Designation: D 4657 – 92 (Reapproved 1998)

An American National Standard

Standard Test Method for Polynuclear Aromatic Hydrocarbons in Water[1]

This standard is issued under the fixed designation D 4657; 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.

1. Scope

1.1 This test method covers the determination of certain polynuclear aromatic hydrocarbons (PAHs) in water and wastewater. The following compounds may be determined by this test method: acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(ghi)perylene, benzo(k)fluoranthene, chrysene, dibenzo(ah)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenathrene, and pyrene. Additional PAHs may also be determined; however, the analyst should demonstrate that the test method is in fact applicable to the specific PAH(s) of interest before applying it to sample analysis. This test method has high sensitivity for the compounds of interest. It is limited to use by analysts familiar with high-performance liquid chromatography (HPLC) or working under close supervision of such persons.

1.2 This test method is applicable to the determination of the compounds in 1.1 in water and wastewater. This test method has been successfully used with distilled water, tap water, surface water, and the following wastewaters: effluent from an oil refinery, blast furnace, and combined coke oven and blast furnace. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices. It presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, component identities should be verified by using two different types of reverse phase HPLC columns, both ultraviolet and fluorescence detection, or gas chromatography/mass spectrometry-spectroscopy screening procedures, or both.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazards statements are given in Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[2]

D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[2]

D 1193 Specification for Reagent Water[2]

D 1253 Test Method for Residual Chlorine in Water[2]

D 3370 Practices for Sampling Water from Closed Conduits[2]

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[2]

D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[2]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

4. Summary of Test Method

4.1 This test method consists of the extraction of 1 L of water with methylene chloride. This extract is then reduced in volume using Kuderna-Danish (K-D) evaporation followed by column chromatography on silica gel. The appropriate fraction from the silica gel chromatography containing the PAHs is again reduced in volume using K-D evaporation and is solvent exchanged with acetonitrile to an exact volume of 1 mL. This concentrated extract is then analyzed for PAH using high-performance liquid chromatography (HPLC).

4.2 The HPLC analysis utilizes reverse phase chromatography using a combination of isocratic and gradient elution. Acetonitrile and water are used as the mobile phase on a Perkin Elmer PAH/10 reverse phase column.[3] Other C-18 reverse phase columns may be used, provided that they yield adequate resolution of the PAHs of interest. Fluorescence or ultraviolet detection depending on the needs is used to monitor the PAH of interest; quantitation is by peak area integration or peak height measurement. Results are reported in micrograms per litre.

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[1] This test method is under the jurisdiction of ASTM Committee D-19 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] *Annual Book of ASTM Standards*, Vol 11.01.

[3] Perkin-Elmer PAH/10 reverse phase column is available from Perkin-Elmer Corporation, 761 Main Ave., Norwalk, CT 06859.

4.3 If interferences are encountered, this test method provides a selected general purpose cleanup procedure to aid the analyst in their elimination.

5. Significance and Use

5.1 Prominent among the group of compounds found in various water supplies and considered to be potential health risks are the polynuclear aromatic hydrocarbons (PAHs). These compounds have been found to occur naturally in water as a result of pyrolytic processes in the environment. Other sources include automobile exhaust, runoff from highways, and municipal and industrial discharges. Several of these compounds have been determined to be at least weak carcinogens even at very low concentrations. For this reason, a method for the detection and quantitation of these compounds in the water environment is necessary.

6. Interferences

6.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts or elevated baselines causing misinterpretation of chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Specific selection of reagents and the purification of solvents by distillation in all glass systems is required. Glassware should be cleaned by washing with soap and water, rinsing with tap water, reagent water (8.2), redistilled acetone, and finally with pesticide quality hexane. If the type and size of glassware permits, it is heated in a muffle furnace to approximately 400°C for 15 to 30 min. Volumetric ware should not be heated in a muffle furnace. Plastics, except TFE-fluorocarbon, can cause interference or absorption, or both, of PAHs and should be avoided.

6.2 The organic constituents in industrial effluents are often present at high concentrations and can pose great difficulty in obtaining accurate and precise measurement of PAH. The use of the fluorescence detector and the column clean-up procedure may eliminate many of these interferences.

6.3 Other PAH compounds may represent interference in certain cases. Since the PAHs listed in 1.1 represent the more commonly encountered nonalkylated PAHs, interference from isomeric, nonalkylated PAHs is minimal. Benzo(e)pyrene elutes earlier than its isomers, benzo(a)pyrene, benzo(b)fluoranthene, and benzo(k)fluoranthene and does not interfere with any compounds listed in 1.1. Alkylated PAHs will elute later than the parent, nonalkylated compound. Consequently, multialkylated naphthalenes (2-ring system) may coelute with fluoranthene (3-ring system). However, the use of both ultraviolet and fluorescence detection allows recognition of such interferences since widely different response ratios will be encountered for the two groups of compounds.

6.4 All reference standards must be demonstrated to be free of extraneous peaks under the conditions of analysis.

7. Apparatus

7.1 *HPLC Gradient System*, capable of constant flow.

7.2 *Reverse Phase Column*, 5- or 10-µm, which yields resolution equivalent or better than Perkin Elmer Reverse Phase Column PAH/10, 2.6 by 250 mm, used to obtain the precision and bias data in the test method. Equivalency is demonstrated in resolution of the analytes, and the analyst meeting or exceeding the single operator precision for the analytes of concern at known concentrations in reagent water by following procedures outlined in Section 16.

7.3 *Fluorescence Detector*, capable of excitation at 280 nm and emission at 389 nm (using a cutoff filter). Other types of fluorescence detectors (for example, grating emission monochromaters) may be used. However, detection limits may vary considerably and will need to be established for the PAHs of interest in the particular application.

7.4 *Ultraviolet detector*, 254-nm with a noise specification of $2 \times 10{-}4$ AU or better.

7.5 *Chromatographic Data System*, having sufficient parameters to accurately follow a sloping baseline, or a 10-mV full-scale stripchart recorder.

7.6 *Chromatographic Column Glass*, 1 by 25 cm with TFE-fluorocarbon stopcock.

7.7 *Kuderna-Danish Evaporative Concentrator*, with the following components:

7.7.1 *Synder Column*, three-ball.

7.7.2 *Micro Snyder Column*, two-ball.

7.7.3 *Evaporative Flask*, 500-mL.

7.7.4 *Receiver Ampule*, 10-mL.

7.7.5 *Ampule Caps*.

7.8 *Water Bath*, heated with concentric ring cover and capable of temperature control (+ 2°C).

7.9 *Graduated Cylinder*, 1000-mL.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type II.

8.3 *Acetonitrile*—Spectral quality.

8.4 *Cyclohexane*—Pesticide residue quality, or equivalent.

8.5 *Methylene Chloride*—Pesticide residue quality, or equivalent.

8.6 *Pentane*—Pesticide residue quality, or equivalent.

8.7 *Silica Gel*—100/120 mesh, Davidson Grade 923. Activate in an oven at 130°C overnight in an uncapped widemouth jar. Maintain at 130°C when not in use.

8.8 *Sodium Hydroxide*.

8.9 *Sodium Sulfate*—Anhydrous.

8.10 *Sodium Thiosulfate*.

8.11 *Sulfuric Acid*, (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

[4] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Analar Standards for Laboratory Chemicals," BDH Ltd., Poole, Dorset, U.K., and the "United States Pharmacopeia."

8.12 *PAH Standards*, analytical reference grade or highest purity available.

9. Hazards

9.1 **Precaution**—Due to the potential for detrimental health effects from handling these compounds, preparation of standards and samples must be done, using extreme care, in an appropriate hood or glove box.

9.2 **Caution**—The analyst should be aware of the fact that sunlight and certain types of fluorescent lights can cause decomposition of PAHs, so appropriate care should be taken during sample storage and preparation.

10. Sampling

10.1 Collect the sample in accordance with Specification D 1192 or Practice D 3370, as applicable.

10.2 Grab samples must be collected in glass containers with TFE-fluorocarbon lined caps. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program.

NOTE 1—Automatic sampling equipment must be free of plastic tubing such as PVC, and other potential sources of contamination, as determined by collecting a reagent water blank with each group of samples.

10.3 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 48 h will elapse before delivery to the laboratory. If the samples will not be extracted within 48 h of collection, adjust the sample to a pH range of 6.0 to 8.0 with sodium hydroxide or sulfuric acid and add 35 mg of sodium thiosulfate per part per million of free chlorine per litre. Free chlorine can be determined using Test Methods D 1253. If samples cannot be returned to the laboratory within 48 h, field measurement of free chlorine will be necessary. Test kits are commercially available for this purpose.[5]

10.4 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

11. Calibration and Standardization

11.1 Calibrate the instrument for each PAH species at four different concentration levels (in acetone or acetonitrile) using the appropriate detector settings. These concentration levels should span the detector range of interest for a particular application and should represent at least one order of magnitude from the lowest to the highest concentration injected.

11.2 Check calibration daily to establish the validity of the above curves by injection of a standard in the middle portion of the calibration range selected in 11.1.

11.3 The elution order and retention times of the various PAHs are provided in Fig. 1 and Table 1, as a guide.

12. Procedure

12.1 *Sample Extraction*:

12.1.1 Mark the water meniscus on the side of the sample bottle. Pour the entire sample into a 2-L separatory funnel. Check the pH with wide-range paper and adjust to within the range of 6 to 8 with sodium hydroxide or sulfuric acid. With each set of samples, 1 L aliquot of reagent water (8.2) is placed in a sampling bottle and processed as described for samples, to serve as a method blank.

12.1.2 Add 60 mL methylene chloride to the sample bottle and shake 30 s to rinse the walls. Retain the bottle for determination of sample volume in 12.1.7. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for 2 min with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250-mL Ehrlenmeyer flask.

12.1.3 Add a second 60-mL volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Ehrlenmeyer flask.

12.1.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3 to 4 in. of anhydrous sodium sulfate, and collect it in a 500-mL Kuderna-Danish (K-D) flask equipped with a 10-mL concentrator tube. Rinse the Ehrlenmeyer flask and column with 20 to 30 mL methylene chloride to complete the quantitative transfer.

12.1.5 Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a steaming hot water bath so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in steam. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, or when distillation ceases, remove the K-D apparatus and allow it to drain for at least 10 min while cooling. If distillation ceases prior to reaching an apparent 1 mL volume, estimate the volume remaining, after cooling, for calculation of the portion of sample to be used in 12.1.6. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately.

12.1.6 Certain highly contaminated samples may not allow concentration of the extract to 1 mL as indicated in 12.1.5. In these cases, add enough methylene chloride to redissolve the residue. Mix thoroughly and use a 5-mL aliquot of the diluted extract for further processing in 12.2. If less than 5 mL is available, record the volume used for use in 13.1. Record the volume of diluted extract (as *D*) in millilitres for use in 13.2.

[5] Portable test kits for free chlorine, available from Hach Chemical Company, Loveland, CO, have been found suitable for this purpose.

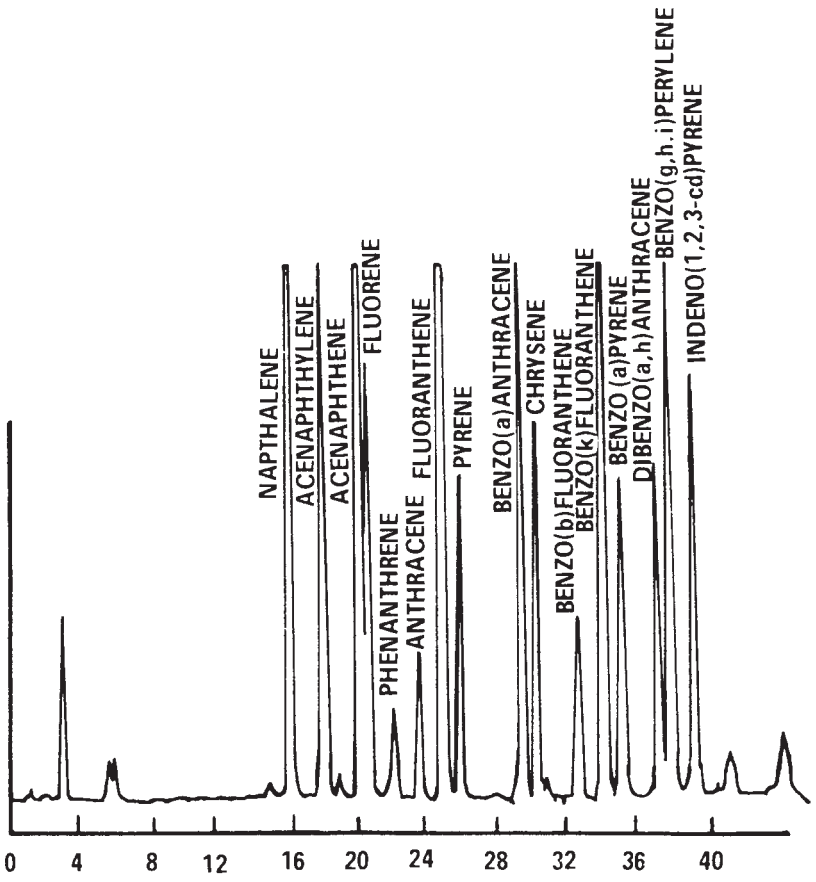

FIG. 1 Fluorescence of PNAs on Reverse Phase Column PE PAH/10 2.6 by 250 mm

TABLE 1 High Performance Liquid Chromatography of PAHs [A]

Compound	Retention Time, min
Naphthalene	16.17
Acenaphthylene	18.10
Acenaphthene	20.14
Fluorene	20.89
Phenanthrene	22.32
Anthracene	23.78
Fluoranthene	25.00
Pyrene	25.94
Benzo(a)anthracene	29.26
Chrysene	30.14
Benzo(b)fluoranthene	32.44
Benzo(k)fluoranthene	33.91
Benzo(a)pyrene	34.95
Dibenzo(a,h)anthracene	37.06
Benzo(ghi)perylene	37.82
Indeno(1,2,3-cd)pyrene	39.21

[A] HPLC conditions are as follows: Reverse phase Perkin-Elmer PAH/10 2.6 by 250 mm column; isocratic elution for 5 min using 40 % acetonitrile/60 % water, then linear gradient elution to 100 % acetonitrile over 25 min; flow rate is 0.5 mL/min.

12.1.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

12.2 *Sample Clean-Up*:

12.2.1 Before the silica gel clean-up technique can be utilized, the extract solvent must be exchanged to cyclohexane. Place the sample extract (in methylene chloride) and a boiling chip in a clean K-D concentrator tube. Add 4 mL of cyclohexane and attach a micro-Snyder column. Prewet the micro-Snyder column by adding 0.5 mL of methylene chloride to the top. Place the micro K-D apparatus on a boiling (100°C) water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of the liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain for at least 10 min while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum of cyclohexane. Adjust the extract volume to about 2 mL.

12.2.2 Place activated silica gel, heated overnight at 130°C, in 50 mL of methylene chloride and pour into a 10-mm inside diameter chromatography column. Gently tap the column to settle the silica gel and elute the methylene chloride. Add a 1-cm layer of anhydrous sodium sulfate to the top of the silica gel bed.

12.2.3 Preelute the column with 40 mL of pentane. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 2 mL of cyclohexane sample extract onto the column, using an additional 2 mL of cyclohexane to complete the transfer.

12.2.4 Just prior to the exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue elution of the column. Discard the pentane eluate.

12.2.5 Elute the column with 25 mL of 40 % methylene chloride/60 % pentane and collect the eluate in a 500-mL K-D flask equipped with a 10-mL concentrator tube. Elution of the column should be at a rate of about 2 mL/min.

12.2.6 Concentrate the collected fraction to less than 10 mL by K-D techniques as in 12.1.5 using pentane to rinse the walls of the glassware.

12.2.7 To the collected fraction, add 4 mL of acetonitrile and a new boiling chip, then attach a micro-Snyder column. Increase the temperature of the hot water bath to 95° to 100°C. Concentrate the solvent as above. After cooling, remove the micro-Snyder column and rinse its lower joint into the concentrator tube with about 0.2 mL of acetonitrile. Adjust the extract volume to 1.0 mL.

12.3 *Sample Analysis*:

12.3.1 Table 1 summarizes the recommended HPLC column, materials and operating conditions for the instrument. Other C-18 reversed phase columns or detector conditions are acceptable, provided that adequate resolution and sensitivity is achieved for the PAHs of interest. An example of the separation achieved by this column is shown in Fig. 1. Calibrate the system daily with a minimum of three injections of a calibration standard near the midpoint of the concentration range of interest, as specified in 11.2.

12.3.2 Inject 5 µL of the sample extract. Record the volume injected and the resulting peak size, in area or peak height units.

12.3.3 If the peak area or peak height exceeds the linear range of the system, dilute the extract and reanalyze.

12.3.4 The ultraviolet detector is recommended for the determination of naphthalene, acenaphthylene, acenaphthane, and fluorene, and the fluorescence detector is recommended for the remaining PAHs.

TABLE 2 Regression Equations for Precision and Bias by Compound and Water Type

Water Type	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene
Applicable concentration range	(10.00–375.00)	(10.00–425.00)	(10.00–260.00)	(10.00–463.00)
Number of observations	96	96	96	96
Distilled water				
Single—analyst precision	$S_R = 0.39X^A - 0.18$	$S_R = 0.36X + 0.29$	$S_R = 0.39X + 0.78$	$S_R = 0.44X - 1.12$
Overall precision	$S = 0.41X + 0.74$	$S = 0.12X + 0.32$	$S = 0.53X + 1.32$	$S = 0.63X - 0.65$
Accuracy	$X = 0.57C^B - 0.70$	$X = 0.69C - 1.89$	$X = 0.52C + 0.54$	$X = 0.56C - 0.52$
Number of data points	80	85	72	88
Tap water				
Single—analyst precision	$S_R = 0.36X + 0.24$	$S_R = 0.38X - 0.01$	$S_R = 0.29X + 0.27$	$S_R = 0.25X + 1.16$
Overall precision	$S = 0.39X + 0.73$	$S = 0.44X - 0.03$	$S = 0.47X + 0.45$	$S = 0.50X - 0.16$
Accuracy	$X = 0.60C - 0.62$	$X = 0.71C - 2.58$	$X = 0.51C - 1.55$	$X = 0.59C - 1.30$
Number of data points	76	87	69	76
Surface water				
Single—analyst precision	$S_R = 0.24X + 1.94$	$S_R = 0.27X + 0.30$	$S_R = 0.17X + 1.48$	$S_R = 0.40X - 0.93$
Overall precision	$S = 0.41X + 1.07$	$S = 0.30X + 0.08$	$S = 0.48X + 0.23$	$S = 0.52X - 0.74$
Accuracy	$X = 0.50C - 0.82$	$X = 0.74C - 2.07$	$X = 0.53C - 0.59$	$X = 0.57C - 0.25$
Number of data points	80	74	66	75
Wastewater (*C*-94)				
Single—analyst precision	$S_R = 0.19X + 1.34$	$S_R = 0.19X + 1.02$	$S_R = 0.35X - 0.79$	$S_R = 0.75X + 1.60$
Overall precision	$S = 0.36X + 0.26$	$S = 0.32X - 0.01$	$S = 0.50X - 0.21$	$S = 0.52X - 1.26$
Accuracy	$X = 0.62C + 0.72$	$X = 0.83C - 1.16$	$X = 0.59C - 0.46$	$X = 0.60C - 0.03$
Number of data points	86	78	73	74
Wastewater (*C*-95)				
Single—analyst precision	$S_R = 0.23X - 0.48$	$S_R = 0.32X - 0.81$	$S_R = 0.24X + 0.33$	$S_R = 0.21X + 2.56$
Overall precision	$S = 0.32X - 1.09$	$S = 0.36X - 0.31$	$S = 0.47X + 0.08$	$S = 0.47X - 0.44$
Accuracy	$X = 0.58C + 1.04$	$X = 0.75C - 0.80$	$X = 0.57C + 0.30$	$X = 0.53C + 0.73$
Number of data points	69	82	69	63
Wastewater (*C*-96)				
Single analyst precision	$S_R = 0.31X + 0.26$	$S_R = 0.17X + 0.57$	$S_R = 0.28X + 0.34$	$S_R = 0.35X + 0.10$
Overall precision	$S = 0.41X - 0.15$	$S = 0.23X + 1.09$	$S = 0.43X - 0.54$	$S = 0.49X - 0.39$
Accuracy	$X = 0.65C - 0.76$	$X = 0.83C - 1.89$	$X = 0.62C + 0.12$	$X = 0.54C + 0.36$
Number of data points	86	80	77	68
Water Type	Phenanthrene	Anthracene	Fluoranthene	Pyrene
Applicable concentration range	(5.00–280.00)	(10.00–400.00)	(0.30–15.00)	(2.00–90.00)
Number of observations	96	96	96	96
Distilled water				
Single—analyst precision	$S_R = 0.28X^A + 0.05$	$S_R = 0.23X + 1.16$	$S_R = 0.22X + 0.06$	$S_R = 0.25X + 0.14$
Overall precision	$S = 0.47X - 0.25$	$S = 0.41X + 0.45$	$S = 0.32X + 0.03$	$S = 0.42X - 0.00$
Accuracy	$X = 0.72C^B - 0.95$	$X = 0.63C - 1.26$	$X = 0.68C + 0.07$	$X = 0.89C - 0.12$
Number of data points	94	78	68	90
Tap water				
Single—analyst precision	$S_R = 0.26X + 0.10$	$S_R = 0.22X + 0.61$	$S_R = 0.23X + 0.01$	$S_R = 0.25X + .02$

TABLE 2 *Continued*

Water Type	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene
Overall precision	$S = 0.35X - 0.16$	$S = 0.41X + 0.10$	$S = 0.32X + .01$	$S = 0.39X + .09$
Accuracy	$X = 0.71C - 0.71$	$X = 0.63C - 2.05$	$X = 0.71C - .03$	$X = 0.68C + .09$
Number of data points	81	77	65	80
Surface water				
Single—analyst precision	$S_R = 0.23X - 0.34$	$S_R = 0.19X + 0.22$	$S_R = 0.27X - .04$	$S_R = 0.22X - 0.10$
Overall precision	$S = 0.37X - 0.62$	$S = 0.34X - 0.69$	$S = 0.44X - .01$	$S = 0.30X - 0.12$
Accuracy	$X = 0.70C - 0.26$	$X = 0.64C - 0.45$	$X = 0.59C + .05$	$X = 0.74C - 0.08$
Number of data points	83	73	67	78
Wastewater (*C*-94)				
Single—analyst precision	$S_R = 0.11X + 0.47$	$S_R = 0.19X + 0.99$	$S_R = 0.12X + .03$	$S_R = 0.17X + 0.15$
Overall precision	$S = 0.26X - 0.22$	$S = 0.39X - 0.41$	$S = 0.35X - .01$	$S = 0.28X - 0.02$
Accuracy	$X = 0.79C - 0.61$	$X = 0.69C - 0.26$	$X = 0.75C - 0.0$	$X = 0.71C + 0.02$
Number of data points	80	78	75	74
Wastewater (*C*-95)				
Single—analyst precision	$S_R = 0.15X - 0.03$	$S_R = 0.19X + 0.10$	$S_R = 0.17X - 0.01$	$S_R = 0.27X - 0.04$
Overall precision	$S = 0.28X - 0.03$	$S = 0.33X - 0.31$	$S = 0.29X + 0.02$	$S = 0.34X - 0.19$
Accuracy	$X = 0.73C - 0.48$	$X = 0.64C - 0.34$	$X = 0.70C + 0.02$	$X = 0.56C + 0.25$
Number of data points	68	77	70	76
Wastewater (*C*-96)				
Single analyst precision	$S_R = 0.35X - 0.50$	$S_R = 0.24X - 0.29$	$S_R = 0.40X - 0.06$	$S_R = 0.20X - 0.00$
Overall precision	$S = 0.38X - 0.28$	$S = 0.35X - 0.91$	$S = 0.38X + 0.03$	$S = 0.25X + 0.14$
Accuracy	$X = 0.70C - 0.47$	$X = 0.66C + 0.08$	$X = 0.75C + 0.01$	$X = 0.77C + 0.01$
Number of data points	88	82	79	77

Water Type	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene
Applicable concentration range	(0.50–16.00)	(2.00–60.00)	(0.20–11.00)	(0.12–6.00)
Number of observations	96	96	96	96
Distilled water				
Single—analyst precision	$S_R = 0.28X^A + 0.04$	$S_R = 0.32X - 0.18$	$S_R = 0.21X + 0.01$	$S_R = 0.44X - 0.01$
Overall precision	$S = 0.34X + 0.02$	$S = 0.56X - 0.22$	$S = 0.38X - 0.00$	$S - 0.69X + 0.01$
Accuracy	$X = 0.73C^B + 0.05$	$X = 0.77C - 0.18$	$X = 0.78C + 0.01$	$X = 0.59C + 0.00$
Number of data points	68	73	73	70
Tap water				
Single precision	$S_R = 0.23X + 0.13$	$S_R = 0.40X - 0.37$	$S_R = 0.24X - 0.00$	$S_R = 0.48X + 0.06$
Overall precision	$S = 0.37X + 0.05$	$S = 0.55X - 0.10$	$S = 0.32X - 0.01$	$S = 0.91X - 0.01$
Accuracy	$X = 0.77C + 0.05$	$X = 0.82C + 0.09$	$X = 0.83C + 0.00$	$X = 0.98C - 0.03$
Number of data points	78	75	75	78
Surface water				
Single—analyst precision	$S_R = 0.18X - 0.01$	$S_R = 0.39X - 0.51$	$S_R = 0.26X - 0.01$	$S_R = 0.19X + 0.16$
Overall precision	$S = 0.34X - 0.05$	$S = 0.50X - 0.20$	$S = 0.48X - 0.03$	$S = 0.76X + 0.01$
Accuracy	$X = 0.76C - 0.02$	$X = 0.77C + 0.39$	$X = 0.73C + 0.01$	$X = 1.02C + 0.04$
Number of data points	65	77	85	74
Wastewater (*C*-94)				
Single—analyst precision	$S_R = 0.24X + 0.03$	$S_R = 0.29X - 0.06$	$S_R = 0.21X - 0.00$	$S_R = 0.18X - 0.01$
Overall precision	$S = 0.32X + 0.06$	$S = 0.44X - 0.09$	$S = 0.39X - 0.02$	$S = 0.47X + 0.01$
Accuracy	$X = 0.73C + 0.12$	$X = 0.97C - 0.28$	$X = 0.80C - 0.01$	$X = 0.61C + 0.03$
Number of data points	77	75	85	63
Wastewater (*C*-95)				
Single—analyst precision	$S_R = 0.28X - 0.04$	$S_R = 0.25X + 0.42$	$S_R = 0.28X - 0.01$	$S_R = 0.46X - 0.07$
Overall precision	$S = 0.43X + 0.04$	$S = 0.48X + 0.10$	$S = 0.42X - 0.02$	$S = 0.68X - 0.01$
Accuracy	$X = 0.69C + 0.03$	$X = 1.22C - 0.56$	$X = 0.90C - 0.00$	$X = 1.09C + 0.03$
Number of data points	79	80	77	66
Wastewater (*C*-96)				
Single—analyst precision	$S_R = 0.18X + 0.00$	$S_R = 0.24X + 0.02$	$S_R = 0.26X - 0.01$	$S_R = 0.22X - 0.00$
Overall precision	$S = 0.32X + 0.04$	$S = 0.45X + 0.14$	$S = 0.37X - 0.01$	$S = 0.69X - 0.03$
Accuracy	$X = 0.76C + 0.00$	$X = 1.01C - 0.07$	$X = 0.90C + 0.00$	$X = 0.99C - 0.05$
Number of data points	79	85	81	68

Water Type	Benzo(a)pyrene	Dibenzo(a,h)anthracene	Benzo(g,h)perylene	Indeno(1,2,3-cd)pyrene
Applicable concentration range	(0.20–15.00)	(0.50–24.00)	(1.00–50.00)	(0.75–22.00)
Number of observations	96	96	96	96
Distilled water				
Single—analyst precision	$S_R = 0.38X^A + 0.01$	$S_R = 0.24X + 2.02$	$S_R = 0.25X + 0.04$	$S_R = 0.29X + 0.02$
Overall precision	$S = 0.53X + 0.01$	$S = 0.45X + 0.03$	$S = 0.58X + 0.10$	$S = 0.42X + 0.01$
Accuracy	$X = 0.56C^B + 0.01$	$X = 0.41C + 0.11$	$X = 0.44C + 0.30$	$X = 0.54C + 0.00$
Number of data points	80	77	82	73
Tap water				
Single—analyst precision	$S_R = 0.29X - 0.01$	$S_R = 0.42X - 0.01$	$S_R = 0.24X - 0.06$	$S_R = 0.33X - 0.04$
Overall precision	$S = 0.53X - 0.00$	$S = 0.44X + 0.04$	$S = 0.29X + 0.00$	$S = 0.38X + 0.02$
Accuracy	$X = 0.54C - 0.02$	$X = 0.68C + 0.09$	$X = 0.71C - 0.07$	$X = 0.70C - 0.05$
Number of data points	84	74	62	67
Surface water				
Single—analyst precision	$S_R = 0.24X - 0.01$	$S_R = 0.34X + 0.04$	$S_R = 0.40X - 0.16$	$S_R = 0.27X - 0.04$
Overall precision	$S = 0.47X - 0.00$	$S = 0.49X - 0.02$	$S = 0.60X - 0.12$	$S = 0.42X - 0.06$

TABLE 2 *Continued*

Water Type	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene
Accuracy	$X = 0.65C + 0.01$	$X = 0.71C - 0.03$	$X = 0.67C + 0.05$	$X = 0.60C + 0.02$
Number of data points	93	80	90	79
Wastewater ($C = 94$)				
Single—analyst precision	$S_R = 0.30X - 0.01$	$S_R = 0.24X + 0.00$	$S_R = 0.25X - 0.04$	$S_R = 0.25X - 0.06$
Overall precision	$S = 0.44X - 0.01$	$S = 0.35X + 0.00$	$S = 0.36X - 0.08$	$S = 0.42X - 0.04$
Accuracy	$X = 0.67C + 0.02$	$X = 0.71C - 0.05$	$X = 0.72C - 0.05$	$X = 0.67C + 0.01$
Number of data points	87	76	68	78
Wastewater ($C = 95$)				
Single—analyst precision	$S_R = 0.31X + 0.01$	$S_R = 0.25X + 0.12$	$S_R = 0.27X + .01$	$S_R = 0.39X - 0.01$
Overall precision	$S = 0.40X - 0.00$	$S = 0.39X - 0.00$	$S = 0.48X - 0.17$	$S = 0.50X + 0.04$
Accuracy	$X = 0.72C - 0.01$	$X = 0.77C + 0.02$	$X = 0.71C + 0.14$	$X = 0.95C - 0.05$
Number of data points	83	72	71	66
Wastewater ($C = 96$)				
Single—analyst precision	$S_R = 0.20X - 0.00$	$S_R = 0.36X - 0.07$	$S_R = 0.34X - 0.17$	$S_R = 0.37X - 0.07$
Overall precision	$S = 0.41X - 0.02$	$S = 0.45X + 0.08$	$S = 0.42X - 0.04$	$S = 0.44X - 0.05$
Accuracy	$X = 0.70C + 0.01$	$X = 0.71C + 0.16$	$X = 0.69C + 0.20$	$X = 0.83C - 0.11$
Number of data points	84	86	77	70

[A] X = Mean recovery, µg/L.
[B] C = True value for the concentration, µg/L.

13. Calculation

13.1 Determine the concentration of individual compounds according to Eq 1.

$$\text{Concentration, µg/L} = (A)\,(B)\,(V_t)/(V_i)\,(V_s) \quad (1)$$

where:

A = calibration factor for chromatographic system, in nanograms material per area (or peak height) unit,
B = peak size in injection of sample extract, in area units,
V_i = volume of extract injected, µL,
V_t = volume of total extract, µL, and
V_s = volume of water extracted, mL.

13.2 If the sample extract required dilution in 12.1.6, use Eq 2:

$$\text{Concentration, µg/L} = (A)\,(B)\,(V_t)/(V_i)\,(V_s) \times \left(\frac{D}{5\ \text{mL}}\right) \quad (2)$$

where:

D = volume of diluted extract, mL.

14. Report

14.1 Report results in micrograms per litre. When duplicate and spiked samples are analyzed, all data obtained should be reported.

15. Precision and Bias [6]

15.1 The equations used for the precision and bias statement are given in Table 2. The precision and bias of this test method by compound and by water types is given in Table 3. Sixteen laboratories participated in this study. Three additional laboratories which participated in the study did not follow the approved analytical procedure and their results were not used in the statistical evaluation of the data.

15.1.1 Based on the precision and bias data, the analyst should establish a criterion of detection for this test method based on Practice D 4210.

15.2 The QA/QC portion of this test method has not been completely established at this time. It is the intent of the ASTM Subcommittee responsible for this test method, that procedures be incorporated into this test method that require a minimum level of QC. These procedures will require at a minimum, a method startup check and ongoing performance checks. The analysts performing the test method will be required to measure their performance against the performance level achieved by the laboratories that participated in the ASTM round robin study done on the test method. These formal QC procedures will be incorporated at such time as they have been officially accepted by the Society.

16. Quality Assurance/Quality Control (QA/QC)

16.1 Before this test method is applied to the analysis of samples of unknown PAH concentrations, the analyst must establish quality control by the procedures recommended in Practice D 4210 and Guide 3856.

16.2 A duplicate sample and known standard must be analyzed each day that an analysis is performed. The duplicate and standard shall meet the limits as established by the control chart before a determination is considered satisfactory.

16.3 A blank and a spiked sample shall be analyzed each day that an analysis is performed. Spiking shall be in accordance with that outlined in the Accuracy Check section of Guide D 3856. The blank shall be low enough that it will not unduly influence the data.

16.4 One sample must be analyzed in duplicate with each group of 10 or less samples. The results must meet the criteria established in Table 2 of this test method before the data for that batch or set of 10 samples is acceptable.

16.5 Other QA/QC portions of this test method have not been completely established at this time. Analysts performing this test method will be required to measure their performance against the performance level achieved by the interlaboratory studies of this test method.

16.6 It is the intention of Subcommittee D19.06 to incorporate formal QA/QC procedures into this test method at such time as they have passed the consensus process and have been officially accepted by the Society.

[6] Precision and bias data are contained in EPA Method Study 20, Method 610 PNAs (Polynuclear Aromatic Hydrocarbons).

TABLE 3 Precision and Bias for Polynuclear Aromatic Hydrocarbons in Water

	± % Bias	Precision, % Relative Standard Deviation			± % Bias	Precision, % Relative Standard Deviation	
		S_r [A]	S_o [B]			S_r [A]	S_o [B]
Napthalene				Benzo(a)anthracene			
Water 1 [C]	−45.72	44	38	Water 1	−23.49	38	36
Water 2 [D]	−42.58	42	37	Water 2	−20.02	47	48
Water 3 [E]	−42.57	45	31	Water 3	−25.55	23	16
Water 4 [F]	−35.23	37	24	Water 4	−18.67	43	29
Water 5 [G]	−38.28	28	21	Water 5	−28.54	34	19
Water 6 [H]	−37.99	40	32	Water 6	−23.87	41	18
Acenaphthylene				Chrysene			
Water 1	−37.26	42	36	Water 1	−25.52	48	26
Water 2	−36.88	44	38	Water 2	−19.61	52	28
Water 3	−33.08	30	27	Water 3	−16.87	44	24
Water 4	−20.66	32	20	Water 4	−13.82	42	27
Water 5	−27.11	36	31	Water 5	−13.02	50	35
Water 6	−22.76	23	17	Water 6	−0.2	49	25
Acenaphthene				Benzo(b)fluoranthene			
Water 1	−45.98	63	45	Water 1	−20.10	38	30
Water 2	−54.74	51	31	Water 2	−16.16	28	24
Water 3	−48.91	50	29	Water 3	−25.26	61	22
Water 4	−42.85	49	29	Water 4	−21.10	30	21
Water 5	−42.44	48	26	Water 5	−9.65	35	24
Water 6	−38.05	40	30	Water 6	−10.07	33	22
Fluorene				Benzo(a)pyrene			
Water 1	−45.75	29	54	Water 1	−42.79	47	32
Water 2	−44.28	48	42	Water 2	−49.00	53	33
Water 3	−43.71	42	28	Water 3	−33.05	47	19
Water 4	−39.73	37	44	Water 4	−30.35	39	25
Water 5	−45.35	42	52	Water 5	−28.88	40	25
Water 6	−44.72	44	36	Water 6	−28.14	32	20
Phenanthrene				Dibenzo(a,h)anthracene			
Water 1	−34.23	36	30	Water 1	−52.16	51	28
Water 2	−33.81	29	30	Water 2	−26.63	49	41
Water 3	−32.09	16	11	Water 3	−31.13	46	40
Water 4	−25.64	19	27	Water 4	−31.75	35	24
Water 5	−30.47	27	14	Water 5	−22.03	39	40
Water 6	−33.37	28	16	Water 6	−18.70	54	28
Anthracene				Benzo(g,h,i)perylene			
Water 1	−41.13	50	46	Water 1	−46.70	66	28
Water 2	−43.58	43	36	Water 2	−31.27	29	20
Water 3	−37.68	22	23	Water 3	−31.54	51	28
Water 4	−31.45	33	34	Water 4	−29.29	30	22
Water 5	−37.49	28	21	Water 5	−24.44	37	28
Water 6	−33.89	21	20	Water 6	−24.24	39	23
Fluoranthene				Ideno(1,2,3-cd)pyrene			
Water 1	−24.94	35	28	Water 1	−43.65	44	32
Water 2	−31.71	33	24	Water 2	−31.97	41	27
Water 3	−35.70	43	23	Water 3	−38.49	32	21
Water 4	−25.17	34	15	Water 4	−32.75	36	16
Water 5	−27.18	31	15	Water 5	−6.81	54	38
Water 6	−23.51	41	35	Water 6	−21.96	37	27
Pyrene				Benzo(k)fluoranthene			
Water 1 [C]	−33.39	42	30	Water 1	−39.88	70	43
Water 2 [D]	−30.91	42	26	Water 2	−9.95	91	50
Water 3 [E]	−26.79	26	19	Water 3	+ 12.54	76	34
Water 4 [F]	−28.23	25	22	Water 4	−30.99	48	17
Water 5 [G]	−30.29	28	26	Water 5	−21.54	68	44
Water 6 [H]	−22.89	29	20	Water 6	−14.71	68	22

[A] S_r = overall precision.
[B] S_o = single operator precision.
[C] *Water 1*—Distilled Water.
[D] *Water 2*—Tap Water.
[E] *Water 3*—Surface Water.
[F] *Water 4*—Wastewater, effluent from oil refinery.
[G] *Water 5*—Wastewater, blast furnace.
[H] *Water 6*—Wastewater, combined coke oven and blast furnace.

17. Keywords

17.1 acenaphthene; acenaphthylene; anthracene; benzo(a)anthracene; benzo(a)pyrene; benzo(b)fluoranthene; chrysene; dibenzo(ah)anthracene; fluoranthene; fluorene; high performance liquid chromatography (HPLC); indeno(1;2;3-cd)pyrene; naphthalene; phenanthrene; polynuclear aromatic

hydrocarbons (PAH); pyrene