



Designation: D 3765 – 02

Standard Test Method for Carbon Black—CTAB (Cetyltrimethylammonium Bromide) Surface Area¹

This standard is issued under the fixed designation D 3765; 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 measurement of the specific surface area of carbon black exclusive of area contained in micropores too small to admit hexadecyltrimethylammonium bromide (cetyltrimethylammonium bromide, commonly referred to as CTAB) molecules. This test method is suitable for characterizing rubber-grade carbon blacks of all types.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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:*

D 1193 Specification for Reagent Water²

D 1799 Practice for Carbon Black—Sampling Packaged Shipments³

D 1900 Practice for Carbon Black—Sampling Bulk Shipments³

D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries³

3. Summary of Test Method

3.1 The isotherm for adsorption of an aqueous solution of CTAB on carbon black has a long horizontal plateau corresponding to a monolayer coverage of the substrate surface from which the adsorbate is not sterically excluded. The CTAB adsorption by carbon black is independent of residual tars and functional groups containing hydrogen and oxygen, etc. Rapid equilibration is achieved by using mechanical stirring and ultrasonic vibration. Titration with dioctyl sodium sulfosuccinate (Aerosol OT⁴) solution to a turbidity maximum end point is used to determine the unadsorbed CTAB after removal of the colloiddally dispersed carbon black by ultrafiltration. All results are scaled by using the Industry Tint Reference Black (ITRB) as a primary standard and taking its accessible surface area to be exactly $83.0 \times 10^3 \text{ m}^2/\text{kg}$.

3.2 Titration of the unadsorbed CTAB with Aerosol OT solution is accomplished by the following:

3.2.1 *Part A*—Automatic Titration.

3.2.2 *Part B*—Manual Turbidity Titration.

4. Significance and Use

4.1 The CTAB molecule is relatively large; so it is not adsorbed in micropores or on surface roughness. Thus, the CTAB surface area reflects only the surface of the carbon black that is available for interaction with rubber molecules.

5. Apparatus

5.1 *Analytical Balance*, 0.1-mg sensitivity.

5.2 *Ultrasonic Cleaning Bath*,⁵ modified to incorporate integral magnetic stirring and vial holder to properly position two sample vials. (If desired, a separate ultrasonic cleaning bath⁶ and a separate magnetic stirrer⁷ may be used.)

5.3 *Magnetic Spinbars*,⁸ chemically resistant covered (polychlorotrifluoroethylene or TFE-fluorocarbon), 6.4 or 4.8-mm ($1/4$ or $3/16$ -in.) diameter, and length nearly equal to the diameter of 50 or 100-cm³ Berzelius beakers, glass vials, or other glass vessels.

5.4 *Microfiltration Membrane Filter Disks*,⁹ 47-mm diameter.

⁴ Aerosol OT is a registered trademark of the American Cyanamid Co., Process Chemicals Dept., Wayne, NM 07470.

⁵ Available from L.A. King Manufacturing Corp., LAKO Division, P.O. Box 2415, Tulsa, OK 74101.

⁶ Millipore Corp., Bedford, MA 01730, Catalog No. XX 66 00900 is satisfactory.

⁷ Sargent magnetic stirrer S-76490 is satisfactory.

⁸ Examples of suitable spinbars are Catalog No. 9235-U7, A. H. Thomas Co., Philadelphia, PA 19105, or Catalog No. S-76497-30, Sargent Welch Scientific Co., Skokie, IL 60076.

⁹ This test is based on the use of three brands of microfiltration membrane: (1) Gelman HT-200, Gelman No. 66199, Baxter Scientific Cat. No. F2988-2, Baxter Scientific Products, 1430 Waukegan Rd., McGraw Park, IL 60085; (2) Microfiltration Systems, Cat. No. A-010A047A, 6800 Sierra Court, Dublin, CA 94566; and (3) Millipore Cat. No. SAIJ076H7 Filters, Millipore Corp., Bedford, MA 01730.

¹ This test method is under the jurisdiction of ASTM Committee D24 on Carbon Black and is the direct responsibility of Subcommittee D24.21 on Adsorptive Properties of Carbon Black.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 09.01.

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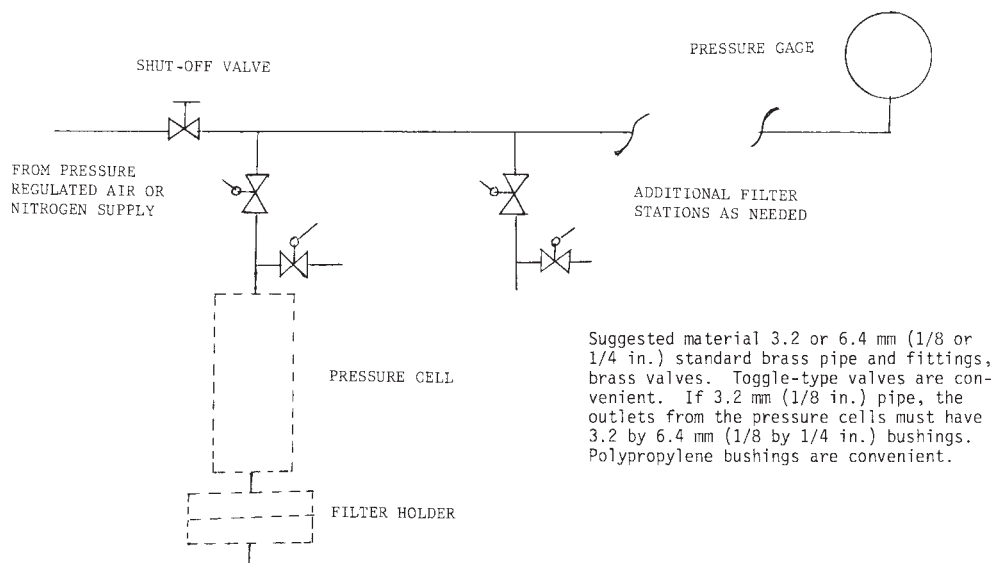


FIG. 1 Pressure Filtration Manifold

Suggested material 3.2 or 6.4 mm (1/8 or 1/4 in.) standard brass pipe and fittings, brass valves. Toggle-type valves are convenient. If 3.2 mm (1/8 in.) pipe, the outlets from the pressure cells must have 3.2 by 6.4 mm (1/8 by 1/4 in.) bushings. Polypropylene bushings are convenient.

5.5 Filter Holder.¹⁰

5.6 Sampling Cylinder, 30-cm³ stainless steel, double end with 6.4-mm (1/4-in.) NPT female openings, suitable for 0.7-MPa (100-psi) pressure.¹¹

5.7 Pressure Manifold, connected to air or nitrogen supply regulated at 0.4 to 0.7 MPa (60 to 100 psi). Fig. 1 shows a schematic diagram of a typical assembly.

5.8 Glass Funnel, small.

5.9 Glass Vials, with plastic screw caps, 28 mm in outside diameter, about 40-cm³ capacity (11-dram size).

5.10 Buret, 50-cm³, 0.1-cm³ divisions, Class A, preferably of automatic refilling and zeroing type (Note 1) with reagent reservoir.

NOTE 1—Automatic burets are usually not certified to Class A tolerance. Such burets should be checked for accuracy, and, if in error by more than 0.05 cm³ at any point, a calibration curve should be prepared and used to correct observed buret readings. Burets with TFE-fluorocarbon manostat valves offer some advantage in ease of stopcock manipulation in delivering small increments of titrant.

5.11 Dispenser-Type Pipet,¹² 50-cm³, attached to a suitable reservoir for CTAB solution.

5.12 Pipet, 10-cm³, Class A.

5.13 Erlenmeyer Flasks, or beakers, 50 or 100-cm³.

5.14 Dropping Bottle, 60-cm³ amber.

5.15 Jar, wide-mouth, plastic screw cap, 118 or 236-cm³ (4 or 8-oz) size.

5.16 Gravity Convection Drying Oven, capable of maintaining 125 ± 5°C.

5.17 Microscope Spotlight.

5.18 TFE-fluorocarbon Pipe Thread Sealing Tape.

5.19 Magnetic Stirrer.

5.20 Containers, suitable for preparation and storage of reagent solutions.

5.21 Automatic Titration Equipment,¹³ with instruction manual.

5.22 Beakers, 100-cm³ Berzelius, tall form, (one furnished with automatic titration equipment).

5.23 Thermometer, to measure temperature in a range from 20 to 40°C.

5.24 Polyethylene Tubing (do not use vinyl tubing).

NOTE 2—All apparatus must be kept chemically clean. Contamination of equipment, water supply, or chemicals by ionic surfactants must be particularly avoided. The filtration equipment, especially the region below the perforated plate in the filter holder, must not be permitted to accumulate carbon black or cleanser residues.

6. Reagents

6.1 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.¹⁴ 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.

¹⁰ This test is based on the use of Swinnex-47 filter holders obtained from Millipore Corp. as Catalog No. SX00 047 00.

¹¹ Hoke, Inc., Kresskill, NJ 07626, No. 4DY30 is suitable.

¹² This test is based on the use of the Universal Repipet, a registered trademark of Labindustries, 1802 Second St., Berkeley, CA 94710.

¹³ This test is based on the use of three sources of automatic titration equipment: (1) Mettler Memotitrator DL40RC, Mettler Instrument Co., Box 71, Highstown, NJ 08520, (2) Brinkman Dosimat 665 Buret, Brinkman Instruments, Inc., Cantiague Rd., Westbury, NY, and (3) ATMAST, available from L. A. King Manufacturing Corp., LAKO Division, P.O. Box 2415, Tulsa, OK 74101. The Probe Colorimeter, also available from Brinkman Instruments, has been found to be an acceptable automatic means of detecting the titration end point. This piece of equipment may be integrated with the Brinkman Dosimat 665 Buret.

¹⁴ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."