Designation: D6209 – 13

Standard Test Method for Determination of Gaseous and Particulate Polycyclic Aromatic Hydrocarbons in Ambient Air (Collection on Sorbent-Backed Filters with Gas Chromatographic/Mass Spectrometric Analysis)[1]

This standard is issued under the fixed designation D6209; 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[2] specifies sampling, cleanup, and analysis procedures for the determination of polycyclic aromatic hydrocarbons (PAH) in ambient air.

1.2 This test method is designed to collect both gas-phase and particulate-phase PAH and to determine them collectively.

1.3 This test method is a high-volume sampling (100 to 250 L/min) method capable of detecting PAH at sub-nanograms per cubic metre (ng/m^3) concentrations with sampling volumes up to 350 m^3 of air.

1.4 This test method has been validated for sampling periods up to 24 h.

1.5 Precision and bias under normal conditions can be expected to be ±35 to 50 %.

1.6 This test method describes a sampling and analysis procedure for PAH that involves collection from air on a combination fine-particle filter and sorbent trap and subsequent analysis by gas chromatography/mass spectrometry (GC/MS).

1.7 The range of this test method is approximately 0.05 to 1000 ng/m^3 of air sampled.

1.8 The values stated in SI units shall be regarded as standard.

1.9 *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.* See also Section 8 for additional safety precautions.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

D3631 Test Methods for Measuring Surface Atmospheric Pressure

E1 Specification for ASTM Liquid-in-Glass Thermometers

E2251 Specification for Liquid-in-Glass ASTM Thermometers with Low-Hazard Precision Liquids

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1356.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *sampling efficiency (SE), n*—ability of the sampler to trap and retain PAH. The percent SE is the percentage of the analyte of interest collected and retained by the sampling medium when it is introduced into the air sampler and the sampler is operated under normal conditions for a period of time equal to or greater than that required for the intended use.

3.2.2 *dynamic retention efficiency, n*—ability of the sampling medium to retain a given PAH that has been added to the sorbent trap in a spiking solution when air is drawn through the sampler under normal conditions for a period of time equal to or greater than that required for the intended use.

4. Summary of Test Method

4.1 *Sampling:*

[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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[2] This test method is based on U. S. Environmental Protection Agency Compendum Method TO-13, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Report No. EPA/600-4-89/018, June 1988, available from the National Technical Information Service, 5285 Port Royal Rd., Springfield, VA 22161, Order No. PB90-11989/AS.

[3] 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.

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TABLE 1 Formulae and Physical Properties of Selective PAH

Compound (Common Name)	Formula	Molecular Weight	Melting Point, °C	Boiling Point,[A] °C	Vapor Pressure, kPa at 25°C
Naphthalene	$C_{10}H_8$	128.18	80.2	218	1.1×10^{-2}
Acenaphthylene	$C_{12}H_8$	152.20	92-93	265-280	3.9×10^{-3}
Acenaphthene	$C_{12}H_{10}$	154.20	90-96	278-279	2.1×10^{-2}
Fluorene	$C_{13}H_{10}$	166.23	116-118	293-295	8.7×10^{-5}
9-Fluorenone	$C_{13}H_8O$	180.21	84	341.5	ca.10^{-5}
Anthracene	$C_{14}H_{10}$	178.24	216-219	340	3.6×10^{-6}
Phenanthrene	$C_{14}H_{10}$	178.24	96-101	339-340	2.3×10^{-5}
Fluoranthene	$C_{16}H_{10}$	202.26	107-111	375-393	6.5×10^{-7}
Pyrene	$C_{16}H_{10}$	202.26	150-156	360-404	3.1×10^{-6}
Cyclopental[*cd*]pyrene	$C_{18}H_{10}$	226.28	ca. 275?	—	ca. 10^{-7}
Benz[*a*]anthracene	$C_{18}H_{12}$	228.30	157-167	435	1.5×10^{-8}
Chrysene	$C_{18}H_{12}$	228.30	252-256	441-448	5.7×10^{-10}
Retene	$C_{18}H_{18}$	234.34	101	390	ca. 10^{-6}
Benzo[*b*]fluoranthene	$C_{20}H_{12}$	252.32	167-168	481	6.7×10^{-8}
Benzo[*k*]fluoranthene	$C_{20}H_{12}$	252.32	198-217	480-481	2.1×10^{-8}
Perylene	$C_{20}H_{12}$	252.32	273-278	500-503	7.0×10^{-10}
Benzo[*a*]pyrene	$C_{20}H_{12}$	252.32	177-179	493-496	7.3×10^{-10}
Benzo[*e*]pyrene	$C_{20}H_{12}$	252.32	178-179	493	7.4×10^{-10}
Benzo[*ghi*]perylene	$C_{22}H_{12}$	276.34	275.278	525	1.3×10^{-11}
Indeno[1,2,3-*cd*]pyrene	$C_{22}H_{12}$	276.34	162-163	—	ca. 10^{-11}
Dibenz[*ah*]anthracene	$C_{22}H_{14}$	278.35	266-270	524	1.3×10^{-11}
Coronene	$C_{24}H_{12}$	300.36	438-440	525	2.0×10^{-13}

[A] Many of these compounds sublime.

4.1.1 An air sample is collected directly from the ambient atmosphere by pulling air at approximately 225 L/min through a fine particulate filter followed by a vapor trap containing polyurethane foam (PUF) or styrene/divinylbenzene polymer resin (XAD-2).[4] Sampling times may be varied from 1 to 24 h, depending on monitoring needs and the detection limits required, so as not to exceed a total sample volume of 350 m^3.

4.2 *Analysis:*

4.2.1 After sampling a fixed volume of air, the particle filter and sorbent cartridge are extracted together in a Soxhlet extractor. The sample extract is concentrated by means of a Kuderna-Danish concentrator (or other validated method), followed by a further concentration under a nitrogen stream, if necessary, and an aliquot is analyzed by gas chromatography/mass spectrometry. The results derived represent the combined gas-phase and particulate-phase air concentrations of each PAH analyzed.

5. Significance and Use

5.1 Polycyclic aromatic hydrocarbons (PAH) as defined by this test method are compounds made up of two or more fused aromatic rings.

5.2 Several PAH are considered to be probable human carcinogens.

5.3 PAH are emitted in the atmosphere primarily through wood or fossil fuel combustion.

5.4 Two- and three-ring PAH are typically present in urban air at concentrations ranging from 10 to several hundred nanograms per cubic metre (ng/m^3); those with four or more rings are usually found at concentrations of a few ng/m^3 or lower.

5.5 PAH span a broad spectrum of vapor pressures (for example, from 1.1×10^{-2} kPa for naphthalene to 2×10^{-13} kPa for coronene at 25°C). Table 1 lists some PAH that are frequently found in ambient air. Those with vapor pressures above about 10^{-8} kPa will be present in the ambient air substantially distributed between the gas and particulate phases. This test method will permit the collection of both phases. However, particulate-phase PAH will tend to be lost from the particulate filter during sampling due to desorption and volatilization.

5.5.1 The distribution between phases depends on ambient temperature, humidity, types and concentrations of PAH and particulate matter, and residence time in the air. PAH, especially those having vapor pressures above 10^{-8} kPa, may vaporize from particulate filters during sampling. Consequently, a back-up vapor trap must be used for efficient sampling.

[4] XAD is a trademark of Rohm and Haas Co., Philadelphia, PA; it is available in the United States solely from Supelco, Inc., Bellefonte, PA. If you are aware of equivalent styrene/divinylbenzene polymer resins, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee[1], which you may attend.

5.6 Separate analyses of the filter and vapor trap will not reflect the original atmospheric phase distributions and should be discouraged.

6. Limitations

6.1 Particulate-phase PAH may be lost from the particle filter during sampling due to desorption and volatilization (**1-6**).[5]

6.1.1 Loss of particulate-associated PAH from the filter depends on the ambient temperature during sampling, humidity, types and concentrations of PAH and particulate matter, and residence time of the PAH on the filter.

6.1.2 During summer months, especially in warmer climates, volatilization from the filter may be as great as 90 % for PAH with vapor pressures above 10^{-6} kPa (**3** and **6**). At ambient temperatures of 30°C and above, as much as 20 % of benzo[*a*]pyrene and perylene (v.p. = 7×10^{-10} kPa) have been found in the vapor trap (**7**).

6.1.3 Separate analysis of the filter will not reflect the concentrations of the PAH originally associated with particles, nor will analysis of the sorbent provide an accurate measure of the gas phase. Consequently, this method calls for coextraction of the filter and sorbent to permit accurate measure of total PAH air concentrations.

6.2 This test method has been evaluated for the PAH shown in Table 1. Other PAH may be determined by this test method, but the user must demonstrate acceptable sampling and analysis efficiencies.

6.2.1 Naphthalene and acenaphthene possess relatively high vapor pressures and may not be efficiently trapped by this test method, especially when PUF is used.

6.2.2 The sampling efficiency for naphthalene has been determined to be about 35 % for PUF and about 60 % for XAD-2.

6.2.3 The user may estimate the sampling efficiencies for PAH of interest by determining dynamic retention efficiency of the sorbent. The percent RE generally approximates the percent SE.

7. Interferences

7.1 Method interferences may be caused by contaminants in solvents, reagents, on glassware, and other sample processing hardware that result in discrete artifacts and elevated baselines, or both, in the detector profiles. Thoroughly clean glass before use (for example, by acid washing, followed by heating to 450°C in a muffle furnace). Check solvents and other materials routinely by running laboratory reagent blanks under the conditions of the analysis to establish that they are free of interfering materials.

7.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. Additional clean-up by column chromatography may be required.

7.3 The extent of interferences that may be encountered using gas chromatographic techniques has not been fully assessed.

7.3.1 Although the GC/MS conditions described allow for resolution of most of the specific PAH compounds covered by this test method, other PAH compounds may interfere.

7.3.2 Some PAH isomers may not be chromatographically resolvable and, therefore, can not be distinguished from each other by MS.

7.3.3 Interferences from some non-PAH compounds, especially oils and polar organic species, may be reduced or eliminated by the use of column chromatography for sample clean-up prior to GC/MS analysis.

7.3.4 The analytical system must be routinely demonstrated to be free of internal contaminants such as contaminated solvents, glassware, or other reagents that may lead to method interferences.

7.3.5 Analyze a laboratory reagent blank for each batch of reagents used to determine if reagents are contaminant-free.

7.4 Exposure to heat, ozone, nitrogen dioxide (NO_2), and ultraviolet (UV) light may cause PAH degradation during sampling, sample storage, and processing.

7.4.1 These problems should be addressed as part of a standard operating procedure prepared by the user.

7.4.2 Use incandescent or UV-filtered fluorescent lighting where possible in the laboratory to avoid photodegradation during analysis.

8. Safety Precautions

8.1 Benzo[*a*]pyrene and several other PAH have been classified as probable human carcinogens. Exercise care when working with these substances.

8.2 Treat all PAH as potential carcinogens.

8.2.1 Weigh pure compounds in a glove box.

8.2.2 Consider unused samples and standards to be toxic waste and properly dispose of them in accordance with regulations.

8.2.3 Regularly check laboratory bench tops and equipment with a UV “black light” for fluorescence indicative of contamination.

9. Apparatus

9.1 *Sampling:*

9.1.1 *Sampling Module*— A typical collection system consisting of a particle filter backed up by a sorbent trap is shown in Fig. 1. It consists of the following:

9.1.1.1 *Metal Filter Holder* (Part 2), capable of holding a 104-mm circular particulate filter supported by a 1.2-mm (16-mesh) stainless-steel screen with 50 % open area. The filter holder is equipped with inert sealing gaskets (for example, polytetrafluoroethylene) placed on either side of the filter.

9.1.1.2 *Metal Cylinder* (Part 1), capable of holding a 65-mm o.d. (60-mm i.d.) by 125-mm borosilicate glass sorbent cartridge. Inert, pliable gaskets (for example, silicone rubber) are used to provide an air-tight seal at each end of the sorbent cartridge. The glass sorbent cartridge is indented 20 mm from the lower end to provide a support for a 1.2-mm (16-mesh) stainless-steel screen that holds the sorbent.

9.1.1.3 The glass sorbent cartridge fits into Part 1, which is screwed onto Part 2 until the sorbent cartridge is sealed

[5] The boldface numbers in parentheses refer to the list of references at the end of this standard.

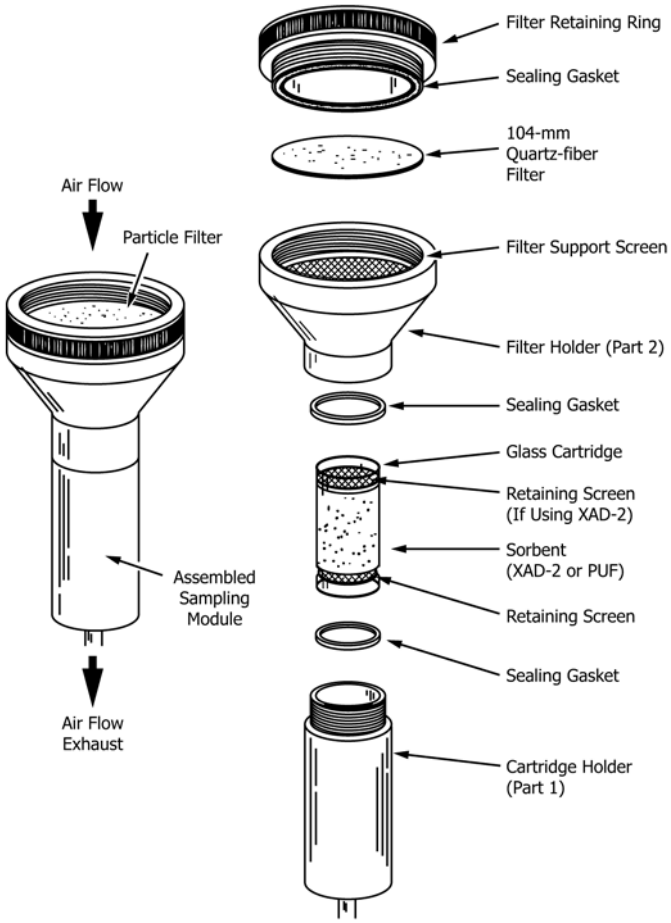

FIG. 1 Typical Sampling Module

between the gaskets. The sampling module is described by Lewis and Jackson **(8)**[4]. Similar sampling modules are commercially available.

9.1.2 *High-volume Pumping System,* capable of providing a constant air flow of up to 250 L/min (15 m^3/h) through the sampling module (9.1.1). A typical air pumping system is shown in Fig. 2. It is equipped with the following components:

9.1.2.1 *Appropriate Flow-control Device:*

9.1.2.2 *Manometer,* to measure pressure drop across the sampling module or other suitable flow measuring device.

9.1.2.3 *Interval Timer.*

9.1.2.4 *Exhaust hose,* to carry exhausted air at least 3 m away from the sampler.

NOTE 1—The sampling system described in 9.1.1 to 9.1.2.4 has been shown to efficiently trap PAH with three or more rings at samples volumes 350 m^3 and lower **(8-16)**. Other samplers utilizing larger filters (for example, 200-mm by 250-mm) and higher capacity sorbent traps (for example, by tandem 77-mm by 62-mm PUF plugs) have been used to collect PAH from larger air volumes (for example, by 700 m^3) **(17-26 and 7)**. If larger sampling volumes or higher flow rates are used, thoroughly evaluate their performance to ensure acceptable sampling efficiencies.

9.1.3 *Flow Calibrator,* a calibrated manometer or other suitable flow measuring device capable of being attached to the inlet of the sampling module (9.1.1).

9.1.4 *Standard Audit Calibration Orifice:*

9.1.5 *Positive-Displacement Rootsmeter:*

9.1.6 *Thermometer*—Precision digital thermometers based on resistance temperature detectors (RTDs), thermistors, thermocouples, or organic liquid-in-glass thermometers (such as Thermometer S18C in Specification E2251) meeting the requirements of specific applications may be used.

9.1.7 *Barometer,* capable of measuring atmospheric pressure to ±0.6 kPa. See Test Method D3631.

9.1.8 *Sample Containers,* airtight, labeled, screw-capped containers (wide mouth, preferably glass jars with PTFE or other noncontaminating sealed lids) to hold filters and sorbent cartridges during transport to the analytical laboratory.

9.1.9 *Ice Chest,* to hold samples at 0°C or below during shipment to the laboratory after collection.

9.1.10 *Field Operations Data Sheets,* for each sample for recording the location and sample time, duration of sample, starting time, and volume of air sampled. See Fig. 3.

9.2 *Sample Preparation:*

9.2.1 *Soxhlet Extractor System,* size 200 mL, with 500 mL flask, and appropriate condenser. If glass sorbent cartridge is extracted without unloading, a 500 mL extractor and 1000 mL flask are required.

9.2.2 *Kuderna-Danish (KD) Concentrators,* size 500 mL, 10 mL graduated concentrator tubes with ground-glass stoppers, and 3-ball macro-Snyder Column.

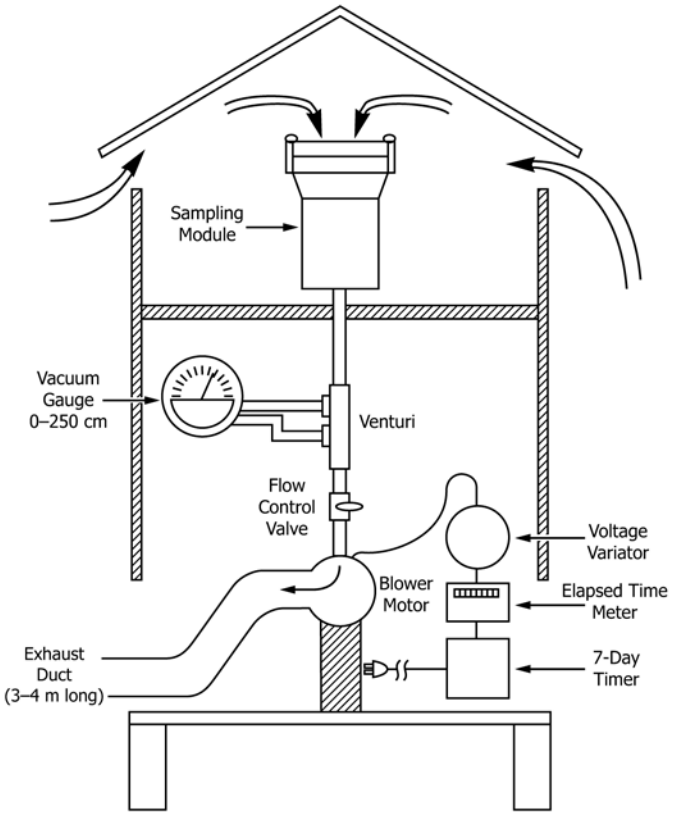

FIG. 2 Typical Air Sampling System With Sampling Module Attached

9.2.3 *Evaporative Concentrators*—microevaporator tubes, 1 mL, micro-Snyder columns (optional), water bath with ±5°C temperature control, nitrogen blow-down apparatus with adjustable flow control.

9.2.4 *Cleanup Column,* chromatography columns; for example, by 160-mm by 11.5-mm i.d.

9.2.5 *Vacuum Oven,* drying oven system capable of maintaining a vacuum at 30 to 35 kPa (flushed with nitrogen (10.1.3.2)) overnight.

9.2.6 *Laboratory Refrigerator/Freezer,* capable of cooling to 4° and –20°C.

9.2.7 *Glove Box,* for handling highly toxic standards, with UV-filtered light source.

9.2.8 *Vials,* 40 mL, borosilicate glass.

9.2.9 *Minivials,* 2 mL, borosilicate glass, with conical reservoir and screw caps lined with PTFE-faced silicone disks, and a vial holder.

9.2.10 *Erlenmeyer Flasks,* 50 mL, borosilicate glass.

9.2.11 *Boiling Chips,* solvent extracted, 0.3 to 0.9-mm (10/40 mesh) silicon carbide or equivalent.

9.2.12 *Spatulas,* PTFE-coated.

9.2.13 *Tweezers and Forceps,* PTFE-coated.

9.2.14 *Muffle Furnace,* capable of heating to 600°C (optional).

9.3 *Sample Analysis:*

9.3.1 *Gas Chromatograph/mass Spectrometer,* analytical system complete with gas chromatograph coupled with a mass spectrometer and data processor, suitable for splitless injection, and all required accessories, including temperature programmer, column supplies, recorders, gases, and syringes.

9.3.2 *GC Columns,* fused silica capillary column (30- to 60-m by 0.25-mm i.d.) coated with crosslinked 5 % phenyl methylsilicone, 0.25 µm film thickness, or other suitable columns.

9.3.2.1 Use ferrules made up of no more than 40 % graphite (for example, 60 % polyimide/40 % graphite) at the GC column injection inlet to avoid possible absorption of PAH.

9.3.3 *Syringes,* sizes 10, 25, 50, 100, and 250 µL for injecting samples into the GC and making calibration, reference standard, and spiking solutions.

10. Reagents and Materials

10.1 *Reagents:*

10.1.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, except where such reagents are not available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

[6] 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 Analar Standards for Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.K., and the United States Pharmacopeia and National Formula, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

DATA SHEET

Start | Stop

Site _____ Barometric Pressure _____ _____

Date _____ Ambient Temperature _____

Operator _____ Sampler Calibration Curve _____ Standard Calibration Curve _____

Sampler No.	Flow Set Point Value	Identification No.		Sampling Period		Total Sampling Time	Flow Rate Indicator		Calibration[1]		
		Filter	PUF or XAD-2	Start	Stop		Start	Stop	Calc. Flow Rate	Std. Flow Rate	Within ±10%?

[1] Must be performed before and after each sampling period.

Date _____

Checked by _____

FIG. 3 Example of Field Operations Data Sheet

10.1.2 *Acetone,* glass distilled, chromatographic quality.

10.1.3 *Compressed Gases:*

10.1.3.1 *Helium Carrier Gas,* ultra-high purity.

10.1.3.2 *Nitrogen,* high purity, for sample concentration.

10.1.4 *Cyclohexane* (optional), glass distilled, chromatographic quality.

10.1.5 *Dichloromethane,* glass distilled, chromatographic quality.

10.1.6 *Diethyl Ether,* reagent grade, preserved with 2 % ethanol.

10.1.7 *n-Hexane,* glass distilled, chromatographic quality.

10.1.8 *Pentane,* glass distilled, chromatographic quality.

10.1.9 *Silica Gel,* high purity grade, type 60, 75–200 µm (70–230 mesh).

10.1.10 *Sodium Sulfate,* Na_2SO_4, anhydrous, reagent grade.

10.1.11 *Toluene* (optional) , glass distilled, chromatographic quality.

10.1.12 *Calibration Standards:*

10.1.12.1 *Internal Standards,* naphthalene - d_8, acenaphthene - d_{10}, phenanthrene - d_{10}, perylene - d_{12}, chrysene - d_{12}, purity 98 % or better.

10.1.12.2 *Extraction Efficiency Standards,* fluorene-d_{10}, pyrene-d_{10}, benzo[*k*]fluoanthrene-d_{12}, or other appropriate deuterated standards, purity 98 % or better. Alternatively or additionally, 2,2'-dibromobiphenyl and 2,2',3,3',4,4',5,5',6,6'-decafluorobiphenyl may be used.

10.2 *Materials:*

10.2.1 *Particulate Filters,* 104-mm micro-quartz-fibre, binderless, acid-washed.

NOTE 2—Glass- or quartz-fibre filters coated or impregnated with polytetrafluoroethylene have been used for collection of particle-associated PAH **(24)**. Validate the performance of these filters before use if used in lieu of those specified.

10.2.2 *Polyurethane Foam,* polyether type, density 22 mg/cm^3, cut into cylinders 76 mm long by 62 mm diameter.

10.2.3 *Adsorbent Resin,* styrene/divinylbenzene polymer (XAD-2), spherical, 500 µm (20 to 60 mesh), precleaned.

10.2.4 *Gloves,* polyester or latex rubber, for handling cartridges and filters.

10.2.5 *Adsorbents* (for sample cleanup), silica gel, high purity grade, type 60, 75 to 200 µm (purified by Soxhlet extraction with dichloromethane (10.1.5) for 6 h at a minimum of 3 cycles per hour, and activated by heating in a foil-covered glass container for 16 h at 450°C).

10.2.6 *Drying Agent*— Sodium sulfate, granular anhydrous (purified by washing with dichloromethane (10.1.5) followed by heating at 450°C for 4 h in a shallow tray).

11. Preparation of Sampling Media

11.1 *Polyurethane Foam*—See 10.2.2.

11.1.1 For initial cleanup, place the PUF plug in the Soxhlet apparatus (9.2.1) and extract it first with acetone (10.1.2) for 14 to 24 h at approximately 4 cycles per h. Follow this by a second Soxhlet extraction for 14 to 24 h at approximately 4 cycles per h with 10 % diethyl ether (10.1.6) in *n*-hexane (10.1.7) or other appropriate solvent to be used in the sample extraction step (13).

11.1.1.1 The PUF plug may be reused if properly cleaned after each use. The number of possible uses before significant deterioration of performance occurs has not been determined, but it should not be used more than six times without verifying that the performance is unchanged.

11.1.1.2 If the PUF plug is reused, 10 % diethyl ether (10.1.6) in *n*-hexane (10.1.7) or the optional extraction solvent, if appropriate, may be used as the solvent for cleanup.

11.1.2 Place the extracted PUF plug in the vacuum oven (9.2.5) connected to an ultra-pure nitrogen (10.1.3.2) gas stream and dry at room temperature for approximately 2 to 4 h (until the plug is no longer swollen).

11.1.3 Place the cleaned and dried PUF plug into the glass sampling cartridge using polyester or latex rubber gloves and PTFE-coated forceps (9.2.13).

11.2 *Styrene/divinylbenzene Resin (XAD-2)*—See 10.2.3.

11.2.1 For initial cleanup of the XAD-2, place a batch of XAD-2 (60 to 100 g) in the Soxhlet apparatus (9.2.1) and extract it with dichloromethane (10.1.5) for 16 h at approximately 4 cycles per h. At the end of the initial Soxhlet extraction, discard the used dichloromethane (10.1.5) and replace it with fresh reagent. Extract once again the XAD-2 resin for 16 h at approximately 4 cycles per h.

11.2.2 Remove the XAD-2 resin from the Soxhlet apparatus (9.2.1), place it in the vacuum oven (9.2.5) connected to an ultra-pure nitrogen (10.1.3.2) gas stream and dry it at room temperature for approximately 4 to 8 h (until the resin particles flow freely).

NOTE 3—The XAD resin may be dried more quickly using a fluidized-bed suspension system with dry nitrogen (10.1.3.2) **(27)**.

11.2.3 Place a stainless steel screen (75-µm, or 200-mesh) or 1-cm thick plug of pre-extracted PUF at the bottom of the hexane-rinsed glass cartridge to retain the XAD-2 resin.

11.2.4 When the XAD-2 resin is dry, pour it into the sampling cartridge to a depth of approximately 5 cm. This will require 55 to 60 g of sorbent. Place another 75-µm (200-mesh) screen or a 1-cm PUF plug on top of the XAD bed to retain the sorbent.

11.2.5 The XAD may be reused if properly cleaned after each use. The number of possible uses before significant deterioration of performance occurs has not been determined, but it should not be used more than six times without verifying that performance is unchanged.

11.3 *Storage*—The loaded sampling cartridge is wrapped with hexane-rinsed aluminum foil, placed in a clean container, and tightly sealed.

11.3.1 In lieu of solvent rinsing, the aluminum foil may be heated for 1 h at 450°C in a muffle furnace.

11.4 *Blank Check*— Analyze at least one assembled cartridge from each batch as a laboratory blank, using the procedures described in Section 13, before the batch is considered acceptable for field use. A blank level of <10 ng/sorbent cartridge for single compounds is acceptable. Ideally, the blank level for a given PAH should be less than 1 % of amount anticipated to be collected for analysis.

11.4.1 Blank levels of <10 ng may not be achievable for naphthalene or phenanthrene. However, since these compounds are typically present in ambient air at relatively high concentrations, a blank level of <50 ng is usually acceptable.

12. Sampling

12.1 *Calibration of The Sampler Flow-control System:*

12.1.1 The air flow through the sampling system must be monitored by a flow-control device or devices. Conduct a multi-point calibration of the flow-control system every six months using standard audit calibration orifice, which is temporally attached to the inlet of the sampler. Alternatively, a high-flow dry gas metre may be used if it has been validated as a transfer standard. Perform a single point calibration before and after each sample collection.

12.1.2 Calibrate the sampler as follows:

12.1.2.1 When new,

12.1.2.2 After major repairs or maintenance,

12.1.2.3 whenever any audit point deviates from the calibration curve by more than 7 %,

12.1.2.4 when using a different collection medium (PUF versus XAD) than that for which the sampler was originally calibrated; or

12.1.2.5 At the frequency specified in the user's manual.

12.1.3 Calibrate the air sampler in the field with a calibrated orifice flow-rate transfer standard (9.1.4).

12.1.3.1 Certify the flow rate transfer standard in the laboratory against a positive-displacement rootsmeter (9.1.5).

12.1.3.2 Recertify flow rate transfer standard once yearly, if the orifice is protected from damage.

12.2 *Determination of Sampling or Dynamic Retention Efficiency:*

12.2.1 Evaluate the efficiency of the sampler for the targeted PAH under the conditions anticipated in the field prior to the initiation of any sampling program, either by determining the *sampling efficiency* directly or estimating it from the *dynamic retention efficiency*. Determination of the efficiency is particularly important if sampling periods exceeding 24 h are planned.

12.2.1.1 The SE is determined by spiking a solution of the compounds of interest (or a representative selection that includes the most volatile PAH) onto a clean particulate filter (10.2.1) backed up with the vapor cartridge, then pulling a volume of air through the assembled sampling module (9.1.1) equivalent to the maximum volume that will be sampled. Add the spiking solution drop wise to the filter, so as to uniformly load it and avoid over-saturation.

12.2.1.2 The RE is determined by spiking the sorbent directly, placing it behind a clean filter (10.2.1) in the sampling module (9.1.1), and otherwise following the same procedure. Inject the spiking solution carefully into the inlet face of the sorbent bed in a manner that will apply the solution uniformly across the face and to a depth of no more than 1 cm. The spiking solution should be in a volatile solvent, such as hexane (10.1.7) or dichloromethane (10.1.5). Spiking levels should correspond to at least three times but no more than ten times the anticipated concentrations of the targeted compounds in the air to be pulled through the sampling medium. Dry the spiked filter or sorbent for about 1 h in a clean, light-protected area prior to pulling air through the system.

12.2.2 Ensure that the calibration sampling rate and sampling period is the same as that planned for the field sampling, and that the ambient temperatures during the test also approximate those expected in the field, especially when warm-weather conditions are anticipated.

12.2.3 When determining the sampling efficiencies, analyze the sorbent and spiked filter (10.2.1) separately and subtract any residue retained by the filter from the initial spike quantity. For determination of dynamic retention efficiencies, analyze only the sorbent.

12.2.4 Calculate the sampling efficiency for a given PAH, in percent, using the following equation:

$$\text{SE},\% = \frac{W}{W_O - W_R} \times 100 \quad (1)$$

where:

W = the mass of PAH extracted from the sorbent after air is pulled through it,
W_O = the mass of PAH initially applied to the filter, and
W_R = the mass of PAH remaining on the filter after air is pulled through it.

12.2.5 Sampling efficiencies should fall between 75 and 125 %, except for naphthalene and acenaphthalene, which may exhibit lower efficiencies, especially with PUF. In no case should sampling efficiencies below 50 % or above 150 % be accepted.

12.2.6 Calculate the dynamic retention efficiency from the following equation:

$$\text{RE},\ \% = \frac{W}{w_o} \times 100 \quad (2)$$

where:

w_o = the mass of PAH initially applied to the sorbent bed.

12.2.7 The percent RE has generally been found to be approximately equal to or slightly lower than the percent SE for semivolatile organic compounds. The same range of acceptability applies to percent RE as to percent SE.

12.3 *Sample Collection:*

12.3.1 See Practice D1357 for general guidance on sampling.

12.3.2 Clean the interior surfaces and gaskets of the sampling module prior to sampling.

12.3.3 Load and unload the sampling module (9.1.1) in a controlled clean environment or at a centralized sample processing area so that the sample handling variables can be minimized.

12.3.4 Load the sorbent-filled glass sampling cartridge into the lower part (Part 1) of the sampling head and attach the filter holder (9.1.1.1) (Part 2) tightly to it (See Fig. 1). With clean PTFE tipped forceps (9.2.13), place the particulate filter (10.2.1) carefully on top of the filter support and secure the filter holder ring over the filter. Assemble and tighten all the module connections.

NOTE 4—Failure to properly tighten connections may result in air leaks and affect sample representativeness.

12.3.5 Locate the sampler in an unobstructed area, at least 2 m from any obstruction to air flow. Stretch out the exhaust hose (9.1.2.4) in the predominant downwind direction to inhibit recycling of air into the sampler.

12.3.6 With the sampling head removed from the sampler and the flow control valve fully open, turn on the pump (9.1.2) and allow it to warm-up for 5 to 10 min.

12.3.7 Attach a test sampling module (9.1.1) loaded with the same type of filter (10.2.1) and sorbent collection cartridge as will be used for sample collection to the air inlet of the sampler. Energize the sampler and open the flow control valve fully. Adjust the flow regulator (for example, by voltage regulator) so that a sample flow rate corresponding to approximately 110 % of the desired flow rate is indicated on the vacuum gage (based on the previously obtained multi-point calibration curve).

12.3.8 Remove the test sampling module (9.1.1) and place the calibration orifice on the sampler. Attach the manometer (9.1.2.2) to the tap on the calibration orifice. Turn the sampler on momentarily and set the zero level of the manometer. Start the sampler again and record the manometer reading once a stable reading is achieved. Turn off the sampler.

12.3.9 Calculate the desired sample flow rate from the calibration curve for the orifice from the data obtained in the previous step, and use the calibration curve for the flow control assembly to calculate the sample flow rate from the data obtained with the test sampling module (9.1.1). Record the calibration data on the Field Data Sheet (Fig. 3). If the two values do not agree within 10 %, inspect the sampler for damage, flow blockage, and so forth. If no obvious problems are found, recalibrate the sampler.

12.3.10 With the sampler turned off, check the zero reading of the vacuum gage. Record the ambient temperature, barometric pressure, elapsed time meter setting, sampler serial number, filter number, and sample number on the Field Data Sheet.

12.3.11 Attach the loaded sampling module (9.1.1) to the sampler and commence sampling.

12.3.12 Activate the elapsed time meter and record the start time.

12.3.12.1 Read and record the flow rates at the beginning and end of the sampling period and at least once a day during the sampling period.

12.3.12.2 Record the ambient temperature and barometric pressure at the beginning and end of the sampling period.

12.3.13 At the end of the desired sampling period, carefully remove the sampling module (9.1.1) to a clean area. Perform a final flow check using the test sampling module (9.1.1). If the calibration deviates by more than 10 % from the initial reading, mark the flow data for that sample as suspect and inspect the sampler, or remove from service, or both.

12.3.14 Carefully remove, while wearing polyester or latex gloves, the sorbent cartridge from the lower sampling module (9.1.1) chamber and place it on hexane (10.1.7)-rinsed aluminum foil (The foil in which it was originally wrapped may be used.). Then carefully remove the particulate filter from its holder with clean PTFE-tipped forceps (9.2.13), fold it in half twice (sample-side inward), and place it inside the glass cartridge on top of the sorbent. Return the cartridge to its original shipping container and write the appropriate information on the label.

12.3.15 Store the sealed sample containers (9.1.6) refrigerated (for example, with solid carbon dioxide) and protected from light for shipment to the laboratory. Store them refrigerated at 4°C or below for no longer than two weeks prior to extraction.

12.4 *Field Blanks:*

12.4.1 Take at least two field blanks per week to the sampling site. If sampling is periodic or large numbers of samples are involved, take at least one blank on each day of sampling. Keep the field blanks in sealed shipping containers and do not expose to air.

13. Sample Preparation

13.1 Set up the Soxhlet extractor (9.2.1) in a normal fashion in a fume hood and add the appropriate amount and volume of extraction solvent to the boiling flask.

13.1.1 If the glass sorbent cartridge is to be extracted without first removing the sorbent, use a 500-mL Soxhlet extractor (9.2.1) and 1000-mL boiling flask, with an extraction solvent volume of 600 mL.

13.1.2 If the sorbent is removed from the cartridge for extraction, use a 200-mL extractor and 500-mL flask, with an extraction solvent volume of 300 mL.

13.1.3 If PUF is the sorbent, use 10 % diethyl ether (10.1.6) in *n*-hexane (10.1.7) as the extraction solvent. Alternatively, cyclohexane (10.1.4) or toluene (10.1.11) may be used for extraction of PUF if first validated by the user **(7, 10, 17, 28, and 29)**.

13.1.4 If XAD-2 resin is the sorbent, use either 10 % diethyl ether (10.1.6) in *n*-hexane (10.1.7) or 100 % dichloromethane (10.1.5) as the extraction solvent. Alternatively, use cyclohexane (10.1.4) or toluene (10.1.11), if first validated by the user.

NOTE 5—Dichloromethane (10.1.5) will extract low-molecular-weight oligimers from PUF and may change its performance characteristics. However, there has been reported use of this solvent for extraction of PAH from PUF that was precleaned by extraction with dichloromethane. The user should be very careful to thoroughly evaluate both sampling and analytical performance before electing to use this solvent with PUF.

13.1.5 Remove the sampling cartridges from the sealed shipping containers using gloved hands and place on solvent-rinsed aluminum foil. Remove the folded particulate filter from the cartridge with hexane (10.1.7)-rinsed tweezers (9.2.13) and place it in the bottom of the Soxhlet extractor (9.2.1). If the glass sorbent cartridge is to be extracted, carefully rinse the outside walls with hexane (10.1.7) before placing it into the extractor on top of the filter. If the sorbent is to be removed for extraction, place it in a pre-extracted Soxhlet thimble for insertion into the extractor (9.2.1), or directly into the extractor.

13.1.6 When PUF is used, remove the PUF plug from the sampling cartridge with tweezers or tongs (9.2.13) and compress it into a 200-mL Soxhlet extractor (9.2.1) for extraction. Rinse the inside walls of the glass sampling cartridge into the extractor with 10 to 20 mL of hexane (10.1.7).

13.1.7 Prepare spiking solutions of the standards in *n*-hexane (10.1.7) or dichloromethane (10.1.5), as appropriate, to a concentration of 50 ng/µL.

13.1.8 Add 20 µL of the extraction efficiency recovery standard solution to the sorbent in the Soxhlet extractor (9.2.1) immediately prior to extraction to monitor recovery.

13.1.9 Add the recovery standard solution to every sample and field blank.

13.1.10 Operate the Soxhlet extractors (9.2.1) for 14- to 24-h (typically overnight) at a reflux rate of about 4 cycles/h. When the extract has cooled, pass it through a drying column containing about 10 g of Na_2SO_4 (10.1.10) and collect in a Kuderna-Danish (K-D) concentrator (9.2.2). Wash the extractor flask and drying column with 100 to 125 mL of *n*-hexane (10.1.7) or dichloromethane (10.1.5), as appropriate, to complete the quantitative transfer.

NOTE 6—Drying with Na_2SO_4 should not be necessary for samples collected during dry weather. However, if XAD-2 is used as the sorbent and drying is not indicated, filter the extract through a clean particulate filter (10.2.1) to remove fine particulate matter of the resin.

13.1.11 Carefully concentrate the extract in the K-D apparatus to 5 mL or less on a water bath at 60 to 65°C.

13.1.11.1 Exercise care to prevent the K-D concentrator tube from going dry.

13.1.11.2 A vacuum rotary evaporator may be used to concentrate the extract to about 5 mL, if it can be demonstrated that acceptable recoveries of internal standards and targeted PAH are achieved.

13.1.12 Carefully rinse the insides of the K-D concentrator flask and Snyder column (9.2.3) with *n*-hexane (10.1.7) or dichloromethane (10.1.5), as appropriate, into the 10-mL concentrator tube. Then place the concentrator in a water bath held at 30 to 40°C and concentrate the extract to 1 mL or less under a gentle stream of nitrogen (10.1.3.2). Alternatively, a micro KD concentrator fitted with a micro-Snyder column maybe used for concentration. Add the internal standards (see 13.4) and adjust the final volume to 1.0 mL.

NOTE 7—When dichloromethane (10.1.5) is used, do not allow the water bath temperature to exceed 30°C.

13.1.12.1 Exercise care to prevent the concentrator tube from going dry.

13.1.13 Adjust the concentrated sample extracts to 1.0 mL and add the internal standard. Mix the sample well and transfer it to sealed brown vials for storage at 4°C or lower until analyzed.

13.1.14 Analyze the final extracts within 30 days.

13.2 *Sample Cleanup:*

13.2.1 *Column Preparation*—Extract silica gel (10.1.9), type 60, in the Soxhlet extractor (9.2.1) with dichloromethane (10.1.5) for 6 h (minimum rate, 3 cycles/h) and then activate by heating in a foil-covered glass container for 16 h at 150°C.

13.2.2 Pack a small piece of glass wool into the bottom of a glass chromatography column of 15- to 25-mL capacity (for example, by 11.5-mm i.d. by 160-mm long) and slurry 10 g of activated silica gel (10.1.9) into the column with pentane (10.1.8). Tap the column gently as the slurry is settling to ensure proper packing. Finally, add 1 g of anhydrous Na_2SO_4 (10.1.10) to the top of the silica gel. Prior to use, rinse the column with pentane (10.1.8) at 1 mL/min for 1 h to remove any trace of contaminants. Preelute with 40 mL of pentane (10.1.8) and discard the eluate.

NOTE 8—Cleanup procedures may not be needed for relatively clean matrix samples.

13.3 *Column Chromatography:*

13.3.1 While the pentane preelutant covers the top of the column, transfer 1 mL of sample extract in *n*-hexane (10.1.7) to the column, and wash with 2 mL of *n*-hexane to complete the transfer. Allow it to elute through the column. Immediately prior to exposure of the Na_2SO_4 (10.1.10) layer to the air, add 25 mL of pentane (10.1.8) and continue the elution. Discard the pentane eluate.

13.3.1.1 If dichloromethane (10.1.5) is used for extraction of the sample, solvent exchange it with *n*-hexane (10.1.7) This may be accomplished by diluting the extract at least 2–fold with hexane and concentrating to 1 mL at 30°C under a purified nitrogen stream. The dilution and concentration process should be repeated at least twice. Alternatively, a micro KD concentrator fitted with a micro-Snyder column may be used for concentration.

13.3.1.2 The pentane fraction contains the aliphatic hydrocarbons collected on the filter/adsorbent combination. If desired, this fraction may be analyzed for specific aliphatic organics. Elute the column at 2 mL/min with 25 mL of dichloromethane (10.1.5) in pentane (10.1.8) (4:6 V/V) and collected in a 50 mL K-D (9.2.2) flask equipped with a 5-mL concentrator tube for concentration to less than 5 mL. Concentrate the concentrate to 1 mL or less under a gentle stream of nitrogen (10.1.3.2) as previously described.

13.3.1.3 An additional elution of the column with 25 mL of methanol will elute polar (oxygenated and nitrated) PAH. This fraction may be analyzed for specific polar PAH.

13.4 *Internal Reference Standards Addition:*

13.4.1 To use this approach, select one or more internal reference standards that are similar in chromatographic behavior to the compounds of interest. For PAH, these are typically the deuterated analogs. Demonstrate that the measurement of the internal reference standard is not affected by method or matrix interferences. The following internal reference standards are suggested for specific PAH as listed below:

Naphthalene - d_8
Naphthalene
Acenaphthene - d_{10}
Acenaphthene
Acenaphthylene
Fluorene
Perylene - d_{12}
Perylene
Benzo[*a*]pyrene
Benzo[*b*]fluoranthene
Benzo[*k*]fluoranthene
Benzo[*ghi*]perylene
Dibenz[*ah*]anthracene
Indeno[1,2,3-*cd*]pyrene
Coronene

Phenanthrene - d_{10}
Anthracene
Fluoranthene
Phenanthrene
Pyrene
Chrysene - d_{12}
Benz[*a*]anthracene
Chrysene
Cyclopenta[*cd*]pyrene

13.4.2 Prepare stock solutions of the appropriate deuterated internal standards, made up to concentrations of 50 ng/µL. Add them to sample extracts to achieve concentrations similar to those expected for the PAH in the samples to be analyzed (for example, add 20 µL of stock solution to the 1-mL sample extract to achieve a 1 ng/µL concentration corresponding to a 3 ng/m^3 air concentration if 325 m^3 of air is sampled). Carefully adjust the final sample volume after addition of the internal standards to 1 mL. Add the internal standards immediately after sample cleanup (if any) and prior to storage in the freezer (9.2.6) pending analysis.

NOTE 9—Deuterated PAH standards contain traces of natural (undeuterated) PAH. If too much deuterated PAH standard is added, possible contamination of the sample from natural PAH in the deuterated standard may interfere with accurate quantitation. Typically, air concentrations of PAH decrease with increasing ring number. Therefore, the concentrations of internal standards added should be lower for the larger PAH (for example, 1 ng/µL for naphthalene-d_8, acenaphthalene-d_{10}, and phenanthrene-d_{10} and 0.1 ng/µL for chrysene-d_{12} and perylene-d_{12})

14. Analysis

14.1 *Instrumentation*—Perform the analyses using a 70-eV electron impact ionization MS (9.3.1) operated in the selected-ion monitoring mode (SIM), with a 30- to 50-m by 0.25-mm fused silica capillary column coated with crosslinked 5 % phenyl methylsilicone, 0.25 µm film thickness, or other suitable column (9.3.2). Typical instrumental parameters are:

14.1.1 Initial column temperature and hold time—60°C for 2 min.

14.1.2 Column temperature program—60 to 290°C at 8°C/min.

NOTE 10—Alternative mass spectrometric instruments, such as ion traps and tandem MS (MS-MS), as well as other ionization techniques or ion monitoring modes, may be used and provide equal or better analytical sensitivity.

14.1.3 Final hold time (at 290°C)—12 min.

14.1.4 Injector—Grob-type, splitless (for 0.5-1 min).

14.1.5 Injector temperature—275 to 300°C.

14.1.6 Transfer line temperature—275 to 300°C.

14.1.7 Source temperature—In accordance with manufacturer's specifications.

14.1.8 Injection volume—1 to 3 µK,

14.1.9 Carrier gas—helium at 30 to 40 cm/s.

NOTE 11—When dichloromethane (10.1.5) is used, the initial column temperature can be lowered to 40°C; however, little, if any improvement in column performance is expected.

14.1.10 For higher resolution (for example, by partial separation of benzo[*b*] and benzo[*k*]fluoranthene) a 4 to 5°C/min column temperature program may be used, with resultant increase in analysis time.

14.2 *Instrument Calibration:*

14.2.1 Prepare calibration standards of native PAH at a minimum of three concentration levels for each PAH of interest, by adding appropriate volumes of one or more stock standards to a volumetric flask. Prepare one of the calibration standards at a concentration near, but above, the minimum detection limit (MDL) and the other concentrations corresponding to the expected range of concentrations found in real samples or to define the working range of the GC/MS (9.3.1) system.

14.2.2 The minimum acceptable ion intensity is instrument dependent. However, do not report quantitative results below the lowest calibration level, sufficiently above the instrument noise level to provide precision between replicate analyses of 20 % relative standard deviation or better. Typically a signal-to-noise ratio of 3:1 is acceptable for compound identification. For quantitation, the signal-to-noise ratio should be at least 7:1.

14.2.3 Prepare the calibration standards so that they contain the appropriate deuterated internal standards at the specified concentration.

14.2.4 Analyze injections (1–3 µL) of each standard solution and plot the area ratio of the primary ion of the analyte and the corresponding internal standard against the concentration or each compound and internal standard. Calculate the response factor (RF_s) for each analyte as followed:

$$RF_s = (A_s C_{is})/(A_{is} C_s) \quad (3)$$

where:

A_s = area of the primary ion for the analyte to be measured,
A_{is} = area of the primary ion for the internal standard,
C_{is} = concentration of the internal standard, ng/µL, and
C_s = concentration of the analyte to be measured, ng/µL.

14.2.5 Select the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next two most intense ions as the secondary ions. Table 2 shows key ions for selected deuterated internal standards. These standards may also serve as retention time standards. Add the internal standards calibration standards and all sample extracts analyzed by GC/MS.

14.2.6 If the RF is constant over the working range (<20 % RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, with RF.

14.2.7 Verify the working calibration curve or RF on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±20 %, repeat the test using a fresh calibration standard. Alternatively, prepare a new calibration curve. The relative retention times for each compound in each calibration run should agree within 0.06 relative retention time units.

14.3 *Analysis:*

14.3.1 Remove the sample extracts from cold storage and allow them to warm to room temperature (if appropriate). Once the GC and MS (9.3.1) are properly set up, inject 1 to 3 µL of each sample extract and record the MS response noted. Select a minimum of two ions per compound for monitoring, with a

TABLE 2 Characteristic Ions for GC/MS Detection of Selected PAH

Compound	Primary	Secondary	
Acenaphthene	154	153	152
Acenaphthene-d_{10}	164	163	162
Acenaphthylene	152	151	153
Anthracene	178	89	179
Benz[*a*]anthracene	228	114	229
Benzo[*a*]pyrene	252	253	126
Benzo[*e*]pyrene	252	253	126
Benzo[*b*]fluoranthene	252	253	126
Benzo[*ghi*]perylene	276	138	277
Benzo[*k*]fluoranthene	252	253	126
Chrysene	228	114	229
Chrysene-d_{12}	240	120	241
Coronene	300	150	301
Cyclopental[*cd*]pyrene	226	113	227
Dibenz[*ah*]anthracene	278	139	279
Fluoranthene	202	101	203
Fluorene	166	165	167
9-Fluorenone	180	152	181
Indeno[1,2,3-*cd*]pyrene	276	138	227
Naphthalene	128	129	127
Naphthalene-d_8	136	137	134
Perylene	252	253	126
Perylene-d_{12}	264	265	132
Phenanthrene	178	179	89
Phenanthrene-d_{10}	188	189	186
Pyrene	202	101	203
Retene	219	234	205
Dibromobiphenyl	312	310	314
Decafluorobiphenyl	334	335	265

minimum dwell time of 100 ms per peak. Typical characteristic ions for selective PAH are outlined in Table 2.

14.3.2 In SIM analysis, analyte identification is based on retention times and qualifier ion ratios. There are no mass spectra to compare. If secondary ions are included for monitoring, method detection limits will be significantly reduced since relative abundances of these ions are low for PAH. Therefore, presence of the primary ion coupled with the relative retention time or index (relative to the corresponding deuterated internal standard) may be more a practical approach to identification when high sensitivity is required.

14.3.2.1 When the ratio (r) of the retention time (RT) of the unknown analyte u to that of the corresponding internal standard I (where $r = RT_u / RT_I$) is used to identify the analyte, the ratio of retention times r_s from the sample chromatogram shall not be greater than 0.4 % of the retention time ratio r_c from the chromatogram of the calibration standard.

14.3.2.2 The value of r shall not be larger than 2 or smaller than 0.5.

14.3.2.3 The retention index of the sample analyte and corresponding standard shall agree within ±2 %.

14.3.3 The abundance ratio of the major characteristic ions of the analyte and corresponding calibration standard should agree within ±30 %. If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, dilute the extract. Add additional internal standard solution to the diluted extract to maintain the required concentration (for example, 1 to 10 ng/µL) of each internal standard in the extract. Reanalyze the diluted extract.

14.3.4 When an analyte has been identified, the quantification of that analyte will be based on the integrated abundance from the monitoring of the primary characteristic ion. Quantitation is accomplished by the internal standard technique. The internal standard used is the one nearest the retention time of that of a given analyte. The peak maxima of specified characteristic ions of the analyte should be coincident within ±0.06 relative retention time units (relative to the retention time of the designated internal standard).

NOTE 12—Carry-over contamination may occur when a sample containing low concentrations of PAH is analyzed immediately after a sample containing high concentrations of PAH or PAH standard solutions. Use a solvent rinse to verify that there is no carry-over.

15. Calculation

15.1 Calculate the concentration of each identified analyte in the sample extract as follows:

$$C_e, \text{ ng/µL} = \frac{(A_x)(C_{is})}{(A_{xs})(RF)} \quad (4)$$

where:

A_x = area of characteristic ion (s) for analyte being measured, and
A_{xs} = area of characteristic ion (s) for internal standard.

15.2 Calculate the air volume from the periodic flow readings taken during sampling using the following equation:

$$V_m = \frac{Q_1 + Q_2 \ldots Q_n}{N} \times \frac{t}{1000} \quad (5)$$

where:

V_m = total sample volume at ambient conditions, m^3,
Q_1, $Q_2 \ldots Q_n$ = flow rates determined at the beginning, end, and intermediate points during sampling, L/min,
N = number of data points, and
t = elapsed sampling time, min.

15.3 Calculate the volume of air sampled at standard conditions of temperature and pressure (25°C and 101 kPa) using the following equation:

$$V_s = V_m \times \frac{P_A}{101} \times \frac{298}{273 + T_A} \quad (6)$$

where:

V_m = total sample flow under ambient conditions, m^3,
P_A = ambient pressure, kPa, and
T_A = ambient temperature, °C.

15.4 Calculate the concentration of each analyte in the air sample as follows:

$$C_a, \text{ ng/m}^3 = \frac{(C_e)(V_e)}{V_s} \quad (7)$$

where:

V_e = final volume of extract, µL

16. Quality Assurance

16.1 Prepare calibration standards every one to two months and check them for accuracy against commercially available PAH standard mixtures. Standard Reference Material (SRM) 1491 from the National Institute for Standards and Technology (NIST), U.S. Department of Commerce, Gaithersberg,

Maryland, U.S.A. is an appropriate standard reference solution. It is certified for 23 PAH.

16.2 Analyze calibration standards immediately before and after each set of samples that are injected into the GC/MS.

16.3 Add a performance standard such as fluoranthene-d_{10} or other suitable surrogate to the purified sample extract prior to analysis to monitor instrument/operator variability.

16.4 Closely monitor the recovery efficiencies of the isotopically-labeled PAH surrogates added to the samples prior to extraction and analysis to ensure the effectiveness of sample work-up and analytical procedures.

16.4.1 The surrogate recoveries should fall between 75 to 125 %. Samples for which surrogate recoveries are less than 50 % or more than 150 % shall be discarded.

16.4.2 Typically, measured PAH analyte concentrations are not corrected for surrogate recovery.

16.5 Perform duplicate analyses on approximately 10 % of the sample extracts to assure acceptable analytical precision.

16.6 To ensure acceptable analytical accuracy, perform periodic analyses of a known standard reference material, such as NIST SRM 1649 (urban dust, with certified values for five PAH).

17. Method Sensitivity

17.1 *Sensitivity*— The sensitivity of this test method is proportional to sample volume. A350 m^3 sample will afford method detection limits of less than 0.05 ng/m^3. Concentration of sample extracts to less than 1 mL in volume prior to analysis will increase sensitivity, but introduce the risk of analyte losses, particularly of 2- and 3-ring PAH. High-resolution mass spectrometry can also improve sensitivity.

18. Precision and Bias

18.1 *Precision*—The precision will vary with sample volume and analyte concentration. Collocated duplicate samples of 150 m^3 of ambient air collected in two U.S. cities over a one-year period have yielded an overall mean standard deviation of 13 % (range 0.03 to 45.3) for 18 PAH (naphthalene through coronene).

18.2 *Bias*—The overall bias of this test method, as determined by analysis of spiked PUF and XAD-2, is approximately ±25 % for PAH with three or more rings.

19. Keywords

19.1 ambient atmospheres; analysis; gas chromatography-mass spectrometry; polycyclic aromatic hydrocarbons; PAH

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