



Designation: D 1993 – 91 (Reapproved 1997)

Standard Test Method for Precipitated Silica-Surface Area by Multipoint BET Nitrogen Adsorption¹

This standard is issued under the fixed designation D 1993; 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 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 Methods D 4820. 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 the standard. The values given 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, and means to deal safely with accidental mercury spills.

2. Referenced Documents

2.1 ASTM Standards:

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

D 4820 Test Methods for Carbon Black—Surface Area by Multipoint B. E. T. Nitrogen Adsorption³

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 (by heating under vacuum) 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 *Classical Glass Vacuum Apparatus*, or equivalent constructed as shown in Fig. 1, including diffusion and vacuum pumps, manometer, gas buret, gas reservoir, and sample cell similar to that illustrated in Fig. 1.

4.2 Optionally, commercial instruments are available⁴ for the measurement of nitrogen surface area by the multipoint BET method. These are automated versions of the vacuum apparatus described herein.

NOTE 1—Automated vacuum 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.

4.3 *Sample Cells*, which, when attached to the vacuum system, will maintain pressure below 1.3 mPa (10 nm Hg).

¹ This test method is under the jurisdiction of ASTM Committee D-11 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 *Annual Book of ASTM Standards*, Vol. 09.01.

⁴ Two commercial automated vacuum instruments found satisfactory are (a) Model ASAP 2400 Accelerated Surface Area and Porosimetry Instrument, available from Micromeritics Instrument Corporation, 800 Goshen Springs Road, Norcross, GA 30071, and, (b) Autosorb Automated Gas Adsorption System, available from Quantachrome Corporation, 5 Aerial Way, Syosset, NY 11791.

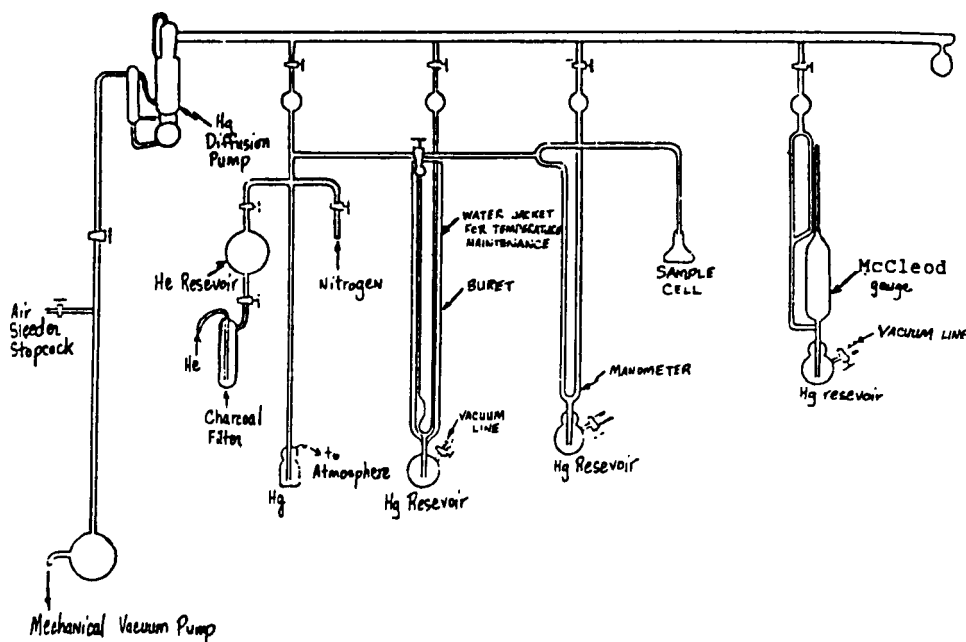


FIG. 1 Glass Vacuum Apparatus

4.4 For automated instruments: sample tubes, filler rods, stoppers, isothermal jacket (if required in manufacturer's procedure), and sample filler tube or powder funnel to fit the neck of the sample tube.

4.5 Dewar Flasks, 1-L size (furnished with commercial instruments).

4.6 McCleod Gage, or equivalent means to measure pressure to less than 1 mPa (8 nm Hg).

4.7 Balance, Analytical, with 0.1-mg sensitivity.

4.8 Heating Mantles, or equivalent, capable of maintaining a temperature of $160 \pm 5^\circ\text{C}$ on the sample.

5. Reagents

5.1 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 (for gas vacuum rack, Fig. 1).

5.2 Liquid Nitrogen.

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

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

5.5 Instrument Grade Mercury (for gas vacuum rack, Fig. 1).

6. Standard Reference Silicas

6.1 None Required—This test method is used to determine surface area of candidate silicas. Reference silicas are available⁵ for checking agreement with data obtained in the inter-laboratory 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 Test Methods D 1799 or D 1900, whichever is appropriate.

8. Preparation of Apparatus

Classical Vacuum Apparatus

NOTE 2—This procedure only need be performed for the initial calibration of the gas buret or when a modification is made to the gas buret.

8.1 Zero the manometer by evacuating both arms of the manometer to a pressure below 1.3 mPa (10 nm Hg) and adjusting the height of the mercury columns to the same zero reading in both arms.

8.2 Determine Gas Buret Constant:

8.2.1 Install a sample cell of approximately 30 cm³ volume on the sample cell position of the apparatus, assuring no vacuum leaks.

8.2.2 Evacuate the sample cell, manometer, and gas buret to a pressure below 1.3 mPa (10 nm Hg).

8.2.3 Immerse the sample cell in a water-ice bath contained in a Dewar flask such that the entire sample bulb and neck are covered.

8.2.4 Fill the gas buret to approximately 50 % of its capacity with helium.

8.2.5 Obtain initial gas buret level and temperature— V_{B1} , T_{B1} (K).

8.2.6 Transfer approximately 2 cm³ of helium to the sample cell.

8.2.7 Read and record the gas buret level and temperature after helium dosing— V_{B2} , T_{B2} (K).

8.2.8 Read and record the pressure in the sample cell after dosing (P_c); and the sample cell temperature, that is, ice-bath temperature T_c (K).

8.2.9 Repeat 8.2.5-8.2.8 at least two times to obtain a total of three data sets.

8.2.10 Remove the sample cell and fill the sample cell with approximately 25 cm³ of instrument grade mercury. Record the mass of the mercury used to ± 0.001 g, W_m .

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 m²/g.