



Designation: D 6209 – 98^{e1}

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 D 6209; 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.

^{e1} NOTE—Paragraph 11.2.2 was corrected editorially in December 1998.

1. Scope

1.1 This test method² 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 meter (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 applica-*

bility of regulatory limitations prior to use. See also Section 8 for additional safety precautions.

2. Referenced Documents

2.1 ASTM Standards:

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres³

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere³

D 3631 Test Methods for Measuring Surface Atmospheric Pressure³

E 1 Specification for ASTM Thermometers⁴

3. Terminology

3.1 *Definitions*— For definitions of terms used in this test method, refer to Terminology D 1356.

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:

4.1.1 An air sample is collected directly from the ambient atmosphere by pulling air at approximately 225 L/min through

¹ This test method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres 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 Compendium 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 Annual Book of ASTM Standards, Vol 11.03.

⁴ Annual Book of ASTM Standards, Vol 14.03.

a fine particulate filter followed by a vapor trap containing polyurethane foam (PUF) or styrene/divinylbenzene polymer resin (XAD-2).⁵ 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 m³.

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 meter (ng/m³); those with four or more rings are usually found at concentrations of a few ng/m³ 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.

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**.⁶

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

⁵ 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 committee¹, which you may attend.

⁶ The boldface numbers in parentheses refer to the list of references at the end of this standard.

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 ₈ O	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[<i>a</i>]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[<i>b</i>]fluoranthene	C ₂₀ H ₁₂	252.32	167-168	481	6.7×10^{-8}
Benzo[<i>k</i>]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[<i>a</i>]pyrene	C ₂₀ H ₁₂	252.32	177-179	493-496	7.3×10^{-10}
Benzo[<i>e</i>]pyrene	C ₂₀ H ₁₂	252.32	178-179	493	7.4×10^{-10}
Benzo[<i>ghi</i>]perylene	C ₂₂ H ₁₂	276.34	275-278	525	1.3×10^{-11}
Indeno[1,2,3- <i>cd</i>]pyrene	C ₂₂ H ₁₂	276.34	162-163	—	ca. 10^{-11}
Dibenzo[<i>ah</i>]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}

^AMany of these compounds sublime.

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 (NO₂), 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 according to 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 between the gaskets. The sampling module is described by Lewis and Jackson (**8**)⁵. 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 m³/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 m³ 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 m³) (**17-26 and**

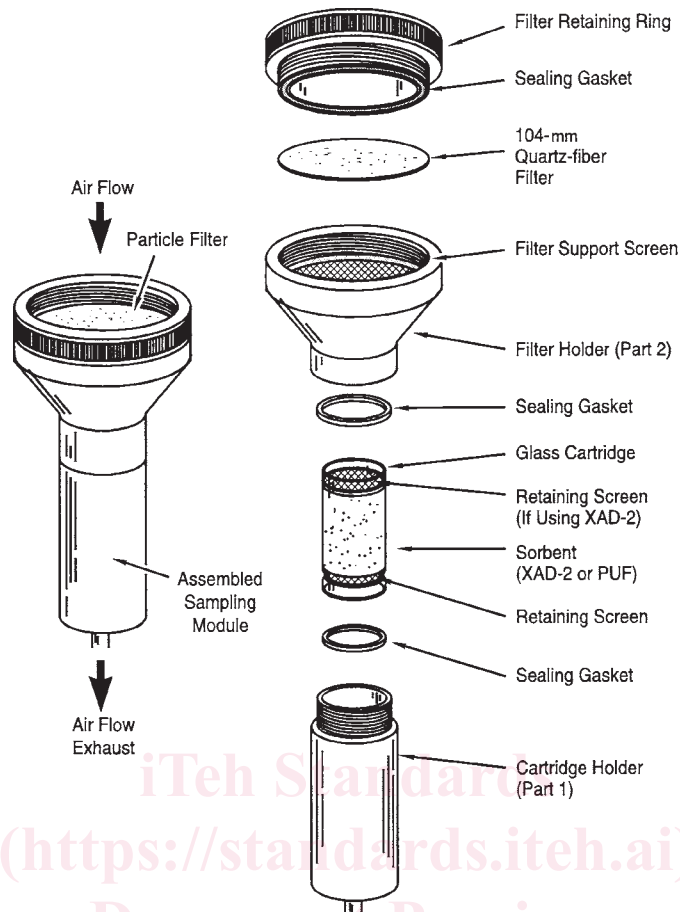


FIG. 1 Typical Sampling Module

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 Rootmeter*:

9.1.6 *Barometer*, ASTM Thermometer 33C, meeting the requirements of Specification E 1 will satisfy the requirements of most applications.

9.1.7 *Thermometer*, capable of measuring atmospheric pressure to ± 0.6 kPa. See Test Method D 3631.

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.

9.2.3 *Evaporative Concentrators*—microevaporator tubes, 1 mL, micro-Snyder columns (optional), water bath with $\pm 5^{\circ}\text{C}$ 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.

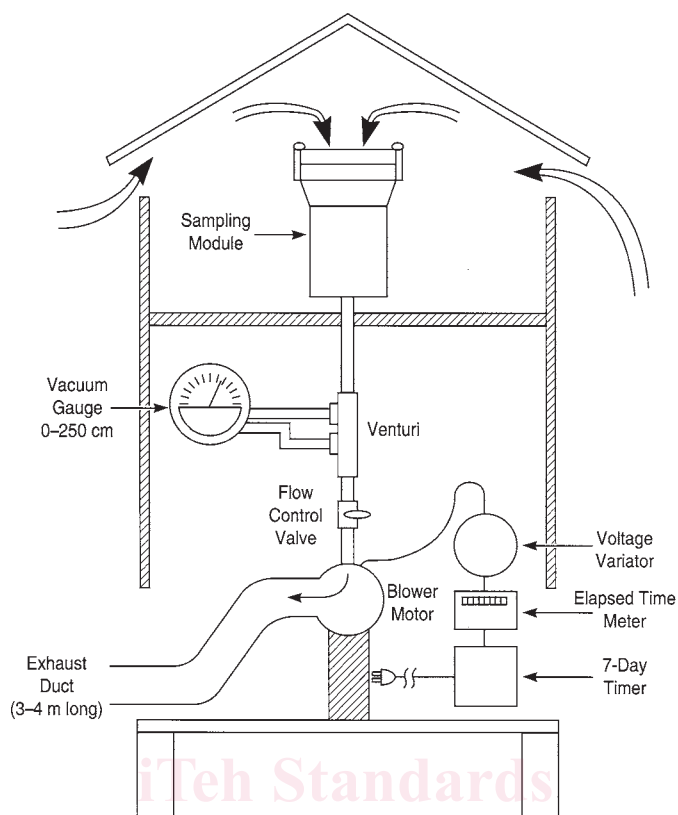


FIG. 2 Typical Air Sampling System With Sampling Module Attached

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.⁷ 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.

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*, Na₂SO₄, anhydrous, reagent grade.

⁷ Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *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.

