



Designation: D7771 – 11

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) 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

D4527 Test Method for Carbon Black—Solvent Extractables

2.2 EPA Standard:

Method 8270D Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)³

2.3 Federal Standard:

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

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.

Current edition approved Nov. 1, 2011. Published December 2011. DOI: 10.1520/D7771-11.

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.

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.

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 consist 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 a specified period of time. The resultant extract is purified by solid-phase extraction (SPE), concentrated down to a known volume, and subsequently analyzed for BaP by gas chromatography with mass spectrometry (GC/MS). The BaP quantification is performed by the means of a deuterated internal standard (isotope dilution).

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.

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 course 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 µL.

6.13 *Microlitre Syringes of Different Volumes*, for example, 10 and 100 µL.

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 ± 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 ± 25°C, used to burn off organic contamination from glass surfaces.

6.19 *Manometer*, capable of pressure readings in the range of 5 ± 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 deuterated internal standard (IS) and of the nondeuterated (native) BaP standards can be purchased prepared from solid materials or individual solutions (Table 1). A concentration range of 80 to 100 µg/cm³ for both the native BaP and d₁₂-benzo(a)pyrene is recommended. All purchased BaP standard materials shall be 98 % pure or better and certified in respect of their purity, concentration level, and authenticity by the manufacturer.

7.2.1 Follow the manufacturer's recommendation on how best to store the standard stock solutions. It is generally accepted to keep them protected from light. They should be checked frequently for signs of degradation or evaporation, especially just before preparing calibration standards from them. The BaP standard stock solutions shall be replaced/recertified on a yearly basis or sooner if comparisons with quality control (QC) samples indicates 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.

7.7 *Silica Solid-Phase Extractor Cartridges*, single-use application, having a volume capacity of approximately 5 cm³ or 2- to 3-cm length by 1-cm diameter.⁶

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.

TABLE 1 Native and Deuterated BaP Compounds

PAH	CAS#	Deuterated PAH	CAS#
Benzo(a)pyrene	50-32-8	d ₁₂ -Benzo(a)pyrene	63466-71-7

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.

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 will then determine the

9. Preparation of Standard Solutions

9.1 The GC/MS instrument is calibrated through five mixtures of the native BaP and deuterated IS. The recommended BaP concentrations are to cover a range of approximately 0.01 to 0.8 $\mu\text{g}/\text{cm}^3$ (ppm) while the IS concentration is kept constant at around 0.3 $\mu\text{g}/\text{cm}^3$. A lower BaP concentration range can be used for the case of high-purity carbon blacks, but the difference between any two concentration levels shall not exceed a factor of four. Furthermore, the IS concentration should maintain an S/N ratio of at least 15/1 for routine instrument performance. Subsections 9.2-9.5 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 cm^3 of five toluene solutions in amber glassware at the concentrations suggested in the following. Cap securely the standard solutions, mix thoroughly, and label.

Native BaP Standard 5	0.85 $\mu\text{g}/\text{cm}^3$
Native BaP Standard 4	0.28 $\mu\text{g}/\text{cm}^3$
Native BaP Standard 3	0.09 $\mu\text{g}/\text{cm}^3$
Native BaP Standard 2	0.03 $\mu\text{g}/\text{cm}^3$
Native BaP Standard 1	0.01 $\mu\text{g}/\text{cm}^3$

9.3 *Preparation of the Deuterated IS Solution*—Using the deuterated IS stock solution described in 7.1, prepare at least 50 cm^3 of a diluted toluene solution in amber glassware at the concentration suggested in the following. Cap securely the standard solutions, mix thoroughly, and label.

IS Standard	3.3 $\mu\text{g}/\text{cm}^3$
-------------	-------------------------------

9.4 *Preparation of the BaP Calibration Solutions*—Into five separate amber GC/MS vials, pipette 1.000 cm^3 of the native BaP standards prepared in 9.2 and 0.100 cm^3 of the IS standard solution prepared in 9.3. Cap securely the amber GC/MS vials, mix thoroughly, and label. The following is obtained:

Cal BaP 5	0.773 $\mu\text{g}/\text{cm}^3$ native BaP + 0.300 $\mu\text{g}/\text{cm}^3$ IS
Cal BaP 4	0.255 $\mu\text{g}/\text{cm}^3$ native BaP + 0.300 $\mu\text{g}/\text{cm}^3$ IS
Cal BaP 3	0.082 $\mu\text{g}/\text{cm}^3$ native BaP + 0.300 $\mu\text{g}/\text{cm}^3$ IS
Cal BaP 2	0.027 $\mu\text{g}/\text{cm}^3$ native BaP + 0.300 $\mu\text{g}/\text{cm}^3$ IS
Cal BaP 1	0.009 $\mu\text{g}/\text{cm}^3$ native BaP + 0.300 $\mu\text{g}/\text{cm}^3$ IS

9.5 All standard solutions shall be stored in amber glassware and kept in a refrigerator ($<6^\circ\text{C}$) when not in use. Care has to be taken not to exceed their shelf life. If any indication on degradation is perceived, the standard has to be prepared anew.

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.

10.5 If repeated cleanings and extractions do not produce clean blanks, certain parts of the glassware may also be baked for at least 6 h in a furnace at, for example, 500°C . This is also valid for glass extraction thimbles if used. It shall be determined with the manufacturer if the glass parts can sustain such temperature—for example, it is unlikely the Soxhlet can sustain this.

10.6 If glass extraction thimbles are used, they should be checked for their drain rate at room temperature by pouring 50 cm^3 of toluene inside the thimble. The time for 40 cm^3 to drip out of the thimble should not exceed 95 s. Otherwise, the thimble is to be discarded. Dry the thimbles with clean nitrogen.

10.7 If glass extraction thimbles are used, pour the 60/80-mesh glass beads into the thimbles to a depth of 1 cm. Sizes other than 60/80 mesh may be used.

10.8 Weigh 10 ± 0.1 g to the nearest 1 mg of the beaded carbon black sample into the dried extraction thimble. Record the exact value as W_{CB} .

10.8.1 Fluffy or powder carbon black should be densified with toluene before extraction. This is accomplished by weighing 10 ± 0.1 g of carbon black into a beaker and adding toluene in approximately 1- cm^3 aliquots and mixing the toluene into the carbon black with a spatula after each aliquot is added. This densifies the carbon black and forms pellets. Add sufficient toluene to densify the entire sample into crude pellets. The beakers shall then be left in the hood overnight to evaporate the solvent. Once the solvent has evaporated, break up the larger of the carbon black pellets with a spatula. The entire amount of pelletized black is then transferred to the thimble.

10.9 Place a plug of glass wool or fold the top of the cellulose thimble above the black. The plug of wool should be placed such that the glass wool is in contact with the carbon black. This facilitates drainage of solvent through the glass wool and into the carbon black bed.

10.10 Add a few glass boiling beads into the clean 250- cm^3 boiling flask and pour approximately 150 cm^3 of toluene. Assemble the extraction apparatus. To maintain temperature uniformity throughout the system, wrap the Soxhlet extractor and the boiling flask with aluminum foil. Record the Soxhlet position number, thimble identification (for glass thimbles), and extraction date.

10.11 *Extraction Settings and Conditions:*

10.11.1 Samples are extracted for 16 h.