Designation: D6845 – 12

Standard Test Method for Silica, Precipitated, Hydrated—CTAB (Cetyltrimethylammonium Bromide) Surface Area[1]

This standard is issued under the fixed designation D6845; 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 precipitated silicas 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 silicas 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:*[2]

D1193 Specification for Reagent Water
D1799 Practice for Carbon Black—Sampling Packaged Shipments
D1900 Practice for Carbon Black—Sampling Bulk Shipments
D4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Summary of Test Method

3.1 The isotherm for adsorption of an aqueous solution of CTAB on silicas 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 silica is independent of functional groups containing hydrogen and oxygen, etc. Rapid equilibration is achieved by using mechanical stirring. Titration with dioctyl sodium sulfosuccinate (Aerosol OT[3]) solution to a turbidity maximum end point is used to determine the unadsorbed CTAB after removal of the colloidally dispersed silica by ultrafiltration.

3.2 Titration of the unadsorbed CTAB with Aerosol OT solution is accomplished by automatic 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 silica that is available for interaction with rubber molecules.

5. Apparatus

5.1 *Analytical Balance,* 0.1 mg sensitivity.

5.2 *Centifuge,* capable of 67 rev/s (4000 r/m).

5.3 *Magnetic Spinbars,*[4]chemically resistant covered (polychlorotrifluoroethylene or TFE-fluorocarbon), 6.4- or 4.8-mm (¼- or ³⁄₁₆-in.) diameter, and length nearly equal to the diameter of 50 or 100 cm^3 Berzelius beakers, glass vials, or other glass vessels.

5.4 *Glass Funnel,* small.

5.5 *Glass Vials,* with plastic screw caps, 28 mm in outside diameter, about 40 cm^3 capacity.

5.6 *Buret,* 50 cm^3, 0.1 cm^3 divisions, Class A, preferably of automatic refilling and zeroing type (see Note 1) with reagent reservoir.

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[1] This test method is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.20 on Compounding Materials and Procedures.

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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.

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

[4] 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.

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 cm^3 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.

5.7 *Dispenser-Type Pipet,*[5] 50 cm^3, attached to a suitable reservoir for CTAB solution.

5.8 *Pipet,* 10 cm^3, Class A.

5.9 *Erlenmeyer Flasks,* or beakers, 50 or 100 cm^3.

5.10 *Dropping Bottle,* 60 cm^3 amber.

5.11 *Jar,* wide-mouth, plastic screw cap, 120 or 240 cm^3 (4- or 8-oz) size.

5.12 *Gravity Convection Drying Oven,* capable of maintaining 105 ± 5°C.

5.13 *Magnetic Stirrer.*

5.14 *Containers,* suitable for preparation and storage of reagent solutions.

5.15 *Automatic Titration Equipment with 550 nm Photoprobe,*[6] with instruction manual.

5.16 *Beakers,* 100 cm^3 Berzelius, tall form (one furnished with automatic titration equipment).

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

5.18 *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.

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.[7] 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type 1 in Specification D1193.

6.3 *Sodium Hydroxide Solution (1M)*—Dissolve 40.0 g NaOH in a 1 dm^3 flask containing 0.5 dm^3 reagent water. After dissolution fill to mark.

6.4 *Buffer Solution of pH 9.6 (0.05 M)*—Prepare buffer solution by dissolving 3.101 g of orthoboric acid (H_3BO_4), 3.708 g of potassium chloride (KCl) and 36.85 cm^3 of sodium hydroxide (NaOH) solution in a 1 dm^3 flask containing 0.5 dm^3 reagent water. After dissolution fill to mark. Verify that the pH of the solution is 9.6 ± 0.1.

6.5 *CTAB Standard Solution*—Dissolve 5.5 g of reagent-grade CTAB[8] in a 1 dm^3 flask containing 350 dm^3 of buffer solution and 500 dm^3 water. After dissolution fill to mark. Homogenize on a magnetic stirrer for 10 h. Allow to stand 24 h before use. Verify that the pH of the solution is 9.6 ± 0.1 before use. If not, adjust the pH with either 0.1 N NaOH solution (too low) or 0.1 N HCl solution (too high). (**Warning—** Storage of the solution below 22°C will result in slow crystallization of the CTAB.)

6.6 *Aerosol OT*[9] Solution 100 % Grade (approximately 0.00389 M)—Dissolve 1.73 g/dm^3 of Aerosol OT solution (100 % solids) in 500 cm^3 distilled or deionized water. Stir vigorously with a magnetic stirrer for 10 h. Allow to stand an additional twelve days before standardization and use. The solution should be capped tightly and stored in a cool place. (Once opened, 100 % Aerosol OT should be stored in a desiccator.)

6.7 *Distilled or Deionized Water.*

6.8 *Octylphenoxy Polyethoxyethanol (Triton X-100*[10]) Solution (0.15 %)—Dissolve 1.5 g in 1 dm^3 of Triton X-100 (100 % liquid) in distilled or deionized water by swirling vigorously with a magnetic stirrer until a homogeneous solution is obtained.

7. Sampling

7.1 No separate practice for sampling silicas is available. However, samples may be taken in accordance with Practices D1799 or D1900.

8. Standardization of Reagents

8.1 Duplicate blanks are determined and averaged.

8.2 Pipet 10 cm^3 of CTAB solution into a beaker.

8.3 Add 50 cm^3 of distilled or deionized water.

8.4 Titrate with Aerosol OT using automatic titrator until endpoint is reached.

8.5 Use average of both repetitions when calculating CTAB of silica sample in Section 10.

9. Procedure

9.1 Dry an adequate portion of sample of silica at 105°C for 2 h and cool in a desiccator.

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

[6] This test is based on the use of two sources of automatic titration equipment: (*1*) Mettler Memotitrator DL21, Mettler Instrument Co., Box 71, Highstown, NJ 08520, and (*2*) Brinkman Dosimat 665 Buret, Brinkman Instruments, Inc., Cantiague Rd., Westbury, NY. 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.

[7] *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*.

[8] Available from J. T. Baker Chemical Co., 222 Red School Lane, Phillipsburgh, NJ 08865, Catalog No. 7N121.

[9] Available from American Cyanamid Co., Process Chemicals Dept., Wayne, NM 07470. Also available as Catalog No. A-349 from Fisher Scientific Co.

[10] Triton X-100 is a registered trademark of Rohm and Haas Co.

TABLE 1 CTAB Surface Area (m^2g)

Material	Average^A	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	s_r	s_R	r	R
Silica A	161.4	1.17	3.19	3.27	8.93
Silica B	194.2	1.03	7.58	2.88	21.21

^A The average of the laboratories' calculated averages.

NOTE 3—If the heating loss of the silica is known, the drying step may be omitted and the observed sample mass corrected for heating loss to obtain the mass of dry sample, *W*.

9.2 Weigh, to 0.1 mg, a suitable sample of the dried silica into a glass vial and record the mass as *W*. Appropriate sample masses may be selected as follows:

Approximate Surface Area, m^2/g (SA)	Sample Mass, g
$SA \leq 90$	0.600
$90 < SA \leq 120$	0.500
$120 < SA \leq 175$	0.400
$175 < SA \leq 220$	0.300
$220 < SA$	0.200

An appropriate sample mass may also be taken as Vo/S_{est} in g, where S_{est} is some estimate of the expected CTAB surface area.

9.3 Insert a magnetic spinbar into the vial. Add 30.0 cm^3 of CTAB solution from the dispensing pipet or buret taking care to prevent foaming of the solution. Cap the vial.

9.4 Place the vial on a magnetic stirrer. Adjust the stirrer to give a vigorous stirring by the spinbar to produce a deep votex without foaming. Stir for 40 min.

9.5 Immediately after completion of the stirring, decant the suspension into a centrifuge tube.

9.6 Separate the silica from the suspension by centrifuging for 20 min at 4000 rpms.

9.7 Pipet a 10.00 cm^3 aliquot of the CTAB solution from the centrifuge tube into a 100 cm^3 beaker containing a TFE-fluorocarbon covered magnetic spin bar 41 mm long by 10 mm in diameter (1.625 by 0.375 in.), taking care to avoid transferring any silica.

9.8 *Titration (Automatic):*

9.8.1 Prepare the automatic titration apparatus according to the instructions furnished with it. Ascertain that the titrant reservoir contains sufficient Aerosol OT solution and that the fluid lines and the pump head are free of air bubbles and have been flushed sufficiently with titrant. Turn the power on and loosen the titrant reservoir cap to admit air as liquid flows out. Adjust the titrant flow rate to 10 cm^3/min.

9.8.2 Lower the 550 nm photo probe into the solution.

9.8.3 Lower the titrant delivery assembly so that the delivery needle is just below the surface of the liquid and open the titrant stopcock.

9.8.4 Set the pump control switch to the "titrate" position and press the "start" button.

9.8.5 After the system stops record the amount of OT dispensed.

9.8.6 Raise the titrant delivery tube clear of the beaker.

9.8.7 Move the pump control to "flush" and allow a few drops of titrant to clear the needle. After the pump stops, close the stopcock and remove the needle from the beaker. Wipe the needle with a clean tissue (do not use solvent).

9.8.8 Remove and rinse the photoprobe with distilled water.

9.8.9 The unit is now ready for another sample.

10. Calculation

10.1 Calculate the CTAB surface area to the nearest 0.1 × 10^3 m^2/g as follows:

$$S = (2V_0 - V) \times 4774/[V_0 \times W(100 - Vol)] \quad (1)$$

where:

S = CTAB surface area of dried silica, 10^3 m^2 /g,
V_0 = volume of OT required to titrate 5 cm^3 of CTAB (Blank),
V = aerosol OT solution required for the 10 cm^3 sample,
W = sample mass, g, and
Vol = volatile matter of silica, %.

11. Report

11.1 Report the following information:

11.1.1 Proper identification of the silica sample and

11.1.2 Result obtained from an individual determination, reported to the nearest 0.1 × 10^3 m^2/g.

12. Precision and Bias[11]

12.1 The precision of this test method is based on an interlaboratory study conducted in 2010. Nine laboratories tested two types of silica samples. Every "test result" represents an individual determination. Each laboratory was instructed to report four replicate test results for each material. Practice E691 was followed for the design and analysis of the data.

12.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "r" value for that material; "r" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

12.1.1.1 Repeatability limits are listed in Table 1.

12.1.2 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the "R" value for that material; "R" is the interval representing the critical

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[11] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D11-1110.

difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

12.1.2.1 Reproducibility limits are listed in Table 1.

12.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

12.1.4 Any judgment in accordance with statements 12.1.1 and 12.1.2 would have an approximate 95 % probability of being correct.

12.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

12.3 The precision statement was determined through statistical examination of 72 results, from nine laboratories, on two different precipitated silica samples. One of the 9 labs has been indicated as being an outlier. These results have been removed from the study.

13. Keywords

13.1 cetyltrimethylammonium bromide; CTAB; silica; surface area by CTAB method; turbidity titration

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