



# 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)<sup>1</sup>

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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method<sup>2</sup> 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 ( $\text{ng}/\text{m}^3$ ) concentrations with sampling volumes up to  $350 \text{ m}^3$  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  $\pm 35$  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  $1000 \text{ ng}/\text{m}^3$  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:*<sup>3</sup>

[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:

<sup>3</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>1</sup> 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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<sup>2</sup> 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.

**TABLE 1 Formulae and Physical Properties of Selective PAH**

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

<sup>A</sup>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).<sup>4</sup> 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<sup>3</sup>.

#### 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.

<sup>4</sup> 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<sup>1</sup>, which you may attend.

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<sup>3</sup>); those with four or more rings are usually found at concentrations of a few ng/m<sup>3</sup> or lower.

5.5 PAH span a broad spectrum of vapor pressures (for example, from 1.1 × 10<sup>-2</sup> kPa for naphthalene to 2 × 10<sup>-13</sup> 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<sup>-8</sup> 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<sup>-8</sup> 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).<sup>5</sup>

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. =  $7 \times 10^{-10}$  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<sub>2</sub>), 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

<sup>5</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.