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*

[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

[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.