# Standard Test Method for Precipitated Silica-Surface Area by Multipoint BET Nitrogen Adsorption[1]

This standard is issued under the fixed designation D1993; 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.

ε¹ NOTE—Editorially corrected 2.1 and related references in February 2016.

## 1. Scope

1.1 This test method covers a procedure which is used to measure the surface area of precipitated hydrated silicas by the conventional Brunauer, Emmett, and Teller (BET)[2] theory of multilayer gas adsorption behavior using multipoint determinations, similar to that used for carbon black in Test Method D6556. This test method specifies the sample preparation and treatment, instrument calibrations, required accuracy and precision of experimental data, and calculations of the surface area results from the obtained data.

1.2 This test method is used to determine the nitrogen surface area of precipitated silicas with specific surface areas in the range of 1 to 50 $hm^2/kg$ (10 to 500 $m^2/g$).

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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.* The minimum safety equipment should include protective gloves, sturdy eye and face protection, and means to deal safely with accidental mercury spills.

## 2. Referenced Documents

2.1 *ASTM Standards:*[3]

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

D6556 Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption

## 3. Significance and Use

3.1 This test method is used to measure the surface area of precipitated, hydrated silicas that is available to the nitrogen molecule using the multipoint (B. E. T.) method.

3.2 Solids adsorb nitrogen and, under specific conditions, the adsorbed molecules approach a monomolecular layer. The quantity in this hypothetical monomolecular layer is calculated using the BET equation. Combining this with the area occupied by the nitrogen molecule yields the total surface area of the solid.

3.3 This test method measures the estimated quantity of nitrogen in the monomolecular layer by adsorption at liquid nitrogen temperature and at several (at least five) partial pressures of nitrogen.

3.4 Before a surface area determination can be made it is necessary that the silica be stripped of any material which may already be adsorbed on the surface. The stripping of adsorbed foreign material eliminates two potential errors. The first error is associated with the weight of the foreign material. The second error is associated with the surface area that the foreign material occupies.

## 4. Apparatus

4.1 Commercial instruments are available[4] for the measurement of nitrogen surface area by the multipoint BET method. These may be of the "flowing gas" or the "vacuum-volumetric" type.

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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] Brunauer, Emmett, and Teller, *Journal of the American Chemical Society*, Vol 60, 1938, p. 309.

[3] 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.

[4] Commercial automated instruments found satisfactory may be obtained from Micromeritics Instrument Corporation, One Micromeritics Drive, Norcross, GA 30093–1877, website: www.micromeritics.com, and Quantachrome Instruments, 1900 Corporate Drive, Boynton Beach, FL 33426, website: www.quantachrome.com.

NOTE 1—Automated instruments will provide results equivalent to the procedure described herein if careful calibration of the instrument, equivalent sample preparation, adherence to manufacturer's instruction for instrument operation, and equivalent data handling and calculations are performed.

4.2 *Sample Cells,* and other peripheral equipment as recommended by the manufacturer for the instrument used.

4.3 *Balance, Analytical,* with 0.1-mg sensitivity.

4.4 *Heating Mantles,* or other sample preparation station, capable of maintaining a temperature of 160 ± 5°C on the sample.

## 5. Reagents

5.1 *Liquid Nitrogen.*

5.2 *Nitrogen Gas,* cylinder, or other source of prepurified nitrogen gas as specified by the manufacturer of the instrument.

5.3 *Helium Gas,* cylinder, or other source of prepurified helium gas, as specified by the manufacturer of the instrument.

## 6. Standard Reference Silicas

6.1 *None Required*—This test method is used to determine surface area of candidate silicas. Reference silicas are available[5] for checking agreement with data obtained in the interlaboratory test used in preparation of this test method.

## 7. Sampling

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

## 8. Sample Preparation Procedure

### *Automated Instrument*

8.1 Weigh (to 0.1 mg) a clean, dry, degassed sample tube with stopper and filler rod if required. Record the mass.

8.2 Transfer a sample of silica to be tested so that the sample tube contains approximately 50 $m^2$ of silica surface area (see Note 2 and 8.2.1).

NOTE 2—If the silica sample contains more than about 6 % moisture, it may be dried at 110°C to 2 to 6 % moisture. A very dry silica (less than 1 % moisture) is difficult to transfer due to static charge buildup.

8.2.1 If the surface area of the silica is unknown, assume a surface area of 7.5 $hm^2/kg$ and weigh out approximately 0.5 g of sample.

8.3 Place the sample assembly (with sample) at the degas station. Degas the sample in accordance with manufacturer's instructions.

8.3.1 The silica must be completely degassed. While samples at normal moisture and moderate surface area are completely degassed in 1 h at 160°C, the inability to hold pressure (in a vacuum-type instrument), moisture condensation in the cold part of the sample cell, or poor reproducibility are indications that longer degassing times may be required. *Do not change the degassing temperature.*

8.4 Set the heating for the desired temperature of 160°C, and degas in accordance with manufacturer's procedure.

NOTE 3—To obtain 160°C sample temperature, a higher temperature on the heater may be necessary. The heater temperature and set point necessary may be determined by way of a temperature sensor in the sample, for example, a thermometer, during a trial run.

8.5 Remove from heat and allow sample and sample tube to cool to room temperature. If moisture is present at the tube neck after 1 h, abort run and pre-dry sample at 110°C in accordance with Note 2 and repeat sample preparation procedure. When cool, remove the sample tube from the degas port in accordance with manufacturer's procedure, stopper, weigh, and record the mass to 0.1 mg. Calculate degas sample weight using weight from 8.1 as tare. The degassed sample weight is inserted into program of calculations.

## 9. Measurement Procedure

### *Automated Instruments*

9.1 For automated system insert prepared tube containing sample into isothermal jacket (if called for in manufacturer's procedure), install on analysis port, and insert run conditions/report options into computer program as required.

9.2 For automated system when partial pressures are requested, select 0.05 and 0.2 and three points between 0.05 and 0.2. Begin run.

9.2.1 Be sure to input degassed weight of sample obtained in 8.5.

9.3 When measurements are complete and sample tube has warmed to room temperature, dry the sample tube, remove it from the instrument, and seal it with its stopper.

## 10. Calculations

10.1 For automated instruments, software automatically calculates results for the chosen reports.

NOTE 4—If the correlation coefficient calculated for the data analysis is low, see Test Method D6556 for a methodology to improve the correlation by discarding one or more points.

## 11. Report

11.1 Report the following information:

11.1.1 Proper sample identification.

11.1.2 Number of data points used to obtain the results.

11.1.3 The nitrogen surface area of the sample reported to the nearest 0.01 $hm^2/kg$.

## 12. Precision and Bias

12.1 This precision and bias section has been prepared in accordance with Practice D4483, which should be referred to for terminology and other statistical calculation details.

12.2 A Type 1 interlaboratory precision was evaluated in April 1990. Both repeatability and reproducibility are short-term. Duplicate determinations were made on each of the test silicas on each of two days, a few days apart. A test result, as specified by this test method, is obtained on one measurement of the surface area.

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[5] Precipitated silica samples are available from Forcoven Products, Inc., 123 Martin Drive, Porter, TX 77365. Samples are available in three surface areas: A, 13.8; B, 5.7; and C, 16.8 $hm^2/kg$.

12.3 Three different precipitated silicas were used, representing low (less than 10.0 hm$^2$/kg), medium (10.0 to 16.0 hm$^2$/kg) and high (greater than 16.0 hm$^2$/kg). These were tested in five laboratories. The tests included the classical vacuum rack (one laboratory) and the automatic instruments (four laboratories).

12.4 The results of the precision calculations for repeatability and reproducibility are given in Table 1 for each of the silicas evaluated.

12.5 Repeatability, *r*, and reproducibility, *R*, vary over the range of surface areas measured.

12.6 *Repeatability*—The repeatability, *r*, of this test method has been established as the appropriate value tabulated in Table 1. Two single test results, obtained with this test method on the same instrument and with the same operator, that differ by more than this tabulated *r* (for any given mean surface area) must be considered as derived from different or nonidentical sample populations.

**TABLE 1 Type 1 Precision of Surface Area of Silica**

| Silica | Mean, hm$^2$/kg | Within Laboratory | | | Between Laboratories | | |
|---|---|---|---|---|---|---|---|
| | | *Sr*, hm$^2$/kg | *r*, hm$^2$/kg | (*r*), | *Sr*, hm$^2$/kg | *R*, hm$^2$/kg | (*R*), |
| A | 13.78 | 0.141 | 0.399 | 2.9 | 0.148 | 0.419 | 3.0 |
| B | 5.67 | 0.079 | 0.223 | 3.9 | 0.094 | 0.267 | 4.71 |
| C | 16.78 | 0.201 | 0.569 | 3.4 | 0.377 | 1.067 | 6.4 |

12.7 *Reproducibility*—The reproducibility, *R*, of this test method has been established as the appropriate value tabulated in Table 1. Two single test results obtained with this test method, in two different laboratories, that differ by more than the tabulated *R* (for any given mean surface area) must be considered as derived from different or nonidentical sample populations.

12.8 Repeatability and reproducibility expressed as a percent of the mean surface area, (*r*) and (*R*), have equivalent application statements as above for *r* and *R*. For the (*r*) and (*R*) statements, the difference in the two single test results is expressed as a percent of the arithmetic mean of the two test results.

12.9 *Bias*—In test method terminology, bias is the difference between an average surface area and the reference (or true) surface area. Reference surface areas do not exist for this test method since the surface area is exclusively defined by this test method. Bias, therefore, cannot be determined.

## 13. Keywords

13.1 nitrogen adsorption surface area; precipitated hydrated silica; silicas; surface area