



Designation: D7771 – 17a

Standard Test Method for Determination of Benzo- α -Pyrene (BaP) Content in Carbon Black¹

This standard is issued under the fixed designation D7771; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the qualitative and quantitative determination of only benzo- α -pyrene (BaP), a specific polycyclic aromatic hydrocarbon (PAH), on carbon black. The procedure involves Soxhlet extraction with toluene and analysis by gas chromatography with mass spectrometry (GC/MS). This method is not intended to test for U.S. Food and Drug Administration (FDA 21 CFR 178.3297) compliance of carbon blacks used for indirect food contact applications.

1.2 *Units*—The values stated in SI units are to be regarded as the standard. No other units of measurement are included in this standard.

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

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

D4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

¹ This test method is under the jurisdiction of ASTM Committee D24 on Carbon Black and is the direct responsibility of Subcommittee D24.66 on Environment, Health, and Safety.

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² 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.

2.2 EPA Standard:³

Method 8270D Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

2.3 Federal Standard:

21 CFR 178.3297 Indirect Food Additives: Adjuvants, Production Aids, and Sanitizers, Colorants for Polymers⁴

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *benzo- α -pyrene, BaP, n*—also known as 3,4-benzopyrene or benzo-a-pyrene is a specific polycyclic aromatic hydrocarbon (PAH) or polynuclear aromatic hydrocarbon that consists of fused aromatic rings with no heteroatom or substituent.

3.1.1.1 *Discussion*—PAHs naturally occur in oil, coal, and tar deposits; are produced by the incomplete combustion of hydrocarbons; and occur in many other products and processes. BaP is a pentacyclic PAH with the formula C₂₀H₁₂, related to pyrene by fusion of a phenylene group in the alpha position.

4. Summary of Test Method

4.1 A portion of carbon black is Soxhlet-extracted with toluene for 16 h. The extract is concentrated and subsequently analyzed for BaP by gas chromatography with mass spectrometry (GC/MS). The BaP quantification is performed by the means of an internal standard.

5. Significance and Use

5.1 This test procedure is used to determine the concentration of BaP extracted from carbon black by the means of a Soxhlet extraction apparatus with toluene.

6. Apparatus

6.1 *Soxhlet Extractor with Reflux Condenser*, 50- or 100-cm³ capacity.

³ Available from United States Environmental Protection Agency (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20004, <http://www.epa.gov/epaoswer/hazwaste/test/new-meth.htm#8270D>.

⁴ Available from the U.S. Government Printing Office, Superintendent of Documents, 732 N. Capital St., NW., Washington, DC 20402-0001.

TABLE 1 Native and Deuterated BaP Compounds

Native PAH	CAS#	Deuterated PAH	CAS#	C13 Labeled PAH	CAS#
Benzo- α -pyrene	50-32-8	d ₁₂ -Benzo- α -pyrene	63466-71-7	13C ₄ -Benzo- α -pyrene	Not Available

6.2 *Extraction Thimbles*, glass or cellulose, approximately 50- to 70-cm³ capacity. For instance, glass extraction thimble of 35-mm diameter by 90-mm height with coarse porosity (70 to 100 μ m similar to Ace Glass Size C, Porosity B, Code-14).

6.3 *Heating Mantle*, compatible with boiling flask described in 6.4.

6.4 *Boiling Flasks for Soxhlet*, for example, 250 cm³.

6.5 *Glass Beads*, approximately 180 to 250 μ m (60/80 mesh) if glass thimbles are used. Need to be very clean or toluene extracted.

6.6 *PTFE or Glass Boiling Beads*, approximately 3 mm.

6.7 *Glass Wool*, need to be very clean or toluene extracted.

6.8 *Rotary Evaporator*, with temperature-controlled water bath, automatic pressure regulation, and solvent-proof membrane vacuum pump.

6.9 *Nitrogen Blow-Down Apparatus*, equipped with a controlled water bath and nitrogen pressure control.

6.10 *Pear-Shaped Flasks for Rotary Evaporator*, for example, 25, 50, and 100 cm³.

6.11 *GC/MS*, with autosampler.

6.11.1 MS with electron impact (EI) capability and single-ion monitoring (SIM) mode.

6.11.2 *GC Capillary Column*, usually a nonpolar GC column composed of 5 % phenyl-methyl silicone coating is used for PAH analysis.

6.11.3 *Deactivated Straight Borosilicate Liner with Small Piece of Deactivated Glass Wool*—This liner may be used as long as peak resolution is satisfactory.

6.11.4 Alternative liner is a split/splitless nondeactivated liner with glass wool (4-mm internal diameter, straight liner). This shall be deactivated with a silanizing agent before use. Another alternative is a split/splitless liner with fluorocarbon liner seals. Such a liner will already contain conditioned silanized glass wool. Other liners can be used if they produce acceptable results.

6.11.5 Gold-plated seal for GC injector port or similar nonreactive seal.

6.11.6 GC/MS amber autosampler vials with polytetrafluoroethylene (PTFE)-coated caps.

6.11.7 Crimping tool.

6.12 *Adjustable Micropipettes*, 1000, 200, and 20 μ L.

6.13 *Microliter Syringes of Different Volumes*, for example, 10 and 100 μ L.

6.14 *Amber Glass Vials*, approximately 4 cm³ with caps (rubber with PTFE back).

6.15 *Amber Volumetric Flasks*, 2, 3, 5, 10, 25, and 100 cm³.

6.16 *Analytical Balance*, with an accuracy of 0.01 mg.

6.17 *Drying Oven*, gravity convection type, capable of maintaining 40 \pm 10°C, used for slowing down the cooling when the glassware is taken out of the muffle furnace.

6.18 *Furnace*, capable of temperature regulation of 500 \pm 25°C, used to burn off organic contamination from glass surfaces.

6.19 *Manometer*, capable of pressure readings in the range of 5 \pm 0.3 kPa.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Separate stock solutions of the native BaP standards and of the internal standard (deuterated or C13-labeled) can be purchased as premade solutions or prepared from solid materials (Table 1).

7.2.1 A concentration range of 80 to 100 μ g/cm³ for the native BaP analyte stock solution is recommended.

7.2.2 A similar concentration range of 80 to 100 μ g/cm³ of the deuterated (d₁₂-benzo- α -pyrene) or isotopically-labeled (13C₄-benzo- α -pyrene) is recommended for the internal standard (IS) stock solution.

7.2.3 All purchased BaP standard materials shall be 98 % pure or better and certified with respect to their purity and concentration by the manufacturer. Follow the manufacturer's recommendation on how best to store the standard solutions. Typically, the compounds are protected from light. They should be checked frequently for signs of degradation or evaporation. The BaP standard stock solutions shall be replaced/recertified on a yearly basis or sooner if comparisons with quality control (QC) samples indicate a problem.

7.3 *Toluene*, suitable for high resolution gas chromatography analysis (99.99 % pure).

7.4 *Acetone*, suitable for high resolution gas chromatography analysis (99.99 % pure).

7.5 *Helium*, GC/MS purity grade.

7.6 *Nitrogen*, analytical purity grade.

⁵ *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 Formulary*, U.S. Pharmacopeial convention, Inc. (USPC), Rockville, MD.

7.7 Silica gel columns for Solid Phase Extraction (SPE) removal of polar compounds.

7.7.1 *Silica SPE Cartridges*, single-use application, having a volume capacity of approximately 1 to 10 cm³.⁶

7.7.1.1 *Preparation of Silica SPE Cartridge*—Follow the manufacturer’s instruction for preparation and use. The typical method of preparation is to wet the cartridge with approximately 10 cm³ of the elution solvent (toluene). Discard the wetting solvent.

7.7.2 *Alternative SPE Method: Silica Gel/13 % H₂O Gravity Column*:

7.7.2.1 *Preparation of a Silica Gel/13 % H₂O Adsorbent*—Pour 200 g silica gel (high purity grade, type 60, particle size 0.063 to 0.200 mm) into a screw cap glass bottle and add 30 g of deionized water in small portions (for example, 2 cm³) using a suitable pipette. After addition of each portion of water, the silica gel bottle is shaken to evenly distribute the wetted silica gel. No aggregation should occur during this process. If so, shaking must be continued until a homogeneous material is obtained. Finally, the closed bottle is shaken for 8 hours by means of an overhead shaker. If properly closed and stored, the adsorbent should be viable for at least 6 months.

7.7.2.2 *Preparation of a Silica Gel/13 % H₂O Gravity Column*—Insert a glass wool plug into the bottom of a pipette tip (for example, 8 to 10 mm inner diameter and 5 cm³ capacity). Place 1 g of the silica gel/13 % H₂O in the column and tap the column gently to settle the silica gel. Cover the adsorbent layer with a glass wool plug and pre-elute the column with 5 cm³ of cyclohexane. Discard the cyclohexane eluate.

8. Hazards

8.1 This test involves hazardous materials, operations, and equipment. This procedure does not attempt to address the safety problems associated with this test. A hazards review shall be conducted by all personnel performing the test. It is the responsibility of the user to review all material safety data sheets (MSDS), manuals, and hazards procedures and establish the appropriate safety measures. Some PAH compounds have been shown to possess mutagenic as well as carcinogenic and teratogenic properties. As such, concentrated extracts of carbon blacks containing PAHs also may possess the same harmful properties. Solvents used are flammable. Appropriate personal protection equipment (PPE) shall be used.

9. Preparation of Standard Solutions

9.1 The GC/MS instrument is calibrated using five solutions of the native BaP and internal standard (IS). The recommended BaP concentrations are to cover a range of 0.0125 to 1.0 µg/cm³ (ppm). Other concentrations may be used as needed for the application. The IS concentration is kept constant within the calibration range. Preferably the IS concentration is in the middle of the selected calibration range (for example, 0.3 to 0.6

µg/cm³). A lower BaP concentration range can be used for the case of high-purity carbon blacks. However, the IS concentration should maintain an S/N ratio of at least 15/1 for routine instrument performance. Subsections 9.2 – 9.4 describe the preparation of the various solutions required.

9.2 *Preparation of Native BaP Standard Solutions for Calibration*—Using the native BaP standard stock solution described in 7.2, prepare at least 10 cm³ of five toluene solutions in amber glassware at the concentrations suggested below. Other concentrations may be used but the difference between any two concentration levels shall not exceed a factor of four. Before diluting to the final solution volume, spike each standard with the appropriate volume (for example, 100 µL IS solution described in 9.3) to give a final IS concentration of 0.500 µg/cm³. Other aliquot volumes and final volumes may be used to obtain the desired concentrations. Cap the standard solutions securely, mix thoroughly, and label.

Native BaP Standard 5	1.00 µg/cm ³
Native BaP Standard 4	0.500 µg/cm ³
Native BaP Standard 3	0.200 µg/cm ³
Native BaP Standard 2	0.0500 µg/cm ³
Native BaP Standard 1	0.0125 µg/cm ³

9.3 *Preparation of Diluted IS Solution*—Using the IS stock solution described in 7.2, prepare a convenient volume (for example, 10 cm³) of diluted internal standard solution that will be later added to samples and calibration standards. A concentration of 50.0 µg/cm³ is suggested for this diluted IS solution in order to achieve a final concentration of 0.500 µg/cm³ in the extract sample.

NOTE 1—Other concentrations within the calibration range can be used as well.

9.4 All standard solutions shall be stored in amber glassware and kept in a refrigerator (<6°C) when not in use. Care has to be taken not to exceed their shelf life. If any indication of degradation is perceived, then new standards have to be prepared.

10. Carbon Black Sample Preparation and Extraction

10.1 All glassware parts coming into contact with the sample shall be BaP free on the basis of the limits of quantification. It is strongly recommended to use separate glassware and extraction units for high-purity carbon blacks and carbon blacks in which higher BaP levels are expected. Blanks should be run on a regular basis.

10.2 Glassware should be rinsed with toluene and acetone after use. The glassware is then dried at 150°C in a laboratory drying oven.

10.3 For low BaP carbon blacks, a pre-extraction of the extraction unit for at least 4 h is recommended. If glass thimbles are not baked in a furnace as described in 10.5, then the thimbles should be included in the 4 h pre-extraction. Cellulose thimbles should be included in the 4 h pre-extraction. In this case, the thimbles are further dried, for example, in a vacuum drying oven prior to use.

10.4 Disposable devices such as cellulose thimbles are rinsed with toluene and dried prior to use, for example, in a vacuum oven.

⁶ The sole source of supply of the Sep-Pak cartridges known to the committee at this time is Waters, 34 Maple Street, Milford, MA 01757 (www.waters.com). If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.