Standard Test Methods for
Precipitated Silica—Surface Area by Single Point B.E.T. Nitrogen Adsorption[1]

This standard is issued under the fixed designation D 5604; 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 These test methods cover a procedure to measure the surface area of precipitated hydrated silicas by, a single point approximation of the Brunauer, Emmett, and Teller (B.E.T.)[2] theory of multilayer gas adsorption. These test methods specify 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 These test methods are used to determine the single point nitrogen surface areas in the range of 10 to 50 hm^2 kg (10 to 500 m^2/g).

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

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.

2. Referenced Documents

2.1 *ASTM Standards:*
D 1799 Practice for Carbon Black—Sampling Packaged Shipments[3]
D 1900 Practice for Carbon Black—Sampling Bulk Shipments[3]
D 1993 Test Method for Precipitated Silica—Surface Area by Multipoint BET Nitrogen Adsorption[3]

3. Summary of Test Methods

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

3.2 These test methods measure the estimated quantity of nitrogen in the monomolecular layer formed by adsorption at liquid nitrogen temperature and at a fractional saturation pressure of 0.30 ± 0.01.

3.3 Before a surface area determination can be made it is necessary that any material which may already be adsorbed on the surface of the silica be removed. Removal of adsorbed foreign material (by heating under vacuum or in a steam of non-adsorbing gas) eliminates two potential errors. The first error is due to the mass of the foreign material. The second error is due to interference by the foreign material to access by nitrogen the silica surface.

4. Significance and Use

4.1 These test methods measure the approximate surface area of precipitated hydrated silicas that is available to the nitrogen molecule using an approximation of the B.E.T. method. While the multi-point version of the B.E.T. method is generally accepted as being less prone to errors arising from the varying surface properties of individual samples, the single-point approximation is often adequate due to the shorter time per test and relative simplicity of the instrumentation needed. Quality control applications and comparative tests on near-identical samples of close chemical and micro-structural composition are likely to be the applications of greatest value.

5. ASTM D11 Standard Reference Silicas

5.1 *None Required*—This test method is used to determine surface area of candidate silicas. Reference silicas are available[4] for determining agreement with data obtained in the

interlaboratory test used for multi-point procedure Test Method D 1993.

TEST METHOD A — SURFACE AREA BY STATIC VOLUMETRIC APPARATUS

6. Apparatus

6.1 *Static-Volumetric Gas Adsorption Apparatus*, with dewar flasks and all other accessories required for operation.

6.2 *Oven*, vacuum-type, capable of temperature-regulation to ±5°C at 110°C. Pressure should be less than 13.5 Pa (0.1 mmHg).

6.3 *Sample Cells*, which, when attached to the adsorption apparatus, will maintain isolation of the sample from the atmospheric pressure equivalent to a helium leak rate of $\leq 10^{-5}$ standard cubic centimeters per minute, per atmosphere of pressure difference.

6.4 *McCleod Gage*, or equivalent means to measure the pressure. (May be part of the adsorption apparatus.)

6.5 *Pressure Gage or Transducer*, known to be accurate to ±0.25 % of reading or ±0.067 kPa (±0.5 mmHg), whichever is greater and covering the 0 to 101.3 kPa (760 mmHg) pressure range. (May be part of the adsorption apparatus.)

6.6 *Analytical Balance*, with 0.1 mg sensitivity.

6.7 *Glass Vials*, small (30 cm^3) glass vials with caps for oven drying samples.

6.8 *Heating Mantle*, or equivalent, capable of maintaining a temperature of 160 ± 5°C.

6.9 *Volumetric Calibration Apparatus*, with valve or stopcock and 6.4 mm tubing adapter to gas adsorption sample connector. See Fig. 1.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall 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 established that they are of sufficiently high purity to use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water (and ice prepared from it) shall be understood to mean distilled water or water of equal purity.
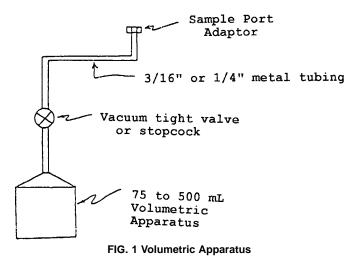
7.3 *Liquid Nitrogen*, 98 % or higher purity.

7.4 *Ultra-High Purity Nitrogen Gas*, cylinder, or other source of prepurified nitrogen gas.

7.5 *Ultra-High Purity Helium Gas*, cylinder, or other source of prepurified helium gas.

8. Sampling

8.1 No separate practice for sampling silicas is available. However, samples may be taken in accordance with Practices

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[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.

FIG. 1 Volumetric Apparatus

D 1799 or D 1900, whichever is appropriate.

9. Preparation and Verification of Calibration of Static-Volumetric Apparatus

NOTE 1—Perform this procedure for initial calibration, periodically for quality control, and following repairs or adjustments. If a commercial apparatus is used, consult the user's manual for specific instructions in carrying out the following steps.

9.1 Attach the very low and atmospheric pressure gages or transducers (see 6.4 and 6.5) to the apparatus and evacuate it, the manifold, and all internal pressure/vacuum sensors to 2.7 Pa (20µ mHg) or below.

9.2 Verify that the internal vacuum sensor(s) are reading correctly and that the internal pressure sensor(s) are reading correctly in the vicinity of zero pressure subject to the expected resolution and stability limits. Make adjustments as needed.

9.3 Close the vacuum path and admit nitrogen gas to build 101.3 kPa ± 1 % (760 mmHg ± 7.6 mmHg) of pressure. Verify that the pressure sensors read the correct pressure to within ±0.25 %. Make adjustments as needed.

9.4 Thoroughly clean and dry an empty sample holder. Attach it to the apparatus and evacuate it to 2.7 Pa (20 µmHg). Apply a 160°C heating mantle and continue evacuation for at least 1 h and until the rate of pressure rise upon temporarily closing off the vacuum path is under .4 Pa (3 µmHg) per minute.

9.5 Perform a sample analysis on this clean empty sample tube at 0.30 ± 0.01 P/P$_o$. Use a P$_o$ of 101.3 kPa (760 mmHg) and a sample mass of 1 g.

9.6 Examine the volume adsorbed quantity obtained. Ideally it should be zero. An error amount exceeding 0.25 standard cubic centimeters is unacceptable and requires correction. An error amount of 0.125 standard cubic centimeter or less is acceptable.

9.7 Obtain a cylindrical or spherical calibration volume made of glass or corrosion resistant metal and having an internal volume between 75 cm^3 and 500 cm^3. It must have a tubing connection and an in-line valve or stopcock as shown in Fig. 1.

9.8 Determine the internal volume below the valve or stopcock by the mass difference when first empty and then

when filled completely with distilled water. Measure the water temperature and correct for the water density to obtain the exact volume of water contained. It may be necessary to immerse the device in boiling water to ensure complete filling and degassing. Repeat the procedure until the calibration volume is known to better than ±0.1 %. Empty the calibration volume and thoroughly dry it overnight in the vacuum oven at 70° ± 5°C.

9.9 Connect the calibrated volume to a sample port of the gas adsorption apparatus, open the valve or stopcock, and evacuate the volume to below 0.0027 kPa (20 μmHg). Continue evacuation for 1 h more. Close off the path to the vacuum source and note whether any rise in pressure occurs. The pressure must remain below 2.7 Pa (20 μmHg) with an increase rate of less than 0.4 Pa (3 μmHg) per minute. When this has been achieved, close the valve or stopcock to retain the vacuum within the calibration volume.

9.10 Leave the closed-off, evacuated calibration volume in place. Raise a dewar flask around the volume and pack wet, crushed ice firmly around the volume as in Fig. 2. Remove any dewars or other equipment that might interfere with a sample run. Start a sample run with a target relative pressure of 0.30 ± 0.01 P/P_o. Use a 1 g sample weight and a P_o of 101.3 kPa (760 mmHg). Upon the beginning of dosing open the valve or stopcock on the evacuated volume and complete the sample run.

9.11 Examine the volume adsorbed. The volume adsorbed should be within ±1 % of the gas volume, V, computed by the following formula:

$$V = \left(\frac{P}{760}\right)V_v = (P/P_o)\left(\frac{P_o}{760}\right)V_v \qquad (1)$$

where P/P_o is the relative pressure at which the point was actually equilibrated and V_v is the internal volume determined by weighing in 9.8.

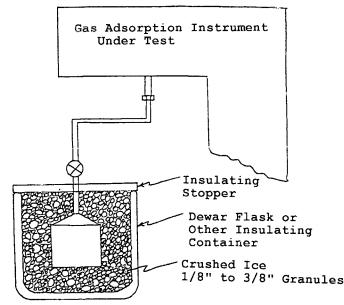9.12 Successful completion of this series of tests indicates that the gas adsorption apparatus meets the basic requirements of adequate vacuum level, compensation for free space errors, linearity, and accuracy of nitrogen gas metering.

10. Sample Preparation Procedure

10.1 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.

10.2 Weigh a sample cell to the nearest 0.0001 g and record the mass. Include the stopper.

10.3 Into the cell, weigh a sample of the silica to be tested that has been dried as required in 10.1, so that the cell contains approximately 50 m^2 of surface area for the silica including stopper.

NOTE 2—When not measuring a standard reference silica, and the type of silica is unknown, assume a surface area of 75 m^2/g and weigh out approximately 0.5 g. Record the combined mass of the cell and silica including stopper.

10.4 With the apparatus at atmospheric pressure, place the sample cell containing the silica onto the degassing apparatus.

10.5 Begin the degassing procedure as appropriate for the apparatus.

10.6 Place a heating mantle or other source of heat around the sample cell and degas the sample at 160 ± 5°C for ½ h or longer as required to obtain and hold a pressure less than 1.3 Pa (10 μmHg) if low pressure degassing is in use. If flowing gas purging is used, all traces of moisture condensing in the top of the tube must be absent. Once the typical degas times have been determined, if desired, future samples can be degassed on the basis of time alone, allowing a reasonable margin of excess time. Some samples will be found to require less than 30 min especially if moisture exposure has been minimal. In these cases, the minimum time which gives a stable surface area may be used for degassing.

10.7 Remove the sample from the heat source and allow the sample cell to cool to room temperature. Continue the flow of purging gas if that technique is in use.

10.8 Go directly to Section 15 and continue the remaining procedures.

TEST METHOD B — SINGLE-POINT SURFACE AREA BY FLOWING GAS APPARATUS

11. Apparatus

11.1 *Flowing gas adsorption apparatus*, with dewar flasks and all other accessories required for operation.

11.2 *Oven*, vacuum-type, capable of temperature-regulation to ±5°C at 110°C. Pressure should be less than 13 Pa (0.1 mmHg).

11.3 *Sample Cells*, which, when attached to the adsorption apparatus, will maintain isolation of the sample from the atmospheric pressure equivalent to a helium leak rate of $\leq 10^{-5}$ standard cubic centimeters per minute, per atmosphere of pressure difference.

11.4 *Analytical Balance*, with 0.1 mg sensitivity.

11.5 *Glass Vials*, small (30 cm^3) glass vials with caps for oven drying samples.

11.6 *Heating Mantle*, or equivalent, capable of maintaining a temperature of 160 ± 5°C.

Gas Adsorption Instrument
Under Test

Insulating Stopper

Dewar Flask or Other Insulating Container

Crushed Ice 1/8" to 3/8" Granules

FIG. 2 Volumetric Apparatus Installed and Readied for Gas Adsorption Instrument Calibration Verification

11.7 *Syringes*, precision, 1 cm^3 and 5 cm^3.

12. Reagents

12.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall 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 established that they are of sufficiently high purity to use without lessening the accuracy of the determination.

12.2 *Purity of Water*—Unless otherwise indicated, references to water (and ice prepared from it) shall be understood to mean distilled water or water of equal purity.

12.3 *Liquid Nitrogen*, 98 % or higher purity.

12.4 Ultra-high purity nitrogen gas; cylinder, or other source of prepurified nitrogen gas.

12.5 Flowing gas systems shall use helium-nitrogen mixtures of concentrations know to ±0.25 % nitrogen content or better and shall contain at the time of exposure to the sample, under one part per million by volume of gases or vapors having boiling points above that of nitrogen.

13. Preparation and Calibration of Flowing Gas Apparatus

Note 3—Perform this procedure for initial calibration, periodically for quality control, and following repairs or adjustments. If a commercial apparatus is used, consult the user's manual for specific instructions in carrying out the following steps.

13.1 For the helium/nitrogen mixture representing the desired P/Po target pressure of 0.30 ± 0.01, perform the following steps.

13.1.1 Establish a stable flow of the gas mixture in the system through a clean, dry, empty sample holder of the size that will be used for the samples on the analysis port(s).

13.1.2 Perform an adsorption/desorption cycle on the empty tube(s) as if a sample were present and record or note the detector responses and the integrated results of each peak.

13.1.3 Both the adsorption and the desorption peaks must integrate to less than 0.03 standard cubic centimeters of nitrogen and the baseline must return to the starting position to within 0.05 % nitrogen equivalent concentration within 5 min of the peak. Failure to achieve this may indicate leaks to or from the atmosphere, contaminated sample tubes, an impure gas mixture, or gas detector malfunctions.

13.1.4 Fill a precision 1 cm^3 syringe from a pure nitrogen source, equilibrate both pressure and temperature with ambient, record the pressure and temperature, and over a 3 s interval smoothly inject the nitrogen into the flowpath at any point between the upstream and downstream detector filaments. Do not allow the syringe to be warmed by the hands. The instrument must yield a response of

$$(1 \text{ cm}^3)\left(\frac{Pa}{101.3}\right)\left(\frac{273.15}{Ta}\right) \tag{2}$$

cubic centimeters of nitrogen where Pa (kPa) is ambient atmosphere pressure and Ta is ambient absolute temperature. Adjust the integrator gain and repeat the process until the error is less than ± 0.03 standard cubic centimeters. Note the integrator gain setting.

13.1.5 Fill a precision 5 cm^3 syringe and repeat the injection as in 13.1.4 except that it will be necessary to inject smoothly over a 10 s interval. The instrument must yield a integrated response five times as great as before to within ±1 % of the value.

$$(5 \text{ cm}^3)\left(\frac{Pa}{101.3}\right)\left(\frac{273.15}{Ta}\right) \tag{3}$$

If the error exceeds 5 %, the instrument is unsuitable or in need of repair. If the error is 1 % to 5 %, adjust the integrator gain and repeat the process until the error is under 1 %. Note the integrator gain setting.

13.2 Many flowing gas instruments have selectable or variable length flow paths. The above tests must be performed on all of the flow paths used for silica surface area measurements. Sample sizes or calibration volumes should be adjusted to keep the respective gas quantities and peak heights involved comparable.

13.3 Successful completion of this series of tests indicates that the flowing gas adsorption apparatus meets the basic requirements of leak freedom, gas mixture purity, cleanliness, detector linearity, and stability.

14. Sample Preparation Procedure

14.1 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.

14.2 Weigh a sample cell to the nearest 0.0001 g and record the mass including the stopper.

14.3 Into the cell weigh a sample of the silica to be tested, that has been dried as required in 14.1, so that the cell contains approximately 10 m^2 of surface area for the silica.

Note 4—When not measuring a standard reference silica, and the type of silica is unknown, assume a surface area of 75 m^2/g and weigh out approximately 0.1 g. Record the combined mass of the cell and silica, including stoppers.

14.4 Seal the sample cell containing the silica onto the degassing apparatus.

14.5 Begin the degassing procedure as appropriate for the apparatus.

14.6 Place a heating mantle or other heat source around the sample cell and degas the sample at 160 ± 5°C for 30 min or longer. Adequate degassing may be determined by degassing in the analysis position and using the detector to indicate when the sample has ceased to evolve adsorbed gases. Once the typical degas times have been determined, future samples can be degassed on the basis of time alone, if desired, allowing a reasonable margin of excess time. Some samples will be found to require less than 30 min especially if moisture exposure has been minimal. In these cases, the minimum time that gives a stable surface area may be used for degassing.

14.7 Remove the heating mantle and allow the sample cell to cool to room temperature.

14.8 Go directly to Section 15 and continue the remaining procedures.

15. Measurement Procedure

15.1 Obtain the user's manual or specific instructions for the

gas adsorption analyzer used and become thoroughly familiar with the procedures.

15.2 Determine the saturation pressure of the liquid nitrogen bath.

15.3 Measure the amount of nitrogen adsorbed at the relative pressure of 0.30 ± 0.01 P/P$_o$. Note that variance in the exact P/P$_o$ value attained will increase the variance of results with more effect on some samples than for others.

15.4 Determine the mass of the cell with dry sample to the nearest 0.0001 g prior to measuring nitrogen adsorption or afterwards. Avoid inconsistent use of helium, as a buoyancy error of one mg per cm^3 of cell volume can occur.

16. Calculations

16.1 Most automated instruments will perform the following computations at the completion of the analysis. The user must verify that the internal computations conform to the following.

16.2 *Sample Mass*:

$$\text{Mass of sample (dried)} = (\text{mass of cell} + \text{sample}) - (\text{mass of cell})$$
$$(\text{Record masses to } \pm 0.0001 \text{ g}) \tag{4}$$

16.3 *Nitrogen Surface Area*:

16.3.1 Calculate total volume of nitrogen adsorbed per gram of specimen to the nearest (0.0001 cm^3/g) as follows:

$$V_{\text{ADS}}/g = \frac{V_{\text{ADS}} \text{ for each dosing in cm}^3}{\text{sample mass}} \tag{5}$$

where:

V_{ADS}/g = total volume of nitrogen adsorbed per gram of silica; in cm^3/kg

16.3.2 Determine the surface area of the silica using the following approximation derived from the B.E.T. equation:

$$\text{Single Point Surface Area} = V_{\text{ads}}/g \, (1 - P/P_o) \times 4.35 \text{ m}^2/\text{cm}^3/g$$

$$\tag{6}$$

where:
P = equilibrium pressure over the sample in kPa,
P_o = saturation vapor pressure of nitrogen in kPa,
4.35 = area occupied by one standard cubic centimeter of nitrogen as a monolayer, each molecule occupying 0.162 nm^2.

17. Report

17.1 Report the following information:

17.1.1 Sample identification.

17.1.2 The data used to obtain the result.

17.1.3 The nitrogen surface area of the sample reported to the nearest 0.1 m^2/g.

18. Keywords

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