Designation: D7363 – 13a

Standard Test Method for
Determination of Parent and Alkyl Polycyclic Aromatics in Sediment Pore Water Using Solid-Phase Microextraction and Gas Chromatography/Mass Spectrometry in Selected Ion Monitoring Mode[1,2]

This standard is issued under the fixed designation D7363; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

Note—Balloted information was included and the year date changed on May 17, 2013.

1. Scope

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. This test method covers the separation of pore water from PAH-impacted sediment samples, the removal of colloids, and the subsequent measurement of dissolved concentrations of the required 10 parent PAHs and 14 groups of alkylated daughter PAHs in the pore water samples. The "24 PAHs" are determined using solid-phase microextraction (SPME) followed by Gas Chromatography/Mass Spectrometry (GC/MS) analysis in selected ion monitoring (SIM) mode. Isotopically labeled analogs of the target compounds are introduced prior to the extraction, and are used as quantification references.

1.2 Lower molecular weight PAHs are more water soluble than higher molecular weight PAHs. Therefore, USEPA-regulated 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 microgram per litre concentrations for low molecular weight PAHs and nanogram per litre concentrations for high molecular weight PAHs.

1.3 The USEPA narcosis model predicts toxicity to benthic organisms if the sum of the toxic units (ΣTU_c) calculated for all "34 PAHs" measured in a pore water sample is greater than or equal to 1. For this reason, the performance limit required for the individual PAH measurements was defined as the concentration of an individual PAH that would yield 1⁄34 of a toxic unit (TU). However, the focus of this method is the 10 parent PAHs and 14 groups of alkylated PAHs (Table 1) that contribute 95 % of the toxic units based on the analysis of 120 background and impacted sediment pore water samples.[3] The primary reasons for eliminating the rest of the 5-6 ring parent PAHs are: *(1)* these PAHs contribute insignificantly to the pore water TU, and *(2)* these PAHs exhibit extremely low saturation solubilities that will make the detection of these compounds difficult in pore water. This method can achieve the required detection limits, which range from approximately 0.01 µg/L, for high molecular weight PAHs, to approximately 3 µg/L for low molecular weight PAHs.

1.4 The test method may also be applied to the determination of additional PAH compounds (for example, 5- and 6-ring PAHs as described in Hawthorne et al.).[4] However, it is the responsibility of the user of this standard to establish the validity of the test method for the determination of PAHs other than those referenced in 1.1 and Table 1.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the*

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[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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[2] Standard methods under the jurisdiction of ASTM Committee D19 may be published for a limited time preliminary to the completion of full collaborative study validation. Such standards are deemed to have met all other D19 qualifying requirements but have not completed the required validation studies to fully characterize the performance of the test method across multiple laboratories and matrices. Preliminary publication is done to make current technology accessible to users of standards, and to solicit additional input from the user community.

[3] Hawthorne, S. B., Grabanski, C. B., and Miller, D. J., "Measured Partitioning Coefficients for Parent and Algae Polycyclic Aromatic Hydrocarbons in 114 Historically Contaminated Sediments: Part I, Koc Values," *Environmental Toxicology and Chemistry*, Vol 25, 2006, pp. 2901–2911.

[4] Hawthorne, S. B., Grabanski, C. B., Miller, D. J., and Kreitinger, J. P., "Solid Phase Microextraction Measurement of Parent and Akyl Polycyclic Aromatic Hydrocarbons in Milliliter Sediment Pore Water Samples and Determination of K_{DOC} Values," *Environmental Science Technology*, Vol 39, 2005, pp. 2795–2803.

TABLE 1 Target PAHs, Toxic Unit Factors and Performance Limits[A]

Analyte	Added d-PAH Internal Standard	d-PAH Internal Std. for Calculation	Conc. for One Toxic Unit, C_{tu}, (ng/mL)	Performance Limit (ng/mL)	Basis for Performance Limit[B]
Naphthalene	A	A	193.47	5.69	B
2-Methylnaphthalene		B	81.69	2.40	B
1-Methylnaphthalene	B	B	81.69	2.40	B
C2-Naphthalenes		A	30.24	0.89	B
C3-Naphthalenes		A	11.10	0.33	B
C4-Naphthalenes		A	4.05	0.12	C
Acenaphthylene		C	308.85	9.03	B
Acenaphthene	C	C	55.85	1.64	B
Fluorene	D	D	39.30	1.16	B
C1-Fluorenes		D	13.99	0.41	B
C2-Fluorenes		D	5.30	0.16	B
C3-Fluorenes		D	1.92	0.06	S
Phenanthrene	E	E	19.13	0.56	B
Anthracene		E	20.72	0.61	B
C1-Phenanthrenes/Anthracenes		E	7.44	0.22	B
C2-Phenanthrenes/Anthracenes		E	3.20	0.09	B
C3-Phenanthrenes/Anthracenes		E	1.26	0.04	B
C4-Phenanthrenes/Anthracenes		E	0.56	0.02	S
Fluoranthene		F	7.11	0.21	B
Pyrene	F	F	10.11	0.30	B
C1-Fluoranthenes/Pyrenes		F	4.89	0.14	C
Benz[a]anthracene		G	2.23	0.066	B
Chrysene	G	G	2.04	0.060	B
C1-Chrysenes/Benz[a]anthracenes		G	0.86	0.025	C

[A] From Hawthorne, S. B., Grabanski, C. B., Miller, D. J., and Kreitinger, J. P., "Solid Phase Microextraction Measurement of Parent and Alkyl Polycyclic Aromatic Hydrocarbons in Milliliter Sediment Pore Water Samples and Determination of K_{DOC} Values," *Environmental Science Technology*, Vol 39, 2005, pp. 2795–2803.

[B] Performance limits were determined as 3 times the background concentrations from the SPME fiber based on the analysis of water blanks ("B"), the lowest calibration standard which consistently yielded a signal to noise ratio of at least 3:1 ("C"), or (for when no calibration standard was available) for the lowest concentrations consistently found in pore water samples with a signal to noise ratio of at least 3:1 ("S"). Detection limits for alkyl PAHs are based on a single isomer.

responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, refer to Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[5]

D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)[6]
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
E178 Practice for Dealing With Outlying Observations

3. Terminology

3.1 *Definitions:*

3.1.1 *calibration standard*—a solution prepared from a secondary standard, stock solution, or both, and used to calibrate the response of the instrument with respect to analyte concentration.

3.1.2 *calibration verification standard (VER)*—the midpoint calibration standard (CS3) that is analyzed daily to verify the initial calibration.

3.1.3 *CS1, CS2, CS3, CS4*—shorthand notation for calibration standards.

3.1.4 *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.

3.1.5 *performance limit*—performance limit for an individual PAH is defined as the concentration of an individual PAH that would yield 1⁄34 of a toxic unit. For a performance limit of an individual PAH, refer to Table 1 (see 4.6).

3.1.6 *deuterated PAH (d-PAH)*—polycyclic aromatic hydrocarbons in which deuterium atoms are substituted for all hydrogens (that is, perdeuterated). In this method, d-PAHs are used as internal standards.

3.1.7 *GC*—gas chromatograph or gas chromatography.

3.1.8 *HRGC*—high resolution GC.

3.1.9 *LRMS*—low resolution MS.

3.1.10 *internal standards*—isotopically labeled analogs (d-PAHs) of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the water samples immediately after completing the flocculation step and transferring the water aliquot to the autosampler vial, and immediately after adding the calibration PAH solution to water calibration standards, but

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[5] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[6] The last approved version of this historical standard is referenced on www.astm.org.

before SPME extraction. The internal standards are used to calculate the concentration of the target analytes or estimated detection limits.

3.1.11 *laboratory blank*—see *method blank.*

3.1.12 *method blank*—an aliquot of reagent water that is extracted and analyzed along with the samples to monitor for laboratory contamination. Blanks should consistently meet concentrations at or less than one-third of the performance limits for individual PAHs stated in Table 1. Alternatively, if the PAH concentrations calculated from the water blank immediately preceding the test samples are <20 % of the test sample concentrations, the blank is acceptable.

3.1.13 *low calibration level (LCL)*—the level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.1.14 *high or upper calibration level (UCL)*—the concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.1.15 *MS*—mass spectrometer or mass spectrometry.

3.1.16 *PAH*—polycyclic aromatic hydrocarbon, or alternately, polynuclear aromatic hydrocarbon.

3.1.17 *percent difference (%D)*—the difference between the analyzed concentration and expected concentration, expressed as a percentage of the expected concentration.

3.1.18 *relative response factor (RRF)*—the empirically determined ratio between the area ratio (analyte to internal standard) and the unit mass of analyte in the calibration standard (area ratio/ng) for available alkyl PAHs in a given homolog and their parent PAH.

3.1.19 *selected ion monitoring (SIM)*—a mode of operation for the mass spectrometer in which specific ions are monitored. This mode of operation differs from the full scan mode, in which the MS acquires all ions within a range. Because the spectrometer is monitoring fewer ions in the SIM mode, more acquisition (dwell) time is possible for each ion. This results in greater instrument sensitivity for the selected ions. Spectral scanning and library searching, used for tentatively identified compounds, are not supported in this mode.

3.1.20 *signal-to-noise ratio*—the ratio of the mass spectrometer response of a GC peak to the background noise signal.

3.1.21 *NIST*—National Institute of Standards and Technology.

3.1.22 *SRM*—Standard reference material obtained from NIST.

4. Summary of Test Method

4.1 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. An autosampler (Leap Technologies Combi-Pal or equivalent) 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-h run sequence to approximately 3 h, while the manual method requires 24-h 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.

AUTOSAMPLER METHOD

4.2 *Pore Water Separation and Preparation*—The pore water is separated from wet sediment samples by centrifugation and supernatant collection. Colloids are removed from the separated pore water samples by flocculation with aluminum potassium sulfate (alum) and sodium hydroxide as described in Hawthorne et al.[4] A second flocculation and centrifugation, followed by supernatant collection completes the colloid removal. The prepared pore water samples are then split into the required number of replicate aliquots (1.5 mL each) and placed into silanized glass autosampler vials. The 7 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.

4.2.1 The SPME fiber should be cleaned at the beginning of each sampling set (and after very contaminated samples) for 1 h by placing in the cleaning chamber under helium flow at 320°C. This can conveniently be performed while the pore waters are being prepared.

4.3 *Solid-Phase Microextraction*—The SPME extraction of the pore water samples is performed using a commercially available (available from Sigma-Aldrich, formerly Supleco, or equivalent) 7 µm film thickness polydimethylsiloxane (PDMS)-coated fused silica fiber for 30 min while the water sample is mixed by the precession of the autosampler mixing chamber at a rate of 250 revolutions per minute. The target PAHs and d-PAH internal standards adsorb to the nonpolar PDMS phase at equivalent rates. The use of the d-PAHs (that is, isotopic dilution) to quantitate the target PAHs compensates for variations in equilibrium partitioning and kinetics.

4.4 *GC/MS SIM Analysis*—Following the sorption period, the SPME fiber is immediately desorbed in a GC/MS injection port in the splitless mode at 320°C for 5 min. The GC/MS system specified uses a 60 m narrow-bore (250 µm ID) HP5-MS or equivalent capillary column to achieve high resolution for PAHs. Following the 5 min desorption period, the SPME fiber is inserted into the cleaning port and additionally cleaned for 15 min under helium flow at 320°C. At the end of the cleaning period, sorption of the next water sample is begun.

4.5 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 quantified by three methods:

4.5.1 PAHs for which an exact deuterated analog is included in the internal standard mix are quantified by isotope dilution.

4.5.2 Parent PAHs (that is, unsubstituted PAHs) for which an exact deuterated analog is not included in the internal standard mix are quantified by reference to a deuterated analog of a PAH with the same number of rings as the analyte.

4.5.3 Alkyl PAHs are quantified using the experimentally determined relative response factors based on each lab's analysis of SRM 1991 and the concentration values listed in Table 2. Relative response factors for the alkyl PAHs are in reference to their parent PAH.

4.6 *Conversion of Quantified Concentration to Toxic Units*—The USEPA narcosis model predicts toxicity to benthic organisms if the sum of the toxic units calculated for all "34 PAHs" measured in a pore water sample is greater than or equal to 1. For this reason, the performance limits required for the individual PAH measurements were defined as the concentration of an individual PAH that would yield 1⁄34 of a toxic unit. See Table 1. This distribution reflects the relative concentrations of PAHs expected to be found in pore water because the lower molecular weight PAHs are more soluble and have lower organic carbon partition coefficients (Koc), and reflects the lower partitioning of lower molecular weight PAHs to the receptor organism since they have smaller octanol/water coefficients (Kow). The performance limits are essentially benchmarks to ensure that the adequate sensitivity is achieved to predict toxicity.

TABLE 2 PAH concentrations in SRM 1991[A, B]

	Mass Fraction, µg/g
Naphthalene	26.0 ± 1.1
2-Methylnaphthalene	11.7 ± 0.5
1-Methylnaphthalene	8.02 ± 0.32
C2-Naphthalenes	21.3 ± 2.8
C3-Naphthalenes	29.5 ± 1.5
C4-Naphthalenes	33.8 ± 4.7
Acenaphthylene	0.5[C]
Acenaphthene	6.83 ± 0.89
Fluorene	3.8 ± 1.0
C1-Fluorenes	5.62 ± 0.27
C2-Fluorenes	7.20 ± 0.39
C3-Fluorenes	5.16 ± 0.50
Phenanthrene	12.1 ± 0.6
Anthracene	3.33 ± 0.43
C1-Phenanthrenes/Anthracenes	10.7 ± 3.2
C2-Phenanthrenes/Anthracenes	15.5 ± 1.9
C3-Phenanthrenes/Anthracenes	15.1 ± 0.2
C4-Phenanthrenes/Anthracenes	10.2 ± 1.1
Fluoranthene	3.54 ± 0.39
Pyrene	5.91 ± 0.16
C1-Fluoranthenes/Pyrenes	6.86 ± 0.54
Benz[a]anthracene	1.79 ± 0.21
Chrysene	1.32 ± 0.15
C1-Chrysenes/ Benz[a]anthracenes	1.54 ± 0.46

[A] Single compound concentrations are reported for parent PAHs and the two methylnaphthalene isomers in the NIST SRM 1991 certificate. All other alkyl-PAH concentrations are reported as the total for each isomeric group. Concentration values should be revised if updated values are reported by NIST. Mass fraction (µg/g) units can be converted to mass/volume units based on the SRM solution density of 1.31 reported in the NIST SRM 1991 certificate.

[B] 95% confidence intervals are reported as described in the NIST SRM 1991 certificate.

[C] Acenaphthylene is reported as possibly unstable in the NIST SRM 1991 certificate. However, this does not affect D7363 results since acenaphthylene calibration is based on calibration solutions prepared with pure parent PAHs.

MANUAL METHOD

4.7 *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 1-cm 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 specified for the autosampler method. A spare GC split/splitless injection port at 320°C and under helium flow can be used for the 15-min cleaning step between samples as well as for the initial 1-h cleaning step at the beginning of each experimental day. Other procedures are the same as for the autosampler method.

5. Significance and Use

5.1 This method directly determines the concentrations of dissolved PAH concentrations in environmental sediment pore water samples. The method is important from an environmental regulatory perspective because it can achieve the analytical sensitivities to meet the goals of the USEPA narcosis model for protecting benthic organisms in PAH contaminated sediments. Regulatory methods using solvent extraction have not achieved the wide calibration ranges from nanograms to milligrams per litre and the required levels of detection in the nanogram-per-litre range. In addition, conventional solvent extraction methods require large aliquot volumes (litre or larger), use of large volumes of organic solvents, and filtration to generate the pore water. This approach entails the storage and processing of large volumes of sediment samples and loss of low molecular weight PAHs in the filtration and solvent evaporation steps.

5.2 This method can be used to determine nanogram to milligram per litre PAH concentrations in pore water. Small volumes of pore water are required for SPME extraction, only 1.5 mL per determination and virtually no solvent extraction waste is generated.

6. Interferences

6.1 Non-target hydrocarbons can cause peaks on selected ion current profiles (SICPs) intended for other PAHs. Pattern recognition must be employed for identifying interfering peaks, and peak series that should not be considered for the homolog or target PAH under consideration. Analysts should be intimately familiar with both parent and alkyl PAH analyses in complex environmental samples. Representative samples having higher PAH concentrations should periodically be analyzed by full scan GC/MS so that pattern recognition of alkyl PAHs (and interfering species) can be verified by their full mass spectra. This procedure is particularly important for newer operators.

6.2 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.

NOTE 1—The use of high purity reagents and solvents helps minimize interference problems.

7. Apparatus

7.1 *Centrifuge,* capable of sustaining 1000 g with cups for securing 40 mL and 20 mL vials.

7.2 *SPME Fiber Holder,* compatible with 7-µm SPME fiber and compatible with either the autosampler or the manual method.

7.3 *SPME Fibers,* 7-µm thick polydimethylsiloxane (PDMS) coating or equivalent.

7.4 *PTFE Coated Stir Bars (Stir Fleas),* of a size effective for stirring 1.5 mL water without vortexing (for manual method only).

7.5 *Magnetic Stir Plate (for manual method only).*

7.6 *SPME Holder Stand (for manual method only) or GC/MS Autosampler,* capable of SPME extraction and injection.

7.7 *Cleaning Port,* capable of purging SPME fibers in a helium-swept atmosphere at 320°C.

7.8 *GC/MS Analysis:*

7.8.1 *Gas Chromatograph* shall have split/splitless injection port for capillary column, temperature program with isothermal hold.

7.8.2 *GC Column,* 60 m × 0.25 mm ID × 0.25 µm film thickness HP5-MS or equivalent.

7.8.3 *Inlet Liner,* 2 mm ID silanized glass.

7.8.4 *GC Inlet,* 320°C, splitless mode.

7.8.5 *Oven Program*—Isothermal 5 min hold at 40°C. Ramp at 50°C/min to 110°C, followed by a temperature ramp of 12°C/min to 320°C (hold for 10 min).

7.8.6 *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 selectively monitoring at least 12 m/z during a period of approximately 1 s and shall meet all manufacturers' specifications.

7.8.7 *GC/MS Interface*—The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beam.

7.8.8 *Data System,* capable of collecting, recording, and storing MS data.

8. Reagents and Materials

8.1 *Purity of Reagents*—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.[7]

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water that meets the purity specifications of Type I or Type II water, presented in Specification D1193.

8.3 *40 mL Vials,* with Teflon-lined caps.

8.4 *20 mL Vials,* with Teflon-lined caps.

8.5 *Silanized 2.0 mL Autosampler Vials.*

8.6 *Internal Standard Stock Solution*—A dichloromethane solution of d-PAH internal standards used for preparing spiking solutions by dilution into acetone (see 12.2).

TABLE 3 Primary Material Hazards

Material	Hazards	Exposure Limit[A]	Signs and Symptoms of Exposure
Alum (Aluminum Potassium Sulfate)	Irritant	2 mg/M^3 TWA	May cause skin irritation, especially under repeated or prolonged contact, or when moisture is present. May irritate or burn the eyes. Dust or mist inhalation at levels above the TLV may cause irritation to the respiratory tract. May irritate the gastrointestinal tract.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Dichloromethane (DCM)	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	2 mg/M^3 TWA	Causes skin irritation, chemical burns, permanent injury or scarring, and blindness. Vinegar is a mild acid that will neutralize lye if it were to make contact with the skin. Harmful if inhaled or ingested. Causes Sore throat, cough labored breathing, shortness of breath, and abdominal pain. Symptoms may be delayed.

[A] Exposure limit refers to the OSHA regulatory exposure limit.

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[7] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.7 *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.

8.8 *Calibration Stock Solution*—A dichloromethane solution of PAHs used for preparing calibration standards (see 12.2).

8.9 *Calibration Spiking Solutions*—A series of solutions prepared by diluting the calibration stock solution with acetone (see 12.2).

8.10 *Calibration Standards*—Prepared by adding internal standard and calibration spiking solutions in reagent water (see 12.2).

8.11 *Acetone.*

8.12 *Dichloromethane* (DCM).

8.13 *Sodium Hydroxide* (NaOH). Use a 1 molar solution in reagent grade water.

8.14 *Aluminum Potassium Sulfate Dodecahydrate*—Alum, $(AlK(SO_4)_2\cdot 12H_2O)$.

8.15 *Alum Solution*—10 wt. % (wt/vol) of alum in reagent grade water.

8.16 *SRM 1991*—Obtained from NIST, Gaithersburg, MD, USA.

9. Hazards

9.1 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 must pass through an activated charcoal filter.

9.2 *Primary Materials Used*—Table 3 contains a summary of the primary hazards listed in the MSDS. A complete list of materials used in the method can be found in the reagents and materials section. Practitioners 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.

10. Sampling and Sample Preservation

10.1 Collect the sediment sample in accordance with Practices D3370 and Specification D1192, as applicable.

10.2 Prior to shipment, the 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 jars with PTFE-lined lids. Great care must be taken to clean the lid of the jar before capping with the lid to avoid leakage of the water during shipment.

10.3 Ship in an ice chest with adequate ice to maintain 0 to 6°C. Store at the laboratory in the dark at 0 to 6°C.

11. Preparation of Apparatus

11.1 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 ID silanized glass.

11.1.3 GC Inlet 320°C, splitless mode.

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

MS Quad Temperature	150°C, maximum 200°C
MS Source Temperature	230°C, maximum 250°C

11.1.5 Set up SIM Groups to monitor the quantitation and internal standard ions. Optimal exact masses should be determined by monitoring 0.1 mass units near the nominal molecular weight of each PAH to determine the exact mass which gives the best signal to noise ratio. Example masses are shown in Table 4. Optimal exact masses should be determined before the initial use of the method, when major maintenance is performed on the mass spectrometer (for example, ion source cleaning), and if the laboratory is having trouble meeting detection limit requirements. Each ion dwell time should be set at 25 ms. Twelve ions are monitored in each group.

NOTE 2—Some ions (for example, m/z 184.1 for C4 naphthalenes) are included in two ion groups to ensure that the target peaks are adequately monitored. Table 4 should be used with the chromatograms in Appendix X1 to aid the analyst in setting proper retention time windows and

TABLE 4 SIM Ion Groups and Typical Retention Time Windows

NOTE 1—Retention times must be verified by the user.

Analyte	SIM Ion Group	Target m/z (typically)^A	Retention Time (min)	
			Start	Stop
Naphthalene	1	128.1	7	17
2-Methylnaphthalene	1	142.1	7	17
1-Methylnaphthalene	1	142.1	7	17
C2-Naphthalenes	1	156.1	7	17
C3-Naphthalenes	1	170.1	7	17
C4-Naphthalenes	1,2	184.1	7	21
Acenaphthylene	1	152.2	7	17
Acenaphthene	1	154.2	7	17
Fluorene	1	166.2	7	17
C1-Fluorenes	2	180.2	17	21
C2-Fluorenes	2	194.2	17	21
C3-Fluorenes	2,3	208.2	17	25
Phenanthrene	2	178.2	17	21
Anthracene	2	178.2	17	21
C1-Phenanthrenes/ Anthracenes	2	192.2	17	21
C2-Phenanthrenes/ Anthracenes	2,3	206.2	17	30
C3-Phenanthrenes/ Anthracenes	2,3	220.2	17	30
C4-Phenanthrenes/ Anthracenes	3	234.2	21	30
Fluoranthene	2,3	202.2	17	30
Pyrene	2,3	202.2	17	30
C1-Fluoranthenes/ pyrenes	3	216.2	21	30
Benz[a]anthracene	3	228.2	21	30
Chrysene	3	228.2	21	30
C1-Chrysenes	3	242.2	21	30
d-PAH Internal Standards				
Naphthalene-d8	1	136.1	7	17
1-Methylnaphthalene-d10	1	152.1	7	17
Acenaphthene-d10	1	164.2	7	17
Fluorene-d10	1	176.2	7	17
Phenanthrene-d10	2	188.2	17	21
Fluoranthene-d10	2,3	212.2	17	30
Pyrene-d10	2,3	212.2	17	30
Chrysene-d12	3	240.2	21	30

[A] Exact masses (to the 0.1 amu) should be optimized for each GC/MS instrument as described in Section 11.1.5.

recognition of target and contaminant peaks, especially for the alkyl clusters.

12. Calibration

12.1 Determine the absolute and relative retention times of the first and last characteristic peak in each homolog with the aid of the examples in Appendix X1.

12.1.1 Set up a SIM program with the necessary ions to acquire all the alkyl-PAH homologs using the ion groups shown in Table 4 and 25 ms dwell time per ion.

12.1.2 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 and the representative chromatograms in Appendix X1. Assure that the SIM windows for the homologs are set to at least 8 s before the first, and 30 s after the last characteristic peaks to assure coverage of the elution range.

12.2 *Analyze Initial Calibration:*

12.2.1 Prepare stock solutions of PAHs and internal standard stock solutions of d-PAHs at approximately the concentrations shown in Table 5. These concentrations were based on the PAH distributions previously determined in 120 sediment pore water samples. 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.

12.2.1.1 Prepare calibration standard spiking solutions. These are prepared by diluting the stock in acetone to give the calibration solution concentrations (CS1–CS4), as described below:

(1) For CS1, take 5 µL stock to 100 mL in acetone.
(2) For CS2 take 50 µL to 100 mL in acetone.
(3) For CS3, take 25 µL to 10 mL in acetone.
(4) For CS4, take 100 µL to 10 mL in acetone.

12.2.1.2 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 5. Spike 10 µL of internal standard spiking solution at the concentrations shown in Table 5 into each vial.

12.2.1.3 Extract and analyze the calibration series.

(1) Extract and analyze two water blank solutions.

(2) Extract and analyze the water calibration solutions, as described in 13.4 and 13.5. Begin with the CS1-spiked sample, followed by sequentially more concentrated calibration standards. Follow by two water blanks.

12.2.1.4 Calculate the performance parameters for the calibration.

(1) Generate ion chromatograms for the optimal exact masses (examples are listed in Table 4) that encompass the expected retention windows of the target analytes. Integrate the selected ion current profiles of the quantitation ions shown in the table. Integration of alkyl clusters should be as the total area of the cluster integrated from the baseline before the first peak in the cluster to the baseline after the last peak in the cluster peaks. Cluster peaks should never be integrated using the valley-to-valley method. The peak areas of non-target peaks (see Appendix X1) must be removed from the alkyl cluster peak area before any calculation.

(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 1. 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 associate 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 (that is, its mass in the vial, not its concentration). Calibration standards are given in Table 5.

TABLE 5 Initial Calibration Standard Series

Analyte	DCM Stock Conc. mg/mL	LCL			UCL
		CS1	CS2	CS3	CS4
		ng/1.5 mL	ng/1.5 mL	ng/1.5 mL	ng/1.5 mL
Naphthalene	41.5	8.3	83	415	1660
1-Methylnaphthalene	23.9	4.78	47.8	239	956
2-Methylnaphthalene	20.4	4.08	40.8	204.	817
Acenaphthylene	9.02	1.80	18.0	90.2	361
Acenaphthene	11.0	2.20	22.0	110	440
Fluorene	7.55	1.51	15.1	75.5	302
Anthracene	0.60	0.120	1.20	6.0	24.0
Phenanthrene	5.5	1.1	11	55	220
Fluoranthene	2.11	0.422	4.22	21.1	84.4
Pyrene	1.8	0.36	3.60	18.0	72.0
Benz[a]anthracene	0.08	0.016	0.16	0.8	3.2
Chrysene	0.03	0.006	0.06	0.3	1.2
Deuterated Analogs of Mix A Compounds	Stock Solution µg/mL	CS1 ng/1.5 mL	CS2 ng ng/1.5 mL	CS3 ng/1.5 mL	CS4 ng/1.5 mL
Naphthalene-d8	5	50.0	50.0	50.0	50.0
1-Methylnaphthalene-d10	6	60.0	60.0	60.0	60.0
Acenaphthene-d10	1.23	12.3	12.3	12.3	12.3
Fluorene-d10	1.2	12.0	12.0	12.0	12.0
Phenanthrene-d10	0.96	9.6	9.6	9.6	9.6
Pyrene-d10	0.84	8.4	8.4	8.4	8.4
Chrysene-d12	0.033	0.33	0.33	0.33	0.33

$$ar\ rat/ng = \frac{[(peak\ area\ cal\ std)/(peak\ area\ d-PAHint\ std)]}{(mass\ of\ std\ in\ cal\ vial)} \qquad (1)$$

where:

$ar\ rat/ng$ = area ratio per ng,

(3) Calculate the mean ar rat/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:

$$\overline{ar\ rat/ng} = \frac{1}{n}\sum_{i=1}^{n}(ar\ rat/ng)_i \qquad (2)$$

where:

$(ar\ rat/ng)_i$ = ar rat/ng calculated for calibration solution "i" using Eq 1, and

n = number of calibration points in the curve.

(4) Calculate the percent relative standard deviation:

$$\%RSD = \frac{SD}{\overline{ar\ rat/ng}} \times 100 \qquad (3)$$

where:

$\overline{ar\ rat/ng}$ = mean ar rat/ng calculated above, and

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

12.3 *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 $r^2 > 0.99$, and the area ratio per ng for each concentration should show a relative standard deviation of <25 % for two- to three-ring PAHs, and <30 % for four-ring PAHs. See Section 16. 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 (for example, 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.

12.3.1 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 detection limits for many labs (and is also below the required detection limits needed for the method, so it does not negatively impact the analyses). In such cases, the lowest calibration standard is ignored, and the "J" level adjusted appropriately. 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 (and adjust the "E" value accordingly), as long as a minimum of a three-point standard curve is generated for each PAH.

12.3.1.1 It is recommended that a 4-point (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.

12.3.2 The signal to noise ratio (S/N) for the GC signals present in every selected ion current profile (SICP) must be ≥10:1 for the labeled internal standards and unlabeled calibration compounds.

12.4 *Calibration Verification*—Continuing calibration is performed daily at the beginning of a 24-h period. The injection of the first continuing calibration begins the 24-h window, within which all pore water samples must be injected. Duplicate daily standards are analyzed.

12.4.1 Into 1.5 mL of reagent water, add 4 µL of the CS3 spiking solution and 10 µL of the d-PAH internal standards.

12.4.2 Analyze duplicate vials of the Calibration Standard Solution CS3. 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.

12.4.3 *Criteria for Acceptable Daily Calibration Check*—The criteria listed below for acceptable calibration must be met at the beginning of each 24-h period that samples are analyzed. 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. If the 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.

12.5 *Method Blanks*—Method blanks are prepared and analyzed daily in duplicate following the continuing calibration and between analysis of replicate sets of the same pore water sample. See 12.5.2.2.

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

12.5.2 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 detection limits are normally controlled by GC/MS sensitivity. However, for lower molecular weight PAHs, atmospheric contaminants can cause significant background peaks, especially for low MW alkyl PAHs. This problem is most likely to be significant in urban areas impacted by atmospheric PAHs (for example, from diesel exhaust), and with laboratories using manual techniques, rather than the SPME autosampler.

12.5.2.1 *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 pore water sample have detectable background concentrations more than ⅓ of the target detection limit given in Table 1, the analyses should not continue until the fiber is sufficiently cleaned as demonstrated by a clean water blank. The mean of the calculated concentrations of the PAHs in the blanks analyzed immediately before and immediately after sample pore waters should be subtracted from the sample pore water concentrations.

12.5.2.2 *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 pore water sample have detectable background concentrations more than ⅓ of the target detection limit, the analyses should not continue until the fiber is sufficiently cleaned as demonstrated by a clean water blank. Alternatively, if the concentrations determined in the blanks are less than 20 % of those found in the related sample, the data can be accepted.

12.6 *Determining Relative Response Factors (RRFs)*—All parent PAHs on the target compound list (and the 1- and 2-methylnaphthalene isomers) are included in the calibration standard, so RRFs are not relevant to the parent PAH since each parent PAH is quantitated based on the same parent PAH in the calibration standard. RRFs for alkyl PAH isomeric clusters are determined by each laboratory by comparing the alkyl cluster ar rat/ng to the ar rat/ng of the related parent PAH as determined by the analysis of a spiked pore water sample prepared from SRM 1991. The RRFs for the alkyl PAHs should be determined every time the 4-point (or 3-point) calibration curve is determined (12.3.1.1). Duplicate 1.5 mL water samples should be prepared using 1.5 mL of reagent grade water, and 10 µL of the same d-PAH internal standard solution used for all samples, calibrations, and blanks. Each vial should be spiked with 10 µL of a 1:10 dilution of NIST SRM 1991 in acetone and analyzed in the same manner as calibration standards. The relative response factor of each alkyl cluster is determined versus its parent PAH using the SRM concentration values for the alkyl cluster and the related parent PAHs from Table 2 and the equation:

$$RRF = \left(ar \quad rat\ /\ ng \quad alkylcluster\right)/\left(ar\ rat/ng\ parent\ PAH\right) \qquad (4)$$

The duplicate RRF values should agree within 10% for the low molecular weight parent PAHs and 15% for the higher molecular weight and more highly alkylated PAHs, or the RRF determinations should be repeated. The mean RRF of the duplicate determinations for each alkyl cluster should be used to calculate alkyl PAH cluster concentrations as in 14.2.3.

13. Procedure

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

13.2 *Holding Times:*

13.2.1 Pore waters must be generated within 28 days of sediment sample collection.

13.2.2 Pore waters must be generated and flocculated as quickly as possible, and then immediately spiked with 10 µL of d-PAH solution.

13.2.3 Solid phase micro-extraction must be completed within 24 h of flocculation.

13.3 *Generation of Pore Water:*

13.3.1 Stir the slurry and transfer approximately 40 mL (containing a solids and liquids in proportion to the slurry

TABLE 6 Example of a 24-h Analytical Sequence[A]

Example Analytical Sequence					
Run Type	Minutes	Cumulative Minutes to Start	Cumulative Minutes to End	Cumulative Hours to Start[A]	Cumulative Hours to End
Standard	50	0	50	0.0	0.8
Standard	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 analyzed within 24 h of the flocculation step (that is, the value for cumulative hours to start must be ≤24).

provided) to a clean 40 mL vial. Cap the vial with a PTFE-lined cap. Place the vials in a centrifuge. Spin for 30 min at approximately 1000 g. Using a new, graduated serological pipette, transfer 10 mL of the supernatant to a new 20 mL vial.

13.3.2 *Flocculation of Pore Water*—Flocculation must be performed no more than 24 h prior to extraction.

13.3.2.1 If a flocculation blank is to be analyzed, create the blank by placing 10 mL of reagent water in a clean 20 mL vial. Process this blank along with pore water samples.

13.3.2.2 Add the working alum solution (see Section 9) to each vial of pore water (and QC samples). The volume of the alum solution should be 1⁄40 th of the sample volume. After the addition, swirl the vial for several rotations to incorporate the solution.

13.3.2.3 Add 3 to 5 drops of NaOH working solution (see Section 9) to each vial. Swirl to incorporate the NaOH.

13.3.2.4 Shake the vial for 15 s.

13.3.2.5 Centrifuge for 30 min at approximately 1000 g.

13.3.2.6 Collect the supernatant into a clean 20 mL vial.

13.3.2.7 Repeat 13.3.2.2 through 13.3.2.6 once.

13.3.2.8 Immediately transfer 1.5 mL aliquots to new silanized autosampler vials and immediately add 10 µL of the internal standard solution. Vials are weighed before and after adding the water sample to determine the exact sample water mass.

NOTE 3—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.

NOTE 4—The SPME fiber should be cleaned at the beginning of each sampling set (and after very contaminated samples) for 1 h by placing in the cleaning chamber under helium flow at 320°C. This can conveniently be performed while the pore waters are being prepared.

13.4 *Extraction and Analysis of Flocculated Pore Water:*

13.4.1 Load the autosampler following the recommended analytical sequence in Table 6. Verify the sequence against documented sequence following the loading process.

13.5 The recommended analytical sequence described in Table 6 is based on a 24-h "clock."

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

13.5.2 Analyze two method blanks (ca. 50 min each).

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

14. Data Analysis and Calculations

14.1 Generate ion chromatograms for the target analytes listed in Table 4 that encompass the expected retention windows of the target analytes (see Appendix X1). Integrate the selected ion current profiles optimized quantitation ions determined in 15.5.1. Typical optimized exact masses are shown in Table 4.

14.1.1 *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:

14.1.1.1 The quantitation ion must be present, with a signal-to-noise ratio of at least 3:1 for environmental samples.

14.1.1.2 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 s of the relative retention times obtained from the continuing calibration (or initial calibration if this applies). Alkyl clusters must be identified based on their relative retention times to the parent PAHs and related d-PAHs, and also by observation of their characteristic fingerprints by an experienced analyst.

14.1.2 *Qualitative Identification Criteria for Total Homolog Groups* (for example, total C2 or C3 alkylnaphthalenes)—Integration of the alkyl PAHs requires hands-on labor from a highly experienced analyst. Retention time windows, like those used for the parent PAHs are inadequate for identifying alkyl clusters (that can be minutes wide). Proper identification of alkyl clusters is critical, as is the proper identification of non-target species that occur at the same nominal mass. Mental pattern recognition must be used to avoid including non-target species that may occur at the same mass and 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 of the integration is required for alkyl clusters.

14.1.2.1 Representative selected ion chromatograms from the analysis of a pore water sample prepared from SRM 1991 for all target species are shown in Appendix X1. The top chromatogram on each page is the d-PAH internal standard used for the parent and alkyl PAHs associated with that parent. For example, the first page shows d8-naphthalene (m/z 136) followed by naphthalene (m/z 128), the two methylnaphthalene isomers (m/z 142), the C2-naphthalene cluster (m/z 156), the C3-naphthalene cluster (m/z 170), and the C4-naphthalene cluster (m/z 184). The chromatogram also shows a typical interference that occurs in sediments for the C4-naphthalene cluster, that is, the dibenzothiophene isomers that occur in the same selected ion chromatogram as the C4-naphthalene cluster. These interfering dibenzothiophenes are crossed out, and the correct cluster for integration (based on full scan analyses of several different contaminated sediment pore waters) are indicated by brackets. Similar designations are used to indicate common interfering peaks and the correct target species in the subsequent chromatograms.

14.1.3 The retention time (RT) of the analyte must be no more than 5 s before the expected RT of the first isomer in the homolog, based on the continuing windowing solution analysis.

14.1.4 The retention time (RT) of the analyte must be no more than 5 s after the expected RT of the last isomer in the homolog, based on the continuing windowing solution analysis.

14.2 *Quantitation for Target Analytes:*

14.2.1 Sample water concentrations for parent PAHs (and 1-methyl- and 2-methylnaphthalene) 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.

$$Concentration\ (ng/mL) = \frac{(area\ sample\ peak)/(area\ d - PAH\ int\ std)}{(ar\ rat/ng\ cal\ std) \times (sample\ weight)} \quad (5)$$

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

14.2.3 The concentrations of alkyl PAH clusters are based on the calibration response of their parent PAH as adjusted for the relative response factor (RRF) for that cluster of species (including SPME and GC/MS responses) determined as described in 12.6. Thus, the concentrations of alkyl clusters are calculated by:

$$Concentration\ (ng/mL) = \quad (6)$$

$$\frac{(area\ sample\ cluster)/(area\ \ d - PAH\ int\ std)}{(ar\ rat/\ \ ng\ parent\ \ \ cal\ std) \times (sample\ weight) \times RRF}$$

NOTE 5—The two methylnaphthalene isomers are individual alkyl peaks (not clusters as in all other alkyl cases) and are treated as parent PAHs in the calculations.

14.2.4 If no peaks are present at a signal to noise value ≥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" (that is, ND) at the reporting limit.

14.2.5 Depending on project objectives, the results may be reported to TDLs or estimated detection limits (EDLs).

14.2.5.1 If project-specific guidance requires analysis-specific EDLs, calculate the detection limit for that compound according to the following equation:

$$Estimated\ Detection\ Limit = \frac{N \times 2.5}{H_{is} \times (ar\ rat/ng)} \quad (7)$$

where:

N = height of peak to peak noise of quantitation ion signal in the region of the ion chromatogram where the compound of interest is expected to elute,

H_{is} = peak height of quantitation ion for appropriate internal standard, and

$ar\ rat/ng$ = mean ar rat/ng of compound obtained during daily calibration.

14.2.5.2 If project-specific guidance requires total toxic units (TTU) to be reported, calculate the toxic units contributed by each compound (or isomeric alkyl-PAH group) according to the following equations:

$$TU_c = result(ng/mL)/\ \ Ctu \quad (8)$$

$$Total\ Toxic\ Units\ (TTU) = \sum_{1}^{34} TU_c \quad (9)$$

where:

TU_c = toxic units for each individual compound or homolog group (unitless),

Ctu = concentration for one toxic unit (ng/mL), see Table 1,

$result$ = individual pore water result for a compound or homolog group (ng/mL), and

TTU = total toxic units for all parent and alkyl PAHs.

14.2.6 Flag all compound results in the sample which were estimated below the lowest calibration level with a "J" qualifier.

14.2.7 Flag all compound results in the sample which were estimated above the upper calibration level with an "E" qualifier.

15. Precision and Bias[8]

15.1 The recommendations of the ASTM task group members were followed in performing the multi-laboratory study. Four environmental sediment samples were selected from archived sediments to represent clean background sediments (low or undetectable pore water PAHs) and impacted sediments. The clean sediments were used for the coal tar spiking (Youden Pair) studies. The impacted sediments were used for the spiking recovery study with d12-benz(a)anthracene and d10-2-methylnaphthalene. Efforts were made to select sediments having a representative range of organic carbon content and texture.

15.2 The quantitations were based on three- or four-point calibration curves as verified by daily analysis of duplicate calibration verification standards at the medium-high concentration level. All labs were instructed that they must meet calibration and blank criteria as stated in the method before reporting data. Prior to sample analysis, the initial calibration curves must have a coefficient of determination greater than 0.990, and the relative response factors must have a relative standard deviation of less than 25 % for two to three-ring PAHs, and less than 30 % for four-ring PAHs. The calibration verification mean relative response factor must agree with those of the initial calibration curve within 20 % for two to three-ring PAHs, and less than 25 % for four-ring PAHs. All blanks must meet the requirement that the concentrations be at or less than 20 % of the Performance Limits for individual PAHs.

15.3 Precision and bias were determined using two different approaches. First, a two-ring (d10-2-methylnaphthalene) and four-ring (d12-benz(a)anthracene) perdeuterated PAH were spiked into pore water that was generated from two impacted sediment samples to form a low- and high-concentration spike. Each laboratory then analyzed these surrogate spikes in duplicate and reported the data. Based on the known concentrations of these surrogate spikes, a true concentration was determined and the percent recovery, overall standard deviation, and bias were calculated using this true concentration.

15.3.1 As part of the second assessment of precision and bias, the pore waters from two clean sediments were spiked using the same NAPL stock solution that was used to prepare the qualifying test sample. Sediments were chosen to minimize, as much as possible, any interference due to the presence of background PAHs. Duplicate SPME pore water PAH analyses of each sample of each Youden Pair were performed by each participating laboratory. The spiking was performed in a manner that produced a low (YP1/YP2),

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[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1190. Contact ASTM Customer Service at service@astm.org.

TABLE 7 Precision and Bias Statement for Low- and High-Concentration Surrogate Spikes

		Low Spike	High Spike
d10-2-Methylnaphthalene	No. of usable values	13	13
	True conc. (c), ng/g	10.02	501
	Mean recovery (Xbar), ng/g	11.37	473
	Percent recovery, %	113 %	94 %
	Overall std. dev. (S_T), ng/g	1.26	45.9
	Overall relative std. dev. (S_T), %	11 %	10 %
	Bias, %	13 %	–6 %
d12-Benz[a]anthracene	No. of usable values	12	14
	True conc. (c), ng/g	0.092	4.60
	Mean recovery (Xbar), ng/g	0.11	4.17
	Percent recovery, %	115 %	91 %
	Overall std. dev. (S_T), ng/g	0.01	0.44
	Overall relative std. dev. (S_T), %	12 %	11 %
	Bias, %	15 %	–9 %

medium (YP3/YP4) and high (YP5/YP6) concentration Youden Pair. (A Youden Pair is a pair of samples that differ in concentration by 20 %). The spiking was performed using the NAPL stock solution that was used to create the qualifying test sample and an 80 % solution of that original NAPL stock solution. All YP samples were randomly coded, and analyzed in a random order. Based on this relationship, for determination of precision and bias, the "true concentrations" of the Youden Pairs were generated from the mean of the replicate analyses of the qualifying test sample.

15.4 As directed in Practice D2777, Section 10.3, the data were evaluated for outliers prior to the calculations of precision and bias. The data were evaluated using the one-sided t-test at the upper 5 % significance level as described in Practice E178, Section 6.

15.4.1 A total of 14 data points (n = 14) were generated for the low and high surrogate-spiked samples (seven independent operators in duplicate). An outlier assessment of the data resulted in the rejection of one of the low- and high-concentration surrogate-spiked d10-2-methlynapthalene samples and two of the low-concentration surrogate-spiked d12-benz(a)anthracene samples.

15.4.2 A total of 14 data points (n = 14) were generated for each analyte for each of the six Youden Pairs (seven independent operators in duplicate for each Youden Pair). An outlier assessment of the data resulted in the rejection of several of the results for each Youden Pair. There was a maximum of one rejected result per analyte per Youden Pair, that is, 1⁄14 or 7 %.

15.4.3 Precision and bias were recalculated for these samples without the outlying observations.

15.5 *Single Analyst Precision Statement:*

15.5.1 The precision statements for the d10-2-methylnaphthalene and d12-benz(a)anthracene perdeuterated PAH spikes are presented in Table 7. Mean percent recoveries ranged from 91 to 115 % and relative standard deviations (RSDs) were less than 12 %.

15.5.2 The precision statements for the Youden Pairs are presented in Table 8. Mean percent recoveries for Youden Pairs YP3 through YP6 ranged between 70 and 130 % for the majority of the PAHs, whereas the mean percent recoveries for YP1 and YP2 were more erratic, lying, at times, well outside this range. RSDs followed a similar trend, and were less than 50 % for the majority of the PAHs, whereas the RSDs for YP1 and YP2 were higher. PAH concentrations for the low Youden Pair (YP1 and YP2) were at, and sometimes below, the PLs for the PAHs presented in Table 1, resulting in a significant amount of variability in the data.

15.6 *Single Analyst Bias Statement:*

15.6.1 The bias statements for the d10-2-methylnaphthalene and d12-benz(a)anthracene perdeuterated PAH spikes are presented in Table 7. Percent bias ranged from 13 to 15 % for the low-concentration spike and –9 to –6 % for the high-concentration spike.

15.6.2 The bias statements for the Youden Pairs are presented in Table 8. Percent bias for Youden Pairs YP3 through YP6 ranged between –33 and 24 % for the majority of the PAHs, whereas the percent bias for YP1 and YP2 were outside this range.

TABLE 8 Precision and Bias Statement for Youden Pairs 1 through 6 (YP1-YP6)

		YP1	YP2	YP3	YP4	YP5	YP6
Naphthalene	No. of usable values	14	13	14	14	14	14
	True conc. (c), ng/g	0.82	1.03	4.11	5.13	20.5	25.7
	Mean recovery (Xbar), ng/g	1.29	1.65	4.58	5.68	20.1	25.2
	Percent recovery, %	158 %	160 %	112 %	111 %	98 %	98 %
	Overall std. dev. (S_T), ng/g	0.42	0.75	0.69	0.96	1.8	2.6
	Overall relative std. dev. (S_T), %	33 %	46 %	15 %	17 %	9 %	10 %
	No. of usable pairs	13		14		14	
	Single-operator std. dev. (S_O), ng/g	0.37		0.37		0.92	
	Analyst relative std. dev. (S_O), %	26 %		7 %		4 %	
	Bias, %	58 %	60 %	12 %	11 %	–2 %	–2 %

TABLE 8 *Continued*

		YP1	YP2	YP3	YP4	YP5	YP6
2-Methylnaphthalene	No. of usable values	14	13	14	14	14	14
	True conc. (c), ng/g	0.41	0.51	2.03	2.54	10.2	12.7
	Mean recovery (Xbar), ng/g	0.64	0.77	2.31	2.88	10.3	12.8
	Percent recovery, %	156 %	152 %	114 %	113 %	101 %	101 %
	Overall std. dev. (S_T), ng/g	0.20	0.29	0.25	0.40	1.0	1.2
	Overall relative std. dev. (S_T), %	32 %	37 %	11 %	14 %	9 %	9 %
	No. of usable pairs	13		14		14	
	Single-operator std. dev. (S_O), ng/g	0.13		0.23		0.38	
	Analyst relative std. dev. (S_O), %	19 %		9 %		3 %	
	Bias, %	56 %	52 %	14 %	13 %	1 %	1 %
1-Methylnaphthalene	No. of usable values	14	13	14	13	14	14
	True conc. (c), ng/g	0.26	0.33	1.32	1.65	6.6	8.2
	Mean recovery (Xbar), ng/g	0.45	0.55	1.54	1.81	6.6	8.2
	Percent recovery, %	171 %	167 %	117 %	110 %	100 %	99 %
	Overall std. dev. (S_T), ng/g	0.17	0.26	0.29	0.29	0.7	0.9
	Overall relative std. dev. (S_T), %	38 %	47 %	19 %	16 %	10 %	11 %
	No. of usable pairs	13		13		14	
	Single-operator std. dev. (S_O), ng/g	0.11		0.20		0.26	
	Analyst relative std. dev. (S_O), %	21 %		12 %		4 %	
	Bias, %	71 %	67 %	17 %	10 %	0 %	–1 %
C2 Naphthalenes	No. of usable values	14	14	14	14	14	14
	True conc. (c), ng/g	0.72	0.90	3.59	4.49	18.0	22.5
	Mean recovery (Xbar), ng/g	1.25	1.36	4.47	5.34	22.2	26.7
	Percent recovery, %	173 %	151 %	124 %	119 %	124 %	119 %
	Overall std. dev. (S_T), ng/g	0.47	0.48	1.11	26 %	5.5	5.8
	Overall relative std. dev. (S_T), %	37 %	35 %	25 %		25 %	22 %
	No. of usable pairs	14		14		14	
	Single-operator std. dev. (S_O), ng/g	0.16		0.52		3.20	
	Analyst relative std. dev. (S_O), %	12 %		11 %		13 %	
	Bias, %	73 %	51 %	24 %	19 %	24 %	19 %
C3 Naphthalenes	No. of usable values	14	13	14	14	14	14
	True conc. (c), ng/g	1.14	1.43	5.72	7.16	28.6	35.8
	Mean recovery (Xbar), ng/g	1.56	1.51	5.68	6.34	28.7	35.0
	Percent recovery, %	136 %	106 %	99 %	89 %	100 %	98 %
	Overall std. dev. (S_T), ng/g	0.69	0.59	1.63	1.48	6.5	7.8
	Overall relative std. dev. (S_T), %	44 %	39 %	29 %	23 %	23 %	22 %
	No. of usable pairs	12		14		14	
	Single-operator std. dev. (S_O), ng/g	0.31		0.95		4.41	
	Analyst relative std. dev. (S_O), %	20 %		16 %		14 %	
	Bias, %	36 %	6 %	–1 %	11 %	0 %	–2 %
C4 Naphthalenes	No. of usable values	11	12	14	14	13	14
	True conc. (c), ng/g	0.84	1.05	4.19	5.23	20.9	26.2
	Mean recovery (Xbar), ng/g	0.97	0.99	3.49	4.18	18.0	23.0
	Percent recovery, %	115 %	94 %	83 %	80 %	68 %	88 %
	Overall std. dev. (S_T), ng/g	0.41	0.43	1.21	1.52	5.9	7.7
	Overall relative std. dev. (S_T), %	42 %	44 %	35 %	36 %	33 %	33 %
	No. of usable pairs	10		14		13	
	Single-operator std. dev. (S_O), ng/g	0.09		0.66		4.61	
	Analyst relative std. dev. (S_O), %	10 %		17 %		22 %	
	Bias, %	15 %	–6 %	–17 %	–20 %	–14 %	–12 %
Acenaphthylene	No. of usable values	12	12	14	13	14	14
	True conc. (c), ng/g	0.09	0.12	0.46	0.58	2.3	2.9
	Mean recovery (Xbar), ng/g	0.74	0.81	0.92	0.43	1.9	2.3
	Percent recovery, %	805 %	699 %	199 %	75 %	84 %	81 %
	Overall std. dev. (S_T), ng/g	1.48	1.46	1.33	0.23	1.3	1.4
	Overall relative std. dev. (S_T), %	199 %	181 %	144 %	52 %	69 %	59 %
	No. of usable pairs	13		13		14	
	Single-operator std. dev. (S_O), ng/g	0.08		0.84		0.36	
	Analyst relative std. dev. (S_O), %	11 %		122 %		17 %	
	Bias, %	705 %	599 %	99 %	–25 %	–16 %	–19 %
Acenaphthene	No. of usable values	14	13	14	14	13	14
	True conc. (c), ng/g	0.19	0.23	0.93	1.16	4.7	5.8
	Mean recovery (Xbar), ng/g	0.24	0.28	0.99	1.20	4.5	5.7
	Percent recovery, %	128 %	121 %	106 %	103 %	97 %	98 %
	Overall std. dev. (S_T), ng/g	0.07	0.07	0.13	0.16	0.2	0.5
	Overall relative std. dev. (S_T), %	28 %	26 %	14 %	14 %	5 %	9 %
	No. of usable pairs	13		14		13	
	Single-operator std. dev. (S_O), ng/g	0.03		0.05		0.27	
	Analyst relative std. dev. (S_O), %	13 %		5 %		5 %	

TABLE 8 *Continued*

		YP1	YP2	YP3	YP4	YP5	YP6
	Bias, %	28 %	21 %	6 %	3 %	–3 %	–2 %
Fluorene	No. of usable values	14	13	14	13	13	14
	True conc. (c), ng/g	0.11	0.14	0.54	0.68	2.7	3.4
	Mean recovery (Xbar), ng/g	0.15	0.19	0.57	0.68	2.5	3.2
	Percent recovery, %	141 %	137 %	105 %	101 %	92 %	94 %
	Overall std. dev. (S_T), ng/g	0.07	0.08	0.11	0.09	0.2	0.3
	Overall relative std. dev. (S_T), %	45 %	41 %	19 %	14 %	7 %	8 %
	No. of usable pairs	13		13		13	
	Single-operator std. dev. (S_O), ng/g	0.02		0.10		0.36	
	Analyst relative std. dev. (S_O), %	14 %		16 %		12 %	
	Bias, %	41 %	37 %	5 %	1 %	–8 %	–6
C1 Fluorenes	No. of usable values	14	12	14	14	14	14
	True conc. (c), ng/g	0.20	0.25	1.00	1.25	5.0	6.3
	Mean recovery (Xbar), ng/g	0.33	0.30	0.96	1.14	4.8	6.0
	Percent recovery, %	166 %	120 %	96 %	91 %	95 %	96 %
	Overall std. dev. (S_T), ng/g	0.15	1.10	0.20	0.21	0.8	1.0
	Overall relative std. dev. (S_T), %	45 %	32 %	21 %	18 %	18 %	16 %
	No. of usable pairs	12		14		14	
	Single-operator std. dev. (S_O), ng/g	0.09		0.10		0.47	
	Analyst relative std. dev. (S_O), %	29 %		10 %		9 %	
	Bias, %	29 %	20 %	–4 %	–9 %	–5 %	–4 %
C2 Fluorenes	No. of usable values	9	8	14	13	14	13
	True conc. (c), ng/g	0.27	0.34	1.37	1.71	6.9	8.6
	Mean recovery (Xbar), ng/g	0.35	0.38	1.25	1.30	5.7	8.6
	Percent recovery, %	129 %	110 %	91 %	76 %	83 %	77 %
	Overall std. dev. (S_T), ng/g	0.12	0.06	0.45	0.31	1.8	1.4
	Overall relative std. dev. (S_T), %	34 %	17 %	36 %	24 %	32 %	21 %
	No. of usable pairs	7				13	
	Single-operator std. dev. (S_O), ng/g	0.08				1.24	
	Analyst relative std. dev. (S_O), %	23 %				20 %	
	Bias, %	29 %	10 %	–9 %	–24 %	–17 %	–23 %
C3 Fluorenes	No. of usable values	1	1	6	7	11	11
	True conc. (c), ng/g	0.29	0.36	1.43	1.78	7.1	8.9
	Mean recovery (Xbar), ng/g	0.48	0.23	0.95	1.23	4.8	6.3
	Percent recovery, %	168 %	64 %	67 %	69 %	67 %	70 %
	Overall std. dev. (S_T), ng/g			0.27	0.34	2.0	2.5
	Overall relative std. dev. (S_T), %			28 %	28 %	43 %	40 %
	No. of usable pairs	0		6		11	
	Single-operator std. dev. (S_O), ng/g	NA[A]		0.10		1.07	
	Analyst relative std. dev. (S_O), %	NA		9 %		19 %	
	Bias, %	NA	36 %	–33 %	–31 %	–33 %	30 %
Phenanthrene	No. of usable values	14	13	14	14	14	14
	True conc. (c), ng/g	0.36	0.45	1.79	2.23	8.9	11.2
	Mean recovery (Xbar), ng/g	0.43	0.49	1.85	2.30	8.8	11.1
	Percent recovery, %	120 %	111 %	104 %	103 %	99 %	100 %
	Overall std. dev. (S_T), ng/g	0.10	0.12	0.22	0.18	0.7	1.0
	Overall relative std. dev. (S_T), %	24 %	24 %	12 %	8 %	8 %	9 %
	No. of usable pairs	13		14		14	
	Single-operator std. dev. (S_O), ng/g	0.07		0.12		0.61	
	Analyst relative std. dev. (S_O), %	15 %		6 %		6 %	
	Bias, %	20 %	11 %	4 %	3 %	–1 %	0 %
Anthracene	No. of usable values	14	14	13	13	13	14
	True conc. (c), ng/g	0.07	0.09	0.36	0.44	1.8	2.2
	Mean recovery (Xbar), ng/g	0.20	0.21	0.39	0.46	1.9	2.5
	Percent recovery, %	277 %	239 %	110 %	104 %	105 %	11 %
	Overall std. dev. (S_T), ng/g	0.32	0.31	0.22	0.21	0.3	0.3
	Overall relative std. dev. (S_T), %	163 %	147 %	55 %	46 %	14 %	13 %
	No. of usable pairs	14		13		13	
	Single-operator std. dev. (S_O), ng/g	0.02		0.04		0.21	
	Analyst relative std. dev. (S_O), %	9 %		9 %		9 %	
	Bias, %	177 %	139 %	10 %	4 %	5 %	11 %
C1 Phenanthrenes/Anthracenes	No. of usable values	13	14	14	14	14	14
	True conc. (c), ng/g	0.62	0.78	3.12	3.90	15.6	19.5
	Mean recovery (Xbar), ng/g	0.62	0.81	2.65	3.22	13.7	17.1
	Percent recovery, %	99 %	103 %	85 %	83 %	88 %	87 %
	Overall std. dev. (S_T), ng/g	0.49	0.67	1.03	1.18	306	4.05
	Overall relative std. dev. (S_T), %	80 %	83 %	39 %	37 %	22 %	24 %
	No. of usable pairs	13		14		14	

TABLE 8 *Continued*

		YP1	YP2	YP3	YP4	YP5	YP6
	Single-operator std. dev. (S_O), ng/g	0.08		0.29		1.29	
	Analyst relative std. dev. (S_O), %	11 %		10 %		8 %	
	Bias, %	–1 %	3 %	–15 %	–17 %	–12 %	–13 %
C2 Phenanthrenes/Anthracenes	No. of usable values	14	14	14	14	14	14
	True conc. (c), ng/g	0.74	0.92	3.69	4.62	18.5	23.1
	Mean recovery (Xbar), ng/g	11.1	1.22	2.86	3.52	13.0	16.1
	Percent recovery, %	150 %	132 %	77 %	76 %	70 %	72 %
	Overall std. dev. (S_T), ng/g	0.92	1.07	1.74	2.22	5.74	7.54
	Overall relative std. dev. (S_T), %	83 %	88 %	61 %	63 %	44 %	45 %
	No. of usable pairs	14		14		14	
	Single-operator std. dev. (S_O), ng/g	0.16		0.71		2.06	
	Analyst relative std. dev. (S_O), %	14 %		22 %		14 %	
	Bias, %	50 %	32 %	–23 %	–24 %	–30 %	–28 %
C3 Phenanthrenes/Anthracenes	No. of usable values	11	13	13	13	14	14
	True conc. (c), ng/g	0.31	0.39	1.55	1.94	7.75.7	9.7
	Mean recovery (Xbar), ng/g	0.86	0.48	1.19	1.41	7.4	7.3
	Percent recovery, %	278 %	123 %	77 %	73 %	74 %	76 %
	Overall std. dev. (S_T), ng/g	1.36	0.77	1.13	1.26	3.42	4.66
	Overall relative std. dev. (S_T), %	158 %	160 %	95 %	89 %	60 %	64 %
	No. of usable pairs	10		13		14	
	Single-operator std. dev. (S_O), ng/g	0.13		0.26		1.21	
	Analyst relative std. dev. (S_O), %	20 %		20 %		19 %	
	Bias, %	178 %	23 %	–23 %	–27 %	–26 %	–24 %
C4 Phenanthrenes/Anthracenes	No. of usable values	2	5	13	13	14	13
	True conc. (c), ng/g	0.23	0.29	1.16	1.45	5.8	7.3
	Mean recovery (Xbar), ng/g	0.35	0.32	1.21	1.44	4.7	4.6
	Percent recovery, %	151 %	111 %	105 %	99 %	81 %	64 %
	Overall std. dev. (S_T), ng/g	0.03	0.05	2.33	2.43	4.96	4.56
	Overall relative std. dev. (S_T), %	8 %	17 %	192 %	169 %	105 %	98 %
	No. of usable pairs	2		13		13	
	Single-operator std. dev. (S_O), ng/g	0.04		0.28		0.80	
	Analyst relative std. dev. (S_O), %	12 %		21 %		17 %	
	Bias, %	51 %	11 %	5 %	–1 %	–19 %	–36 %
Fluoranthene	No. of usable values	14	13	14	14	14	14
	True conc. (c), ng/g	0.10	0.12	0.49	0.62	2.5	3.1
	Mean recovery (Xbar), ng/g	0.12	0.14	0.50	0.61	2.3	2.9
	Percent recovery, %	125 %	116 %	101 %	99 %	94 %	95 %
	Overall std. dev. (S_T), ng/g	0.03	0.04	0.07	0.07	0.22	0.29
	Overall relative std. dev. (S_T), %	26 %	30 %	14 %	11 %	10 %	10 %
	No. of usable pairs	13		14		14	
	Single-operator std. dev. (S_O), ng/g	0.02		0.03		0.19	
	Analyst relative std. dev. (S_O), %	19 %		6 %		7 %	
	Bias, %	25 %	16 %	1 %	–1 %	–6 %	–5 %
Pyrene	No. of usable values	14	13	14	14	14	14
	True conc. (c), ng/g	0.17	0.21	0.85	1.06	4.2	5.3
	Mean recovery (Xbar), ng/g	0.20	0.23	0.86	1.05	4.1	5.3
	Percent recovery, %	116 %	107 %	101 %	99 %	98 %	99 %
	Overall std. dev. (S_T), ng/g	0.04	0.04	0.09	0.10	0.35	0.47
	Overall relative std. dev. (S_T), %	20 %	18 %	10 %	9 %	8 %	9 %
	No. of usable pairs	13		14		14	
	Single-operator std. dev. (S_O), ng/g	0.03		0.05		0.30	
	Analyst relative std. dev. (S_O), %	15 %		6 %		6 %	
	Bias, %	16 %	7 %	1 %	–1 %	–2 %	–1 %
C1 Fluoranthenes/pyrenes	No. of usable values	14	14	14	14	14	14
	True conc. (c), ng/g	0.20	0.25	1.01	1.26	5.1	6.3
	Mean recovery (Xbar), ng/g	0.17	0.19	0.80	0.99	4.4	5.8
	Percent recovery, %	83 %	76 %	79 %	79 %	86 %	92 %
	Overall std. dev. (S_T), ng/g	0.07	0.07	0.27	0.35	1.32	2.08
	Overall relative std. dev. (S_T), %	41 %	36 %	34 %	35 %	30 %	36 %
	No. of usable pairs	14		14		14	
	Single-operator std. dev. (S_O), ng/g	0.03		0.13		0.65	
	Analyst relative std. dev. (S_O), %	18 %		15 %		13 %	
	Bias, %	–17 %	–24 %	–21 %	–21 %	–14 %	–8 %
Benz[a]anthracene	No. of usable values	13	14	13	14	13	14
	True conc. (c), ng/g	0.07	0.08	0.34	0.42	1.7	2.1
	Mean recovery (Xbar), ng/g	0.06	0.08	0.28	0.34	1.5	2.0
	Percent recovery, %	94 %	94 %	83 %	80	91 %	96 %
	Overall std. dev. (S_T), ng/g	0.01	0.02	0.02	0.05	0.23	0.22

TABLE 8 *Continued*

		YP1	YP2	YP3	YP4	YP5	YP6
	Overall relative std. dev. (S_T), %	19 %	19 %	8 %	14 %	15 %	11 %
	No. of usable pairs	13		13		13	
	Single-operator std. dev. (S_O), ng/g	0.01		0.05		0.34	
	Analyst relative std. dev. (S_O), %	15 %		16 %		19 %	
	Bias, %	–6 %	–6 %	–17 %	–20 %	–9 %	–4 %
Chrysene	No. of usable values	14	14	14	14	13	14
	True conc. (c), ng/g	0.06	0.07	0.30	0.37	1.5	1.9
	Mean recovery (Xbar), ng/g	0.07	0.08	0.30	0.37	1.4	1.7
	Percent recovery, %	111 %	108 %	99 %	98 %	92 %	93 %
	Overall std. dev. (S_T), ng/g	0.01	0.01	0.04	0.06	0.22	0.22
	Overall relative std. dev. (S_T), %	15 %	14 %	14 %	18 %	16 %	13 %
	No. of usable pairs	14		14		13	
	Single-operator std. dev. (S_O), ng/g	0.01		0.03		0.25	
	Analyst relative std. dev. (S_O), %	10 %		9 %		16 %	
	Bias, %	11 %	8 %	–1 %	–2 %	–8 %	–7 %
C1 Chrysenes	No. of usable values	13	12	14	14	14	14
	True conc. (c), ng/g	0.07	0.09	0.35	0.44	1.8	2.2
	Mean recovery (Xbar), ng/g	0.09	0.10	0.33	0.39	1.4	1.8
	Percent recovery, %	126 %	111 %	93 %	87 %	80 %	80 %
	Overall std. dev. (S_T), ng/g	0.02	0.03	0.06	0.08	0.34	0.54
	Overall relative std. dev. (S_T), %	24 %	27 %	19 %	21 %	24 %	30 %
	No. of usable pairs	12		14		14	
	Single-operator std. dev. (S_O), ng/g	0.01		0.03		0.23	
	Analyst relative std. dev. (S_O), %	11 %		9 %		15 %	
	Bias, %	26 %	11 %	–7 %	–13 %	–20 %	–20 %
Total PAH_{24} (sum of 24 PAH compounds)	No. of usable values	14	14	14	14	13	14
	True conc. (c), ng/g	8.3	10.4	41.7	52.1	209	261
	Mean recovery (Xbar), ng/g	11.5	14.1	41.3	49.1	191	242
	Percent recovery, %	138 %	135 %	99 %	94 %	92 %	93 %
	Overall std. dev. (S_T), ng/g	5.2	5.3	9.1	9.6	28	15 %
	Overall relative std. dev. (S_T), %	45 %	38 %	22 %	19 %	15 %	
	No. of usable pairs	14		14		13	
	Single-operator std. dev. (S_O), ng/g	2.6		2.5		39	
	Analyst relative std. dev. (S_O), %	20 %		6 %		18 %	
	Bias, %	38 %	35 %	–1 %	–6 %	–8 %	–7 %

[A] NA: Not applicable (either analyte not detected in the associated sample or it was rejected as an outlier).

15.7 The graphs and linear regression equations show the relationship between standard deviation and concentration, and mean recovery and concentration for representative PAHs (naphthalene, 2-methylnaphthalene, phenanthrene, and C1-chrysenes) (see Figs. 1-4). The figures show the linearity of precision and accuracy with increasing concentration.

16. Quality Control Criteria

16.1 *Initial Calibration:*

16.1.1 The following acceptance criteria will be used for initial calibration: *(1)* The signal to noise (S/N) ratio for the GC signals present in every selected ion current profile (SICP) must be ≥10:1 for the labeled internal standards and calibration compounds; *(2)* 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 $r^2 > 0.99$. The calibration curve must not

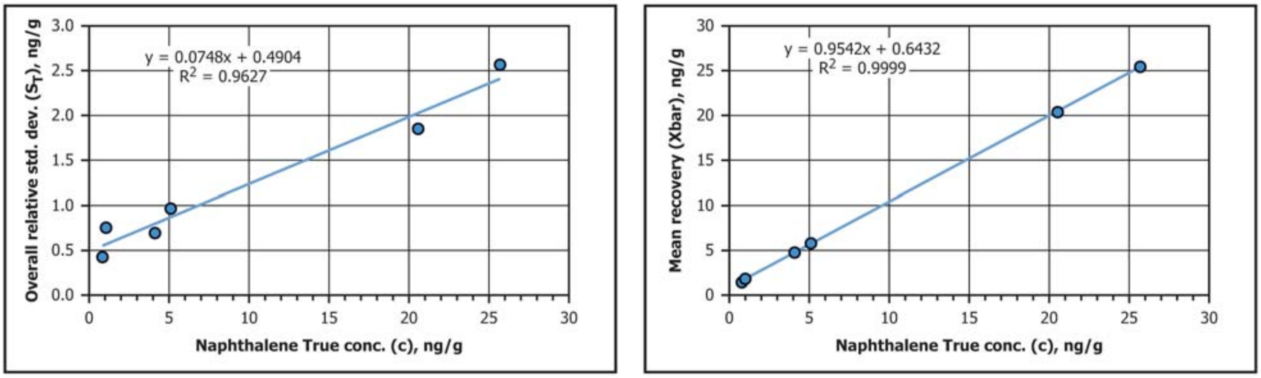

FIG. 1 Naphthalene Standard Deviation and Mean Recovery versus Youden Pair Concentration

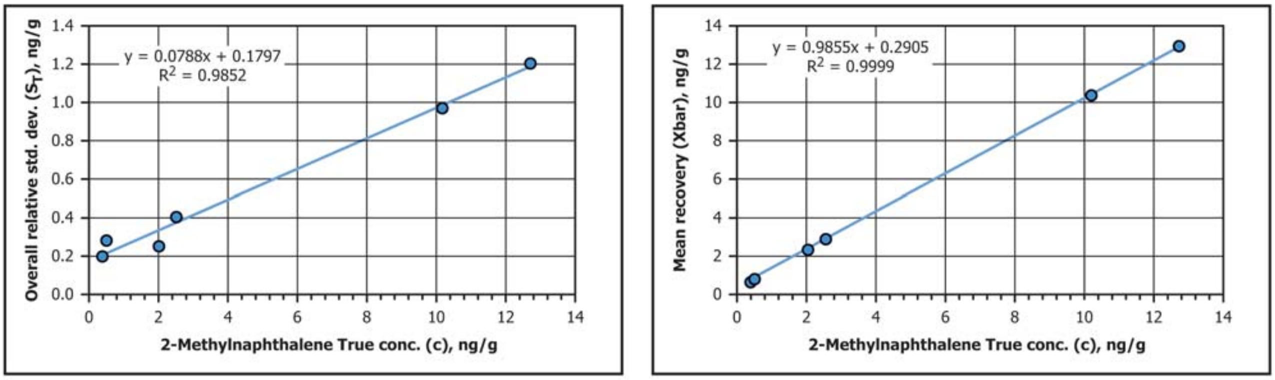

FIG. 2 2-Methylnaphthalene Standard Deviation and Mean Recovery versus Youden Pair Concentration

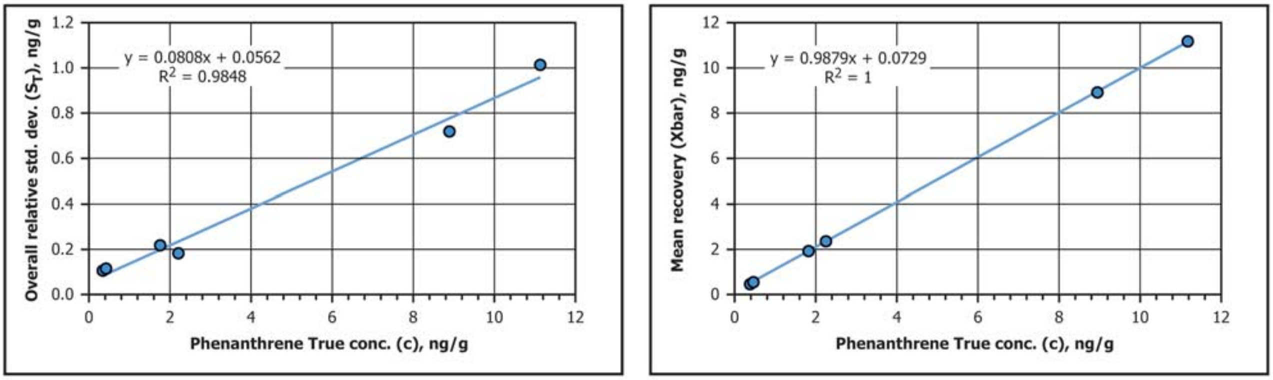

FIG. 3 Phenanthrene Standard Deviation and Mean Recovery versus Youden Pair Concentration

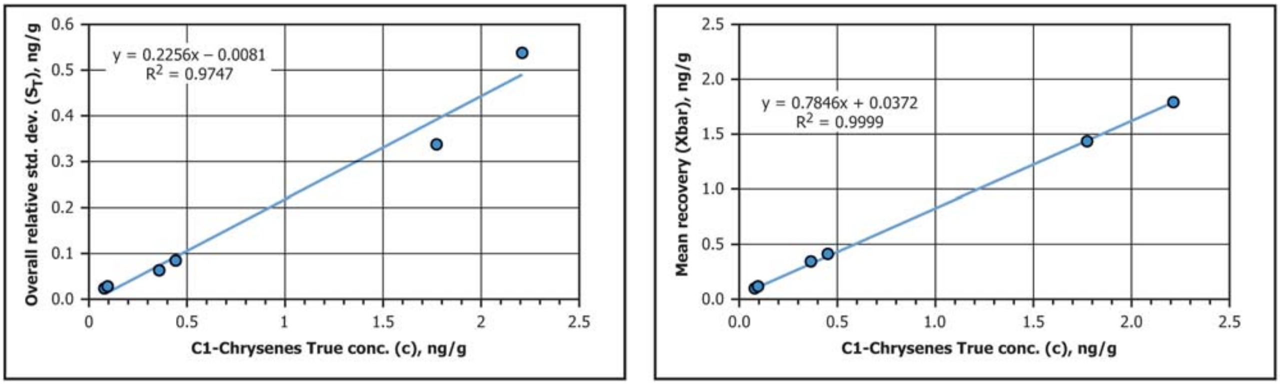

FIG. 4 C1-Chrysenes Standard Deviation and Mean Recovery versus Youden Pair Concentration

be forced through the origin; *(3)* The number of calibration standards may be reduced from four to three based on the criteria in 12.3 of this test method.

16.1.2 The following corrective action will be adopted for initial calibration: *(1)* Initial calibration must be re-established if the RSD(s) exceed the limit(s); *(2)* The calibration will not be re-established in response to a nonconforming RSD if the sample results are less than the Performance Limit.

16.2 *Daily Duplicate Calibration Verifications:*

16.2.1 The following acceptance criteria will be used for daily duplicate calibration verifications: *(1)* The S/N ratio for the GC signals present in every SICP must be ≥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 less than ±20 % for low molecular weight PAHs of the mean values established during the initial calibration.

16.2.2 The following corrective action will be adopted for daily duplicate calibration verifications if the first acceptance criterion is not satisfied: a new initial calibration curve must be established before sample extracts can be analyzed.

16.3 *Flocculation Blanks:*

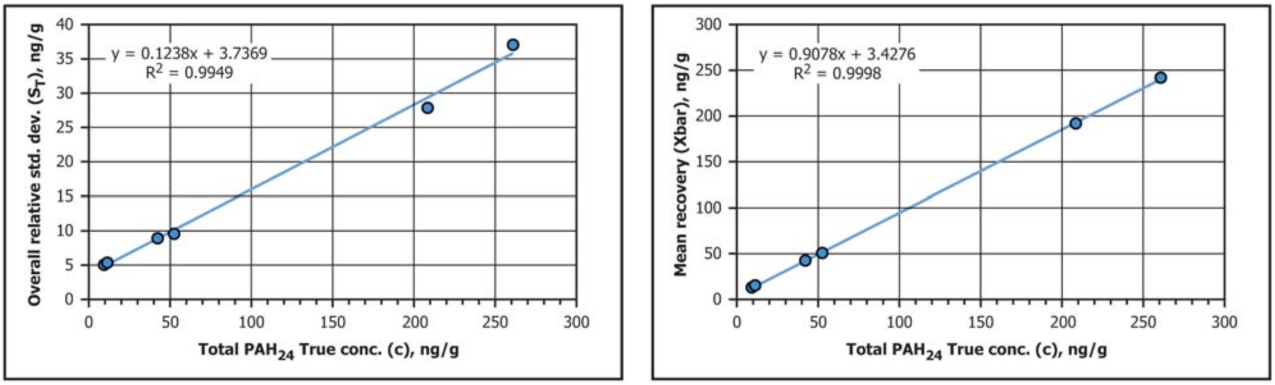

FIG. 5 Total PAH_{24} Standard Deviation and Mean Recovery versus Youden Pair Concentration

16.3.1 The following acceptance criterion will be used for flocculation blanks: Prepared as needed to assess contamination from flocculation reagents and handling. Target analytes must not be detected above ⅓ of the target detection limits or >20 % of the associated sample result(s).

16.3.2 The following corrective action will be adopted for flocculation blanks: Locate the source of the contamination; correct the problem. Re-extract and reanalyze associated samples that are less than ten times the level of the contaminants present in the method blank.

16.4 *Extraction and Analytical Blanks:*

16.4.1 The following acceptance criterion will be used for extraction and analytical blanks: Analyzed between every sample to monitor the baseline. Target analytes must not be detected above ⅓ of the target detection limits or >20 % of the associated sample result(s).

16.4.2 The following corrective action will be adopted for extraction and analytical blanks: Locate the source of the contamination; correct the problem. Re-extract and reanalyze associated samples that are less than ten times the level of the contaminants present in the method blank.

16.5 *Signal to Noise Ratio:*

16.5.1 The following acceptance criterion will be used for signal to noise ratio: The signal to noise (S/N) ratio for the GC signals present in every selected ion current profile (SICP) must be ≥3:1 for target compounds in environmental samples and ≥10:1 for the labeled internal standards.

16.5.2 The following corrective action will be adopted for signal to noise ratio: Reanalyze the sample unless obvious matrix interference is present.

APPENDIX

(Nonmandatory Information)

X1. ION PLOTS

X1.1 Selected ion chromatograms (nominal masses) from an analysis of pore water spiked with SRM 1991 including the d-PAH internal standards (top chromatogram of each page), and the related target parent and alkyl PAHs. Target species are indicated with brackets, and interfering species are marked with an "X." See Table 3 for a list of d-PAH internal standards and their related target analyte PAHs. See Table 4 for typical m/z values for d-PAH internal standards and target PAHs.

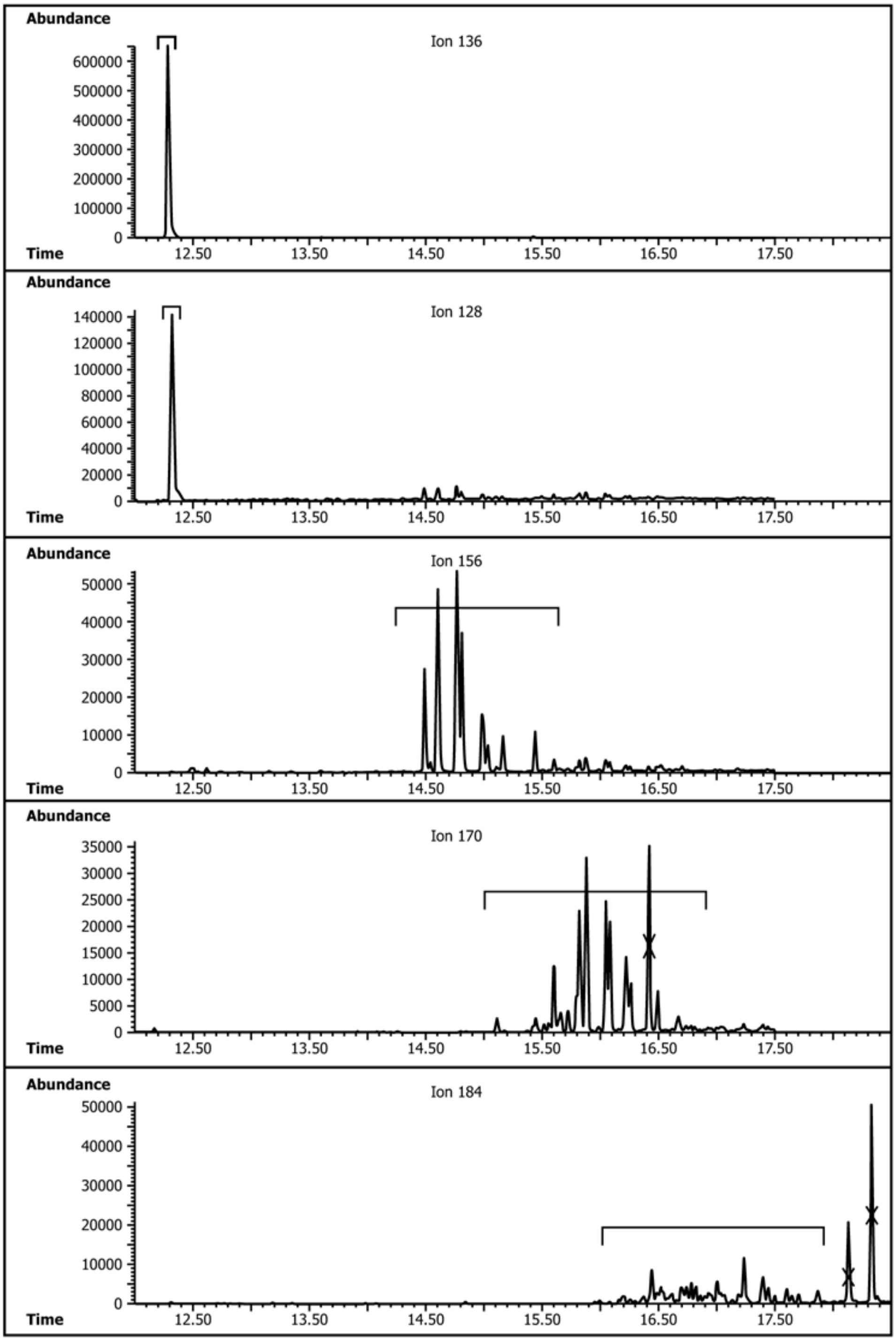

FIG. X1.1 Naphthalenes

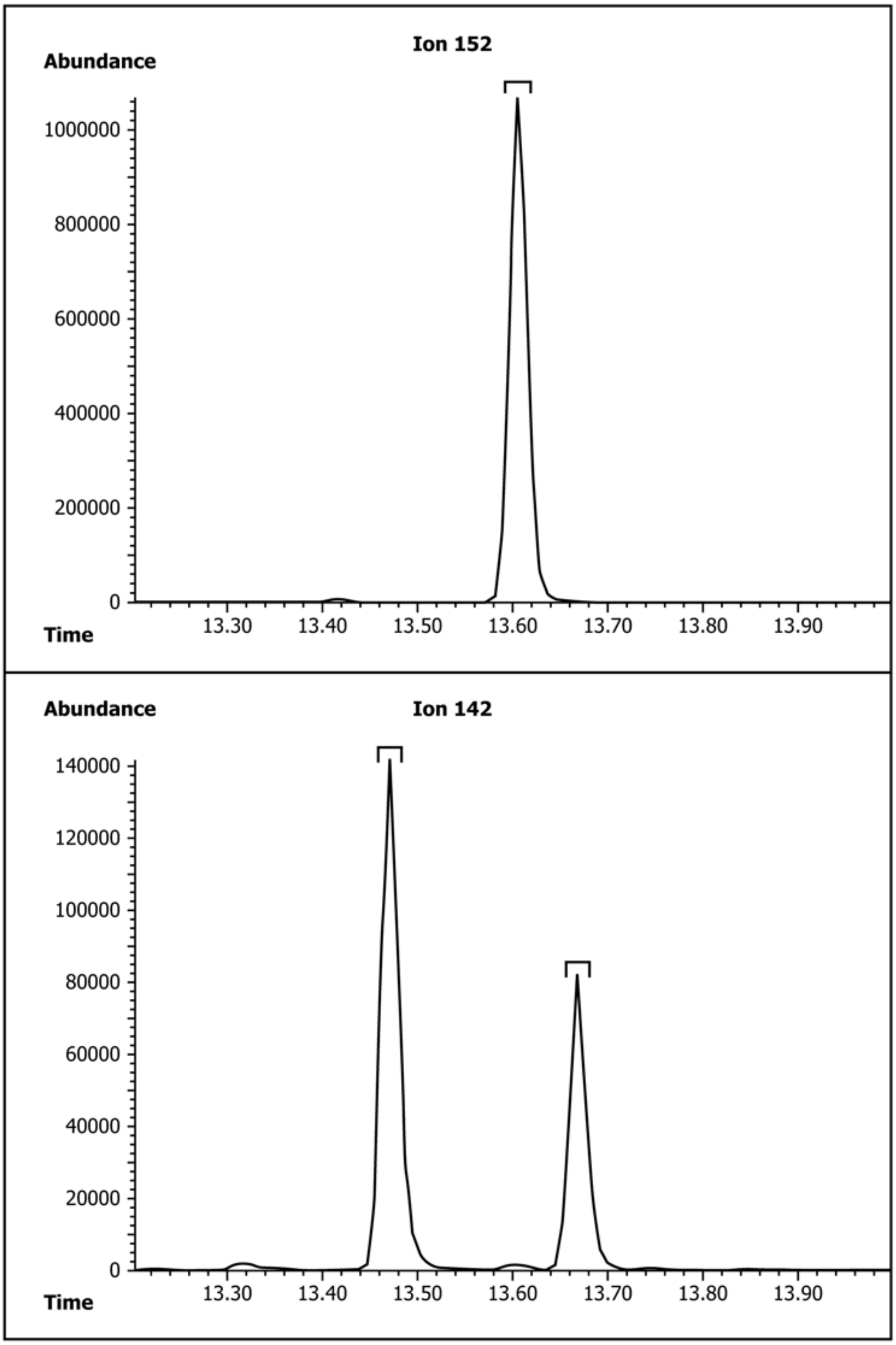

FIG. X1.2 Methylnaphthalenes

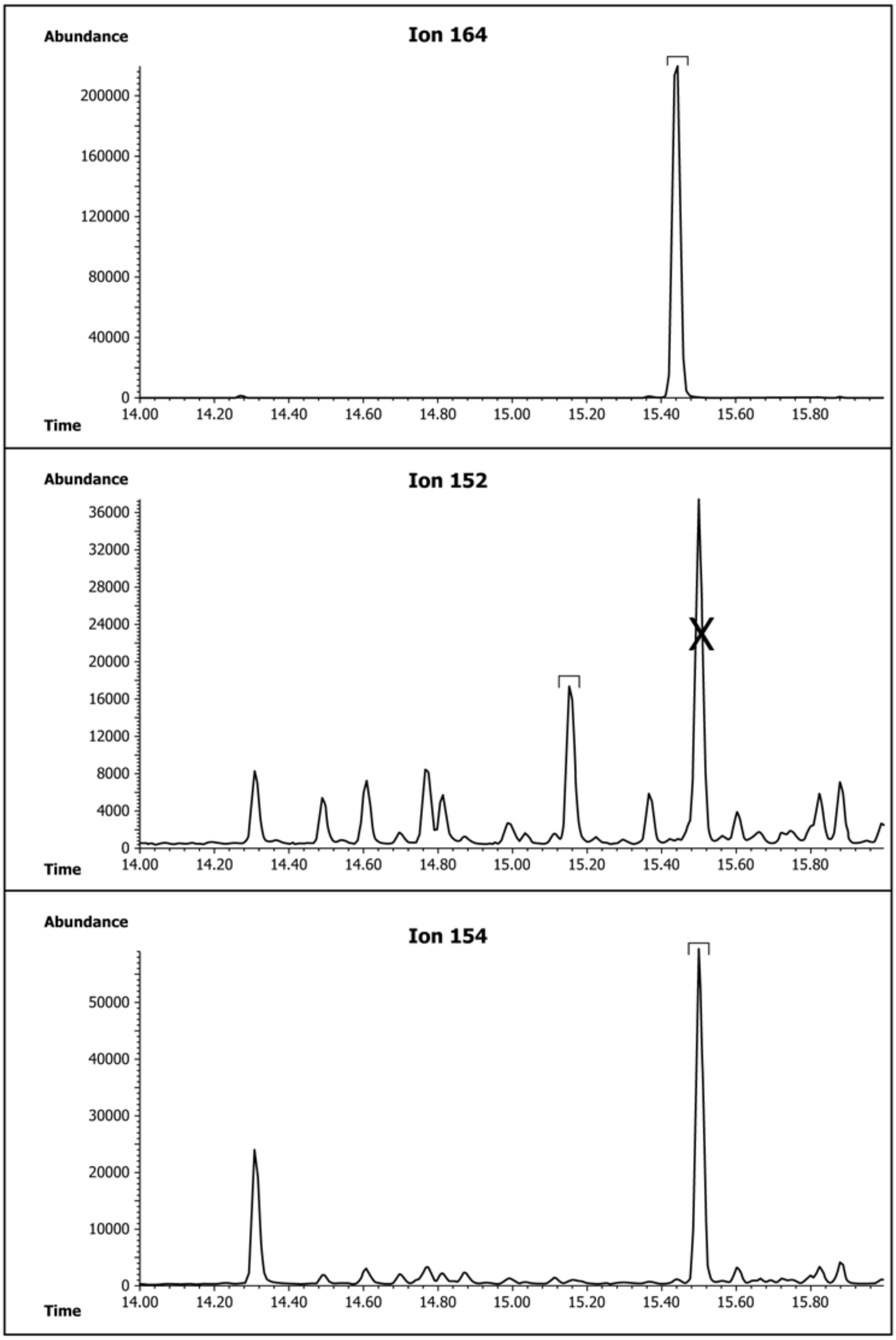

FIG. X1.3 Acenaphthylene/Acenaphthene

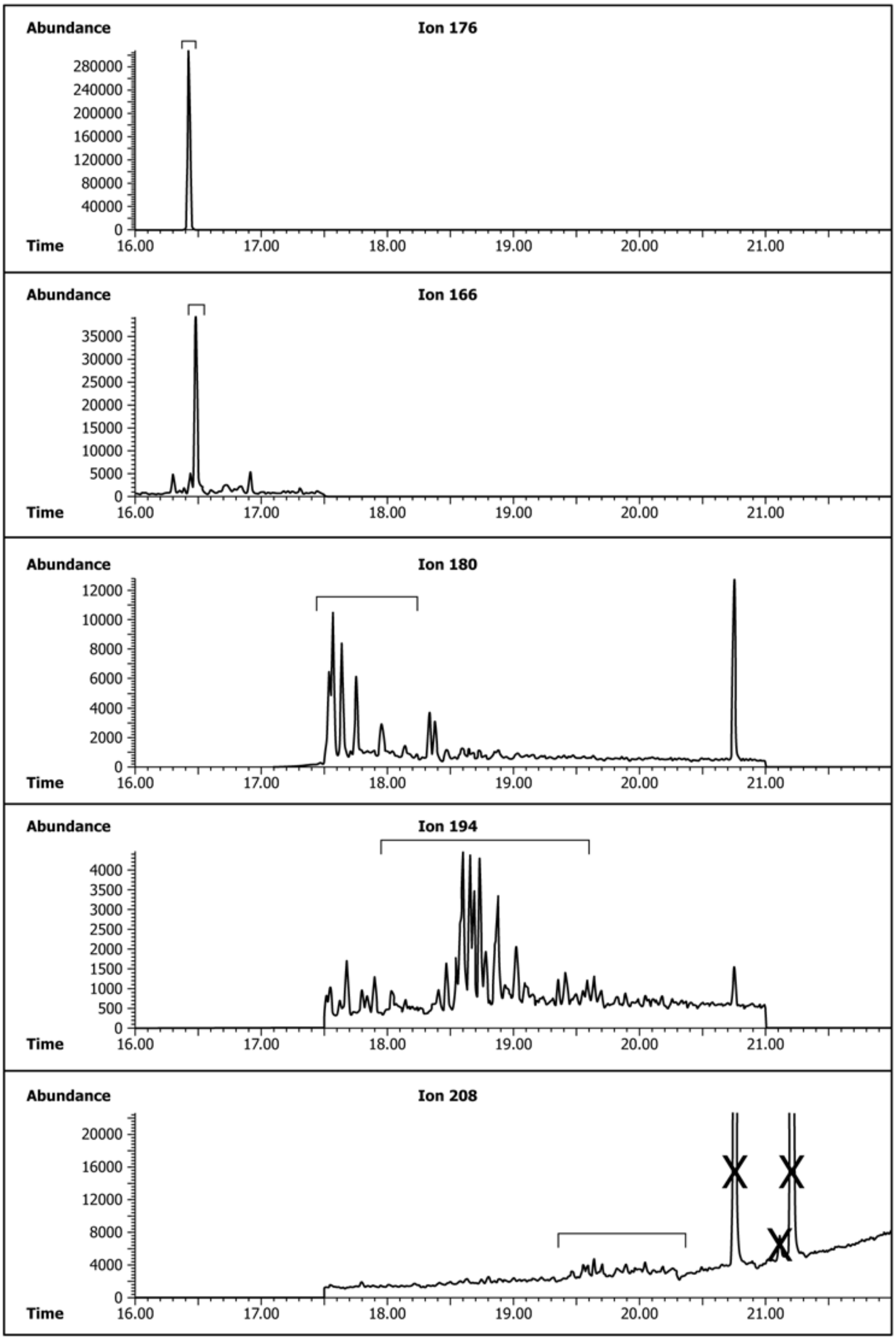

FIG. X1.4 Fluorenes

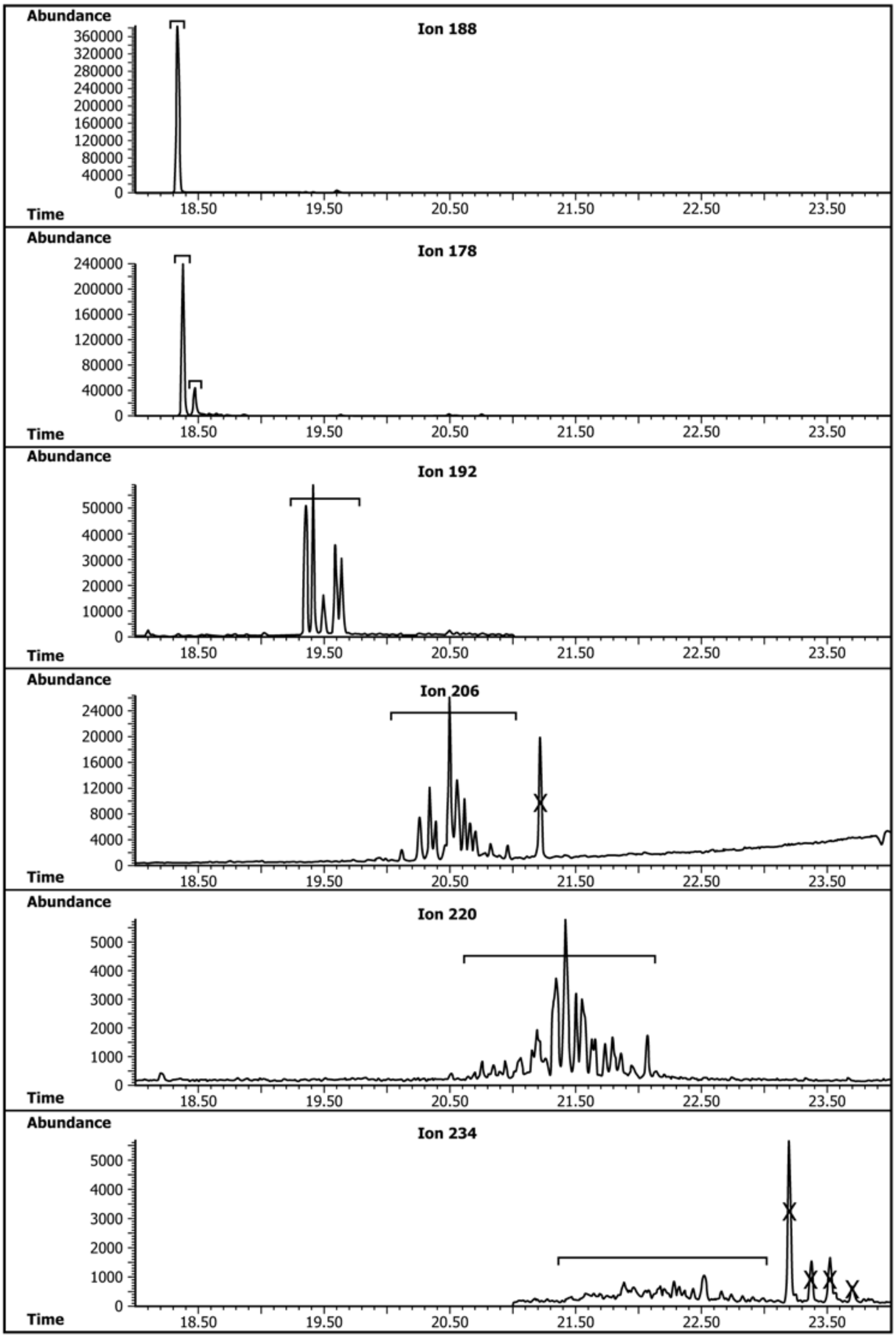

FIG. X1.5 Phenanthrenes/Anthracenes

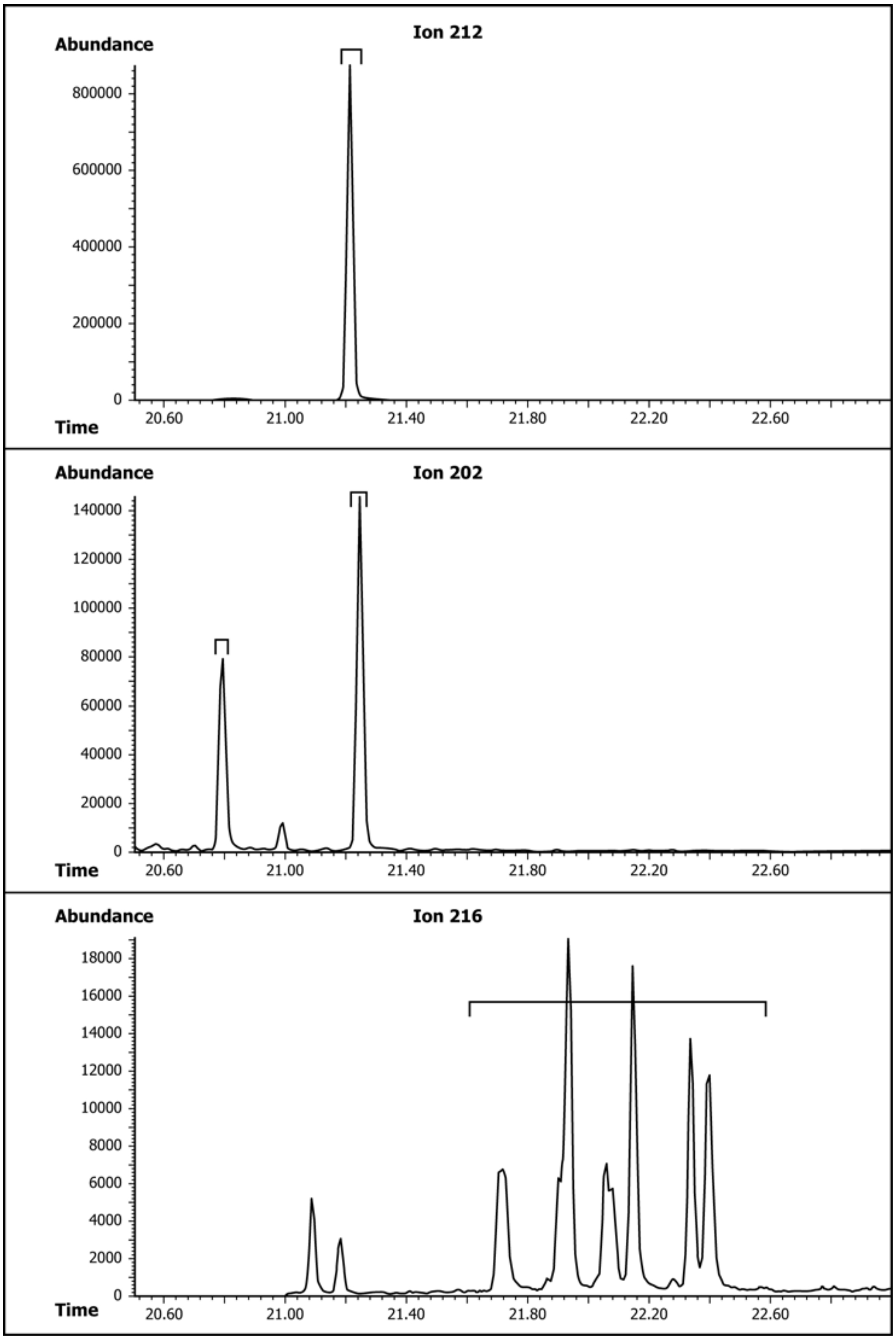

FIG. X1.6 Fluoranthenes/Pyrenes

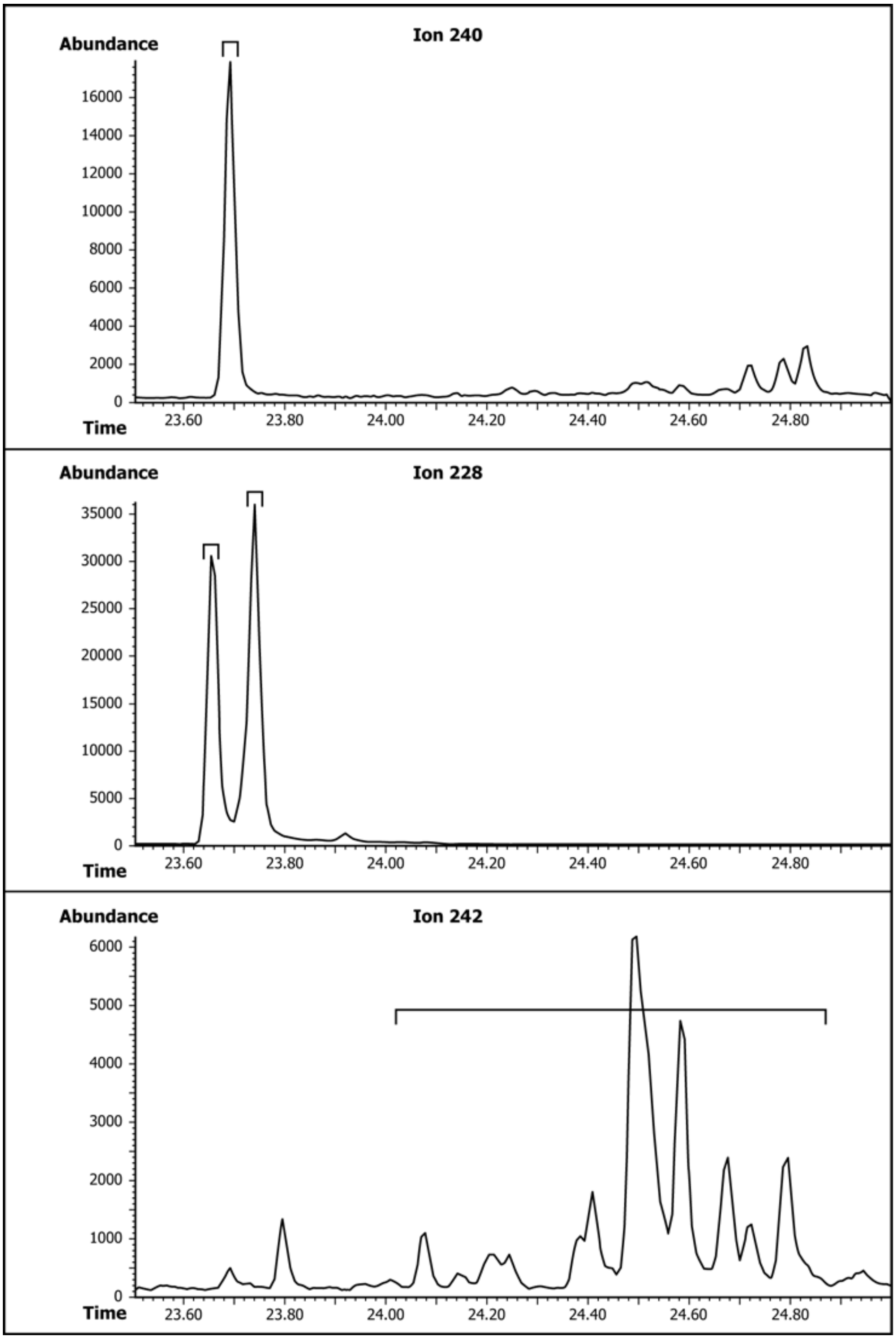

FIG. X1.7 Benz[a]anthracenes/Chrysenes

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