



Designation: D 5816 – 99

Standard Test Methods for Carbon Black—External Surface Area by Multipoint Nitrogen Adsorption¹

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1. Scope

1.1 These test methods cover the determination of the external surface area of carbon blacks by the statistical thickness surface area (STSA) method.

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 1799 Practice for Carbon Black—Sampling Packaged Shipments²

D 1900 Practice for Carbon Black—Sampling Bulk Shipments²

D 4820 Test Methods for Carbon Black—Surface Area by Multipoint B.E.T. Nitrogen Adsorption²

3. Significance and Use

3.1 These test methods are used to measure the external surface area of carbon black. These techniques are based on the statistical thickness method using a carbon black model. The external surface area is defined as the specific surface area that is accessible to rubber. The external surface area excludes the micropore area, pore diameters less than 20 Å.

4. Apparatus

4.1 *Multipoint Static-Volumetric Gas Adsorption Apparatus*, with Dewar flasks and all other accessories required for operation.

4.2 *Sample Cells* that, when attached to the adsorption apparatus, will maintain isolation of the sample from the atmosphere equivalent to a helium leak rate of $<10^{-5}$ cm³/min, per atmosphere of pressure difference.

¹ These test methods are under the jurisdiction of ASTM Committee D-24 on Carbon Black and are the direct responsibility of Subcommittee D24.21 on Adsorptive Properties of Carbon Black.

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² *Annual Book of ASTM Standards*, Vol 09.01.

4.3 *Analytical Balance*, with 0.1 mg sensitivity.

4.4 *Heating Mantle or Equivalent*, capable of maintaining a temperature of $300 \pm 10^\circ\text{C}$.

4.5 *Oven, Gravity Convection*, capable of maintaining a temperature of $125 \pm 5^\circ\text{C}$.

5. Reagents

5.1 *Liquid nitrogen*, 98 % or higher purity.

5.2 *Ultra high-purity nitrogen gas*, cylinder, or other source of prepurified nitrogen gas.

5.3 *Ultra high-purity helium gas*, cylinder, or other source of prepurified helium gas.

6. Sampling

6.1 Samples shall be taken in accordance with Practice D 1799 and Practice D 1900.

7. Sample Preparation Procedure

7.1 Dry a portion of the carbon black to be tested at 125°C for 1 h. If the carbon black is known to be substantially free of moisture, or subsequent preparation steps are known to be adequate for moisture removal, then this step may be omitted.

7.2 Weigh a sample cell to the nearest 0.1 mg and record the mass.

7.3 Weigh into the cell approximately 0.4 g of the carbon black to be tested.

NOTE 1—For carbon black powder samples, add enough carbon black to give a depth of approximately 2 in. in straight wall sample tubes, or fill the sample bulb for bulb-type sample cells.

7.4 Flow Degassing:

7.4.1 Open the helium control valve and insert the delivery tube into the sample tube, and allow to purge for a minimum of 1 min.

7.4.2 Place a heating mantle or other source of heat around the sample cell and degas the sample at $300 \pm 10^\circ\text{C}$ for $\frac{1}{2}$ h or longer to ensure that all traces of moisture condensing in the top of the tube are absent.

7.4.3 Once the typical degassing 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 $\frac{1}{2}$ h, especially if moisture exposure has been minimal. In these cases, the minimum time that gives a stable surface area may be used for degassing.

7.4.4 After degassing, the sample tube may be moved directly to the analyzer. Otherwise, remove the sample tube from the heat source and continue the flow of purging gas until it is ready for analysis.

7.4.5 Go directly to Section 8 and continue the remaining steps of the procedure.

7.5 Vacuum Degassing:

7.5.1 With the apparatus at atmospheric pressure, place the sample cell containing the carbon black onto the degassing apparatus.

7.5.2 Begin the degassing procedure as appropriate for the apparatus.

7.5.3 Place a heating mantle or other source of heat around the sample cell and degas the sample at $300 \pm 10^\circ\text{C}$ for $\frac{1}{2}$ h or longer as required to obtain and hold a pressure less than 1.4 Pa (10 mm Hg).

7.5.4 Once the typical degassing 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 $\frac{1}{2}$ h, especially if moisture exposure has been minimal. In these cases, the minimum time that gives a stable surface area may be used for degassing.

7.5.5 Go directly to Section 8 and continue the remaining steps of the procedure.

8. Measurement Procedure

8.1 Refer to the user's manual or specific instructions for the multipoint gas adsorption analyzer to be used, and become thoroughly familiar with the procedures.

8.2 Fill the Dewar with liquid nitrogen and allow it to reach temperature equilibrium, generally 1 h.

8.3 Accurately determine the saturation pressure of the liquid nitrogen bath by running replicate determinations until two consecutive saturation pressure values agree within 0.13 kPa (1 mm Hg).

8.4 Determine the free space of the sample cell by measurement with helium or by calculation using an assumed carbon black density of 1.9 g/cm^3 .

8.5 Obtain a minimum of four data points in the 0.2 to 0.5 relative pressure (P/P_o) range. A data point consists of the relative pressure of equilibrium and the total amount of nitrogen gas adsorbed by the sample at that relative pressure. The data points should be at as near equal spacing in P/P_o range as possible.

8.6 Determine the mass of the cell with dry sample to the nearest 0.1 mg. This may be done before or after measuring nitrogen adsorption. Avoid inconsistent use of helium, as a buoyancy error of 1 mg/cm^3 of cell volume can occur. As an alternative, the carbon black mass may be determined directly by pouring it from the sample cell into a tared weighing pan, taking care to remove all of the carbon black.

9. Calculations

9.1 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 method.

9.2 Sample Mass:

$$\text{sample mass (dried)} = (\text{mass of cell} + \text{sample}) - (\text{mass of cell}) \quad (1)$$

Record masses to nearest 0.1 mg.

9.3 Statistical Thickness Surface Area:

9.3.1 Calculate the total volume of nitrogen adsorbed per g of carbon black to the nearest 0.0001 cm^3 as follows:

$$V_{\text{ADS/g}} = \frac{V_{\text{ADS for each dosing in cm}^3}}{\text{sample mass}} \quad (2)$$

where:

$V_{\text{ADS/g}}$ = total volume of nitrogen adsorbed per g of black in cm^3/g .

9.3.2 Determine the STSA of the black using a plot of the V versus the statistical layer thickness (t).

9.3.3 Plot t on the X axis versus V_a on the Y axis, for data sets having P/P_o in the range of 0.2 to 0.5.

where:

P = manometer pressure in kPa,

P_o = saturation vapor pressure of nitrogen in kPa,

V_a = $V_{\text{ADS/g}}$, total volume of nitrogen adsorbed per g of black in standard cm^3/g , and

t = statistical layer thickness of carbon black = $0.88 (P/P_o)^2 + 6.45 (P/P_o) + 2.98$.

NOTE 2—Standard linear regression calculations can be used to determine the slope of this function.

9.3.4 Calculate the STSA to the nearest $0.1 \text{ m}^2/\text{g}$ as follows:

$$\text{STSA} = M \times 15.47 \quad (3)$$

where:

M = slope of the V_a - t plot, and

15.47 = conversion of the nitrogen gas to liquid volume, and conversion of units to m^2/g .

10. Report

10.1 Report the following information:

10.1.1 Proper sample identification,

10.1.2 The data points used to obtain the results, and

10.1.3 The statistical thickness surface area of the sample reported to the nearest $0.1 \text{ m}^2/\text{g}$.

11. Precision and Bias

11.1 These precision statements have been prepared in accordance with Practice D 4483. Refer to this practice for terminology and other statistical details.

11.2 The precision results in this precision and bias section give an estimate of the precision of this test method with the materials used in the particular interlaboratory program described below. The precision parameters should not be used for acceptance or rejection testing of any group of materials without documentation that they are applicable to those particular materials and the specific testing protocols of the test method. Any appropriate value may be used from Table 1

11.3 A type 1 inter-laboratory precision program was conducted as detailed in Table 2. Both repeatability and reproducibility represent short term (daily) testing conditions. The testing was performed using two operators in each laboratory performing the test once on each of two days (total of four