the shipping/receiving dock.

15. REFERENCES

15.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update I, Revision 1, July 1992. Methods 3005A and 3010A

15.2. Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Method 200.7, Revision 4.4, May 1994

15.3. Methods for the Determination of Metals in Environmental Samples, Supplement 1 (EPA/600/R-94/111), Method 200.8, Determination of Trace Elements in Waters by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, 1994

15.4. PT-MT-001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010B/6010C/6010D and Method 200.7

15.5. PT-MT-002, Analysis of Metals by Inductively Coupled Plasma/Mass Spectrometry (ICPMS) for Methods 200.8, 6020/6020A/6020B

15.6. PT-QA-021, TestAmerica Pittsburgh QC Program

15.7. PT-QA-007, Method Detection Limits

15.8. PT-QA-024, Subsampling

15.9. PT-QA-M-001, TestAmerica Pittsburgh’s Laboratory Quality Assurance Manual

15.10. SOP PT-QA-016, Nonconformance & Corrective Action System

15.11. SOP PT-QA-001, Employee Orientation and Training

15.12. SOP PT-HS-001, Appendix D, Waste Collection, Accumulation and Storage

15.13. SOP PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability

15.14. SOP PT-QA-031, Internal Chain of Custody

16. METHOD MODIFICATIONS

16.1. Modifications applicable to SW-846 reference methods.

16.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

16.1.2. The referenced methods as well as Table 3-1 of SW-846 refer to the use of a 100 mL aliquot for digestion. This SOP requires the use of a 50 mL sample size to reduce waste generation. The use of reduced sample volumes are supported in EPA's document "Response to Public Comments Background Document, Promulgation of the Second Update to SW-846, Third Edition" dated November 3, 1994. This document stated "..flexibility to alter digestion volumes is addressed and "allowed" by the table (3-1) and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples..." EMSL-Ci has also taken the stance that "reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology." Additionally, in written correspondence from the Office of Solid Waste, Olliver Fordham stated " As a "representative sample" can be assured, scaling causes no loss of precision and accuracy in the analysis."

16.2. Modifications Specific to Method 3010A

16.2.1. Section 10.13.7 of this SOP requires the sample be reduced to a volume of 5 - 10 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the digestion tube should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the digestion tube so as to prevent the loss of critical analytes through volatilization.

16.2.2. The scope of 3010A has been expanded to include silver based on comparison studies with 7760A. Method 3010A consistently demonstrated improved accuracy and precision over Method 7760A in the matrices tested (reagent water, surface water and TCLP leachate) up to a concentration of 1 ppm silver.

17. ATTACHMENTS

17.1. Figure 1 – Method 3005A Flowchart

17.2. Figure 2 – Method 3010A Flowchart

17.3. Figure 3 – Method 200.7 Flowchart

17.4. Figure 4 – Method 200.8 Flowchart

17.5. Figure 5 – Example of a Lab Aqueous pH Preservation Form

17.6. Appendix A – Tables

17.6.1. Table I – Approved Preparation Method Analytes – SW846

17.6.2. Table II – Approved Preparation Method Analytes – NPDES

17.6.3. Table III – ICP/ICPMS Matrix Spike and Aqueous Laboratory Control Sample Levels

17.6.4. Table IV – TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

17.6.5. Table V – Summary of Quality Control Requirements

17.7. Appendix B – TALS Metals Prep Example Worksheets

17.8. Appendix C – Contamination Control Guidelines

17.9. Appendix D – Example Template for Hotblock Thermometer Rotation

18. REVISION HISTORY

18.1. Revision 7, 8/24/07
18.2. Revision 7.1, 10/11/07
18.3. Revision 8, 1/31/2009
18.4. Revision 9, 2/8/2010

18.5. Revision 10, 6/23/2010
18.6. Revision 11, 5/8/2012
18.7. Revision 12, 6/22/2014
18.8. Changes to current revision

SOP section	Change from	Change to	Reason
Entire SOP	beaker	digestion tube	Correction
1.4, 1.6, 2.1 and 10.11		Clarified that Method 3005A is used for TCLP leachate digestion for West Virginia samples	Clarification
1.7		Added "When dissolved metals analysis is requested the samples must be field filtered at the time of collection and prior to digestion using Method 3005A."	Method requirement
3.5 and 3.6		Added definitions of TALS and NCM	Clarification
5.1 and 13.1		Added reference to PT-HS-001	Correction
6.8		Added Class A in front of graduated cylinder	Correction
6.14		Plastic digestate storage bottles are purchased from Environmental Express	Correction
Table under section 8	≤6.0℃	>0.0℃ but ≤6.0℃	SOP Review Sheet format
8.1		Noted that preservation must be verified at the time of receipt by the laboratory.	Clarification
8.2	24 hours	15 minutes	Correction
8.2.3		Added Use "Filtration – Field Filtered, 15 Minutes" NCM for samples filtered for dissolved metals in the lab.	Clarification
10 throughout & 16.1.2	Removed reference to use of sample weight instead of volume		Correction
10.1		Noted that the Hotblock diagram is used to chart the position used to take the daily temperature of the Hotblock to ensure thermometer rotation.	Correction
10.9.3		Added a NOTE under this section which indicates the lab uses 5 mL of sample volume for TCLP digestates to minimize matrix interferences	Clarification
10.14.1	2 mL of 1:1 HNO_3	1 mL of 1:1 HNO_3	Correction

10.13.2 and 10.14.2		Added text to note the 80-85℃ temperature is for uncovered samples and 90-95℃ temperature is used for covered samples	Clarification
10.13.2 and 10.14.2		Added a NOTE under these samples to explain that if samples have >1% suspended solids by visual inspection to add sample volume containing no more than 1g of solid to the digestion tube and increase acid volume accordingly and proceed with digestion	Clarification
10.14		Reduced sample volume to 50 mL and volume of 1:1 HNO_3 to 1 mL and 0.5 mL for 1:1 HCl; proportionality is kept therefore this is not a method modification	Correction
10.14.10	Removed “Take a 25 mL aliquot of the 50 mL sample…” since this statement is no longer necessary		Correction
16.9	Removed the 200.8 Prep method modification since it is no longer necessary		Correction
17.9 and Appendix D		Added Example of Template for Hotblock Thermometer Rotation diagram	Clarification
Figure 1 & 2	Removed 50g beaker	Digestion tube	Correction
Figure 2	Step 6: 15-20 mL	Step 6: 5-10 mL	Correction
Figure 3	Beaker 80-85℃	Digestion tube 90-95℃ (80-85℃, uncovered) Added Cool in front of filter	Correction
Figure 4	Beaker Heat at 80-85℃ Removed “Dilute to 25 mL…”	Digestion tube Cover, Heat at 90-95℃ (80-85℃, uncovered) Added Cool in front of filter Added Dilute to 50 mL…	Correction
Table III	As 200 (ICP); As 2000 (ICP) Se 200 (ICP); Se 2000 (ICP) Tl 200 (ICP); Tl 2000 (ICP)	As 50 (ICP); As 500 (ICP) Se 50 (ICP); Se 500 (ICP) Tl 50 (ICP); Tl 500 (ICP)	Correction
Table IV	Ba - RL 10000 Cd - RL 100 Se - RL 250	Ba - RL 2000 Cd - RL 500 Se - RL 500	Correction

	Ba – Spike Level 50000 Cd – Spike Level 1000 Cr – Spike Level 5000 Se – Spike Level 1000 Ag – Spike Level 1000	Ba – Spike Level 20000 Cd – Spike Level 500 Cr – Spike Level 2000 Se – Spike Level 5000 Ag – Spike Level 500	

FIGURE 1 - METHOD 3005A

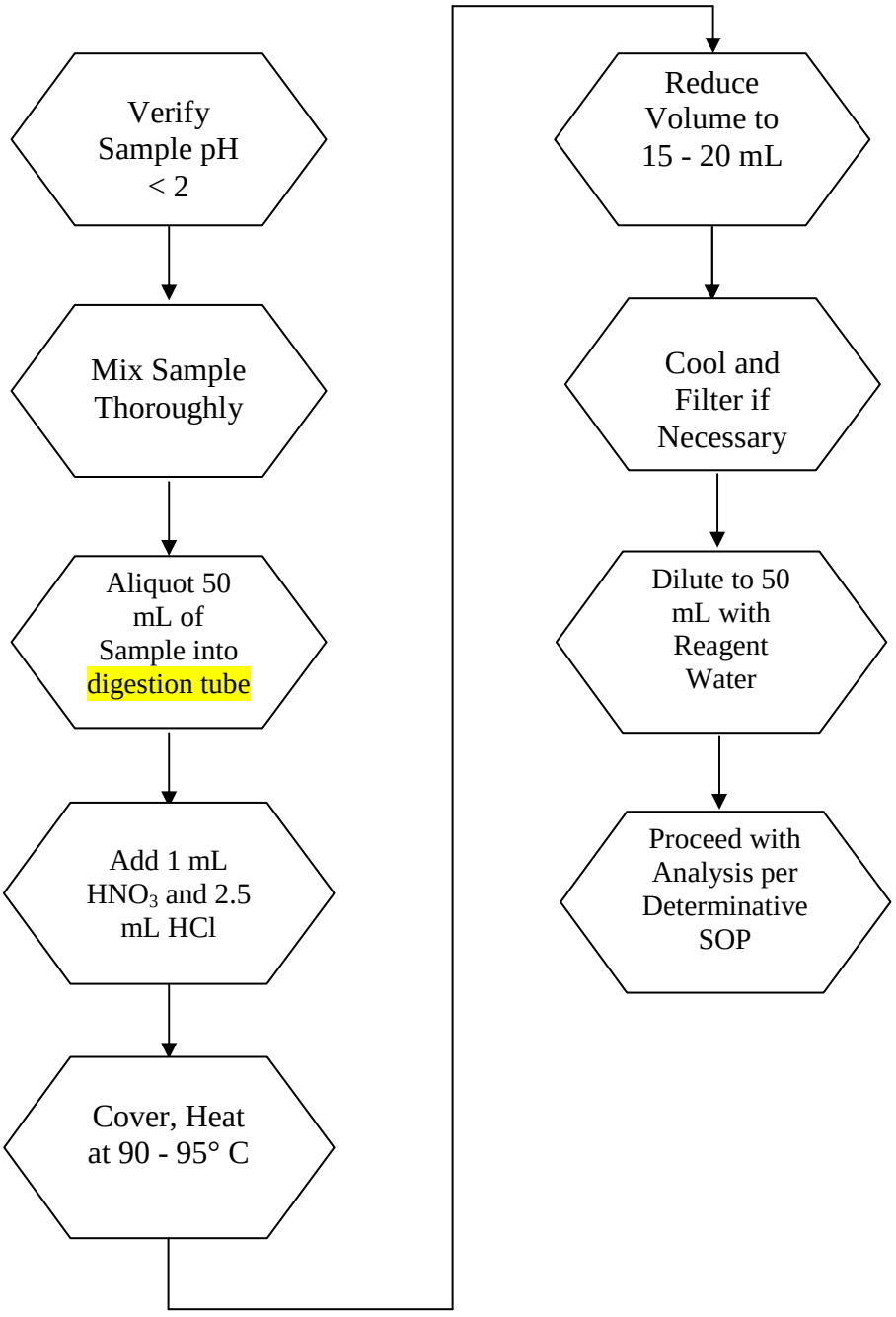

FIGURE 2 - METHOD 3010A

FIGURE 3 - METHOD 200.7

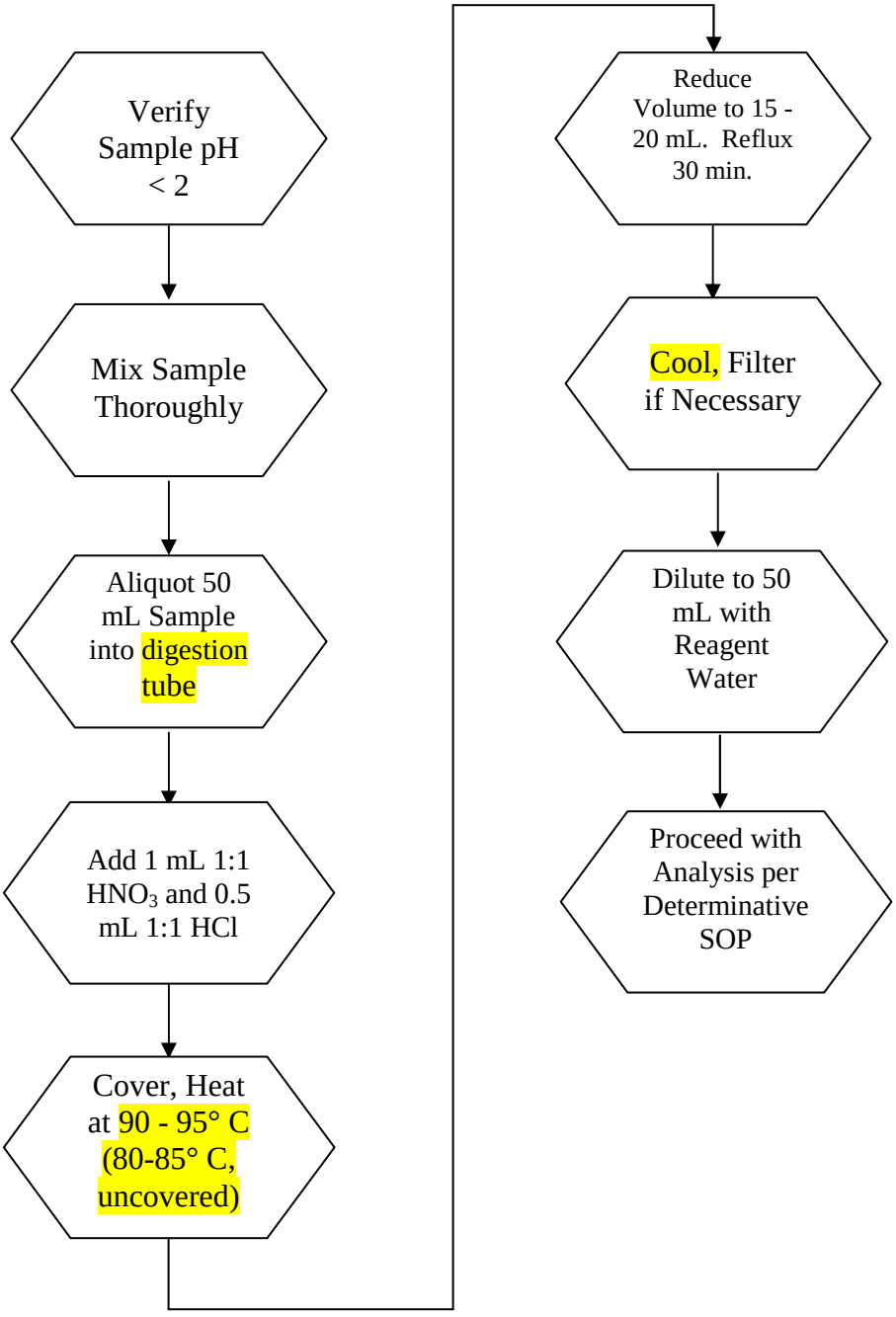

FIGURE 4 - METHOD 200.8

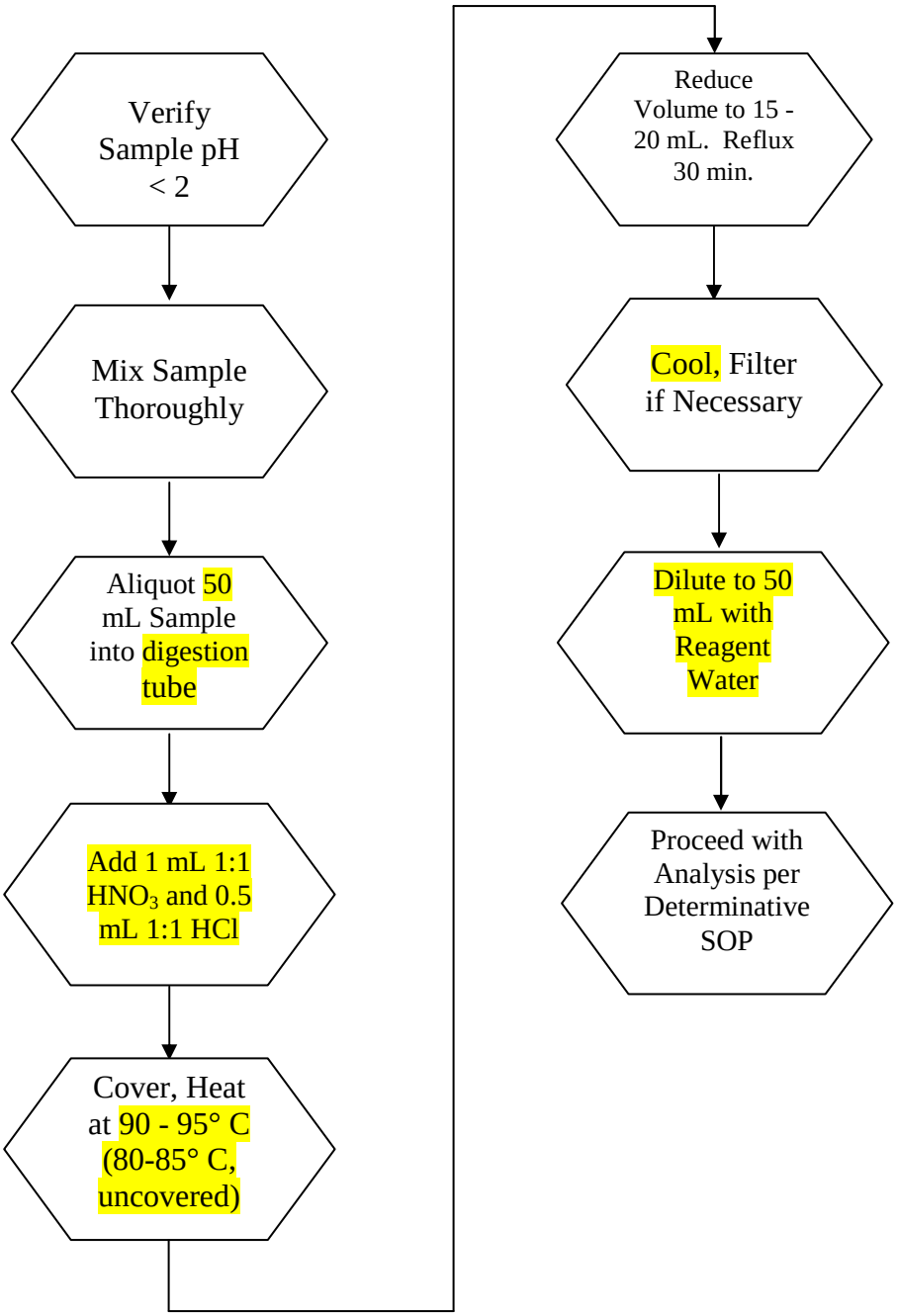

FIGURE 5 – EXAMPLE OF A LAB AQUEOUS PH PRESERVATION FORM

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Client ID	Lab ID	Bottle Type	pH initial	Amount acid (mL)	Date/Time	Initials	pH final	Date/Time	Initials

pH (initial) Strip lot #_____

pH (final) Strip lot #_____

Acid lot #_____

Login- complete **pH initial information**, place purple sticker on bottle lid, put comment in TALs submit paperwork to metals prep.

Metals prep- complete pH final information, scan and attach this document to the prep batch.

APPENDIX A

TABLES

TABLE I
Approved Preparation Method Analytes - SW846

ELEMENT	Symbol	CAS Number	3005A	3010A
Aluminum	Al	7429-90-5	X	X
Antimony	Sb	7440-36-0	X	X
Arsenic	As	7440-38-2	X	X
Barium	Ba	7440-39-3	X	X
Beryllium	Be	7440-41-7	X	X
Cadmium	Cd	7440-43-9	X	X
Calcium	Ca	7440-70-2	X	X
Chromium	Cr	7440-47-3	X	X
Cobalt	Co	7440-48-4	X	X
Copper	Cu	7440-50-8	X	X
Iron	Fe	7439-89-6	X	X
Lead	Pb	7439-92-1	X	X
Magnesium	Mg	7439-95-4	X	X
Manganese	Mn	7439-96-5	X	X
Molybdenum	Mo	7439-98-7	X	X
Nickel	Ni	7440-02-0	X	X
Potassium	K	7440-09-7	X	X
Selenium	Se	7782-49-2	X	X
Silver	Ag	7440-22-4	X	X
Sodium	Na	7440-23-5	X	X
Thallium	Tl	7440-28-0	X	X
Vanadium	V	7440-62-2	X	X
Zinc	Zn	7440-66-6	X	X

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 12.0 of the SOP are met.

TABLE II
Approved Preparation Method Analytes - NPDES

ELEMENT	Symbol	CAS Number	200.7
Aluminum	Al	7429-90-5	X
Antimony	Sb	7440-36-0	X
Arsenic	As	7440-38-2	X
Boron	B	7440-42-8	X
Barium	Ba	7440-39-3	X
Beryllium	Be	7440-41-7	X
Cadmium	Cd	7440-43-9	X
Calcium	Ca	7440-70-2	X
Chromium	Cr	7440-47-3	X
Cobalt	Co	7440-48-4	X
Copper	Cu	7440-50-8	X
Iron	Fe	7439-89-6	X
Lead	Pb	7439-92-1	X
Magnesium	Mg	7439-95-4	X
Manganese	Mn	7439-96-5	X
Molybdenum	Mo	7439-98-7	X
Nickel	Ni	7440-02-0	X
Potassium	K	7440-09-7	X
Selenium	Se	7782-49-2	X
Silicon	Si	7631-86-9	X
Silver	Ag	7440-22-4	X
Sodium	Na	7440-23-5	X
Thallium	Tl	7440-28-0	X
Vanadium	V	7440-62-2	X
Zinc	Zn	7440-66-6	X

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 12.0 of the SOP are met.

TABLE III
ICP/ICPMS Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/ MS Level * (ug/l)
Aluminum	200	2000
Antimony	50	500
Arsenic	50 (ICP), 4 (ICPMS)	500 (ICP), 40 (ICPMS)
Barium	200	2000
Beryllium	5	50
Cadmium	5	50
Calcium	5000	50000
Chromium	20	200
Cobalt	50	500
Copper	25	250
Iron	100	1000
Lead	50 (ICP), 2 (ICPMS)	500 (ICP), 20 (ICPMS)
Lithium	100	1000
Magnesium	5000	50000
Manganese	50	500
Molybdenum	100	1000
Nickel	50	500
Potassium	5000	50000
Selenium	50 (ICP), 1 (ICPMS)	500 (ICP), 10 (ICPMS)
Silver	5	50
Sodium	5000	50000
Strontium	100	1000
Thallium	50 (ICP), 5 (ICPMS)	500 (ICP), 50 (ICPMS)
Vanadium	50	500
Zinc	50	500
Boron	100	1000
Silica	1000	10000
Tin	200	2000
Titanium	100	1000

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 0.5 mL working spike (7.3) to 50 mL of sample.

TABLE IV
TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	RL (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)
Arsenic	500	5000	5000
Barium	2000	100000	20000
Cadmium	500	1000	500
Chromium	500	5000	2000
Lead	500	5000	5000
Selenium	500	1000	5000
Silver	500	5000	500

TABLE V
Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA[(1)]	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: PT-MT-001 and PT-MT-002	Redigest and reanalyze samples associated with the method blank.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: PT-MT-001 and PT-MT-002	Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples (SW-846 Methods) or one per every 10 or fewer samples (200.7/200.8).	Refer to determinative SOPs: PT-MT-001 and PT-MT-002	Reprep not required unless preparation error suspected.
Matrix Spike Duplicate	See Matrix Spike	Refer to determinative SOPs: PT-MT-001 and PT-MT-002	See Corrective Action for Matrix Spike.

APPENDIX B – TALS METALS PREP EXAMPLE WORKSHEETS

Metals/Inorganics Prep Worksheet

(Used for Collecting Prep Info)

Batch Number: 180-33196
Method Code: 180-3010A-180

Analyst: Shook, Caitlin N

Batch Open: 4/13/2012 10:50:00AM
Batch End: 4/13/2012 2:50:00PM

Preparation, Total Metals

	Input Sample Lab ID	Input Sample Lab ID (Analytical Method)	SDG	Matrix	Initial Amount	Final Amount	Due Date	Analytical TAT	Div Rank	Comments
1		MB~180-33196/1 N/A	N/A		50 mL	50 mL	N/A	N/A	N/A	
2		LCS~180-33196/2 N/A	N/A		50 mL	50 mL	N/A	N/A	N/A	
3		180-9781-A-1 (6010_DOD)	N/A	Water	50 mL	50 mL	5/1/12	13_Days - R	N/A	
4		180-9781-A-2 (6010_DOD)	N/A	Water	50 mL	50 mL	5/1/12	13_Days - R	N/A	
5		180-9781-A-3 (6010_DOD)	N/A	Water	50 mL	50 mL	5/1/12	13_Days - R	N/A	
6		180-9781-A-4 (6010_DOD)	N/A	Water	50 mL	50 mL	5/1/12	13_Days - R	N/A	
7		180-9781-A-5 (6010_DOD)	N/A	Water	50 mL	50 mL	5/1/12	13_Days - R	N/A	
8		180-9781-A-6 (6010_DOD)	N/A	Water	50 mL	50 mL	5/1/12	13_Days - R	N/A	
9		180-9781-A-7 (6010_DOD)	N/A	Water	50 mL	50 mL	5/1/12	13_Days - R	N/A	
10		180-9781-A-7~MS (6010_DOD)	N/A	Water	50 mL	50 mL	5/1/12	13_Days - R	N/A	
11		180-9781-A-7~MSD (6010_DOD)	N/A	Water	50 mL	50 mL	5/1/12	13_Days - R	N/A	
12		180-9781-A-8 (6010_DOD)	N/A	Water	50 mL	50 mL	5/1/12	13_Days - R	N/A	
13		180-9781-A-9 (6010_DOD)	N/A	Water	50 mL	50 mL	5/1/12	13_Days - R	N/A	
14		180-9781-A-10 (6010_DOD)	N/A	Water	50 mL	50 mL	5/1/12	13_Days - R	N/A	
15		180-9562-G-2 (6010_DOD)	N/A	Water	50 mL	50 mL	5/3/12	18_Days - R	N/A	

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APPENDIX B – TALS METALS PREP EXAMPLE WORKSHEETS (cont.)

Metals/Inorganics Prep Worksheet

(Used for Collecting Prep Info)

Batch Number: 180-33196 Analyst: Shook, Caitlin N Batch Open: 4/13/2012 10:50:00AM

Method Code: 180-3010A-180 Batch End: 4/13/2012 2:50:00PM

16		180-9662-G-3 (6010_DOD)	N/A	Water	50 mL	50 mL	5/3/12	18_Days - R	N/A	
17		180-9662-G-4 (6010_DOD)	N/A	Water	50 mL	50 mL	5/3/12	18_Days - R	N/A	
18		180-9662-G-5 (6010_DOD)	N/A	Water	50 mL	50 mL	5/3/12	18_Days - R	N/A	

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APPENDIX B – TALS METALS PREP EXAMPLE WORKSHEETS (cont.)

Metals/Inorganics Prep Worksheet

(Used for Collecting Prep Info)

Batch Number: 180-33196
Method Code: 180-3010A-180

Analyst: Shook, Caitlin N

Batch Open: 4/13/2012 10:50:00AM
Batch End: 4/13/2012 2:50:00PM

Batch Notes

Lot # of hydrochloric acid	5mL 368638
Lot # of Nitric Acid	3mL 377036
Vendor of Reagent used	Mallinckrodt
Digestion Tube/Cup Lot #	1107184
Hot Block ID number	#3
ID number of the thermometer	IP03 (-1.0)
Uncorrected Temperature	95
Oven, Bath or Block Temperature 1	94
Uncorrected Temperature 2	NA
Oven, Bath or Block Temperature 2	NA
Filter Paper Lot Number	NA
Pipette ID	03F95602
Person who witnessed spiking	CS
First Start time	10:50
First End time	14:50
Batch Comment	METALS C7

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APPENDIX B – TALS METALS PREP EXAMPLE WORKSHEETS (cont.)

Metals/Inorganics Prep Worksheet

(Used for Collecting Prep Info)

Batch Number: 180-33196
Method Code: 180-3010A-180

Analyst: Shook, Caitlin N

Batch Open: 4/13/2012 10:50:00AM
Batch End: 4/13/2012 2:50:00PM

Comments

180-9662-G-3	Method Comments:	DoD QSM 3.0 & SC
180-9662-G-4	Method Comments:	DoD QSM 3.0 & SC
180-9662-G-5	Method Comments:	DoD QSM 3.0 & SC
Login Comments for Job 9662:		Please extract and analyze samples ASAP so that any necessary re-extracts can be extracted while still within hold.
		Report only one result per compound/analyte.
180-9662-G-2	Method Comments:	DoD QSM 3.0 & SC

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APPENDIX B – TALS METALS PREP EXAMPLE WORKSHEETS (cont.)

Metals/Inorganics Prep Worksheet

(Used for Collecting Prep Info)

Batch Number: 180-33196
Method Code: 180-3010A-180

Analyst: Shook, Caitlin N

Batch Open: 4/13/2012 10:50:00AM
Batch End: 4/13/2012 2:50:00PM

Reagent Additions Worksheet

Lab ID	Reagent Code	Amount Added	Final Amount	By	Witness
LCS 180-33196/2	MTAPITTMSA_00006	0.5 mL	50 mL		
LCS 180-33196/2	MTAPITTMSBREV_00001	0.5 mL	50 mL		
LCS 180-33196/2	MTAPITTMSC_00011	0.5 mL	50 mL		
180-9781-A-7 MS	MTAPITTMSA_00006	0.5 mL	50 mL		
180-9781-A-7 MS	MTAPITTMSBREV_00001	0.5 mL	50 mL		
180-9781-A-7 MS	MTAPITTMSC_00011	0.5 mL	50 mL		
180-9781-A-7 MSD	MTAPITTMSA_00006	0.5 mL	50 mL		
180-9781-A-7 MSD	MTAPITTMSBREV_00001	0.5 mL	50 mL		
180-9781-A-7 MSD	MTAPITTMSC_00011	0.5 mL	50 mL		

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APPENDIX B – TALS METALS PREP EXAMPLE WORKSHEETS (cont.)

Metals/Inorganics Prep Worksheet

(Used for Collecting Prep Info)

Batch Number: 180-33196
Method Code: 180-3010A-180

Analyst: Shook, Caitlin N

Batch Open: 4/13/2012 10:50:00AM
Batch End: 4/13/2012 2:50:00PM

Other Reagents:

Reagent	Amount/Units	Lot#:

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APPENDIX B – TALS METALS PREP EXAMPLE WORKSHEETS (cont.)

Metals Worksheet

Batch Number: 180-33196
Method: 3010A
Analyst: Shook, Caitlin N

Date Open: Apr 13 2012 10:50AM
Batch End: Apr 13 2012 2:50PM

Lab ID	Client ID	Method Chain	Basis	Initial weight/volume of sample	Final weight/volume of sample	MTAPITTMSA_00008	MTAPITTMSBREV_00001	MTAPITTMSC_00011
MB~180-33196/1				50 mL	50 mL			
LCS~180-33196/2				50 mL	50 mL	0.5 mL	0.5 mL	0.5 mL
180-9781-A-1	S12MW0070028	3010A, 6010_DOD	T	50 mL	50 mL			
180-9781-A-2	S12MW0080028	3010A, 6010_DOD	T	50 mL	50 mL			
180-9781-A-3	S12MW0090028	3010A, 6010_DOD	T	50 mL	50 mL			
180-9781-A-4	S12MW0010028	3010A, 6010_DOD	T	50 mL	50 mL			
180-9781-A-5	S12MW0010028-D	3010A, 6010_DOD	T	50 mL	50 mL			
180-9781-A-6	S12MW0011028	3010A, 6010_DOD	T	50 mL	50 mL			
180-9781-A-7	S12MW0012028	3010A, 6010_DOD	T	50 mL	50 mL			
180-9781-A-7~MS	S12MW0012028	3010A, 6010_DOD	T	50 mL	50 mL	0.5 mL	0.5 mL	0.5 mL
180-9781-A-7~MSD	S12MW0012028	3010A, 6010_DOD	T	50 mL	50 mL	0.5 mL	0.5 mL	0.5 mL
180-9781-A-8	S12MW0013028	3010A, 6010_DOD	T	50 mL	50 mL			
180-9781-A-9	S12-FB041112	3010A, 6010_DOD	T	50 mL	50 mL			
180-9781-A-10	S12-EB041112	3010A, 6010_DOD	T	50 mL	50 mL			
180-9662-G-2	PAI-03-MW-01SR	3010A, 6010_DOD	T	50 mL	50 mL			
180-9662-G-3	PAI-03-MW-02DR	3010A, 6010_DOD	T	50 mL	50 mL			
180-9662-G-4	PAI-03-MW-03SR	3010A, 6010_DOD	T	50 mL	50 mL			
180-9662-G-5	PAI-03-MW-04SR	3010A, 6010_DOD	T	50 mL	50 mL			

Lot # of hydrochloric acid:	5mL 368638
Lot # of Nitric Acid:	3mL 377036
Vendor of Reagent used:	Mallinckrodt
Digestion Tube/Cup Lot #:	1107184
Hot Block ID number:	#3
ID number of the thermometer:	IP03 (-1.0)
Uncorrected Temperature:	95 Degrees C
Oven, Bath or Block Temperature 1:	94 Degrees C
Uncorrected Temperature 2:	NA Degrees C
Oven, Bath or Block Temperature 2:	NA Degrees C
Filter Paper Lot Number:	NA
Pipette ID:	03F95602
Person who witnessed spiking:	CS
First Start time:	10:50
First End time:	14:50

Page 1 of 2

APPENDIX B – TALS METALS PREP EXAMPLE WORKSHEETS (cont.)

Metals Worksheet

Batch Number: 180-33196
Method: 3010A
Analyst: Shook, Caitlin N

Date Open: Apr 13 2012 10:50AM
Batch End: Apr 13 2012 2:50PM

Comments

Lab ID	Client ID	Method Chain	Basis	Analysis comment
MB~180-33196/1				
LCS~180-33196/2				
180-9781-A-1	S12MW0070028	3010A, 6010_DOD	T	
180-9781-A-2	S12MW0080028	3010A, 6010_DOD	T	
180-9781-A-3	S12MW0090028	3010A, 6010_DOD	T	
180-9781-A-4	S12MW0010028	3010A, 6010_DOD	T	
180-9781-A-5	S12MW0010028-D	3010A, 6010_DOD	T	
180-9781-A-6	S12MW0011028	3010A, 6010_DOD	T	
180-9781-A-7	S12MW0012028	3010A, 6010_DOD	T	
180-9781-A-7~MS	S12MW0012028	3010A, 6010_DOD	T	
180-9781-A-7~MSD	S12MW0012028	3010A, 6010_DOD	T	
180-9781-A-8	S12MW0013028	3010A, 6010_DOD	T	
180-9781-A-9	S12-FB041112	3010A, 6010_DOD	T	
180-9781-A-10	S12-CD041112	3010A, 6010_DOD	T	
180-9662-G-2	PAI-03-MW-01SR	3010A, 6010_DOD	T	
180-9662-G-3	PAI-03-MW-02DR	3010A, 6010_DOD	T	
180-9662-G-4	PAI-03-MW-03SR	3010A, 6010_DOD	T	
180-9662-G-5	PAI-03-MW-04SR	3010A, 6010_DOD	T	

Batch Comment: METALS C7

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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 nitric 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 or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile 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.

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 soak with nitric acid prior to routine cleaning.

APPENDIX D
Example of Template for Hotblock Thermometer Rotation

This is a Controlled Document. When Printed it Becomes Uncontrolled.

TestAmerica
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Pittsburgh
WI No.: PT-QA-WI-017 R2
Effective Date:7/30/2014
Page No.: 1 of 1

Template for Hotblock Thermometer Rotation - Diagram 1

Directions: Select a starting point on the template and mark an "X" on the selected slot with a dry erase marker. Record the slot ID selected in the TALS Batch information. Continue in this fashion until all slots are "X"ed out, then wipe the laminated diagram clean and begin again.

A1	A2	A3	A4	A5	A6
B1	B2	B3	B4	B5	B6
C1	C2	C3	C4	C5	C6
D1	D2	D3	D4	D5	D6
E1	E2	E3	E4	E5	E6
F1	F2	F3	F4	F5	F6
G1	G2	G3	G4	G5	G6
H1	H2	H3	H4	H5	H6
I1	I2	I3	I4	I5	I6

Virginia Zusman
Quality Assurance Manager
7/30/2014
Date

Roseann Ruyechan
Inorganics Department Manager
7/30/2014
Date

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: GC/MS Analysis for Semivolatile Organics

Methods: SW-846 8270C & 8270D

Approvals (Signature/Date):

7/19/2016	7/18/2016
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1.0 Scope and Application

1.1 This procedure is based upon SW846 methods 8270C and 8270D, utilizes best practices, and is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from many types of solid matrices, soils and aqueous matrices.

1.1.1 Direct injection of a sample may be used in limited applications.

1.1.2 Refer to Table 1 for the list of compounds applicable for this method. Note that the compounds are listed in approximate retention time order. This method may be amenable to additional compounds. If non-standard analytes are required, they must be validated by the procedures described in section 12.2 before sample analysis.

1.2 The following compounds may require special treatment when being determined by this method:

- Benzidine can be subject to oxidative losses during solvent concentration and exhibits poor chromatography. Neutral extraction should be performed if this compound is expected.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be distinguished from diphenylamine.
- Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 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.
- 3-Methylphenol cannot be separated from 4-methylphenol by the conditions specified in this method. They are reported as 3 and 4-methylphenol.
- Hexachlorophene and famphur analysis are not quantitatively reliable by this method.
- 1,2-diphenylhydrazine is unstable even at room temperature and readily decomposes to form azobenzene. Given the stability problems, it would be acceptable to calibrate for 1,2-diphenylhydrazine using azobenzene and the results for either of these compounds should be reported as a combined concentration.
- Pyridine may perform poorly at the GC injection port temperatures listed in this SOP. Lowering the injection port temperature may reduce the amount of degradation.

1.3 The standard reporting limit (RL) of this method for determining an individual compound is approximately 330 µg/kg (wet weight) for soil/sediment/tissues samples, 33 µg/kg (wet weight) for low level soil/sediment/tissues samples, 2 - 400

mg/kg for wastes (dependent on matrix and method of preparation), 10 µg/L for groundwater samples and 1.0 µg/L for low level groundwater samples. Some compounds have higher reporting limits. Refer to Table 1 for specific RLs. Reporting limits will be proportionately higher for sample extracts that require dilution.

1.4 Certain clients may require specific project or program QC that may supersede the requirements presented in this section. Project specific QAPP's should be developed to address these requirements.

1.5 Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP PT-QA-016. The NCM shall be filed in the project file and addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

1.6 On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated in PT-QA-M-001, the Quality Assurance Manual.

2.0 Summary of Method

2.1 Aqueous samples are extracted with methylene chloride using either a continuous extractor (Method 3520C) or a separatory funnel (Method 3510C). TCLP samples are usually extracted by separatory funnel. TestAmerica Pittsburgh performs both routine and low level water analyses with the final extract volume at 10 mL and 1.0 mL respectively.

2.2 Solid samples are extracted with methylene chloride / acetone using Soxhlet extraction. TestAmerica Pittsburgh performs both routine and low level soil analyses with the final extract volume at 5.0 mL and 0.5 mL respectively.

2.3 Waste dilution is used for samples that are miscible with the solvent.

2.4 Extraction procedures are detailed in the following SOPs:

- PT-OP-001 Extraction of Organic Compounds from Waters, Based on SW-846 3500 Series and 600 Series Methods
- PT-OP-026 Extraction of Organic Compounds from Solids, Sediments, Tissue and Wipes Based on SW-846 3500 Series
- PT-OP-028 Cleanup of Organic Compounds from Waters, Solids, Sediments, Tissue and Wipes Based on SW-846 3600 Series and CarboPrep90 Methods

2.5 Qualitative identification of the analytes in the extract is performed using the retention time and the relative abundance of characteristic ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

3.0 Definitions

3.1 TALS – TestAmerica Laboratory Information Management System

3.2 NCM – Non-Conformance Memo – a system within TALS for the lab to communicate to project management and others when there is an anomaly seen with the samples or batch, or a QC failure.

3.3 Definitions of terms used in this SOP may be found in the glossary of the Pittsburgh Laboratory Quality Assurance Manual (PT-QA-M-001).

4.0 Interferences

4.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample. Cleanup procedures may help to eliminate select interferences, as follows:

- Method 3640A, Gel-Permeation Chromatography - Removes higher molecular weight hydrocarbons by size exclusion chromatography, which is most frequently used for biological samples

- Method 3660B, Sulfur Cleanup – If a sulfur peak is detected, copper or mercury can be used to treat the extract and remove the sulfur

- Other, more aggressive cleanup procedures listed in SW-846 may be used for select compounds listed in this procedure, but may cause degradation of some of the more reactive compounds. Consult with a technical expert in the laboratory for more difficult interference problems.

  Details concerning cleanup steps are described in the organic extraction SOP PT-OP-028.

4.2 Contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts may cause method interferences. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section (Section 9.4). Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If interference is detected, it is

necessary to determine if the source of interference is in the preparation and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.3 The use of high purity reagents, solvents, and gases helps to minimize interference problems.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.5 Phthalate contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-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

5.1.1 Eye protection with side-shields that protect against splash, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

NOTE: Latex and vinyl gloves provide no protection against the organic solvents used in this method. Nitrile or similar gloves must be used.

5.1.2 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 must cool them to room temperature prior to working on them.

5.1.3 The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.1.4 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 before performing any maintenance.

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. 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.

Materials with Significant or Serious Hazard Rating

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.
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.

(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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Gas chromatograph/mass spectrometer system: an 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 should be directly coupled to the source.

6.2 Column: 30 m x 0.32 mm I.D. x 0.50-µm film thickness fused-silica capillary column coated with 5% diphenyl/95% dimethyl polysiloxane(Restek Rtx®-5MS or

equivalent). Alternate columns are acceptable if they provide acceptable performance.

6.3 Mass Spectrometer: Capable of scanning from 35 to 500 u (previously "amu") every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) that meets all of the criteria in Table 4 when 50 ng of the GC/MS tuning standard is injected through the GC/MS.

6.4 Autosampler: HP7683 Autosampler or equivalent.

6.5 GC/MS Interface: Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.6 Data System: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have 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 the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended.

6.7 Syringe: 10 µL Hamilton Laboratory grade syringes or equivalent. The 10 µL syringe is used for the Agilent ALS to be able to inject 2.0 µL.

6.8 Carrier gas: Ultra high-purity helium.

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

The preparation of standards, surrogates and spiking solutions is documented in the TALS Reagent Module. Formulary reports can be generated upon request.

7.1 An eight-point calibration curve is prepared (a minimum of five is required) when average response factors or linear regression curve fitting is used. Six calibration points are required for second-order curve fits. The low point should be at or below the reporting limit. Refer to Table 9 for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit and the high standard defines the range of the calibration.

7.2 An internal standard (IS) solution is prepared. Compounds in the IS Mix are acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10.

7.2.1 Internal standards are added to all calibration standards and extracts to result in a final concentration of 4 µg/mL. For example, if the volume of an extract aliquot used was 100 µL, 1 µL of a 40 µg/mL internal standard solution would be added to the aliquot.

7.3 Surrogate Standard Spiking Solution: Prepare as indicated in the extraction SOPs. Typically surrogate solutions are purchased. Surrogate compounds and levels are listed in Table 8.

Acid Surrogates	**Base Surrogates**
2-Fluorophenol	2-Fluorobiphenyl
2,4,6-tribromophenol	Terphenyl-d4
Phenol-d5	Nitrobenzene-d5

7.4 GC/MS Tuning Standard: A methylene chloride solution containing 25 ng/ul of decafluorotriphenylphosphine (DFTPP) is prepared and injected on to the column. Pentachlorophenol, benzidine, and DDT should also be included in the Tuning Standard at 25 ng/ul.

7.5 Laboratory Control / Matrix Spiking Solution: Prepare as indicated in the extraction SOPs. The spike solution is purchased with a certificate of analysis and contains all routinely analyzed target analytes. Appendix IX compounds and other specially requested compounds are included in the LCS/MS/MSD as requested by the client, and at least biannually.

7.6 All standards are stored away from any light source at >0.0℃ but ≤6.0 °C (-10 °C recommended). The standard stock solutions expire after one year from preparation date or at the earliest expiration date assigned by the vendor to any parent standard, whichever is earlier. The working standards prepared from the stock standards are replaced every 6 months. The continuing calibration standard should be replaced every week, when there are visible signs of degradation, or when the standard fails to meet QC criteria.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Samples and extracts are stored at >0.0℃ but ≤ 6.0ºC. Samples and extracts should be stored in suitable glass containers with Teflon lined caps. Extracts will be kept for at least 30 days after invoicing.

Matrix	Sample Container	Min. Sample Size	Preservation	Extraction Holding Time	Analysis Holding Time
Waters	1 liter amber	1 Liter	Cool, >0.0℃ but ≤ 6.0ºC	7 Days	40 Days from extraction
Soils[1]	4oz Jar	15 grams	Cool, >0.0℃ but ≤ 6.0ºC	14 Days	40 Days from extraction

[1] Includes solids, sludges, sediments, and organic liquid wastes.

9.0 Quality Control

9.1. Control Limits

9.1.1 In-house statistical control limits, based on historical analytical data, must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be reviewed at least annually. The recovery limits are set using the mean recovery +/- 3 standard deviations for surrogates, MS and LCS Precision limits for matrix spikes / matrix spike duplicates are mean relative percent difference +/- 3 standard deviations.

9.1.2 Precision limits for the MS/MSD pair results are the absolute value of the mean relative percent difference (RPD) +3 standard deviations.

9.1.3 All QC, even failing compounds, must be entered into TALS so that realistic statistical control limits can be generated.

9.1.4 Refer to the QC program SOP, PT-QA-021, for further details of control limits.

9.2 The following QC are performed with each preparation batch. Spiking is done to the original sample volume prior to extraction.

Quality Controls	Frequency	Acceptance Limits
Method Blank (MB)	1 per preparation batch[1]	< 1/2 RL
Laboratory Control Sample (LCS)[2]	1 per preparation batch[1]	Statistical limits are maintained in TALS
Matrix Spike (MS)[2,3]	1 per preparation batch[1]	Statistical limits are maintained in TALS. MS is not used for batch control.
Matrix Spike Duplicate (MSD)[2,3]	1 per preparation batch[1]	Statistical limits are maintained in TALS. MSD is not used for batch control.
Surrogates[2]	All samples and QC	Statistical limits are maintained in TALS

[1]A preparation batch is a maximum of 20 samples plus the associated prepared QC.

[2]Statistical control limits are developed and updated as per SOP PT-QA-021. LCS for batches with samples from South Carolina must meet 70-130% recovery limits for all target compounds, 60-140% for poor performers.

[3]The parent sample used for MS/MSD is randomly selected, unless specifically requested by a client.

9.3 The following QC are performed along with each analysis batch. Standards are prepared by the GCMS analyst. Internal standards are added to the extracts prior to analysis. NOTE: Initial Calibration is not performed with each analytical batch.

Analytical QC	Frequency	Acceptance Limits
Tune check (DFTTP)	1 per 12 hr clock, prior to any standards or samples	See Table 4
Initial Calibration Curve (ICAL)	Every 6 months or more often as needed, minimum 5 points	8270C: ≤15%RSD 8270D: ≤ 20%RSD see section 10.2
Initial Calibration Verification	After each ICAL	8270C: List 1 ≤30%D, List 2 ≤50%D [1] 8270D: ≤30%D, see section 10.2.8
Calibration Verification Standard	1 per 12 hr clock, prior to any samples	8270C: CCC ≤20%D, List 1 ≤25%D, List 2 ≤ 50%D [1] 8270D ≤ 20%D, see section 10.2.9.3
Internal Standards	All samples and QC	50– 200% Response in mid-level of ICAL

[1] Refer to Table 2 for List 1 and List 2 compounds

9.4 One Method Blank (MB) is analyzed along with each batch of 20 or fewer samples of the same matrix. MBs are spiked with surrogates and internal standards.

9.4.1 The MB must not contain any analyte of interest at or above ½ the reporting limit. For any analyte detected above the MDL in the MB, associated samples results will be reported with a "B" qualifier. If the MB is contaminated above ½ the RL, reanalyze the blank once. If the failure repeats, re-extraction of the associated samples is required unless one of the following situations exists. Blank subtraction is not permitted.

- If the analyte is a common laboratory contaminant (phthalate esters) the data may be reported with B qualifiers if the concentration of the analyte is not more than 5x the reporting limit. Results are reported using the "Method Blank – Report, Common Lab Contaminant < 5x RL" NCM.

- If the affected compound is not detected above the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers and using the "Method Blank – Report, ND" NCM.

- If the sample concentrations are greater than 10x the concentration seen in the MB, results may be reported with qualifiers and using the "Method Blank – Report, 10X" NCM.

- If reanalysis of the batch is not possible due to limited sample volume or other constraints, the PM should be contacted for direction on how to proceed. If the data must be reported, affected compounds are qualified with a "B" in the associated samples, and appropriate comments are made in the case narrative.

9.4.2 The MB must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the sample analysis is free of contamination. All non-conforming blanks will be documented in an NCM and, if reported, the reasons for reporting the data will be summarized. For example, if surrogate recoveries are low, re-extraction and/or reanalysis of the blank and affected samples will normally be required. If the surrogate recoveries are high in the MB only, results for samples may be reported along with narration. The PM must be contacted and consultation with the client should take place for how to proceed.

9.5 One Laboratory Control Samples (LCS) is analyzed along with each batch of 20 or fewer samples of the same matrix. The matrix of the LCS matches that of the MB. The compounds must be spiked at a concentration equivalent to 20 ng/µL, depending on the analyte, unless a special QAS states a specific level. The LCS

contains all routine analytes of interest (See Table 2). Appendix IX or other specialty analytes are added as required by client project, and at least once every 2 years. If any target analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur (see marginal exceedance allowance in section 9.5.3). Samples associated with a failed LCS must be reanalyzed unless one of the following situations exists:

9.5.1 If the LCS recovers above the control limits, and the affected compound is not detected above the RL in the associated samples, results may be reported with qualification and using the "LCS/LCSD - %R High" NCM.

9.5.2 If reanalysis of the batch is not possible due to limited sample volume or will be past the analytical holding time, the PM must be notified and the client input sought on how to proceed. If the data must be reported, all associated sample results are qualified, and appropriate comments are made in a narrative to document the situation.

9.5.3 For SW846 methods, when there are more than 11 target analytes in the LCS, NELAC allows a specified number of results to fall beyond the LCS control limit (3 standard deviations), but within the marginal exceedance (ME) limits, which are set at 4 standard deviations around the mean of historical data. The number of marginal exceedances allowed is based on the number of analytes in the LCS, as shown in the following table:

Allowed Marginal Exceedances

# of Analytes in LCS	# of Allowed MEs
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

- If more analytes exceed the LCS control limits than is allowed, or if any analyte exceeds the ME limits, the LCS fails and corrective action is necessary. Marginal exceedances must be sporadic and random, which is defined as no more than 2 failures in 3 consecutive batches. If the same analyte repeatedly fails the LCS control limits, it is an indication of a systematic problem, and this is tracked through the review of LCS control charts. The source of the error must be identified and corrective action taken.
- ME limits are determined using the same annual control charts as the LCS control limits.

- Use of marginal exceedances is not permitted for South Carolina work. Control Limits for South Carolina projects are 70-130% with poor performers at 60-140%. See Table 11 for list of poor performers.

NOTE: Due to the nature of Safety Kleen samples, an LCS/LCSD will always be analyzed for QC purposes, in accordance with client instructions.

9.6 One Matrix Spike / Matrix Spike Duplicate (MS/MSD) pair is required to be analyzed with every batch of 20 or fewer samples. The sample used for MS/MSD analysis is chosen at random from the batch unless a client specifies a sample for QC. Spiked compounds and recovery limits are the same as those established for the LCS. Precision limits are calculated from control charts run on an annual basis.

9.6.1 Batch quality is not controlled on the MS/MSD acceptance alone because the sample matrix is being tested. The initial corrective action for MS/MSD failures will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). If the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. Only parent sample results will be qualified associated with MS/MSD failures.

9.6.2 If the recovery for any control component is outside QC limits for both the MS/MSD and the LCS, the laboratory operation is out of control and corrective action must be taken according to the LCS section above.

9.6.3 If a MS/MSD is not possible due to limited sample, it is acceptable to run only an MS, or the LCS may be analyzed in duplicate. RPD of the LCS and LCSD are compared to the matrix spike limits. Document this situation using the “MS/MSD/DUP – Insufficient Volume” NCM.

9.6.4 The matrix spike/duplicate must be analyzed at the same dilution as the unspiked, or parent, sample, even if some matrix spike compounds will be diluted out.

9.7 Surrogates are spiked into all samples and QC to monitor both the analytical system and the effect of the sample matrix on it. Surrogate compounds and spiking levels are provided in Table 8. Surrogate recovery limits are statistically determined annually using historical data. If recovery of any surrogate is outside limits, corrective action is required.

9.7.1 If surrogate recovery is above the control limits, and none of the associated compounds are detected above the RL, results may be reported using the “Surrogate – High, ND” NCM.

9.7.2 Samples that have major matrix interference, which is obvious from the chromatogram, will not be rerun for confirmation of matrix interference. Results will be reported using the "Surrogate – Matrix" NCM.

9.7.3 The decision to reanalyze or flag the data should be made in consultation with the PM and client if neither of the above applies. It is only necessary to reprepare/reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect.

9.7.4 If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and re-preparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then reanalysis or flagging of the data is required.

9.7.5 Surrogate evaluation for dilutions

9.7.5.1 Samples analyzed straight and up to a 5X should have a reportable value for the surrogates above 10% unless there is obvious sample matrix. If surrogates are outside QC limits and no obvious matrix is visible, these samples will go back for re-extraction provided there are no technical reasons why re-extraction should not be done. No "D" qualifier will be applied in TALS.

9.7.5.2 Samples analyzed at 6X and up to and including a 10X may have a reportable value less than 10% for the surrogate results. At these dilutions, if surrogates are outside QC limits and no obvious matrix is visible, these samples will NOT require re-extraction due to the dilution performed, because sample matrix in conjunction with the dilution may cause reportable surrogate results to be less than 10%. No "D" qualifier will be applied in TALS.

9.7.5.3 Samples analyzed at 11X and up to and including a 50X will have their surrogates considered not monitored. In these instances, the values for the surrogates will be reported and a "D" qualifier will be applied in TALS denoting that the surrogate value being reported is from a diluted analysis and the results are not monitored.

9.7.5.4 Samples analyzed at a 51X and above will have their surrogates considered diluted out. The surrogate values will be reported as "0" on the quantitation report and a "D" qualifier will be applied in TALS denoting that the surrogate value being reported is from a diluted analysis and the results will be considered diluted out or not calculated.

9.8 Internal standards (IS) are added to all QC and samples to monitor system performance and adjust for minor changes over time and from sample matrices. The response of the IS must be within 50 – 200% of the response seen in the mid-level standard of the Initial Calibration Curve. If IS response is outside this range, it indicates either a drift in instrument response, or an adverse effect of the sample matrix and corrective action is required.

9.8.1 The internal standard compounds and target compounds associated with each IS are listed in Table 6.

9.8.2 If IS response falls outside the acceptance range in a MB or LCS, this may indicate a drift in instrument response from the ICAL, and a new initial calibration curve must be analyzed if the failures repeats.

9.8.3 IS failure in a sample or MS/MSD may be caused by the matrix. If volume is available, the sample should be reanalyzed to confirm, unless the matrix interference is obvious. If the bad matrix is obvious, results for the associates compounds are considered as estimated and may be reported along with the "ISTD – Matrix" NCM.

9.8.4 If the sample matrix effect is not obvious, and the sample cannot be reanalyzed due to limited volume or holding time, results for the associates compounds are considered as estimated and may be reported along with the "ISTD – No RX/Rerun" NCM.

9.8.5 Internal standards Dioxane-d8 and TBA-d9 apply to only 1 or 2 target analytes that are not always included in the list being reported. If these ISs are outside the control limits, and the associated compounds are not reported, the "ISTD – Non-Targets Affected" NCM may be applied, and results reported without qualification.

9.8.6 Internal standards are also used to monitor for retention time shifts. See section 10.5.2 for details.

9.9 Instrument Blank - Instruments must be evaluated for contamination during each 12-hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of methylene chloride with the internal standards added. It is evaluated in the same way as the method blank.

9.10 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents and approved by a supervisor and QA Manager.

10 Procedure

10.1 Sample Preparation - Samples are prepared according to the following organic preparation SOPs, as applicable:

- PT-OP-001 Extraction of Organic Compounds from Waters, Based on SW-846 3500 Series and 600 Series Methods
- PT-OP-026 Extraction of Organic Compounds from Solids, Sediments, Tissue and Wipes Based on SW-846 3500 Series

- PT-OP-028 Cleanup of Organic Compounds from Waters, Solids, Sediments, Tissue and Wipes Based on SW-846 3600 Series and CarboPrep90 Methods

10.2 Calibration - The instrument is tuned for DFTPP, calibrated initially with an eight point calibration curve (minimum of a five levels required), and verified each 12-hour shift with one or more continuing calibration standard(s). Recommended instrument conditions are listed in Table 3.

10.2.1 All standards and extracts are allowed to warm to room temperature before injecting.

10.2.2 Instrument Tuning

10.2.2.1 Prior to any GCMS analytical sequence, including calibration, the instrument parameters for the tune and subsequent sample analyses within that sequence must be set. Prior to tuning/auto-tuning the mass spec, the parameters may be adjusted within the specifications set by the manufacturer or the analytical method. These generally do not need any adjustment but it may be required based on the current instrument performance. If the tune verification does not pass it may be necessary to clean the source or perform additional maintenance. Any maintenance is documented in the maintenance log.

10.2.2.2 At the beginning of every twelve-hour shift when analyses are to be performed, the GC/MS system must be checked to see if the acceptance criteria are achieved for DFTPP (decafluorotriphenylphosphine). See Table 4.

10.2.2.3 Inject 25 ng/ul of the GC/MS tuning standard (Section 7.4) into the GC/MS system. Part of the purpose of the tune is to demonstrate sensitivity and analyzing solutions at higher concentrations does not support this purpose. Tune failures may be due to saturation and a lower DFTPP concentration may be warranted. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 4 are achieved.

10.2.2.4 Acceptable means of passing DFTPP are as follows:

- Tune evaluations usually utilize the "Autofind" function and are 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. The peak apex, or the scan immediately before the apex, or the scan immediately after the apex, or the average of these three scans may be used.

10.2.2.5 Options or if Auto Tune Fails:

- Sometimes the instrument does not always correctly identify the apex on some peaks when the peak is not perfectly shaped. In this case, manually identify and average the apex peak +/- 1 scan and background correct as in 10.2.2.4 above. This is consistent with EPA 8270D.
- A single scan at the Apex (only) may also be used for the evaluation of the tune. For SW 846 methods, background correction is still required.
- Adjustments such as adjustments to the repeller and ion focus lenses, adjusting the EM Voltage, etc. may be made prior to tune verification as long as all of the subsequent injections in the 12 hour tune cycle are analyzed under the same MS tune settings and it is documented in the run sequence log and/or maintenance log that an adjustment was made. Necessary maintenance is performed and documented in instrument log. If changes are made to EM Voltage or other parameters that can result in changes to response and/or instrument sensitivity, a new initial calibration curve must be run under the new conditions prior to sample analysis.
- Cleaning the source or other maintenance may be performed and then follow steps for tune evaluation above. Note: If significant maintenance was performed, see methods 8000C then the instrument may require recalibration prior to proceeding.
- Tune evaluation printouts must include the chromatogram and spectra as well as the Tune evaluation information. In addition, the verifications must be sent directly to the printer or pdf file (no screen prints for DFTPP tunes). This ability should be built into the instrument software.
- Since the limits are expressed in whole percentages, the results may be rounded to whole percentage before comparing to criteria when assessing the tune verification against the tune requirements. However, the comparison to the criteria is usually done automatically by the software and if the printout says “Fail” then there would have to be documentation of the hand calculation on the raw data and comparison to the criteria if the lab intends to still accept the tune. In most cases the analyst is better off performing an adjustment and rerunning the tune standard.
- All MS tune settings must remain constant between running the tune check and all other samples. It is recommended that a

separate tune method not be used, however a separate method may be used as long as the MS conditions between the methods are the same as the sample analysis method and tracked so any changes that are made to the analysis method are also made to the tune method.

- If the instrument has a built in macro that checks the DFTPP, use of this macro with no manual manipulation is also acceptable and preferred (assuming, of course that the correct ion ratios are being checked).

10.2.2.6 If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

10.2.2.7 The GC/MS tuning standard should also be used to evaluate the inertness of the chromatographic system. The acceptance criteria for the peak tailing factor for benzidine is < 2.0 and pentachlorophenol is < 2.0. DDT breakdown must be <20%. Refer to section 11 for the appropriate calculations.

10.2.3 **Initial Calibration**

10.2.3.1 Internal Standard (IS) Calibration Procedure: Internal standards are listed in Table 6. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation.

10.2.3.2 Compounds are assigned to the IS with the closest retention time.

10.2.3.3 Prepare calibration standards at eight (a minimum of five required) concentration levels for each parameter of interest when average response factors or linear regression curve fits are used. Six standards must be used for a quadratic least-squares calibration. It may also be useful to analyze six calibration levels and use the lower five for most analytes and the upper five for analytes that have poor response.

10.2.3.4 Generally, it is not acceptable to remove points from a calibration. If calibration acceptance criteria are not met, the normal corrective action is to examine conditions such as instrument maintenance and accuracy of calibration standards. Any problems must be fixed and documented in the run log or maintenance log. Then the calibration standard(s) must be reanalyzed.

10.2.3.5 If no problems are found or there is documented evidence of a problem with a calibration point (e.g., obvious misinjection explained in the run log), then one point might be rejected, but

only if all of the following conditions are met:

- The rejected point is the highest or lowest on the curve, i.e., the remaining points used for calibration must be contiguous; and
- The lowest remaining calibration point is still at or below the project reporting limit; and
- The highest remaining calibration point defines the upper concentration of the working range, and all samples producing results above this concentration are diluted and reanalyzed; and
- The calibration must still have the minimum number of calibration levels required by the method, i.e. five levels for calibrations modeled with average response factors or linear regressions, or six levels for second-order curve fits.

10.2.3.6 Add the internal standard mixture to result in a 4-ng/µL final concentration. (For example, if the volume of the calibration standard used is 1.0 mL, add 10 µL of the 400 µg/mL internal standard). The concentrations of all analytes are listed in Table 9.

10.2.3.7 Analyze each calibration standard and tabulate the area of the primary characteristic m/z against the concentration for each compound and internal standard. Standard concentrations are listed in Table 9. Calculate the response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in Section 11. No sample analysis may be performed unless these criteria are met.

10.2.4 Selection of Calibration Curve Fit Type

10.2.4.1 Average Response Factor

- If all analyte RSDs in the initial calibration are ≤ 15% for method 8270C or ≤20% for method 8270D, then all analytes may use average response factor for calibration.
- If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with RSD >15% for method 8270C or >20% for method 8270D for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve fit, then the appropriate curve should be used for quantitation.
- If analyte RSDs in the initial calibration are >15% for method 8270C or >20% for method 8270D, then calibration using an alternative curve fit, must be used for those analytes. Linear or

quadratic curve fits may be used. Use of 1/Concentration^2 weighting is recommended to improve the accuracy of quantitation at the low end of the curve. The analyst should consider instrument maintenance to improve the linearity of response.

10.2.4.2 Linear Regression

- A weighted linear regression may be used even if the average response factor curve is acceptable.
- If linear regression is used the calibration must employ weighting by 1/Amt or 1/(Amt)^2. A minimum of 5 points are required. The coefficient of determination (r^2) must be > 0.990.
- When using Linear Regression, recalculate the concentration of the low calibration point (or the point that corresponds to the RL). Acceptance criteria is ± 30% of true value. Poor performers have an expanded criteria of ± 40%. Poor performers are considered are listed in Table 11.
- If the readback criteria fails for any analyte, sample detects should be reanalyzed under passing critiera. If reanalysis is not possible, the result must be flagged as estimated, or described in the narrative.
- For non-detects, reanalysis is not required, and flagging is not required.

10.2.4.3 Quadratic Regression

- In some cases the response/concentration relationship may be non-linear. In these cases quadratic regression may be used.
- Quadratic fits must only be used where an average or weighted linear fit is clearly inappropriate. **Quadratic curve fits are not allowed for analysis of South Carolina samples.**
- Force through zero is allowed, but should be necessary only rarely.
- A minimum of 6 points are required for a quadratic curve, and the coefficient of determination (r^2) must be > to 0.990. Additional checks are required to ensure that a quadratic fit is appropriate:
- The calibration plot must be inspected to ensure that the curve does not flatten out (i.e., slope = 0) or become negative within the range of the calibration

- Where a quadratic curve fit is applied- all chromatograms for all samples must be inspected for off scale peaks in the retention time range of the analyte.
- When using Quadratic fits, recalculate the concentration of the low calibration point (or the point that corresponds to the RL) Acceptance criteria is ± 70% of true value.
- If the readback criteria fails for any analyte, sample detects should be reanalyzed under passing criteria. If reanalysis is not possible, the result must be flagged as estimate, or the situation described in the narrative.
- For non-detects, if the readback failed with high recovery, reanalysis is not required, and flagging is not required. If the readback failed low, samples should be reanalyzed. If reanalysis is not possible, the result must be flagged as estimate, or the situation described in the narrative.

10.2.4.4 Linear Regression (unweighted)

- Unweighted linear should be used only where other available fits are clearly inappropriate.
- If unweighted linear regression is used, a minimum of 5 points are required. The coefficient of determination (r2) must be > 0.990.
- When using Unweighted Linear Regression, recalculate the concentration of the low calibration point (or the point that corresponds to the RL) Acceptance criteria is ± 30% of true value. Poor performers have an expanded criteria of ± 40%.
- If this readback criteria fails for any analyte, sample detects should be reanalyzed under passing criteria. If reanalysis is not possible, the result must be flagged as estimate, or the situation described in the narrative.
- For non-detects, if the readback failed with high recovery, reanalysis is not required, and flagging is not required. If the readback failed low, samples should be reanalyzed. If reanalysis is not possible, the result must be flagged as estimate, or the situation described in the narrative.

10.2.4.5 For method 8270D only, if more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.990) for alternate curve fits, then the chromatographic system is considered too reactive for analysis to begin. Clean or replace the injector liner and/or column, then repeat the calibration

procedure. Minimum response factors should be met, especially for the low level standard.

10.2.4.6 Any analyte that fails both the RSD and the correlation requirement must have any positive result flagged as estimated and the non-conformance must be explained in the case narrative.

10.2.4.7 Any individual analyte that fails the minimum response factor (see Table 10) must have a demonstration of sensitivity in the analytical batch to report non-detects. Detected results may be reported without qualification.

- The demonstration of sensitivity is analysis of a low level CCV (LODV) at or below the reporting limit. The criterion for passing a LODV is detection only and a passing LODV allows non-detects to be reported without flagging.
- The LODV would be analyzed immediately after the mid-level CCV.
- Table 10 is used as guidance for the minimum response factors, however the RFs may be modified if appropriate (for example, especially if low level analysis is performed).

10.2.4.8 Table 11 lists TestAmerica Pittsburgh's poor performing compounds and the criteria used to evaluate these compounds.

10.2.5 Weighting of Calibration Data Points

In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason, it is preferable to increase the weighting of the lower concentration points. 1/Concentration2 weighting (often called 1/X2 weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability. Because the data system does not indicate the type of weighting used, the analyst must make a notation on the initial calibration form as to the weighting used (e.g. 1/x or $1/x^2$).

10.2.6 Low level Standard 30% Readback (linear curve fit only)

Analytes using linear calibration fit should have the readback concentration of the low level standard evaluated. The readback concentration should be within 30% of the true value, although other criteria may be applicable. Any sample with detects for analytes that fail the readback criteria, and are using linear calibration must be flagged as estimated, or described in the

narrative. Flagging is not required for any samples with non-detects for analytes the fail the readback criteria.

10.2.7 If time remains in the 12-hour period initiated by the DFTPP injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration, Section 10.2.9.

NOTE: Quantitation is always performed using the calibration curve or average response factor from the initial curve, not the continuing calibration.

10.2.8 Second Source Calibration Verification Requirements: An initial calibration verification containing all components from a second source (an alternate vendor or a unique lot from the same vendor) must be analyzed after the initial calibration. The measured concentrations for all analytes of the second source standard must be within ± 30% of the expected value (50% for List 2 compounds for method 8270C). Table 11 lists TestAmerica Pittsburgh's poor performing compounds and the criteria used to evaluate these compounds for second source ICV purposes for method 8270D.

10.2.8.1 If the SOP limits are exceeded, a fresh ICV standard is prepared and analyzed. If failure repeats, the ICAL and ICV should be reanalyzed.

10.2.8.2 If sample results must be reported associated with a failed ICV due to holding time or sample volume limitations, inform the Project Manager to get directions from the client. If results must be reported, describe the issue in the narrative or flag as an estimate. For samples from Pennsylvania, sample results must be flagged.

10.2.9 Continuing Calibration Verification (CCV)

10.2.9.1 At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. A 25-ng/µL injection of DFTPP must result in a mass spectrum for DFTPP, which meets the criteria given in Table 4.

10.2.9.2 Following a successful DFTPP analysis, the continuing calibration verification (CCV) standard(s) are analyzed. The standard(s) must contain all semivolatile analytes, including all required surrogates. A mid-level calibration standard is used for the CCV.

10.2.9.3 The following criteria must be met for the CCV to be acceptable:

- For method 8270C, all CCC compounds must have %D ≤20%. List 1 compounds that are not CCC compounds must have %D ≤25%, with an allowance for up to 4 non-CCC compounds to

have %D up to 40%. List 2 compounds must have %D ≤50%.

- For method 8270D, all routine compounds (CCC and non-CCC) must have percent difference or drift (%D) ≤ 20%. Appendix IX compounds may have %D up to 40%. See Table 11 for poor-performer and Appendix IX compound list.
- Due to the large numbers of compounds that may be analyzed by this method, it is expected that some compounds will fail to meet the criterion.
    - For method 8270C, List 2 compounds are given a wider acceptance range of ≤ 50%D. See Table 2 for List 2 compounds.
    - For method 8270D, up to 20% of the compounds in the standard are allowed to fail exceed 20%D. If the criterion is not met for more than 20% of the compounds included in the calibration, then corrective action must take place prior to the analysis for samples. Any compound with a %D or Drift >20% must be narrated using the "CCV – Outside Criteria; Estimated Value (EPA 8270D/8260C)" NCM.
    - In cases where compounds fail, they may still be reported as non-detects if recovery was high, or if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations where the failed compound is present, the concentrations must be reported as estimated values (J flagged).
- Each of the most common target analytes in the CCV must meet the minimum response factors listed in Table 10. If they are not met, the system is evaluated, and corrective action takes place 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. Table 10 is used as guidance for the minimum response factors, however the RFs may be modified if appropriate (for example, especially if low level analysis is performed). Any individual analyte that fails the minimum response factor (see Table 10) must have a demonstration of sensitivity in the analytical batch to report non-detects. The demonstration of sensitivity is analysis of a low level CCV (LODV) at or below the reporting limit. The LLCCV would be analyzed immediately after the mid-level CCV. The criterion for passing a LODV is detection only and a passing LODV allows non-detects to be reported without flagging. Currently, TALs

does not allow for the upload of the LODVs, thus they will be monitored using the instrument runlog.

10.2.9.4 The internal standard response of the CCV must be within 50 - 200% of the response in the same level of the corresponding calibration. If any internal standard retention time in the CCV changes by more than 30 seconds from that of the same level of the corresponding initial calibration, the chromatographic system must be inspected for malfunctions and corrections made, as required.

10.2.4.5 Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the DFTPP have passed. (A sample injected less than or equal to 12 hours after the DFTPP is acceptable.)

10.2.4.6 Table 11 lists TestAmerica Pittsburgh's poor performing compounds and the criteria used to evaluate these compounds for ICAL, ICV and CCV purposes.

10.2.4.7 Any sample detects for an analyte that fails the SOP CCV criteria must be flagged as an estimated or described in the narrative. Sample results (both ND and detects) associated with a compound outside 20%D in the CCV must be flagged for samples from Pennsylvania.

10.3 Sample Analysis Procedure

10.3.1 QC standards and sample extracts are stored at >0.0℃ but ≤ 6.0°C, protected from light in screw cap vials equipped with unpierced Teflon lined septa. Allow standards and sample extracts to warm to room temperature prior to injection.

10.3.2 Calibrate the instrument as described in Section 10.2. Depending on the target compounds required by the client, it may be necessary to use more than one set of calibration standards.

10.3.3 All samples must be analyzed using the same instrument conditions as the preceding continuing calibration verification (CCV) standard.

10.3.4 Add internal standard to an aliquot of the extract to result in a 4-ng/µL concentration (for example, 1.0 µL of internal standard solution at, 400 µg/mL in 100 µL of extract). Mix thoroughly before injection into the instrument.

10.3.5 Inject the aliquot into the GC/MS system using the same injection technique as used for the standards.

10.3.6 The data system will determine the concentration of each analyte in the extract using calculations in Section 11. Quantitation is based on the initial calibration, not the continuing calibration verification.

10.3.7 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst (see CA-Q-S-002, Acceptable Manual Integration Practices) or automatically by the data system. The minimum documentation required includes a hard copy of original data system peak integration and a similarly scaled hard copy showing the manual integration with analyst 's electronic initials/name, date and reason for manual integration.

10.3.8 Target compounds identified by the data system are evaluated using the criteria listed in Section 11.1.

10.3.9 Library searches of peaks present in the chromatogram that are not target compounds, i.e., Tentatively Identified Compounds (TIC), may be performed if required by the client. They are evaluated using the criteria in Section 11.2.

10.3.10 Analysis of extracts from tissue samples follows the same procedure as other samples as described in this SOP.

10.4 Dilutions

10.4.1 If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be between the 4 and 10 ng on column concentration. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range. See Table 12, which shows how dilutions are prepared.

10.4.2 Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are significantly less than two times the height of the internal standards, the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgment. For example, samples containing organic acids may need to be analyzed at a higher dilution to avoid destroying the column.

10.4.2 Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will be reported only at client request.

10.5 Retention Time Criteria for Samples

10.5.2 If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

10.6 Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP PT-WC-020 for determination of percent moisture.

10.7 Troubleshooting Guide

10.7.1 Daily Instrument Maintenance

In addition to the checks listed in Appendix A, the following daily maintenance should be performed.

- Clip Column as necessary.
- Install new or cleaned injection port liner as necessary.
- Install new septum as necessary.
- Install new or cleaned gold seal and washer as necessary.
- Perform mass calibration as necessary.
- Refill rinse autosampler vials with clean methylene chloride.

10.7.2 Major Maintenance

10.7.2.1 A new initial calibration is necessary following certain maintenance procedures. These maintenance procedures include changing or reversing the column, cleaning or changing the repeller, cleaning the source, replacing the multiplier, and replacing the “top board” or RF-related electronics. Refer to the manufacturer's manual for specific guidance.

10.7.3 In contrast, some maintenance procedures should not automatically require recalibration of the instrument. These maintenance procedures include changing septa, compressed gas cylinders, autosampler syringes, moisture traps, PTFE transfer lines, column fittings or inlet liners. Other procedures include cleaning the MS source, breaking off or changing the guard column, changing an injection port or filaments and cleaning the inlet.

10.7.3.1 Whenever such procedures are performed, the analyst must demonstrate that the results for a CCV meet the acceptance criteria in section 10.8.15.3 before the analysis of any samples. Otherwise, recalibration is required.

11 Calculations / Data Reduction

11.1 Qualitative Identification

An analyte is identified by retention time, the relative abundances of characteristic ions and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NBS library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions.

NOTE: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.

11.1.1 The sample component relative retention time must compare to within ± 0.06 RRT units of the relative retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

11.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

11.1.3 The characteristic ions of a compound must maximize in the same scan or within one scan of each other.

11.1.4 The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%.)

11.1.5 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

11.1.6 Mass chromatogram searches:

Certain compounds are unstable in the calibration standard and cannot be calibrated in the normal way. In particular, the compound hexachlorophene (CAS 70-30-4) falls into this category, and is required for Appendix IX analysis. For this analyte a mass chromatogram search is made.

11.1.6.1 Hexachlorophene - Display the mass chromatograms for mass 196, mass 198 and mass 209 for the region of the chromatogram from at least 2 minutes before chrysene-d12 to at least 4 minutes after chrysene-d12. If peaks for both ions coincide then the analyst evaluates the spectrum for the presence of hexachlorophene. No quantitation is possible.

11.2 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 will be determined by the type of analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches shall the mass spectral interpretation specialist assign a tentative identification. Following are guidelines for making tentative identification:

11.2.1 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

11.2.2 The relative intensities of the major ions should agree to within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30% and 70%.)

11.2.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

11.2.4 Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or the presence of co-eluting compounds.

11.2.5 Ions present in the reference spectrum, but not in the sample spectrum, should be 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.

11.2.6 Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

11.3 Isomers with identical mass spectra and close elution times pose problems for definitive identification. The following compounds fall into this category:

Aniline and bis(2-chloroethyl) ether
Dichlorobenzenes
Methylphenols
Trichlorophenols
Phenanthrene, anthracene
Fluoranthene, pyrene
Benzo(b) and (k)fluoranthene
Chrysene, benzo(a)anthracene

Identification of these compounds requires both experience and extra precautions on the part of the analyst. Specifically, the analyst must more closely scrutinize the comparison of retention times between the unknown and the calibration

standard. The analyst must also check that all isomers have distinct retention times.

11.4 A second category of problem compounds consist of the poor responders or compounds that chromatograph poorly. The integrations for these types of compounds should be checked manually. The following compounds are included in this category:

Benzoic acid
Chloroanilines
Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol
3,3'-Dichlorobenzidine
Benzyl alcohol
4,6-Dinitro-2-methylphenol
Atrazine
Famphur
Benzidine
2,2'- Oxybis (1-Chloropropane)

11.5 Calculating the Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{RF} \times 100\%$$

Where:

RF = Mean of RFs from the initial calibration for a compound
SD = Standard deviation for the mean RF from the initial calibration for a compound

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(RF_i - \overline{RF}\right)^2}{n-1}}$$

RFi = RF for each of the calibration levels
n = Number of RF values

11.6 Calculating the Continuing Calibration Percent Drift

$$\%Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

Where:

C actual = Known concentration in standard
C found = Measured concentration using selected quantitation method

11.7 Calculating the Concentration in the Extract

The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration.

11.7.1 Average Response Factor Calibration

If the average of all the RSDs of the response factors in the initial calibration is ≤20%, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is}\overline{RF}}$$

Where:

Cex = Concentration in the extract, µg/mL
Rx = Response for the analyte
Ris = Response for the internal standard
Cis = Concentration of the internal standard
$\overline{RF}$ = Average response factor

11.7.2 Linear Fit Calibration

$$C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$$

Where:

Cex = Concentration in the extract, µg/mL
Rx = Response for the analyte
Ris = Response for the internal standard
Cis = Concentration of the internal standard
A = Intercept of linear calibration line
B = Slope of linear calibration line

11.7.3 Quadratic Fit Calibration

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}}{R_{is}}\right)$$

Where:

Cex = Concentration in the extract, µg/mL
Rx = Response for the analyte
Ris = Response for the internal standard
Cis = Concentration of the internal standard
A = Intercept
B = Factor for the linear term of the quadratic calibration function
C = Factor for the curvature term of the quadratic calibration function

11.8 Calculating the Concentration in the Sample

11.8.1 Calculation for Aqueous Samples

$$\text{Concentration, } \mu\text{g / L} = \frac{C_{ex} V_t}{V_o}$$

Where:

Cex = Concentration in the extract

Vt = Volume of total extract in µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1-mL extract will mean that Vt = 10,000 µL. If half of the base/neutral extract and half of the acid extract are combined, then Vt = 2,000.)

Vo = Volume of the sample that was extracted (mL)

11.8.2 Calculation for Sediment, Soil, Sludge, and Waste Samples

Results for sediments, sludges, and soils are usually calculated on a dry-weight basis, and for waste, on a wet-weight basis.

$$\text{Concentration, } \mu\text{g / kg} = \frac{C_{ex} V_t}{W_s D}$$

Where:

Cex = Concentration in the extract
Vt = Volume of total extract in µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1-mL extract will mean that Vt = 10,000 µL. If half of the base/neutral extract and half of the acid extract are combined, then Vt = 2,000.)
Ws = Weight of sample extracted or diluted in grams

D = (100 - % moisture in sample)/100, for a dry-weight basis or 1 for a wet-weight basis

11.9 MS/MSD Percent Recovery Calculation

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

Where:
SSR = Spike sample result
SR = Sample result
SA = Spike added

11.10 Calculating the Relative Percent Difference (RPD) MS/MSD Pair

$$RPD = \frac{\left|MS_R - MSD_R\right|}{(MS_R + MSD_R)/2} \times 100$$

Where:
RPD = Relative percent difference
MSR = Matrix spike result
MSDR = Matrix spike duplicate result

11.11 Relative Response Factor Calculation

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:
Ax = Area of the characteristic ion for the compound being measured
Ais = Area of the characteristic ion for the specific internal standard
Cx = Concentration of the compound being measured (µg/L)
Cis = Concentration of the specific internal standard (µg/L)

11.12 Calculation of TICs

The calculation of TICs (tentatively identified compounds) is identical to the above calculation (11.11) with the following exceptions:

Ax = Area of the total ion chromatogram for the compound being measured
Ais = Area of the total ion chromatogram for the nearest internal standard without interference
RF = 1

11.13 Calculating Percent DDT Breakdown

$$\% \text{ DDT breakdown} = \frac{\text{DDEarea} + \text{DDDarea}}{\text{DDTarea} + \text{DDEarea} + \text{DDDarea}}$$

The areas for the 235 ion are used for this calculation.

11.14 Calculating the Peak Tailing Factor

$$TailingFactor = \frac{BC}{AB}$$

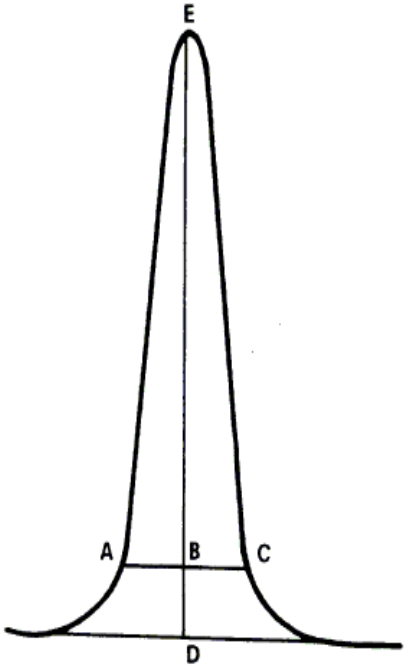
Where:

Peak width (AC) is measured at 10% peak height, and divided into two line segments at the peak centroid, so that.

AC = AB + BC, with

AB = left-hand segment

BC = right-hand segment



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

12 Method Performance

12.1 The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilities – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual and SOP PT-QA-001, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Method Detection Limit Study – A Method Detection Limit (MDL) study, as described in the QA Manual and SOP PT-QA-007, must be performed initially, annually and any time a significant change is made to the analytical system.

13 Pollution Control

13.1 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" and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

14 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 PT-HS-001 (note a Waste Disposal SOP or manual). The following waste streams are produced when this method is carried out.

14.1.1 Solvent waste generated from cleaning operations and out of specification standards. This waste is placed in a waste container identified as "Methylene Chloride Waste", Waste #2 or "Mixed Flammable Solvent Waste", Waste #3.

14.1.2 Sample extracts in vials. This waste is placed in containers identified as "Vials & Extracts", Waste #7.

14.1.3 Sylon Waste. This waste is collected in a container identified as "Sylon (5%) / Toluene Waste", Waste #20.

15 References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Revision 3, December 1996, Method 8270C

15.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update V, Revision 5, July 2014, Method 8270D

15.3 USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, OSWER 9240.1-05A-P, PG99-963-506, EPA540/R-99/008, October 1999

15.4 PT-OP-001 Extraction of Organic Compounds from Waters, Based on SW-846 3500 Series and 600 Series Methods

15.5 PT-OP-026 Extraction of Organic Compounds from Solids, Sediments, Tissue and Wipes Based on SW-846 3500 Series

15.6 PT-OP-028 Cleanup of Organic Compounds from Waters, Solids, Sediments, Tissue and Wipes Based on SW-846 3600 Series and CarboPrep90 Methods

15.7 SOP PT-QA-001, Employee Orientation and Training

15.8 SOP CA-Q-S-002, Acceptable Manual Integration Practices

15.9 SOP PT-QA-007, Determination of Method Detection Limits (MDL)

15.10 SOP PT-QA-016, Nonconformance and Corrective Action System

15.11 SOP PT-QA-018, Technical Data Review Requirements

15.12 SOP PT-QA-021, Quality Control Program

15.13 Pittsburgh Laboratory Quality Assurance Manual (PT-QA-M-001)

15.14 SOP CA-Q-W-007, Technical Guidance on Quality Control for SW-846 Method 8270D

15.15 PT-HS-001, Pittsburgh Facility Addendum EH&S Manual to the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention"

15.16 PT-SR-001, Sample Receipt & Login

15.17 PT-QA-031, Internal Chain of Custody

16 Method Modifications:

16.1 Modifications from Reference Method

16.1.1 The quantitation and qualifier ions for some compounds have been added to the list of those, which are recommended in SW-846 in order to improve the reliability of qualitative identification.

17 Attachments

Table 1 - TestAmerica Pittsburgh Routine and Low Level Standard Reporting Limits (RLs)

Table 2 **-** Reportable Compounds for TestAmerica Pittsburgh Standard Tests

Table 3 - Suggested Instrument Conditions

Table 4 - DFTPP Key Ions and Ion Abundance Criteria

Table 5 - Characteristic Ions for Routine and Appendix IX Compounds

Table 6 - Semivolatile Internal Standards with Corresponding Analytes assigned for Quantitation

Table 7 - 8270D TCLP LCS Compounds

Table 8 - 8270D Surrogate Compounds

Table 9 - Routine and Appendix IX Standard Calibration Levels, µg/mL

Table 10 - Minimum Response Factor Criteria for Initial and Continuing Calibration Verification

Table 11 - Method 8270D Poor Performers and Laboratory Acceptance Criteria

Table 12 - TestAmerica Pittsburgh GCMS Semivolatile Dilution Calculation Table

Appendix A - Instrument Maintenance Schedules - Mass Spectrometer & Gas Chromatograph

19.0 Revision History

19.1 Revision 0, 1/31/2009.

19.2 Revision 1, 7/27/2009

19.3 Revision 2, 5/15/2012.

19.4 Revision 3, 9/27/2013

19.5 Revision 4, 1/26/2016

19.6 Revision 5, 4/20/2016

19.7 Changes to current revision

SOP section	Change from	Change to	Reason
10.2.2.5 bullet 3		Add if changes are made to EM Voltage a new calibration curve is required.	Clarification

Table 1
TestAmerica Pittsburgh Standard and Low Level Reporting Limits (RLs)[1]

Compound	CAS #	Standard RL Aqueous (µg/L)	Standard RL Soil (µg/kg)	Low Level RL Aqueous (µg/L)	Low Level RL Soil (µg/kg)
1,1'-Biphenyl	92-52-4	10	330	1.0	33
1,2,4,5-Tetrachlorobenzene	95-94-3	10	330	1.0	33
1,2,4-Trichlorobenzene	120-82-1	10	330	1.0	33
1,2-Dichlorobenzene	95-50-1	10	330	1.0	33
1,2-Diphenylhydrazine	122-66-7	10	330	1.0	33
1,3,5-Trinitrobenzene	99-35-4	10	330	1.0	33
1,3-Dichlorobenzene	541-73-1	10	330	1.0	33
1,3-Dinitrobenzene	99-65-0	10	330	1.0	33
1,4-Dichlorobenzene	106-46-7	10	330	1.0	33
1,4-Dinitrobenzene	100-25-4	10	330	1.0	33
1,4-Dioxane	123-91-1	20	660	2.0	66
1,4-Naphthoquinone	130-15-4	10	330	1.0	33
1-Chloronaphthalene	90-13-1	10	330	1.0	33
1-Methylnaphthalene	90-12-0	2	66	0.2	6.6
1-Naphthylamine	134-32-7	10	330	1.0	33
2,2'-oxybis[1-chloropropane] [2]	108-60-1	10	330	1.0	33
2,3,4,6-Tetrachlorophenol	58-90-2	10	330	1.0	33
2,3,5,6-Tetrachlorophenol	935-95-5	10	330	1.0	33
2,4,5-Trichlorophenol	95-95-4	10	330	1.0	33
2,4,6-Trichlorophenol	88-06-2	10	330	1.0	33
2,4-Dichlorophenol	120-83-2	10	330	1.0	33
2,4-Dimethylphenol	105-67-9	10	330	1.0	33
2,4-Dinitrophenol	51-28-5	50	1650	5.0	165
2,4-Dinitrotoluene	121-14-2	10	330	1.0	33
2,6-Dichlorophenol	87-65-0	10	330	1.0	33
2,6-Dinitrotoluene	606-20-2	10	330	1.0	33
2-Acetylaminofluorene	53-96-3	10	330	1.0	33
2-Chloronaphthalene	91-58-7	2	66	0.2	6.6
2-Chlorophenol	95-57-8	10	330	1.0	33
2-Methylnaphthalene	91-57-6	2	66	0.2	6.6
2-Methylphenol	95-48-7	10	330	1.0	33
2-Naphthylamine	91-59-8	10	330	1.0	33
2-Nitroaniline	88-74-4	50	1650	5.0	165
2-Nitrophenol	88-75-5	10	330	1.0	33
2-Picoline	109-06-8	10	330	1.0	33
2-Toluidine	95-53-4	10	330	1.0	33
3,3'-Dichlorobenzidine	91-94-1	10	330	1.0	33

Compound	CAS #	Standard RL Aqueous (µg/L)	Standard RL Soil (µg/kg)	Low Level RL Aqueous (µg/L)	Low Level RL Soil (µg/kg)
3,3'-Dimethylbenzidine	119-93-7	50	1650	5.0	165
3-Methylcholanthrene	56-49-5	10	330	1.0	33
3-Nitroaniline	99-09-2	50	1650	5.0	165
4,4'-Methylene bis(2-chloroaniline)	101-14-4	10	330	1.0	33
4,6-Dinitro-2-methylphenol	534-52-1	50	1650	5.0	165
4-Aminobiphenyl	92-67-1	10	330	1.0	33
4-Bromophenyl phenyl ether	101-55-3	10	330	1.0	33
4-Chloro-3-methylphenol	59-50-7	10	330	1.0	33
4-Chloroaniline	106-47-8	10	330	1.0	33
4-Chlorophenyl phenyl ether	7005-72-3	10	330	1.0	33
4-Methylphenol	106-44-5	10	330	1.0	33
4-Nitroaniline	100-01-6	50	1650	5.0	165
4-Nitrophenol	100-02-7	50	1650	5.0	165
4-Nitroquinoline-1-oxide	56-57-5	50	1650	5.0	165
6-Methylchrysene	1705-85-7	10	330	1.0	33
7,12-Dimethylbenz(a)anthracene	57-97-6	10	330	1.0	33
Acenaphthene	83-32-9	2	66	0.2	6.6
Acenaphthylene	208-96-8	2	66	0.2	6.6
Acetophenone	98-86-2	20	660	2.0	66
Acrylamide	79-06-1	10	330	1.0	33
alpha,alpha-Dimethyl phenethylamine	122-09-8	50	1650	5.0	165
Aniline	62-53-3	10	330	1.0	33
Anthracene	120-12-7	2	66	0.2	6.6
Aramite, Total	140-57-8	10	330	1.0	33
Atrazine	1912-24-9	20	660	2.0	66
Benzaldehyde	100-52-7	20	660	2.0	66
Benzidine	92-87-5	200	6600	20.0	660
Benzo[a]anthracene	56-55-3	2	66	0.2	6.6
Benzo[a]pyrene	50-32-8	2	66	0.2	6.6
Benzo[b]fluoranthene	205-99-2	2	66	0.2	6.6
Benzo[g,h,i]perylene	191-24-2	2	66	0.2	6.6
Benzo[k]fluoranthene	207-08-9	2	66	0.2	6.6
Benzoic acid	65-85-0	50	1650	5.0	165
Benzyl alcohol	100-51-6	10	330	1.0	33
Bis(2-chloroethoxy)methane	111-91-1	10	330	1.0	33
Bis(2-chloroethyl)ether	111-44-4	10	330	1.0	33
Bis(2-ethylhexyl) phthalate	117-81-7	20	660	2.0	66
Butyl benzyl phthalate	85-68-7	10	330	1.0	33
Caprolactam	105-60-2	50	1650	5.0	165
Carbazole	86-74-8	10	330	1.0	33
Chlorobenzilate	510-15-6	10	330	1.0	33

Compound	CAS #	Standard RL Aqueous (µg/L)	Standard RL Soil (µg/kg)	Low Level RL Aqueous (µg/L)	Low Level RL Soil (µg/kg)
Chrysene	218-01-9	2	66	0.2	6.6
Diallate	2303-16-4	10	330	1.0	33
Dibenz(a,h)anthracene	53-70-3	2	66	0.2	6.6
Dibenz[a,h]acridine	226-36-8	10	330	1.0	33
Dibenzofuran	132-64-9	10	330	1.0	33
Diethyl phthalate	84-66-2	10	330	1.0	33
Dimethoate	60-51-5	10	330	1.0	33
Dimethyl phthalate	131-11-3	10	330	1.0	33
Di-n-butyl phthalate	84-74-2	10	330	1.0	33
Di-n-octyl phthalate	117-84-0	10	330	1.0	33
Dinoseb	88-85-7	10	330	1.0	33
Diphenylamine [3]	122-39-4	10	330	1.0	33
Disulfoton	298-04-4	10	330	1.0	33
Ethyl methanesulfonate	62-50-0	10	330	1.0	33
Ethyl Parathion	56-38-2	10	330	1.0	33
Famphur	52-85-7	100	3300	10.0	330
Fluoranthene	206-44-0	2	66	0.2	6.6
Fluorene	86-73-7	2	66	0.2	6.6
Hexachlorobenzene	118-74-1	10	330	1.0	33
Hexachlorobutadiene	87-68-3	10	330	1.0	33
Hexachlorocyclopentadiene	77-47-4	10	330	1.0	33
Hexachloroethane	67-72-1	10	330	1.0	33
Hexachloropropene	1888-71-7	10	330	1.0	33
Hexadecane	544-76-3	10	330	1.0	33
Indene	95-13-6	2	66	0.2	6.6
Indeno[1,2,3-cd]pyrene	193-39-5	2	66	0.2	6.6
Isodrin	465-73-6	10	330	1.0	33
Isophorone	78-59-1	10	330	1.0	33
Isosafrole	120-58-1	10	330	1.0	33
Kepone	143-50-0	40	1320	4.0	132
Methapyrilene	91-80-5	10	330	1.0	33
Methyl methanesulfonate	66-27-3	10	330	1.0	33
Methyl parathion	298-00-0	10	330	1.0	33
Methyl Phenols,Total	1319-77-3	20	660	2.0	66
Naphthalene	91-20-3	2	66	0.2	6.6
n-Decane	124-18-5	10	330	1.0	33
Nitrobenzene	98-95-3	20	660	2.0	66
N-Nitro-o-toluidine	99-55-8	10	330	1.0	33
N-Nitrosodiethylamine	55-18-5	10	330	1.0	33
N-Nitrosodimethylamine	62-75-9	10	330	1.0	33

Compound	CAS #	Standard RL Aqueous (µg/L)	Standard RL Soil (µg/kg)	Low Level RL Aqueous (µg/L)	Low Level RL Soil (µg/kg)
N-Nitrosodi-n-butylamine	924-16-3	10	330	1.0	33
N-Nitrosodi-n-propylamine	621-64-7	10	330	1.0	33
N-Nitrosodiphenylamine	86-30-6	10	330	1.0	33
N-Nitrosomethylethylamine	10595-95-6	10	330	1.0	33
N-Nitrosomorpholine	59-89-2	10	330	1.0	33
N-Nitrosopiperidine	100-75-4	10	330	1.0	33
N-Nitrosopyrrolidine	930-55-2	10	330	1.0	33
n-Octadecane	593-45-3	10	330	1.0	33
o,o',o''-Triethylphosphorothioate	126-68-1	10	330	1.0	33
p-Dimethylamino azobenzene	60-11-7	10	330	1.0	33
Pentachlorobenzene	608-93-5	10	330	1.0	33
Pentachloroethane	76-01-7	10	330	1.0	33
Pentachloronitrobenzene	82-68-8	10	330	1.0	33
Pentachlorophenol	87-86-5	10	330	1.0	33
Phenacetin	62-44-2	10	330	1.0	33
Phenanthrene	85-01-8	2	66	0.2	6.6
Phenol	108-95-2	10	330	1.0	33
Phenylmercaptan	108-98-5	10	330	1.0	33
Phorate	298-02-2	10	330	1.0	33
p-Phenylene diamine	106-50-3	200	6600	20.0	660
Pronamide	23950-58-5	10	330	1.0	33
Pyrene	129-00-0	2	66	0.2	6.6
Pyridine	110-86-1	10	330	1.0	33
Quinoline	91-22-5	10	330	1.0	33
Safrole, Total	94-59-7	10	330	1.0	33
Sulfotepp	3689-24-5	10	330	1.0	33
Thionazin	297-97-2	10	330	1.0	33

[1]The TestAmerica Pittsburgh Standard of standards are the standards normally used at TestAmerica Pittsburgh. These standards include normal TCL compounds and Appendix IX compounds necessary to accommodate the majority of client compound requests.

[2]2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether.

[3] Diphenylamine can't be separated from N-Nitrosodiphenylamine. Hits for the compound will be reported as N- Nitrosodiphenylamine.

Table 2

Reportable Compounds for TestAmerica Pittsburgh Standard Tests

Analytes	CAS #	Routine Standard of Standards Compounds	APPIX Standard of Standards Compounds	TCLP
1,1'-Biphenyl	92-52-4	List 2		
1,2,4,5-Tetrachlorobenzene	95-94-3	List 2		
1,2,4-Trichlorobenzene	120-82-1	List 1		
1,2-Dichlorobenzene	95-50-1	List 2		
1,2-Diphenylhydrazine	122-66-7	List 2		
1,3,5-Trinitrobenzene	99-35-4		X	
1,3-Dichlorobenzene	541-73-1	List 1		
1,3-Dinitrobenzene	99-65-0	List 2		
1,4-Dichlorobenzene	106-46-7	CCC		X
1,4-Dinitrobenzene	100-25-4		X	
1,4-Dioxane	123-91-1	List 2		
1,4-Naphthoquinone	130-15-4	List 2		
1-Chloronaphthalene	90-13-1		X	
1-Methylnaphthalene	90-12-0	List 2		
1-Naphthylamine	134-32-7		X	
2,2'-oxybis[1-chloropropane]	108-60-1	List 2		
2,3,4,6-Tetrachlorophenol	58-90-2	List 2		
2,3,5,6-Tetrachlorophenol	935-95-5	List 2		
2,4,5-Trichlorophenol	95-95-4	List 1		X
2,4,6-Trichlorophenol	88-06-2	CCC		X
2,4-Dichlorophenol	120-83-2	CCC		
2,4-Dimethylphenol	105-67-9	List 1		
2,4-Dinitrophenol	51-28-5	List 2		
2,4-Dinitrotoluene	121-14-2	List 1		X
2,6-Dichlorophenol	87-65-0	List 2		
2,6-Dinitrotoluene	606-20-2	List 1		
2-Acetylaminofluorene	53-96-3		X	
2-Chloronaphthalene	91-58-7	List 1		
2-Chlorophenol	95-57-8	List 1		
2-Methylnaphthalene	91-57-6	List 1		

Analytes	CAS #	Routine Standard of Standards Compounds	APPIX Standard of Standards Compounds	TCLP
2-Methylphenol	95-48-7	List 1		X
2-Naphthylamine	91-59-8	List 2		
2-Nitroaniline	88-74-4	List 2		
2-Nitrophenol	88-75-5	CCC		
2-Picoline	109-06-8		X	
2-Toluidine	95-53-4		X	
3,3'-Dichlorobenzidine	91-94-1	List 2		
3,3'-Dimethylbenzidine	119-93-7		X	
3-Methylcholanthrene	56-49-5		X	
3-Nitroaniline	99-09-2	List 2		
4,4'-Methylene bis(2-chloroaniline)	101-14-4		X	
4,6-Dinitro-2-methylphenol	534-52-1	List 2		
4-Aminobiphenyl	92-67-1		X	
4-Bromophenyl phenyl ether	101-55-3	List 1		
4-Chloro-3-methylphenol	59-50-7	CCC		
4-Chloroaniline	106-47-8	List 2		
4-Chlorophenyl phenyl ether	7005-72-3	List 1		
4-Methylphenol	106-44-5	List 1		X
4-Nitroaniline	100-01-6	List 2		
4-Nitrophenol	100-02-7	List 2		
4-Nitroquinoline-1-oxide	56-57-5		X	
6-Methylchrysene	1705-85-7		X	
7,12-Dimethylbenz(a)anthracene	57-97-6	List 2		
Acenaphthene	83-32-9	CCC		
Acenaphthylene	208-96-8	List 1		
Acetophenone	98-86-2	List 2		
Acrylamide	79-06-1		X	
alpha,alpha-Dimethyl phenethylamine	122-09-8		X	
Aniline	62-53-3	List 2		
Anthracene	120-12-7	List 1		
Aramite, Total	140-57-8		X	
Atrazine	1912-24-9	List 2		

Analytes	CAS #	Routine Standard of Standards Compounds	APPIX Standard of Standards Compounds	TCLP
Benzaldehyde	100-52-7	List 2		
Benzidine	92-87-5	List 2		
Benzo[a]anthracene	56-55-3	List 1		
Benzo[a]pyrene	50-32-8	CCC		
Benzo[b]fluoranthene	205-99-2	List 1		
Benzo[g,h,i]perylene	191-24-2	List 1		
Benzo[k]fluoranthene	207-08-9	List 1		
Benzoic acid	65-85-0	List 2		
Benzyl alcohol	100-51-6	List 2		
Bis(2-chloroethoxy)methane	111-91-1	List 1		
Bis(2-chloroethyl)ether	111-44-4	List 1		
Bis(2-ethylhexyl) phthalate	117-81-7	List 2		
Butyl benzyl phthalate	85-68-7	List 2		
Caprolactam	105-60-2	List 2		
Carbazole	86-74-8	List 2		
Chlorobenzilate	510-15-6		X	
Chrysene	218-01-9	List 1		
Diallate	2303-16-4		X	
Dibenz(a,h)anthracene	53-70-3	List 1		
Dibenz[a,h]acridine	226-36-8		X	
Dibenzofuran	132-64-9	List 1		
Diethyl phthalate	84-66-2	List 2		
Dimethoate	60-51-5		X	
Dimethyl phthalate	131-11-3	List 2		
Di-n-butyl phthalate	84-74-2	List 2		
Di-n-octyl phthalate	117-84-0	CCC		
Dinoseb	88-85-7		X	
Diphenylamine[1]	122-39-4	CCC		
Disulfoton	298-04-4		X	
Ethyl methanesulfonate	62-50-0		X	
Ethyl Parathion	56-38-2		X	
Famphur	52-85-7		X	

Analytes	CAS #	Routine Standard of Standards Compounds	APPIX Standard of Standards Compounds	TCLP
Fluoranthene	206-44-0	CCC		
Fluorene	86-73-7	List 1		
Hexachlorobenzene	118-74-1	List 1		X
Hexachlorobutadiene	87-68-3	CCC		X
Hexachlorocyclopentadiene	77-47-4	List 2		
Hexachloroethane	67-72-1	List 1		X
Hexachloropropene	1888-71-7		X	
Hexadecane	544-76-3	List 2		
Indene	95-13-6	List 2		
Indeno[1,2,3-cd]pyrene	193-39-5	List 2		
Isodrin	465-73-6		X	
Isophorone	78-59-1	List 1		
Isosafrole	120-58-1		X	
Kepone	143-50-0		X	
Methapyrilene	91-80-5		X	
Methyl methanesulfonate	66-27-3		X	
Methyl parathion	298-00-0		X	
Methyl Phenols,Total	1319-77-3	List 1		
Naphthalene	91-20-3	List 1		
n-Decane	124-18-5	List 2		
Nitrobenzene	98-95-3	List 1		X
N-Nitro-o-toluidine	99-55-8		X	
N-Nitrosodiethylamine	55-18-5		X	
N-Nitrosodimethylamine	62-75-9	List 2		
N-Nitrosodi-n-butylamine	924-16-3		X	
N-Nitrosodi-n-propylamine	621-64-7	List 1		
N-Nitrosodiphenylamine	86-30-6	CCC		
N-Nitrosomethylethylamine	10595-95-6		X	
N-Nitrosomorpholine	59-89-2		X	
N-Nitrosopiperidine	100-75-4		X	
N-Nitrosopyrrolidine	930-55-2	List 2		
n-Octadecane	593-45-3	List 2		

Analytes	CAS #	Routine Standard of Standards Compounds	APPIX Standard of Standards Compounds	TCLP
o,o',o''-Triethylphosphorothioate	126-68-1		X	
p-Dimethylamino azobenzene	60-11-7		X	
Pentachlorobenzene	608-93-5		X	
Pentachloroethane	76-01-7		X	
Pentachloronitrobenzene	82-68-8		X	
Pentachlorophenol	87-86-5	CCC		X
Phenacetin	62-44-2		X	
Phenanthrene	85-01-8	List 1		
Phenol	108-95-2	CCC		
Phenylmercaptan	108-98-5		X	
Phorate	298-02-2		X	
p-Phenylene diamine	106-50-3		X	
Pronamide	23950-58-5		X	
Pyrene	129-00-0	List 1		
Pyridine	110-86-1	List 2		X
Quinoline	91-22-5		X	
Safrole, Total	94-59-7		X	
Sulfotepp	3689-24-5		X	
Thionazin	297-97-2		X	

[1] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

[2] Diphenylamine is a required compound for Appendix IX. N-nitrosodiphenylamine decomposes in the injection port to form diphenylamine. Therefore these two compounds cannot be distinguished. Diphenylamine is not included in the calibration standard.

[3] Hexachlorophene is a required analyte for Appendix IX. This compound is not stable, and therefore not included in the calibration standard. The characteristic ions for hexachlorophene are searched for in the chromatogram via a library search (TIC).

List 1 and List 2 designations are for method 8270C ICAL and CCV evaluations.

Table 3 Suggested Instrument Conditions	
Mass Range:	35 - 500 amu
Scan Time:	≤ 1 second/scan
Initial Column Temperature/Hold Time:	40 °C for 1 minute
Column Temperature Program:	40 - 320 °C at 11.5 °C/min.
Final Column Temperature/Hold Time:	320 °C (until at least one minute after Benzo(g,h,i)perylene has eluted)
Total Run Time	0.5 min based on the last compound of CCAL
Injector Temperature:	250 - 300°C
Transfer Line Temperature:	250 - 300°C
Source Temperature:	According to manufacturer's specifications
Injector:	Grob-type, split / splitless
Sample Volume:	1 or 2 µl
Carrier Gas:	Helium at 30 cm /sec.

Table 4 DFTPP Key Ions and Ion Abundance Criteria	
Mass	Ion Abundance Criteria
51	30 - 60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40 - 60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5 - 9% of mass 198
275	10 - 30% of mass 198
365	>1% of mass 198
441	Present, but less than mass 443
442	>40% of mass 198
443	17 - 23% of mass 442

Table 5
Characterisitic Ions for Routine and Appendix IX Compounds

Analytes	CAS #	Primary	Secondary	Tertiary
1,1'-Biphenyl	92-52-4	154	153	76
1,2,4,5-Tetrachlorobenzene	95-94-3	216	214	218
1,2,4-Trichlorobenzene	120-82-1	180	182	145
1,2-Dichlorobenzene	95-50-1	146	148	111
1,2-Diphenylhydrazine	122-66-7	77	182	105
1,3,5-Trinitrobenzene	99-35-4	213	75	120
1,3-Dichlorobenzene	541-73-1	146	148	111
1,3-Dinitrobenzene	99-65-0	168	75	76
1,4-Dichlorobenzene	106-46-7	146	148	111
1,4-Dinitrobenzene	100-25-4	168	75	122
1,4-Dioxane	123-91-1	88	58	57
1,4-Naphthoquinone	130-15-4	158	104	102
1-Chloronaphthalene	90-13-1	162	127	164
1-Methylnaphthalene	90-12-0	142	141	115
1-Naphthylamine	134-32-7	143	115	116
2,2'-oxybis[1-chloropropane]	108-60-1	45	77	121
2,3,4,6-Tetrachlorophenol	58-90-2	232	230	131
2,3,5,6-Tetrachlorophenol	935-95-5	237	230	131
2,4,5-Trichlorophenol	95-95-4	196	198	200
2,4,6-Trichlorophenol	88-06-2	196	198	200
2,4-Dichlorophenol	120-83-2	162	164	98
2,4-Dimethylphenol	105-67-9	107	121	122
2,4-Dinitrophenol	51-28-5	184	63	154
2,4-Dinitrotoluene	121-14-2	165	63	89
2,6-Dichlorophenol	87-65-0	162	164	63
2,6-Dinitrotoluene	606-20-2	165	89	63
2-Acetylaminofluorene	53-96-3	181	180	223
2-Chloronaphthalene	91-58-7	162	164	127
2-Chlorophenol	95-57-8	128	64	130
2-Methylnaphthalene	91-57-6	142	141	115

Analytes	CAS #	Primary	Secondary	Tertiary
2-Methylphenol	95-48-7	108	107	79
2-Naphthylamine	91-59-8	143	115	116
2-Nitroaniline	88-74-4	65	92	138
2-Nitrophenol	88-75-5	139	65	109
2-Picoline	109-06-8	93	66	92
2-Toluidine	95-53-4	106	107	77
3,3'-Dichlorobenzidine	91-94-1	252	254	126
3,3'-Dimethylbenzidine	119-93-7	212	213	211
3-Methylcholanthrene	56-49-5	268	252	253
3-Nitroaniline	99-09-2	138	108	92
4,4'-Methylene bis(2-chloroaniline)	101-14-4	231	266	268
4,6-Dinitro-2-methylphenol	534-52-1	198	51	105
4-Aminobiphenyl	92-67-1	169	168	170
4-Bromophenyl phenyl ether	101-55-3	248	250	141
4-Chloro-3-methylphenol	59-50-7	107	144	142
4-Chloroaniline	106-47-8	127	129	65
4-Chlorophenyl phenyl ether	7005-72-3	204	206	141
4-Methylphenol	106-44-5	108	107	79
4-Nitroaniline	100-01-6	138	92	108
4-Nitrophenol	100-02-7	139	109	65
4-Nitroquinoline-1-oxide	56-57-5	190	128	160
6-Methylchrysene	1705-85-7	242	239	241
7,12-Dimethylbenz(a)anthracene	57-97-6	256	241	120
Acenaphthene	83-32-9	153	152	154
Acenaphthylene	208-96-8	152	151	153
Acetophenone	98-86-2	105	77	51
Acrylamide	79-06-1	71	55	44
alpha,alpha-Dimethyl phenethylamine	122-09-8	58	91	42
Aniline	62-53-3	93	66	65
Anthracene	120-12-7	178	179	176
Aramite, Total	140-57-8	185	135	63
Atrazine	1912-24-9	200	173	215
Benzaldehyde	100-52-7	77	105	106
Benzidine	92-87-5	184	92	185

Analytes	CAS #	Primary	Secondary	Tertiary
Benzo[a]anthracene	56-55-3	228	229	226
Benzo[a]pyrene	50-32-8	252	253	125
Benzo[b]fluoranthene	205-99-2	252	253	125
Benzo[g,h,i]perylene	191-24-2	276	138	277
Benzo[k]fluoranthene	207-08-9	252	253	125
Benzoic acid	65-85-0	122	105	77
Benzyl alcohol	100-51-6	108	79	77
Bis(2-chloroethoxy)methane	111-91-1	93	95	123
Bis(2-chloroethyl)ether	111-44-4	93	63	95
Bis(2-ethylhexyl) phthalate	117-81-7	149	167	279
Butyl benzyl phthalate	85-68-7	149	91	206
Caprolactam	105-60-2	113	55	56
Carbazole	86-74-8	167	166	168
Chlorobenzilate	510-15-6	251	139	253
Chrysene	218-01-9	228	226	229
Diallate	2303-16-4	86	43	234
Dibenz(a,h)anthracene	53-70-3	278	139	279
Dibenz[a,h]acridine	226-36-8	279	280	278
Dibenzofuran	132-64-9	168	139	84
Diethyl phthalate	84-66-2	149	177	150
Dimethoate	60-51-5	87	93	125
Dimethyl phthalate	131-11-3	163	194	164
Di-n-butyl phthalate	84-74-2	149	150	104
Di-n-octyl phthalate	117-84-0	149	167	43
Dinoseb	88-85-7	211	163	147
Diphenylamine[1]	122-39-4	169	168	167
Disulfoton	298-04-4	88	97	89
Ethyl methanesulfonate	62-50-0	79	109	97
Ethyl Parathion	56-38-2	109	97	291
Famphur	52-85-7	218	125	93
Fluoranthene	206-44-0	202	101	203
Fluorene	86-73-7	166	165	167
Hexachlorobenzene	118-74-1	284	142	249
Hexachlorobutadiene	87-68-3	225	223	227

Analytes	CAS #	Primary	Secondary	Tertiary
Hexachlorocyclopentadiene	77-47-4	237	235	272
Hexachloroethane	67-72-1	117	201	199
Hexachloropropene	1888-71-7	213	215	211
Hexadecane	544-76-3	57	43	71
Indene	95-13-6	116	115	63
Indeno[1,2,3-cd]pyrene	193-39-5	276	138	277
Isodrin	465-73-6	193	66	195
Isophorone	78-59-1	82	95	138
Isosafrole	120-58-1	162	104	131
Kepone	143-50-0	272	274	237
Methapyrilene	91-80-5	58	97	72
Methyl methanesulfonate	66-27-3	80	79	65
Methyl parathion	298-00-0	109	125	263
Methyl Phenols,Total	1319-77-3	108	107	79
Naphthalene	91-20-3	128	129	127
n-Decane	124-18-5	43	57	71
Nitrobenzene	98-95-3	77	123	65
N-Nitro-o-toluidine	99-55-8	152	77	106
N-Nitrosodiethylamine	55-18-5	102	44	57
N-Nitrosodimethylamine	62-75-9	74	42	44
N-Nitrosodi-n-butylamine	924-16-3	84	57	41
N-Nitrosodi-n-propylamine	621-64-7	70	42	101
N-Nitrosodiphenylamine	86-30-6	169	168	167
N-Nitrosomethylethylamine	10595-95-6	88	42	43
N-Nitrosomorpholine	59-89-2	116	56	86
N-Nitrosopiperidine	100-75-4	114	42	55
N-Nitrosopyrrolidine	930-55-2	100	41	42
n-Octadecane	593-45-3	57	43	71
o,o',o''-Triethylphosphorothioate	126-68-1	198	121	93
p-Dimethylamino azobenzene	60-11-7	120	225	77
Pentachlorobenzene	608-93-5	250	248	252
Pentachloroethane	76-01-7	117	119	167
Pentachloronitrobenzene	82-68-8	237	142	214
Pentachlorophenol	87-86-5	266	264	268

Analytes	CAS #	Primary	Secondary	Tertiary
Phenacetin	62-44-2	108	179	109
Phenanthrene	85-01-8	178	179	176
Phenol	108-95-2	94	65	66
Phenylmercaptan (Benzenethiol)	108-98-5	110	66	109
Phorate	298-02-2	121	75	260
p-Phenylene diamine	106-50-3	108	80	107
Pronamide	23950-58-5	173	175	255
Pyrene	129-00-0	202	200	203
Pyridine	110-86-1	79	52	
Quinoline	91-22-5	129	102	128
Safrole, Total	94-59-7	162	104	77
Sulfotepp	3689-24-5	97	322	202
Thionazin	297-97-2	97	96	143
2-Fluorobiphenyl (Surrogate)	321-60-8	172	171	170
2-Fluorophenol (Surrogate)	367-12-4	112	64	63
2,4,6-Tribromophenol (Surrogate)	118-79-6	330	332	141
Nitrobenzene-d5 (Surrogate)	4165-60-0	82	128	54
Phenol-d5 (Surrogate)	4165-62-2	99	42	71
Terphenyl-d14 (Surrogate)	1718-51-0	244	122	212
1,4-Dichlorobenzene-d4 (Internal Standard)	3855-82-1	152	150	115
Naphthalene-d8 (Internal Standard)	1146-65-2	136	68	54
Acenapthene-d10 (Internal Standard)	15067-26-2	164	162	160
Phenanthrene-d10 (Internal Standard)	1517-22-2	188	94	80
Chrysene-d12 (Internal Standard)	1719-03-5	240	120	236
Perylene-d12 (Internal Standard)	1520-96-3	264	260	265

[1]Diphenylamine can't be separated from N-Nitrosodiphenylamine. Hits for the compound will be reported as N- Nitrosodiphenylamine.

Table 6

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-Trichlorobenzene	1,1-Biphenyl
1,3-Dichlorobenzene	1-Methylnaphthalene	1,2,4,5-Tetrachlorobenzene
1,4-Dichlorobenzene	2,4-Dichlorophenol	1,3-Dinitrobenzene
1,4-Dioxane	2,4-Dimethylphenol	1,4-Dinitrobenzene
2,2'-oxybis[1-Chloropropane]	2,6-Dichlorophenol	1,4-Naphthoquinone
2-Chlorophenol	2-Methylnaphthalene	1-Chloronaphthalene
2-Fluorophenol (surrogate)	2-Nitrophenol	1-Naphthylamine
2-Methylphenol	4-Chloro-3-methylphenol	2,3,4,6-Tetrachlorophenol
2-Picoline	4-Chloroaniline	2,3,5,6-Tetrachlorophenol
2-Toluidine	4-Chlorophenol	2,4,5-Trichlorophenol
4-Methylphenol	a,a-Dimethyl phenethylamine	2,4,6-Trichlorophenol
Acetophenone	Acetophenone	2,4-Dinitrophenol
Acrylamide	Benzoic acid	2,4-Dinitrotoluene
Aniline	bis(2-Chloroethoxy)methane	2,6-Dinitrotoluene
Benzaldehyde	Caprolactam	2-Chloronaphthalene
Benzyl alcohol	Hexachlorobutadiene	2-Fluorobiphenyl (surrogate)
bis(2-Chloroethyl) ether	Hexachloropropene	2-Naphthylamine
Ethyl methanesulfonate	Hexadecane	2-Nitroaniline
Hexachloroethane	Isophorone	3-Nitroaniline
Indene	Naphthalene	4-Chlorophenyl phenyl ether
Methyl methanesulfonate	Nitrobenzene	4-Nitroaniline
Methyl Phenols, Total	Nitrobenzene-d_5 (surrogate)	4-Nitrophenol
n-Decane	n-Nitrosodi-butylamine	Acenaphthene
n-Nitrosodiethylamine	n-Nitrosopiperidine	Acenaphthylene
n-Nitrosodimethylamine	o,o',o"-Triethylphosphorothioate	Dibenzofuran
n-Nitroso-di-n-propylamine	p-Phenylene diamine	Diethyl phthalate
n-Nitrosomethylethylamine	Quinoline	Dimethyl phthalate
n-Nitrosomorpholine	Safrole	Fluorene
n-Nitrosopyrrolidine	Thionazin	Hexachlorocyclopentadiene
n-Octadecane		Isosafrole
Pentachloroethane		n-Nitro-o-toluidine
Phenol		Pentachlorobenzene
Phenol-d_5		
Phenylmercaptan (Benzenethiol)		
Pyridine		
Phenanthrene-d_{10}	**Chrysene-d_{12}**	**Perylene-d_{12}**
4-Aminobiphenyl	1-Methylnaphthalene	3-Methylcholanthrene
1,2-Diphenylhydrazine	2-Acetylaminofluorene	7,12-Dimethylbenz(a)anthracene
1,3,5-Trinitrobenzene	3,3'-Dichlorobenzidine	Benzo(a)pyrene
2,4,6-Tribromphenol (surrogate)	3,3'-Dimethylbenzidine	Benzo(b)fluoranthene
4,6-Dinitro-2-methylphenol	4,4'-Methylene bis(2-chloroaniline)	Benzo(g,h,i)perylene
4-Bromophenyl phenyl ether	6-Methylchrysene	Benzo(k)fluoranthene
4-Nitroquinoline oxide	Aramite, Total	Dibenz(a,h)anthracene

Table 6

Semivolatile Internal Standards with Corresponding Analytes assigned for Quantitation

Phenanthrene-d_{10} (cont.)	**Chrysene-d_{12} (cont.)**	**Perylene-d_{12} (cont.)**
Anthracene	Benzidine	Dibenz[a,h]acridine
Atrazine	Benzo(a)anthracene	Di-n-octyl phthalate
Carbazole	Butyl benzyl phthalate	Indeno(1,2,3-cd)pyrene
Diallate	Chlorobenzilate	
Dimethoate	Chrysene	
Di-n-butyl phthalate	Famphur	
Dinoseb	Kepone	
Diphenylamine	p-Dimethyl aminoazobenzene	
Disulfoton	Pyrene	
Ethyl Parathion	Terphenyl-d_{14} (surrogate)	
Fluoranthene		
Hexachlorobenzene		
Isodrin		
Methapyrilene		
Methyl Parathion		
n-Nitrosodiphenylamine		
Pentachloronitrobenzene		
Pentachlorophenol		
Phenacetin		
Phenanthrene		
Phenol		
Phenol-d_5		
Phenylmercaptan (Benzenethiol)		

Table 7 8270D TCLP LCS Compounds	
LCS Compounds[1]	**Spiking Level, µg/mL, added to extract[2]**
1,4-Dichlorobenzene	50
2,4-Dinitrotoluene	50
Hexachlorobenzene	50
Hexachlorobutadiene	50
Hexachloroethane	50
2-Methylphenol	50
3&4-Methylphenol	100
Nitrobenzene	50
Pentachlorophenol	50
Pyridine	50
2,4,5-Trichlorophenol	50
2,4,6-Trichlorophenol	50

[1] Recovery limits for the LCS and for matrix spikes are generated from historical data and are maintained by the QA group.

[2] TCLP's are either extracted via Separatory Funnel at a 200 mL initial volume and concentrated to a final volume of 10 mL or at a 1000 mL initial volume and concentrated to a final volume of 10 mL.

Table 8 8270D Surrogate Compounds		
Surrogate Compounds	**Routine 8270D Spiking Concentration µg/mL**	**Low Level 8270D Spiking Concentration µg/mL**
Nitrobenzene-d5	200	20
2-Fluorobiphenyl	200	20
Terphenyl-d14	200	20
Phenol-d5	200	20
2-Fluorophenol	200	20
2,4,6-Tribromophenol	200	20

[1] Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 9

Routine and APPIX Standard Calibration Levels, µg/mL (for 2 µl injection)

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8
1,2,4,5-Tetrachlorobenzene	0.2	1.0	2.0	5.0	10	20	30	40
1,2,4-Trichlorobenzene	0.2	1.0	2.0	5.0	10	20	30	40
1,2-Dichlorobenzene	0.2	1.0	2.0	5.0	10	20	30	40
1,2-Diphenylhydrazine (as Azobenzene)	0.2	1.0	2.0	5.0	10	20	30	40
1,3,5-Trinitrobenzene	0.2	1.0	2.0	5.0	10	20	30	40
1,3-Dichlorobenzene	0.2	1.0	2.0	5.0	10	20	30	40
1,3-Dinitrobenzene	0.2	1.0	2.0	5.0	10	20	30	40
1,4-Dichlorobenzene	0.2	1.0	2.0	5.0	10	20	30	40
1,4-Dinitrobenzene	0.2	1.0	2.0	5.0	10	20	30	40
1,4-Naphthoquinone	0.2	1.0	2.0	5.0	10	20	30	40
1-Naphthylamine	0.2	1.0	2.0	5.0	10	20	30	40
2,2'-oxybis(1-chloropropane)[1]	0.2	1.0	2.0	5.0	10	20	30	40
2,3,4,6-Tetrachlorophenol	0.2	1.0	2.0	5.0	10	20	30	40
2,4,5-Trichlorophenol	0.2	1.0	2.0	5.0	10	20	30	40
2,4,6-Trichlorophenol	0.2	1.0	2.0	5.0	10	20	30	40
2,4-Dichlorophenol	0.2	1.0	2.0	5.0	10	20	30	40
2,4-Dimethylphenol	0.2	1.0	2.0	5.0	10	20	30	40
2,4-Dinitrophenol	0.4	2.0	4.0	10	20	40	60	80
2,4-Dinitrotoluene	0.2	1.0	2.0	5.0	10	20	30	40
2,6-Dichlorophenol	0.2	1.0	2.0	5.0	10	20	30	40
2,6-Dinitrotoluene	0.2	1.0	2.0	5.0	10	20	30	40
2-Acetylaminofluorene	0.2	1.0	2.0	5.0	10	20	30	40
2-Chloronaphthalene	0.2	1.0	2.0	5.0	10	20	30	40
2-Chlorophenol	0.2	1.0	2.0	5.0	10	20	30	40
2-Methylnaphthalene	0.2	1.0	2.0	5.0	10	20	30	40
2-Methylphenol	0.2	1.0	2.0	5.0	10	20	30	40
2-Naphthylamine	0.2	1.0	2.0	5.0	10	20	30	40
2-Nitroaniline	0.2	1.0	2.0	5.0	10	20	30	40
2-Nitrophenol	0.2	1.0	2.0	5.0	10	20	30	40
2-Picoline	0.2	1.0	2.0	5.0	10	20	30	40
3,3'-Dichlorobenzidine	0.2	1.0	2.0	5.0	10	20	30	40
3,3'-Dimethylbenzidine	0.2	1.0	2.0	5.0	10	20	30	40
3-Methylcholanthrene	0.2	1.0	2.0	5.0	10	20	30	40
3-Nitroaniline	0.2	1.0	2.0	5.0	10	20	30	40
4,6-Dinitro-2-methylphenol	0.4	2.0	4.0	10	20	40	60	80
4-Aminobiphenyl	0.2	1.0	2.0	5.0	10	20	30	40
4-Bromophenyl phenyl ether	0.2	1.0	2.0	5.0	10	20	30	40
4-Chloro-3-methylphenol	0.2	1.0	2.0	5.0	10	20	30	40
4-Chloroaniline	0.4	2.0	4.0	10	20	40	60	80
4-Chlorophenyl phenyl ether	0.2	1.0	2.0	5.0	10	20	30	40
4-Methylphenol	0.2	1.0	2.0	5.0	10	20	30	40
4-Nitroaniline	0.2	1.0	2.0	5.0	10	20	30	40
4-Nitrophenol	0.4	2.0	4.0	10	20	40	60	80
4-Nitroquinoline-1-oxide	0.2	1.0	2.0	5.0	10	20	30	40

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8
5-Nitro-o-toluidine	0.2	1.0	2.0	5.0	10	20	30	40
6-Methylchrysrene	0.2	1.0	2.0	5.0	10	20	30	40
7,12-Dimethylbenz(a) anthracene	0.2	1.0	2.0	5.0	10	20	30	40
a,a-Dimethyl-phenethylamine	0.2	1.0	2.0	5.0	10	20	30	40
Acenaphthene	0.2	1.0	2.0	5.0	10	20	30	40
Acenaphthylene	0.2	1.0	2.0	5.0	10	20	30	40
Acetophenone	0.2	1.0	2.0	5.0	10	20	30	40
Aniline	0.2	1.0	2.0	5.0	10	20	30	40
Anthracene	0.2	1.0	2.0	5.0	10	20	30	40
Aramite 1 & 2	0.2	1.0	2.0	5.0	10	20	30	40
Benzidine	0.2	1.0	2.0	5.0	10	20	30	40
Benzo(a)anthracene	0.2	1.0	2.0	5.0	10	20	30	40
Benzo(a)pyrene	0.2	1.0	2.0	5.0	10	20	30	40
Benzo(b)fluoranthene	0.2	1.0	2.0	5.0	10	20	30	40
Benzo(g,h,i)perylene	0.2	1.0	2.0	5.0	10	20	30	40
Benzo(k)fluoranthene	0.2	1.0	2.0	5.0	10	20	30	40
Benzoic Acid	0.4	2.0	4.0	10	20	40	60	80
Benzyl alcohol	0.2	1.0	2.0	5.0	10	20	30	40
Bis(2-chloroethoxy)methane	0.2	1.0	2.0	5.0	10	20	30	40
Bis(2-chloroethyl)ether	0.2	1.0	2.0	5.0	10	20	30	40
Bis(2-ethylhexyl)phthalate	0.2	1.0	2.0	5.0	10	20	30	40
Butyl benzyl phthalate	0.2	1.0	2.0	5.0	10	20	30	40
Carbazole	0.2	1.0	2.0	5.0	10	20	30	40
Chrysene	0.2	1.0	2.0	5.0	10	20	30	40
Diallate 1 & 2	0.2	1.0	2.0	5.0	10	20	30	40
Dibenz(a,h)anthracene	0.2	1.0	2.0	5.0	10	20	30	40
Dibenzofuran	0.2	1.0	2.0	5.0	10	20	30	40
Diethylphthalate	0.2	1.0	2.0	5.0	10	20	30	40
Dimethoate	0.2	1.0	2.0	5.0	10	20	30	40
Dimethyl phthalate	0.2	1.0	2.0	5.0	10	20	30	40
Di-n-butyl phthalate	0.2	1.0	2.0	5.0	10	20	30	40
Di-n-octylphthalate	0.2	1.0	2.0	5.0	10	20	30	40
Dinoseb	0.2	1.0	2.0	5.0	10	20	30	40
Disulfoton	0.2	1.0	2.0	5.0	10	20	30	40
Ethyl methanesulfonate	0.2	1.0	2.0	5.0	10	20	30	40
Famphur	0.3	1.5	3.0	7.5	15	30	45	60
Fluoranthene	0.2	1.0	2.0	5.0	10	20	30	40
Fluorene	0.2	1.0	2.0	5.0	10	20	30	40
Hexachlorobenzene	0.2	1.0	2.0	5.0	10	20	30	40
Hexachlorobutadiene	0.2	1.0	2.0	5.0	10	20	30	40
Hexachlorocyclopentadiene	0.2	1.0	2.0	5.0	10	20	30	40
Hexachloroethane	0.2	1.0	2.0	5.0	10	20	30	40
Hexachloropropene	0.2	1.0	2.0	5.0	10	20	30	40
Indeno(1,2,3-cd)pyrene	0.2	1.0	2.0	5.0	10	20	30	40
Isodrin	0.2	1.0	2.0	5.0	10	20	30	40
Isophorone	0.2	1.0	2.0	5.0	10	20	30	40

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8
Isosafrole 1 + 2	0.2	1.0	2.0	5.0	10	20	30	40
Kepone	0.8	4.0	8.0	20.0	40	80	120	160
Methapyrilene	0.2	1.0	2.0	5.0	10	20	30	40
Methyl methanesulfonate	0.2	1.0	2.0	5.0	10	20	30	40
Methyl parathion	0.2	1.0	2.0	5.0	10	20	30	40
Naphthalene	0.2	1.0	2.0	5.0	10	20	30	40
Nitrobenzene	0.2	1.0	2.0	5.0	10	20	30	40
N-Nitrosodiethylamine	0.2	1.0	2.0	5.0	10	20	30	40
N-nitrosodimethylamine	0.2	1.0	2.0	5.0	10	20	30	40
n-Nitrosodi-n-butylamine	0.2	1.0	2.0	5.0	10	20	30	40
N-Nitroso-di-n-propylamine	0.2	1.0	2.0	5.0	10	20	30	40
N-Nitrosodiphenylamine	0.2	1.0	2.0	5.0	10	20	30	40
N-Nitrosomethylethylamine	0.2	1.0	2.0	5.0	10	20	30	40
N-Nitrosomorpholine	0.2	1.0	2.0	5.0	10	20	30	40
N-Nitrosopiperidine	0.2	1.0	2.0	5.0	10	20	30	40
N-Nitrosopyrrolidine	0.2	1.0	2.0	5.0	10	20	30	40
o,o,o-Triethyl-Phosphorothioate	0.2	1.0	2.0	5.0	10	20	30	40
o-Toluidine	0.2	1.0	2.0	5.0	10	20	30	40
p-(Dimethylamino) azobenzene	0.2	1.0	2.0	5.0	10	20	30	40
Parathion, Ethyl	0.2	1.0	2.0	5.0	10	20	30	40
p-Chlorobenzilate	0.2	1.0	2.0	5.0	10	20	30	40
Pentachlorobenzene	0.2	1.0	2.0	5.0	10	20	30	40
Pentachloroethane	0.2	1.0	2.0	5.0	10	20	30	40
Pentachloronitrobenzene	0.2	1.0	2.0	5.0	10	20	30	40
Pentachlorophenol	0.4	2.0	4.0	10	20	40	60	80
Phenacetin	0.2	1.0	2.0	5.0	10	20	30	40
Phenanthrene	0.2	1.0	2.0	5.0	10	20	30	40
Phenol	0.2	1.0	2.0	5.0	10	20	30	40
Phorate	0.2	1.0	2.0	5.0	10	20	30	40
p-Phenylenediamine	0.2	1.0	2.0	5.0	10	20	30	40
Pronamide	0.2	1.0	2.0	5.0	10	20	30	40
Pyrene	0.2	1.0	2.0	5.0	10	20	30	40
Pyridine	0.2	1.0	2.0	5.0	10	20	30	40
Safrole	0.2	1.0	2.0	5.0	10	20	30	40
Sulfotepp	0.2	1.0	2.0	5.0	10	20	30	40
Thionazin	0.2	1.0	2.0	5.0	10	20	30	40

[1]2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether.

Table 10

Minimum Response Factor Criteria for Initial and Continuing Calibration Verification

Analyte	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl)ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-oxybis(1-chloropropane)[1]	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800
2-Nitroaniline	0.010
Dimethylphthalate	0.010
Acenaphthylene	0.900
2,6-Dinitrotoluene	0.200
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
Dibenzofuran	0.800
4-Nitrophenol	0.010
2,4-Dinitrotoluene	0.200
Diethylphthalate	0.010
Fluorene	0.900
4-Chlorophenylphenylether	0.400

Table 10

Minimum Response Factor Criteria for Initial and Continuing Calibration Verification

Analyte	Minimum Response Factor (RF)
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
N-Nitrosodiphenylamine	0.010
4-Bromophenylphenylether	0.100
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butylphthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butylbenzylphthalate	0.010
Benzo(a)Anthracene	0.800
3,3'-Dichlorobenzidine	0.010
Chrysene	0.700
Bis(2-ethylhexyl)phthalate	0.010
Di-n-octylphthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

Table 11: Poor Performers and Laboratory Acceptance Criteria

Routine Poor Performers	ICAL %RSD	ICV %D	CCAL %D	
1,4-Dioxane	50%	50%	**40%**	
2,2 oxybis 1-Chloropropane	50%	50%	20%	
2,4-Dinitrophenol	50%	50%	**40%**	
2-Naphthylamine	50%	50%	**40%**	
3,3'-Dichlorobenzidine	50%	50%	**40%**	
4,6-Dinitro-2-methylphenol	50%	50%	20%	
4-Nitrophenol	50%	50%	20%	
Atrazine	50%	50%	**40%**	
Benzaldehyde	50%	50%	**40%**	
Benzidine	50%	50%	**40%**	
Benzoic acid	50%	50%	**40%**	
Benzyl alcohol	50%	50%	20%	
Caprolactam	50%	50%	20%	
Di-n-octylphthalate	50%	50%	20%	
Hexachlorocyclopentadiene	50%	50%	20%	
N-nitrosopyrrolidine	50%	50%	20%	
Pentachlorophenol	50%	50%	20%	
Pyridine	50%	50%	20%	
Methylmethane sulfonate	50%	50%	**40%**	
2,4 Dimethylphenol	50%	50%	20%	
South Carolina Poor Performers	**ICAL %RSD**	**ICV %D**	**CCAL %D**	**LCS Limits %Recovery**
1,4-Dioxane	50%	50%	**40%**	60-140%
2,2 oxybis 1-Chloropropane	50%	50%	20%	60-140%
2,4-Dinitrophenol	50%	50%	**40%**	60-140%
2-Naphthylamine	50%	50%	**40%**	60-140%
3,3'-Dichlorobenzidine	50%	50%	**40%**	60-140%
4,6-Dinitro-2-methylphenol	50%	50%	20%	60-140%
4-Nitrophenol	50%	50%	20%	60-140%
Atrazine	50%	50%	**40%**	60-140%
Benzaldehyde	50%	50%	**40%**	60-140%
Benzidine	50%	50%	**40%**	60-140%
Benzoic acid	50%	50%	**40%**	60-140%
Benzyl alcohol	50%	50%	20%	60-140%
Caprolactam	50%	50%	20%	60-140%
Di-n-octylphthalate	50%	50%	20%	60-140%
Hexachlorocyclopentadiene	50%	50%	20%	60-140%
N-nitrosopyrrolidine	50%	50%	20%	60-140%
Pentachlorophenol	50%	50%	20%	60-140%
Pyridine	50%	50%	20%	60-140%
Methylmethane sulfonate	50%	50%	**40%**	50-150%
2,4 Dimethylphenol	50%	50%	20%	50-150%

Table 11: Poor Performers and Laboratory Acceptance Criteria (cont.)

Appendix IX Poor Performers	ICAL %RSD	ICV %D	CCAL %D
1,3,5-Trinitrobenzene	50%	50%	**40%**
1,4-Naphthoquinone	50%	50%	**40%**
1-Naphthylamine	50%	50%	**40%**
2-Acetylaminofluorene	50%	50%	**40%**
2-Picoline	50%	50%	**40%**
3,3'-Dimethylbenzidine	50%	50%	**40%**
3-Methylcholanthrene	50%	50%	**40%**
4,4'-Methylene bis(o-chloroan	50%	50%	**40%**
4-Aminobiphenyl	50%	50%	**40%**
4-Nitroquinoline 1-oxide	50%	50%	**40%**
5-Nitro-o-toluidine	50%	50%	**40%**
6-methylchrysene	50%	50%	**40%**
a,a-Dimethyl-phenethylamine	50%	50%	**40%**
Aramite 1	50%	50%	**40%**
Aramite 2	50%	50%	**40%**
Diallate 1	50%	50%	**40%**
Diallate 2	50%	50%	**40%**
Dibenz(a,h)acridine	50%	50%	**40%**
Dimethoate	50%	50%	**40%**
Dinoseb	50%	50%	**40%**
Disulfoton	50%	50%	**40%**
Ethyl methanesulfonate	50%	50%	**40%**
Famphur	50%	50%	**40%**
Hexachloropropene	50%	50%	**40%**
Isodrin	50%	50%	**40%**
Isosafrole 1	50%	50%	**40%**
Kepone	50%	50%	**40%**
m-Dinitrobenzene	50%	50%	**40%**
Methapyrilene	50%	50%	**40%**
Methyl parathion	50%	50%	**40%**
N-Nitrosodiethylamine	50%	50%	**40%**
N-Nitrosodi-n-butylamine	50%	50%	**40%**
N-Nitrosomethylethylamine	50%	50%	**40%**
N-Nitrosomorpholine	50%	50%	**40%**
N-Nitrosopiperidine	50%	50%	**40%**
O,O,O-Triethyl phosphorothioa	50%	50%	**40%**
o-Toluidine	50%	50%	**40%**
Parathion	50%	50%	**40%**
p-Chlorobenzilate	50%	50%	**40%**
p-Dimethylamino azobenzene	50%	50%	**40%**
Pentachlorobenzene	50%	50%	**40%**

Table 11: Poor Performers and Laboratory Acceptance Criteria (cont.)

Appendix IX Poor Performers	ICAL %RSD	ICV %D	CCAL %D
Pentachloroethane	50%	50%	**40%**
Pentachloronitrobenzene	50%	50%	**40%**
Phenacetin	50%	50%	**40%**
Phorate	50%	50%	**40%**
p-Phenylene diamine	50%	50%	**40%**
Pronamide	50%	50%	**40%**
Safrole	50%	50%	**40%**
Sulfotepp	50%	50%	**40%**
Thionazin	50%	50%	**40%**

Appendix 9 compounds allowed outliers on ICAL %RSD. Outliers will be noted in an NCM.

Appendix 9 compounds allowed outliers on ICV %D. Outliers will be noted in an NCM.

Table 12: TestAmerica Pittsburgh GCMS Semivolatile Dilution Calculation Table

Dilution Required 100 uL F.V.	Amount of Sample uL	Amount of $MeCl_2$ uL	Amount of IS (if none added) uL	Amount of IS uL (if added)	Final Volume uL
1.5	66.7	33.3	1	0.33	100
2	50	50	1	0.5	100
3	33.3	66.7	1	0.67	100
4	25	75	1	0.75	100
5	20	80	1	0.8	100
6	16.7	83.3	1	0.83	100
7	14.3	85.7	1	0.86	100
8	12.5	87.5	1	0.88	100
9	11.1	88.9	1	0.89	100
10	10	90	1	0.9	100
11	9.1	90.9	1	0.91	100
12	8.3	91.7	1	0.92	100
13	7.7	92.3	1	0.92	100
14	7.1	92.9	1	0.93	100
15	6.7	93.3	1	0.93	100
20	5	95	1	0.95	100
25	4	96	1	0.96	100
30	3.3	96.7	1	1	100
35	2.85	97.15	1	1	100
40	2.5	97.5	1	1	100
45	2.2	97.8	1	1	100
50	2	98	1	1	100
55	1.8	98.2	1	1	100
60	1.7	98.3	1	1	100
65	1.5	98.5	1	1	100
70	1.4	98.6	1	1	100
75	1.3	98.7	1	1	100
80	1.25	98.75	1	1	100
85	1.18	98.82	1	1	100
90	1.11	98.89	1	1	100
95	1.05	98.95	1	1	100
100	1	99	1	1	100
150	0.67	99.33	1	1	100
200	0.5	99.5	1	1	100
250	0.4	99.6	1	1	100
300	0.33	99.67	1	1	100
350	0.29	99.71	1	1	100
400	0.25	99.75	1	1	100
500	0.2	99.8	1	1	100

APPENDIX A

Instrument Maintenance Schedules - Mass Spectrometer & Gas Chromatograph

MASS SPECTROMETER Instrument Maintenance Schedule				
Daily	**Weekly**	**As Needed**	**Quarterly**	**Annually**
Check for sufficient gas supply. Check for correct column flow and/or inlet pressure	Check mass calibration (PFTBA or FC-43).	Check level of oil in mechanical pumps and diffusion pump if vacuum is insufficient. Add oil if needed between service contract maintenance.	Check vacuum, relays, gas pressures, and flows.	Replace the exhaust filters on the mechanical rough pump every 1 to 2 years.
Check temperatures of injector, detector. Verify temperature programs.		Replace electron multiplier when the tuning voltage approaches the maximum and/or when sensitivity falls below required levels.	Check vacuum, relays, gas pressures and flows	Change the oil in the mechanical rough pump.
Check inlets, septa.		Clean source, including all ceramics and lenses. Source cleaning is indicated by a variety of symptoms, including inability of the analyst to tune the instrument to specifications, poor response, and high background contamination.		
Check baseline level.		Repair/replace jet separator.		
Check values of lens voltages, electron multiplier, and relative abundance and mass assignments of the calibration compounds.		Replace filaments when both filaments burn out or performance indicates the need for replacement.		

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Analysis of Metals by Inductively Coupled Plasma/Mass Spectrometry (ICPMS)

Method(s): EPA 200.8, SW-846 6020, 6020A

Approvals (Signature/Date):			
	3/16/2015		3/13/2015
Roseann Ruyechan Inorganics Department Manager	Date	Steve Jackson Regional Safety Coordinator	Date
	3/17/2015		3/12/2015
Virginia Zusman Quality Assurance Manager	Date	Debbie Lowe Laboratory Director	Date

1. SCOPE AND APPLICATION

This method is applicable to the determination of metals by inductively coupled plasma mass spectrometry (ICP-MS) by EPA Method 6020, 6020A and EPA Method 200.8.

This method is applicable to drinking, surface, and saline waters, soil, sediment, wipe, tissue and waste samples. (Use of the collision reaction cell technology is not allowed for drinking water analysis using method 200.8.)

Reporting Limits

The standard reporting limits for metals analyzed by ICP-MS are listed in Table 1. Upon client request, results below the standard reporting limit but above the current method detection limit (MDL) may be reported and qualified as “estimated”.

Methods are based on the requirements of SW-846 methods 6020 and 6020A.

Elements that may be determined using this procedure include: Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Si, Ag, Sr, Tl, Sn, Ti, V, Zn, Ca, Mg, K, P, Cs and Na.

- Successful Ag analysis may require all solutions to be prepared as described, but with the addition of hydrochloric acid to 1% (v/v). This may degrade performance for As, Se and V.
- Collision Cell Technology (CCT) is used in analysis for Al, Sb, As, Ba, Cd, Co, Cr, Cu, Fe, Pb, Mg, Mo, Na, Ni, P, Se, Sr, Tl, V, and Zn.
- CCT is not used when analyzing for Be, B, Ca, K, Li, Mn, Sc, Si and Ti.

Additional elements may be analysed using this procedure, provide all appropriate QC measure are evaluated and found acceptable.

On occasion clients may require slight modifications to this SOP. These modifications are handles as indicated in the Quality Assurance Manual (PT-QA-M-001), current version.

2. SUMMARY OF METHOD

Samples requiring preparation are processed as in PT-IP-002 (Acid Digestion of Soils by SW 846 Method 3050B), and PT-IP-003 (Acid Digestion of Aqueous Samples by SW 846 Methods 3005a, 3010A and EPA 200.7 and 200.8)

The sample solution is introduced into a pneumatic nebulizer via a peristaltic pump. The nebulizer generates a fine aerosol by bringing the solution into contact with a high velocity flow of argon gas at its tip. The nebulized sample is sorted by droplet size in the spray chamber. Large droplets are rejected, while smaller particles are transported with the gas stream into the plasma.

The argon plasma operates with a continuously applied radio frequency (RF) field to give a high-energy discharge consisting of argon atoms, ions and electrons. The hottest part of the plasma can attain 6000-8000 K. In the plasma, aerosol droplets undergo evaporation, atomization and ionization. Ions are sampled through an aperture in a metal cone (sampler) at atmospheric pressure, into the expansion region at about 2 mbar and subsequently through an aperture in a second metal cone (skimmer) into the intermediate chamber.

An electrostatic ion lens system focuses the ion beam through a differential aperture into the analyser chamber, at about 10-7 mbar. The ions are filtered by mass-to-charge ratio in microsecond timescales by the quadrupole. The selected mass is detected by a discrete dynode electron multiplier. The multiplier has two simultaneous modes of operation: pulse count and analogue. The combination of these two modes allows seamless detection spanning 8 - 9 orders of magnitude. A detector "cross-calibration" is required for the analogue counts to be converted to equivalent pulse counts. The output from the detector is proportional to the concentration of the element in the aspirated solution, hence the concentration of unknown samples may be calculated when the instrument response is calibrated with standards of known concentration.

The linear range may vary from instrument to instrument and is dependant upon the sensitivity determined by the optimization parameters. This should be determined by the individual laboratory. In the test study at TestAmerica Pittsburgh, the linear ranges listed below were obtained:

2.1.1. Table A - Test study linear ranges for the X5 ICP-MS

Elements	Linear Range (mg/L)
Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Ag, Tl, V, Zn	2.0 – 25.0
Al, Ca, Mg, K Na, Fe	100 - 1500

Calibration standard concentrations are listed below.

2.1.2. Table B - Calibration standard concentrations for analysis of water and waste

Elements	Calibration Range (mg/L)
Al, Mn	1.0
Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Ni, Se, Ag, Tl, V, Zn	0.20
Ca, Mg, K Na, Fe	100
Fe	50
B, Mo, Sn, Sr, Ti	0.20
Si	10

3. DEFINITIONS

TALS – TestAmerica Laboratory Information Management System

Please refer to the glossary in the Laboratory Quality Assurance Manual (PT–QA-M-001) for definitions of general terms.

See appendix for Glossary of Abbreviations.

4. INTERFERENCES

Isobaric interferences. Elemental isobaric interferences occur when different elements have isotopes at the same nominal mass, e.g. ^{114}Cd and ^{114}Sn. Problematic elemental isobaric interferences for these methods are listed in Table 3. The correction factors given in Table C are based on theoretical isotopic abundance ratios and may require adjustment.

Table C - Isobaric Interferences and Correction Equations

m/z	Element	Interferent	Correction
58	Ni	Fe	58Ni=58M-0.0040*56Fe
64	Zn	Ni	64Zn=64M-0.0440*60Ni
82	Se	Kr	82Se=82M-1.0010*83Kr
114	Cd	Sn	114Cd=114M-0.0270*118Sn
115	In	Sn	115In=115M-0.0140*118Sn
123	Sb	Te	123Sb=123M-0.1240*125Te
138	Ba	Ce	138Ba=138M-0.0030*140Ce

Abundance Sensitivity - Abundance sensitivity is the ability of the quadrupole to separate a low intensity peak from an adjacent high intensity peak. An example of the requirement of this is the detection of low concentrations of manganese (m/z 55) in the presence of high concentrations of iron (m/z 56). Quadrupole resolution and bias can be adjusted during set-up to resolve these signals.

Isobaric Polyatomic Ion Interferences - Polyatomic ions are produced by chemical reaction in the plasma and the interface region. If these polyatomic ions have the same nominal mass to charge (m/z) ratio as an element a polyatomic interference is observed. The principle polyatomic species for this method are listed in Table 4. Some of the correction factors given in Table 4 are based on theoretical isotopic abundance ratios and may require adjustment. Other factors were derived empirically. The stability of the empirical factors was determined during the test study at Thermo Electron. It was found that the factors require little or no adjustment and can be transferred between similarly configured X5 instruments. These interferences can also be eliminated by use of Collision Cell Technology (CCT). This technology introduces a 93% Helium and 7% Hydrogen gas into the instrument before the sample reaches the quadruple. This gaseous mixture collides with the polyatomic formed bonds to break them. For example, the gaseous mixture will break the ArCl (Mass 75) bond leaving Ar^{40} and Cl^{35} as separate masses, therefore the only element detected at Mass 75 is arsenic.

Table D - Isobaric Polyatomic Interferences and Correction Equations

m/z	Element	Interferent	Correction
51	V	ClO	51V = 51M-3.0460*53ClO 53ClO = M53-0.114*52Cr
52	Cr	ArC, ClOH	52Cr = 52M-0.0050*13C
56	Fe	CaO	56Fe = 56M-0.1500*43Ca
56	Co	CaO, CaOH	59Co = 59M-0.0046*43Ca
60	Ni	CaO	60Ni = 60M-0.0020*43Ca
75	As	ArCl	75As = 75M-3.000*77ArCl 77ArCl = 77M-0.8000*82Se 82Se = 82M-1.0010*83Kr
111	Cd	MoO	111Cd = 111M-0.9820*108MoO 108MoO = 108M-0.712*106Cd

Physical Interferences - Physical interferences include transport effects, ionization effects and deposition effects in the sample introduction system, plasma and interface, which result in signal suppression and signal drift. Transport effects arise from variations in solution properties, e.g. viscosity or surface tension, which affect nebulization efficiency and aerosol droplet size. The concentration of dissolved matter will affect the ionization efficiency of the elements in the plasma and will cause a mass-dependant suppression effect and contribute to space-charge effects. Dissolved matter may also condense on the cones, altering the ion beam profile. This normally manifests itself as a time-dependant downward signal drift. To reduce the severity of these effects it is advised that the total dissolved solids concentration of solutions aspirated should be limited to <0.05%. Samples known to contain higher dissolved solids concentrations should be diluted. Signal suppression and drift can be corrected, to a degree, with the use of internal standardization techniques. Since these effects can be mass-dependant and may be related to the ionization potential of the element, a multiple-element internal standard approach should be used.

Memory Effects - Memory effects occur when the signal for an element from a sample contributes to the signal of a subsequent sample. This effect can be severe for certain elements due to their physico-chemical properties, e.g. mercury. This effect is minimised by aspirating a wash solution between samples. A monitored wash can be used in order to ensure that element signals recover to the background level.

Common molecular ion interferences for ICPMS are given in Table 6 at the end of this SOP.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-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.

Specific Safety Concerns or Requirements

5.1.1. The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

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.

Table E – Known Hazardous Materials

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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Eye protection that protects against splash, laboratory coat, and chemically resistant 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.

The waste pumped from the spray chamber is corrosive and must be handled with care, especially if large volume containers are used, as these may be heavy and awkward to carry. Empty the waste vessel daily to reduce the quantity that must be disposed each time and to keep weight to a minimum. Protective clothing, including hand and eye protection must be worn when handling this waste.

The wash solution is corrosive and must be handled with care. This solution must be prepared and stored in a vessel made of a robust acid-resistant material with a tight fitting lid that it is resistant to breakage if dropped. Large volumes of this solution will be heavy and may be awkward to carry. Ensure adequate provision for transporting the vessel, i.e. suitable handles on the vessel, minimum distance between the preparation area and the instrument. Use a cart to transport the vessel where necessary or ask for assistance in carrying.

Many of the concentrated metal standard solutions are toxic and must be handled with care. Skin and eye protection should be worn when handling and inhalation of vapours must be prevented.

Fumes generated by the plasma can be hazardous and must be removed from the laboratory with an extraction system as detailed in the X Series site planning guide. If the extraction system is faulty do not attempt to use the instrument. The extraction system should be inspected on a regular basis.

The plasma emits strong UV light and is harmful to vision.

5.1.2. ***WARNING:*** **AVOID looking directly at the plasma.**

The plasma is a source of radio frequency (RF) radiation and intense, ultra-violet radiation that can damage the eyes. This radiation is normally contained by the system, but operators must be aware of the dangers. The instrument must be properly maintained by qualified service personnel. Never attempt to defeat hardware interlocks – they are there for your safety.

Should the plasma need to be extinguished in an emergency, open the torch box door. This will immediately cut-off the power to the plasma RF generator, extinguishing the plasma. After extinguishing the plasma, the torch, torch box, cones and cone housing may remain very hot for some time. Operators must be aware of this fact and allow cooling time prior to handling these components.

There are high voltage components inside the instrument. Routine maintenance does not require access to any of the electronic components. If an electronic fault is suspected, a qualified service engineer must be called. Do not attempt to tamper with electronic components yourself.

Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported **immediately** to a laboratory supervisor and/or the EHSC.

6. EQUIPMENT AND SUPPLIES

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

Instrumentation

6.1.1. Thermo Scientific X Series ICP-MS fitted with Xi interface and Y-connector for on-line internal standard addition

6.1.2. Cetac ASX-510 autosampler

6.1.3. Thermo Scientific Plasma Lab software, version 3.51

Supplies

6.1.4. Ultrapure water system capable of delivering de-ionized, polished water of at least 18 MΩ cm

6.1.5. Thermo Scientific Yellow/orange tab peristaltic pump tubes (~0.5 mm ID)

6.1.6. Thermo Scientific White/white tab peristaltic pump tubes (~1 mm ID)

6.1.7. A range of adjustable pipettes, such as Rainin pipettes. Adjustable pipettes with a capacity of 0.1 mL, 1 mL, and 10 mL are recommended. These must be calibrated regularly to ensure accurate volumes are delivered.

Refer to Appendix 3 at the end of this document and SOP PT-QA-022 for routine instrument maintenance procedures

7. REAGENTS AND STANDARDS

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard. Quantities different than what is specified can be made provided that the ratios remain the same.

General Reagents

7.1.1. **Laboratory Water** - All laboratory water used in these procedures must be of very high quality, purified with a reverse osmosis system and polished with an ion exchange system to give a final product of resistivity >18 MΩ cm.

7.1.2. **Hydrochloric Acid** (sp. gr. 1.18) - Hydrochloric acid must be at least Romil “SPA”, J.T. Baker “Instra Analyzed”, BDH/Merk “Analar”, Fisher “Optima” - grade or equivalent. Hazards – corrosive, causes severe burns.

7.1.3. **Nitric Acid** (sp. gr. 1.42) - Nitric acid must be at least Romil “SPA”, J.T. Baker “Instra Analyzed”, BDH/Merk “Analar”, Fisher “Optima” - grade or equivalent. Hazards – oxidising and corrosive, causes severe burns.

7.1.4. **2 % (m/v) Nitric Acid** - This reagent is used for the calibration blank, ICB, CCB, sample dilution and solution preparation. Add 5 mL of Conc of HNO3 to DI water and dilute to 250 mL.

7.1.5. For Standard preparation refer to TALS Reagent Module. Composition of standards and concentration are given in Tables 2-5.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time	Reference
Water	250 mL Plastic bottle	100 mL	pH <2 preserved with HNO_3	180 days from collection	40 CFR Part 136
Soil/Wipes	4 oz. clear glass jar	2 grams	≤ 6°C, but not frozen	180 days from collection	40 CFR Part 136
Tissues	4 oz. clear glass jar	2 grams	Frozen until ready to prepare	180 days from collection	40 CFR Part 136
Sediments	4 oz. clear glass jar	100 grams	≤ 6°C, but not frozen	180 days from collection	40 CFR Part 136

Aqueous samples for total metals must be digested before analysis using an appropriate digestion procedure. Method 200.8 has its own digestion specifications that are followed by the laboratory. Method 3005A is used for total recoverable metals, total metals and dissolved metals and method 3010A is used for TCLP metals by 6020 and 6020A. These are covered in the SOP PT-IP-003. Upon consultation with the client dissolved samples can forego digestion to help prevent contamination when very low detection limits are required.

Soil, wipe, tissue and waste samples should be digested before analysis using an appropriate digestion procedure. Method 3050B of SW846 is the appropriate digestion procedure. The SOP for 3050B is PT-IP-002.

Dissolved metals samples that are filtered directly into a nitric acid preserved container may be digested immediately following the filtration.

9. QUALITY CONTROL

Summary of Quality Control Requirements

QC Code	Method(s)	QC Name	Purpose	Frequency	Limits
ICV	6020, 6020A, 200.8	Initial Calibration Verification	Checks the calibration against a second calibration source	After initial calibration	90-110%
ICB	6020, 6020A, 200.8	Initial Calibration Blank	Initial check of read-back at blank level	After initial calibration	<CRQL (1)
CRI/ LLICV/LLCCV[2]	6020, 6020A, 200.8	Contract Required Quantitation Limit Check	Checks accuracy at the required limit of quantitation	After each calibration. [2]	50-150% (1) 70-130%(6020A)[2]
ICSA	6020, 6020A, 200.8	Interference Check Solution A	Checks for freedom from interference	After initial calibration	For RL < 10 ±3 CRQL, RL > 10 ± RL or ±20% of the true value (whichever is the greater) [3]
ICSAB	6020, 6020A, 200.8	Interference Check Solution AB	Checks that elements are accurately measured in an interference-producing matrix	After initial calibration	80-120% of true value
CCV	6020, 6020A, 200.8	Continuing Calibration Verification	A continuing periodic check on accuracy and drift	After each calibration and every 10 samples	90-110%
CCB	6020, 6020A, 200.8	Continuing Calibration Blank	A continuing periodic check on the read-back at blank levels	After each calibration and every 10 samples	<CRQL (1)
MB	6020, 6020A, 200.8	Method Blank	Identify contamination	Once every 20 samples per matrix	< RL except for common lab contaminants at < 5 X RL. common lab contaminants < RL.
LCS	6020, 6020A,	Laboratory	Checks the	Once every 20	80-120%

QC Code	Method(s)	QC Name	Purpose	Frequency	Limits
	200.8	Control Sample	accuracy of the entire analytical process	samples per matrix	85-115% - 200.8
MS/MSD	6020, 6020A, 200.8	Matrix Spike/Matrix Spike Duplicate	Accuracy and precision	For 6020, 6020A and DoD once every 20 samples – For 200.8 every 10 samples	6020 and 6020A: 75-125%, RPD ± 20% 200.8: 70-130, RPD ±20%
DUP	6020, 6020A, 200.8	Duplicate	Checks the reproducibility of results by analyzing an unknown sample in duplicate	Once every 20 samples per matrix	±20% Relative Percentage Difference (RPD)
PDS	6020, 6020A	Post Digestion Spike	Checks the recovery of elements spiked into an unknown sample after preparation (digestion) – Performed if MS/MSD criteria not met.	Once every 20 samples per matrix	75 – 125% (6020 and 6020A)
SER	6020, 6020A, 200.8	Serial Dilution	Checks for matrix effects by assessing the variation of results for an unknown sample before and after dilution	Once every 20 samples per matrix	±10% of the original undiluted result after dilution correction for sample results ≥ 50 X MDL or IDL.

(1) For Method 6020 and 200.8, limit is 50-150%.

(2) For Method 6020A the CRI is also analyzed at the end of the analytical sequence.

(3) For batches containing samples from Wisconsin, the ICSA must be <RL for all elements.

Batch QC

9.1.1. Method Blank (MB)

The method blank consists of reagent water, or Teflon chips for non-aqueous matrix batches, containing all reagents specific to the method that is carried through the entire preparation and analysis procedure with the samples. The method blank is used to identify any system and process interferences or contamination of the

analytical system that may lead to the reporting of elevated element concentrations or false positive data.

- MB must not contain any target elements at or above the Reporting Limit (RL). Certain programs may require a more stringent evaluation of the method blank, for instance, that the blank not contain any elements of interest at a concentration greater than ½ the reporting limit or greater than the MDL. Check projects for specific criteria.
- Samples associated with MBs contaminated above the RL (or other limit per project specifications) must be reanalyzed or re-digested and reanalyzed, unless one of the following situations exists.
- If the element is a common laboratory contaminant (copper, iron, zinc), the data may be reported with qualifiers if the concentration of the element in the MB is less than five times the RL. The "Method Blank – Report, Common Lab Contaminant <5x RL" NCM must be used when reporting such data as well as the qualifier flag.

If the method blank is contaminated and associated sample concentrations are > 10x the MB concentration, results may be reported and using the "Method Blank – Report, 10X" NCM.

- If the contaminated element is not detected above the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers and using the "Method Blank – Report, ND" NCM.
- If none of the above situations applies, and reanalysis is not possible due to sample volume or other problem, the project manager must be notified and the client contacted with the details. If results are to be reported, they must be properly qualified and the nonconformance described in the case narrative.

9.1.2. Laboratory Control Sample (LCS)

The LCS consists of reagent water, or Teflon chips for non-aqueous matrix batches, spiked with the elements listed in Tables 9 and 10, unless otherwise requested by the client. The LCS is carried through the entire preparation and analysis procedure with the samples, and is used to monitor for bias and method performance with each batch. Results must be within 85-115% of the true value for method 200.8, or 80-120% for methods 6020/6020A.

9.1.2.1. If any element in the LCS is outside the control limits, corrective action must occur:

- Check calculations,
- Check instrument performance,
- Reanalyze the LCS, and if still outside of control limits,
- Evaluate the data, and/or
- Re-digest and reanalyze all samples in the QC batch.

9.1.2.2. Re-digestion/reanalysis is not required if recovery of the LCS is above the control limits, up to 140%, and the affected element is not detected above the RL in the associated sample.

9.1.2.3. If reanalysis is not possible, the project manager must be notified and the client contacted with the details. If results are to be reported, they must be properly qualified and the nonconformance described in the case narrative.

9.1.3. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

The MS and MSD are spiked into separate portions of a client sample prior to any digestion steps, and are carried through all the preparation and analytical steps along with the samples. Samples for MS/MSD are chosen at random from all client samples in the batch, unless a client has specified a sample to be used. The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

Some programs require a Matrix Duplicate (MD) and Matrix Spike (MS) in lieu of an MS/MSD. When a MD/MS is performed the MS is evaluated for accuracy (% recovery) and the MD is evaluated for precision (RPD). Percent recovery must be within 70-130% for method 200.8 and 75-125% for methods 6020/6020A. The %RPD must be $\leq$20% for all methods.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that element in the Laboratory Control Sample (LCS). If the recovery of the element in the LCS is within limits, then the laboratory operation is in control and results may be reported with the parent sample and MS/MSD (or MD) qualified and the nonconformance described in the case narrative.
- If the recovery for any component is outside QC limits for both the matrix spike/spike duplicate and the LCS, the process is out of control and corrective action must be taken. Corrective action will include re-digestion and reanalysis of the batch.
- If the concentration of the element in the parent sample is greater than 4 times the amount of spike added, then routine control limits may not apply. Recoveries are still evaluated, however reanalysis is not required. Results are reported with qualifiers and the condition described in the case narrative.

9.1.4. Post-Digestion Spike Samples (PDS)

- For methods 6020 and 6020A, a post digestion spike will be run on a sample if the MS/MSD for recovery falls outside of 75-125%. For 6020 and 6020A the default matrix spike protocol is a “post digestion spike”. However, TestAmerica Pittsburgh will perform a conventional matrix spike and spike duplicated as the default matrix QC. We will perform the “PDS” only where the conventional matrix spike fails. We believe that this approach will provide more complete matrix information than the default requirements.

- A post digestion spike is a matrix spike added to the already digested portion of the parent sample.
- If the PDS also fails, then matrix effects are confirmed. The software calculates this based on the following equation:

  %Repeatability = 100 * (Spk-Orig)/Tru

  Where, Spk is the spiked sample result and Orig is the original sample result and Tru is the True spiked concentration value. If a result is outside the required range, an NCM will be written stating the recovery was outside of the control limits.
- **A Post Digestion Spike is not required for method 200.8.**

9.1.5. Serial Dilution Samples (SER)

- Some regulatory programs such as require a dilution test to be performed for each matrix within an analytical batch determination. If the element concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should be performed.
- The software calculates this based on the following equation:

  %Repeatability = 100 * Ser/Orig

  Where, Ser is the dilution corrected serial diluted sample result and Orig is the original sample result. If a result is outside the required range, the data should be assessed carefully and samples may require reanalysis.
- The results of the dilution (corrected for the dilution factor) must agree with the original sample results within 10%. Only elements for which the original sample result is ≥50x the MDL are evaluated.

Instrument QC

9.1.6. Mass Spectrometer Tuning Check must be performed daily prior to calibration.

- Peak resolution must be < 0.90 amu at 10% peak height for methods 6020/6020A and ≤0.90 amu at 5% peak height for method 200.8.
- Mass calibration must be within ± 0.1 amu from the actual value for the 6 tuning elements (Be, Ce, Co, In, Mg and Pb).
- See section 10.2.2 for additional details.

9.1.7. Initial Calibration is performed daily using a single calibration standard and a blank for each element. Refer to Table 2 for standard concentrations.

9.1.8. Linear Range Verification (LR) - The linear range is determined semi-annually (2x/year) for each element on the standard list. See Section 12 for details of the linear range verification.

9.1.9. The internal standard (IS) intensities in samples must be within 60 to 125% of the IS

intensities for the Calibration Blank for method 200.8, 30% to 120% for method 6020 and 70 to 120% for method 6020A. If this criterion is not met, the sample will be diluted and reanalyzed until the IS recoveries are within the limits. If the upper control limit is exceeded, the analyst should review the data for the presence possible contribution from the native sample. IS failures must be documented in the case narrative.

- For method 6020 the internal standard intensity in the ICV, ICB, CCV and CCB should be within 20% of the IS intensity in the calibration blank of the initial calibration. If not, the analyst should check for any instrument anomalies and continue if none are noted.
- For method 200.8 the IS acceptance range does not vary from the 60 to 125% noted above.
- For method 6020A the IS acceptance range does not vary from the 70 to 120% noted above.

9.1.10. Interference Check Solutions (ICSAs) - The "true" value will be taken as zero, unless otherwise indicated in the solution manufacturer's literature. The software automatically checks for compliance with the above, based on a "true" value of zero. If a result falls outside this range, the analysis must be terminated and the samples associated must be reanalyzed. Interference Check Solution Spike Recoveries (ICSABs) - The software automatically checks for compliance with the above, based on the values indicated in (Tables 4 and 5). If a result falls outside this range, the analysis must be terminated and the samples associated must be reanalyzed.

NOTE: For ICSA associated with samples from Wisconsin, all elements must be <RL.

9.1.11. Initial Calibration Verification (ICV) - Calibration accuracy is verified by analyzing a second source standard (ICV). Recoveries for the ICV must be within 90-110% of the true value. If ICV recovery is outside control limits, determine the source of the failures and repeat the Initial Calibration and ICV analysis.

9.1.12. Initial Calibration Blank (ICB) - An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. Certain programs, may require a more stringent evaluation of ICB, for instance, that the blank not contain any elements of interest at a concentration greater than ½ the reporting limit or greater than the MDL.

9.1.13. CRQL Check Standard (CRI)

- For method 6020 and 6020A the CRI check is at the RL. The CRI/LLICV/LLCCV must be analyzed at the beginning (200.8/6020/6020A) and end (6020A only) of the analytical sequence. The CRI is a low level quantitation check sample which is prepared and analyzed daily with each analytical batch. Recovery must be within 50-150% for methods 200.8 and 6020, and within 70-130% for method 6020A.

- If any element is outside the range indicated, the standard may be re-run once. If the results fall within the required values upon re-run, no further corrective action

need be taken. If still outside the acceptable range, the analysis shall be terminated, the problem corrected and the affected samples reanalyzed.

- For 6020A, if the closing CRI recovers high and outside of criteria, the sample results may be reported if sample concentrations are ≥10X the CRI concentration or < the RL.

9.1.14. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard (CCV) and blank (CCB).

- CCV recovery is checked by the software, based on the true values, and must be within 90-110% of the true value. If outside this range, the analysis must be terminated, the problem corrected and the samples since the last valid CCV must be re-analyzed. If an element recovers >110% in the CCV, up to 120%, and the element is not detected above the RL in any bracketed sample, sample results may be reported with qualifier and using the "CCV - %D, High, Sample ND" NCM.
- The CCB result must fall within ± RL from zero, unless all bracketed samples have concentrations ≥10X the CCB concentration or concentrations < the RL. (Certain programs, may require a more stringent evaluation of the CCB, for instance, that the blank not contain any elements of interest at a concentration greater than ½ the reporting limit.) The analyst should refer to the project notes provided by the PM to identify when this is an issue and if so what the corrective actions to take for exceedances.)
- Sample results may only be reported when bracketed by valid CCV/CCB pairs, unless one of the situations described above exists. If a mid-run CCV or CCB fails, the CCV or CCB may be reanalyzed once and accepted if there is a reason for the initial out-of-control event such as carryover from a high concentration sample. Otherwise, if the CCV or CCB fails, the analysis for the affected element must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed.
- Refer to Section 10.9 for an illustration of the appropriate rerun sequence.

10. PROCEDURE

Sample Preparation

10.1.1. Refer to SOPs PT-IP-002 (Acid Digestion of Soils by SW 846 Method 3050B) and PT-IP-003 (Acid Digestion of Aqueous Samples by SW 846 Methods 3005A, 3010A and EPA 200.7 and 200.8) for sample digestion procedures.

Calibration

10.1.2. Instrument start-up

Follow the instrument start-up procedure outlined in the Thermo X-Series ICP-MS Operator's Manual.

10.1.3. Instrument Tuning

10.1.3.1. Aspirate a 20 ppb tuning solution containing all of the tuning elements. The 6020/6020A tuning elements are Li, Co, In, and Tl. The instrument manufacturer monitors Mg, Ce, Be & Pb for instrument performance.

10.1.3.2. Mass calibration and resolution checks must be documented and included as part of the raw data package.

10.1.3.3. Resolution must be < 0.90 amu at 5% peak height for the 6 tuning (Be, Ce, Co, In, Mg, & Pb) for 200.8/6020/6020A.

10.1.3.4. Mass calibration must be within ± 0.1 amu from the actual value for the 6 tuning elements (Be, Ce, Co, In, Mg, & Pb) or the mass calibration must be adjusted.

10.1.3.5. A "daily" performance check must be performed. This uses the same tuning solution as above with 5 replicates. The 6 tuning elements must have RSDs below 5%. The oxides ratio must be below 5%. If any of these conditions are not met repairs or optimization procedures must be performed until these specifications are met.

10.1.3.6. Recommended analytical isotopes and additional masses that maybe monitored are given in Table 7. Recommended isotopes and additional masses that may be monitored are given in Table 8.

10.1.4. Initial Calibration

10.1.4.1. Calibration consists of a blank and the following calibration standards (STD1, STD 2X, and STD 3X see Table 2 for concentrations) in accordance with the manufacturer's procedure. Use the average of three integrations for both calibration and sample analyses.

10.1.4.2. Following the STD, STD2X & STD3X, a second source ICV and ICB are analysed.

10.1.4.3. For 6020/6020A, following the ICV/ICB pair, the CRI/RLV is run before the ICSA is analyzed. The CRI/RLV is analyzed again at the end of the sequence for 6020A.

10.1.4.4. For 6020, 6020A, following the ICSA, analyze the ICSAB. The ICSAB must be within ± 20% of the true value. For method 200.8 ICSA and ICSAB is also analyzed although not required by the method.

10.1.4.5. Internal standards are added to all standards and samples by the instrument automatically during analysis.

10.1.5. Continuing Calibration:

10.1.5.1. Following every 10 samples (including lab QC), analyze a CCV/CCB pair. These must be within ± 10% of the true value for analysis to continue. For methods 6020/6020A, a CCV/CCB pair should also be analyzed immediately after the ICSAB.

10.1.5.2. All samples must be bracketed by an acceptable CCV/CCB pair. Where a CCV/CCB fails the samples preceding it back to the last acceptable CCV/CCB must be reanalyzed.

10.1.6. Instrument Set-up

10.1.6.1. Configure the X Series with the standard sample introduction equipment, i.e. a glass concentric nebulizer, glass impact bead spray chamber and a one-piece torch with 1.5mm ID injector tube. A Peltier spray chamber cooling unit is optional. Ensure that the Xi interface cones are fitted. These are standard with the X5 instrument and an option for the X7. They can be identified as follows:

Xi Sampler - 1.1 mm orifice, no nipple, no holes around the flat circumference

Xi Skimmer - Small pointed skimmer mounted in a copper adapter with two screws

Yellow/orange tab peristaltic pump tubes (6.2.2) should be used for sample and internal standard uptake. Connect the liquid output end of the peristaltic pump tubes to the 1.0 mm (OD) barbed fitting screwed into the Y connector. Note that the barbed fitting may require tightening with a pair of grips to ensure a good fluid-tight seal. The mixed output flow should be connected to the nebulizer. See diagram in Appendix 6 for plumbing schematic. A white/white tab peristaltic pump tube (6.2.3) should be connected to the spray chamber drain outlet at one end and to a tube running into a waste vessel at the other and wound on the pump to draw the waste liquid away from the spray chamber.

10.1.6.2. Perform the daily maintenance as outlined in Appendix 3.

10.1.6.3. Switch the instrument into the *Operate* state by clicking the *ON* button at the top of the screen. During the automated ignition sequence, the following processes occur:

i. Torch purge with argon gas

ii. RF power match

iii. Plasma ignition

iv. Slide valve open

v. Electronics on

This process takes about two minutes. Upon successful ignition, the software will display *Operate* in the *Instrument State* bar. If the event of unsuccessful ignition, the software will display an error message and/or place a message in the *Technician Event Log*. Upon unsuccessful ignition, inspect the sample introduction equipment and torch, ensuring a good gas-seal at each connection and ensuring the torch is not misaligned or damaged. If all appears satisfactory, the ignition may be attempted again. If the ignition process consistently fails, contact your local Thermo service agent for advice.

10.1.6.4. Once the instrument is in the *Operate* state, it should be left for 30 minutes to reach thermal equilibrium prior to starting analytical measurements. The optimization (tuning), performance testing and instrument set-up calibrations may be performed after 15 minutes. Ensure that the peristaltic pump is operated at a default analytical speed of 30%. This is done by clicking on *Instrument*, *Configurations*, *Configuration Editor*, *View Selected Accessories* (network icon), *Peristaltic Pump*, *Connect* (chain icon). Set pump speed to 30% using the slider bar and adjust the *Settle Time* to 15 seconds and click on *Apply*. Click *OK* to close the dialogue box.

10.1.6.5. During the initial 15 minutes, the system can be “conditioned” by aspirating the system thoroughly with 2% nitric acid + 1% HCL solution prior to continuing.

10.1.6.6. Instrument tuning (optimization) is performed using a 20 µg/L Tune Solution, aspirated through the sample uptake tube. Optimization may not be necessary from day to day if the sample introduction system and cones have not been adjusted in any way and if the instrument fulfils the performance requirements given below. If the instrument gives performance exceeding the requirements shown below, proceed to 10.2.5.7. Otherwise, tune the instrument manually or using *Autotune* while aspirating 20 µg/L Tune Solution through the sample probe. *Autotune*, using an appropriately defined sequence is advised (see Appendix 4).

The final conditions must give the following:

^{9}Be	< 500
^{115}In	< 10,000
^{208}Pb	< 10,000

$^{156}CeO/^{140}Ce$ <0.05

The Collision Cell Technology (CCT) aspirates the same 20 ug/L Tune Solution listed above using a CCT defined instrument sequence. The CCT sequence uses all the same modes(lense/stage/nebulizar/ settings) as the standard tune. The CCT gaseous mixture is gradually added during the CCT tune sequence. The final CCT tune conditions must give the following:

^{115}In > 10,000 cps

$^{208}Se/Ar\text{-}Ar$ < 200 cps

If the above criteria are met, proceed to 10.2.5.7. If the above criteria are not met, do not proceed. Check that the tune solution was prepared properly and remake if necessary. If the sensitivity is below the minimum requirement, a new detector plateau may be required (see Appendix 6), the cones may require cleaning (see Appendix 8), or the nebulizer or sample uptake lines may have become blocked or may not be properly clamped on the peristaltic pump. If the CeO/Ce ratio is >0.05, the nebulizer gas flow can be reduced and/or the sampling depth increased, obtaining a corresponding reduction in oxide formation. Recheck the above parameters after taking any remedial action.

10.1.6.7. Save the satisfactory instrument settings by clicking on the disk icon on the Tune page. Note that this is not necessary if Autotune has been used, as the instrument settings are saved automatically (unless manual adjustments have been made after autotuning).

10.1.6.8. Set-up the resolution as described in Appendix 5.

10.1.6.9. Perform a cross-calibration (and mass-calibration and detector voltage setup if required) as explained in Appendix 6. Note that retuning may be necessary after performing this routine.

10.1.6.10. Aspirate Tune solution and run a *Performance Report* (see Appendix 4) to confirm the mass-calibration, resolution, minimum sensitivity and maximum cerium oxide requirement and to verify instrument stability. The performance report acquires five consecutive one-minute runs and calculates the percentage relative standard deviation (RSD) of the five measurements for each isotope. The RSD of the elemental elements in the performance report must be <5%. If the performance report passes, proceed to (10.3). If the performance report fails, check:

a. Liquid uptake tubes for kinks or other damage

b. Condition and position of the peristaltic pump tubing

c. Tightness of the peristaltic pump clamp screws (these should be just tight enough to draw liquid through the tube smoothly)

d. Joints of all sample introduction components, ensuring a good seal

e. Nebulizer for blockage

f. Salt deposition on cones

Remedy the above as necessary and repeat the test. Note that retuning may be required if any sample introduction components are adjusted or replaced.

Note: Resolution set-up may require adjustment if the resolution check fails (see Appendix 5). Note that the quadrupole and hexapole bias strongly influence abundance sensitivity (Pole Bias should be kept >+4V and Hexapole Bias <-3V).

If the measured mass position for each mass in the performance report is not within ±0.1 amu of the nominal mass position, a new mass-calibration must be performed (see Appendix 6).

Sample Analysis

10.1.7. Open the method template by clicking on *Templates* and then <TESTAMERICA PITTSBURGH ICPMS ANALYSIS> or <TA PITT CCT ICPMS Analysis>. The method template will be opened. This contains all the saved analytical parameters and only the sample list need be amended. For work flow chart refer to Appendix 11.

NOTE: The CCT Template uses both the standard and CCT modes. First the instrument analyzes in standard mode for non-CCT elements (Be, B, Ca, K, Li, Mn, Sc, Si and Ti), then it switches to CCT mode which adds the CCT gaseous mixture to analysis for the CCT elements (Al, **As,** B, Ba, Cd, Co, **Cr,** Cu, Fe, Mg, Mo, Na, Ni, P, Pb, Sb, **Se,** Sn, Sr, Tl, **V** and Zn. Critical CCT elements are bolded). The instrument stabilizes for 20 seconds and then analysis for the CCT elements.

10.1.8. Go to *Sample List*. This grid contains all the information about calibration, QC and samples to be run. The calibration and QC concentration information is already stored. Enter all unknown samples into the list in the appropriate order below the existing calibration and QC samples by overwriting the sample label fields. Delete any QC samples that do not apply to the required method. (If sample list changes are to be made permanent to the method, save the method as a *Template*, by going to *File*, *Save as Template*. Enter a new name to create an amended method, or use the same name to overwrite the current one.)

10.1.9. Once all the sample information is added, check the required autosampler positions have been correctly entered. Amend as necessary. To sequentially renumber positions, add the correct position required for the initiation of the sequence and right mouse click on the first correctly numbered cell. A pop-up menu will appear. Select *Renumber autosampler positions* from this. Ensure that all samples have one survey

run and 3 main runs and a probe depth of 155mm.

10.1.10. Save the experiment run by clicking on the *File* menu, then *Save as*. Enter the required file name, e.g. *X50103A* and click *Save*.

10.1.11. To print the sample list, go to *Reports* and check the *Sample List* box. Click the refresh icon. The sample list will be displayed in a printable format. Press the print icon. Note that this can only be done with PlasmaLab version 2.3 and above.

Loading the Autosampler

10.1.12. Pour the required samples into pre-cleaned 15ml polypropylene test tubes (5.1.4). To avoid contamination, a small amount of the solution to be analyzed can be poured into the tube and then discarded. This will rinse out any residual contamination.

10.1.13. Pour blanks, standards and QCs (positioned in rack 0) into pre-cleaned 50ml polypropylene tubes. To avoid contamination, a small amount of the solution to be analyzed can be poured into the tube and then discarded. This will rinse out any residual contamination. Note that **2% nitric acid** (7.1.4) is used as the calibration blank, ICB, and CCB.

10.1.14. For the **serial dilution** sample(s), dispense 2.00±0.02 mL of the original sample into a pre-cleaned 15 mL polypropylene test-tube and add 8.00±0.08 mL of 2% nitric acid (7.1.4). Mix well. This is a 5-fold dilution.

10.1.15. Place the tubes for each sample into the appropriate position in the rack according to the sample list. Note that the autosampler works on a two-dimensional grid position system by rack number (0-4). See Appendix 9 for autosampler position map.

Initiating Analysis

10.1.16. Place the sample probe into the autosampler arm and the internal standard probe into the internal standard solution.

10.1.17. Go to *Instrument*, *Tune* and click on the accessories dialog icon. Click on *Autosampler* and then on the chain icon to connect. The autosampler should initialize. Ensure that the probe is at the correct height by positioning it so that its tip just protrudes through the hole in the bottom of the arm. Click on the *Go to Wash* icon (faucet) to send the probe to the wash station. Ensure that the wash solution is being correctly delivered to the wash station via the peristaltic pump at the rear of the autosampler. Allow at least 2 minutes for the liquid to be delivered to the sample introduction system.

10.1.18. Click on the experiment to be run. Click the *Queue* icon and then *Append* and *OK*. The analysis has now been initiated.

10.1.19. To monitor the progress of the analysis, right-mouse click on the *MS* icon at the

bottom-right of the screen and select *Open Service Window* from the pop-up menu. The Service Window hovers over the current application window until moved or closed and displays the current instrument activity. This window is also used **to stop an analysis** if required. This is done by clicking on the ^{x}***Q*** **icon**.

10.1.20. To view results as they are generated, click on the experiment icon and go to the *Results* tab. Click on the *Refresh* button or the refresh icon (green circular arrows on a page) to calculate the results from the data obtained.

10.1.21. To view calibration plots, click on the *Calibration Data* tab. The calibration for each element can be viewed by clicking on the required isotope in the *Element* box. Each subsequent set of calibrations (calibration block) can be displayed by selecting the required calibration block from the drop-down combo box, e.g. *FQ Block 1*, *FQ Block 2*, etc. FQ denotes a Fully-Quantitative calibration and SQ denotes a Semi-Quantitative calibration, i.e. a response curve generated from the *FQ* calibrations. The SQ response curve is used to calculate semi-quantitative concentrations if required.

10.1.22. To view data, click on the *Numerical Results* tab. The *Element Dilution Conc.* tab is a tabular display of the calculated corrected concentrations for each element. These values have been corrected for internal standardization, external drift correction (if used), and dilution (where entered). The *Mass Uncorrected ICPS* tab shows the uncorrected raw data for each measured mass in units of integrated counts per second (ICPS). The *Element ICPS* tab shows integrated counts per second data that has been mathematically corrected for blank deduction, internal standardization, drift correction (if used), and dilution (as appropriate). The *Survey* tabs show the data integrated from the survey scan for each sample. Any concentrations displayed in the survey page will be semi-quantitative only.

10.1.23. To edit the amount of data on screen (filter the results display), click on the filter icon (funnel and lightening). Alter the numerical values or the check boxes to select the required data to display and click on *OK*. To jump directly to a particular sample of interest, find the sample in the drop-down combo box at the top of the data display and click on it.

10.1.24. To display mass-spectra, click on the *Spectra* tab. Display the spectrum for a particular sample by double-clicking on the sample name in the selection box on the left of the screen. Note that several spectra may be overlaid by double-clicking on each sample to be displayed. To zoom into a particular area, click the zoom icon (magnifying glass) and click and drag on the spectral display to zoom into the required area. The dashed-lines represent data acquired in the analogue mode of the detector whilst the solid-lines represent pulse-count data. To remove the noise associated with analogue detection at low signal levels, point at the display and right-mouse click to bring up a menu. Go to *View Options* and then click on *Eliminate Analogue Noise*. To identify a peak, click on it and wait for the options for that mass to be displayed in the box above the spectral display. To fingerprint a spectrum, double click on the species to fingerprint in the options box. This will overlay the isotopic pattern for the selected species, based on the lowest relative intensity signal for the

pattern masses. The spectra may be navigated by using the arrow buttons above the display. Allow the arrow cursor to hover over each button for an on-screen explanation of its function.

Post-Analysis Data Processing

10.1.25. Internal Standards

10.1.25.1. Check the internal standard recovery percentage for each internal standard isotope used for every sample. The percentage for each isotope must be within the range 30-120% for method 6020, 70 – 120% for method 6020A and 60 – 125% for method 200.8.

10.1.25.2. If above 120%, check that the other internal standard isotopes show similar deviation. If not, this may be due to the presence of the internal standard element in the sample. This is particularly common with the isotopes of Li, Sc and Y in environmental materials. If this is the case, the affected internal standard isotope may be excluded for the sample affected, as follows. Go to the *Sample List*.

Find the sample affected and select it in the list by clicking on the box in the left-hand column. Click *Show Advanced* and go to *Internal Standards*. Click on *New Internal Standard Set*. Select the affected isotope(s) in the *Internal Standards* box on the right. Remove the affected isotope from the *Internal Standards* box by using the left hand arrow button (<<). Recalculate the results for this sample by going back to *Results* and clicking on *Refresh*.

10.1.25.3. If any internal standard isotope is outside the required range (see section 10.6.1.1) and all other internal standard isotopes show similar values for that sample, the instrument may have drifted, or the sample may be producing a suppression or enhancement effect. Find the nearest blank following the sample in question and check its internal standard results. If these are similarly reduced or elevated, the instrument has drifted and the samples must be reanalyzed from the last compliant blank. If the blank does not exhibit similar drift, the sample must be producing a suppression or enhancement effect due to its matrix. In this case the sample must be re-analyzed after a five-fold (1+4) for CLP or a ten-fold (1+9) dilution for 6020/6020A to reduce the matrix effect.

Initial Calibration

10.1.26. Open a new dataset using the date and instrument in the title. For instance the first run (A) on instrument 2 on JAN 1, 2003 would be X30101A.

10.1.27. Open the appropriate method if one already exists or create a new one for the elements to be quantitated in the run. Solicit the assistance of a senior ICP-MS operator in creating a new method.

10.1.28. See Tables 7, 8, and 9 for recommended isotopes and interference

equations for commonly analyzed elements.

10.1.29. If no recommended isotopes are given for the element to be analyzed, consult a senior ICP-MS operator or appropriate reference.

10.1.30. See Table 10 for commonly used internal standards.

10.1.31. All masses which could affect data quality should be monitored to determine potential interferences either simultaneously during an analytical run or in a separate scan.

10.1.32. Internal standards are added to all standards and samples by the instrument prior to analysis.

10.1.33. Use of an existing autosampler table is suggested. A read delay of 45 to 60 seconds is used between all analyses.

10.1.34. Calibration consists of a blank and a single calibration standard (see Table 2 for concentrations) in accordance with the manufacturer's procedure. Use the average of three integrations for both calibration and sample analyses.

The order of analysis for the initial QC samples and calibration should be:

1. Rinse
2. Performance Report (Tune Check)
3. STD1 (Blank)
4. STD2 (All elements except B, Mo, Sb, Si, Sn and Ti)
5. STD3 (B, Mo, Sb, Si, Sn and Ti)
6. ICV (Second source, must be ± 10% of true value)
7. ICB
8. CRI / RLV/LLICV (Reporting Limit Verification Standard)
9. ICSA (Interference check solution.)
10. ICSAB (Interference check solution, ± 20% of true value)
11. CCV
12. CCB
13. Prep QC such as LCS or MB, followed by samples (up to 10 runs)
14. CCV
15. CCB
16. CRI / RLV/LLCCV (Method 6020A only at the end of the analytical sequence)

17. CCV
18. CCB

10.1.35. To continue the analytical run, add an additional 10 runs followed by a CCV/CCB, and repeat for up to 24 hours.

10.1.36. Analysis sequence when out-of-control QC is observed: Recalibrate and rerun all affected samples (including initial QC)

11. CALCULATIONS / DATA REDUCTION

All pertinent calculations are performed by the Plasma LAB software. Elemental equations used to calculate results are given in Table 9.

Reporting Requirements

11.1.1. Units are ug/L or mg/L for aqueous samples and mg/kg for soil samples and ug/wipe for wipe samples.

11.1.2. If dilutions were required due to insufficient sample, interferences, or other problems, the laboratory reporting limits are multiplied by the dilution factor.

11.1.3. Document any non-standard procedures or anomalies by using the TALS NCM Module.

Data Package Requirements

11.1.4. A complete data package consists of: the daily tuning package, the method printout, run log, standards documentation, level 1 checklist, and all raw data.

11.1.5. Level I review will be completed by the analyst.

11.1.6. Level II review will be completed by a senior level laboratory analyst familiar with the technical aspects of ICP-MS and in accordance with the ICP-MS DATA REVIEW checklists. The instrument operator of an analytical run may not perform the Level II review for that run.

12. METHOD PERFORMANCE

12.1. The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2. Demonstration of Capabilities – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3. Method Detection Limit Study – A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is

made to the analytical system.

Instrumentation Detection Limit (IDL) 6020 – IDL for each element must be determined for each element wavelength used on each instrument. The IDL must be determined quarterly for method 6020/6020A for the standard elements listed in Appendix A. For method 200.8 IDLs will be determined annually. If the instrument is adjusted in any way that may affect the IDL, the IDL for that instrument must be redetermined.

12.3.1. For 6020 the IDLs shall be determined by performing a blank analysis on 3 non-consecutive days with 7 consecutive measurements per day. The IDL is calculated by summing the standard deviations of the measurements from each day. For 200.8 the IDL is determined by performing 10 replicate blank analysis and multiplying the resulting standard deviation by 3.

12.3.2. Each measurement must be performed as though it were a separate analytical sample.

12.3.3. Each measurement must be followed by a rinse and/or any other procedure normally performed between the analyses of separate samples.

12.3.4. The IDL measurement must consist of the same number of replicates used for analytical samples with the average result used for reporting.

Instrument detection limits (IDLs) 6020A – IDLs are useful means to evaluate the instrument noise level and response changes over time for each element 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. It may be helpful to compare the calculated IDLs to the established lower limit of quantitation, however, it should be understood that the lower limit of quantitation needs to be verified according to the guidance in Section 9.2.6.

12.3.5. IDLs in µg/L can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should 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.

Linear Range Verification (LR) - The linear range is determined semi annually (2x/year) for each element on the standard list. Some regulatory programs, such as AFCEE, may require more frequent determinations.

12.3.6. To determine the linear range, analyze 3 standards at increasing concentration up to 90% of the last concentration where the element was within 10% of true value is considered the upper linear range.

12.3.7. An alternative is to prepare a higher concentration standard and run this in the analytical run. If this standard is within 10% of the expected value this value can be used as the upper linear range. If this option is chosen, then note the action in

an anomaly.

13. 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." and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

14. 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 PT-HS-001 (the facility addendum). The following waste streams are produced when this method is carried out.

14.1.1. Acid waste consisting of sample and rinse solution. This waste is collected in waste containers identified as "Acid Waste", Waste #33. It is neutralized to a pH between 6 and 9 and then discharged down a lab sink.

14.1.2. Expired Metals Standards. This waste is collected in waste containers identified as "Acid Waste with Metals", Waste #6.

15. REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, Method 6020, Inductively Coupled Plasma – Mass Spectrometry, Revision 0, September, 1994

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update IV, Method 6020A, Inductively Coupled Plasma – Mass Spectrometry, Revision 1, February, 2007

Methods for the Determination of Metals in Environmental Samples, Supplement 1 (EPA/600/R-94/111), Method 200.8, Determination of Trace Elements in Waters by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, 1994

Thermo Electron X Series ICPMS Users' Manual

SOP PT-HS-001, Pittsburgh Facility Addendum EH&S Manual

SOP PT-QA-006, Procurement of Standards and Materials; Labelling and Traceability

SOP PT-QA-007, Method Detection Limits

SOP PT-QA-016, Nonconformance & Corrective Action System

SOP PT-QA-018, Technical Data Review Requirements

SOP PT-QA-021, TestAmerica Pittsburgh QC Program

SOP PT-QA-022, Equipment Maintenance

SOP PT-QA-024, Subsampling, current version.

SOP PT-QA-031, Internal Chain of Custody

PT-QA-M-001, Pittsburgh Laboratory Quality Assurance Manual

16. METHOD MODIFICATIONS

Use of Collision Cell Technology is an allowed method modification for SW-846 methods. Use for method 200.8 is not allowed for drinking water analysis, but may be used for waste waters.

Sample analysis using Collision Cell Technology must meet all method criteria in the same manner as analysis without it, including IDL, MDL, IDOC, Calibration and all batch QC.

17. ATTACHMENTS

Table 1 – Standard Element List and Reporting Limits

Table 2 – Composition of the CAL Standard

Table 3 – Composition of the ICV Standard

Table 4 – Composition of the ICSA Standard

Table 5 – Composition of the ICSAB Standard

Table 6 – Common Molecular Ion Interferences in ICP-MS

Table 7 – Recommended Analytical Isotopes And Additional Masses That May Be Monitored

Table 8 – Recommended Isotopes And Additional Masses That May Be Monitored

Table 9 – Elemental Equations Used To Calculate Results

Table 10 – Internal Standards and Limitations Of Use

Table 11 - TestAmerica Pittsburgh Metals Dilution Calculation Table

Appendix 1 Cleaning Procedure for Glass- and Plastic-ware

Appendix 2 Wash Solution Preparation Instructions

Appendix 3 Daily Instrument Maintenance

Appendix 4 Autotune and Performance Reports

Appendix 5 Resolution Setup

Appendix 6 Instrument Calibrations

Appendix 7 Sample Introduction Plumbing Diagram

Appendix 8 Procedure for Cleaning Sample Introduction Equipment and Cones

Appendix 9 Autosampler Position Map

Appendix 10 Spiking Levels

Appendix 11 Work Flow Chart

18. REVISION HISTORY

Revision 5, 5/19/08

Revision 6, 3/31/2009

Revision 7, 7/27/2009

Revision 8, 3/1/2011

Revision 9, 5/8/2012

Revision 10, 8/02/2013

Changes to current revision

SOP SECTION	Change from	Change to	Reason
Cover	QAM – Violet Fanning	QAM –Virginia Zusman	Change in personnel
Entire SOP		Removed all reference to DoD and PT-QA-029	Correction
1.2 & 1.5		Added Collision Cell Technology (CCT) scope	Clarification
2 through 5	Tables 1, 2, 3, 4 and Hazardous Materials	Tables A, B, C, D and E	Clarification from Tables 1-4 at the end of the SOP
4.2		Added text to describe CCT's role in interference removal	Clarification
5.1 and 13.1		Added reference to PT-HS-001	Correction
5.	MSDS	SDS	Due to change in industry standard language
6.1.1 & 6.1.2		Added Thermo Scientific	Clarification
6.1.3		Added Thermo software	Clarification
6.3	PT-QA-M-001	Appendix 3 and SOP PT-QA-022	Correction
9.1.10 NOTE	Added	ICSA associated with samples from Wisconsin all elements must be <RL.	Correction

9.2.1 through 9.3.9		Added details for corrective actions and reporting data associated with failed QC	Clarification
9.3.1		Added tune criteria to Instrument QC	Clarification
9.3.2		Added Initial Calibration information to Instrument QC	Clarification
9.3.6	Split ICV and ICB sections	Added ICV acceptance criteria	Clarification
9.3.8		Clarified the 6020 and 6020A CRI requirements; added text to discuss when data can be reported when 6020A closing CRI fails.	Clarification
9.3.8		Added “unless all bracketed samples had concentrations 10X the CCB concentration or concentrations < RL” to the end of the third sentence	Clarification
9.4.9	Split CCV and CCB criteria into bullets	Added CCV recovery criteria and details for reporting results with QC failures	Clarification
10.2.2.3	Removed 6020/6020A resolution criteria since we follow200.8 criteria for everything		Correction
10.2.2.5		Added “5 replicate” to daily tune	Clarification
10.2.5.4	15%; 10 seconds	30%; 15 seconds	Correction
10.2.5.6	>0.025	>0.05; added CCT tuning resolution requirements	Correction
10.3.1		Added information for CCT analysis	Clarification
11.2.3	Removed section since TALS takes care of rounding		Correction
12.1	Added	Supervisor responsibility text from SOP Checklist	SOP Review Sheet format
12.2	Added	IDOC text from SOP Checklist	SOP Review Sheet format
12.3	Added	MDL text from SOP Checklist	SOP Review Sheet format
15.4	Removed reference to 6020 CLP M since we no longer perform CLP analysis		Correction
15.13		Added reference to PT-QA-031 ICOC SOP	Correction
Table 1		Updated RL’s for B, Ca, Mg, K and Na	Correction

Table 11 and Appendix 10	Removed DOD information		
Appendix 8, 3a	Removed 0.05% nitric acid	Replaced with deionized water	Correction
Appendix 8, 4f	Removed “between 20 minutes and 1 hour”	Updated to “20 minutes”	Correction

Tables:

TABLE 1

STANDARD ELEMENT LIST AND REPORTING LIMITS*

Element	Symbol	CAS #	Aqueous RL mg/L	Aqueous QC SPIKE mg/L	Soil/Tissue RL mg/Kg	Soil/Tissue QC SPIKE mg/kg	Wipe RL ug/wipe	Wipe QC SPIKE ug/wipe
Aluminum	Al	7429-90-5	0.03	2.0	3.0	200	1.5	100
Antimony	Sb	7440-36-0	0.002	0.50	0.2	50	0.1	25
Arsenic	As	7440-38-2	0.001	0.04	0.1	4	0.05	100
Barium	Ba	7440-39-3	0.010	2.0	1.0	200	0.5	100
Beryllium	Be	7440-41-7	0.001	0.05	0.1	5	0.05	2.5
Boron	B	7440-42-8	0.02	1.0	2.0	100	1.0	50
Cadmium	Cd	7440-43-9	0.001	0.05	0.1	5	0.05	2.5
Calcium	Ca	7440-70-2	0.500	50	50	5000	25	2500
Chromium	Cr	7440-47-3	0.002	0.2	0.2	20	0.1	10
Cobalt	Co	7440-48-4	0.0005	0.5	0.05	50	0.025	25
Copper	Cu	7440-50-8	0.002	0.25	0.2	25	0.1	12.5
Iron	Fe	7439-89-6	0.05	1.0	5.0	100	2.5	50
Lead	Pb	7439-92-1	0.001	0.02	0.1	2	0.05	25
Magnesium	Mg	7439-95-4	0.500	50	50	5000	25	2500
Manganese	Mn	7439-96-5	0.005	0.5	0.5	50	0.25	25
Molybdenum	Mo	7439-98-7	0.005	1.0	0.5	100	0.25	50
Nickel	Ni	7440-02-0	0.001	0.5	0.1	50	0.05	25
Potassium	K	7440-09-7	0.500	50	50	5000	25	2500
Phosphorus	P	7723-14-0	0.500	1.0	0.05	100	25	5000
Selenium	Se	7782-49-2	0.005	0.01	0.5	1	0.25	100
Silver	Ag	7440-22-4	0.001	0.05	0.1	5	0.05	2.5
Sodium	Na	7440-23-5	0.500	50	50	5000	25	2500
Strontium	Sr	7440-24-6	0.005	1.0	0.5	100	0.25	50
Tin	Sn	7440-31-5	0.005	2.0	0.5	200	0.25	100

TABLE 1								
STANDARD ELEMENT LIST AND REPORTING LIMITS*								
Element	**Symbol**	**CAS #**	**Aqueous RL mg/L**	**Aqueous QC SPIKE mg/L**	**Soil/Tissue RL mg/Kg**	**Soil/Tissue QC SPIKE mg/kg**	**Wipe RL ug/wipe**	**Wipe QC SPIKE ug/wipe**
Titanium	Ti	7440-03-26	0.005	1.0	0.5	100	0.25	50
Thallium	Tl	7440-28-0	0.001	0.05	0.1	5	0.05	100
Vanadium	V	7440-62-2	0.001	0.5	0.1	50	0.05	25
Zinc	Zn	7440-66-6	0.005	0.5	0.5	50	0.25	25

***** *Note: These are the routine reporting limits for most sample types. Lower reporting limits may be achievable for special projects. Difficult sample matrices may cause reporting limits to be raised.*

TABLE 2			
Composition of the Calibration Standards			
Element	**Concentration ug/mL**	**Element**	**Concentration ug/mL**
Ag	0.200	Mo	0.200
Al	1.00	Na	100
As	0.200	Ni	0.200
B	0.200	P	2.5
Ba	0.200	Pb	0.200
Be	0.200	Sb	0.200
Ca	100	Se	0.200
Cd	0.200	Si	10
Co	0.200	Sn	0.200
Cr	0.200	Sr	0.200
Cu	0.200	Ti	0.200
Fe	50	Tl	0.200
K	100	V	0.200
Mg	100	Zn	0.200
Mn	1.0		

TABLE 3
Composition of the ICV Standard

Element	Concentration ug/mL	Element	Concentration ug/mL
Ag	0.08	Mo	0.08
Al	0.4	Na	40
As	0.08	Ni	0.08
B	0.08	P	2
Ba	0.08	Pb	0.08
Be	0.08	Sb	0.08
Ca	40	Se	0.08
Cd	0.08	Si	4.0
Co	0.08	Sn	0.08
Cr	0.08	Sr	0.08
Cu	0.08	Ti	0.08
Fe	20	Tl	0.08
K	40	V	0.08
Mg	40	Zn	0.08
Mn	0.4		

TABLE 4
Composition of the ICSA Standard

Element	Concentration ug/mL	Element	Concentration ug/mL
Al	100	P	100
Ca	100	S	100
Fe	100	C	200
K	100	Cl^-	1000
Mg	100	Mo	2.0
Na	100	Ti	2.0

TABLE 5
Composition of the ICSAB Standard

Element	Concentration ug/mL	Element	Concentration ug/mL
Ag	0.02	Na	100
Al	100	Ni	0.02
As	0.02	Pb	0.02
B	0.05	Sb	0.02
Ba	0.02	Se	0.05
Be	0.02	Si	0.50
Ca	100	Sn	0.10
Cd	0.02	Sr	0.02
Co	0.02	Ti	2.0
Cr	0.02	Tl	0.02
Cu	0.02	V	0.02
Fe	100	Zn	0.025
K	100	P	100
Mg	100.0	S	100
Mn	0.0225	C	200
Mo	2.00	Cl-	1000

TABLE 6[1]

COMMON MOLECULAR ION INTERFERENCES IN ICP-MS

Molecular Ion	Mass	Element	Molecular Ion	Mass	Element
BACKGROUND MOLECULAR IONS					
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 IONS – Chloride					
$^{35}Cl0^+$	51	V	$^{37}Cl0H^+$	54	Cr
$^{35}Cl0H^+$	52	Cr	$^{35}Cl0^+$	51	V
$^{37}Cl0^+$	53	Cr	$^{35}Cl0H^+$	52	Cr
$Ar^{35}Cl^+$	75	As	$Ar^{37}Cl^+$	77	Se
MATRIX MOLECULAR IONS – Sulfate					
$^{32}SO^+$	48		$^{34}SOH^+$	51	V
$^{32}SOH^+$	49		SO_2^+, S_2^+	64	Zn
$^{34}SO^+$	50	V, Cr			
$Ar^{32}S^+$	72		$Ar^{34}S^+$	74	
MATRIX MOLECULAR IONS – Phosphate					
PO^+	47		PO_2^+	63	Cu
POH^+	48				
ArP^+	71				
MATRIX MOLECULAR IONS – Group I, II Metals					
$ArNa^+$	63	Cu	$ArCa^+$	80	
ArK^+	79				
MATRIX OXIDES[3]					
TiO	62-66	Ni, Cu, Zn	MoO	108-116	Cd
ZrO	106-112	Ag, Cd			

[1] *From Method 200.8, Section 13.2.6*
[2] *Method elements or internal standards affected by the molecular ions.*

[3]Oxide interferences will normally be very small and will only impact the method elements when present at relatively high concentrations. Some examples of matrix oxides are listed of which the analyst should be aware. It is recommended that Ti and Zr isotopes be monitored in solid waste samples, which are likely to contain high levels of these elements. Mo is monitored as a method element.

TABLE 7

RECOMMENDED ANALYTICAL ISOTOPES AND ADDITIONAL MASSES THAT MAY BE MONITORED [1]

Isotope	Element of Interest	Isotope	Element of Interest
27	Aluminum [2]	80,**78**,**82**,**76**,**77**,74	Selenium
121,123	Antimony [2]	**107**,**109**	Silver [2]
75	Arsenic [2]	**23**	Sodium [2]
138,**137**,136,**135**,134,132,130	Barium [2]	203, **205**	Thallium [2]
9	Beryllium [2]	**51**,**50**	Vanadium [2]
114,112,**111**,110,113,116,106,**108**	Cadmium [2]	**66**, **68**	Zinc [2]
42,**43**,**44**,46,48	Calcium [2]	83	Krypton
52,**53**,**50**,54	Chromium [2]	72	Germanium
59	Cobalt [2]	139	Lanthanum
63,**65**	Copper [2]	140	Cerium
56,**54**,**57**,58	Iron [2]	129	Xenon
206,207,**208**	Lead [2]	**118**	Tin
24,**25**,**26**	Magnesium [2]	105	Palladium
55	Manganese [2]	47,**49**	Titanium
98,96,92,97,94,95	Molybdenum	125	Tellurium
58,**60**,62,**61**,64	Nickel [2]	69	Gallium
39	Potassium [2]	35,37	Chlorine

[1] *From Method 6020 CLP-M, Table 9*

[2] *Element approved for ICP-MS determination by SW846 Method 6020 CLP-M*

NOTE: Isotopes recommended for analytical determination are **bolded**.

TABLE 8			
RECOMMENDED ISOTOPES AND ADDITIONAL MASSES THAT MAY BE MONITORED			
Rare Earth Elements	**ICPMS Preferred Mass**	**Elemental Equations**	**Additional Masses**
Lanthanum	138.906		
Cerium	139.905		
Praseodymium	140.907		
Neodymium	141.908	-0.125266 * ^{140}Ce	142.910, 144.912
Samarium	151.920	-0.012780 * ^{157}Gd	144.912
Europium	152.929		
Gadolinium	157.924	-0.004016 * ^{163}Dy	156.934
Terbium	158.925		
Dysprosium	163.929	-0.047917 * ^{166}Er	
Holmium	164.930		
Erbium	165.930		
Thulium	168.934		
Ytterbium	173.939	-0.005935 * ^{178}Hf	171.937
Lutetium	174.941		

TABLE 8A			
RECOMMENDED ISOTOPES AND ADDITIONAL MASSES THAT MAY BE MONITORED			
Rare Earth Elements			
Other Elements			
Boron	11.009		
Calcium	43.956		
Cesium	132.905		
Galium	68.926		
Germanium	71.922		
Gold	196.967		
Hafnium	177.944		176.944
Holmium	164.930		
Iridium	192.963		
Lithium	7.016		
Tungsten	183.951	-0001242* ^{189}Os	
Uranium	238.050		
Yttrium	88.905		
Zirconium	238.050		
Niobium	92.906		
Palladium	104.905		
Phosphorus	30.994		
Platinum	194.965		
Rhenium	186.965	-0.099379 * ^{189}Os	
Rhodium	102.905		
Rubidium	84.912		
Ruthenium	101.904	-0.045678 * ^{105}Pd	
Scandium	44.956		
Strontium	87.906		
Tantalum	180.948		
Tellurium	127.905	-0.072348 * ^{129}Xe	
Thorium	232.03		

TABLE 9

ELEMENTAL EQUATIONS USED TO CALCULATE RESULTS

Element	Elemental Equation	Note
Al	(1.000) (^{27}C)	
Sb	(1.000) (^{121}C)	
As	(1.000) (^{75}C) - (3.1278)[^{77}C) - (1.0177)(^{78}C)]	Correction for chloride interference with adjustment for Se77. ArCl 75/77 ratio may be determined from the reagent blank.
Ba	(1.000) (^{137}C)	
Be	(1.000) (^{9}C)	
Cd	(1.000) (^{111}C) - (1.073) [(^{108}C) - (0.712) (^{106}C)]	Correction of MoO interference. An additional isobaric elemental correction should be made if palladium is present.
Cr	(1.000) (^{52}C)	In 0.4% v/v HCl, the background from ClOH will normally be small. However the contribution may be estimated from the reagent blank.
Co	(1.000) (^{59}C)	
Cu	(1.000) (^{63}C)	
Pb	(1.000) (^{206}C) + (1.000) (^{207}C) + (1.000) (^{208}C)	Allowance for isotopic variability of lead isotopes.
Mn	(1.000) (^{55}C)	
Mo	(1.000) (^{98}C) - (0.146) (^{99}C)	Isobaric elemental correction for ruthenium.
Ni	(1.000) (^{60}C)	
Se	(1.000) (^{82}C)	Some argon supplies contain krypton as an impurity. Selenium is corrected for Kr82 by background subtraction.
Ag	(1.000) (^{107}C)	
Tl	(1.000) (^{205}C)	
Th	(1.000) (^{232}C)	
U	(1.000) (^{238}C)	
V	(1.000) (^{51}C) - (3.127) [(^{53}C) - (0.113) (^{52}C)]	Correction of chloride inference with adjustment for Cr53. Cl0 51/53 ratio may be determined from the reagent blank.
Zn	(1.000) (^{66}C)	
Internal Standards		

TABLE 9 ELEMENTAL EQUATIONS USED TO CALCULATE RESULTS		
Bi	(1.000) (^{209}C)	
In	(1.000) (^{115}C) -(0.0149) (^{118}C)	Isobaric elemental correction for tin.
Ge	(1.000) (^{72}C)	
Sc	(1.000) (^{45}C)	
Tb	(1.000) (^{159}C)	
Tm	(1.000) (^{169}C)	
Y	(1.000) (^{89}C)	

* Method elements or internal standards affected by the molecular ions. C = Calibration blank subtracted counts at specified mass.

TABLE 10 INTERNAL STANDARDS AND LIMITATIONS OF USE		
Internal Standard	Mass	Possible Limitation
Lithium	6	a
Scandium	45	Polyatomic Ion Interference
Germanium	72	
Yttrium	89	a, b
Rhodium	103	
Indium	115	Isobaric Interference by Sn
Terbium	159	
Holmium	165	
Thulium	169	
Lutetium	175	
Bismuth	209	a

a May be present in environmental samples.

b In some instruments Yttrium may form measurable amounts of YO^+ (105 amu) and YOH^+ (106 amu). If this is the case, care should be taken in the use of the cadmium elemental correction equation.

Table 11 - TestAmerica Pittsburgh Metals Dilution Calculation Table

DILUTION REQUIRED	Dilution Formula
2	5 mL sample : 5 mL Matrix Blank
5	2 mL sample : 8 mL Matrix Blank
10	1 mL sample : 9 mL Matrix Blank
25	0.4 mL sample : 9.6 mL Matrix Blank
50	0.2 mL sample : 9.8 mL Matrix Blank
100	0.1 mL sample : 9.9 mL Matrix Blank

Appendices

Appendix 1

Cleaning Procedure for Glass- and Plastic-ware

All glassware and plastic-ware coming into contact with samples, reagents and standards must be cleaned in the following manner. Plastic pipette tips may be cleaned in the same manner by soaking them in a suitable plastic container.

1) Completely fill the container to be leached with 10% nitric acid solution (6.1.5) and fit the lid.
2) Leave soaking for at least 12 hours.
3) Empty the container of acid and rinse thoroughly with laboratory water (6.1.1). Note that the acid may be collected and re-used until it becomes too contaminated.
4) Allow the vessel to air-dry in a clean area (preferably Class-1000 or better). If no such clean area is available, the container should be allowed to dry in the cleanest possible environment, or may be emptied of residual water as much as is possible and re-capped.
5) Containers should be capped ready for use and stored in the cleanest area available.
6) If pre-cleaned containers are to be stored for long periods (weeks to months) prior to use, it is most effective to store them full of laboratory water (6.1.1). This must be discarded and the containers rinsed thoroughly with laboratory water (6.1.1) and dried before use.

Appendix 2

Wash Solution Preparation Instructions (2% Nitric Acid (v/v))

A large volume of this solution is required for supply to the autosampler rinse station in order to wash the probe between samples. These instructions detail the preparation procedure for 2.5 L of this solution that is normally sufficient for one day of analytical use. The procedure may be scaled up or down as required.

1) Into a 2.5 L container (pre-cleaned as per Appendix 1), add 500±450 mL of laboratory water (6.1.1)
2) Add 50±10 mL of concentrated nitric acid (6.1.3)
3) Make to 2.50±0.25 L with laboratory water (6.1.1)
4) Mix well

Notes:

If preparing larger quantities simply scale-up quantities proportionally.

If analyzing for Ag, add hydrochloric acid at 1% by adding 50±10 mL of concentrated hydrochloric acid (6.1.2) after step 2.

Appendix 3

Daily Instrument Maintenance

1) Wipe all instrument, autosampler and surrounding bench surfaces with a damp wipe – continual cleanliness is important for the minimization of contamination
2) Check Wash Solution volume and remake if necessary (see Appendix 2)
3) Empty Waste Vessel according to laboratory disposal policy
4) Check the condition of all peristaltic pump tubes and replace if required (it is recommended to replace these daily although this may not be necessary with lower sample loads)
5) Check condition of sample introduction system and cones and clean and/or replace as necessary (see Appendix 8)
6) Ensure instrument fume-extraction system is operational

Appendix 4

Autotune and Performance Reports

Description

Autotune is a *PlasmaLab* software tool that allows the X Series to be optimized in a consistent, routine manner, giving reproducible levels of performance and saving the operator time and effort. It works by following a pre-defined sequence, optimizing individual instrument parameters in turn. Default sequences are provided with the software upon installation and a further customized sequence is provided on the CD accompanying this productivity pack.

Performance Reports are a *PlasmaLab* software tool that allows the X Series performance to be checked on a daily basis. The *Performance Report* can be set-up to give information about instrument sensitivity, stability, background, oxide species, doubly charged species, mass-calibration validity and peak resolution. Like *Autotune*, the *Performance Report* is user definable but defaults are provided with the software. Customized *Performance Reports* are provided on the CD accompanying this package.

The philosophy of use of these tools is as follows. After the sample introduction system or the cones have been removed and replaced or upon using the instrument for the first time or following major adjustments, the full *Autotune* sequence should be used to properly optimize the system. This takes about 15 minutes. From this, an *Autotune Update* sequence can be automatically created. This is a shortened version of the optimization sequence and will take about 5 minutes to run. The performance of the X Series is, in general, very stable from day-to-day, meaning that large amounts of optimization are not normally needed on a daily basis. To check whether optimization is needed, a *Performance Report* can be run initially. The results of this tell the operator if the system requires resolution adjustment, re-mass-calibration, or re-optimization. If the required sensitivity, background, stability or oxide performance is not satisfied, an *Autotune* should be run (the faster *Autotune Update* is normally sufficient). The *Performance Report* should then be repeated to ensure that the problem has been resolved.

Installing the EPA Autotune Sequence

To install the custom Autotune sequence, follow the instructions below:

1) Insert the CD in the CD ROM drive of the instrument operating PC. Wait for it to autorun and install the Productivity Pack by following the prompts after clicking on *Install*.
2) Ensure that PlasmaLab version 2.2 (or higher) has been installed
3) In PlasmaLab, go to *Instrument*, *Tune* and click on the down arrow button next to the *Autotune* icon (musical note).
4) Point to *Tools* in the menu and then select *Import Autotune Sequences*

5) Click *Next* in the Autotune Wizard
6) Click on *Browse* and find the path

C:/Program Files/ThermoElemental/PlasmaLab/Data

7) Select *EPA Autotune Sequence* and click on *Open*
8) Click on *Next*
9) Select *EPA – Xi Interface* and click on *Next*
10) Click on *Finish*

Installing the EPA Performance Reports

To install the custom Performance Reports, follow the instructions below:

1) Ensure the Pack is installed from the CD as described above
2) Ensure that PlasmaLab version 2.2 (or higher) has been installed
3) In PlasmaLab, go to *Instrument*, *Tune* and click on the down arrow button next to the *Performance Report* icon (musical note on page).
4) Point to *Tools* in the menu and then select *Import Performance Report*
5) Click *Next* in the Performance Report Wizard
6) Click on *Browse* and find the path for the CD ROM drive

   C:/Program Files/ThermoElemental/PlasmaLab/Data
7) Select *EPA 6020 Report* and click on *Open*
8) Click on *Next*
9) Select *EPA 6020 2.1* and click on *Next*
10) Click on *Finish*

To install the second Performance Report, follow instructions 1) to 10) above, selecting the alternative Performance Report name, i.e. *EPA ILM05_2D Report*.

Running Autotune from the Tune Page

To run an Autotune Sequence, follow the instructions below:

1) In PlasmaLab go to *Instrument*, *Tune* and click on the *Autotune* icon (musical note)
2) Select *Run an Existing Autotune Sequence* and click on *Next*
3) Select the required sequence, e.g. *EPA Xi Interface*, or *EPA Xi Interface – Update* and click on *Next*

4) Ensure that the indicated solution is being aspirated (through both probes if on-line internal standard addition is being used) and allow sufficient time for the solution to be transported into the nebulizer

5) Click on *Finish*

The selected Autotune sequence will now be run. To monitor its progress, observe the processes indicated at the bottom left of the PlasmaLab screen and open the Service Window (double-click on *MS* icon at the bottom right of the screen). A printable *Autotune Report* is generated at the end of the sequence. To continue, this report must be closed. To access this report upon closure, go to *Instrument*, *Configurations*, *Configuration Editor* and point to the appropriate *Instrument Settings* line. Open a pop-up menu by right-clicking and use the *View Tune Report* selection.

Running a Performance Report from the Tune Page

To run a Performance Report, follow the instructions below:

1) In PlasmaLab go to *Instrument*, *Tune* and click on the *Performance Report* icon (musical note on a page)

2) Select *Run an Existing Performance Report* and click on *Next*

3) Select the required sequence, e.g. *EPA ILM05 / 6020*, or *EPA 6020* and click on *Next*

4) Ensure that the indicated solution is being aspirated (through both probes if on-line internal standard addition is being used) and allow sufficient time for the solution to be transported into the nebulizer

5) Click on *Finish*

The selected *Performance Report* will now be run. To monitor its progress, open the Service Window (double-click on *MS* icon at the bottom right of the screen). A printable *Performance Report* is generated at the end of the sequence. To access this report upon closure, go to *Instrument*, *Tune*, and click on the down arrow to the right of the Performance Report icon. Point at *Tools* and then select *View Performance Report Results*. Select the required Performance Report to view and click *OK*.

Running Performance Reports and Autotune in an Experiment

It is also possible to automate the running of these procedures using an instrument setup sample within an experiment. To do this, insert an *Instrument Setup Sample* at the beginning of the Sample List by selecting the first sample and using a right-mouse-click menu to *Insert New Before*. Define the *Sample Type* for this new sample as *Instrument Setup* and click on *Show Advanced*. Click on the *Instrument Performance Tests* tab and setup the Performance Report and Autotune functions following the logic and using the drop-down combo boxes to select the next action. An example would be as follows:

Acquire Performance Report	*EPA ILM05.2 / 6020*
If mass calibration verification fails then	*Abort the Queue*

If the Performance Report fails then	*Autotune using EPA – Xi Interface*
If the Autotune fails then	*Abort the experiment*
If the Autotune passes then	*re-run the Performance Report*
If the Performance Report fails again then	*Abort the Queue*

When Performance Reports and Autotunes are acquired in this way, the results are stored as part of the experiment report. Note that since this method of acquiring the report is done using the autosampler, the solution concentration should be adjusted if on-line internal standard addition is to be used, e.g. if the addition dilutes the samples 1:1, the solution concentration should be doubled to get an accurate measure of sensitivity.

Appendix 5

Resolution Set up

With the instrument in *Operate* mode, aspirate 10-µg/L Tune solution (6.4.1) (through both probes if using on-line internal standard addition). Go to *Instrument*, *Tune* and stop the real time display (RTD) using the square stop icon. Change the display mode from *Time vs ICPS* to *ICPS on the full mass range*. Insert Be as the mass to monitor and change the spacing to 10, the dwell to 1 ms and the channels to 200. Disable all other masses in the grid. Restart the RTD by clicking on the triangular play icon. The software will display the scanned peak for mass 9, Be. To adjust the resolution, go to the *Global* tab and use the slider bar marked *Standard resolution*. This must be set up to give a peak width of less than 0.75 amu at 5% peak height. This is typically reached at a setting of between 100 and 200. If high-resolution mode is to be used, this can be setup by changing the resolution setting on the RTD to *High*. The High Resolution peak width is typically set at about 0.4 amu at 5% peak height, again with values typically between 100 and 200. Note that this method does not use High-resolution mode. Each resolution mode should be checked with several other masses across the mass range, typically 55Mn, 115In, 203Tl and 238U are used. Special attention should be paid to the resolution setup for Mn. This is measured at m/z 55, which is adjacent to both iron and argon oxide at mass 56. These high signals must be properly resolved from the low Mn signal in standard resolution mode. When the correct resolution settings are achieved, save the setting using the disk icon. **Note that a new mass-calibration must always be performed after adjustment of the resolution.**

Appendix 6

Instrument Calibrations

There are three instrument calibrations that are fundamental for obtaining good quality data on the X Series. These are:

1) Mass-calibration
2) Detector Plateau and Analogue voltage set routines
3) Detector cross-calibration.

Mass calibration sets the quadrupole scan parameters to give the correct measured mass positions. The detector plateau sets the optimum voltage on the ion or pulse counting section of the discrete dynode detector. The analogue voltage set routine applies an appropriate voltage on the analogue part of the detector to obtain a cross-calibration factor of approximately 20,000 for a mid-mass isotope. The detector calibration, or cross-calibration, calculates the correction factor, for each measured mass, between the two detector modes, pulse counting and analogue. All three calibrations may be performed in a single routine, or may be performed separately.

Mass Calibration

A mass-calibration must be performed whenever the resolution settings are adjusted, as this will affect the apparent mass position. Mass-calibration must be performed when the Performance Report shows that measured peak positions are >0.1 amu from their nominal position. Mass-calibrations are best performed using a solution containing as many elements as possible or with every element required for analysis at the very least. The solution should contain Li and U as these are used as low and high mass datum points. An appropriate concentration solution be used (one that gives between **100,000-1,500,000 cps** for each mass to be calibrated is appropriate). To perform a mass calibration, follow the instructions below.

1) Click *Experiment*
2) Select *Create New Experiment*
3) Click *OK*
4) Select the *Default* database
5) Click *Open*
6) Go to *Sample List*
7) Click the *Report* check box in the sample list grid
8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*
9) Click on the *Show Advanced* button

10) Click on the *Instrument Calibrations* tab

11) Check the *Mass-Calibration* box

12) There is an option to *Update current mass-calibration* or form a *New mass-calibration*. Unless a major hardware change has been performed, the *Update current mass-calibration* option should be selected.

13) Click *Queue*

14) Save the experiment with an appropriate name, e.g. *masscal 090902* and click *Save*

15) Click *Append*

16) Click *OK*

Mass-calibration will now be performed.

To view the mass-calibration results, go to *Instrument*, *Calibrations*, *Mass-Calibration*. A mass-calibration for each of the two resolution modes is displayed in the graph of Peak Width and Error (y) versus Mass (x). The current mass-calibration is indicated by the row(s) displayed in green. To display alternative mass-calibrations, click on the appropriate date/time-stamped line in the top grid. The Performance Report function can be used to check mass-calibration accuracy (see Appendix 4).

Detector Plateau and Analogue Voltage Set

These routines can be performed separately, but it is advised to run them simultaneously as described here. The necessary frequency of these calibrations depends upon the amount of signal the detector is exposed to, i.e. how many samples are analyzed, which elements and what concentrations. For most laboratories running a moderate sample load, this procedure may be run weekly. Up to three masses may be used in this procedure, however here, the use of a single mass is described. A solution that gives a countrate of between **100,000-1,500,000 cps** is appropriate. The default mass used here is indium (m/z 115), so this must be present in the solution for the routine to work. For an X5 instrument, an appropriate concentration would typically be between 10 and 100 µg/L, depending upon the sensitivity of the system. To perform this routine, follow the instructions below.

1) Click *Experiment*

2) Select *Create New Experiment*

3) Click *OK*

4) Select the *Default* database

5) Click *Open*

6) Go to *Sample List*

7) Click in the *Report* check box in the sample list grid

8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*

9) Click on the *Show Advanced* button

10) Click on the *Instrument Calibrations* tab

11) Check *the Set analogue voltage* box

12) Set the *Number of iterations* to *2*

13) Click *Queue*

14) Save the experiment with an appropriate name, e.g. *plateau 090902* and click *Save*

15) Click *Append*

16) Click *OK*

The voltage setup will now be performed. To view the plateau, go to *Instrument*, *Calibrations*, *Detector Plateau*. A graph of signal intensity (y) versus voltage (x) is displayed. The "knee" inflexion on this plot corresponds to the plateau voltage. This is automatically selected and applied to the detector by the software.

Detector Calibration (Cross-Calibration)

This routine must be performed whenever the detector voltages are altered and daily prior to analysis of samples. The solution used must contain all the elements to be measured as an absolute minimum. The more elements present, the better. All elements should ideally be set at a concentration that gives between **500,000 and 1,500,000cps**. To perform the detector calibration, follow the instructions below:

1) Click *Experiment*

2) Select *Create New Experiment*

3) Click *OK*

4) Select the *Default* database

5) Click *Open*

6) Go to *Sample List*

7) Click in the *Report* check box in the sample list grid

8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*

9) Click on the *Show Advanced* button

10) Click on the *Instrument Calibrations* tab

11) Check the *Detector Calibrate* box

12) Click *Queue*

13) Save the experiment with an appropriate name, e.g. *xcal 090902* and click *Save*

14) Click *Append*

15) Click *OK*

The detector calibration will now be performed. To view the cross-calibration grap, go to *Instrument*, *Calibrations*, *Detector Cross-Calibration*. A graph of cross-calibration factor (y) versus mass (x) is displayed. **Use the data table to check that all analytical masses of interest have been used in the cross-calibration**. If not, the cross-calibration factor will be estimated from the equation of the graph. This may result in error.

All Routines in One

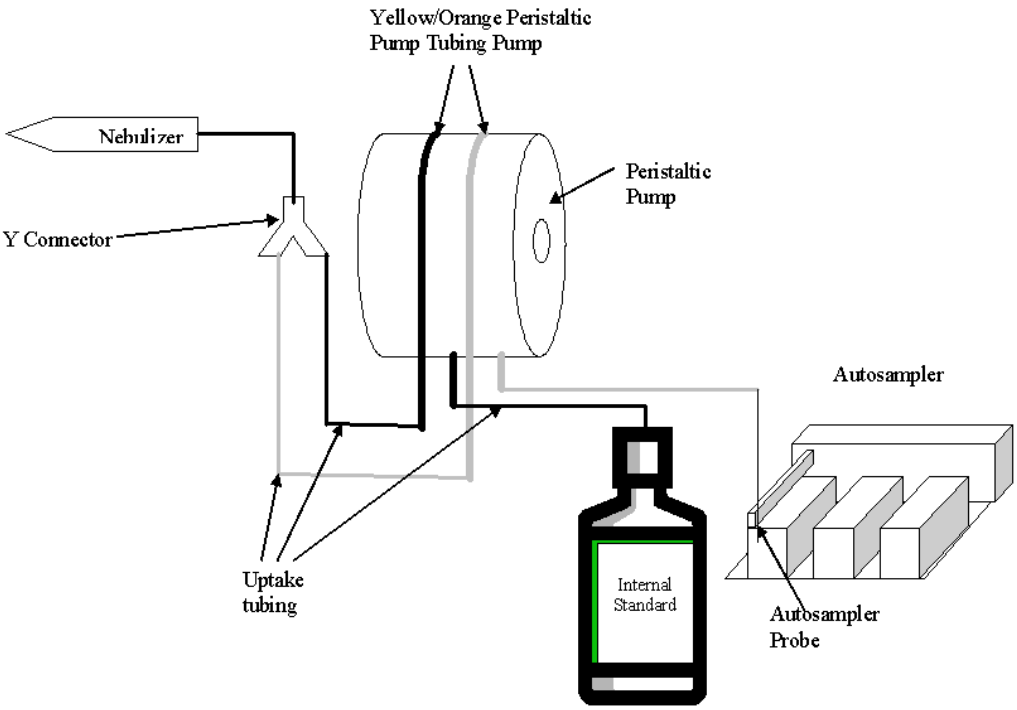
It is possible to run all three of the above routines on a single run if the solution used conforms to all of the criteria spelt out above. To do this, follow the instructions below.

1) Click *Experiment*
2) Select *Create New Experiment*
3) Click *OK*
4) Select the *Default* database
5) Click *Open*
6) Go to *Sample List*
7) Click in the *Report* check box in the sample list grid
8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*
9) Click on the *Show Advanced* button
10) Click on the *Instrument Calibrations* tab
11) Check the *Mass calibration*, *Detector Calibrate* and *Set analogue voltage* boxes
12) Set the *Number of iterations* to *2*
13) Click *Queue*
14) Save the experiment with an appropriate name, e.g. *instr cal 090902* and click *Save*
15) Click *Append*
16) Click *OK*

The instrument calibrations will now be performed. Each parameter can be viewed as described above.

Appendix 7

Sample Introduction Plumbing Diagram



Appendix 8

Procedure for Cleaning Sample Introduction Equipment and Cones

1) Ensure that the instrument is in the *vacuum* or *shutdown* state (i.e. the plasma is OFF and the slide valve is SHUT)
2) Dismantle the sample introduction system as follows:

a) Remove the gas connection from the nebulizer
b) Remove the sample input plug from the nebulizer
c) Remove the metal clip on the spray chamber to elbow joint
d) Remove the drain plug from the spray chamber
e) Slide the spray chamber and nebulizer away from the elbow
f) Carefully slide the nebulizer out of the spray chamber and set both pieces aside in a safe place
g) Open the torch box and the internal Faraday cage
h) Pull the gas connections away from the torch
i) Undo the torch catch
j) Remove the metal clip on the elbow to torch joint
k) Carefully remove the torch from the load coil and set aside in a safe place
l) Remove the elbow by sliding it out of the torch box bulkhead toward spray chamber end
m) Slide the torch box away from the mass spectrometer to reveal the interface
n) Use the flat metal cone tool to undo the locking ring over the sample cone
o) Carefully remove the sample cone and set aside in a safe place
p) Carefully unscrew and remove the skimmer cone from the interface using the cylindrical aluminium tool and set aside in a safe place

3) Clean the cones as follows.

a) Carefully place the cones into a large beaker and fill with sufficient deionized water.
b) Place the beaker in an ultrasonic bath for about 10 minutes or until surface deposition has been removed
c) Carefully remove the cones from the solution and rinse thoroughly with deionised water
d) Allow the cones to air-dry prior to refitting

4) Clean the sample introduction equipment as follows.

e) Carefully place the glass sample introduction components into a large beaker and fill with sufficient 10% nitric acid to cover all components

f) Place in an ultrasonic bath for 20 minutes

g) Carefully remove the glass components and rinse thoroughly with deionised water

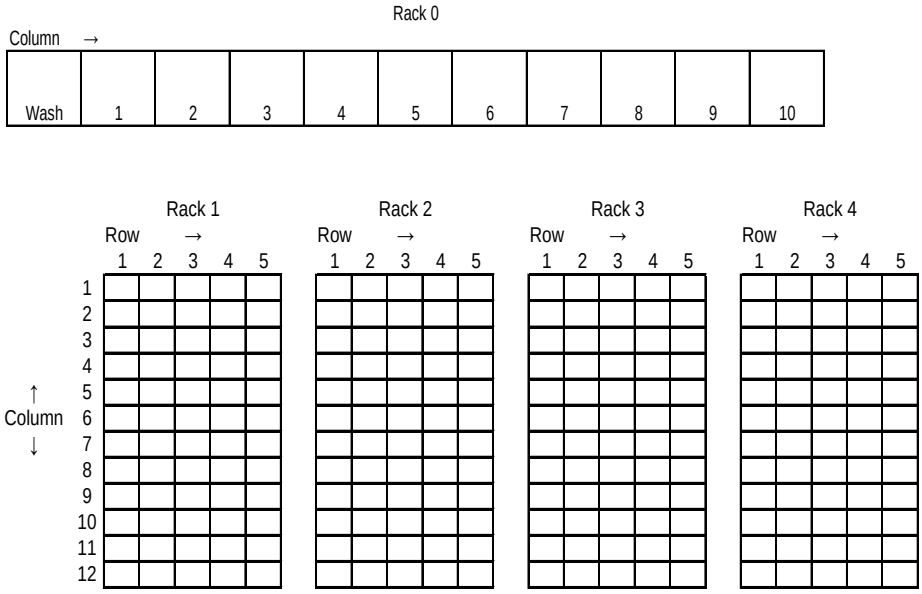
h) Allow to air-dry prior to refitting

5) Reassemble the components in the reverse order to disassembly

Note: Occasionally, glass sample introduction components crack when the ultrasonic cleaning procedure is used. To avoid this, the components may be soaked in acid, as above, for 12 hours, without ultrasonic treatment.

Appendix 9

Autosampler Position Map



NB: This map is only applicable for CETAC ASX-500/510 autosamplers fitted with 60 position racks.

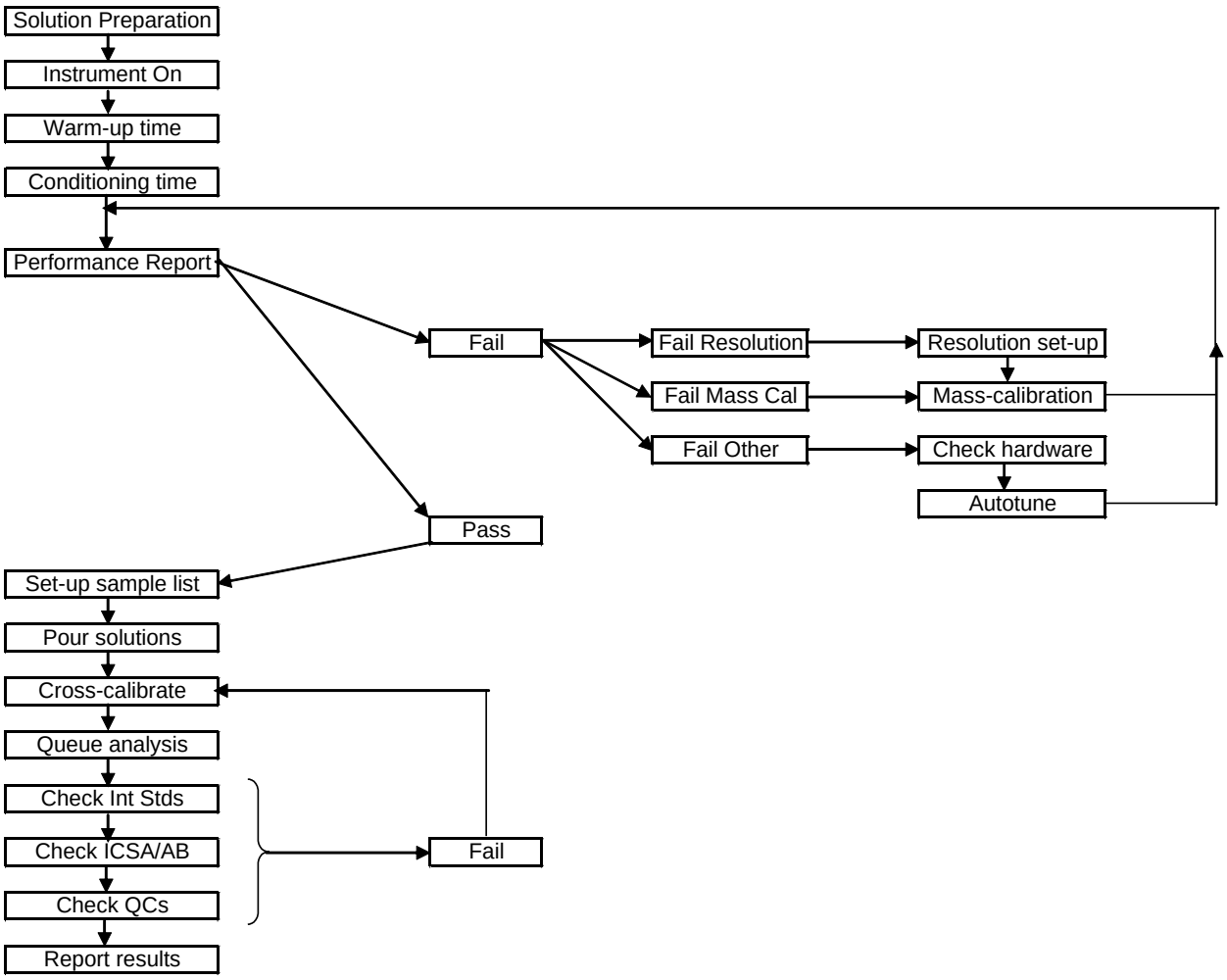
Appendix 10

Spiking Levels

(Concentration in Final Solution Based on Instructions Within this Document)

Element	Spike Value (µg/L)
Al	2000
Sb	500
As	40
Ba	2000
Be	50
Cd	50
Cr	200
Co	500
Cu	250
Pb	20
Mn	500
Ni	500
Se	10
Ag	50
Tl	50
V	500
Zn	500

Appendix 11
Work Flow-Chart



Title: Extractable Residue (Lipids) from Animal Tissue

SOP # PT-OP-011 (Extractable Residue – Lipids)

Approvals (Signature/Date):

Sharon Bacha Organics Department Manager	4/17/2016 Date	Steve Jackson Regional Safety Coordinator	4/6/2016 Date
Virginia Zusman Quality Assurance Manager	4/5/2016 Date	Deborah L. Lowe Laboratory Director	4/8/2016 Date
Roseann Ruyechan Inorganics Department Manager	4/11/2016 Date		

1.0 Scope and Application

1.1 This SOP describes the procedure for determining organic solvent extractable residue from fish tissue. Normally this residue is predominantly lipid material from the tissue, but it may include other non-polar material as well (e.g. petroleum hydrocarbons).

1.2 This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above.

1.3 On occasion clients may request modifications to this SOP. These modifications are handled following as indicated PT-QA-M-001, Quality Assurance Manual.

2.0 Summary of Method

2.1 A 10-gram aliquot of homogenized tissue is extracted via soxtherm. The extract is dryed and evaporated to dryness. The residue remaining after evaporation is determined gravimetrically. TestAmerica Pittsburgh is certified to perform this procedure and it is referenced on the scope of accreditation as SOP (00416) OP-011.

3.0 Definitions

3.1 Refer to the glossary in the Laboratory Quality Assurance Manual (PT-QA-M-001), current version.

3.2 TALS – TestAmerica Laboratory Information Management System

3.3 NCM – Non-Conformance Memo – a system within TALS for the lab to communicate to project management and others when there is an anomaly seen with the samples or batch, or a QC failure.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-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.

5.2 Nitrile gloves should be used when performing this extraction. Latex and vinyl gloves provide no significant protection against the organic solvents used in this SOP and should not be used.

5.3 Ultrasonic disrupters can produce high intensity noise and must be used in an area with adequate noise protection.

5.4 The following is a list of the materials used in this method, which have a serious or significant hazard rating. 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
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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5 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.

5.6 Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.7 The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.8 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported immediately to a laboratory supervisor and/or the EH&S coordinator.

6.0 Equipment and Supplies

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Syringe or positive displacement pipette: 1 mL

6.2 Analytical balance, capable of accurately weighing ± 0.0001 g

6.3 Toploader Balance: >100 g capacity, accurate ± 0.1 g

6.4 Soxtherm Model S 306A

6.5 Soxtherm thimbles

6.6 Horizon SpeedVap 9000II

6.7 70 ml Disposable Evaporation Pan

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the SDS prior to the use of any reagent or standard.

7.1 Reagents

7.1.1 Methylene chloride, pesticide grade or equivalent

7.1.2 Sodium sulfate (Na_2SO_4), Granular, Anhydrous: Purify by heating at 400℃ a minimum of two hours.

7.2 Standards

7.2.1 Fish Oil (Sigma): purchased commercially

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 The tissue samples are stored frozen and are to be extracted within 1 year of sample collection.

8.2 The extracts are stored at ambient temperature and analyzed within forty (40) days of extraction.

9.0 Quality Control

9.1 The following quality control samples are prepared with each batch of samples**.**

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 per preparation batch[1]	< RL
Laboratory Control Sample (LCS)	1 per preparation batch[1]	30-150%
Laboratory Control Sample Duplicate (LCSD)	1 per preparation batch[1]	30-150%; ± 25% RPD
Sample Duplicate (SD)	1 per preparation batch[1]	± 25% D

[1]A batch is limited to 20 samples.

9.2 Method Blank: The method blank is carried through the entire analytical procedure, including preparation and analysis. The method blank consists of 10.0 grams of sodium sulfate. The method blank 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.

9.2.1 The method blank must not contain any analyte of interest at or above the reporting limit. If the MB has a result at or above the RL all associated samples must be re-extracted along with an acceptable MB unless one of the following criteria is met.

- Evaluate the sample results. If associated samples are non-detect, results for those samples may be reported with the NCM “Method Blank – Report, ND”.
- If associated samples have concentrations that are greater than 10 times the MB concentration, those results may be reported with the NCM “Method Blank – Report, 10X”.
- If reanalysis is not possible due to limited sample quantity, the laboratory project manager will be notified to inform the client. Results shall be reported flagged with a “B” qualifier and the NCM “Method Blank – Insufficient Sample”.
- If reanalysis will be outside of holding time, the client must be notified and approval from the client must be obtained for the reanalysis. If reanalysis is performed past holding time, both the initial and reanalysis results must be included in the report.

9.3 Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD): The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. The LCS/LCSD consists of 10.0 grams of sodium sulfate spiked with 1.0 g of Fish Oil (Section 7.2.1).

9.3.1 On-going monitoring of the LCS through control charting recoveries provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2 Recovery of the LCS and LCSD must be within 30 – 150%. If recovery is outside this range for either standard, all associated samples must be re-extracted with an acceptable LCS/LCSD unless one of the following criteria is met.

- Evaluate the sample results. If LCS recovery is above control limits and associated samples are non-detect, results for those samples may be reported with the NCM "LCS/LCSD - %R High". Samples associated with low LCS recovery, or samples with detected Lipids associated with high LCS recovery must be redistilled and reanalyzed.

- If reanalysis is not possible due to limited sample quantity, the laboratory project manager will be notified to inform the client. Results shall be reported flagged with a "*" qualifier and the NCM "LCS/LCSD – Insufficient Sample".

- If reanalysis will be outside of holding time, the client must be notified and approval from the client must be obtained for the reanalysis.

9.4 Sample Duplicate: One sample per analytical batch must be analyzed in duplicate. The Duplicate is a separate portion of sample that is taken through all extraction and analytical steps along with the sample batch.

9.4.1 The %RPD between the sample and Duplicate results must be $\leq$ 25%. If the %RPD limit is exceeded, and sample and duplicate results are above 5x the reporting limit, sample and duplicate should be reanalyzed. If sample and duplicate results are <5x the reporting limits, results should agree within a difference of the reporting limit concentration.

9.4.2 If the %RPD exceeds the control limit, examine the sample. If the matrix is too varied to be properly homogenized, report the results along with the "Sample Duplicate - %RPD, non-homogeneous" NCM. Results of the parent sample must be flagged.

10.0 Procedure

10.1 Calibration and Standardization

10.1.1 Not Applicable

10.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.3 Lipid Extraction Procedure (Organic Prep Department)

10.3.1 Weigh 10.0 g of the homogenized tissue into a soxtherm thimble. Record the weight to the nearest 0.1 g in the TALS AD Batch worksheet. Add sodium sulfate until no free liquid is present in sample. NOTE: Record the actual weight that is extracted and record the Final Volume as 10 mL in the TALS worksheet so that the prep factor will be properly applied to the RL.

10.3.2 Add 120 mL of methylene chloride.

10.3.3 Extract at 150℃ for approximately 2 hours.

10.3.4 After 2 hours. remove from soxtherm and cool.

10.3.5 Transfer to a pre-weighed 40-mL VOA vial. Rinse the soxtherm apparatus with 2 additional portions of methylene chloride and add to the vial.

10.4 Lipid Analytical Procedure (Wet Chemistry Department)

10.4.1 Calibrate the analytical balance at 2 mg and 1000 mg using class “S” weights before and after each batch of samples is weighed.

10.4.2 Calibration shall 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, recalibrate the balance.

10.4.3 Mark 1 disposable evaporation pan with an ID for each sample and QC. Weigh the pans using an analytical balance, and record the weights in the TALS AD Batch worksheet.

10.4.4 Place a phase separation filter paper into a filter funnel. Rinse with methylene chloride and dispose of the rinsate.

10.4.5 Filter the extract through the phase separator filter paper into a pre-weighed 70 mL evaporation pan. Rinse the collection flask and filter paper twice with approximately 5 mL portions of methylene chloride.

10.4.6 Place pans into the SpeedVap and evaporate to dryness. The SpeedVap is set to

50°C.

10.4.7 After all the liquid has evaporated from the pan, place it in a desiccator for at least one hour.

10.4.8 Weigh the pans on an analytical balance and record the weights to the nearest 0.1 mg.

10.4.9 Determine the Lipid concentration using the equation in section 11.

10.5 Analytical Documentation

10.5.1 Record all information in the TALS LIMS worksheet for Percent Lipid extraction and analysis. See example Percent Lipids Extraction and Analysis Worksheets in the Attachments at the end of the SOP.

11.0 Calculations / Data Reduction

11.1 Sample Results are calculated by the TALS method using the following equation:

$$Concentration(\%) = \frac{(A - B)}{W} \times 100$$

Where: A = Weight of beaker + residue, g
B = Weight of the beaker, g
W = Weight of sample extracted, g

11.2 Duplicate Sample Relative Percent Difference calculation:

$$RPD = \frac{|X_1 - X_2|}{\left(\frac{X_1 + X_2}{2}\right)} \times 100\ \%$$

Where: X1 = Original Result
X2 = Duplicate Result

11.3 Percent Recovery (%R) Calculation:

$$\%R = \frac{\text{observed value}}{\text{true value}} \times 100\ \%$$

12.0 Method Performance

12.1 The supervisor has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use, and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilities – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Method Detection Limit Study – MDLs are not performed for this procedure. No results are reported below the Reporting Limit.

13.0 Pollution Control

13.1 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" and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

13.2 This method does not contain any specific modifications that serve to minimize or prevent pollution.

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 PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1 Extracted solid samples contaminated with methylene chloride. This waste is collected in waste container identified as "Lab Trash Waste", Waste #12.

14.1.2 Used sodium sulfate contaminated with methylene chloride from the extract drying step. This waste is collected in waste container identified as "Lab Trash Waste", Waste #12.

14.1.3 Assorted flammable solvent waste from various glassware rinses. This waste is collected in waste containers identified as "Mix Flammable Solvent Waste", Waste #3.

14.1.4 Methylene chloride waste from various glassware rinses. This waste is collected in waste containers identified as “Methylene Chloride Waste”, Waste #2.

14.1.5 Miscellaneous disposable glassware contaminated with solvents and sample residue. This waste is collected in waste container identified as “Lab Trash Waste”, Waste #12.

15.0 References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, Method 8290 Sections 6.7, 7.2.2, 7.3.3, and Method 3550.

15.2 United States Army Corps of Engineers Waterways Experiment Station. May 1995. A Comparison of Three Lipid Extraction Methods. Technical Note EEDP-01-35. 3909 Halls Ferry Road, Vicksburg, Mississippi 39180-6199.

15.3 PT-QA-M-001, TestAmerica Pittsburgh Laboratory Quality Assurance Manual

15.4 PT-OP-026, Extraction of Organic Compounds from Solids, Sediments, Tissues and Wipes, SW846 3500-series methods

15.5 PT-HS-001, Pittsburgh Facility Addendum to TestAmerica Corporate Environmental to TestAmerica Corporate Environmental Health & Safety Manual (CW-E-M-001)

15.6 PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability

15.7 PT-QA-012, Selection and Calibration of Balances and Weights

15.8 PT-QA-016, Nonconformance & Corrective Action System

15.9 PT-QA-031, Internal Chain of Custody

16.0 Method Modifications

16.1 None

17.0 Attachments

17.1 Attachment 1 - Example Percent Lipids TALS Extraction Worksheet

17.2 Attachment 2 - Example Percent Lipids TALS Analytical Worksheet

18.0 Revision History

18.1 Revision 4, 08/18/09

18.2 Revision 5, 3/4/2014

18.3 Changes to current revision

SOP section	Change from	Change to	Reason
Cover	QAM – Violet Fanning	QAM –Virginia Zusman	Change in personnel
3.2 & 3.3		Added definitions for TALS and NCM	Clarification
5.1, 13.1 and 15.6		Added reference to PT-HS-001, Pittsburgh's Facility Addendum EH&S Manual	Correction
7.1.3	Fish Oil moved to standard section 7.2.1		Clarification
9.6 and 9.7			Correction
10.3.5		Added rinse the soxtherm apparatus with 2 portions of methylene chloride	Correction
10.4.3		Added mark pans with ID for samples and QC	Clarification
10.4.4 and 10.4.5	Removed "sodium sulfate" since it is no longer used by Wet Chemistry		Correction
11.2		Added equation for Sample/Duplicate %RPD	Clarification
11.3		Added equation for LCS/LCSD %Recovery	Clarification
15.4	PT-OP-001	PT-OP-026	SOP numbering change for solid extraction
15.6 15.7 15.8 15.9 15.10		PT-HS-001 PT-QA-031	SOP reference additions

ATTACHMENTS

Attachment 1 - Example Percent Lipids TALS Extraction Worksheet

Organic Prep Worksheet

Batch Number: 180-88324
Method: 3541
Analyst: Geehring, Kevin

Date Open: Oct 30 2013 7:10AM
Batch End: Oct 30 2013 9:30AM

Lab ID	Client ID	Method Chain	Basis	Initial weight/volume of sample	Final weight/volume of sample	OP Fish Oil_00003
MB~180-88324/1				10.0 g	10.0 mL	
LCS~180-88324/2				10.0 g	10.0 mL	1.0 g
LCSD~180-88324/3				10.0 g	10.0 mL	1.0 g
180-26510-A-1-B		3541, Percent_Lipids	T	10.0 g	10.0 mL	
180-26510-A-2-B		3541, Percent_Lipids	T	10.0 g	10.0 mL	
180-26510-A-3-B		3541, Percent_Lipids	T	10.0 g	10.0 mL	
180-26510-A-4-B		3541, Percent_Lipids	T	10.1 g	10.0 mL	
180-26510-A-5-B		3541, Percent_Lipids	T	10.1 g	10.0 mL	
180-26510-A-5-B~DU		3541, Percent_Lipids	T	10.1 g	10.0 mL	
180-26510-A-6-B		3541, Percent_Lipids	T	10.0 g	10.0 mL	
180-26510-A-7-B		3541, Percent_Lipids	T	10.1 g	10.0 mL	
180-26510-A-8-B		3541, Percent_Lipids	T	10.0 g	10.0 mL	
180-26510-A-9-B		3541, Percent_Lipids	T	10.0 g	10.0 mL	
180-26510-A-10-B		3541, Percent_Lipids	T	10.0 g	10.0 mL	
180-26510-A-11-B		3541, Percent_Lipids	T	10.1 g	10.0 mL	
180-26510-A-12-B		3541, Percent_Lipids	T	10.1 g	10.0 mL	
180-26510-A-13-B		3541, Percent_Lipids	T	10.0 g	10.0 mL	
180-26510-A-14-B		3541, Percent_Lipids	T	10.1 g	10.0 mL	
180-26510-A-15-B		3541, Percent_Lipids	T	10.0 g	10.0 mL	
180-26510-A-16-B		3541, Percent_Lipids	T	10.1 g	10.0 mL	
PB~180-88168/17-A				10.0 g	10.0 mL	

First Start time: NA
Person's name who did the prep: kg bp
Person's name who witnessed reagent drop: NA
First End time: NA

SOP Number: NA
Balance ID: 1120122641
Person's name who did the concentration: kg
Concentrator ID: NA

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Organic Prep Worksheet

Batch Number: 180-68324
Method: 3541
Analyst: Geehring, Kevin

Date Open: Oct 30 2013 7:10AM
Batch End: Oct 30 2013 9:30AM

Concentration Start Time:	NA
Concentration End Time:	NA
Concentration Temperature:	NA Celsius
Na2SO4 Lot Number:	1002415
DCM/CG2 ID:	NA
Silica Gel Lot Number:	NA
Boiling Chips ID:	NA
Solvent:	Methylene chloride
Vendor lot number:	1000447
Exchange Solvent Name:	NA
Exchange Solvent Lot #:	NA
Blank Soil Lot Number:	NA
Magnesium Sulfate Lot #:	1000405
N-evap #:	NA
N-evap temperature:	NA Degrees C
Uncorrected N-evap Temperature:	NA Degrees C
Florisil Lot #:	NA
TBA Lot #:	NA
Acid used for Clean Up Reagent:	NA
Pipette ID:	NA
Syringe Lot #:	NA
Soxtherm Unit:	5 6 7 8
Soxtherm Temperature:	NA
ID number of the thermometer:	NA
Glass Wool ID:	NA

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Organic Prep Worksheet

Batch Number: 180-88324
Method: 3541
Analyst: Geehring, Kevin

Date Open: Oct 30 2013 7:10AM
Batch End: Oct 30 2013 9:30AM

Lab ID	Client ID	Method Chain	Basis	Analysis comment	Comments
MB~180-88324/1					
LCS~180-88324/2					
LCSD~180-88324/3					
180-26510-A-1-B		3541, Percent_Lipids	T		
180-26510-A-2-B		3541, Percent_Lipids	T		
180-26510-A-3-B		3541, Percent_Lipids	T		
180-26510-A-4-B		3541, Percent_Lipids	T		
180-26510-A-5-B		3541, Percent_Lipids	T		
180-26510-A-5-B~DU		3541, Percent_Lipids	T		
180-26510-A-6-B		3541, Percent_Lipids	T		
180-26510-A-7-B		3541, Percent_Lipids	T		
180-26510-A-8-B		3541, Percent_Lipids	T		
180-26510-A-9-B		3541, Percent_Lipids	T		
180-26510-A-10-B		3541, Percent_Lipids	T		
180-26510-A-11-B		3541, Percent_Lipids	T		
180-26510-A-12-B		3541, Percent_Lipids	T		
180-26510-A-13-B		3541, Percent_Lipids	T		
180-26510-A-14-B		3541, Percent_Lipids	T		
180-26510-A-15-B		3541, Percent_Lipids	T		
180-26510-A-16-B		3541, Percent_Lipids	T		
PB~180-88168/17-A					

Batch Comment: NA

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Attachment 2 - Example Percent Lipids TALS Analytical Worksheet.

General Chemistry Worksheet

Batch Number: 180-87785
Method: Lipids
Analyst: McLaughlin, Jeremiah W

Date Open: Oct 24 2013 2:33PM
Batch End:

Lab ID	Client ID	Method Chain	Basis	Final weight/volume of sample	Sample Tare Weight	Weight of Residue and Dish	RawResidue
MB~180-87698/1-A		Percent_Lipids		10.0 mL	2.5458 g	2.5462 g	0.0004 g
LCS~180-87698/2-A		Percent_Lipids		10.0 mL	2.5696 g	3.5399 g	0.9703 g
LCSD~180-87698/3-A		Percent_Lipids		10.0 mL	2.5838 g	3.4495 g	0.8657 g
180-24841-A-61-D		Percent_Lipids	T	10.0 mL	2.5556 g	2.5592 g	0.0036 g
180-24841-A-62-D		Percent_Lipids	T	10.0 mL	2.5557 g	2.6573 g	0.1016 g
180-24841-A-63-D		Percent_Lipids	T	10.0 mL	2.5790 g	2.5832 g	0.0042 g
180-24841-A-64-D		Percent_Lipids	T	10.0 mL	2.5734 g	2.7385 g	0.1651 g
180-24841-A-65-D		Percent_Lipids	T	10.0 mL	2.5719 g	2.5794 g	0.0075 g
180-24841-A-66-D		Percent_Lipids	T	10.0 mL	2.5720 g	2.8314 g	0.2594 g
180-24841-A-67-D		Percent_Lipids	T	10.0 mL	2.5780 g	2.5849 g	0.0069 g
180-24841-A-68-D		Percent_Lipids	T	10.0 mL	2.5857 g	2.8401 g	0.2544 g
180-24841-A-69-D		Percent_Lipids	T	10.0 mL	2.5845 g	2.5918 g	0.0073 g
180-24841-A-70-D		Percent_Lipids	T	10.0 mL	2.5897 g	2.6140 g	0.0243 g
180-24841-A-71-D		Percent_Lipids	T	10.0 mL	2.5621 g	2.5651 g	0.003 g
180-24841-A-72-D		Percent_Lipids	T	10.0 mL	2.5568 g	2.6311 g	0.0743 g
180-24841-A-73-D		Percent_Lipids	T	10.0 mL	2.6060 g	2.6104 g	0.0044 g
180-24841-A-74-D		Percent_Lipids	T	10.0 mL	2.5651 g	2.6675 g	0.1024 g

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Extraction of Organic Compounds from Solids, Sediments, Tissue and Wipes

Method(s): SW846 3500 Series

Approvals (Signature/Date):

7/19/2016	7/20/2016
Sharon Bacha Date Organics Department Manager	Steve Jackson Date Regional Safety Coordinator
7/18/2016	7/18/2016
Virginia Zusman Date Quality Assurance Manager	Deborah L. Lowe Date Laboratory Director

1.0 SCOPE AND APPLICATION

1.1 This SOP describes procedures for preparation (extraction) of semivolatile organic analytes in soil, sediment, tissue, waste and wipe matrices for analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS). The procedures are based on SW-846 methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.2 Extraction procedures for the following determinative methods are covered:

8081A, 8081B, 8082, 8082A 8141A, 8141B, 8270C and 8270D.

1.2.1 For sediment samples being analyzed in support of Dredged Material Management programs, method modifications are often necessary, to compensate for the high moisture content, to meet project goals. This may include increased sample weight or decreased final extract volumes. Typically these volume modifications are up to a factor of 2.

1.3 The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

1.4 On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated PT-QA-M-001, Quality Assurance Manual.

2.0 SUMMARY OF METHOD

2.1 High Level (Client Specific) Sonication Extraction

A measured weight of sample, typically 2 grams, is mixed with anhydrous sodium sulfate to for a free flowing powder. This is solvent extracted once using an microtip ultrasonic horn.

2.2 Accelerated Soxhlet (Soxtherm®) Extraction

A measured weight of sample, typically 15 g, or one whole wipe sample is mixed with anhydrous sodium sulfate and magnesium sulfate to form a free flowing powder. This is extracted with an accelerated soxtherm unit.

2.3 Concentration

Procedures are presented for drying and concentration of the extract to final volume for analysis.

3.0 DEFINITIONS

3.1 Definitions of terms used in this SOP may be found in the glossary of the Pittsburgh Quality Assurance Manual (PT-QA-M-001).

3.2 TALS – TestAmerica Laboratory Information Management System

3.3 NCM – Non-Conformance Memo – a system within TALS for the lab to communicate to project management and others when there is an anomaly seen with the samples or batch or a QC failure.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2 Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-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.

5.2 Samples containing or suspected to contain cyanide or sulfide concentrations at or greater than 250 ppm or 500 ppm, respectively, shall be processed in a fume hood.

5.3 Nitrile gloves should be used when performing this extraction. Latex and vinyl gloves provide no significant protection against the organic solvents used in this SOP, and should not be used.

5.4 During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard. The KD apparatus and glass separatory funnels have ground glass joints, which can become stuck. Technicians must use Kevlar or other cut/puncture resistant gloves when separating stuck joints.

5.5 Ultrasonic disrupters can produce high intensity noise and must be used in an area with adequate noise protection.

5.6 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[i]	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-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.
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.

[i] Exposure limit refers to the OSHA regulatory exposure limit.

5.7 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 become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.8 The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit. Use of methylene chloride for glassware cleaning should be avoided as far as possible.

5.9 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported immediately to a laboratory supervisor or EH&S coordinator.

6.0 EQUIPMENT AND SUPPLIES

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Glassware should be cleaned with soap and water, rinsed with water and dried in an oven at 400°C for at least 2 hours. Alternatively the glassware can be solvent rinsed with acetone or methanol followed by methylene chloride after the water rinse.

6.2 Equipment and supplies for extraction procedures

EQUIPMENT AND SUPPLIES	High Level Sonication	Accelerated Soxtherm	Conc
20 or 40 mL VOA Vials	X		
Solvent Dispenser Pump or 100 mL Graduated Cylinder	X		
Boiling Chips: Contaminant free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent).		X	X
Cooling Condensers		X	
Heating Mantle: Rheostat controlled		X	
Auto-timer for heating mantle		X	
Beakers: 250 & 400 mL, graduated	X	X	
Balance: >100 g capacity, accurate ±0.1 g	X	X	
Soxtherm® Extractor Gerhardt Model S 306A		X	
Glass Thimbles		X	
Sonicator (at least 300 watts)	X		
Sonicator horn, microtip	X		
Kuderna-Danish (K-D) Apparatus: 500 mL			X
Concentrator Tube: 10 mL, attached to K-D with clips			X
Snyder Column: Three-ball macro			X
Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5℃) up to 95℃. The bath m ust be used in a hood or with a solvent recovery system.			X
Vials: Glass, 2 mL, 4 mL, and 10 mL capacity with Teflon®-lined screw-cap			X
Nitrogen Blowdown Apparatus			X
Nitrogen: reagent grade.			X
Culture tubes: 10 mL, 16 mmx100 mm			X
Syringe: 1 mL	X	X	
Phase Separation Paper	X	X	
Glass Wool	X	X	
Glass Funnel: 75 X 75 mm	X	X	X
Disposable Pipettes	X	X	X
Aluminum foil	X	X	X
Paper Towels	X	X	X
Ottawa Sand		X	

7.0 REAGENTS AND STANDARDS

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the SDS prior to the use of any reagent or standard.

7.1 Reagents for Extraction Procedures

All reagents must be ACS reagent grade or better unless otherwise specified.

REAGENTS	High Level Sonication	Accelerated Soxtherm	Conc.
Sodium sulfate (Na_2SO_4), Granular, Anhydrous: Purify by heating at 400℃ a minimum of two hours.	X	X	
Magnesium Sulfate, Anhydrous powder		X	
Extraction/Exchange Solvents: Methylene chloride, hexane, acetone, pesticide quality or equivalent	X	X	X
Acetone: Used for cleaning	X	X	X
50:50 Sodium Sulfate/Magnesium Sulfate	X	X	

7.2 Standards

7.2.1 Stock Standards

Stock standards are purchased as certified solutions or prepared from neat. Semivolatile stock standards are stored at $\leq 6.0^{o}$C. All stock standards must be protected from light. Stock standard solutions must be replaced after one year (from the time of preparation, if prepared in house, or from the time the ampule is opened if purchased.) Standards must be allowed to come to room temperature before use.

7.2.2 Surrogate Spiking Standards

Prepare or purchase surrogate spiking standards at the concentrations listed in Table 2. Surrogate spiking standards are prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.2.3 Matrix Spiking and Laboratory Control Spiking Standards.

The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 3. Spiking standards are purchased or prepared as dilutions of the stock standards. Spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Matrix	Sample Container	Min. Sample Size	Preservation	Extraction Holding Time	Analysis Holding Time
Soils[1]	4oz Jar	15 grams	Cool, >0.0˚C but ≤ 6.0ºC	14 Days	40 Days from extraction
Sediment	4oz Jar	30 grams	Cool, >0.0˚C but ≤ 6.0ºC	14 Days	40 Days from extraction
Tissues	4oz Jar	15 grams	Frozen	1 year	40 Days from extraction
Wipes	4 oz jar	1 wipe	Cool, >0.0˚C but ≤ 6.0ºC	14 Days	40 Days from extraction

[1] Soils include solids, sludges, and organic liquids (wastes).

8.1 For method 8141B, solid sample extraction must be started within 7 days of collection.

8.2 Some, but not all, states accept a 1 year holding time for PCB solid samples. The holding time in TALS is set to 14 days to reflect those states/projects that will not accept this extended holding time. Confirm with QA or the Project Manager that a longer holding time may be applied per project.

9.0 QUALITY CONTROL

9.1 Insufficient Sample Volume Provided

9.1.1 If insufficient sample is available to process a MS/MSD, then an LCS Duplicate may be processed. The LCS pair is then evaluated according to the MS/MSD criteria. Use of a LCS pair in place of a MS/MSD must be documented. Because subsamples cannot be taken from a wipe sample for MS/MSD analyses, wipe samples will always be processed with a LCS/LCSD.

9.1.2 It is acceptable to prepare an MS without an MSD, if there is sufficient sample available for only one QC.

9.2 Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count for 20 samples in a preparation batch. Field QC samples are included.

9.3 The following quality control samples are prepared with each batch of samples. For QC control limits, refer to the individual analytical methods SOPs and TALS.

Quality Controls	Frequency
Method Blank (MB)	1 per preparation batch[1]
Laboratory Control Sample (LCS)	1 per preparation batch[1]
Matrix Spike (MS)[2]	1 per preparation batch[1]
Matrix Spike Duplicate (MSD)[2]	1 per preparation batch[1]
Surrogates	All samples and QC

[1]A preparation batch is limited to 20 samples.

[2]The sample used for MS/MSD is randomly selected, unless specifically requested by a client.

9.4 Method Blank

A method blank consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the method blank at the same level as the samples. The method blank is used to identify any background interference or contamination of the analytical system, which may lead to the reporting of elevated concentration levels or false positive data.

9.4.1 Solid method blanks use the same target weight of sodium sulfate as the extracted weights of the associated samples, spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

NOTE: For batches containing samples from South Carolina, certified clean Ottawa sand is used as a blank matrix, in addition to the sodium sulfate.

9.4.2 Method blanks for wipes consist of clean, unused gauze pads (that are the same as those used for the associated wipe samples) that are spiked with the surrogates and carried through the entire analytical procedure, including any cleanup steps.

9.5 Laboratory Control Sample (LCS)

Laboratory Control Samples are well characterized, laboratory-generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure, including any cleanup steps.

9.5.1 The LCS is made up in the same way as the method blank but spiked with the LCS standard as well as surrogates. (See section 9.4.1 and 9.4.2.)

9.6 Surrogates

9.6.1 Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.6.2 Each applicable sample, blank, LCS and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

9.7 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second spiked aliquot of the same sample, which is prepared and analyzed along with the sample and matrix spike.

10.0 PROCEDURE

Procedures for high level sonication extraction (10.1), accelerated soxtherm extraction (10.2), waste dilution (10.3) and extract concentration (10.4) are presented in this section.

10.1 High Level Sonication Procedure

10.1.1 Refer to Figure 1 – High Level Sonication Extraction flowchart.

10.1.1.1 Weigh 2 g of sample into a 20 mL vial. Record the weight to the nearest 0.1 g in the appropriate column on the TALS LIMS worksheet. Use 2 g of sodium sulfate for the method blank and the LCS.

10.1.1.2 Add 2 grams of sodium sulfate to each sample and mix well.

10.1.1.3 Add 1 mL of surrogate to all samples including QC samples. Add 1 mL of the matrix spike solution to the LCS, MS and MSD. Depending on the test, surrogate and matrix spike solutions at higher concentrations may need to be prepared. If necessary, the preparation of these solutions will be documented in the standards database in TALS LIMS.

Add the surrogates and matrix spiking compounds to the sample aliquot after mixing the sample with the sodium sulfate drying agent. This will be done in accordance with the memorandum from the USEPA dated August 5, 2010, which supersedes previous Method instructions (see Attachment 1). The EPA points out in the memorandum that adding surrogates and other spiked compounds to environmental and QC samples prior to mixing with drying agents may cause major recovery issues depending on the analyte and/or the matrix.

10.1.1.4 Add 9.0 mL of extraction solvent (8.0 mL to the LCS, MS, MSD) so that the final volume is 10.0 mL. The extraction solvent is as follows:

- For organochlorine pesticides, organophosphorus pesticides, and PCBs (Aroclors and congeners), the solvent is hexane.
- For GC/MS semivolatiles, the solvent is methylene chloride.

10.1.1.5 Place the bottom surface of a 1/8” tapered microtip attached to a 1/2” horn approximately ½ inch below the surface of the solvent, but above the solid layer.

10.1.1.6 Sonicate each sample for 2 minutes. A Fisher Scientific 550 sonicator is used, the output should be set at 10 with mode switch on pulse, and the percent-duty cycle knob set at 100% full power.

10.1.1.7 Loosely pack a disposable Pasteur pipette with 2 to 3 cm of glass wool. Filter the extract through the glass wool into a suitable container.

10.1.1.8 If the samples do not require cleanups or additional concentration, than the extract is ready for analysis

10.1.1.9 If cleanups (SOP PT-OP-028) or additional concentration (10.4) are required, collect a standard volume (i.e., 5.0 mL, which represents ½ of the extract). Either account for the "loss" of half of the extract in the final sample calculations, or concentrate the extract to ½ of the standard final volume to compensate for the loss.

10.1.2 High Level Procedure - Calgon Samples

10.1.2.1 Weigh 2 g of sample into a 40 mL vial. Record the weight to the nearest 0.1 g in the appropriate column on the TALS LIMS worksheet. Use 2 g of sodium sulfate for the method blank and the LCS.

10.1.2.2 Add 2 grams of sodium sulfate to each sample and mix well.

10.1.2.3 Add 1 mL of surrogate to all samples including QC samples. Add 1 mL of the matrix spike solution to the LCS, MS and MSD. Depending on the test, surrogate and matrix spike solutions at higher concentrations may need to be prepared. If necessary, the preparation of these solutions will be documented in the standards database.

NOTE: Add the surrogates and matrix spiking compounds to the sample aliquot after mixing the sample with the sodium sulfate drying agent. This will be done in accordance with the memorandum from the USEPA dated August 5, 2010, which supersedes previous Method instructions (see Attachment 1). The EPA points out in the memorandum that adding surrogates and other spiked compounds to environmental and QC samples prior to mixing with drying agents may cause major recovery issues depending on the analyte and/or the matrix.

10.1.2.4 Add 19.0 mL of extraction solvent (18.0 mL to the LCS, MS, MSD) so that the final volume is 20.0 mL. The extraction solvent is as follows:

10.1.2.5 For organochlorine pesticides, organophosphorus pesticides, and PCBs (Aroclors and congeners), the solvent is hexane.

10.1.2.6 For GC/MS semivolatiles, the solvent is methylene chloride.

10.1.2.7 Shake each sample for 2 minutes.

10.1.2.8 Loosely pack a disposable Pasteur pipette with 2 to 3 cm of glass wool. Filter the extract through the glass wool into a suitable container.

10.1.2.9 If the samples do not require cleanups or additional concentration, than the 20 mL extract is ready for analysis

10.1.2.10 If cleanups (PT-OP-028) or additional concentration (10.4) are required, collected a standard volume (i.e., 10.0 mL, which represents ½ of the extract). Either account for the "loss" of half of the extract in the final sample calculations, or concentrate the extract to ½ of the standard final volume to compensate for the loss.

10.1.3 Sonicator Tuning:

10.1.3.1 Tune the sonicator according to manufacturer's instructions. The sonicator must be tuned at least every time a new horn is installed.

10.2 Accelerated Soxhlet (Soxtherm®):

Refer to Figure 2 – Accelerated Soxtherm Extraction (Soxtherm) flowchart.

10.2.1 Decant and discard any water layer on a sediment/soil sample. **Note:** For sediment samples associated with most Dredged Material Management projects, the water layer is considered part of the whole sediment and should not be decanted, but re-mixed into the sample. Check project requirements before decanting any water layer. Homogenize the sample by mixing thoroughly.

10.2.2 Tissue samples should be homogenized prior to extraction. Discard any foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials consult with the client. Document in the TALS LIMS worksheet if a water layer was discarded.

10.2.3 For wipe samples, the entire contents of the original sample container will be extracted (i.e., no subsample will be taken) following the procedure for solid samples.

10.2.4 Remove surrogate and matrix spiking solutions from the refrigerator and allow these solutions to warm to room temperature.

10.2.5 Weigh 15 g of sample ± 0.5 g (30 g for sediments due to the assumption of 50% moisture) into a beaker, recording the weight to the nearest 0.1 g on the TALS LIMS worksheet. Use 15 g of 50:50 sodium sulfate/magnesium sulfate for the method blank and LCS. Add 15 g of anhydrous 50:50 sodium sulfate/magnesium sulfate and mix well. The mixture should have a free flowing texture. If not, add more sodium sulfate. Add the sample/50:50 sodium sulfate/magnesium sulfate mixture to a soxtherm thimble, but do not pack the thimble tightly. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the thimble is required.

10.2.5.1 Sample weights less than 15 g but over 5 g may be used if the appropriate reporting limits can be met.

10.2.6 Prepare a method blank, LCS and MS/MSD for each batch as specified in Section 9 of this SOP, using sodium sulfate as the matrix. Use a new, clean gauze pad as the blank matrix for wipe samples and follow the procedure for extraction of solid samples. The weight of 50:50 sodium sulfate/magnesium sulfate used should be approximately the weight of soil used in each sample.

10.2.7 Add the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Add the appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to PT-OP-WI-001 for details of the spiking solutions. Record spiking volumes and standard numbers on the TALS LIMS worksheet. Return spiking solutions promptly to refrigerator.

NOTE: Add the surrogates and matrix spiking compounds to the sample aliquot after mixing the sample with the sodium sulfate drying agent. This will be done in accordance with the memorandum from the USEPA dated August 5, 2010, which supersedes previous Method instructions (see Attachment 1). The EPA points out in the memorandum that adding surrogates and other spiked compounds to environmental and QC samples prior to mixing with drying agents may cause major recovery issues depending on the analyte and/or the matrix.

Note: The same volume of surrogates and matrix spiking compounds is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

10.2.8 Place thimble in beaker containing clean boiling chips and add approximately 140 mL of solvent (see below). Place beakers into positions on the accelerated soxtherm unit. Run the appropriate program for the extraction solvent. Periodically, check the system for leaks at the joints.

10.2.8.1 For organochlorine pesticides, organophosphorus pesticides, and PCBs (Aroclors and congeners), the extraction solvent is 1:1 hexane/acetone except if GPC cleanup is being done. If GPC cleanup is being done, the extraction solvent is 1:1 methylene chloride/acetone.

10.2.8.2 For all other parameters, the extraction solvent is 1:1 methylene chloride/acetone.

10.2.9 Upon completion of the program, remove the beaker from the accelerated soxtherm unit and dispose of the extracted sample.

10.2.10 Collect the extract in a K-D or other glass container. Rinse the flask that contained the solvent extract with 5-10 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

10.2.11 Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 10.4 for concentration and PT-OP-028 for cleanup.

10.3 Waste Dilution:

10.3.1 This method is used for materials that are soluble in an organic solvent.

10.3.2 Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

10.3.3 Transfer 10 mL of the solvent to be used for dilution into a Teflon capped vial. Mark the meniscus on the vial, and then discard the solvent.

10.3.4 Tare the vial, and then transfer approximately 1g of sample to the vial. Record the weight to the nearest 0.1 g.

10.3.5 Add 1 mL of surrogate solution to each sample. Add 1 mL of matrix spike solution to the MS, MSD and LCS. Depending on the test, surrogate and matrix spike solutions at higher concentrations may need to be prepared. If necessary, the preparation of these solutions will be documented in the standards database.

10.3.6 Dilute to 10 mL with the appropriate solvent (hexane for organochlorine pesticides, organophosphorus pesticides, and PCBs (Aroclors and congeners); acetonitrile for PAHs by HPLC; methylene chloride for GC/MS semivolatiles).

10.3.7 Add 2 g $\pm$ 0.1 g sodium sulfate to the sample. Cap and shake for 2 minutes.

10.3.8 Add 4-5 g sodium sulfate to a small funnel. The funnel can be plugged with glass wool or phase separation filter paper may be used to hold the sodium sulfate.

10.3.9 Pour the sample through the funnel, collecting as much as possible in a clean vial. Do NOT rinse the funnel with additional solvent, and do NOT concentrate the sample. The final volume is defined as 40 mL for method 8082 and 10 mL for method 8270.

10.3.10 Label the sample, which is now ready for cleanup or analysis.

10.4 Concentration:

According to the type of sample and any cleanup procedures needed, different final solvents and volumes will be required. Refer to Table 1 for the appropriate final volumes and concentrations.

Refer to Figure 3 – Concentration and Cleanup flowchart.

10.4.1 Kuderna-Danish (KD) Method:

10.4.1.1 Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL KD flask. For procedures where the final volume is 10 mL, a 250 mL Erlenmyer flask may be used as an alternative to the KD flask.

10.4.1.2 Add one or two clean boiling chips and the dried extract to be concentrated to the KD flask and attach a three ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column (this is important to ensure that the balls are not stuck and that the column will work properly).

10.4.1.3 Place the KD apparatus on a water bath (80-90^{o}C) so that the tip of the concentrator tube is submerged. The water level should not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter but the chambers should not flood.

10.4.1.4 Concentrate to 5-15 mL. If the determinative method requires a solvent exchange add the appropriate exchange solvent (see Table 1) to the top of the Snyder Column, and then continue the water bath concentration back down to 1-4 mL. Refer to Table 1 for details on final volumes. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: Add an additional boiling chip with the addition of exchange solvent.

An alternative technique for solvent exchange is to replace the macro Snyder column and KD flask with a micro Snyder column, concentrate to approximately 1 mL, add 10 mL of exchange solvent, and concentrate back down to 1 mL. The extract must be cool before the macro Snyder assembly is removed.

Note: It is very important not to concentrate to dryness as analytes will be lost.

10.4.1.5 Remove the KD apparatus from the water bath and allow it to cool for a minimum of 10 minutes. If the level of the extract is above the level of the concentrator tube joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

10.4.1.6 If the final volume is 5 or 10 mL the extract may be made up to volume in the graduated KD tube or transferred to a 12 mL vial previously marked at the appropriate volume level. Document the final volume. Otherwise proceed to section 10.4.2.

10.4.2 Nitrogen Evaporation to Final Concentration

10.4.2.1 Transfer the entire extract to a calibrated evaporation tube. Rinse the concentrator tube with 1-2 mL of the appropriate solvent and transfer the solvent rinsate to the evaporation tube.

10.4.2.2 Place the tube in a warm water bath that is at approximately 35^{o}C and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but should not create splattering of the extract.

10.4.2.3 During the course of the evaporation rinse the sides of the evaporation tube twice with approximately 1 mL of clean solvent. The first rinse should be about half way through the process, with the second rinse when the solvent volume gets close to 1 mL. Concentrate the solvent accurately to the calibrated volume line and transfer the extract to the appropriate storage vial.

Note: It is very important not to concentrate to dryness as analytes will be lost.

Vial Calibration Note: Using a Class A volumetric pipette dispense the appropriate volume of solvent into the vial being calibrated, mark the meniscus and use this vial when marking the final volume line on subsequent sample vials. See SOP PT-QA-026 and work instruction PT-QA-WI-008 for details.

10.4.2.4 An alternative technique is to follow the previous steps concentrating the solvent to slightly below the required final volume and then drawing the extract into a syringe. Rinse the evaporation tube with a small amount of solvent and draw additional solvent into the syringe to make up the accurate final volume.

Note: The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

11.0 CALCULATIONS / DATA REDUCTION

Not applicable.

12.0 METHOD PERFORMANCE

12.1 The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilities – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Method Detection Limit Study – A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

13.0 POLLUTION CONTROL

13.1 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" and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

13.2 Within the constraints of following the methodology in this SOP, use of organic solvents should be minimized.

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 PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1 Methylene Chloride extraction waste. This waste is collected in waste containers identified as "Methylene Chloride Waste", Waste #2.

14.1.2 Extracted water samples. This waste is collected in a waste container identified as “Extraction Water”, Waste #35. The bottom organic layer is drained into a container identified as “Methylene Chloride Waste”, Waste #2. The remaining aqueous layer is neutralized to a pH between 6 and 9 and discharged down lab sink/ drain.

14.1.3 Used sodium sulfate and glass wool or filter paper contaminated with methylene chloride from the extract drying step. This waste is collected in a container identified as “Lab Trash Waste”, Waste #12.

14.1.4 Assorted flammable solvent waste from various rinses. This waste is collected in waste containers identified as “Mixed Flammable Solvent Waste”, Waste 3.

14.1.5 Methylene chloride waste from various rinses. This waste is collected in waste containers identified as “Methylene Chloride Waste”, Waste #2.

14.1.6 Miscellaneous disposable glassware contaminated with acids, caustics, solvents and sample residue. This waste is collected in a container identified as “Lab Trash Waste”, Waste #12.

15.0 REFERENCES – CROSS-REFERENCES

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B, 3541 and 3550B

15.2 Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Update IV, Methods 3500C, Method 3550C and Method 3620C, Rev. 3, February 2007

15.3 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update IV, Revision 2, February 2007, Method 8141B

15.4 “Spiking (Prior To vs. After Sample Drying) Issue in SW-846 Organic Extraction Methods” Memorandum, United States Environmental Protection Agency, Washington DC, 20460. Dated August 5, 2010

15.5 Pittsburgh Laboratory Quality Assurance Manual (PT-QA-M-001)

15.6 SOP PT-QA-001, Employee Training and Orientation.

15.7 SOP PT-QA-003, Glassware Clean-up for Organic/Inorganic Procedures

15.8 SOP PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability

15.9 SOP PT-QA-007, Determination of Method Detection Limits (MDL)

15.10 SOP PT-QA-008, Thermometer Calibration and Temperature Monitoring

15.11 SOP PT-QA-012, Selection and Calibration of Balances and Weights

15.12 SOP PT-QA-016, Nonconformance and Corrective Action System

15.13 SOP # PT-QA-021, Quality Control Program

15.14 SOP PT-QA-026, Container Accuracy Verification – Gravimetric

15.15 SOP PT-QA-031, Internal Chain of Custody

15.16 Pittsburgh Facility Addendum EH&S Manual, PT-HS-001.

15.17 PT-OP-WI-001, TestAmerica Pittsburgh Organic Prep Work Instruction for Initial/Final Volumes, Exchange Solvents, LCS and Matrix Spiking Components and Concentrations

16.0 METHOD MODIFICATIONS

16.1 Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.0 ATTACHMENTS

17.1 Table 1 – Initial Extraction Weight Adjustments for Sediment Samples (based on % Solids), Method 8270C and 8270D.

17.2 Table 2 – Initial Extraction Weight Adjustments for Sediment Samples (based on % Solids), Methods 8081A, 8081B, 8082, 8082A, 8141A and 8141B

17.3 Figure 1 – Sonication Extraction

17.4 Figure 2 – Accelerated Soxtherm Extraction (Soxtherm)

17.5 Figure 3 – Concentration and Cleanup

17.6 Attachment 1 - USEPA Memorandum on Spiking Prior to vs. After adding drying agent.

18.0 REVISION HISTORY

18.1 Revision 0, 10/2/2015

18.2 Changes to current revision

SOP section	Change from	Change to	Reason
throughout	Removed references to methohd 8151A and herbicides		Procedure addressed in separate SOP
9.4.1		Add note that Ottawa sand must be used as clean matrix for MB and LCS for batches with	Correction

		samples from SC.	

Table 1
Initial Weights and Final Volumes per Matrix and Method

Method	Matrix	Initial Sample Weight (g)	Surrogate & Matrix Spike Volume (mL)	Final Extract Volume (mL)
Semivolatiles				
8270 / 3541	Soil	15		5.0
	Sediment	30		5.0
	Tissue	15		5.0
8270_LL / 3541_LL	Soil	15		0.5
	Sediment	30		0.5
8270 / 3550	Solid	2.0		20
8270 / 3580	Solid	1.0		10
Pesticides				
8081 / 3541	Soil	15		20
	Sediment	15		10
	Tissue	15		20
8081_LL / 3541_LL	Soil	15		1.0
	Sediment	30		0.5
8081 / 3580	Solid	1.0		40
PCBs				
8082 / 3541	Soil	15		20
	Sediment	15		10
	Tissue	15		20
8082_LL / 3541_LL	Soil	30		1.0
	Sediment	30		1.0
8082 Congeners				
8082 / 3541	Soil	10		20
	Sediment	10		10
O-P Pesticides				
8141 / 3541	Soil	15		2.5
	Sediment	24		2.0
	Tissue	15		2.5
8141_LL / 3541_LL	Soil	30		1.0

Figure 1 – High Level Sonication Extraction

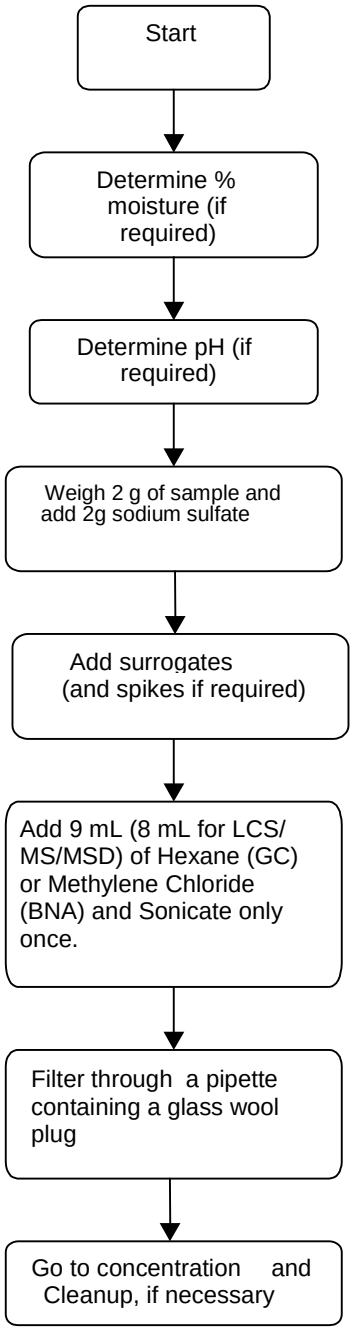


Figure 2 - Accelerated Soxtherm Extraction (Soxtherm®)

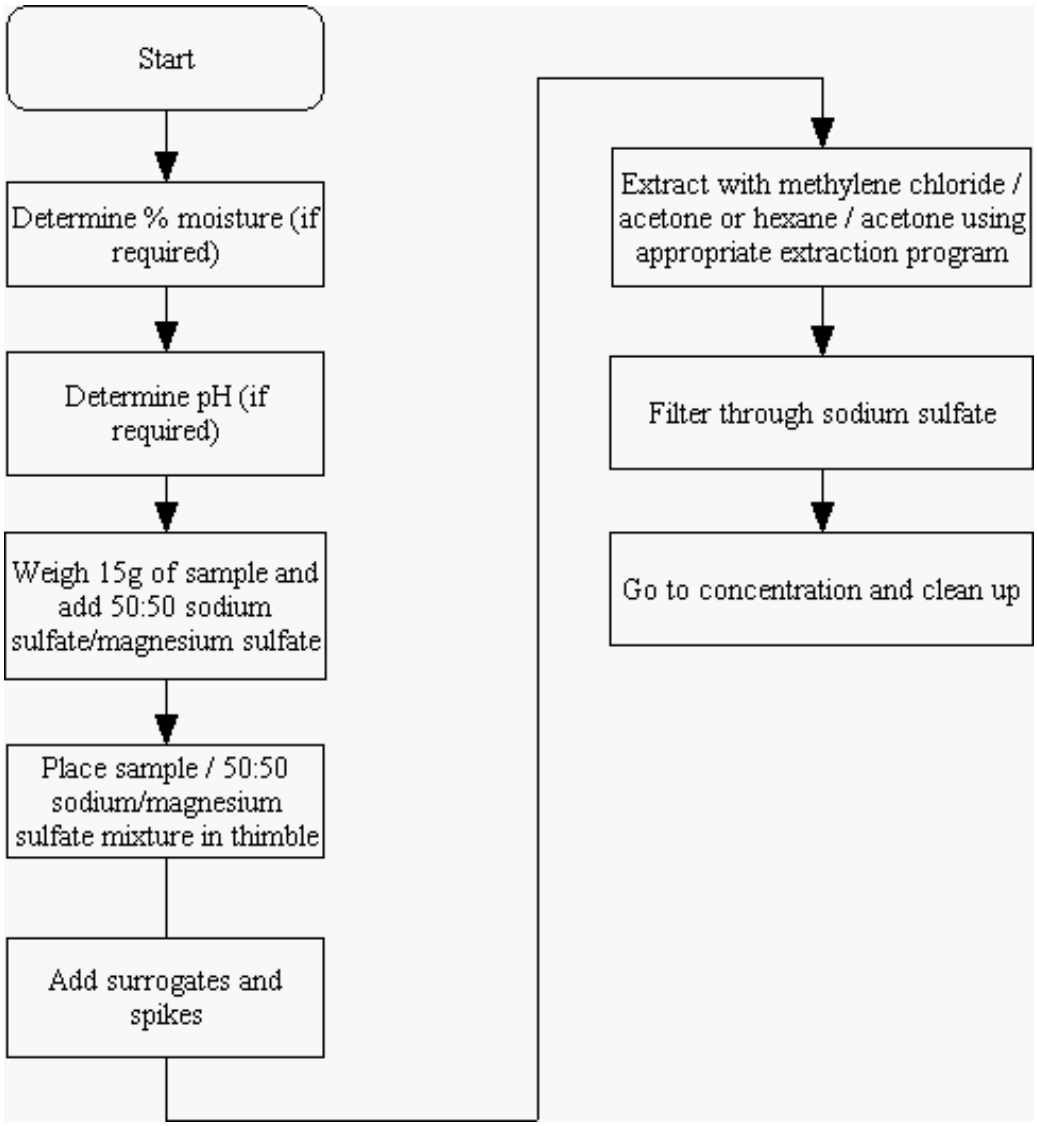
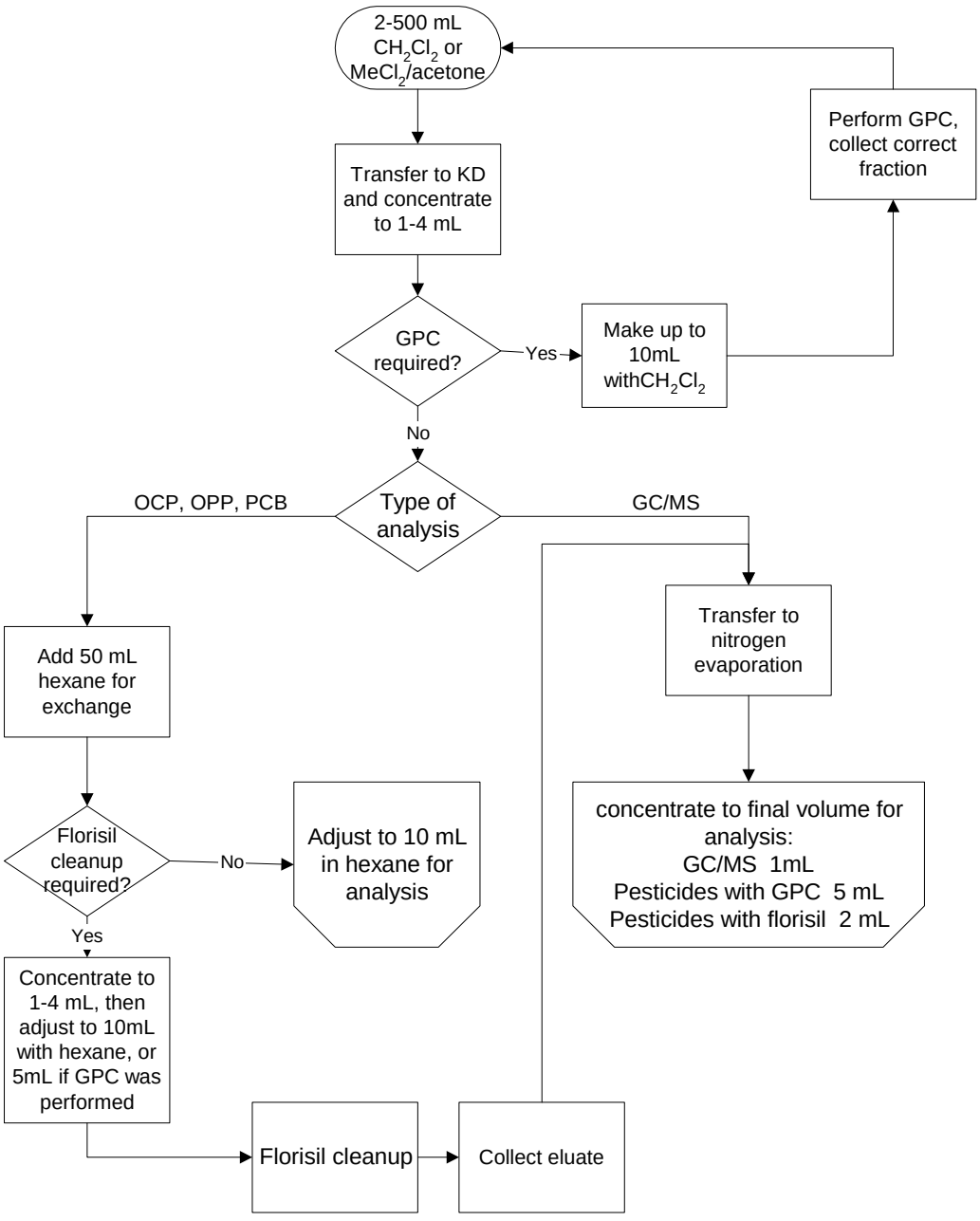


Figure 3 - Concentration and Cleanup



ATTACHMENT 1: MEMORANDUM from USEPA concerning Spiking Procedures in SW-846 Solid Extraction methods.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF SOLID WASTE
AND EMERGENCY RESPONSE

AUG 5 2010

MEMORANDUM

SUBJECT: Spiking (Prior To vs. After Sample Drying) Issue in SW-846 Organic Extraction Methods

FROM: James Michael, Chief, Waste Characterization Branch
Materials Recovery and Waste Management Division (MC-5304P)
Office of Resource Conservation and Recovery, USEPA

TO: EPA Regional Laboratory Directors I-X
EPA Regional QA Officers I-X
User Community for the SW-846 Methods Manual

This letter is to inform you that the Office of Resource Conservation and Recovery (ORCR, formally OSW) is currently evaluating a quality control (QC) spiking inconsistency that commercial and EPA regional laboratories raised for the extraction of semivolatile and nonvolatile organic compounds in solids. In the interim, we are recommending that you not follow the cautionary notes in three SW-846 methods, specifically the notes in Section 9.3.1 of Method 3500C (for organic extraction and sample preparation), and Section 11.5 of Method 3545A (pressurized fluid extraction) and Section 11.3 of Method 3550C (ultrasonic extraction).

These cautionary notes were inserted into three Update IV SW-846 methods that were published on January 3, 2008 (73 FR 486-489). These notes state that, "it is CRITICAL that any compounds added to a sample, including surrogates, are added to the sample aliquot PRIOR TO any additional processing steps. This means that the surrogates and matrix spike compounds should be added to the sample PRIOR TO adding drying agents such as sodium sulfate to solid samples." The note in Method 3500C further states that, "As each 3500 series extraction procedure is revised, the order of the procedural steps will be made consistent with this note. However, until such time as all those methods are revised, the instructions in this note SUPERSEDE those in each extraction method."

Commercial and EPA Regional laboratories have pointed out that adding surrogates and other spiked compounds to environmental and QC samples prior to mixing with drying agents may cause major recovery issues depending on the analyte and/or the matrix. Additional instructions requiring evaporation of the solvent from the surrogate and spiking solutions compound the problem. For example, when the spike solutions are added to a clay sample, they may roll off without absorption to the matrix. The spiking solvent could evaporate quickly, before the solutions can be effectively mixed with the sample. Spiking in this manner has been

shown to cause considerable losses of the more volatile and light-sensitive compounds, resulting in poor recovery. One study showed recovery for more than 1/3 of the semivolatile analyte list can easily drop 50-100%.

In addition, we found that there is no such cautionary note in two other organic extraction methods that were published at the same time as the three above mentioned methods. These two methods, specifically Methods 3546 (microwave extraction) and 3562 (super critical fluid extraction), recommend spiking surrogates and other compounds after the sample drying procedure.

At this time ORCR is evaluating the information and records that were used in support of said spiking procedural change; communicating with commercial labs; and reviewing Department of Defense and Contract Laboratory Program protocols to verify what spiking protocols the analytical community is following. We plan on working with commercial and EPA Regional laboratories to acquire data for ORCR's consideration to resolve this spiking inconsistency and revise those three methods as necessary. Until that time, ORCR recommends that you not follow the language in these notes.

Should you have question regarding this issue, please contact Shen-yi Yang, of my staff at (703) 308-0437.

cc: Shen-yi Yang, MRWMD
Kim Kirkland, MRWMD
Charles Sellers, MRWMD
Mark Baldwin, MRWMD

2

Title: Cleanup of Organic Compounds from Waters, Solids, Sediments, Tissue and Wipes

Method(s): SW846 3600 Series and CarboPrep 90

Approvals (Signature/Date):

11/4/2015	11/4/2015
Sharon Bacha Date	Steve Jackson Date
Organics Department Manager	Regional Safety Coordinator
11/4/2015	11/4/2015
Virginia Zusman Date	Deborah L. Lowe Date
Quality Assurance Manager	Laboratory Director

This SOP was formerly part of PT-OP-001

1.0 SCOPE AND APPLICATION

1.1 This SOP describes cleanup procedures that are appropriate for the target analytes of interest. These cleanup procedures are applied to the extracts prepared by one of the extraction methods, to eliminate sample interference.

1.2 Cleanup procedures for the following determinative methods are covered: 8081A, 8081B, 8082, 8082A, 8082A Congeners, 8141A, 8141B, 8270C and 8270D.

1.3 On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated PT-QA-M-001, Quality Assurance Manual.

2.0 SUMMARY OF METHOD

2.1 Cleanup Procedures are presented for removing interferents from sample extracts.

3.0 DEFINITIONS

3.1 Definitions of terms used in this SOP may be found in the glossary of the Pittsburgh Quality Assurance Manual (PT-QA-M-001).

3.2 TALS – TestAmerica Laboratory Information Management System

3.3 NCM – Non-Conformance Memo – a system within TALS for the lab to communicate to project management and others when there is an anomaly seen with the samples or batch or a QC failure.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2 Florisil and Silica Gel cartridges may contain phthalate esters which can interfere with many method analytes, not just the phthalate esters themselves; the copper technique for sulfur cleanup requires that the copper powder be very reactive, however care must be taken to remove all traces of the acid used to prepare the copper in order to avoid degradation of some analytes; the sulfuric acid/permanganate technique will not destroy chlorinated benzenes, chlorinated naphthalenes and a number of chlorinated pesticides; and the CarboPrep Cartridge method interferes with TCMX surrogate recovery, however the Carboprep Quick method does not show the same issue.

5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-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.

5.2 Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

5.3 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[i]	Signs and symptoms of exposure
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.
Florisil	**Irritant**	**TLV 10mg/m^3 PEL 5mg/m^3**	**May cause irritation if inhaled or adsorbed through the skin.**
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.
Sulfuric Acid[ii]	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.
Copper Powder	Flammable Irritant	1 mg/m^3 - TWA	If swallowed, wash out mouth with water, provided person is conscious, then call a physician; if inhaled, remove to fresh air, CPR if not breathing and oxygen if difficulty in breathing; In case of skin contact, flush the affected area for 15 minutes with water. Remove contaminated clothing and shoes and call a physician; In case of contact with the eyes, flush with water for at least 15minutes. Assure adequate flushing by separating the eyelids with the fingers. Call a physician.
Tetrabutyl-ammonium hydrogen sulfate	Irritant	None listed	Irritant to the skin, eyes, digestive tract (if swallowed) and respiratory tract (if inhaled). Flush skin and eyes with water for 15 minutes, then seek medical attention; If ingested, DO NOT induce vomiting, instead rinse mouth and drink 2-4 cupfuls of milk or water, then seek medical attention; If inhaled, get fresh air immediately. If difficulty in breathing persists give oxygen then seek medical attention.
Sodium sulfite	Irritant	5 mg/m^3 - TWA	Inhalation may cause irritation to the mucous membranes of the upper respiratory tract. Ingestion may cause gastric irritation by the liberation of sulfurous acid. Large doses may result in circulatory disturbances, diarrhea and CNS depression. Estimated fatal dose is 0.5 to > 5g/kg. May cause skin and eye irritation, redness and pain.
Potassium Permanganate	Oxidizer	5 mg/m^3 – for Mn compounds	Causes irritation to the respiratory tract. Symptoms may 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.
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.

[i] Exposure limit refers to the OSHA regulatory exposure limit.
[ii] Always add acid to water to prevent violent reactions.

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 become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor or EH&S coordinator.

6.0 EQUIPMENT AND SUPPLIES

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Equipment and Supplies for Cleanup Procedures

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid	Silica Gel	CarboPrep 90	Acid-Base Partition
Gel permeation chromatography system (GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc. or Zymark Benchmate or equivalent).	X						
Bio Beads: (S-X3) -200-400 mesh, 70 gm (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent).	X						
Chromatographic column: 700 mm x 25 mm ID glass column. Flow is upward.	X						
Ultraviolet detector: Fixed wavelength (254 nm) and a semi-prep flow-through cell.	X						
Strip chart recorder, recording integrator, or laboratory data system.	X						
Syringe: 10 mL with Luerlok fitting.	X						
Syringe filter assembly, with disposable 5 um filter discs, Millipore No. LSWP 01300 or equivalent.	X						
Chromatographic column: 250 mm long x 10 mm ID; with Pyrex glass wool at the bottom and a Teflon stopcock (for silica gel cleanup).	X						
Vacuum system for eluting multiple cleanup cartridges. Vac Elute Manifold - Analytichem International, J.T. Baker, or Supelco (or equivalent). The manifold design must ensure that there is no contact between plastics containing phthalates and sample extracts.		X					
Vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.		X					
Vacuum pressure gauge.		X					
Rack for holding 10 mL volumetric flasks in the manifold.		X					
Mechanical shaker or mixer: Vortex Genie or equivalent.			X	X			
Separatory Funnels with Ground-Glass Stoppers: 125 m L or 250 mL			X				X

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid	Silica Gel	CarboPrep 90	Acid-Base Partition
Erlenmeyer Flasks: 125 mL	X						X
Disposable Pipettes		X	X	X			
Culture tubes: 10 mL, 16 mmx100 mm	X	X	X	X	X	X	
0.45µm syringe filter						X	

7.0 REAGENTS AND STANDARDS

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

7.1 Reagents for Cleanup Procedures

REAGENTS	GPC	Florisil	Sulfur	Acid	Silica Gel	CarboPrep 90	Acid-Base Partition
Methylene Chloride	X						X
Florisil: 500 mg or 1 g cartridges with stainless steel or Teflon frits (catalog 694-313, Analytichem, 24201 Frampton Ave., Harbor City, CA, or equivalent.)		X					
Tetrabutylammonium hydrogen sulfate			X				
Sodium sulfite			X				
Tetrabutylammonium (TBA) sulfite reagent: Prepare reagent by dissolving 3.39 g of Tetrabutylammonium hydrogen sulfate in 100 mL organic-free reagent water. Extract this solution 3 times with 20 mL portions of hexane. Discard the hexane extracts. Add 25 g sodium sulfite to the water solution.			X				
2-Propanol			X				
Copper powder: remove oxides (if powder is dark) by treating with 1N nitric acid, rinse with organic-free reagent water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.						X	
Sulfuric acid, Concentrated				X			
Sodium hydroxide, Pellets		X					
Sodium hydroxide, 10N: Dissolve 40 g of NaOH in 100 mL of reagent water		X					X
Silica Gel Cartridge – Restek Part No. 24038					X		
Hexane				X	X		
CarboPrep 90 SPE Cartridge						X	
CarboPrep 90 Bulk Reagent						X	
1 :1 Sulfuric Acid							X

7.2 Standards

7.2.1 GPC calibration solution: prepare or purchase a solution in methylene chloride that contains the following analytes in the concentrations listed below:

Analyte	mg/mL
Corn Oil	25.0
Bis (2-ethylhexyl) phthalate	1.0
Methoxychlor	0.2
Perylene	0.02
Sulfur	0.08

NOTE: Sulfur is not very soluble in methylene chloride; however, it is soluble in warm corn oil. Therefore, weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds. This standard expires 6 months after preparation.

8.0 SAMPLE COLLECTION PRESERVATION, SHIPMENT AND STORAGE

8.1 Holding Times are not applicable to Cleanup procedures.

9.0 QUALITY CONTROL

9.1 All QC extracted with the sample batch according to SOP PT-OP-001 or PT-OP-026 is put through the clean-up procedure along with the samples.

10.0 PROCEDURE

10.1 Cleanup Techniques may be used to remove interfering peaks, and /or to remove materials that may cause column deterioration and/ or loss of detector sensitivity.

10.2 Gel Permeation Chromatography (GPC)

GPC is a generally applicable technique which can be used for cleanup of extracts for Semivolatiles (8270), Organochlorine pesticides (8081A/8081B), PCBs (8082/8082A), and Organophosphorus Pesticides (8141A/8141B) analysis. It is capable of separating high molecular weight material from the sample analytes, and so is particularly useful if tissue or vegetable matter is part of the sample, and for many soil samples.

Note: GPC systems include the GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc., or equivalent. For GPC instrument operation see Appendix A.

10.2.1 GPC Column Preparation

10.2.1.1 Weigh out 70 g of Bio Beads (SX-3) into a 400-mL beaker.

10.2.1.2 Add approximately 300 mL of methylene chloride and stir gently.

10.2.1.3 Cover with aluminum foil and allow the beads to swell for a minimum of two hours. Maintain enough solvent to sufficiently cover the beads at all times.

10.2.1.4 Position and tighten the outlet bed support (top) plunger assembly in the tube by inserting the plunger and turning it clockwise until snug. Install the plunger near the column end but no closer than 5 cm (measured from the gel packing to the collar).

10.2.1.5 Turn the column upside down from its normal position with the open end up. Place the tubing from the top plunger assembly into a waste beaker below the column.

10.2.1.6 Swirl the bead/solvent slurry to get a homogeneous mixture and pour the mixture into the open end of the column. Transfer as much as possible, with one continuous pour, trying to minimize bubble formation. Pour enough to fill the column. Wait for the excess solvent to drain out before pouring in the rest. Add additional methylene chloride to transfer the remaining beads and to rinse the beaker and the sides of the column. If the top of the gel begins to look dry, add more methylene chloride to rewet the beads.

10.2.1.7 Wipe any remaining beads and solvent from the inner walls of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

10.2.1.8 Push the plunger until it meets the gel, and then compress the column bed about 4 cm.

10.2.1.9 Connect the column inlet to the solvent reservoir and place the column outlet tube in a waste container. Pump methylene chloride through the column at a rate of 5 mL/min. for one hour.

10.2.1.10 After washing the column for at least one hour, connect the column outlet tube to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. Placing a restrictor (made from a piece of capillary tubing of 1/16"OD x 10/1000”ID x 2”) in the outlet tube from the UV detector will prevent bubble formation, which causes a noisy UV baseline. The restrictor will not affect the flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi back-pressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

10.2.1.11 When the GPC column is not to be used for several days, connect the column inlet and outlet lines to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, re-swelled, and re-poured as described above. If drying occurs, pump methylene chloride through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify that retention volumes have not changed.

10.2.2 Initial Calibration of the GPC Column

10.2.2.1 Before use, the GPC must be calibrated based on monitoring the elution of standards with a UV detector connected to the GPC column.

10.2.2.2 Pump solvent through the GPC column for 2 hours. Verify that the flow rate is 4.5-5.5 mL/min. Corrective action must be taken if the flow rate is outside this range. Record the column pressure (should be 6-10 psi) and room temperature (22^{o}C is ideal).

Note: Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared.

10.2.2.3 Inject the calibration solution and retain a UV trace that meets the following requirements (See resolution calculation in section 10.1.1.7.1):

10.2.2.4 Peaks must be observed and should be symmetrical for all compounds in the calibration solution.

10.2.2.5 Corn oil and phthalate peaks must exhibit >85% resolution.

10.2.2.6 Phthalate and methoxychlor peaks must exhibit >85% resolution.

10.2.2.7 Methoxychlor and perylene peaks must exhibit >85% resolution.

10.2.2.8 Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

10.2.2.9 A UV trace that does not meet the above criteria indicates the need for system maintenance and/or the need for a new column.

10.2.3 Determine appropriate collect and dump cycles.

10.2.3.1 The calibrated GPC program for organochlorine pesticides/PCB Aroclors should dump >85% of the phthalate and should collect >95% of the methoxychlor and perylene. Use a wash time of 10 minutes.

10.2.3.2 For GC/MS semivolatile and PAHs by HPLC extracts, initiate a column eluate collection just before the elution of bis (2-ethylhexyl) phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Stop collection before sulfur elutes. Use a wash time of 10 minutes after the elution of sulfur.

10.2.3.3 For PCB Congeners and Organophosphorus pesticides, this collection window should be appropriate but needs to be verified with spike solutions containing all analytes of interest.

10.2.3.4 Reinject the calibration solution after appropriate dump and collect cycles have been set.

10.2.3.5 Measure and record the volume of collected GPC eluate in a graduated cylinder.

10.2.3.6 The retention times for both bis(2-ethylhexyl) phthalate and perylene must not vary more than +/- 5% between calibrations.

10.2.4 GPC calibration check

10.2.4.1 Check the calibration of the GPC immediately after the initial calibration and at least every 7 days thereafter, while the column is in use. Ensure that UV trace requirements, flow rate and column pressure criteria are acceptable. Also, the retention time shift must be <5% when compared to retention times in the last calibration (previous week) UV trace. This means checking the retention time shift against the previous week's calibration and the RT shift must be <5%.

10.2.4.2 Inject the calibration solution, and obtain a UV trace. If the retention times of bis(2-ethylhexyl)phthalate or perylene have changed by more than ± 5% use this run as the start of a new initial calibration. Otherwise, proceed with the

recovery check. Excessive retention time shifts may be caused by poor laboratory temperature control or system leaks, an unstabilized column, or high laboratory temperature causing outgassing of methylene chloride. Pump methylene chloride through the system and check the retention times each day until stabilized.

10.2.5 GPC Recovery Check for Organochlorine Pesticides/ PCB Aroclors

10.2.5.1 The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Two recovery check solutions are used. The first mixture is prepared by diluting 1.0 mL of the organochlorine pesticide matrix spiking solution (See PT-OP-WI-001) to 10 mL in methylene chloride. The second mixture is prepared by diluting 1 mL of the PCB Aroclor matrix spiking solution (see PT-OP-WI-001) to 10 mL with methylene chloride.

10.2.5.2 Load the pesticide matrix spike mixture, the PCB mixture, and a methylene chloride blank onto the GPC using the GC dump and collect values.

Note: If the analysis is for PCB Aroclors only, then the pesticide recovery check is not necessary.

10.2.5.3 After collecting the GPC calibration check fraction, concentrate, solvent exchanging to hexane. Adjust the final volume to 5.0 mL, and analyze by GC/EC. Refer to concentration, section 10.2.

10.2.5.4 The methylene chloride blank may not exceed more than one half the reporting limit of any analyte. And if the recovery of each of the single component analytes is 80-110% and if the Aroclor pattern is the same as previously run standards, then the analyst may use the column. If the above criteria are not met, there may be a need for system maintenance.

10.2.6 GPC Recovery Check for All other Semivolatiles

10.2.6.1 The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Dilute 1.0 mL of the GC/MS semivolatiles matrix spiking solution (PT-OP-WI-001) to 10 mL in methylene chloride for GC/MS Semivolatiles and PAHs by HPLC. For PCB Congeners and Organophosphorus pesticides, a solution containing all analytes of interest should be prepared in 10 mL of methylene chloride.

10.2.6.2 Load the spike mixture and a methylene chloride blank onto the GPC using the semivolatiles dump and collect values.

10.2.6.3 After collecting the GPC recovery check fraction, concentrate to 0.5 mL, and analyze by GC/MS for the GC/MS Semivolatiles and PAHs by HPLC. Analyze by GC/ECD for the PCB Congeners and GC/FPD for the Organophosphorus pesticides. Refer to the concentration section 10.2.

10.2.6.4 Recovery of the spiked analytes should be at least 60%. The blank should not contain any analytes at or above the reporting limit. If these conditions are met the column may be used for sample analysis. Otherwise correct the contamination problem, or extend the collect time to improve recovery of target analytes.

10.2.7 Sample Extract Cleanup

10.2.7.1 Reduce the sample extract volume to 1-2 mL, then adjust to 10 mL with methylene chloride prior to cleanup. This reduces the amount of acetone in the extract. Refer to section 10.2.

10.2.7.2 Start the pump and let the flow stabilize for 2 hours. The solvent flow rate should be 4.5-5.5 mL/min. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22^{o}C. The normal backpressure is 6-10 psi.

10.2.7.3 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol:water solution (by visual comparison) must be diluted and loaded into several loops.

10.2.7.4 Samples being loaded onto the GPC should be filtered with a 5 micron (or less) filter disk. Attach a filter to a 10 mL Luerlok syringe and filter the 10 mL sample extract into the sample tube.

10.2.7.5 Load the filtered samples into the proper sample tubes and place on the GPC.

Note: For the GPC Autoprep Model 1002A, wash the loading port with methylene chloride after loading each sample loop in order to minimize cross contamination. This step is automated on the GPC Autoprep 1002B.

10.2.7.6 Set the collect, dump, and wash times determined by the calibration procedure.

10.2.7.7 Switch to the run mode and start the automated sequence. Process each sample using the collect and dump cycle times established by the calibration procedure.

10.2.7.8 Collect each sample in a suitable glass container. Monitor sample volumes collected.

10.2.7.9 Any samples that were loaded into 2 or more positions must be recombined.

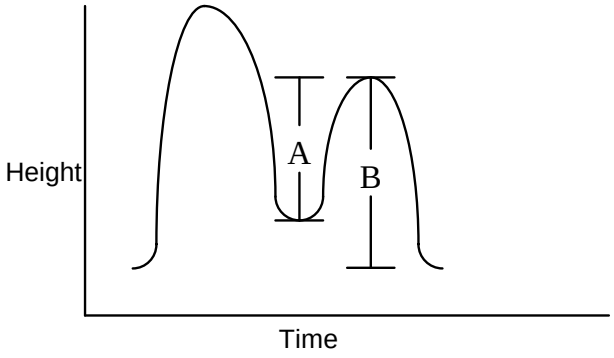
10.2.7.10 Concentrate semivolatile sample extracts to 0.5 mL in methylene chloride. Refer to the concentration section 10.2.

10.2.7.11 Solvent exchange pesticide/PCB sample extracts into hexane and concentrate to 5.0 mL. Refer to the concentration section 10.2.

10.2.8 Calculations

10.2.8.1 Resolution: To calculate the resolution between two peaks on a chromatograph, divide the depth of the valley between the peaks by the peak height of the smaller peak being resolved and multiply by 100.

Resolution Calculation



$$\% \text{ Resolution } = \frac{A}{B} \times 100$$

Where: A = depth of valley to height of smaller peak

B = peak height of smaller peak

10.2.8.2 Dump Time

Mark on the chromatograph the point where collection is to begin. Measure the distance from the injection point. Divide the distance by the chart speed. Alternatively the collect and dump times may be measured by means of an integrator or data system.

$$\text{Dump time (min)} = \frac{\text{Distance (cm) from injection to collection start}}{\text{Chart speed (cm / min)}}$$

10.2.8.3 Collection Time

$$\text{Collection time (min)} = \frac{\text{Distance (cm) between collection start and stop}}{\text{Chart speed (cm / min)}}$$

10.3 Florisil Cartridge Cleanup

Florisil cleanup is generally used for organochlorine pesticides (8081A/8081B/608) and PCB (8082/8082A/608), although it may be applied to other analytes. It separates compounds of different polarity from the target analytes. Sections 10.2.1 through 10.2.8 outline the procedure for organochlorine pesticides, while section 10.2.9 outlines modifications required for PCBs.

Note 1: Systems for eluting multiple cleanup cartridges include the Supelco, Inc. Solid Phase Extraction (SPE) assembly, or equivalent.

10.3.1 Before Florisil cleanup sample volume must be reduced to 10 mL (5 mL if GPC cleanup was used) and the solvent must be hexane. Refer to SOP PT-OP-001 or PT-OP-026 for details of extract concentration.

10.3.2 Attach a vacuum manifold to a vacuum pump or water aspirator with a trap installed between the manifold and the vacuum. Adjust the vacuum in the manifold to 5-10 psi.

10.3.3 Place one Florisil cartridge into the vacuum manifold for each sample extract. Prior to cleanup of samples, pre-elute each cartridge with 5 mL of hexane/acetone (9:1). Adjust the vacuum applied to each cartridge so that the flow through each cartridge is approximately 2 mL/min. Do not allow the cartridges to go dry.

10.3.4 Just before the cartridges go dry, release the vacuum to the manifold and remove the manifold top.

10.3.5 Place a rack of clean labeled 12 mL concentrator tubes into the manifold and replace the manifold top. Make sure that the solvent line from each cartridge is placed inside the appropriate tube.

10.3.6 After the clean tubes are in place, vacuum to the manifold is restored and 2.0 mL of the extract is added to the appropriate Florisil cartridge.

10.3.7 The organochlorine pesticides/aroclors in the extract concentrates are then eluted through the column with 8 mL of hexane/acetone (90:10) and are collected into the 10 mL culture tube or concentrator tube held in the rack inside the vacuum manifold.

10.3.8 Transfer the extract to a graduated concentrator tube and concentrate the extract to 2 mL. Refer to the N-evap concentration Section 10.3.

Note 1: A cartridge performance standard must be run with each lot of Florisil cartridges.

Note 2: Florisil cartridge performance check--every lot number of Florisil must be tested before use. Add 0.5 ug/mL of 2,4,5-trichlorophenol solution and 0.5 mL of Organochlorine Pesticide Calibration Standard Mix A (midpoint concentration) to 4 mL hexane. Reduce volume to 0.5 mL. Add the concentrate to a pre-washed Florisil cartridge and elute with 9 mL hexane/acetone [(90:10)(v/v)]. Rinse cartridge with 1.0 mL hexane two additional times. Concentrate eluate to 1.0 mL final volume and transfer to vial. Analyze the solution by GC/EC. The test sample must show 80 to 120% recovery of all pesticide analytes with <5% trichlorophenol recovery, and no peaks interfering with target compounds can be detected. This standard has a lifetime of six months. Alternatively, this standard may be purchased as a stock solution.

10.3.9 Modifications for PCBs

Pre-elute the cartridge with 4 mL hexane. Add 2 mL of the sample extract and elute with 3 mL hexane. The eluant will contain the PCBs together with any heptachlor, aldrin, 4,4'DDE and part of any 4,4'DDT. Any BHC isomers, heptachlor epoxide, chlordane, endosulfan I and II, endrin aldehyde and endrin sulfate and methoxychlor will be retained on the column and can be eluted in a separate fraction with 8 mL 90:10 hexane:acetone if required.

10.4 Sulfur Removal

Sulfur cleanup is generally applied to sample extracts for analysis by methods 8081A/8081B, 8082/8082A, and 608 because the Electron Capture Detector (ECD) responds strongly to sulfur. It is performed after GPC and/or Florisil cleanup, if necessary.

10.4.1 Sulfur can be removed by one of two methods: copper or tetrabutylammonium sulfite (TBA) according to laboratory preference. The TBA procedure is the laboratory default procedure. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipette, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

10.4.2 Sulfur Removal with Copper

10.4.2.1 Transfer 1.0 mL of sample extract into a centrifuge or concentrator tube.

10.4.2.2 Add approximately 2 g of cleaned copper powder to the sample extract tube.

10.4.2.3 Mix for one minute on a mechanical shaker.

10.4.2.4 If the copper changes color, sulfur was present. Repeat the sulfur removal procedure until the copper remains shiny.

10.4.2.5 Transfer the supernate to a clean vial.

10.4.3 Sulfur Removal with Tetrabutylammonium (TBA) Sulfite Reagent

10.4.3.1 Transfer 1.0 mL of sample extract into a culture tube.

10.4.3.2 Add 1.0 mL TBA sulfite reagent and 2 mL 2-propanol to the sample extract. Cap and shake for 1 minute. If clear crystals (precipitated sodium sulfite) form, sufficient sodium sulfite is present.

10.4.3.3 If a precipitate does not form, add sodium sulfite in approximately 0.1g portions until a solid residue remains after repeated shaking.

10.4.3.4 Add 5 mL organic free reagent water and shake for 1 minute. Allow sample to stand for 5-10 minutes. (Centrifuge if necessary to separate the layers). Transfer the sample extract (top layer) to a vial. The final volume is defined as 1.0 mL in section 10.1.3.3.1.

10.5 Sulfuric Acid Cleanup

This cleanup is only performed on extracts requiring PCB analysis (Aroclors and Congeners) because most organic matter is destroyed by sulfuric acid.

10.5.1 Add approximately 2-5 mL of concentrated sulfuric acid to 2 mL of sample extract in a Teflon capped vial.

Caution: There must be no water present in the extract or the reaction may shatter the sample container.

10.5.2 Shake or vortex for about thirty seconds and allow extract to settle. (Centrifuge if necessary)

10.5.3 Remove the sample extract (top layer) from the acid using a Pasteur pipette and transfer to a clean vial.

10.5.4 **Caution:** It is not necessary to remove all the extract since the final volume is already determined. Transfer of small amounts of sulfuric acid along with the extract will result in extremely rapid degradation of the chromatographic column.

10.5.5 If the sulfuric acid layer becomes highly colored after shaking with the sample extract, transfer the hexane extract to a clean vial and repeat the cleanup procedure until color is no longer being removed by the acid, or a maximum of 5 acid cleanups.

10.5.6 Properly dispose of the acid waste.

10.6 Silica Gel Cleanup

This cleanup is only performed on extracts requiring PCB analysis (Aroclors and Congeners).

10.6.1 A 1g silica gel cartridge, Restek part number 24038 or equivalent, is utilized.

10.6.2 Condition the cartridge with 4 mL of Hexane. Slowly open the cartridge valves to allow the hexane to pass through the sorbent beds to the lower frit. Allow a few drops per cartridge to pass through the manifold to remove all air bubbles. Close the valves and allow the solvent to soak the entire sorbent bed for 5 minutes.

10.6.3 Slowly open cartridge valves to allow the hexane to pass through the cartridge. Close the cartridge valve when there is still approximately 1 mm of solvent above the sorbent bed.

10.6.4 Transfer 2 ml of sample to the cartridge. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2mL per minute.

10.6.5 When the entire extract has passed through the cartridge, but before the cartridge becomes dry, rinse the sample vial with 0.5mL of solvent, and add to the cartridge to complete the quantitative transfer.

10.6.6 Close the cartridge valve ensuring that the cartridge never goes dry.

10.6.7 Place a test tube into the sample rack corresponding to the cartridge position.

10.6.8 Add 5mL of hexane to the cartridge. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve and collect the eluate into the test tube. Close the cartridge valve. Remove sample and concentrate down to the final volume using an N-Evap, see section 10.3. This eluate will contain the PCBs as well as Heptachlor, Aldrin, 4,4'-DDE, and 4,4'-DDT.

10.7 CarboPrep 90 Cleanup

This cleanup is only performed on extracts requiring analysis for Organichlorine Pesticides and/or PCBs.

10.7.1 Cartridge Method

10.7.1.1 Put approximately 2 ml of sample extract into a test tube and mark the sample volume on the tube.

10.7.1.2 Condition the cartridge by adding 2 ml of methylene chloride and allowing it to drip through the cartridge. Do not allow the cartridge packing to go dry in this or any subsequent step, until the final rinse has been completed.

10.7.1.3 Add 2 ml of hexane/methylene chloride (80%/20%) mixture and allow it to drip through the cartridge until almost empty.

10.7.1.4 Add the sample extract to the cartridge and place the test tube under the cartridge to collect the liquid as it drips through.

10.7.1.5 Rinse 3 times with 2 ml aliquots of hexane/methylene chloride (80%/20%) mixture, while not allowing the cartridge to go dry. After the final rinse, use a pipette bulb to force out all of the remaining liquid in the cartridge.

10.7.1.6 Concentrate the sample extract back down to the original volume according to the mark on the test tube using the N-Evap process in section 10.3. The extract is now ready for analysis.

10.7.1.7 **NOTE:** When using the Carboprep Cartridge Method the recovery of the TCMX surrogate is poor.

10.7.2 Quick Method

10.7.2.1 Add a half scoop of Carboprep 90 to approximately 2 ml of sample extract. Swirl for about one minute and allow the extract to settle. Add a half scoop of Copper Granules to 1 mL of sample or a whole scoop to 2 mL of sample, cap the vial and shake vigorously for 2 miuntes. Pipette out an aliquot of extract and filter through a 0.45 µm syringe filter. The extract is now ready for analysis.

10.7.2.2 Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. Any affected samples are re-analyzed.

10.7.2.3 Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

10.7.2.4 Compounds extracted from the sample matrix to which the detector will respond, such as single-component chlorinated pesticides, including the DDT analogs (DDT, DDE, and DDD).

Note: A standard of the DDT analogs should be injected to determine which of the PCB or Aroclor peaks may be subject to interferences on the analytical columns used. There may be substantial DDT interference with the last major Aroclor 1254 peak in some soil and sediment samples.

10.8 Acid-Base Partition

10.8.1 Place 10 mL of the solvent extract from a prior extraction procedure into a 125 mL or 250 mL separatory funnel.

10.8.2 Add 20 mL of methylene chloride to the separatory funnel.

10.8.3 Slowly add 20 mL of prechilled DI water which has been previously adjusted to a pH of 12-13 with 10N sodium hydroxide.

10.8.4 Seal and shake the separatory funnel for at least 2 minutes with periodic venting to release excess pressure.

10.8.5 Allow the organic layer to separate from the aqueous phase for a minimum of 10 minutes. If the emulsion interface between layers is more the one-third the size of the solvent layer, use mechanical techniques such as stirring, filtration of the emulsion through glass wool, centrifugation or other physical methods to complete the phase separation.

10.8.6 Drain off the aqueous phase into a 125 Erlenmeyer flask. Repeat the extraction 2 more times using 20 mL aliquots of dilute sodium hydroxide (pH 12-13) collecting the aqueous into the same 125 mL Erlenmeyer flask as the initial phase.

10.8.7 Water soluble organic acids and phenols will be primarily in the aqueous phase. Base/neutral analytes will be in the methylene chloride. If the analytes of interest are only in the aqueous phase, discard the methylene chloride and proceed to section 10.8.8. If the analytes of interest are only in the methylene chloride, discard the aqueous phase and proceed to section 10.8.10.

10.8.8 Externally cool the 125 mL Erlenmeyer flask with ice while adjusting the aqueous phase to a pH of 1-2 with 1:1 Sulfuric Acid. Quantitatively transfer the cool aqueous phase to a clean 125 mL separatory funnel. Add 20 mL of methylene chloride to the separatory funnel and shake it for at least 2 minutes. Allow the methylene chloride to separate from the aqueous phase and collect the methylene chloride in an Erlenmeyer flask.

10.8.9 Add 20 mL of methylene chloride to the separatory funnel and extract a pH 1-2 a second and third time combining the extracts in the Erlenmeyer flask.

10.8.10 Dry the necessary fraction, acid or base/neutral, by passing it througha funnel containing anhydrous sodium sulfate. Collect the dried fraction in another Erlenmeyer flask. Rinse the Erlenmeyer flask which contained the solvent and pour through the anhydrous sodium sulfate to complete the quantitative transfer.

10.8.11 The fractions are now ready to be concentrated to the required final volume, proceed to section 10.9.

10.9 Concentration:

10.9.1 According to the type of sample and any cleanup procedures needed, different final solvents and volumes will be required. Refer to PT-OP-WI-001 for the appropriate final volumes and concentrations.

10.9.2 Refer to Figure 1 – Concentration and Cleanup flowchart.

11.0 CALCULATIONS / DATA REDUCTION

Not applicable

12.0 METHOD PERFORMANCE

12.1 The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilities – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

13.0 POLLUTION CONTROL

13.1 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" and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

13.2 Within the constraints of following the methodology in this SOP, use of organic solvents should be minimized.

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 PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1 Methylene Chloride extraction waste. This waste is collected in waste containers identified as "Methylene Chloride Waste", Waste #2.

14.1.2 Extracted water samples. This waste is collected in a waste container identified as "Extraction Water", Waste #35. The bottom organic layer is drained into a container identified as "Methylene Chloride Waste", Waste #2. The remaining aqueous layer is neutralized to a pH between 6 and 9 and discharged down lab sink/ drain.

14.1.3 Used sodium sulfate and glass wool or filter paper contaminated with methylene chloride from the extract drying step. This waste is collected in a container identified as "Lab Trash Waste", Waste #12.

14.1.4 Assorted flammable solvent waste from various rinses. This waste is collected in waste containers identified as "Mixed Flammable Solvent Waste", Waste 3.

14.1.5 Methylene chloride waste from various rinses. This waste is collected in waste containers identified as "Methylene Chloride Waste", Waste #2.

14.1.6 Spent sulfuric acid waste is collected in a container identified as "Acid Waste", Waste #5.

14.1.7 Miscellaneous disposable glassware contaminated with acids, caustics, solvents and sample residue. This waste is collected in a container identified as "Lab Trash Waste", Waste #12.

15.0 REFERENCES

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3600C, 3620B, 3640A, 3650B, 3660B, and 3665A

15.2 Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Update IV, Method 3620C, Rev. 3, February 2007

15.3 Restek CarboPrep 90 SPE Cartridge procedure

15.4 Pittsburgh Laboratory Quality Assurance Manual (PT-QA-M-001)

15.5 SOP PT-QA-001, Employee Training and Orientation

15.6 SOP PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability

15.7 SOP PT-QA-012, Selection and Calibration of Balances and Weights

15.8 SOP PT-QA-016, Nonconformance and Corrective Action System

15.9 SOP PT-QA-021, Quality Control Program

15.10 SOP PT-QA-026, Container Accuracy Verification – Gravimetric

15.11 SOP PT-QA-031, Internal Chain of Custody

15.12 Pittsburgh Facility Addendum EH&S Manual, PT-HS-001

15.13 PT-OP-WI-001, TestAmerica Pittsburgh Organic Prep Work Instruction for Initial/Final Volumes, Exchange Solvents, LCS and Matrix Spiking Components and Concentrations

16.0 METHOD MODIFICATIONS

16.1 None

17.0 ATTACHMENTS

17.1 Figure 1 – Concentration and Cleanup

17.2 Appendix A – GPC Operation

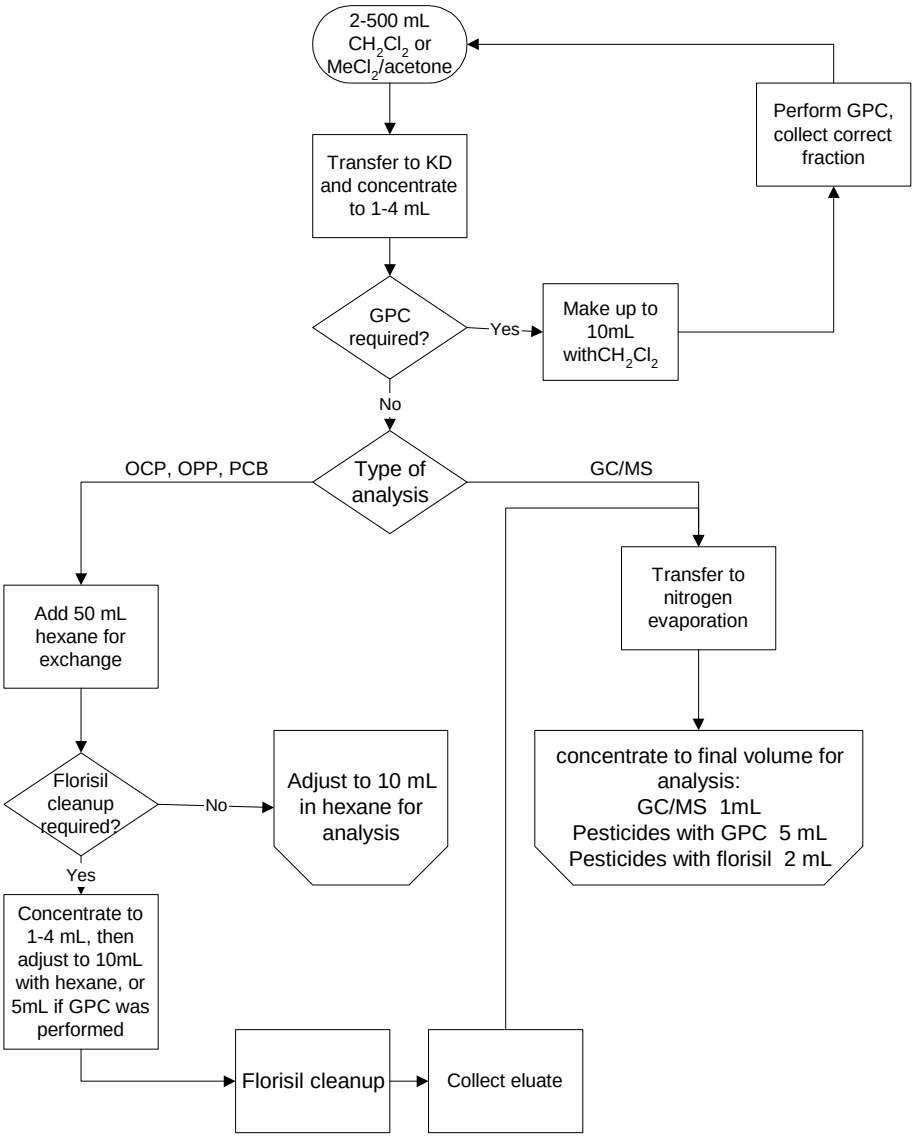
18.0 REVISION HISTORY

18.1 Original issue, 9/15/2015

18.2 Revision 1, 11/xx/2015

SOP section	Change from	Change to	Reason
Table under 5.3		Added NaOH to the Table	Correction
Table under section 6.1 and 7.1		Added the Acid-Base Partition equipment, supplies and reagents	Correction
10.8		Added Acid-Base Partition Procedure.	Correction
15.1		Added 3650B the Acid-Base Partition Method reference	Correction

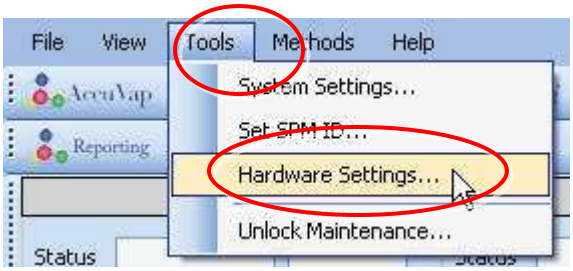
Figure 1 - Concentration and Cleanup



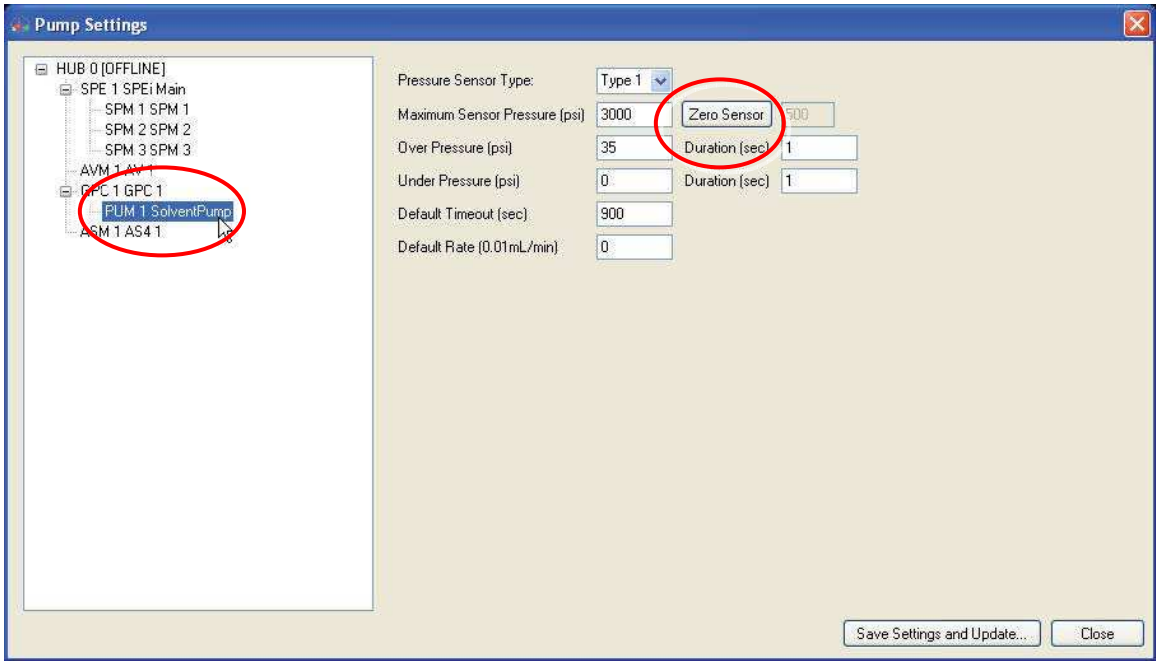
Appendix A
PrepLinc Software, J2 Brand, GPC Instrument Operation:

1. Fill the solvent reservoir with methylene chloride and allow the solvent to acclimate to room temperature.

2. Zero the solvent pump by clicking on Tools then Hardware Settings,



which will pop-up the Pump Settings Screen, where you will click on PUM 1 SolventPump and finally 'Zero Sensor' to zero the pressure when there is no back pressure on the system.

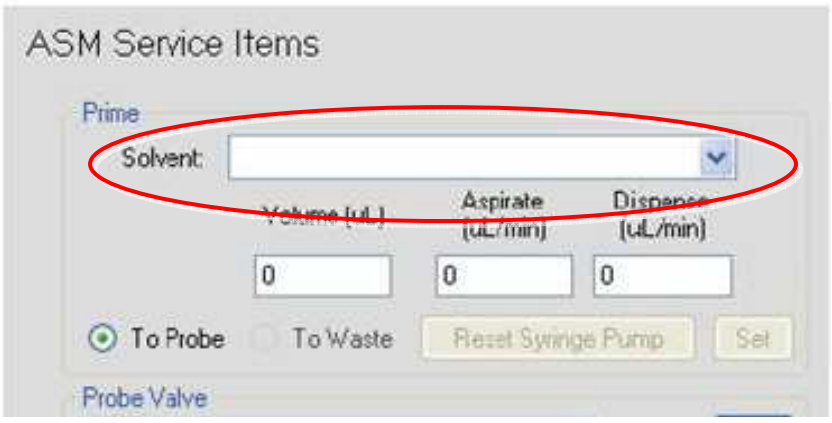


The pump should run for approximately one hour before starting the sequence to allow the pump to equilibrate. Equilibration allows the column pressure and the solvent flow rate to stabilize before the run begins.

3. Upon initialize the solvent pump the GPC column is also brought on line by clicking the GPC box, followed by the Sequence Editor box, then the Column Position box to place the column 'In-line'. Once the column is in position enter the flow rate, i.e. 5 mL/min, in the box next to the

Pump Rate button then click the Pump Rate button to prime the column. (see snapshot below).

4. Prime the syringe by first clicking the 'AS4' button, 'Service Items' then select the solvent to be used to prime the syringe and finally click 'Set' (see snapshot below). After the syringe finishes priming, the column pressure should read between 8 and 12 psi.



5. Load each sample in a disposable test tube after nitrogen blowdown. Pour 10 mls of sample in an empty test tube and mark all others using a calibrated tube.

6. Place the samples in the sample tray starting with the first sample in the front most left slot and place each successive sample behind the first working toward the back of the tray.

7. Follow the same procedure as in 10.2.5.7 for the placement of the corresponding collection tubes.

8. Enter a Sequence by clicking on the 

Sequence Editor icon on the Menu Toolbar.

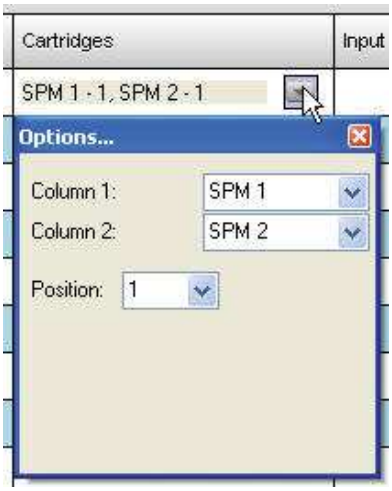
9. The Sequence Editor is where the sample processing is defined and the samples are cued. The Sequence Editor is in a spreadsheet-like format. The columns are defined as follows:

Sequence Editor

	Sample	Priority	Status	Device	Method	Inject Volume (uL)	Cartridges	Input Tray	Output Tray	Type	ID	Batch
1		☐	UNPROCESSED									
2		☐	UNPROCESSED									
3		☐	UNPROCESSED									
4		☐	UNPROCESSED									
5		☐	UNPROCESSED									
6		☐	UNPROCESSED									
7		☐	UNPROCESSED									
8		☐	UNPROCESSED									
9		☐	UNPROCESSED									
10		☐	UNPROCESSED									
11		☐	UNPROCESSED									
12		☐	UNPROCESSED									
13		☐	UNPROCESSED									

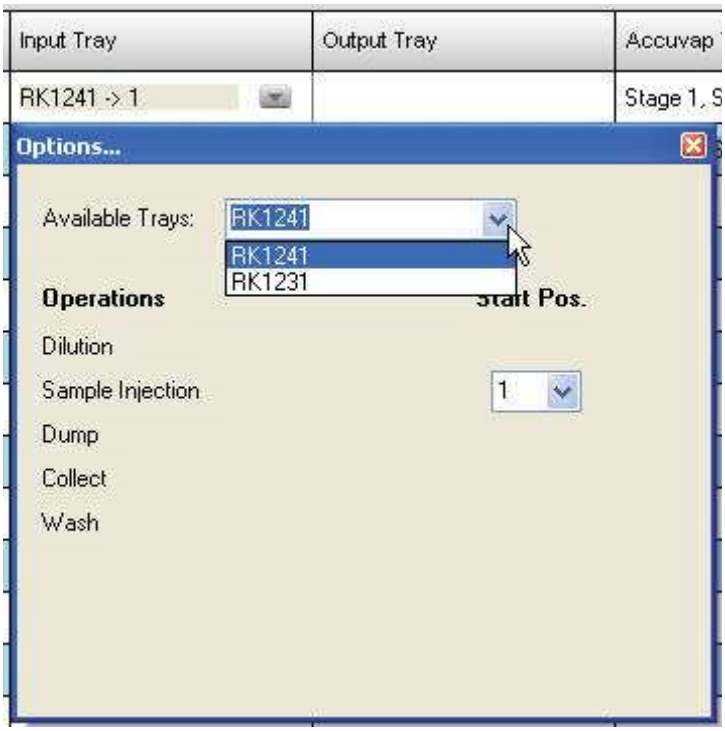
- Line ID #: The first column indicates the line number of the sequence. The line number does not always correspond to the sample number.
- Sample: Indicates the sample number. There can be multiple lines for a sample, like in the case of a Linc method that process samples through multiple methods on multiple devices.
- Priority: Check this box if the sample should be processed before other samples that are ahead of it in the que. The samples that are marked "Priority" will be processed in their numerical order.
- Status: Shows the status of the current sample. "Unprocessed", "Processing" or "Processed".
- Device: Select the device for the process. If a Linc method will be used, choose "Linc" from the list.
- Method: Choose the method for the sample to be processed with by clicking the folder icon and browsing for the method.
- Inject Volume: This field will automatically fill with the volume of sample defined in the chosen method.

- Click the down arrow to view options. It is possible to choose a different column number. The system will default to sample 1 being processed through column 1, etc.



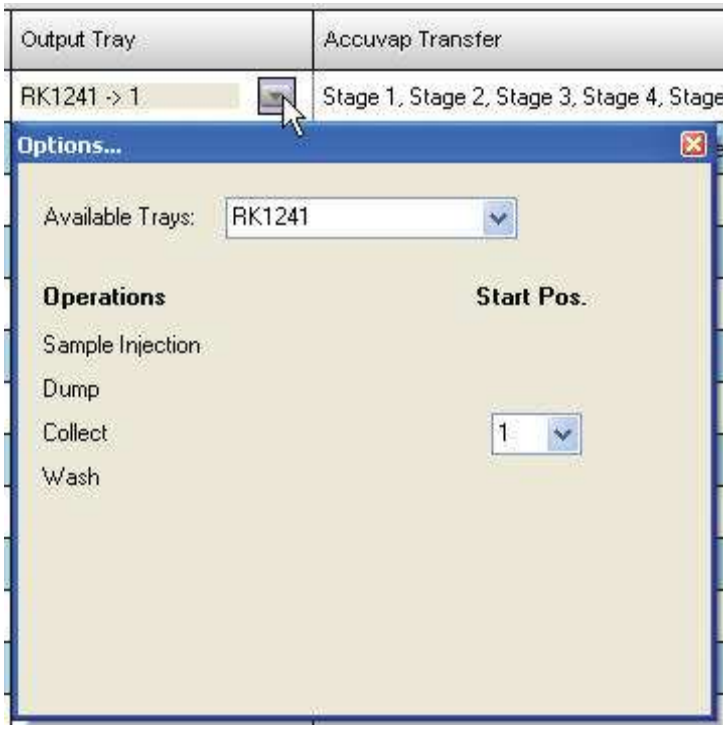
- Input: Click the down arrow to define the tray holding the sample and the position of the sample vial. Choose a tray from the drop-down list in the "Available Trays" field. A summary of the method will be displayed. To the right of the Sample Injection step there is a list of the vial positions to choose from. Choose the vial number for the specified tray where the sample will be located.

View for example GPC Method



- Output: Click the down arrow to define the tray where the sample will be collected after processing. This field will only be active when the AccuVap is **NOT** used for concentration prior to final collection.
- Choose a tray for the drop-down list in the "Available Tray" field. A summary of the method will be displayed. For every possible collection there will be a number choice to the right. Choose the vial where the sample will be collected. Multiple samples can be collected into the same vial, but care must be given to ensure the vial is large enough to hold all collections.

View for example GPC Method



- Type, ID and Batch: These fields are available for the user to define the sample in the sequence. Enter sample ID number, Batch identification number and Type of sample (QC,Blank, sample, etc). Or use these fields in any way desired for reporting purposes.

- Example Sequence Views -

GPC Only Method

Device	Method	Volume	Cartridges	Input	Output	Accuvap
GPC 1	Simple GPC	5000		RK1241 (90) - 1	RK1255 - 1	

Nothing is displayed in the "Cartridges" or "AccuVap" fields because the method does not involve these devices.

SPE Single Column Method

Device	Method	Volume	Cartridges	Input	Output	Accuvap
SPE 1	SPErevElu	004000	SPM_1 - 1	RK1241 (90) - 1	RK1255 - 1	

The "Cartridges" field shows that only one column is being used for each sample. The "AccuVap" field is blank.

GPC with SPE Method

Device	Method	Volume	Cartridges	Input	Output	Accuvap
GPC 1	GPCwSPE	000000	SPM_1 - 1	RK1241 (90) - 1	RK1255 - 1	

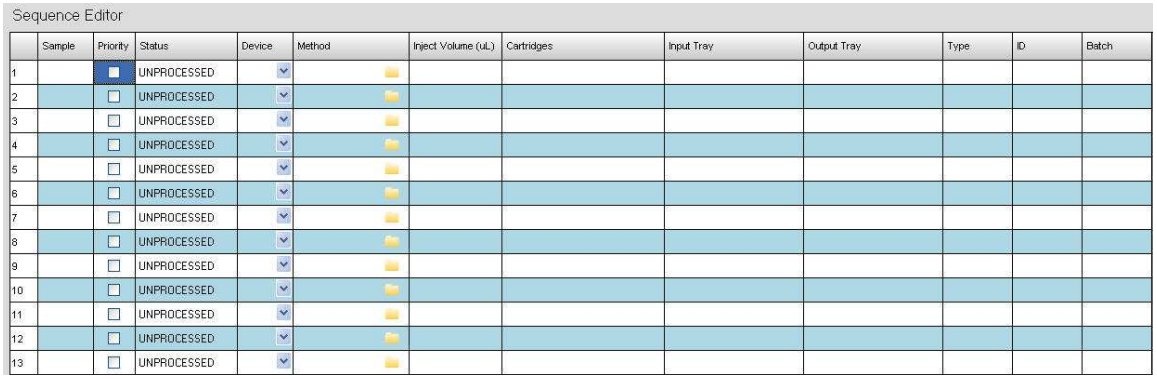
The "Cartridges" field shows which SPE column will be inline with the GPC for that GPC sample. The "AccuVap" field is blank.

GPC Column Calibration Method

Device	Method	Volume	Cartridges	Input	Output	Accuvap
GPC 1	CO770_CAL	5000		RK1241 (90) - 1		

Nothing is displayed in the "Cartridges" or "AccuVap" fields because the method does not involve these devices. There is nothing displayed in the "Output" field because there is no collect fraction for the method. When you click the down arrow there is no vial position number to choose from:

10. After all samples have been added to the sequence click 'Start' and you will then be prompted to name and save the sequence. Once the sequence has been saved, the GPC will automatically start the run.
11. As each sample is processed, the color on the sample tray will be light green and will change to dark green in the 'Status Column' after the sample processing is completed (see snapshot below).



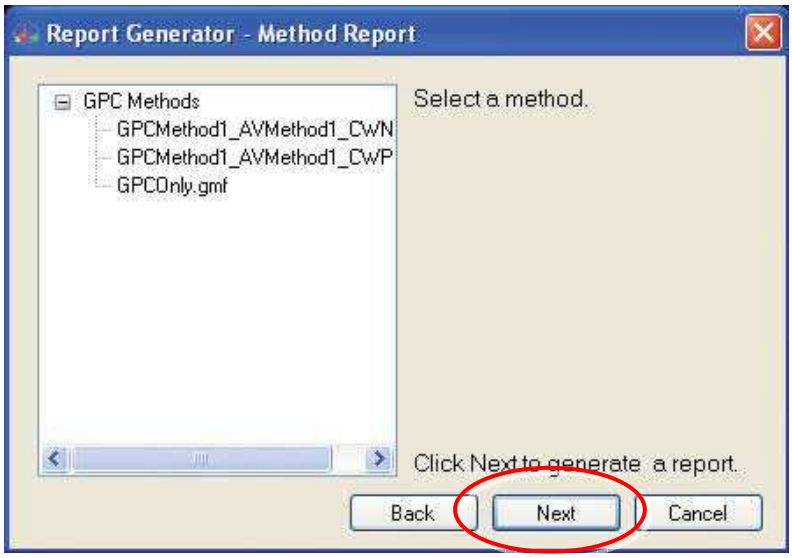
12. Reporting - The PrepLinc software contains a set of pre-defined reports that the user can print for a sequence, a particular sample or to see the parameters of a particular method.

- A Reporting Wizard guides the user through report creation. Click on the "Reporting" button on the toolbar.

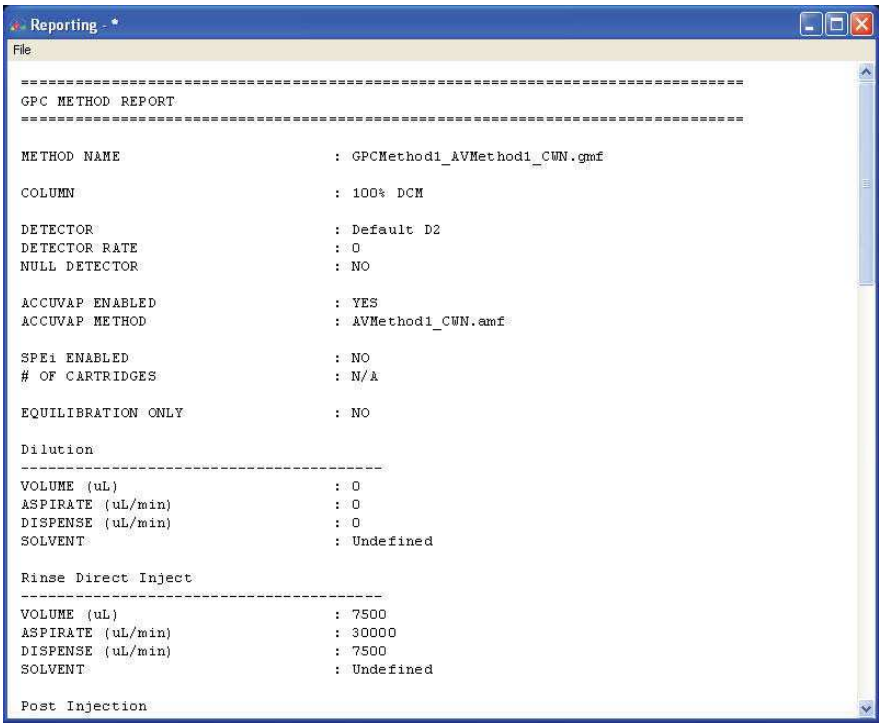
- From the first screen of the Wizard, select the report type you would like to generate.

- Method Report
  The method report lists all the parameters for the selected saved method. After choosing "Method Report" from the list, click the Next button.

  A list of the saved method for that module will be displayed. Click on the method desired for the report and click the Next button.



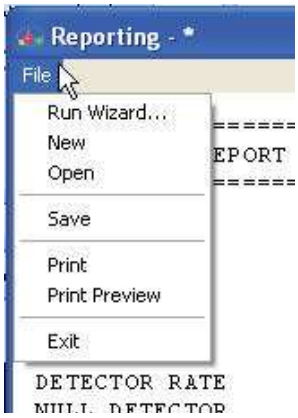
The report will appear in the “Report Generator” window.



The example report shown above is for a GPC Cleanup method. Every parameter available for a GPC method and it’s the corresponding value is listed.

- Printing & Saving Reports

To Print or Save the displayed report, click on the “File” drop-down menu button at the top of the Report Generator window. Select the action desired from the list.



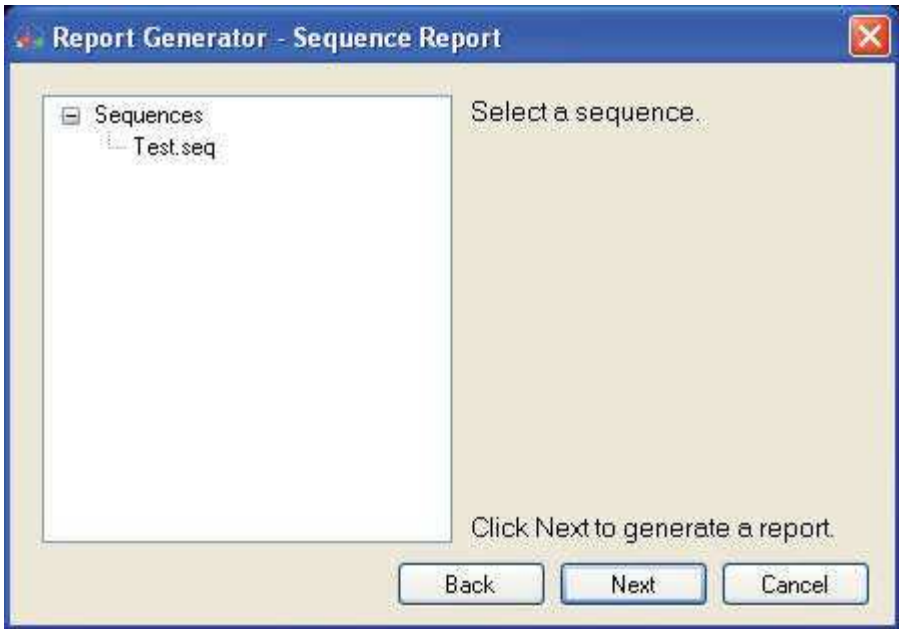
- Generate Another Report

From the File drop-down menu, choose “Run Wizard” to start the Reporting Wizard over again.

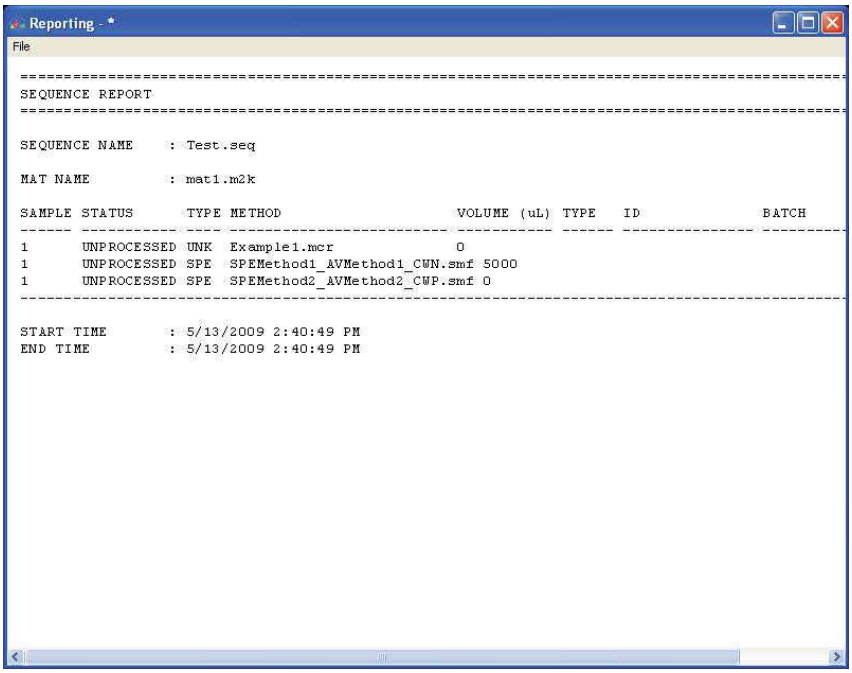
- Sequence Report

The Sequence Report is a list of all the samples processed, the method used to processes them and any errors that occurred during a given sequence. The Sequence Report also shows the time and date the sequence was processed. The Sequence Report can only be generated once the sequence is completed processing.

After choosing Sequence Report from the first screen of the Wizard, a list of completed sequences will be displayed. Choose the desired sequence and click the Next button.



The report will appear in the “Report Generator” window.

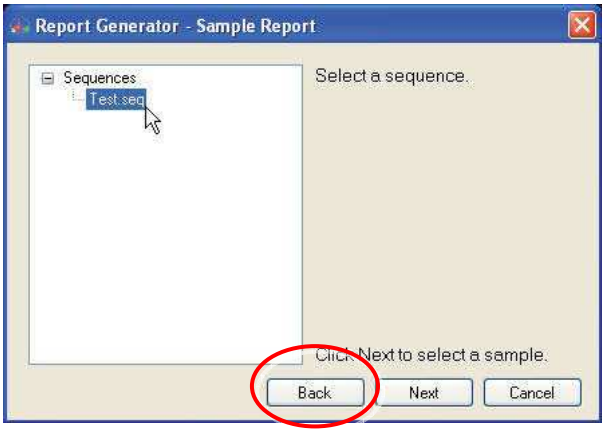


The example report above shows what will be reported for each sequence: Sequence Name, Mat Name, list of samples processed, Sequence Start and End times.

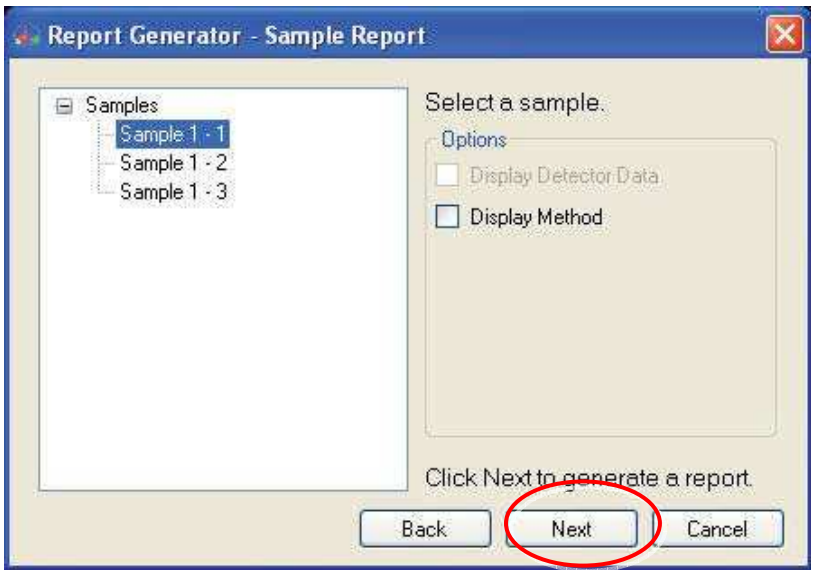
- Sample Report

The Sample Report lists details of a particular sample within a sequence.

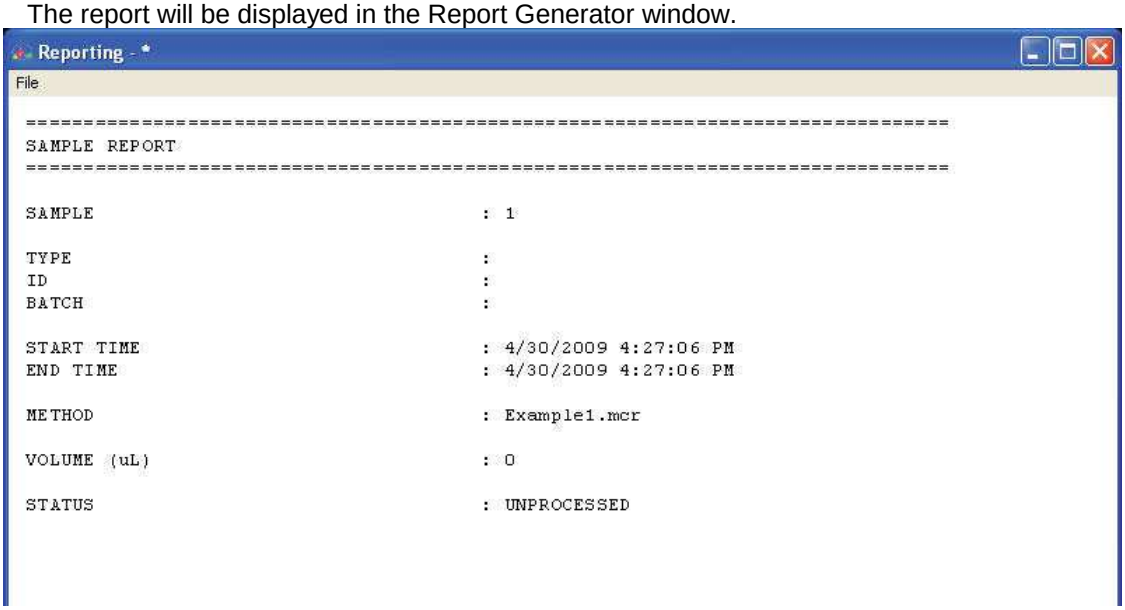
After choosing “Sample Report” from the first wizard screen, a list of processed sequences. Choose the sequence name in which the sample was processed and click the Next button.



A list of the samples processed in the chosen sequence will be displayed on the next screen. Choose the name of the sample desired for the report from the list. If there is detector data saved for the sample, the "Display Detector Data" check box will be active to the right. The option is also given to include detailed method information on the Sample Report. If either of these options are desired, click the appropriate check box and click the Next button.



The report will be displayed in the Report Generator window.

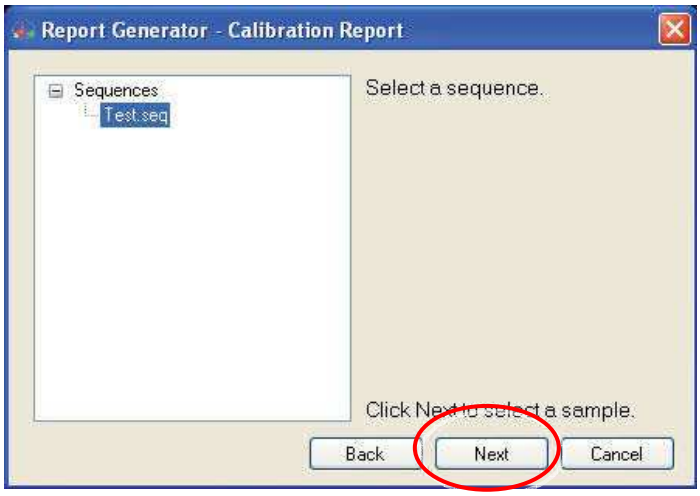


The Sample Report contains information about the sample that is not displayed on the Sconce Report.

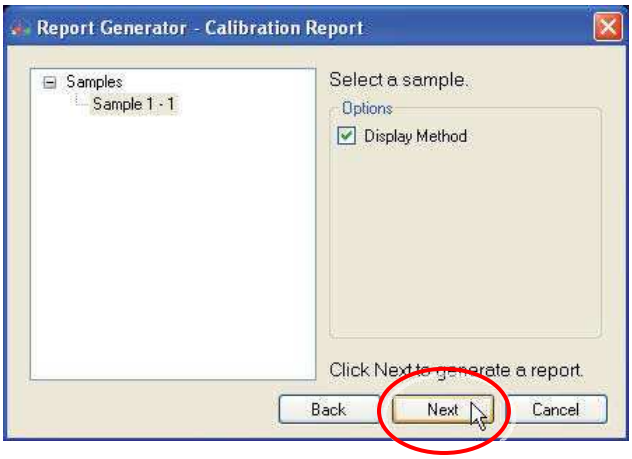
- Column Calibration Report

The Column Calibration Report shows the annotated chromatogram,sample information and resolution pass/fail results. The report can also show the full method summary for the sample, if desired.

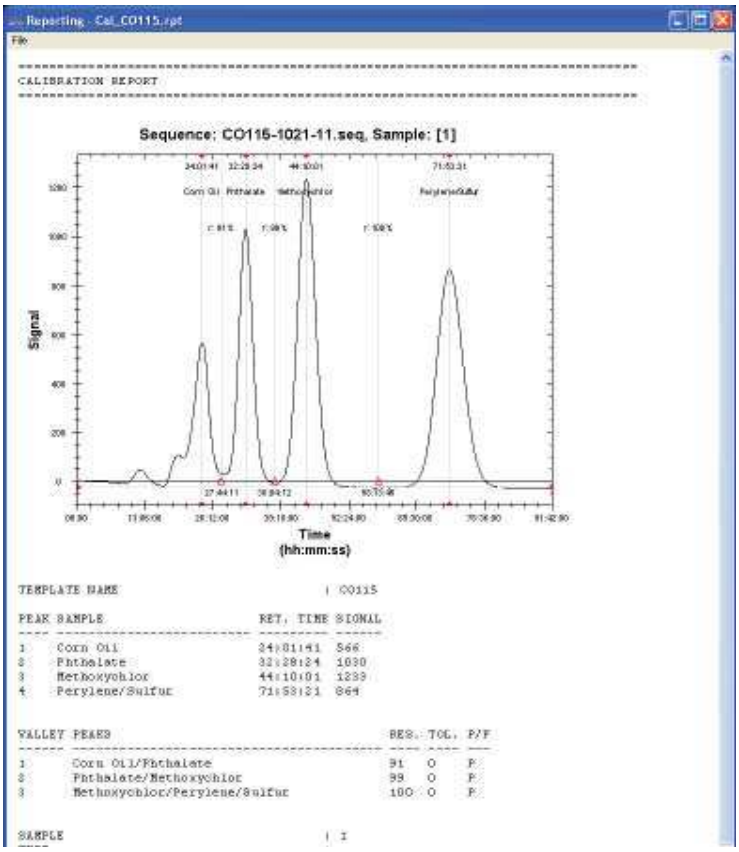
After choosing “Column Calibration Report” from the first wizard screen, a list of processed sequences will be displayed. Choose the appropriate sequence and click the Next button.



A list of the samples processed in the sequence will be displayed on the next screen. Choose the name of the calibration sample from the list. The Option “Display Method” will become active. Click the check box if you would like the method details to be included in the Column Calibration Report. Click the Next button.



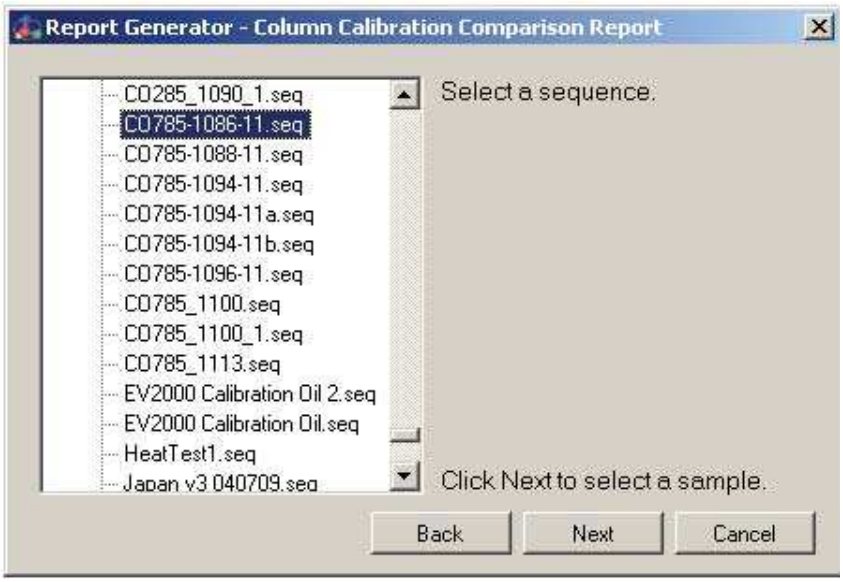
The report will be displayed in the Report Generator window.

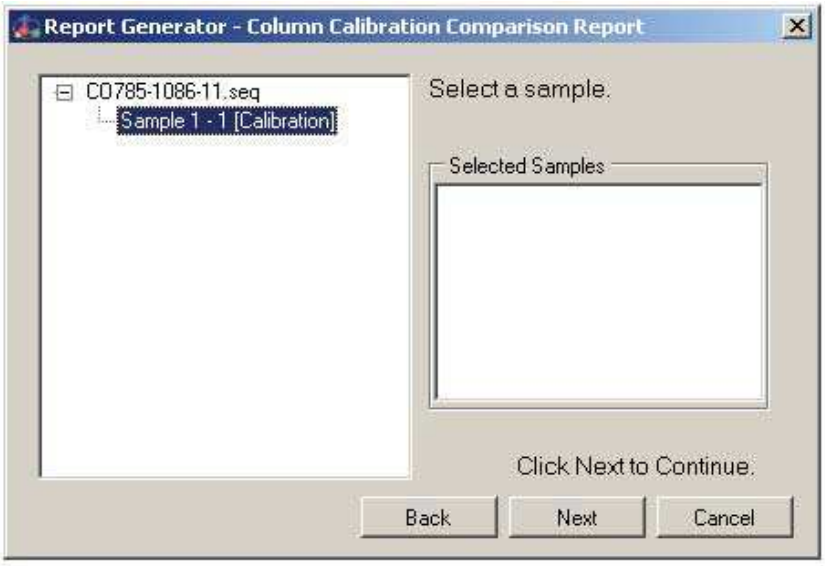


- Column Calibration Comparison Report

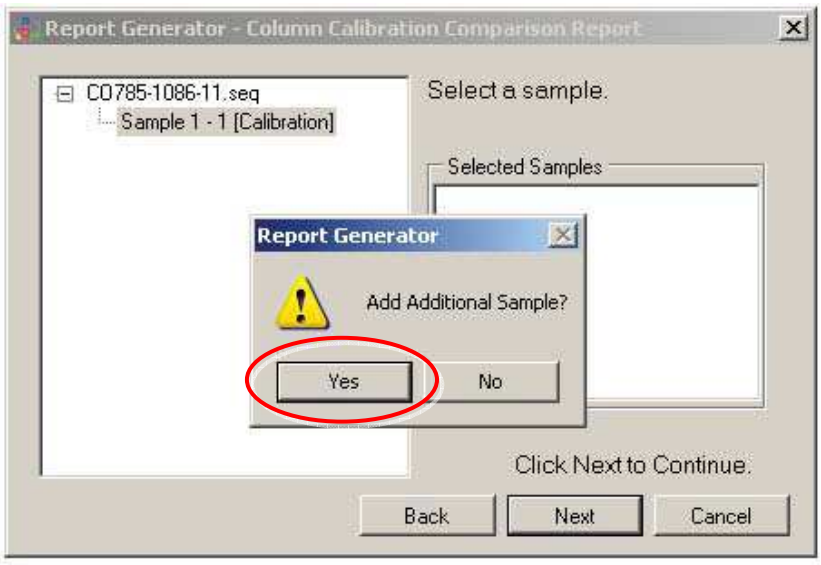
  The Column Calibration Comparison Report takes information from two annotated chromatograms and compares certain data from them to determine a pass/fail for the calibration based on EPA methods.

  After choosing “Column Calibration Comparison Report” from the first wizard screen, a list of processed sequences will be displayed. Choose the appropriate sequence and click the Next button. Choose the sample number in the Sequence that corresponds to the calibration.

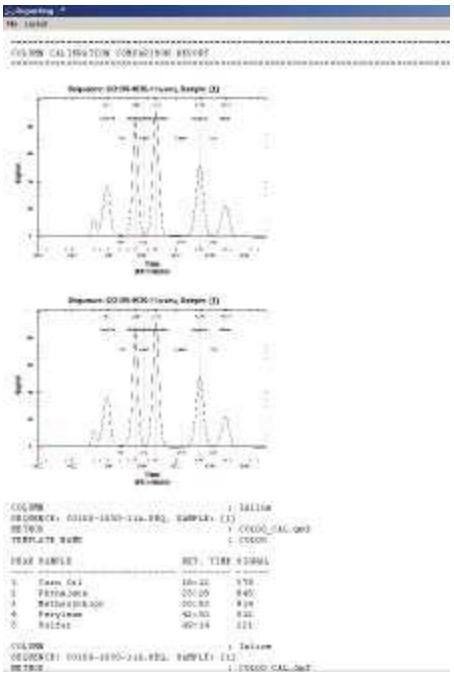


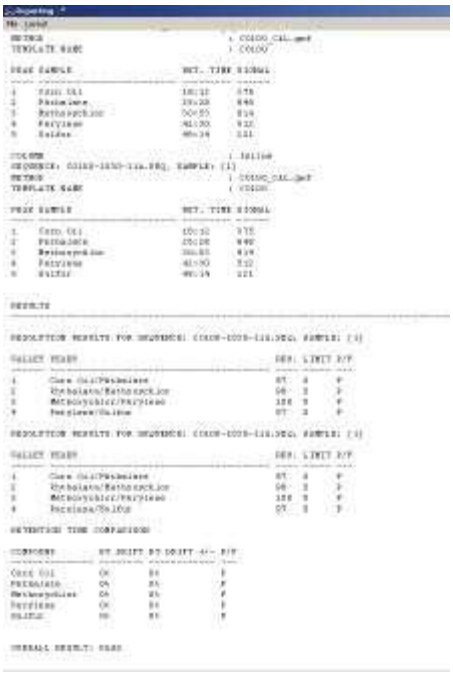


To add an additional sample for comparison, click Yes.



You will then repeat the steps above to choose the Sequence and Sample for comparison. The report that is generated will look similar to the images below. It will show summary information for each sample and then the comparison pass/fail indications.





TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Handling and Preparation of Biota and Tissue Samples

Approvals (Signature/Date):

1/29/2016	1/29/2016
Larry Matko Date	Steve Jackson Date
Technical Director	Regional Safety Coordinator
1/28/2016	2/1/2016
Violet Zusman Date	Deborah L. Lowe Date
Quality Assurance Manager	Laboratory Director

Formerly PT-LP-001_R0

1. SCOPE

1.1. This program standard is followed by TestAmerica's Sediment and Tissue Laboratories, as part of the minimum standards required for program endorsement. The guidance has been reviewed and approved by the Sediment & Tissue Product Manager, multiple Technical Specialists and Operations Manager. It is intended to assure proper practices in the handling of marine and terrestrial biological tissue samples, which may include animal, or plant species collected for food consumption, bioaccumulation, food web or ecological risk studies. This SOP describes the laboratory procedure for the homogenization and extraction of biota and tissue samples in preparation for analysis by a variety of chromatographic procedures.

2. SUMMARY

2.1. No comprehensive regulatory guidance exists for handling tissue samples. The procedures for handling fish and shellfish are based primarily on Section 7 of Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1, Fish Sampling and Analysis, Third Edition, November 2000 (EPA 823-B-00-007), but also on more than 20 years of experience in tissue analysis in support of a variety of state, federal and private research programs.

2.2. In studies of protein structure, very gentle cell lysis techniques are used, to preserve the proteins for analysis. However, in the analysis of metals, and persistent bioaccumulating organics, protein damage is not a concern. Cell lysis may be accomplished by acidification, or by high speed maceration (e.g. Tissumizer or Polytron). Homogenization is performed by processing with a blender, food processor, or macerator, beyond the point where the material is uniform in appearance. Size reduction and processing with a food grinder may be necessary prior to homogenization.

2.3. Because of the variety of species morphology, detailed resection instructions are limited to a few examples. Specific resection guidance may be developed on a project specific basis.

2.4. On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated PT-QA-M-001, Quality Assurance Manual.

3. DEFINITIONS

3.1. Biota: flora and fauna. For this SOP, all reference to "biota" refers to plant material.

3.2. Tissue: an aggregate of cells usually of a particular kind together with their intercellular substance that form one of the structural materials of a plant or animal. For this SOP, all reference to "tissue" refers to structural materials from an animal.

3.3. TALS – TestAmerica Laboratory Information Management System

3.4. Please refer to the glossary in the Quality Assurance Manual PT-QA-M-001 for additional definitions.

4. INTERFERENCES

4.1. Method interference may be caused by contaminants in solvents, reagents, glassware and other sample processing equipment that can cause interference and/or elevated baselines in chromatography. All reagents and solvents used during this procedure should be reagent grade or high purity in order to minimize interference. All glassware must be cleaned in accordance with the laboratory's cleaning procedure. See section 10.11.5 for equipment cleaning procedures.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual PT-HS-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-toed, nonabsorbent shoes are a minimum.

5.2. Specific Safety Concerns or Requirements

5.3. Eye protection against splashing, laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. Nitrile gloves must be used. Latex gloves may be used for methanol. Cut resistant gloves must be worn when handling fillet knives.

5.4. Exposure to chemicals must be maintained as low as reasonably achievable; therefore all samples must be opened, transferred and prepared in a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. Laboratory procedures such as repetitive use of pipettes, repetitive transferring of extracts and manipulation of filled separatory funnels and other glassware represent a significant potential for repetitive motion or other ergonomic injuries. Laboratory associates performing these procedures are in the best position to realize when they are at risk for these types of injuries. Whenever a situation is found in which an employee is performing the same repetitive motion, the employee shall immediately bring this to the attention of their supervisor, manager, or the EH&S staff. The task will be analyzed to determine a better means of accomplishing it.

5.6. The following is a list of the materials used in this method, which have a serious or significant hazard rating. 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
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
1– Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1. Equipment used in processing samples for organics analysis should be of stainless steel, anodized aluminum, borosilicate glass, polytetrafluoroethylene (PTFE), ceramic, or quartz. Polypropylene and polyethylene (plastic) implements, gloves, and containers are a potential source of contamination by organics and should not be used. If a laboratory chooses to use these materials, there should be clear documentation that they are not a source of contamination.

6.2. Filleting should be done on glass or PTFE cutting boards that are cleaned properly between fish or on cutting boards covered with heavy duty aluminum foil that is changed after each filleting. Tissue should be removed with clean, high quality, corrosion-resistant stainless steel or quartz instruments or with knives with titanium blades and PTFE handles. Fillets or tissue homogenates may be stored in borosilicate glass, quartz, or PTFE containers with PTFE-lined lids or in heavy duty aluminum foil.

6.3. Prior to preparing each composite sample, utensils and containers should be washed with detergent solution, rinsed with tap water, soaked in pesticide-grade acetone, and rinsed with organic-free, distilled, deionized water. Work surfaces should be cleaned with pesticide-grade acetone, washed with distilled water, and allowed to dry completely. Knives, fish scalers, measurement boards, etc., should be cleaned with pesticide-grade acetone followed by a rinse with contaminant-free distilled water between each sample.

6.4. “Cuisinart” or “Ninja” Brand Food Processor.

6.5. High quality stainless steel knives or Titanium coated knives.

6.6. Cut-Resistant Gloves

6.7. Stainless Steel Chum Grinder

7. REAGENTS

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

7.1. 20% Nitric Acid (HNO_3) Solution: Prepared by using 800 mL of DI water and slowly adding 200 mL of concentrated nitric acid to it (other proportionally equivalent volumes can be prepared).

7.2. Reagent Water: RO water filtered through a Nanopure System

7.3. Alkaline Liquid Detergent: Contrex

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Plant, fish, shellfish, and turtle samples, once logged in and released for laboratory processing are stored at less than -10^{o} C. Size reduction and grinding may be done with the tissue in a partially frozen state. Depending on the size of the specimens, allow them to partially thaw at room temperature.

8.2. General recommendations for holding times are given in Table 1. These holding times are based on guidance that is sometimes administrative rather than technical in nature; there are no promulgated holding time criteria for tissues (U.S. EPA, 1995). Holding times specifically outlined in analytical methods or project QAPPs will supersede those given in the table below.

Table 1 Sample Storage and Holding Times

Analyte	Matrix	Sample Container	Preservation	Holding Time[a]
Mercury	Tissue	Plastic, Borosilicate glass, quartz, PTFE	Freeze at less than -10^{o}C	28 days [b,e]
Other Metals	Tissue	Plastic, Borosilicate glass, quartz, PTFE	Freeze at less than -10^{o}C	6 months [c,e]
Organics	Tissue	Borosilicate glass, PTFE, quartz, aluminum foil	Freeze at less than -10^{o}C	1 year [d,e]
Lipids	Tissue	Borosilicate glass, PTFE, quartz, aluminum foil	Freeze at less than -10^{o}C	1 year [e]

Adapted from table 7-1, Guidance For Assessing Chemical Contaminant Data For Use in Fish Advisories, Volume 1, Fish Sampling and Analysis, Second Edition, September 1995 (EPA 823-R-95-007)

[a]Maximum holding times recommended by the EPA (1995).

[b]This maximum holding time is also recommended by the PSEP (1990). The California Department of Fish and Game (1990) and the USGS National Water Quality Assessment Program (Crawford and Luoma, 1993) recommend a maximum holding time of 6 months for all metals, including mercury.

[c]This maximum holding time is also recommended by the California Department of Fish and Game (1990), the 301(h) monitoring program (EPA 1986), and the USGS National Water Quality Assessment Program (Crawford and Luoma, 1993). The PSEP (1990) recommends a maximum holding time of 2 years.

[d]This maximum holding time is also recommended by the PSEP (1990). The California Department of Fish and Game (1990), and the USGS National Water Quality Assessment Program (Crawford and Luoma, 1993) recommend a more conservative maximum holding time of 1 year at $\leq$ 10oC for dioxins/furans.

[e]NOAA recommends a maximum holding time of < 3 months.

9. QUALITY CONTROL

9.1. Tissue processing requires specialized quality assurance measures in addition to those required in the analytical standard operating procedures.

9.2. Because isolation and recovery of target analytes from tissues requires performance characteristics not demonstrated by standard soil methods, the laboratory must demonstrate recovery and sensitivity in a natural matrix. Examples of this type of demonstration would be an RL or MDL check, or MDL Study

9.3. Routine quality control samples may be used, and homogenization and/or resection blanks are recommended as optional QC. The reference matrices shown in Table 4-1 should be used, unless otherwise approved by the Sediments & Tissues Operations Manager.

Table 2 - Reference Matrices

Analyte Type	Homogenization Blanks	Purge/Digestion/Extraction Blanks
Volatile Organics	Sample-equivalent weight of DI water	Sample-equivalent weight of DI water
Extractable Organics	Sample-equivalent weight of DI water	Sample-equivalent weight of DI water
Metals	Sample-equivalent weight of DI water	Sample-equivalent weight of DI water
Butyltins	Sample-equivalent weight of DI water	Sample-equivalent weight of DI water
Methyl Mercury	Sample-equivalent weight of DI water	Sample-equivalent weight of DI water

9.4. To avoid cross-contamination, all equipment used in sample processing (i.e., filleting, homogenizing, and compositing) should be cleaned thoroughly before each composite sample is prepared. Suggested sample processing equipment and cleaning procedures by analysis type are discussed in Section 11.15.1. Other procedures may be used if it can be demonstrated, through the analysis of appropriate blanks, that no contamination is introduced.

9.5. Verification of the efficiency of cleaning procedures should be documented through the analysis of homogenization blanks.

9.6. Homogenization blanks: The general procedure for homogenization blanks follows:

9.7. Log in a sample as a homogenization blank along with the field samples. A daily homogenization blank should be produced.

9.8. When homogenization work is being organized, randomly select a position to insert the homogenization blank, after the first field sample has been homogenized, but before the last field sample has been homogenized.

9.9. For the homogenization blank, place 50 to 250 mL of reagent water into the piece of equipment that is being used for homogenization, depending on the amount needed for all subsequent analyses. Select an amount near the lowest mass processed on the field samples – so that a worst-case (low dilution) effect is tested.

9.10. Process the reagent water by pouring it over resection blades and cutting surface; blending it as a field sample, and transferring it to a labeled glass jar for future preparation for analysis.

9.11. Extraction/digestion of the homogenization blank should be performed using the same weight of blank material as used for the samples.

9.12. Quality Control Batch

The batch must contain a homogenization blank and a matrix spike/matrix spike duplicate, when requested. (In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD). If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSDs.

9.13. Calibration

9.13.1. On a daily basis, calibrate any balances to be used in accordance with laboratory SOP PT-QA-012.

10. PROCEDURE

10.1. Individual specimens for resection should be unwrapped and inspected carefully to ensure that they have not been compromised in any way (i.e., not properly preserved during shipment). Any specimen deemed unsuitable for further processing and analysis should be returned to storage until permission to proceed, or a replacement samples is obtained

10.2. If a wet weight is to be determined for each specimen; all samples should be weighed in balances that are properly calibrated and of adequate accuracy and precision to meet program data quality objectives. Fish shipped on wet or blue ice should be weighed directly on a foil-lined balance tray or in a new tared sample jar. If using, the foil lining should be replaced after each weighing. Frozen fish (i.e., those

shipped on dry ice) should be weighed in clean, tared, noncontaminating containers if they will thaw before the weighing can be completed.

Note: Liquid from the thawed whole fish sample will come not only from the fillet tissue but from the gut and body cavity, which would not be part of a final fillet sample. Consequently, inclusion of this liquid with the sample may result in an overestimate of target analyte and lipid concentrations in the fillet homogenate. Nevertheless, it is recommended, as a conservative approach, that all liquid from the thawed whole fish sample be kept in the container as part of the sample. All weights should be recorded to the nearest 0.1gin the TALS Tissue Prep Batch, see Figure 1..

10.3. Each fish within the selected target species should be measured to determine total body length (cm). To be consistent with the convention used by most fisheries biologists in the United States, the maximum body length is defined as the length from the anterior-most part of the fish (Lip) to the tip of the longest caudal fin ray (Anderson and Gutreuter, 1983).

10.4. Aging, Sex Determination and Evaluation of Morphological Anomalies are options for which no standard practices are defined. They may be supported with project specific guidelines, if adequate training is completed by the staff performing the work.

10.5. Whole Body Processing

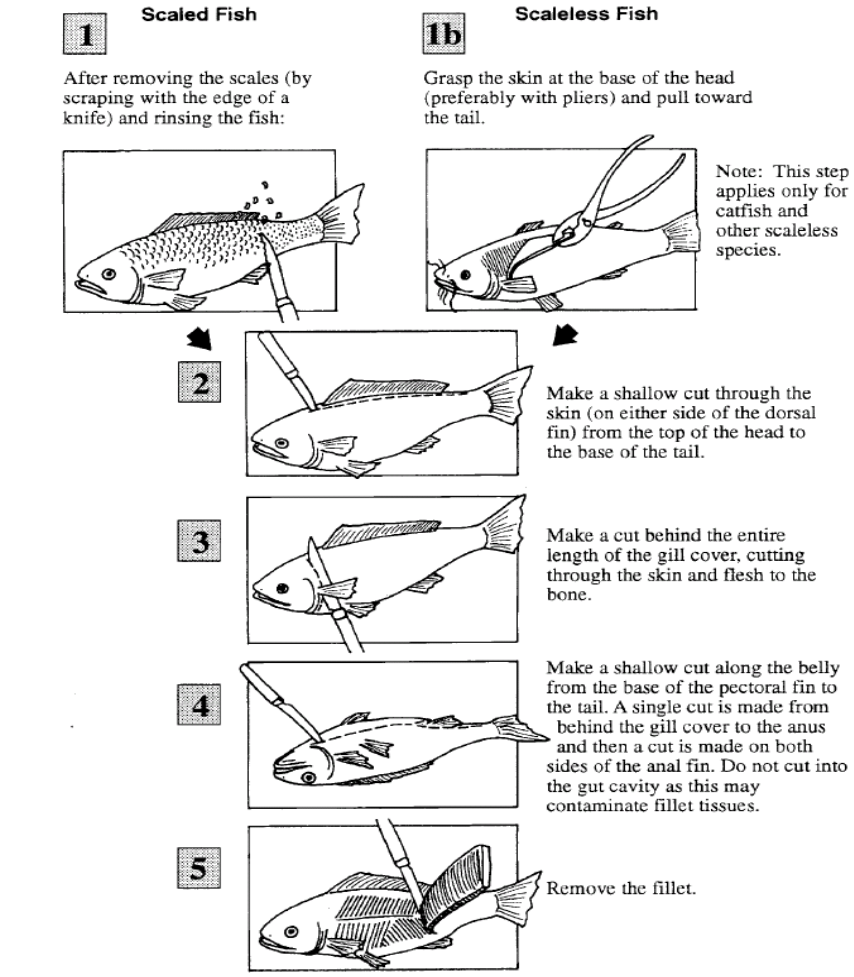
10.5.1. For whole body processing, the samples will be inspected, weighed and measured. Proceed to section 10.11.

10.6. Scaling or Skinning

10.6.1. Fish with scales should be scaled and any adhering slime removed by washing with DI or reagent water prior to filleting. (Note do not wash if whole fish is being prepared). Fish without scales (e.g., catfish) should be skinned prior to filleting. These fillet types are recommended because it is believed that they are most representative of the edible portions of fish prepared and consumed by sport anglers.

10.6.2. A fish is scaled by laying it flat on a clean glass or PTFE cutting board or on one that has been covered with heavy duty aluminum foil and removing the scales and adhering slime by scraping from the tail to the head using the blade edge of a clean stainless steel, ceramic, or titanium knife. Cross-contamination is controlled by rinsing the cutting board and knife with contaminant-free distilled water between fish. If an aluminum-foil-covered cutting board is used, the foil should be changed between fish. The skin should be removed from fish without scales by loosening the skin just behind the gills and pulling it off between knife blade and thumb or with pliers as shown in Figure 6-1. Once the scales and slime have been scraped off or the skin removed, the outside of the fish should be washed with contaminant-free distilled water and it should be placed on a second clean cutting board for filleting.

Figure 6-1



Source: U.S. EPA, 1991d.

10.7. Filleting Fish

10.7.1. Filleting should be conducted only by or under the supervision of an experienced individual. Cut resistance, talc- or dust-free, gloves must be worn. Prior to filleting, hands should be washed with soap and rinsed thoroughly in tap water, followed by distilled water. Specimens should come into contact with noncontaminating surfaces only. Fish should be filleted on glass or PTFE cutting boards that are cleaned properly between fish or on cutting boards covered with heavy duty aluminum foil that is changed between fish (Puget Sound Estuary Program, 1990d, 1990e).

10.7.2. Care must be taken to avoid contaminating fillet tissues with material released from inadvertent puncture of internal organs. Note: If the fillet tissue is contaminated by materials released from the inadvertent puncture of the internal organs during resection, the state may eliminate the fillet tissue as a sample or, alternatively, the fillet tissue should be rinsed in contaminant-free, deionized distilled water and blotted dry. Regardless of the procedure selected, a notation should be made in the sample processing record. Ideally, fish should be filleted while ice crystals are still present in the muscle tissue. Therefore, if fish have been frozen, they should not be allowed to thaw completely prior to filleting. Fish should be thawed only to the point where it becomes possible to make an incision into the flesh. Clean, high-quality stainless steel, ceramic, or titanium utensils should be used to remove one or both fillets from each fish, as necessary. The general procedure recommended for filleting fish is illustrated in Figure 6-1.

10.7.3. The belly flap should be included in each fillet. Any dark muscle tissue in the vicinity of the lateral line should not be separated from the light muscle tissue that constitutes the rest of the muscle tissue mass. Care must be exercised to avoid excessive quantities in the tissue sample

10.7.4. Record the weight of each fillet in the TALS batch.

10.8. Resecting for the edible portions of shellfish

10.8.1. The samples should consist only of those tissues that the population of concern might reasonably be expected to eat. Edible tissues should be clearly defined in site-specific sample processing protocols. A brief description of the edible portions used should also be provided on the sample processing record.

10.8.2. General procedures for removing edible tissues from a variety of shellfish are illustrated in Appendix A.

10.8.3. Thawing of frozen shellfish samples should be kept to a minimum during tissue removal to avoid loss of liquids. Shellfish should be rinsed well with laboratory reagent water prior to tissue removal to remove any loose external debris.

10.9. Bivalve mollusks (oysters, clams, mussels, and scallops) typically are prepared by severing the adductor muscle, prying open the shell, and removing the soft tissue. The soft tissue includes viscera, meat, and body fluids.

10.9.1. Byssal threads from mussels should be removed with a knife before shucking and should not be included in the composite sample.

10.9.2. Edible tissue for crabs typically includes all leg and claw meat, back shell meat, and body cavity meat. Internal organs generally are removed. Inclusion of the hepatopancreas should be determined by the eating habits of the local

population or subpopulations of concern. If the crab is soft-shelled, the entire crab should be used in the sample. Hard- and soft-shelled crabs must not be combined in the same composite.

10.9.3. Typically, shrimp and crayfish are prepared by removing the cephalothorax and then removing the tail meat from the shell. Only the tail meat with the section of intestine passing through the tail muscle is retained for analysis. (Confirm that the project is not scoped for thorax-sucking consumers)

10.9.4. Edible tissue for lobsters typically includes the tail and claw meat. If the tomalley (hepatopancreas) and gonads or ovaries are consumed by local populations of concern, these parts should also be removed and analyzed separately.

10.10. Other Resection Techniques

10.10.1. Segregation of hepatopancreas, gut contents, shell material, adipose, or fat plugs, skin, etc for project specific, target organ studies require differing procedures for differing species. These procedures should be addressed as project-specific requirements.

10.10.2. If fillets or other resected tissues are to be homogenized immediately, they should be placed in a pre-cleaned certified glass jar or PTFE homogenization container. If samples are to be analyzed for metals only, plastic homogenization containers may be used. To facilitate homogenization, it may be necessary or desirable to chop each fillet into smaller pieces using a titanium or stainless steel knife prior to placement in the homogenization container.

10.10.3. If tissues are to be homogenized later, they should be wrapped in heavy duty aluminum foil or placed in a pre cleaned jar The individual fillets from each fish should be kept together. Stored at less than -10^{o} C until homogenization.

10.11. Homogenization of Tissue Samples

10.11.1. To ensure even distribution of contaminants throughout tissue samples and to facilitate extraction and digestion of samples, the fillets from individual fish should be homogenized prior to analysis. Grinding may be required to facilitate homogenization.

10.11.2. Samples should be ground and homogenized using an automatic grinder or high speed blender, homogenizer or macerator. Large fillets may be cut into 2.5-cm cubes with high-quality stainless steel or titanium knives or with a food grade saw prior to homogenization.

Note: Whole fish that are too large to fit through the grinder throat should not be held by hand while slicing through tough tissues. Cut resistant gloves must be worn

during slicing or sawing. If, for whole body preparation, fish heads exceed 2-1/2 inches in width, or 2 lb in weight, alternatives include using random or targeted borings through the fish, removing the head prior to size reduction/homogenization or rejection of the sample should be selected.

Note: If nickel and chromium data quality objective cannot be met using high quality stainless steel, the project may require the use of tantalum or titanium blades rather than stainless steel.

10.11.3. Grinding and homogenization of tissue is easier when it is partially frozen. Chilling the grinder/blender briefly with a few chips of dry ice will also help keep the tissue from sticking to it.

10.11.4. The sample should be ground until it appears to be homogeneous. Continue the homogenization for an additional time, of approximately 25% of the time required to reach apparent homogeneity. No chunks of tissue or skin should remain in the sample homogenate because these may not be extracted or digested efficiently and could bias the analytical results. Dry ice may be used to facilitate breakage of tough tissues.

Note: Samples greater than 12 inches or samples with weight measurements that exceed 1-2 pounds should be homogenized in a stainless steel meat grinder prior to use of the titanium blade. If the sample is extremely large homogenization with a knife may be necessary. If the homogenized tissue sample cannot fit into a single container, pass the sample through the meat grinder multiple times, homogenize the slurry and transfer to multiple containers.

10.11.5. Between each sample the equipment must be cleaned. Disassemble the homogenization equipment (i.e., blender, grinder, or other device) and thoroughly clean **all surfaces and parts** that contact the sample. Similarly, clean all knives, cutting boards, and other utensils used.

At a minimum:

Wash with a detergent solution (phosphate- and scent-free) and warm tap water
Rinse three times with warm tap water
Rinse three times with deionized (DI) water
Rinse with acetone
Rinse three times with DI water
Rinse with (not soak in) 20% nitric acid
Rinse three times with DI water
Allow the components to air dry

10.12. Homogenization of Biota Samples

10.12.1. Plant tissue preparation differs depending on the type of plant, exposure pathways and contaminants being studied. Therefore a single procedure is not described. However, some example procedures are provided in this section.

10.12.2. Preparation of leaves and/or seed heads for analysis of metals and semivolatile organics.

10.12.3. Take an aliquot of the sample for"as received" percent moisture by oven drying ~105℃. Do not use this value for dry weight correction, but report separately.

10.12.4. Wash the sample lightly with distilled, deionized water to remove dust particles. Limit the amount of time the sample comes in contact with rinse water to as short a time as possible. Do not scrub or wipe the surface.

10.12.5. Remove excess water.

10.12.6. Chop or blend the sample so that no individual pieces exceed 0.5 cm wide in any dimension. This may be done using ceramic scissors where metals are of concern.

10.12.7. Mix the chopped sample thoroughly.

10.12.8. Take an aliquot to determine percent moisture by oven drying ~105℃. Use this value to calculate percent moisture for dry weight correction.

10.12.9. Proceed to extraction or digestion with appropriate aliquots.

10.12.10. Between individual samples clean the equipment per section 10.11.5.

10.13. Extraction and Concentration

10.13.1. Sample extraction and concentration steps should follow those in the specific method being carried out. Refer to laboratory SOP for specific method instructions.

10.13.2 Specific extraction procedures are detailed in sample preparation SOPs, where the procedure is scoped for tissue analysis. The following constraint is placed on procedures for extraction, within TestAmerica's Sediment and Tissue Laboratories, If the homogenization step has included maceration or blending with dry ice to a uniform appearance, extractions may be performed by Soxhlet, accelerated Soxhlet or Sonication.

10.14. Sample Cleanup

10.14.1. For tissue samples GPC and Silica Gel cleanups are recommended for elimination of lipids in the extracts. See specific methods for details.

10.15. Immediately following concentration, all sample extracts must be stored in a refrigerator maintained at a temperature of >0.0ºC but ≤6.0℃ in order to maintain thermal preservation.

11. CALCULATIONS/DATA REDUCTION

11.1. Not applicable

12. METHOD PERFORMANCE

12.1. Use method specific performance criteria from specific analytical method SOPs.

13. POLLUTION CONTROL

13.1. 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" and the Pittsburgh Facility Addendum EH&S Manual PT-HS-001.

14. 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 specific laboratory procedures outlined in their applicable SOP.

14.1.1. Acetone waste is collected in waste containers identified as "Mixed Flammable Solvent Waste", Waste 3.

14.1.2. Debris created by this method is collected in a container identified as "Lab Trash Waste", Waste #12.

14.1.3. Fish Tissue can be disposed of in the normal waste (dumpster) unless it is known to be above the TCLP Limits then the waste is disposed of in Waste 44.

15. REFERENCES

15.1. US EPA, Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1, Section 7 Fish Sampling and Analysis, Second Edition (EPA 823-R-95-007) September 1995

15.2. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1, Fish Sampling and Analysis, Third Edition, November 2000 (EPA 823-B-00-007)

15.3. US EPA, Office of Water, Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS. (EPA-821-R-00-002). December 1999

15.4. US EPA, Office of Water, Method 1699, Pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS. (EPA-821-R-08-001) December 2007

15.5. The Water Resources Research Institute, North Carolina State University. Publication UNC-SG-88-02 UNC Sea Grant, Raleigh, NC 1988

15.6. U.S. EPA Office of Water's National Coastal Condition Assessment (NCCA). Statement of Work "Fish Tissue Sample Preparation, Homogenization, and Distribution Procedures for the National Coastal Condition Assessment Human Health Fish Tissue Indicator"

15.7. Pittsburgh Laboratory Quality Assurance Manual (PT-QA-M-001)

15.8. Pittsburgh Facility Addendum EH&S Manual, PT-HS-001

15.9. SOP PT-QA-012, Selection and Calibration of Balances and Weights

15.10. SOP PT-QA-016, Nonconformance and Corrective Action System

15.11. SOP PT-QA-031, Internal Chain of Custody

16. METHOD MODIFICATIONS

16.1. Not applicable

17. ATTACHMENTS

17.1. Appendix A – Adapted from Appendix L of EPA 823-B-00-007. General Procedures for Removing Edible Tissues from Shellfish

17.2. Figure 1 – Example of TALS Tissue Prep Batch

18. REVISION HISTORY

18.1. New SOP, 1/27/2014

18.2. Changes to current revision

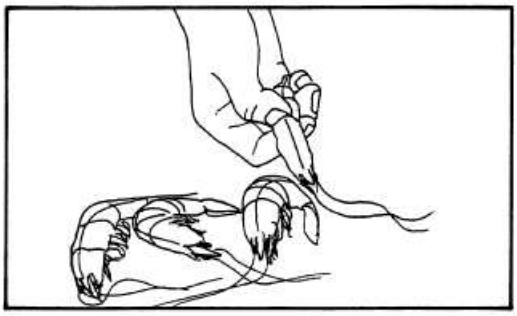
SOP section	Change from	Change to	Reason
Entire SOP		Updated section numbering where necessary	Correction
SOP Number	PT-LP-001 R0	PT-OP-030 R1	Correction
Cover Page	Violet Fanning as QAM	Virginia Zusman as QAM	Personnel change
4.1 and 10.12.10	Section reference 11.5.1	Section reference 10.11.5	Correction
5.1, 13.1 and 15.8		Added reference to PT-HS-001	Correction
5.6	MSDS	SDS	Compliance with industry naming convention
7.1	Acetone	20% Nitric Acid	Correction
9.13.1		Added SOP number PT-QA-012 for Balance Calibration	Clarification
NOTE under section 10.2	Record weights to nearest 0.1 g on worksheets	Record weights to nearest 0.1 g in TALS Tissue Prep batch	Correction
10.5	Section 11.13 reference	Section 10.11 reference	Correction
10.11.5	5% Nitric Acid	20% Nitric Acid	Correction
NOTE under section 10.14.1	4±2℃	≥0.0℃ but ≤6.0℃	Correction
15.7, 15.8, 15.9, 15.10 and 15.11		Added reference to PT-QA-M-001, PT-HS-001, PT-QA-012, PT-QA-016 and PT-QA-031, respectively	SOP reference additions
17.2, 17.3 and 17.4 and Figures 1, 2 and 3	Removed reference to the old logsheets to record data	Added 17.2 and Figure 1 to reference the TALS Tissue Prep batch for recording data	Correction

Appendix A - General Procedures for Removing Edible Tissues from Shellfish

Heading, peeling and deveining shrimp

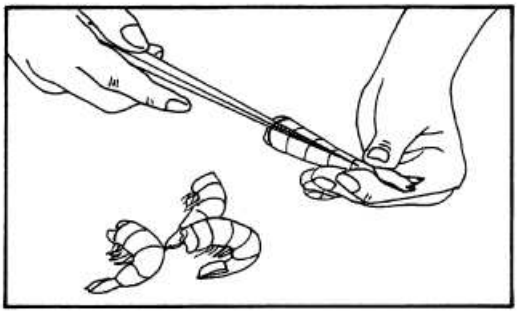
1

To head a shrimp, hold it in one hand. With your thumb behind shrimp head, push head off. Be sure to push just the head off so that you do not lose any meat.



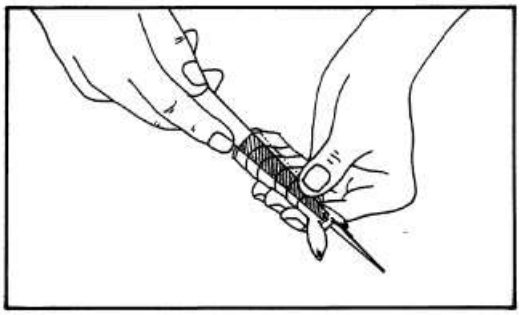
2

If using a deveiner, insert it at head end, just above the vein.



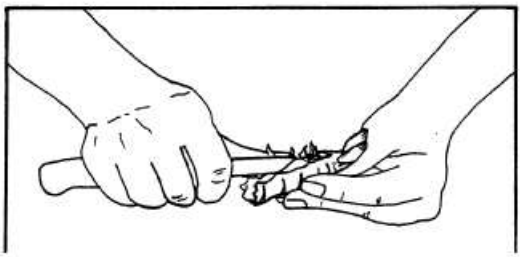
3

Push through shrimp to the tail and split and remove shell. This removes vein at the same time.



4

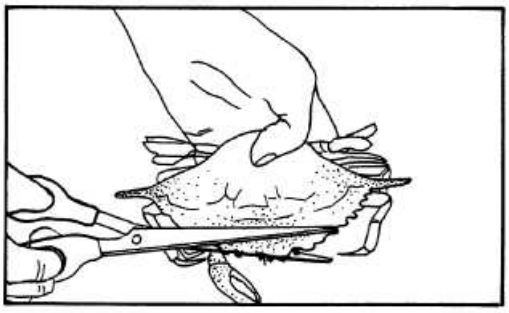
If you prefer to use a paring knife, shell shrimp with your fingers or knife. Then use knife to gently remove vein.



Source: UNC Sea Grant. 1988. Publication UNC-SG-88-02. The Water Resources Research Institute, North Carolina State University, Raleigh, NC.

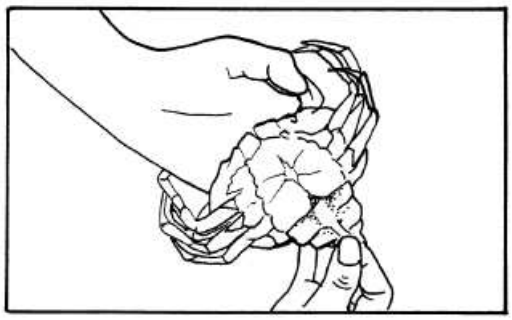
1

Hold crab in one hand and cut across body just behind eyes to remove eyes and mouth.



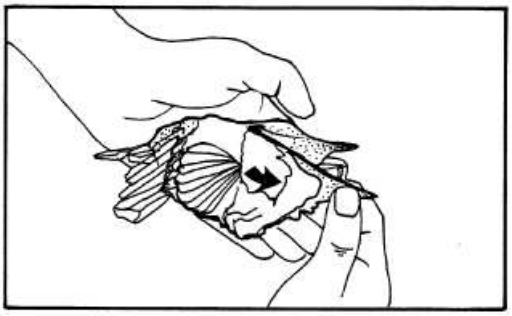
2

Turn crab on its back. Lift and remove apron and vein attached to it.



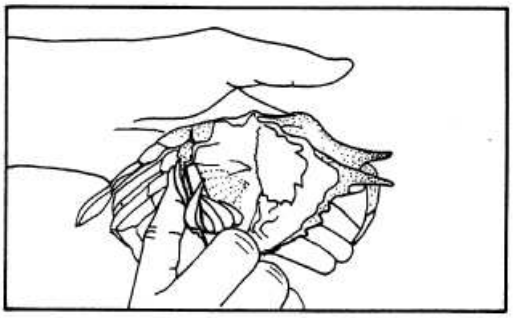
3

Turn crab over and lift one side of top shell.



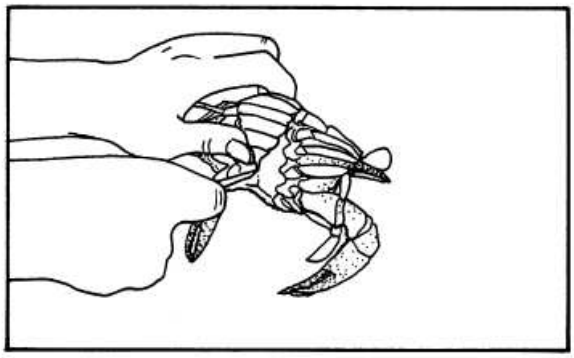
4

With a small knife, scrape off grayish-feathery gills. Repeat procedure on other side.



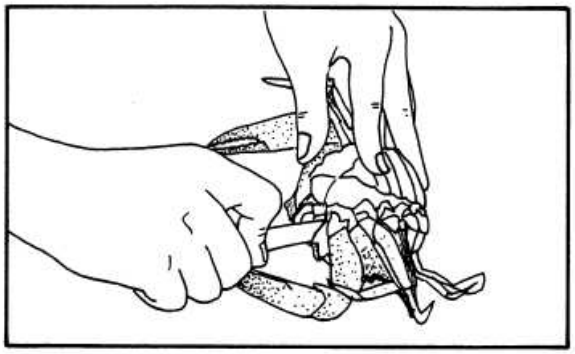
1

Hold crab in one hand. Turn crab over and stab straight down at point of apron with a knife.



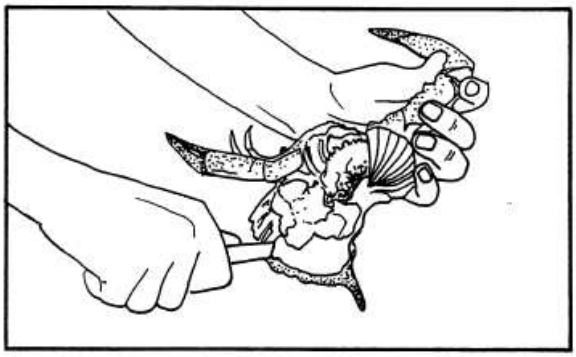
2

Make two cuts from this point to form a V-pattern that will remove mouth.



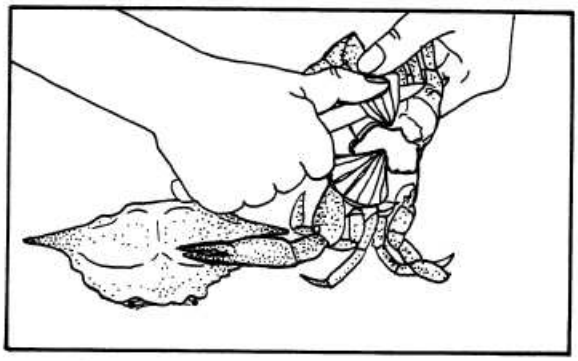
3

Do not remove knife after making second cut. Firmly press crab shell to cutting surface without breaking back shell. With other hand, grasp crab by legs and claws on the side where you are holding knife, and pull up. This should pull crab body free from back shell.



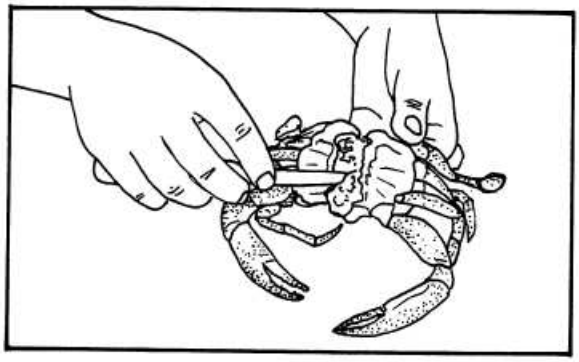
4

Remove gray, feathery gills, which are attached just above legs. Cut and scrape upward to remove gills.



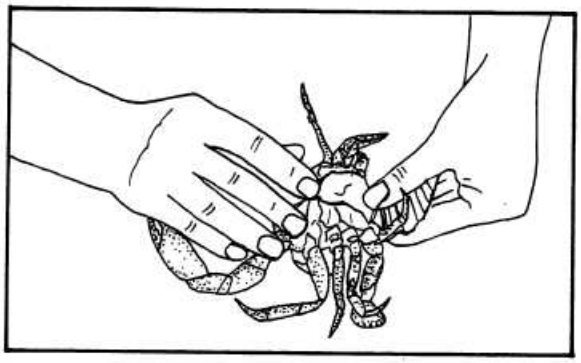
5

Remove all loose material—viscera and eggs—from body cavity.



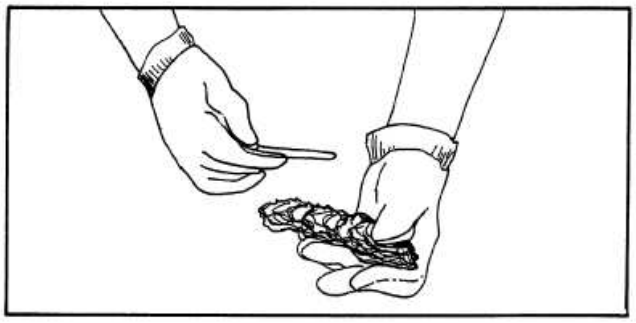
6

If apron did not come loose with shell, remove it.



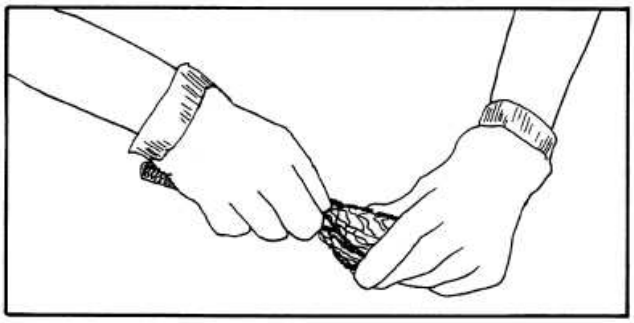
1

Oyster shells are especially sharp; be sure to wear gloves to protect your hands. Chip off a small piece of shell from the thin lip of the oyster until there is a small opening.



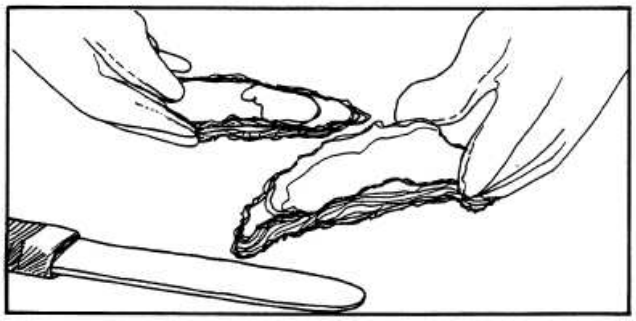
2

Insert knife blade into the opening and cut muscle free from top and bottom shells.



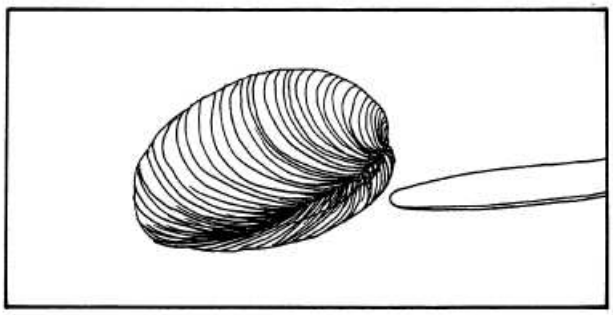
3

Remove oyster meat from the shell.



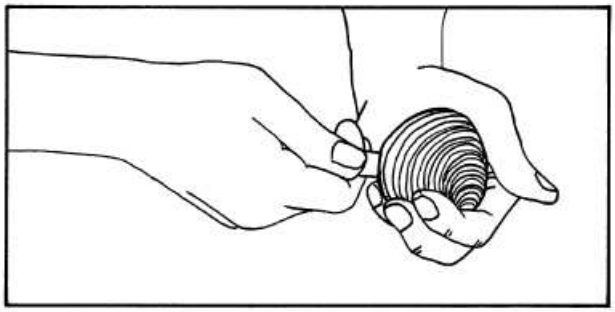
1

In the back of clam near the hinge is a black ligament. Toward the front where ligament ends is a weak spot. Insert your knife at this spot.



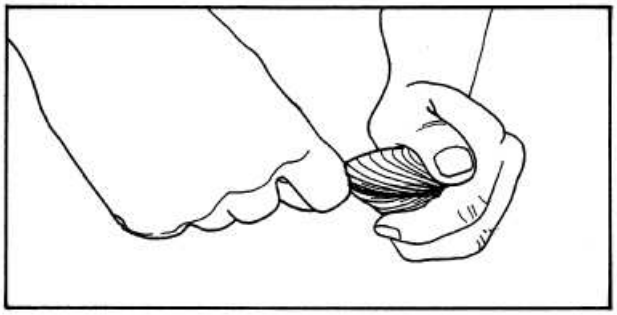
2

Inside are two muscles. Run the knife around the shell to sever both muscles.



3

Now insert the knife blade into the front of the shell and separate the two shells.



4

Scrape the meat free from the top and bottom shell.

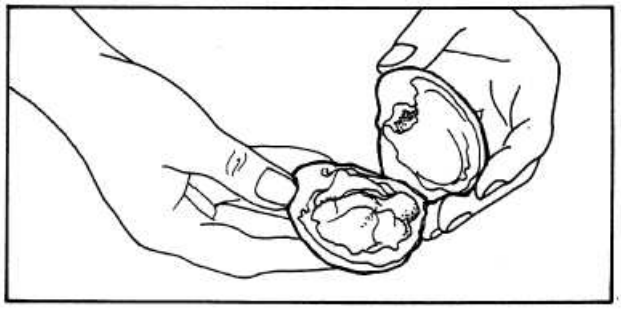
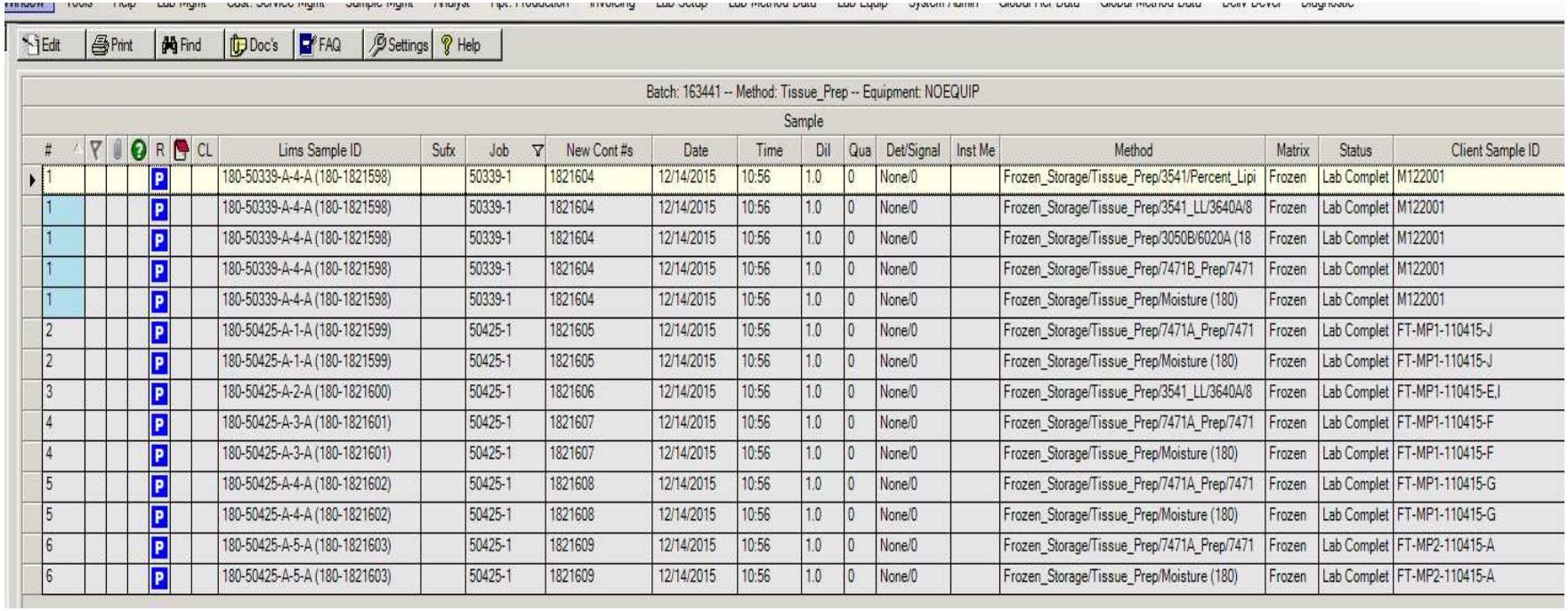


Figure 1 – Example of TALS Tissue Prep Batch

#	Lims Sample ID	New Cont #s	Date	Time	Dil	Matrix
1	180-50339-A-4-A (180-1821598)	1821604	12/14/2015	10:56	1.0	Frozen
2	180-50425-A-1-A (180-1821599)	1821605	12/14/2015	10:56	1.0	Frozen
3	180-50425-A-2-A (180-1821600)	1821606	12/14/2015	10:56	1.0	Frozen
4	180-50425-A-3-A (180-1821601)	1821607	12/14/2015	10:56	1.0	Frozen
5	180-50425-A-4-A (180-1821602)	1821608	12/14/2015	10:56	1.0	Frozen
6	180-50425-A-5-A (180-1821603)	1821609	12/14/2015	10:56	1.0	Frozen

Figure 1 – Example of TALS Tissue Prep Batch (cont.)



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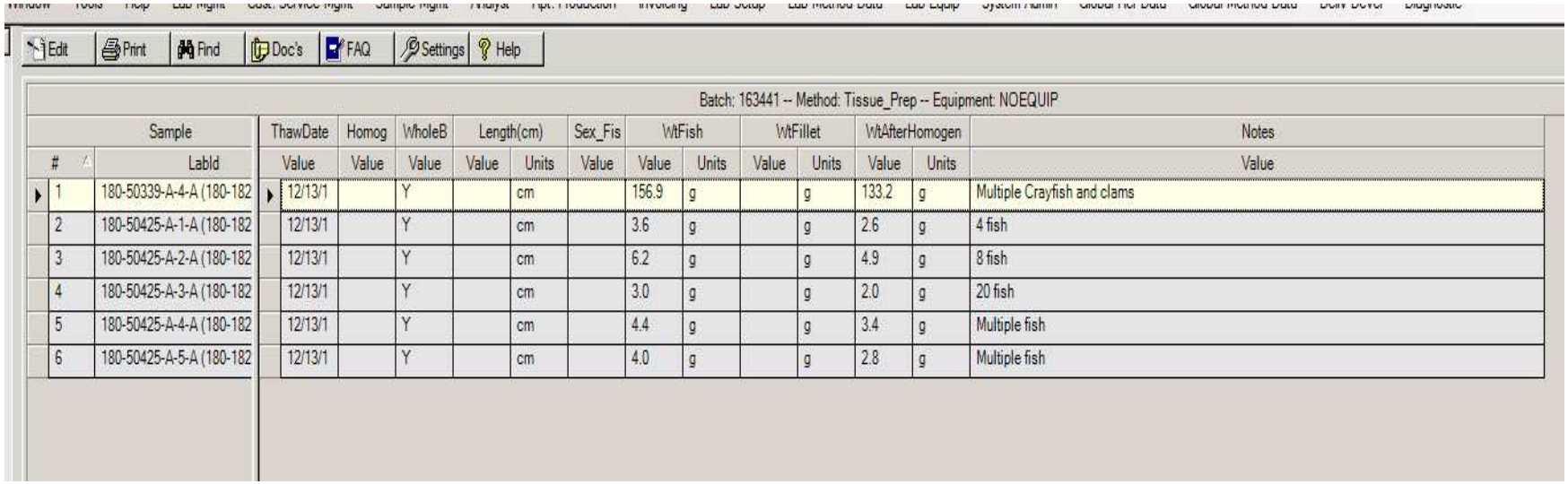
Batch: 163441 -- Method: Tissue_Prep -- Equipment: NOEQUIP

Sample

#	R	CL	Lims Sample ID	Sufx	Job	New Cont #s	Date	Time	Dil	Qua	Det/Signal	Inst Me	Method	Matrix	Status	Client Sample ID
1	P		180-50339-A-4-A (180-1821598)		50339-1	1821604	12/14/2015	10:56	1.0	0	None/0		Frozen_Storage/Tissue_Prep/3541/Percent_Lipi	Frozen	Lab Complet	M122001
1	P		180-50339-A-4-A (180-1821598)		50339-1	1821604	12/14/2015	10:56	1.0	0	None/0		Frozen_Storage/Tissue_Prep/3541_LL/3640A/8	Frozen	Lab Complet	M122001
1	P		180-50339-A-4-A (180-1821598)		50339-1	1821604	12/14/2015	10:56	1.0	0	None/0		Frozen_Storage/Tissue_Prep/3050B/6020A (18	Frozen	Lab Complet	M122001
1	P		180-50339-A-4-A (180-1821598)		50339-1	1821604	12/14/2015	10:56	1.0	0	None/0		Frozen_Storage/Tissue_Prep/7471B_Prep/7471	Frozen	Lab Complet	M122001
1	P		180-50339-A-4-A (180-1821598)		50339-1	1821604	12/14/2015	10:56	1.0	0	None/0		Frozen_Storage/Tissue_Prep/Moisture (180)	Frozen	Lab Complet	M122001
2	P		180-50425-A-1-A (180-1821599)		50425-1	1821605	12/14/2015	10:56	1.0	0	None/0		Frozen_Storage/Tissue_Prep/7471A_Prep/7471	Frozen	Lab Complet	FT-MP1-110415-J
2	P		180-50425-A-1-A (180-1821599)		50425-1	1821605	12/14/2015	10:56	1.0	0	None/0		Frozen_Storage/Tissue_Prep/Moisture (180)	Frozen	Lab Complet	FT-MP1-110415-J
3	P		180-50425-A-2-A (180-1821600)		50425-1	1821606	12/14/2015	10:56	1.0	0	None/0		Frozen_Storage/Tissue_Prep/3541_LL/3640A/8	Frozen	Lab Complet	FT-MP1-110415-E,I
4	P		180-50425-A-3-A (180-1821601)		50425-1	1821607	12/14/2015	10:56	1.0	0	None/0		Frozen_Storage/Tissue_Prep/7471A_Prep/7471	Frozen	Lab Complet	FT-MP1-110415-F
4	P		180-50425-A-3-A (180-1821601)		50425-1	1821607	12/14/2015	10:56	1.0	0	None/0		Frozen_Storage/Tissue_Prep/Moisture (180)	Frozen	Lab Complet	FT-MP1-110415-F
5	P		180-50425-A-4-A (180-1821602)		50425-1	1821608	12/14/2015	10:56	1.0	0	None/0		Frozen_Storage/Tissue_Prep/7471A_Prep/7471	Frozen	Lab Complet	FT-MP1-110415-G
5	P		180-50425-A-4-A (180-1821602)		50425-1	1821608	12/14/2015	10:56	1.0	0	None/0		Frozen_Storage/Tissue_Prep/Moisture (180)	Frozen	Lab Complet	FT-MP1-110415-G
6	P		180-50425-A-5-A (180-1821603)		50425-1	1821609	12/14/2015	10:56	1.0	0	None/0		Frozen_Storage/Tissue_Prep/7471A_Prep/7471	Frozen	Lab Complet	FT-MP2-110415-A
6	P		180-50425-A-5-A (180-1821603)		50425-1	1821609	12/14/2015	10:56	1.0	0	None/0		Frozen_Storage/Tissue_Prep/Moisture (180)	Frozen	Lab Complet	FT-MP2-110415-A

Figure 1 – Example of TALS Tissue Prep Batch (cont.)



Batch: 163441 -- Method: Tissue_Prep -- Equipment: NOEQUIP

Sample		ThawDate	Homog	WholeB	Length(cm)		Sex_Fis	WtFish		WtFillet		WtAfterHomogen		Notes
#	LabId	Value	Value	Value	Value	Units	Value	Value	Units	Value	Units	Value	Units	Value
1	180-50339-A-4-A (180-182	12/13/1		Y		cm		156.9	g		g	133.2	g	Multiple Crayfish and clams
2	180-50425-A-1-A (180-182	12/13/1		Y		cm		3.6	g		g	2.6	g	4 fish
3	180-50425-A-2-A (180-182	12/13/1		Y		cm		6.2	g		g	4.9	g	8 fish
4	180-50425-A-3-A (180-182	12/13/1		Y		cm		3.0	g		g	2.0	g	20 fish
5	180-50425-A-4-A (180-182	12/13/1		Y		cm		4.4	g		g	3.4	g	Multiple fish
6	180-50425-A-5-A (180-182	12/13/1		Y		cm		4.0	g		g	2.8	g	Multiple fish

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Percent Moisture, Solids, Ash, Organic Matter in Soil Samples

Methods: SM 2540G and ASTM D2974-07a

Approvals (Signature/Date):

8/27/2014	8/28/2014
Roseann Ruyechan Date	Steve Jackson Date
Inorganics Department Manager	Regional Safety Coordinator
8/27/2014	8/27/2014
Virginia Zusman Date	Deborah L. Lowe Date
Quality Assurance Manager	Laboratory Director

1.0 Scope and Application

1.1 This method is applicable to the determination of the moisture content of soil, rock and soil-aggregate mixtures, and products. This method is also used to determine the ash content in oil, liquid (non-aqueous, i.e. sludges) and petroleum samples.

1.2 On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated in PT-QA-M-001, Quality Assurance Manual.

2.0 Summary of Method

2.1 A homogenous sample is dried at 103°C to 105°C (to determine moisture), and 500 ± 50°C (to determine Ash). The weight loss of the sample at 103-105°C represents the moisture content and the residue the total solids.

2.2 The Ash content is the percentage of the total solids that remain after burning at 450-550°C.

2.3 Percent organic matter, or volatile solids, is equal to 100% (of the total solids) - the % ash. Therefore the % organic matter is defined as the percentage of combustible material found in the sample based on dry weight.

3.0 Definitions

3.1 Please refer to the glossary in the Quality Assurance Manual- PT-QA-M-001 for additional definitions.

3.2 TALS – TestAmerica LIMS

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2 Non-homogeneous samples may give erratic results.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-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

5.1.1 After heating, sample containers will present a burn hazard. Tongs or heat resistant gloves must be used when handling samples after heating in the oven or muffle furnace.

5.2 Primary Materials Used

5.2.1 There are no materials used in this method that have a serious or significant hazard rating.

5.3 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.

5.4 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor and/or the EHSC.

6.0 Equipment and Supplies

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this sop can be met.

6.1 Analytical balance: capable of accurately weighing ± 0.0001 g

6.2 Drying Oven, 103°C ± 2°C

6.3 Muffle furnace, 550°C ± 50°C

6.4 Desiccators

6.5 Evaporating dishes, various sizes, capable of being heated above 550°C

6.6 Wooden Spatula

6.7 Aluminum pans

7.0 Reagents and Standards

7.1 Not Applicable

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Samples are not chemically preserved.

8.2 Samples are stored in plastic or glass containers at ≥0.0˚C but ≤ 6.0°C.

8.3 There is no method recommended holding time for solid samples for these tests. The lab will assign a 28 day holding time internally.

9.0 Quality Control

9.1 A duplicate sample is analyzed with every set of 10 or fewer samples.

9.1.1 The acceptable range between the sample and sample duplicate is %RPD less than or equal to 20 percent.

9.1.2 If the %RPD is outside criteria, check calculations and verify balance calibration. Reanalyze the samples once and evaluate results vs the initial sample/duplicate. If the failure repeats, report data with an NCM and narrative description of the initial and second data sets.

10.0 Procedure

10.1 Calibration and Standardization

10.1.1 Balances are calibrated as needed, and proper balance operation is verified daily, prior to sample analysis, bracketing the range of weights used. See SOP PT-QA-012 for balance calibration and verification details.

10.1.2 Oven temperature must be checked daily and recorded in the oven temperature log. Oven and muffle furnace temperatures at the time of analysis are documented in the batch information in TALS.

10.2 Total Solids – 2540G

10.2.1 Preparation of evaporating dish: If volatile solids or ash content are to be measured, ignite a clean evaporating dish at 500± 50°C for one hour in a muffle furnace. If only total solids is being measured, an aluminum pan baked at 103-105°C may be used. Cool dishes to room temperature in desiccator before use. Dishes may be store in desiccator until ready for use.

10.2.2 Preparation of sample: Rocks, stones, twigs, leaves, or other foreign matter which interfere with homogenizing the sample must be carefully removed and the remaining sample mixed thoroughly so that a representative sample will be obtained. Where it has been necessary to remove artifacts, the action taken and artifacts removed from the sample must be adequately described by the analyst in a narrative provided with the sample data. If there is doubt concerning the proper handling of sample artifacts (due to the nature of the particular sample or project), the laboratory supervisor and project manager must determine the procedure to be followed, and the resulting actions must be documented in a narrative provided with the sample data. For volatile solid samples and samples analyzed for percent dry solids, supernatant liquids are mixed into the sample.

10.2.3 Place weighing dish plus 5 - 10g sample in a drying oven maintained at 103°C ± 2°C. If samples contain enough liquid to flow readily, use 25 to 50 g of sample for analysis. Sample handling and drying must be conducted in a well ventilated area.

10.2.4 Dry the sample for a minimum of 12 hours. Remove the sample from the oven and cool in a dessicator at least 30 minutes. If dried less than 12 hours, it must be documented that constant weight was attained by repeating the dry/desiccate/weight cycle, with a minimum of one hour drying time in each cycle, until a change in weight of no greater than 0.05g or 4% (whichever is greater), is seen between start weight and final weight of last cycle.

10.3 Ash (Fixed) and Volatile Solids:

10.3.1 Transfer the dried residue from Section 10.2.4 to a muffle furnace at 500± 50°C and ignite for one hour. (If the residue contains large amounts of organic matter, first ignite it over a gas burner and under a fume hood in the presence of adequate air to lessen losses due to reducing conditions and to avoid odors in the laboratory.) Cool in desiccator to room temperature and weigh.

10.3.2 Return the sample to the muffle furnace for an additional 30 minutes. Cool in a desiccator to room temperature and weigh. Repeat burning, cooling and weighing until a constant weight is obtained. Constant weight is defined as a change in weight of no greater than 0.05g or 4% (whichever is greater), between start weight and final weight of last cycle.

10.4 Any deviations from this procedure must be documented as a nonconformance, with a cause and corrective action described.

10.5 Organic matter is determined by subtracting percent ash content from one hundred.

11.0 Calculations / Data Reduction

11.1 Percent Total Solids:

$$\frac{(A - B)}{(C - B)} \times 100$$

Percent Volatile Solids or Organic Matter:

$$\frac{(A - D)}{(A - B)} \times 100$$

Percent Ash (Fixed) Solids:

$$\frac{(D - B)}{(A - B)} \times 100$$

Where:

A = Weight of dried residue and dish, mg

B = Weight of dish

C = Weight of wet sample and dish, mg

D = Weight of residue and dish after ignition, mg

11.2 Percent Moisture

%Moisture = 100% - % Total Solids

11.3 Report all results to the nearest 0.1 percent. Report furnace temperature used for ash content determinations.

11.4 Duplicate Sample, Relative Percent Difference (RPD):

$$RPD = \frac{|X_1 - X_2|}{\left(\frac{X_1 + X_2}{2}\right)} \times 100$$

Where:

X_1 = Original Result

X_2 = Duplicate Result

12.0 Method Performance

12.1 The supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

13.0 Pollution Control

13.1 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."

13.2 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 Safety Manual for "Waste Management and Pollution Prevention.

13.3 This method does not contain any specific modifications that serve to minimize or prevent pollution.

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 PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1 Used Soil Samples – This waste is collected in containers identified as "Lab Trash", Waste #12.

15.0 References / Cross-References

15.1 Standard Methods for the Examination of Water and Waste Water, Method 2540G, 2011

15.2 ASTM Standard D 2974-07a, Standard Test Methods for Moisture, Ash, and Organic Matter of Peat Materials, 2008

15.3 PT-QA-012, Selection and Calibration of Balances and Weights

15.4 PT-QA-016, Nonconformance & Corrective Action System

15.5 PT-QA-021, Quality Assurance Program

15.6 PT-QA-024, Subsampling

15.7 PT-QA-M-001, Pittsburgh Laboratory Quality Assurance Manual

15.8 PT-HS-001, Pittsburgh Facility Addendum EH&S Manual

16.0 Method Modifications

16.1 The ash/organic content temperature (550±50°C) requirement from SM2540G is used in place of either method C (440°C) or D (750°C) from ASTM D 2974-07a.

17.0 Attachments

17.1 All sample preparation and analysis information will be documented electronically in TALS LIMS. All the documents associated with an analysis will be electronically available for inclusion in the final report.

17.2 Organic Matter Worksheet

18.0 Revision History

18.1 Revision 4, 11/7/08

18.2 Revision 5, 10/14/2009

18.3 Revision 6, 1/21/2012

18.4 Revision 7, 8/28/2014

SOP section	Change from	Change to	Reason
Cover	Technical Analyst – Mike Wesoloski Steve Jackson – Health & Safety Manager/ Coordinator QAM – Nasreen DeRubeis	Inorganics Department Manager – Roseann Ruyechan Regional Safety Coordinator QAM –Virginia Zusman	Change in personnel
Entire SOP	Removed Updated	DoD references PT-LQAM to PT-QA-M-001	Voluntarily withdrew from the program SOP numbering change
1.1	Added	Added “and products” to the end of the first sentence	Clarification
1.2	Added	SOP Checklist text on modifications	SOP Review Sheet format
3.1	Sample Duplicate definition	Reference for glossary in QA Manual	SOP Review Sheet format
3.2	QC Batch definition	TALS – TestAmerica LIMS	Clarification

5.1	Removed	Radiation Safety Manual	Does not pertain to this facility
5.2	Changed	MSDS to SDS	Due to change in industry standard language
5.2.1	Removed statement for VITON gloves		Clarification
6	Added	Text from SOP Review Checklist for this section	SOP Review Sheet format
6.6	Removed Top-loader balance		Clarification
8	Updated	≤6˚C to ≥0.0˚C but ≤6.0 ˚C	Correction
9.1.2	Added	Verify balance calibration…. If failure repeats, NCM and narrative	Clarification
10.1.1	Added	Balances are calibrated as needed…verified bracketing the range of weights used. See SOP PT-QA-012.	Clarification
10.2.3	Added	If samples contain enough liquid to flow readily, use 25 to 50g of sample for analysis	To match method weights (SM2540G)
10.2.4	change in weight of no greater than 0.01g	change in weight of no greater than 0.05g, or a change of less than 4% of the sample weight	To match method requirement (SM2540G)
10.3.2	Added	Requirement for repeated heating, cooling and weighing to constant weight	To match method requirement (SM2540G)
12.1	Added	Supervisor responsibility text from SOP Checklist	SOP Review Sheet format
15.2	Removed	Reference to ILM04.0	No longer perform CLP analysis
15.5, 6, 7, 9, 13, 14	Removed references to methods/SOP not used for this procedure		Clarification
15.13 (now 15.7)	PT-LQAM	PT-QA-M-001	QA Manual ID change
5 and 15.8	added	Reference to Pittsburgh EH&S Manual PT-HS-001	Clarification

General Chemistry Worksheet

Batch Number: 180-25593
Method: SM 2540G
Analyst: Cox, Chrissy M

Date Open: Jan 10 2012 10:27AM
Batch End:

Lab ID	Client ID	Method Chain	Basis	CrucibleID	Empty Dish Weight	Wt of Dish and sample prior to drying	Final weight/volume of sample	First Weighing	Second Weighing
180-7343-A-2	1311B Free Sand I12742	2540G	T	11	27.75 g	37.08 g	9.33 g	36.54 g	36.54 g
180-7343-A-2-DU		2540G	T	Z15	29.51 g	38.94 g	9.43 g	38.40 g	38.40 g

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General Chemistry Worksheet

Batch Number: 160-25593
Method: SM 2540G
Analyst: Cox, Chrissy M

Date Open: Jan 10 2012 10:27AM
Batch End:

Lab ID	Client ID	Method Chain	Basis	Third Weighing	Weight of Residue and Dish	Weight after ignition 1	Weight after ignition 2	Weight after ignition 3	Weight at 550 C
160-7343-A-2	1311B Free Sand I12742	2540G	T	36.54 g	36.54 g	36.55 g	36.54 g	36.55 g	36.55 g
160-7343-A-2-DU		2540G	T	38.40 g	38.4 g	38.40 g	38.39 g	38.40 g	38.4 g

General Chemistry Worksheet

Batch Number: 160-25593
Method: SM 2540G
Analyst: Cox, Chrissy M

Date Open: Jan 10 2012 10:27AM
Batch End:

Lab ID	Client ID	Method Chain	Basis	Calculation Message
160-7343-A-2	1311B Free Sand I12742	2540G	T	OK
160-7343-A-2-DU		2540G	T	OK

Oven ID: 2/3
Oven, Bath or Block Temperature 1: 104/550 Celsius
Perform Calculation (0=No, 1=Yes): 1

General Chemistry Worksheet

Batch Number: 160-25593
Method: SM 2540G
Analyst: Cox, Chrissy M

Date Open: Jan 10 2012 10:27AM
Batch End:

Comments

Lab ID	Client ID	Method Chain	Basis	Analysis comment
160-7343-A-2	1311B Free Sand I12742	2540G	T	
160-7343-A-2-DU		2540G	T	

Batch Comment: oven 2- 10:32 1/10/12 - 08:44 1/11, oven 3- 08:55-09:55 0 1/11/12

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Attachment B
GeoExplorer 6000 Series Datasheet

DATASHEET

GEOEXPLORER 6000 SERIES
GEOXH HANDHELD

KEY FEATURES

220 channel GNSS receiver with real-time H-Star technology
Decimeter accuracy faster than ever before

Floodlight satellite shadow reduction technology
More positions and increased accuracy in tough environments

Sunlight readable display
4.2" polarized screen for unmatched clarity in bright sunlight

3.5G modem option
Integrated cellular for Internet connectivity in the field

5 megapixel autofocus camera
Capture high quality photographs and link directly to features

High capacity removable battery
More than 8 hours operation on a single charge and swap-and-go battery replacement in the field

DECIMETER ACCURACY, TRIMBLE PRODUCTIVITY, HANDHELD CONVENIENCE

The Trimble® GeoExplorer® 6000 series takes GNSS productivity to a whole new level. Bringing together the essential functionality for high-accuracy field work in one device, the GeoXH™ handheld delivers real-time decimeter (10 cm / 4 inch) accuracy positioning, high quality photo capture, and integrated Internet connectivity options.

Together with the latest field software enhancements and GNSS innovations—including Trimble Floodlight™ satellite shadow reduction technology—the GeoXH handheld establishes a new standard for GNSS system performance and handheld data capture.

Decimeter accuracy without the wait

For field workers recording the location of buried infrastructure, distinguishing between closely spaced assets, or relocating buried equipment, the GeoXH handheld delivers the accuracy and speed required to ensure that the work of recording new asset locations or navigating back to previously captured assets is fast and reliable.

The GeoXH handheld is equipped with a 220 channel GNSS receiver capable of tracking GPS and GLONASS satellites together with an integrated dual-frequency (L1/L2) GNSS antenna. In conjunction with Trimble field software, the GeoXH handheld uses Trimble H-Star™ technology to deliver decimeter accuracy in the field, eliminating the need for back-office processing and giving the confidence that the job is done right while still on site.

Floodlight satellite shadow reduction

Trees and buildings create satellite shadows, limiting the environments where reliable high-accuracy GNSS data collection can be performed. Using the innovative Trimble Floodlight satellite shadow reduction technology, the GeoXH handheld continues to deliver productive, usable positioning data in areas where legacy GNSS receiver systems cannot.

With Floodlight technology, the GeoXH receiver can compute positions even with very weak satellite signals. Floodlight technology increases the number of positions that are gathered in difficult locations, and boosts accuracy in those places where normally only low accuracy data is available. With the GeoXH handheld, field crews can now work with fewer disruptions, meaning better data, faster, at less cost.

Never-seen-before display performance

The GeoXH handheld includes a sunlight-optimized display designed specifically for outdoor operation. It maintains exceptional clarity in all outdoor conditions, including direct sunlight. Text is crisp and easy to read. Background maps and photos are rich and vibrant. At 4.2" (10.7 cm), the display is also big, so the touch panel is spacious and easy to control.

Work online, anywhere, cable-free

With the GeoXH handheld, wireless connectivity options including cellular, Wi-Fi and Bluetooth® technology ensure that field workers can remain in contact with the office and each other, even from remote locations.

An optional integrated 3.5G cellular modem allows continuous network and Internet access to real-time map data, web-based services, VRS™ corrections, and live update of field information.

Bluetooth technology also enables wireless connection to other external devices such as Bluetooth-enabled laser range finders, barcode scanners, or underground pipe locators.

High quality photo capture

A photograph is often the best way to capture information about an asset, event, or site. The GeoXH handheld includes a 5 megapixel autofocus camera with geo-tagging capability. The camera can be controlled by the TerraSync™ software and other third-party applications, so photo capture and linking of images to GIS features is seamless and simple to integrate with existing data capture workflows.

Designed for work

The GeoExplorer 6000 series was designed with a single goal in mind—delivering a high-accuracy handheld GNSS system that works faster, longer, and in more places than any other.

The Lithium-Ion battery provides up to 8 hours of GNSS operation on a single charge, and can be swapped on-the-go without shutting down the device—enabling near-continuous operation and minimizing field worker downtime.

The GeoXH handheld is powered by a super-fast OMAP 3503 series processor and 256 MB RAM. With 2 GB of internal storage and the capacity to add an additional 32 GB via SDHC card, the GeoXH handheld has the capacity and power needed to work with high resolution maps and the most complex datasets.

The fully ruggedized IP65 construction is designed to withstand the harshest environments. Wherever field workers go, they can take the GeoXH handheld with the confidence that the equipment can handle the toughest conditions.

These smart design features combine with unprecedented accuracy and productivity to deliver the ultimate high performance handheld field solution.

The GeoXH handheld. Designed for work.

Trimble®

GEOEXPLORER 6000 SERIES GEOXH HANDHELD

SYSTEM SUMMARY

- Dual-frequency GNSS receiver and antenna with Everest™ multipath rejection technology and Trimble Floodlight satellite shadow reduction technology
- Sunlight readable 4.2" polarized screen
- Optional integrated 3.5G cellular modem
- Integrated Wi-Fi and Bluetooth wireless technology
- 5 megapixel autofocus camera
- Windows Mobile® 6.5 (Professional edition)
- Rugged and water-resistant design

SIZE AND WEIGHT

Height . . . . . 234 mm (9.2 in)
Width . . . . . 99 mm (3.9 in)
Depth . . . . . 56 mm (2.2 in)
Weight (inc. battery) . . . . . 925 g (2.0 lb)

GNSS

Receiver . . . . . Trimble Maxwell™ 6 GNSS chipset
Channels . . . . . 220 channels
Systems . . . . . GPS, GLONASS, SBAS
GPS L1C/A, L2C, L2E
GLONASS L1C/A, L1P, L2C/A, L2P
SBAS[1] . . . . . WAAS/EGNOS/MSAS
Update rate . . . . . 1 Hz
Time to first fix . . . . . 45 s (typical)
NMEA-0183 support . . . . . Optional
RTCM support RTCM2.x/RTCM3.x
CMR support . . . . . CMR/CMR+/CMRx

GNSS ACCURACY (HRMS) AFTER CORRECTION[2]

Real-time H-Star[2] . . . . . 10 cm + 1 ppm
Real-time code corrected
  VRS or local base . . . . . 75 cm + 1 ppm
  SBAS (WAAS/MSAS/EGNOS) . . . . . < 1 m
H-Star postprocessed . . . . . 10 cm + 1 ppm
Code postprocessed . . . . . 50 cm + 1 ppm
Carrier postprocessed
  After 45 minutes . . . . . 1 cm + 2 ppm

TEMPERATURE

Operation . . . . . –20 °C to +50 °C (–4 °F to 122 °F)
Storage . . . . . –30 °C to +70 °C (–22 °F to 158 °F)
Charging . . . . . 0 °C to +45 °C (32 °F to 113 °F)

MECHANICAL SHOCK

Drop . . . . . 1.2 m (4 ft) plywood over concrete
Vibration . . . . . Method 514.5

ALTITUDE & HUMIDITY RATINGS

Relative humidity . . . . . 95% non-condensing
Maximum operating altitude . . 3,658 m (12,000 ft)
Maximum storage altitude . . . . 5,000 m (16,400 ft)

INGRESS PROTECTION

Water/Dust IP65

BATTERY

Type . . . . . Rechargeable, removable Li-Ion
Capacity . . . . . 11.1V 2.5 AH
Charge time . . . . . 4 hours (typical)

BATTERY RUN TIME[3]

GNSS only . . . . . 10 hours
GNSS & VRS over BT . . . . . 9.5 hours
GNSS & VRS over Wi-Fi . . . . . 8.5 hours
GNSS & VRS over Cellular modem . . . . . 5 hours
Standby time . . . . . 50 days

BUTTONS & CONTROLS

- Power key
- Left & right application keys
- Camera key

CONNECTORS & INPUTS

- Internal microphone and speaker
- Mini USB connector
- DE-9 serial via optional USB to serial converter
- External power connector
- SIM socket
- SDHC card socket

CAMERA

Still mode . . . . . Autofocus 5 MP
Still image format . . . . . JPG
Video mode . . . . . Up to VGA resolution
Video file format . . . . . WMV with audio

CELLULAR[4] & WIRELESS[5]

UMTS/HSDPA . . . . . 850/900/2100 MHz
GPRS/EDGE . . . . . 850/900/1800/1900 MHz
Wi-Fi . . . . . 802.11 b/g
Bluetooth . . . . . Version 2.1 + EDR

DISPLAY

Type . . . . . Transflective LED-backlit LCD
Size . . . . . 4.2" (diagonal)
Resolution 480x640
Luminance . . . . . 280 cd/m^2

HARDWARE

Processor . . . . . TI OMAP 3503
RAM . . . . . 256 MB
Flash . . . . . 2 GB
External storage . . . . . SD/SDHC up to 32 GB

LANGUAGES

- English (US), Spanish, French, German, Italian, Portuguese (Brazilian), Chinese (Simplified), Korean, Japanese, Russian

IN THE BOX

- GeoExplorer 6000 series handheld
- Pouch
- Hand strap
- USB data cable
- Rechargeable battery pack
- AC Power adaptor
- Screen protector kit
- Spare stylus & tether
- Documentation

OPTIONAL ACCESSORIES

- Tornado™ external GNSS antenna
- 1.5 m & 5 m external antenna cable
- Range pole kit for external antenna
- Backpack kit for external antenna
- Vehicle mount
- Hard carry case
- TDL 3G cellular modem
- GeoBeacon receiver
- Null modem cable
- USB to serial converter cable

SOFTWARE COMPATIBILITY

- TerraSync™ software
- Trimble GPScorrect™ extension for Esri ArcPad software
- Trimble GPS Controller software
- GNSS Connector software
- GPS Pathfinder® Office software
- Trimble GPS Analyst™ extension for Esri ArcGIS Desktop software
- Third party NMEA-based applications[6]

1 SBAS (Satellite Based Augmentation System). Includes WAAS available in North America only, EGNOS available in Europe only and MSAS available in Japan only.
2 HRMS refers to Horizontal Root Mean Squared accuracy, 1-sigma (68%). Except in conditions where most GNSS signals are affected by trees, or buildings, or other objects. The following factors increase the availability of specified H-Star accuracy: availability of GPS & GLONASS data at the base station(s) used for corrections, longer elapsed time tracking uninterrupted L1/L2 carrier phase data, use of the optional external Tornado antenna, tracking of more satellites with L2 measurements, shorter distance to the base station(s), and use of more (than one) base stations for postprocessing. Specified H-Star accuracy can normally be achieved for baseline lengths of 100 km or less. H-Star accuracy is typically achieved within 2 minutes. 45 minute carrier postprocessed accuracy is limited to data collected within 10 km of the base station. Except when using VRS corrections, accuracy varies with proximity to base station by +1 ppm for code postprocessing and real-time. Carrier postprocessed accuracy varies with proximity to base station by +2 ppm.
3 Tested by Trimble with default system settings at 21°C ambient. Actual run time will vary with conditions of use.
4 3.5G edition handhelds only. The GeoXH 3.5G edition handheld is PTCRB certified and can operate on supported networks that do not require carrier certification. Consult with your local reseller for more information.
5 Bluetooth and Wi-Fi type approvals are country specific. GeoExplorer 6000 series handhelds have Bluetooth and Wi-Fi approval in the U.S. and in most European countries. For further information please consult your local reseller.
6 NMEA output is an optional upgrade.

Specifications subject to change without notice.

bg Wi Fi CERTIFIED®

Bluetooth®

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