Standard Operating Procedure
Analytical Method

TITLE: Analysis of Base/Neutral and Acid (BNA) Compounds by GC/MS

DEPARTMENT: Semivolatile Organics

APPLICATION: This method is used to determine the concentration of various BNA compounds in water, solid waste and biological tissue samples. Appendix A contains the compounds that may be determined by this method and the detection limits for each compound in reagent water.

REFERENCES: Test Methods for Evaluating Solid Wastes
SW846 Method 8000B (Revision 2, December 1996)
SW846 Method 8270C (Revision 3, December 1996)

Code of Federal Regulations
USEPA Method 625 40CFR Pt. 136, App. A, Ch. 1 (7-1-88 Ed.)

PROCEDURE SUMMARY:

This method provides the gas chromatographic conditions for the separation of the compounds in the extract for the quantitative analysis by mass spectrometry. A volume of a sample extract is injected into a gas chromatograph (GC) and compounds in the effluent are analyzed by mass spectrometry (MS).

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SAMPLE EXTRACT HANDLING AND STORAGE

Store all extracts at 4° ± 2° C in the dark in Teflon-sealed containers until analysis is complete. Sample extracts must be analyzed within 40 days from time of extraction.

INTERFERENCES:

Method interferences may be caused by contaminants (primarily phthalate esters) in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total 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. Contact with common plastics or rubber products must be avoided.

Matrix interference's may be caused by contaminants that are co-extracted from the sample. The extent of matrix interference's will vary considerably from source to source. The GPC (Gel Permeation Chromatography) cleanup procedure is available for cleaning up the sample extract. The extraction personnel initially determine the need for GPC cleanup. The analyst can request that the sample extracts have GPC cleanup prior to the addition of Internal Standards. This is usually determined by visual inspection of the sample extract or by historical data. Tissue samples should routinely be cleaned by GPC.

APPARATUS AND MATERIALS:

GC/MS:	Hewlett Packard (HP) GC5890 series / MSD5970, MSD5972 or equivalent, capable of scanning 35-500 amu at 1 sec/scan.
GC Autosampler:	HP7673 or equivalent.
Data Processor:	HP ChemStation (acquiring) / HP ChemServer-Target 3 (analysis) or equivalent.
Printer:	HP Laserjet 4 or equivalent
Syringes:	10-1000 µL Gastight syringes (Hamilton series 1000 or equivalent).
Autosampler Vials:	2 mL with crimp top caps.
GC Column:	Rtx-5MS capillary column, 30 m x 0.32 mm I.D. x 0.5 um df with guard column or XTI-5 capillary column, 30 m x 0.25 mm I.D. x 0.25 um df with guard column (Restek or equivalent).

Note: The conditions below are typical conditions for this method. The actual conditions used for each instrument will be adjusted to optimize instrument performance.

GC Column Conditions:

Carrier gas -	Helium	Injector temperature -	280° C
Flow rate -	1.2 mL/min.	Splitless Injection Flow Rate -	50-60 mL/min.
Linear velocity -	43.1 cm/sec.	Auxillary E pressure control -	50 psi
Detector temp. -	290° C		

Inlet B Pressure Program:

Initial Pressure-	0.2 psi
Initial Time -	0.10 min.
Level 1 Rate -	99 psi/min.
Final 1 Pressure -	10 psi
Final 1 Time -	0.40 min.
Level 2 Rate-	99 psi/min.
Final 2 Pressure-	0.2 psi
Final 2 Time -	1.2 min.
Level 3 Rate -	0.3 psi/min.
Final 3 Pressure -	10 psi
Final 3 Time -	0.0 min.

GC Temperature Program:

Initial temp. -	40° C
Initial time -	2 min.
Rate 1 -	10° C/min.
Final 1 temp. -	300° C
Final 1 time -	0.0 min.
Rate 2 -	16 C/min.
Final 2 temp. -	320 C
Final 2 time -	7 min.

REAGENTS:

Solvents: Methylene chloride and acetone pesticide grade.

Stock Standards Solutions: Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or an independent source. Shelf-life of standard solutions is 12 months from the date of preparation.

Calibration Standards: Standard Mixtures containing all compounds including surrogate compounds at 6 concentration levels are prepared from the stock solutions. Each calibration solution is spiked with 40 ng of internal standard solution. One of the concentration levels should be at a concentration near, but above, the method detection limit. This low standard of the calibration curve is the reporting limit known as the estimated quantitation limit (EQL). Shelf-life of the calibration solutions is 6 months from the date of preparation.

Internal Standards: A commercially prepared standard mix at a concentration of 4000 µg/mL is used. This solution is certified by the manufacturer (Restek). Shelf-life of standard solution is 6 months from the date of preparation. See Appendix B.

Surrogate Standards: Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or an independent source. Shelf-life of standard solutions is 6 months from the date of preparation. See Appendix B.

Matrix Spike/Laboratory Control Sample Standards: A commercially prepared stock standard solution is used at a concentration of 100 µg/mL certified by the manufacturer. See Appendix C for the list of compounds in the matrix spike mix. See Appendix G for the list of compounds in the Laboratory Control Sample spike mix.

GC/MS Tuning Standard: Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or an independent source. Shelf-life of standard solutions is 6 months from the date of preparation. See Appendix B.

GC/MS INITIAL CALIBRATION:

1. GC/MS tuning standard: Inject 1 µL of 50 ng of Decafluorotriphenylphosphine (DFTPP). The average of three scans (the apex and the scan before and after the apex) may be used. Background subtraction is required and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. Compare the mass listing to the tuning criteria in appendix D. The tuning criteria <u>must</u> be met in order to continue calibration or sample analysis.

   All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

   The DFTPP tuning standard should include 50 ng each of the following additional compounds, pentachlorophenol, benzidine and DDT in order to assess GC column performance and injection port inertness. The degradation of DDT to DDE and DDD should not exceed 20%. If any observable DDD or DDE peaks are present the % Breakdown must be calculated as shown below and recorded in the injection log.

   The responses for benzidine and pentachlorophenol should be normal with no peak tailing. If peak tailing is observed, the peak tailing factor must be calculated as illustrated in Appendix J. The tailing factor for Benzidine must be less than 3.0 and less than 5.0 for pentachlorophenol. The tailing factor must be recorded in the injection log if calculated.

$$\%\ \text{DDT Breakdown} = \frac{\text{Total peak area of (DDD + DDE)}}{\text{(DDD + DDE + DDT)}} \times 100\%$$

   If Breakdown and tailing are not observed, note that DFTPP criteria has been met in the injection log.
   If degradation of DDT is excessive and/or the chromatography for benzidine or pentachlorophenol is poor the injection port may require cleaning and replacement of the glass liner, liner insert, and the gold seal. Also 6-12 inches of the column should be cut off. This preventative must be performed prior to sample analysis. If the response for pentachlorophenol continues to be very poor or absent then the column may need to be replaced.

2. Inject 1 µL of each of the calibration standard solutions, SSTD010, SSTD020, SSTD050, SSTD080, SSTD120, and SSTD160. Determine the response factors (RF), the average RF and percent relative standard deviation (%RSD) for each compound.

A. $RF = (A_x C_{is})/(A_{is} C_x)$

Where: A_x = Area of the characteristic ion for the compound being measured
A_{is} = Area of the characteristic ion for the specific internal standard
C_{is} = Concentration of the specific internal standard
C_x = Concentration of the compound being measured

B. $\%RSD = 100[SD/RF_{ave}]$

The %RSD should be less than or equal to 15% for each compound. The %RSD <u>must</u> not exceed 30% for the Calibration Check Compounds (CCC). (See Appendix D).

Linearity - If the %RSD is less than or equal to 15%, then the average RF is used for calculating the concentration of the compound being measured. If the %RSD exceeds 15%, the analyst must choose the best calibration option for quantitation purposes. Linear regression, quadratic regression, and third order polynomial are the other options used for analyte quantitation. It is not the intent to allow non-linear calibration to be used to compensate for detector saturation at higher concentration or to avoid proper instrument maintenance. Non-linear calibration may not be employed for analytes previously shown to exhibit linear calibration. When the linear model is used, the correlation coefficient must be greater than or equal to 0.99.

South Carolina requires the use of a linear calibration model. Either the %RSD is less than 15% and the average RF is used for quantitation or a linear regression with a correlation coefficient greater than or equal to 0.99 must be used for all analytes listed in SW 846 Method 8270C. Any single point within the calibration curve may be re-run if it appears there was a problem with the injection. Since a calibration curve generally consists of more than 5 calibration standards, some of the responses from the upper end of the curve do not need to be included to reduce the data. At least 5 standards must be used to generate the calibration curve. Dilutions must be performed if the concentration of an analyte exceeds the concentration of the highest calibration standard in the curve used to quantify the sample.

C. The System Performance Check Compounds (SPCC) <u>must</u> have a minimum RF of 0.050 (See Appendix D).

If these criteria are not met, corrective action is required such as cleaning or replacing the injection port liner and/or capillary column or, recalibration.

If the CCCs are not included in the list of analytes for a project, then all required analytes must meet the 30% RSD criterion.

3. Analysis of Initial Calibration Verification Standard

   In order to consider the initial calibration acceptable, an Initial Calibration Verification Standard (ICV) must be analyzed prior to sample analysis. The ICV standard must be from a second source and meet the same criteria as the Continuing Calibration Verification (CCV) standard before the initial calibration may be considered valid.

4. GC/MS Daily Calibration:

   A. GC/MS Tuning Standard (DFTPP). Inject 1 µL of 50 ng DFTPP and compare the mass listing to the acceptance criteria in Appendix D. The tuning standard must precede each 12-hour analysis sequence.

   B. A midpoint calibration standard (50 ppm) must precede sample analysis. The calibration check response factors are compared to average response factors from the initial calibration.

      1. The SPCCs must meet the minimum RF criteria of 0.050.

      2. The CCCs must meet the percent difference (%D) criteria.

$$\%D = \frac{RF_{ave} - RF}{RF_{ave}} X100$$

      If the percent difference for any compound is greater than 20%, this is considered a warning limit. If the percent difference for each of the CCCs is less than or equal to 20%, then the initial calibration is assumed valid and analysis of samples may proceed. If the 20% criterion is not met for CCCs, corrective action must be taken. Corrective action will consist of re-calibration and instrument maintenance if necessary. If the CCCs are not analytes required for the project, then all required analytes must meet the 20% drift criterion.

      3. If the retention time for any internal standard in the continuing calibration check standard changes by more than 30 seconds from that in the mid-point standard level in the most recent calibration sequence, the chromatographic system must be inspected for any malfunction and corrective action must be made.

      4. The area counts of the internal standard peaks must be within 50-200% of the area counts obtained in the mid-point standard of the initial calibration curve.

SAMPLE ANALYSIS:

1. All samples, method blanks, laboratory control samples and matrix spikes must be analyzed within 12 hours of a valid DFTPP tuning standard.

2. All samples, method blanks, laboratory control samples, and matrix spike extracts are spiked with 40 ng of internal standard solution mix just prior to analysis.

   The internal standard areas of the samples, method blanks, laboratory control samples, and matrix spikes must fall within a factor of two (-50% to +100%) range from the preceding midpoint calibration check standard. In addition, the relative retention times of the internal standards for each sample analysis must fall within a ± 30 second window defined by the midpoint calibration check standard.

3. Surrogate recoveries are calculated using the following equation:

   $$\text{Surrogate \% Recovery} = (C_{ex} / C_s) \times 100$$

   Where: C_{ex} = Concentration of analyte in the extract (mg/L).
   C_s = Calculated concentration of analyte spiked into extract based on amount spiked (mg/L).

   Compare the surrogate recoveries according to the specific matrix to the recovery limits in appendix E. These limits are updated annually.

4. Qualitative sample analysis:

   A. The relative retention time (RRT) for the sample component must compare within ± 0.06 RRT units of the standard component.

   B. The mass spectrum for a sample component should compare to the spectrum of the standard component. Note: These criteria do not overrule the judgment of the analyst.

      1. All ions present in the standard mass spectrum greater than 10% should be present in the sample spectrum.

      2. The relative intensities of those ions must agree within ± 30% of those ions in the reference spectrum.

5. Quantitative sample analysis:

   When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the extracted ion current profile (EICP) of the primary characteristic ion. See Appendix A for primary ion (1°) of each compound. A dilution of the sample shall be performed for any analyte that exceeds the high calibration point of the calibration.

   Calculation of the Concentration of the analyte in the extract (C_{ex}).

   $$(C_{ex}) = (A_x C_{is})/(A_{is} RF)$$

   Where: A_x = Area of the characteristic ion for the compound being measured
   A_{is} = Area of the characteristic ion for the specific internal standard
   C_{is} = Concentration of the specific internal standard

RF = Average Response factor from calibration curve.

Water:

$$\text{concentration } (\mu g/L) = \frac{(C_{ex})(V_F)(DF)}{(V_o)}$$

Soil/Tissue:

$$\text{concentration } (\mu g/kg) = \frac{(C_{ex})(V_F)(DF)}{(W_s)(D)}$$

Where: C_{ex} = Concentration of analyte in the extract (ug/mL)
DF = Dilution factor (if applicable)
V_o = Initial sample volume (L)
V_F = Final extract volume (mL)
W_s = Initial sample weight extracted (kg)
D = % solids (if applicable)

Tissue samples are generally reported on an "as is"' basis and are not dry weight corrected.

QUALITY CONTROL:

1. The method blank must meet the surrogate limits (see appendix E). If the blank fails these criteria, all of the associated samples, matrix spikes and laboratory control spikes must be re-extracted.

2. The results of the method blank must be (a.) less than the laboratory's reporting limit (see Appendix A), (b.) less than 5% of the regulatory limit associated with an analyte, or (c.) less than 5% of the sample result for the same analyte, whichever is greater. If the blank contains contamination, the source must be located and eliminated.

3. The sample surrogate recovery acceptance criteria are listed in Appendix E. One acid and one base surrogate are allowed to be outside of the acceptance criteria without performing corrective action. **For samples from the State of South Carolina,** if any sample fails these criteria, the sample must be re-extracted unless it is demonstrated to be a matrix effect.

4. Every batch of samples must contain a Laboratory Control Sample (LCS). The LCS is used to verify method performance in the event of poor recoveries in the Matrix Spike or Matrix Spike Duplicate. The control limits for the LCS should fall within the prescribed limits (see Appendix G).

   Since an extensive number of compounds are spiked into the LCS, a small percentage of sporadic marginal failures may be tolerated (i.e., will not trigger re-extraction and analysis of the entire batch). See Appendix I for amount of sporadic failures allowed. The control limits for the LCS must fall within the prescribed limits (see Appendix G). See the METHOD EXCEEDANCES section for exceptions to this tolerance. If more analytes are