METHOD 8272

PARENT AND ALKYL POLYCYCLIC AROMATICS IN SEDIMENT PORE WATER BY SOLID-PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY IN SELECTED ION MONITORING MODE

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generation its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 The U.S. Environmental Protection Agency (USEPA) narcosis model for benthic organisms in sediments contaminated with polycyclic aromatic hydrocarbons (PAHs) is based on the concentrations of dissolved PAHs in the interstitial water or pore water in sediment. Method 8272 covers the separation of pore water from PAH-impacted sediment samples, the removal of colloids, and the subsequent measurement of dissolved concentrations of the 10-parent PAHs and two alkylated daughter PAHs in the pore water samples. This method directly determines the concentrations of dissolved PAHs in environmental sediment pore water, groundwater, and other water samples. The following polycyclic aromatic hydrocarbons (PAHs) have been determined by this method and other PAH compounds may also be amenable to analysis by this method:

Analyte	CAS No[a]
Naphthalene	91-20-3
2-Methylnaphthalene	91-57-6
1-Methylnaphthalene	90-12-0
Acenaphthylene	208-96-8
Acenaphthene	83-32-9
Fluorene	86-73-7
Phenanthrene	85-01-8
Anthracene	120-12-7
Fluoranthene	206-44-0
Pyrene	129-00-0
Benz(a)anthracene	56-55-3
Chrysene	218-01-9

[a]: Chemical Abstract Registry Number

NOTE: Method 8272 is specifically for the determination of dissolved PAHs in interstitial water or pore water in sediment samples only. If the heavy molecular weight PAHs that may be present in the particulates are of concern, additional determinative extraction and analysis methods are required to measure suspended and sediment-based (i.e., total) PAHs.

Regulatory methods using solvent extraction have not achieved the wide calibration ranges from nanograms to milligrams per liter and the necessary levels of detection in the nanogram per liter range. In addition, conventional solvent extraction methods require large aliquot volumes (liter or larger), the use of large volumes of organic solvents, and filtration to generate the pore water. Solvent extraction entails the storage and processing of large volumes of sediment samples and may result in the loss of low molecular weight PAHs in the filtration and solvent evaporation steps.

This method can be used to determine nanogram to milligram per liter PAH concentrations in pore water. Small volumes of pore water are needed for solid phase microextraction (SPME), only 1.5 mL per determination, and virtually no solvent extraction waste is generated.

1.2 Lower molecular weight PAHs are more water soluble than higher molecular weight PAHs. Therefore, PAH concentrations in pore water samples vary widely due to differing saturation water solubilities that range from 0.2 µg/L for indeno[1,2,3-cd]pyrene to 31,000 µg/L for naphthalene. This method can accommodate the measurement of milligram per liter concentrations for low molecular weight PAHs and nanogram per liter concentrations for high molecular weight PAHs, such as benz(a)anthracene and chrysene and any other four-five ring PAHs that can be determined by this method.

1.3 This method can achieve the necessary lower limits of quantitation, which range from approximately 0.06 µg/L for high molecular weight PAHs, to approximately 9 µg/L for low molecular weight PAHs.

1.4 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600 and 8000). For additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance, analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography/mass spectrometers and skilled in the

interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Pore water is separated from wet sediment samples by centrifugation and supernatant collection. The groundwater and tap water samples begin preparation with the colloid removal step. Colloids are removed from the separated pore water, groundwater, and tap water samples by flocculation with aluminum potassium sulfate (alum) and sodium hydroxide. A second flocculation and centrifugation step, followed by supernatant collection, completes the colloid removal.

2.2 The PAHs are determined using SPME followed by gas chromatography/mass spectrometry (GC/MS) analysis in selected ion monitoring (SIM) mode. Either the use of an autosampler, or a manual approach can be used to perform the SPME extraction and the subsequent injection of collected analytes into the GC/MS. Isotopically labeled analogs of the target compounds are introduced prior to the extraction, and are used as quantitation references.

2.3 The mass spectrometer is operated in the SIM mode for the molecular ions of the target PAHs and d-PAHs to achieve low limits of detection. Analyte concentrations are quantitated by either of two methods: (1) parent PAHs (i.e., unsubstituted PAHs) for which an exact deuterated analog is not included in the internal standard mix are quantitated by reference to a deuterated analog of a PAH with the same number of rings as the analyte, or (2) PAHs for which an exact deuterated analog is included in the internal standard mix are quantitated by isotope dilution.

2.4 Test Method Options: Either the use of an autosampler or a manual approach may be used to perform the SPME extraction and the subsequent injection of collected analytes into the GC/MS. An autosampler is much preferred over the manual method because: (1) the autosampler yields lower and more reproducible blanks, (2) the manual method requires the use of a stir bar that can cause sample cross-contamination, (3) the manual method is highly labor-intensive and requires multiple timed manipulations per analysis leading to operator fatigue and resultant errors, and (4) the autosampler reduces the technician time required to prepare samples for a 24-hour run sequence to approximately 3 hours, while the manual method requires 24 hour operator attendance. Therefore, the method procedures are written assuming the use of an autosampler, with modifications to the autosampler procedures listed for the manual method.

2.4.1 Autosampler Method

2.4.1.1 Pore Water Separation and Preparation: Pore water is separated from wet sediment samples by centrifugation and supernatant collection. The groundwater and tap water samples begin preparation with the colloid removal step. Colloids are removed from the separated pore water, groundwater, and tap water samples by flocculation with aluminum potassium sulfate (alum) and sodium hydroxide. A second flocculation and centrifugation, followed by

supernatant collection completes the colloid removal. The prepared water samples are then split into the number of replicate aliquots needed and placed into silanized glass autosampler vials. The 8 perdeuterated PAH internal standards (d-PAHs) are then added immediately. All of the water preparation steps beginning with the centrifugation and ending with the addition of d-PAH internal standards should be conducted continuously and in the minimum amount of time possible.

The SPME fiber should be cleaned at the beginning of each sampling set (and after very contaminated samples) while the water samples are being prepared.

2.4.1.2 Solid-Phase Microextraction: The SPME extraction of the water samples is performed using a commercially available polydimethylsiloxane (PDMS)-coated fused silica fiber while the water sample is mixed by the precession of the autosampler mixing chamber. The target PAHs and d-PAH internal standards adsorb to the nonpolar PDMS phase at equivalent rates. The use of the d-PAHs (i.e., isotopic dilution) to quantitate the target PAHs compensates for variations in equilibrium partitioning and kinetics.

2.4.1.3 GC/MS SIM Analysis: Following the sorption period, the SPME fiber is immediately desorbed to a GC/MS injection port in the splitless mode. Following the desorption period, the SPME fiber is inserted into the cleaning port and additionally cleaned. At the end of the cleaning period, sorption of the next water sample is begun.

2.4.2 Manual Method

Alternate Procedures for Manual Method: Samples are prepared as for the autosampler method, except that a small Teflon-coated stir bar is placed in the silanized autosampler vial prior to adding the water and d-PAH internal standard solution. A new stir bar should be used for each sample, calibration standard, and blank to avoid cross-contamination caused by carryover on the stir bar. To perform the SPME step, the vial is set on a stir plate and the stirring rate adjusted so that no large vortex is formed. The SPME fiber should be inserted into the water so that the entire-active length is exposed to the water sample, but not so low that the fiber comes into contact with the stir bar or that the metal needle sheath contacts the water. All time sequences should be the same as described for the autosampler method. A spare GC split/splitless injection port under helium flow can be used for the cleaning step between samples as well as for the initial cleaning step at the beginning of each working day.

2.5 This method includes specific calibration, sample analysis, and quality control steps that supersede the general requirements provided in Method 8000.

3.0 DEFINITIONS

Refer to the SW-846 Chapter One, Chapter Four and appendix of terms and definitions for potentially applicable definitions.

3.1 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 HP5973 include SIM mode and Low Mass Resolution Mode.

3.2 Lower Limit of Quantitation – The lower limit of quantitation (LLOQ) for each individual PAH is defined as the concentration of an individual PAH that would yield 1/34 of a toxic unit (see Sec. 3.4). Due to the differences in saturation solubilities for the PAH compounds recommended in this method the LLOQ will also vary for each compound. Ideally, the exact LLOQ should be at or below those recommended in Table 3 for optimum method performance. However, the actual LLOQs should be a project planning decision based on the desired project-specific data quality objectives. For example lower limits of quantitation of each individual PAH refer to Table 3. See Ref. 2 in Sec. 16.0 for additional details.

3.3 Solid Phase Microextraction (SPME): Solid phase microextraction has been used for the determination of PAHs in water samples. SPME utilizes a commercially available 7 micron thick polydimethylsiloxane (PDMS)-coated fused silica fiber. The target PAHs and d-PAH internal standards adsorb to the nonpolar PDMS phase at equivalent rates. PAHs are extracted onto the fiber from the sediment pore water for 30 minutes before they are desorbed into the GC/MS injection port.

3.4 Toxic Units - Using contaminated site sediment PAH concentrations and sediment organic carbon content, equilibrium partitioning (EqP) is used to predict the pore water concentrations of the PAHs, which are equivalent to the bioavailable concentrations for the hydrocarbon narcosis model. Alternatively, the pore water concentrations can be directly measured to more accurately determine the bioavailable concentrations than is possible using sediment concentrations and the EqP model. The analyte list in Sec. 1.1 can be expanded as described in Refs. 2 and 7 to include the alkyl PAHs necessary to calculate total toxic units based on hydrocarbon narcosis theory. For a more detailed discussion of toxic units and their application see Ref. 6 in Sec. 16.0.

4.0 INTERFERENCES

4.1 Non-target hydrocarbons can cause peaks on selected ion current profiles (SICPs) intended for other PAHs. Analysts should be familiar with both parent and alkyl PAH analyses in complex environmental samples.

4.2 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. The use of high purity reagents and solvents helps minimize interference problems.

4.3 For lower molecular weight PAHs, atmospheric contaminants can cause significant background peaks. This problem is most likely to be significant in urban areas impacted by atmospheric PAHs (e.g, from diesel exhaust), and with laboratories using manual techniques, rather than the SPME autosampler.

5.0 SAFETY

This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

This section does not list common laboratory glassware (e.g., beakers and flasks).

The mention of trade names or commercial products in this method is for illustrative purposes only, and does not constitute an EPA endorsement of exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance for the intended application has been demonstrated and documented.

6.1 Centrifuge capable of sustaining 1000 g with cups for securing 40-mL and 20-mL vials.

6.2 SPME fiber holder compatible with 7-µm SPME fiber and compatible with either the autosampler or the manual method.

6.3 SPME fused silica fibers coated with 7 µm film thickness polydimethylsiloxane (PDMS) from Sigma-Aldrich (formerly Supelco®) or equivalent.

6.4 PTFE coated stir bars (stir fleas) of a size effective for stirring 1.5 mL water without vortexing (for manual method only).

6.5 Magnetic stir plate (for manual method only).

6.6 SPME holder stand (for manual method only) or GC/MS autosampler capable of SPME extraction and injection (LEAP Technologies Combi-Pal or equivalent).

6.7 Cleaning port, capable of purging SPME fibers in a helium-swept atmosphere at 320 °C.

6.8 40-mL vials with Teflon-lined caps.

6.9 20-mL vials with Teflon-lined caps.

6.10 Silanized 2.0-mL autosampler vials.

6.11 GC/MS Analysis

6.11.1 Gas Chromatograph – Shall have split/splitless injection port for capillary column, temperature program with isothermal hold.

6.11.2 GC column – 60 m x 0.25 mm ID x 0.25 μm film thickness HP5-MS or equivalent. The column listed in this section was the column used in developing the method. The listing of this column in this method is not intended to exclude the use of other columns that are available or that may be developed. Laboratories may use this or another column provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

6.11.3 Inlet liner 2 mm i.d. silanized glass.

6.11.4 GC inlet 320 °C, splitless mode.

6.11.5 Oven program: Isothermal 5 minute hold at 40 °C. Ramp at 50 °C /minute to 110 °C, followed by a temperature ramp of 12 °C/minute to 320 °C (Hold for 10 min).

6.11.6 Mass Spectrometer – Electron impact ionization with the ionization energy optimized for best instrument sensitivity (typically 70 eV), stability and signal to noise ratio. Shall be capable of repetitively and selectively monitoring at least 12 separate m/zs during a period of approximately 1 second.

6.11.7 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 spectral information obtained throughout the duration of the chromatographic program. The computer should have software that can search any GC/MS data file for the SIM ions collected during each time window and that can plot such ion abundances.

7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals must 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 sufficiently high purity to permit its use without lessening the accuracy

of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 Reagent water: Deionized water, free of the analytes of interest. Water that meets the purity specifications of HPLC-grade water, or equivalent.

7.3 Internal standard stock solution. A dichloromethane solution of d-PAH internal standards used for preparing spiking solutions by dilution into acetone (see Sec. 11.3).

7.4 Internal standard spiking solution. A dilution of the internal standard stock solution in acetone used to spike d-PAH internal standards into all sample, calibration, and blank water vials (see Sec. 11.3).

7.5 Calibration stock solution. A dichloromethane solution of PAHs used for preparing calibration standards (see Sec. 11.3).

7.6 Calibration Spiking Solutions. A series of solutions prepared by diluting the calibration stock solution with acetone (see Sec. 11.3).

7.7 Calibration Standards. Prepared by adding internal standard and calibration spiking solutions in reagent water (see Sec. 11.3).

7.8 Acetone (CH_3COCH_3)

7.9 Dichloromethane (DCM) (CH_2Cl_2)

7.10 Sodium Hydroxide (NaOH). 1 M NaOH - Slowly add 10 g NaOH pellets to 125 mL reagent water and stir until completely dissolved. Fill the flask to 250 mL. Wear goggles and be aware of heat of solution. Store in a plastic container.

7.11 Aluminum Potassium Sulfate Dodecahydrate ($AlK(SO_4)_2 \cdot 12H_2O$).

7.12 Alum Solution: Add 20g ($AlK(SO_4)_2 \cdot 12H_2O$) to 80 mL reagent water.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Four, "Organic Analytes." Prior to shipment, the sediment samples should be mixed well. Sieve the slurry of sediment and site water through a 2-mm screen to remove debris. If the sieved slurry is to be stored or shipped before use, store in 250-mL to 1-L glass jars fitted with PTFE-lined lids. Great care must be taken to clean the lid of the jar before capping the jar with the lid to avoid leakage of the water during shipment. Groundwater and tap water samples should be stored in 250-mL to 1-L glass bottles fitted with PTFE-lined caps.

8.2 Ship samples in an ice chest with adequate ice to maintain 0-6 °C. Store the samples at the laboratory in the dark at 0-6 °C. Do not allow the samples to freeze.

8.3 Once the sample preparation process has begun, pore waters must be generated and flocculated as quickly as possible, but must be done within 28 days of

sediment sample collection. Pore water, groundwater, and tap water samples must then be immediately spiked with 10 µL of d-PAH solution following flocculation.

8.4 Solid phase micro-extraction must be completed within 24 hours of flocculation for pore water, groundwater, and tap water samples.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a quality assurance project plan (QAPP) or a sampling and analysis plan (SAP), which translates project objectives and directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference and inspection.

9.2 Refer to Method 8000 for specific determinative method QC procedures. Refer to Method 3500 for QC procedures to ensure the proper operation of the various sample preparation techniques. If an extract cleanup procedure is performed, refer to method 3600 for the appropriate QC procedures. Any more specific QC procedures provided in this method will supersede those noted in Methods 8000, 3500, or 3600.

9.3 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. Any more specific QC procedures provided in this method will supersede those noted in Method 8000.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. Analyze seven replicates, or any other suitable number based on the project planning objectives, of an initial demonstration of performance (IDP) solution. The IDP solution is a reagent water or field sample matrix solution fortified with the method analytes and internal standards at known concentrations. Ideally, the IDP solution should be prepared by an independent analyst. The mean and standard deviation of the seven values should then be calculated and compared to the test method accuracy and precision guidance values in Sec. 13.0.

If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff is trained or significant changes in instrumentation are made. See

Method 8000 for further information on how to accomplish a demonstration of proficiency.

9.5 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are free from contaminants and interferences. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed in the retention time window of any analyte that would prevent the determination of the analyte, determine the source and eliminate it, if possible, before processing any samples. The blanks should be carried through all stages of sample preparation and analysis. When new chemicals or reagents are received, the laboratory should monitor the preparation and/or analysis blanks associated with the samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents. This initial and continuing monitoring is accomplished through the analysis of extraction and analytical method blanks analyzed between every calibration verification standard and sample to monitor the baseline. See Table 4. Target analytes must not be detected above 1/3 of the lower limits of quantitation or greater than 20% of the associated sample result(s).

Should the acceptance criteria not be met for any extraction and analytical blank, locate the source of the contamination and correct the problem. Re-extract and reanalyze the associated samples that are less than ten times the level of the contaminant(s) present in the method blank.

9.6 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (i.e., precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate and a laboratory control sample (LCS) in each analytical batch. The use of deuterated analogs as internal standards makes the addition of surrogates unnecessary. Any method blanks, matrix spike samples, and replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.6.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix duplicate must be based on knowledge of the samples in the sample batch. If samples are expected to contain target analytes, laboratories may use a matrix spike and duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike/matrix duplicate pair. See Method 3500 for instructions on preparing the matrix spike standard. The same standard may be used as the laboratory control standard (LCS) and the spiking solution should be the same source as used for the initial calibration standards to restrict the influence of standard accuracy on the determination of

recovery through preparation and analysis. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD.

9.6.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, where appropriate. As noted in Sec. 9.6.1, the LCS is ideally prepared from the same source stock standard that is used to prepare the calibration standards. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Consult Method 8000 for information on developing acceptance criteria for the LCS.

9.6.3 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for evaluating method performance should be developed using the guidance in Method 8000.

9.7 Initial Calibration. The following acceptance criteria must be used for initial calibration: (i) The signal to noise (S/N) ratio for the GC signals present in every SICP must be $\geq$ 10:1 for the labeled internal standards and calibration compounds; (ii) The percent relative standard deviation (RSD) for the mean area ratio/ng for labeled internal standards and the calibration compounds must be less than 30% for high molecular weight PAHs and less than 25% for low molecular weight PAHs, and the r^2 must be greater than 0.99. The calibration curve must not be forced through the origin; and (iii) the number of calibration standards may be reduced from four to three based on the criteria in Sec. 11.4.1 of this procedure.

There must be an initial calibration of the GC/MS system as described in Sec. 11.3. In addition, the initial calibration curve should be verified immediately after performing the standard analyses using a second source standard (prepared using standards different from the calibration standards if available). It is assumed after this method is formally published that various standard vendors will offer other sources than the current single standard mix source option. Should an independent source or possibly another lot number from the same standard source used to prepare the calibration standards not be available during planned sample analyses, the initial calibration should be verified using the continuing calibration standard. The suggested acceptance limits for this initial calibration verification analysis are 70 - 130%. Alternative acceptance limits may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding these results could be used for screening purposes and would be considered estimated values.

The initial calibration must be re-established if the RSD(s) exceed the limit(s). However, it is not necessary to re-establish the initial calibration in response to a nonconforming RSD if the reported sample result(s) are less than the lower limits of quantitation and the signal to noise ratio and r^2 criteria are met.

9.8 Continuing Calibration Verification. The following acceptance criteria must be used for the daily duplicate calibration verifications: (1) The S/N ratio for the GC signals present in every SICP must be $\geq$ 10:1 for the labeled internal standards and the calibration compounds; (2) The percent differences for the measured area ratio/ng of all analytes must be within ±25% for high molecular weight PAHs and within ±20% for low molecular weight PAHs of the mean values established during the initial calibration.

The calibration verification standard should be prepared from the same stock standard source as is used for the initial calibration curve standards.

Should the acceptance criteria for the daily duplicate calibration verifications not be met, a new initial calibration curve must be established before sample extracts can be analyzed.

9.9 The signal to noise (S/N) ratio for the GC signals present in every SICP must be $\geq$ 3:1 for any target analyte in environmental samples and $\geq$ 10:1 for the labeled internal standards.

Should the acceptance criteria for any sample and/or labeled internal standard signal to noise ratio not be met, the sample should be reanalyzed unless obvious matrix interference is present.

10.0 CALIBRATION AND STANDARDIZATION

See Sec. 11.0 for calibration and standardization information.

11.0 PROCEDURE

11.1 To prepare the apparatus, set up the GC system using the following parameters.

11.1.1 GC Column Agilent HP-5MS column (0.25 µm film thickness, 0.25 mm ID) or equivalent.

11.1.2 Inlet liner 2-mm i.d. silanized glass.

11.1.3 GC Inlet 320 °C, splitless mode.

11.1.4 Oven program: Isothermal 5 minute hold at 40 °C. Ramp at 50 °C/minute to 110 °C, followed by a temperature ramp of 12 °C/minute to 320 °C. (Hold for 10 min.)

MS Quad Temperature: 150 °C, maximum 200 °C

MS Source Temperature: 230 °C, maximum 250 °C

11.2 SIM Group Set Up

11.2.1 Set up a SIM program with the necessary ions to acquire all the PAHs using the ion groups shown in Table 1 and set a 25 msec dwell time per ion.

11.2.2 Update the expected retention times in the method section of the quantitation software using the d-PAH internal standards of previous runs as relative retention time markers.

11.3 Establish Initial Calibration

The following initial calibration guidance is based on data generated during the method development process. The recommended calibration concentrations listed in Table 2 were based on the PAH distributions previously determined in 120 sediment pore water samples and take into account the water solubilities of each individual PAH compound. These are the recommended calibration standard concentrations for optimum method performance. However, other concentrations may be used provided acceptable method performance can be attained.

11.3.1 Prepare stock solutions of PAHs and internal standard stock solutions of d-PAHs at approximately the concentrations shown in Table 2. Stocks are prepared in DCM. Spiking solutions are prepared by dilution of intermediate stocks in acetone. For calibration solutions, spiking solutions are added to reagent water.

11.3.1.1 Prepare calibration standard spiking solutions. These are prepared by adding acetone to the stock to give the calibration solution concentrations (CS1-CS4), as described below.

11.3.1.1.1 For CS1, take 5 µL stock to 100 mL in acetone.

11.3.1.1.2 For CS2 take 50 µL to 100 mL in acetone.

11.3.1.1.3 For CS3, take 25 µL to 10 mL in acetone.

11.3.1.1.4 For CS4, take 100 µL to 10 mL in acetone.

11.3.1.2 Spike 4 µL of each calibration solution into 1.5 mL of reagent water to give a calibration series with the low calibration limits (LCLs) and upper calibration limits (UCLs) shown in Table 2. Spike 10 µL of internal standard spiking solution at the concentrations shown in Table 2 into each vial.

11.3.1.3 Extract and analyze the calibration series.

11.3.1.3.1 Extract and analyze two method blank solutions.

11.3.1.3.2 Extract and analyze the water calibration solutions, as described in Secs. 11.4 and 11.5. Begin with the CS1-spiked sample, followed by sequentially more concentrated calibration standards. Follow by two water blanks.

11.3.1.4 Calculate the performance parameters for the calibration.

11.3.1.4.1 Generate ion chromatograms for the masses listed in Table 1 that encompass the expected retention windows of the target analytes. Integrate the selected ion current profiles of the quantitation ions shown in the table.

11.3.1.4.2 Calculate the area ratio (analyte peak area divided by internal standard peak area) per unit mass of analyte, using the area of the appropriate internal standard listed in Table 3.

Quantitative calculations are based on a comparison of the area ratio per ng from the calibration and sample waters. The area ratio per ng is calculated for calibration runs by dividing the calibration peak area by the peak area of its most closely associated d-PAH internal standard (the deuterated parent PAH, in most cases), and dividing this result by the ng of the calibration PAH present in the vial (i.e., its mass in the vial, not its concentration). Calibration standards are given in Table 2.

(area ratio/ng) = [(peak area cal. std)/(peak area d-PAH)]/(mass of std in cal vial)

11.3.1.4.3 Calculate the mean area ratio/ng. The mean relative response factor for these duplicate daily calibration standards should agree with those from the 4-point (or 3-point) standard curve within 20% for the two- and three-ring PAHs, and within 25% for the four-ring PAHs. No sample data will be reported if these calibration criteria are not met. Calculate the mean area ratio/ng and the standard deviation of the relative response factors for each calibration standard solution using the following equations:

$$\overline{\text{area ratio/ng}} = \frac{1}{\text{n}} \sum_{i=1}^{n} (\text{area ratio/ng})_{\text{i}}$$

Where:

$(\text{area ratio/ng})_i$ = area ratio/ng calculated for calibration solution "i" using the equation in Sec. 11.3.1.4.2.

n = The number of calibration points in the curve.

11.3.1.4.4 Calculate the percent relative standard deviation.

$$\%\text{RSD} = \frac{\text{SD}}{\overline{\text{area ratio/ng}}} \times 100$$

Where:

$\overline{\text{area ratio/ng}}$ = Mean area ratio/ng calculated above.

SD = The sample standard deviation of the replicate area ratio/ng values used to calculate the mean area ratio/ng.

11.4 Criteria for acceptable initial calibration. Prior to analyzing any samples, the standard curves are prepared using the identical analysis procedures as used for sample waters. To be acceptable, the linearity of each PAH standard curve should be r^2 greater than 0.99, and the relative response factor per ng for each concentration should show a relative standard deviation of less than 25% for two- to three-ring PAHs, and less than 30% for four-ring PAHs. If an 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., injector malfunction) repeat the individual analysis and recalculate the percent relative standard deviation. If the calibration is acceptable, document the problem and proceed; otherwise repeat the initial calibration. Additionally, prior to sample analyses the initial calibration should be verified using a check standard mix that is prepared from an independent source as the calibration standards. Should an independent source or possibly another lot number from the same standard source used to prepare the calibration standards not be available during planned sample analyses, the initial calibration should be verified using the continuing calibration check standard.

11.4.1 Because of the large range of calibration concentrations required, the wide range of water solubilities of the individual PAHs, and the desire to require only one stock calibration solution, some PAHs may only have a three point linear calibration curve that meets the above criteria. This is most likely to occur for the higher molecular weight PAHs, because the dilution of lowest calibration standard is likely to be below the lower limit of quantitation required for the method, so it does not negatively impact the analysis. In such

cases, the lowest calibration standard is ignored. Less frequently, the highest concentrations of the lowest molecular weight PAHs may exceed the linear dynamic range of the GC/MS response. In such cases the laboratory should investigate lowering the MS multiplier voltage to autotune voltage or slightly below and rerun the calibration curve. If the highest calibration standard still exceeds the detector linearity, it is acceptable to reject the highest concentration for those specific PAHs, as long as a minimum of a three-point standard curve is generated for each PAH.

It is recommended that a 4- (or 3-) point initial calibration be established every two weeks, when continuing calibration criteria are not met, or when service is performed on the GC/MS instrument system.

11.4.2 The S/N for the GC signals present in every SICP must be $\geq$ 10:1 for the labeled internal standards and unlabeled calibration compounds.

11.5 Continuing calibration check is performed daily at the beginning of a 24-hour period. The injection of the first continuing calibration begins the 24-hour window, within which all pore water samples must be injected. Duplicate daily standards are analyzed.

11.5.1 To prepare the continuing calibration check solution, into 1.5 mL of reagent water, add 4 µL of the CS3 calibration check spiking solution and 10 µL of the d-PAH internal standards.

11.5.2 Analyze duplicate vials of the continuing calibration check standard solution. Use the same data acquisition parameters as those used during the initial calibration. Check for GC resolution and peak shape. If peak shape or retention times are unacceptable, perform column and injector maintenance. If this fails to correct the problem, the column must be replaced and the calibration repeated.

11.5.3 Criteria for Acceptable Daily Calibration Check. The criteria listed below for acceptable calibration must be met at the beginning of each 24-hour period that samples are analyzed. The mean relative response factor for the duplicate daily calibration standards should agree with those from the 4-point (or 3-point) standard curve within 20% for the two- and three-ring PAHs, and within 25% for the four-ring PAHs. No sample data will be reported if these calibration criteria are not met. If the continuing calibration check criteria are not met, identify the root cause, perform corrective action and repeat the continuing calibration. If the second consecutive continuing calibration check does not meet acceptance criteria, additional corrective action must be performed.

Additionally, after establishment of the 4-point calibration curve, the raw peak areas of each d-PAH for each subsequent daily calibration check, method blank, and sample analyses must be greater than or equal to 50% of the mean raw peak area for each d-PAH internal standard established for the 4-point calibration curve.

11.5.4 The S/N for the GC signals present in every SICP must be $\geq$ 10:1 for the labeled internal standards and unlabeled calibration compounds.

11.6 Method blanks are prepared and analyzed daily in duplicate following the continuing calibration and between analyses of replicate sets of the same pore water sample. See Sec. 11.6.2.2.

11.6.1 For each method blank, add 10 µL of the d-PAH internal standards solution into 1.5 mL of reagent water.

11.6.2 Two types of sources of background PAHs must be considered. For the higher molecular weight PAHs, typical GC/MS criteria for signal to noise are appropriate, since their lower limits of quantitation are normally controlled by GC/MS sensitivity. However, for lower molecular weight PAHs, atmospheric contaminants can cause significant background peaks.

11.6.2.1 Background PAHs from Ambient Air – Concentrations of each PAH in the water blanks should be calculated in the same manner as a sample. Should the blank prior to the subsequent water sample have any detectable background concentration greater than 1/3 of the example lower limits of quantitation given in Table 3, the analyses should not continue until the fiber is sufficiently cleaned as demonstrated by a clean reagent water blank.

11.6.2.2 Carryover from Highly Contaminated Samples – Carryover blanks are analyzed between each new pore water sample (not including replicates). Significant carryover can occur if the previous sample was highly contaminated. Should the blank prior to the subsequent water sample have any detectable background concentrations more than 1/3 of the example lower limits of quantitation given in Table 3, the analyses should not continue until the fiber is sufficiently cleaned as demonstrated by a clean reagent water blank. Alternatively, if the concentrations determined in the blanks are less than 20% of those found in the associated sample(s), the data may be accepted.

11.7 At the laboratory, store samples and extracts in the dark at 0 to 6 °C.

NOTE: Once the sample preparation process has begun, pore waters must be generated and flocculated as quickly as possible, but must be done within 28 days of sediment sample collection. Pore water, groundwater, and tap water samples must then be immediately spiked with 10 µL of d-PAH solution following flocculation.

Solid phase micro-extraction must be completed within 24 hours of flocculation for pore water, groundwater, and tap water samples.

11.8 Generation of pore water from sediment samples.

Stir the slurry and transfer approximately 40 mL (containing a solids and liquids in proportion to the slurry provided) to a clean 40 mL vial. Cap the vial with a PTFE-lined

cap. Place the vials in a centrifuge. Spin for 30 minutes at 1000 g. Using a new, graduated serological pipette, transfer 10 mL of the supernatant to a new 20 mL vial.

11.9 Flocculation of pore water samples.

11.9.1 Once the process has begun, immediately add the working alum solution (see Sec. 7.0) to each vial of water (and QC samples). The volume of the alum solution should be 1/40th of the sample volume. After the addition, swirl the vial for several rotations to incorporate the solution.

11.9.2 Add 3-5 drops of NaOH working solution (see Sec. 7.0) to each vial. Swirl to incorporate the NaOH.

11.9.3 Shake the vial for 15 seconds.

11.9.4 Centrifuge for 30 minutes at 1000 g.

11.9.5 Collect the supernatant into a clean 20 mL vial.

11.9.6 Repeat Secs. 11.10.1 through 11.10.5 once.

11.9.7 Immediately transfer 1.5 mL aliquots to new silanized autosampler vials and immediately add the internal standard solution as described below. Vials are weighed before and after adding the water sample to determine the exact sample water mass.

11.10 Extraction and analysis of flocculated pore water, groundwater, and tap water samples.

11.10.1 Split the prepared water samples into the required number of replicate samples, placing 1.5 mL aliquots of each into a new silanized glass autosampler vials. For QC samples, add 1.5 mL of reagent water.

NOTE: The SPME fiber should be cleaned at the beginning of each sampling set (and after highly contaminated samples) for one hour by placing in the cleaning chamber under helium flow at 320 °C. This can conveniently be performed while the pore waters are being prepared.

11.10.2 Immediately add 10 µL of the d-PAH solution to each sample and QC sample.

NOTE: All of the water preparation steps beginning with the centrifugation and ending with the addition of d-PAH internal standards should be conducted continuously and in the minimum amount of time possible.

11.10.3 Load the autosampler following the recommended analytical sequence in Table 4. Verify the sequence against documented sequence following the loading process.

11.11 The recommended analytical sequence described in Table 4 is based on a 24-hour “clock.”

11.11.1 Two continuing calibration check standards are analyzed (100 min.). The sequence begins with analysis of the first continuing calibration standard.

11.11.2 Analyze two method blanks (50 min. each).

11.11.3 Analyze pore water samples (in duplicate at a minimum) (50 min. each).

11.12 Generate ion chromatograms for the masses listed in Table 1 that encompass the expected retention windows of the target analytes. Integrate the selected ion current profiles of the quantitation ions shown in the table.

For a gas chromatographic peak to be identified as a target analyte, it must meet all of the following qualitative identification criteria for individual analytes.

11.12.1 The quantitation ion must be present, with a S/N of at least 3:1 for environmental samples.

11.12.2 The relative retention time (RRT) of the parent PAHs (and the 2- and 1- methylnaphthalene compounds) compared to the RRT for the labeled-standards must be within ± 3 seconds of the relative retention times obtained from the continuing calibration (or initial calibration if this applies).

11.13 Quantitation for Target Analytes

Results need to be reported in the units commensurate with their intended use and all dilutions need to be taken into account when computing final results.

Sample water concentrations are calculated by dividing the peak area of the sample peak by the peak area of its d-PAH internal standard, and then dividing the result by the calibration area ratio per ng, and dividing that result by the sample water weight.

$$\text{Concentration (ng/mL)} = \frac{(\text{area sample peak})/(\text{area d-PAH peak})}{(\text{area ratio per ng cal.std}) / (\text{sample weight})}$$

The mean calibration area ratio per ng values from the daily calibration check runs is used for sample concentration calculations (assuming QA/QC checks with the full calibration curve meet criteria).

NOTE: The two methylnaphthalene isomers are individual alkyl peaks and are treated as parent PAHs in the calculations.

11.13.1 If no peaks are present at a S/N $\geq$ 3 to 1 in the region of the ion chromatogram where the compounds of interest are expected to elute, report the result as “Not Detected” (i.e., ND) at the reporting limit.

11.13.2 Depending on project objectives, the results may be reported to lower limit of quantitation which is typically defined as 1/34 of a toxic unit. See Sec. 3.2 for additional information related to the lower limit of quantitation.

12.0 DATA ANALYSIS AND CALCULATIONS

See Secs. 11.12 and 11.13 for calculations.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance goals for users of the methods. Instead, performance goals should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Tables 5 through 12 present precision and bias data from three independent laboratories for spiked reagent water, groundwater, and two sediment pore water matrices. The PAH-impacted sediment samples were collected from an aluminum smelter site and a manufactured gas plant (MGP) site. These data are provided for guidance purposes only.

For the inter-laboratory validation study (ILV), the pore waters were spiked with 12 two- to four-ring PAHs at levels approximately 5 times and 50 times above the performance limit concentrations except for the five heavier PAHs, whose spike levels were based on the saturation solubility of the individual compounds. The highest molecular weight PAHs (i.e. benz(a)anthracene and chrysene), were spiked at five times the lower limit of quantitiation in the high level samples, instead of 50-fold, because of solubility limitations. In the low-level samples, benz(a)anthracene and chrysene were spiked at concentrations less than lower limit of quantitiation for these compounds. Therefore, based on the custodial laboratory recommendation, the low-level spike results for benz(a)anthracene and chrysene were not reported.

Seven replicate SPME analyses of the spiked sample pore waters were performed on each sample by each participating laboratory. Statistical outliers were determined and omitted using a one sided t-test at the 1% significance interval. All statistical outliers were traceable to one replicate analysis of the low-level groundwater sample from one participating laboratory. The high outlying results were caused by ambient (i.e., background) PAH contamination at the laboratory.

13.2.1 PAH concentration had no significant effect on the accuracy and reproducibility of the technique. The ILV recoveries for both the low and high-level spiked pore water samples (smelter and MGP sediments) ranged from 68 to 107 percent. The recoveries for both the low and high-level spiked aqueous samples (reagent water and groundwater) ranged from 81 to 108 percent.

13.2.2 It was assumed that the calculated standard deviation using the combined data from all three participating laboratories was equivalent to the

overall standard deviation (S_T). Replicate determinations of sample PAH concentrations typically had relative standard deviations (RSDs) less than 25 percent for the aqueous samples (reagent water and groundwater), with RSDs less than 33% for the impacted sediment samples (smelter and MGP sediments).

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in the laboratory operation. The USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

In keeping with USEPA goals this method uses a minimum of hazardous materials and results in only small amounts of hazardous waste.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

15.1 The USEPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

15.2 Some of the reagents and solutions used in this method as well as the effluent from the chromatograph contain PAHs and should be handled and disposed of in an approved manner.

16.0 REFERENCES

1. American Society for Testing Methods (ASTM), E178-02, "Standard Practice for Dealing with Outlying Observations," Volume 14.02.

2. S. B. Hawthorne, C. B. Grabanski, D. J. Miller and J. P. Kreitinger, “Solid Phase Microextraction Measurement of Parent and Alkyl Polycyclic Aromatic Hydrocarbons in Milliliter Sediment Pore Water Samples and Determination of K_{DOC} Values,” *Environ. Sci. Technol*, 39, 2795-2803, 2005.

3. D. I. Thal, “Preparation of Flocculated Pore Waters and Analysis of Parent and Alkyl Polycyclic Aromatic Hydrocarbons by Isotope Dilution Solid Phase Microextraction/Gas Chomatography/Mass Spectrometry (SPME/GC/MS) (Hawthorne Method),” Standard Operating Procedure KNOX-ID-0019, ©Severn Trent Laboratories. 2006.

4. S. B. Hawthorne, C. B. Grabanski, and D. J. Miller, “Measured Partitioning Coefficients for Parent and Alkyl Polycyclic Aromatic Hydrocarbons in 114 Historically Contaminated Sediments: Part I, Koc Values,” *Environmental Toxicology and Chemistry,* 25, 2901-2911, 2006.

5. U.S. EPA (OSWER), “Development and Validation of SW-846 Methods, Phase 2: Formal Validation,” April, 1992. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/methdev.pdf

6. U. S. Environmental Protection Agency, “Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures,” EPA/600/R-02/013, Office of Research and Development, Washington D.C., November 2003.

7. American Society for Testing Methods (ASTM), D7363-07, “Standard Test Method For Determination Of Parent Alkyl Polycyclic Aromatics in Sediment Pore Water Using Solid Phase Microextraction and Gas Chromatography/Mass Spectrometry in Selected Ion Monitoring Mode,” Volume 11.02.

8. D. Mackay and W.U. Shiu, Aqueous solubility of polynuclear aromatic-hydrocarbons, J. Chem. Eng. Data 22 (1977), pp. 399–402.

9. Syracuse Research Corporation, Environmental Database <http://www.syrres.com/esc/chemfate.htm>

17.0 TABLES AND FIGURES

The following pages contain the tables and figures referenced by this method.

TABLE 1

SIM TARGET IONS AND RETENTION TIME WINDOWS

Analyte	Carbon 12 (amu)	Hydrogen 1.007825 (amu)	Mass of Compound (amu)	SIM Ion Group	Target m/z	Retention Time[a] (min) Start	Stop
Naphthalene	10	8	128.063	1	128.1	7	17
1-Methylnaphthalene	11	10	142.078	1	142.1	7	17
2-Methylnaphthalene	11	10	142.078	1	142.1	7	17
Acenaphthylene	12	8	152.063	1	152.1	7	17
Acenaphthene	12	10	154.078	1	154.1	7	17
Fluorene	13	10	166.078	1	166.1	7	17
Anthracene	14	10	178.078	2	178.1	17	21
Phenanthrene	14	10	178.078	2	178.1	17	21
Fluoranthene	16	10	202.078	2,3	202.1	17	30
Pyrene	16	10	202.078	2,3	202.1	17	30
Benz(a)anthracene	18	12	228.094	3	228.1	21	30
Chrysene	18	12	228.094	3	228.1	21	30
d-PAH Internal Standards		Deuterium 2.014102 (amu)					
Naphthalene-d8	10	8	136.113	1	136.1	7	17
1-Methylnaphthalene-d10	11	10	152.141	1	152.1	7	17
Acenaphthene-d10	12	10	164.141	1	164.1	7	17
Fluorene-d10	13	10	176.141	1	176.1	7	17
Phenanthrene-d10	14	10	188.141	2	188.1	17	21
Fluoranthene-d10	16	10	212.141	2,3	212.1	17	30
Pyrene-d10	16	10	212.141	2,3	212.1	17	30
Chrysene-d12	18	12	240.169	3	240.2	21	30

[a]: Retention times must be verified by the user.

TABLE 2

INITIAL CALIBRATION STANDARD SERIES

Analyte	DCM Stock Conc. mg/mL	LCL CS1 ng/1.5 mL	CS2 ng/1.5 mL	CS3 ng/1.5 mL	UCL CS4 ng/1.5 mL
Naphthalene	42	8.3	83	415	1660
1-Methylnaphthalene	24	4. 8	48	239	956
2-Methylnaphthalene	20	4.1	41	204	817
Acenaphthylene	9.0	1.8	18	90	361
Acenaphthene	11	2.2	22	110	440
Fluorene	7.6	1.5	15	76	302
Anthracene	0.60	0.12	1.2	6.0	24
Phenanthrene	5.5	1.1	11	55	220
Fluoranthene	2.1	0.42	4.2	21	84
Pyrene	1.8	0.36	3.6	18	72
Benz(a)anthracene	0.08	0.02	0.16	0.80	3.2
Chrysene	0.03	0.006	0.06	0.30	1.2
Deuterated Analogs of Mix A Compounds	Stock Solution	CS1	CS2	CS3	CS4
Naphthalene-d8	5	50	50	50	50
1-Methylnaphthalene-d10	6	60	60	60	60
Acenaphthene-d10	1.2	12	12	12	12
Fluorene-d10	1.2	12	12	12	12
Phenanthrene-d10	0.96	9.6	9.6	9.6	9.6
Fluoranthene-d10	0.93	9.3	9.3	9.3	9.3
Pyrene-d10	0.84	8.4	8.4	8.4	8.4
Chrysene-d12	0.033	0.33	0.33	0.33	0.33

TABLE 3

EXAMPLE TOXIC UNIT FACTORS AND LOWER LIMITS OF QUANTITATION (LLOQ)

Analyte	Added d-PAH Internal Standard	d-PAH Internal Std. for Calculation	SPME-GC/MS RRF vs. Parent	Conc. For One Toxic Unit, C_{tu}, (ng/mL)	LLOQ (ng/mL)
Naphthalene	A	A	1.00	193	5.7
2-Methylnaphthalene		B	1.00	82	2.4
1-Methylnaphthalene	B	B	1.00	82	2.4
Acenaphthylene		C	1.00	307	9.0
Acenaphthene	C	C	1.00	56	1.6
Fluorene	D	D	1.00	39	1.2
Phenanthrene	E	E	1.00	19	0.56
Anthracene		E	1.00	21	0.61
Fluoranthene	F	F	1.00	7.1	0.21
Pyrene	G	G	1.00	10	0.30
Benz(a)anthracene		H	1.00	2.2	0.07
Chrysene	H	H	1.00	2.0	0.06

Data taken from Ref. 6.

TABLE 4

EXAMPLE OF A 24-HOUR ANALYTICAL SEQUENCE[a]

Run Type	Minutes	Cumulative Minutes to Start	Cumulative Minutes to End	Cumulative Hours to Start[a]	Cumulative Hours to End
Verification Std.	50	0	50	0.0	0.8
Verification Std.	50	50	100	0.8	1.7
Blank	50	100	150	1.7	2.5
Blank	50	150	200	2.5	3.3
Sample	50	200	250	3.3	4.2
Sample	50	250	300	4.2	5.0
Blank	50	300	350	5.0	5.8
Blank	50	350	400	5.8	6.7
Sample	50	400	450	6.7	7.5
Sample	50	450	500	7.5	8.3
Blank	50	500	550	8.3	9.2
Blank	50	550	600	9.2	10.0
Sample	50	600	650	10.0	10.8
Sample	50	650	700	10.8	11.7
Blank	50	700	750	11.7	12.5
Blank	50	750	800	12.5	13.3
Sample	50	800	850	13.3	14.2
Sample	50	850	900	14.2	15.0
Blank	50	900	950	15.0	15.8
Blank	50	950	1000	15.8	16.7
Sample	50	1000	1050	16.7	17.5
Sample	50	1050	1100	17.5	18.3
Blank	50	1100	1150	18.3	19.2

[a] The last pore water sample must be injected within 24 hours of the flocculation step. (i.e., The value for cumulative hours to start must be $\leq$ 24.)

TABLE 5

REAGENT WATER LOW-LEVEL PRECISION AND BIAS DATA

Analyte	True Value (ng/mL)	Number of Retained Values	Overall Mean Recovery (ng/mL)	Overall Mean Recovery (%)	Overall Standard Deviation (S_T)	Relative Standard Deviation (ng/mL)
Naphthalene	28	21	27	99	2.9	11
2-Methylnaphthalene	14	21	12	91	1.7	14
1-Methylnaphthalene	16	21	15	97	1.8	12
Acenaphthylene	6.0	21	5.5	92	0.74	13
Acenaphthene	7.3	21	6.9	94	0.77	11
Fluorene	5.0	21	4.8	96	0.49	10
Phenanthrene	3.7	21	3.5	96	0.34	10
Anthracene	0.40	21	0.32	81	0.10	30
Fluoranthene	1.4	21	1.4	97	0.18	13
Pyrene	1.2	21	1.2	97	0.14	12
Benz(a)anthracene	0.05	21	NR	NR	NR	NR
Chrysene	0.02	21	NR	NR	NR	NR

NR: Not reported.

TABLE 6

REAGENT WATER HIGH-LEVEL PRECISION AND BIAS DATA

Analyte	True Value (ng/mL)	Number of Retained Values	Overall Mean Recovery (ng/mL)	Overall Mean Recovery (%)	Overall Standard Deviation (S_T)	Relative Standard Deviation (ng/mL)
Naphthalene	277	21	263	95	30	11
2-Methylnaphthalene	136	21	118	87	22	19
1-Methylnaphthalene	159	21	150	94	20	13
Acenaphthylene	60	21	56	94	9.6	17
Acenaphthene	73	21	70	96	8.4	12
Fluorene	50	21	48	96	6.0	12
Phenanthrene	37	21	35	96	4.6	13
Anthracene	4.0	21	3.6	89	0.70	20
Fluoranthene	14	21	13	96	1.8	14
Pyrene	12	21	11	95	1.5	13
Benz(a)anthracene	0.53	21	0.48	91	0.04	7.4
Chrysene	0.20	21	0.20	99	0.02	7.6

TABLE 7

GROUNDWATER LOW-LEVEL PRECISION AND BIAS DATA

Analyte	True Value (ng/mL)	Number of Retained Values	Overall Mean Recovery (ng/mL)	Overall Mean Recovery (%)	Overall Standard Deviation (S_T)	Relative Standard Deviation (ng/mL)
Naphthalene	28	20	26	93	1.6	6.1
2-Methylnaphthalene	14	20	13	93	1.1	8.8
1-Methylnaphthalene	16	20	15	92	0.98	6.7
Acenaphthylene	6.0	21	5.4	90	0.51	9.4
Acenaphthene	7.3	20	6.6	91	0.40	6.1
Fluorene	5.0	20	4.6	91	0.26	5.7
Phenanthrene	3.7	21	3.6	99	0.36	10
Anthracene	0.40	21	0.42	105	0.03	7.9
Fluoranthene	1.4	20	1.3	93	0.07	5.1
Pyrene	1.2	21	1.1	92	0.07	6.4
Benz(a)anthracene	0.05	21	NR	NR	NR	NR
Chrysene	0.02	21	NR	NR	NR	NR

NR: Not reported.

TABLE 8

GROUNDWATER HIGH-LEVEL PRECISION AND BIAS DATA

Analyte	True Value (ng/mL)	Number of Retained Values	Overall Mean Recovery (ng/mL)	Overall Mean Recovery (%)	Overall Standard Deviation (S_T)	Relative Standard Deviation (ng/mL)
Naphthalene	277	21	254	92	23	9.0
2-Methylnaphthalene	136	21	118	86	16	13
1-Methylnaphthalene	159	21	145	91	15	11
Acenaphthylene	60	21	54	90	4.9	9.1
Acenaphthene	73	21	69	94	5.3	7.7
Fluorene	50	21	47	94	2.7	5.7
Phenanthrene	37	21	37	101	6.6	18
Anthracene	4.0	21	3.9	97	0.56	14
Fluoranthene	14	21	13	92	0.86	6.7
Pyrene	12	21	11	90	0.61	5.7
Benz(a)anthracene	0.53	21	0.48	91	0.05	11
Chrysene	0.20	21	0.18	88	0.02	8.7

TABLE 9

ALUMINUM SMELTER SEDIMENT LOW-LEVEL PRECISION AND BIAS DATA

Analyte	True Value (ng/mL)	Number of Retained Values	Overall Mean Recovery (ng/mL)	Overall Mean Recovery (%)	Overall Standard Deviation (S_T)	Relative Standard Deviation (ng/mL)
Naphthalene	28	21	27	99	2.9	11
2-Methylnaphthalene	14	21	13	96	1.3	9.9
1-Methylnaphthalene	16	21	15	97	1.7	11
Acenaphthylene	6.0	21	6.2	102	0.54	8.8
Acenaphthene	7.3	21	7.1	96	0.59	8.4
Fluorene	5.0	21	4.9	97	0.42	8.6
Phenanthrene	3.7	21	3.6	99	0.37	10
Anthracene	0.54	21	0.58	107	0.10	18
Fluoranthene	2.5	21	2.3	93	0.46	20
Pyrene	1.7	21	1.5	87	0.33	22
Benz(a)anthracene	0.15	21	NR	NR	NR	NR
Chrysene	0.20	21	NR	NR	NR	NR

NR: Not reported.

TABLE 10

ALUMINUM SMELTER SEDIMENT HIGH-LEVEL PRECISION AND BIAS DATA

Analyte	True Value (ng/mL)	Number of Retained Values	Overall Mean Recovery (ng/mL)	Overall Mean Recovery (%)	Overall Standard Deviation (S_T)	Relative Standard Deviation (ng/mL)
Naphthalene	277	21	260	94	42	16
2-Methylnaphthalene	136	21	111	81	29	26
1-Methylnaphthalene	159	21	147	92	26	18
Acenaphthylene	60	21	60	99	14	24
Acenaphthene	73	21	70	95	11	16
Fluorene	50	21	48	96	7.2	15
Phenanthrene	37	21	34	93	5.6	16
Anthracene	4.0	21	4.2	104	0.63	15
Fluoranthene	14	21	14	99	2.4	17
Pyrene	12	21	11	94	1.8	16
Benz(a)anthracene	0.63	21	0.49	78	0.04	8.5
Chrysene	0.37	21	0.30	81	0.05	18

TABLE 11

MGP SEDIMENT LOW-LEVEL PRECISION AND BIAS DATA

Analyte	True Value (ng/mL)	Number of Retained Values	Overall Mean Recovery (ng/mL)	Overall Mean Recovery (%)	Overall Standard Deviation (S_T)	Relative Standard Deviation (ng/mL)
Naphthalene	28	21	26	95	2.1	8.1
2-Methylnaphthalene	14	21	13	92	1.2	9.3
1-Methylnaphthalene	16	21	15	92	1.3	8.6
Acenaphthylene	6.0	21	5.6	92	0.48	8.6
Acenaphthene	7.3	21	6.7	91	0.51	7.6
Fluorene	5.0	21	4.6	91	0.34	7.5
Phenanthrene	3.7	21	3.3	91	0.21	6.4
Anthracene	0.40	21	0.34	85	0.08	24
Fluoranthene	1.4	21	1.3	92	0.11	8.4
Pyrene	1.2	21	1.1	92	0.09	7.8
Benz(a)anthracene	0.05	21	NR	NR	NR	NR
Chrysene	0.02	21	NR	NR	NR	NR

NR: Not reported.

TABLE 12

MGP SEDIMENT HIGH-LEVEL PRECISION AND BIAS DATA

Analyte	True Value (ng/mL)	Number of Retained Values	Overall Mean Recovery (ng/mL)	Overall Mean Recovery (%)	Overall Standard Deviation (S_T)	Relative Standard Deviation (ng/mL)
Naphthalene	277	21	257	93	36	14
2-Methylnaphthalene	136	21	118	87	24	21
1-Methylnaphthalene	159	21	148	93	22	15
Acenaphthylene	60	21	58	96	9.0	16
Acenaphthene	73	21	70	95	9.8	14
Fluorene	50	21	48	95	6.9	14
Phenanthrene	37	21	35	94	5.4	16
Anthracene	4.0	21	3.5	87	1.1	30
Fluoranthene	14	21	13	94	2.0	16
Pyrene	12	21	11	94	1.6	14
Benz(a)anthracene	0.53	21	0.43	81	0.05	12
Chrysene	0.20	21	0.19	93	0.02	8.8