Designation: ~~D6556 – 17~~ D6556 – 19

Standard Test Method for
Carbon Black—Total and External Surface Area by Nitrogen Adsorption[1]

This standard is issued under the fixed designation D6556; 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 determination of the total surface area by the Brunauer, Emmett, and Teller (B.E.T. NSA) theory of multilayer gas adsorption behavior using multipoint determinations and the external surface area based on the statistical thickness surface area 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* (The minimum safety equipment should include protective gloves, sturdy eye and face protection).

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D1799 Practice for Carbon Black—Sampling Packaged Shipments
D1900 Practice for Carbon Black—Sampling Bulk Shipments
D3765 Test Method for Carbon Black—CTAB (Cetyltrimethylammonium Bromide) Surface Area (Withdrawn 2007)[3]
D4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

3. Summary of Test Method

3.1 The total and external surface areas are measured by evaluating the amount of nitrogen adsorbed, at liquid nitrogen temperature, by a carbon black at several partial pressures of nitrogen. The adsorption data is used to calculate the NSA and STSA values.

4. Significance and Use

4.1 This test method is used to measure the total and external surface area of carbon blacks based on multipoint nitrogen adsorption. The NSA measurement is based on the B.E.T. theory and it includes the total surface area, inclusive of micropores, pore diameters less than 2 nm (20 Å). The external surface area, based on the statistical thickness method (STSA), is defined as the specific surface area that is accessible to rubber.

4.2 CTAB Surface Area (formerly Test Method D3765) has been withdrawn. The CTAB value may be estimated from the STSA value using Eq 1. The equation is based on a linear regression of the STSA and CTAB measured values of the SRB 5 standards.

$$CTAB = STSA*1.0170 + 2.6434 \tag{1}$$

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5. Apparatus

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

5.2 *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 $<10^{-5}$ cm^3/min, per atmosphere of pressure difference.

5.3 *Balance, Analytical,* with 0.1 mg sensitivity.

5.4 *Heating Mantle or Equivalent,* capable of maintaining a temperature of $300 \pm 10°C$.

5.5 *Oven, Gravity Convection,* capable of maintaining a temperature of $125 \pm 10°C$.

6. Reagents

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

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

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

7. Sampling

7.1 Samples may be taken in accordance with Practices D1799 and D1900.

8. Sample Preparation Procedure

8.1 Dry a portion of carbon black 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.

8.2 Condition an empty sample cell for a minimum of 10 min at the same conditions intended for degassing the sample. Weigh the empty sample cell to the nearest 0.1 mg and record the mass.

8.3 Weigh approximately 0.4 g of the carbon black into the sample cell.

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 approximately 0.4 g for bulb-type sample cells.

8.4 *Flow Degassing:*

8.4.1 Open the gas control valve and insert the delivery tube into the sample tube, and allow purging with either helium or nitrogen for a minimum of 1 min.

8.4.2 Place a heating mantle or other source of heat around the sample cell and degas the sample at $300 \pm 10°C$ for ½ h or longer to ensure that all traces of moisture condensing in the top of the tube are absent. The minimum degassing time that gives a stable surface area (that is, a surface area that does not increase with additional degassing) may be used for degassing.

NOTE 2—For carbon blacks at their moisture pickup equilibrium, like standard reference blacks, longer degassing times likely will be required in order to achieve stable results. It has been found that for SRB B8 and SRB C8, it is necessary to extend the degassing time to at least 60 min in order to reliably obtain the target NSA and STSA values. This may be true for other high structure and high porosity carbon blacks.

8.4.3 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 ½ 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.

8.4.4 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.

8.4.5 Go directly to Section 9 and continue the remaining steps of the procedure.

8.5 *Vacuum Degassing:*

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

8.5.2 Begin the degassing procedure as appropriate for the apparatus.

8.5.3 Place a heating mantle or other source of heat around the sample cell and degas the sample at $300 \pm 10°C$ for ½ h or longer as required to obtain and hold a pressure less than 1.4 Pa (10 µm Hg).

NOTE 3—Attention! One-half hour vacuum degassing may be inadequate for some grades and may result in statistically different results to flow degassing.

8.5.4 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 ½ 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 (see Note 2).

8.5.5 Go directly to Section 9 and continue the remaining steps of the procedure.

9. Measurement Procedure

9.1 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. There are numerous instruments available that offer a variety of saturation vapor pressure (P_o) measurement options and Dewar sizes.

9.2 Fill the Dewar with liquid nitrogen (LN2) and allow it to reach temperature equilibrium. The Dewar should be refilled approximately once per hour or between each analysis. The time required to reach equilibrium is dependent upon Dewar size and quality.

9.2.1 *Small Dewar (<1 L)*—Fill and cover the Dewar for a minimum of 2 h prior to use. The Dewar should be cleaned and dried at the end of each day.

9.2.2 *Large Dewar (>1 L)*—Fill and cover the Dewar for a minimum of 16 h prior to use, unless continuous P_o measurements are employed. For continuous P_o, use a 2-h Dewar equilibration. Once equilibration is reached, a large Dewar can maintain this equilibration for several days if kept filled and covered. The cleaning frequency is left to the discretion of the operator, but is not to exceed once per week.

9.3 Following is a list of P_o measurement options:

9.3.1 *Continuous P_o* (measurement at each relative pressure point)—This method is considered the best practice. When available with the instrument and software package, it is recommended to use this option.

9.3.2 *Single P_o Per Analysis*—Although this value can be measured before, during, or after the run, a P_o value measured at the end of the analysis is preferred, since STSA is calculated from the last data points acquired and is significantly influenced by P_o values. This method requires that a P_o value be determined prior to initiating any measurements to ensure equilibrium of the Dewar as described in 9.4. Subsequently, a new P_o value is measured for each run, which is used for calculating NSA/STSA values.

9.3.3 *Daily P_o*—This method is used when evidence of a stable Dewar is present and no changes in atmospheric pressure greater than 0.13 kPa (1 mm Hg) occur.

9.3.4 *Calculated P_o*—This method calculates a P_o value by measuring atmospheric pressure and adding a value between 1.3 and 2.6 kPa (10 and 20 mm Hg). The operator is responsible for determining the constant used in their laboratory; however, 2.0 kPa (15 mm Hg) is most commonly used.

9.4 With the exception of continuous P_o measurements, it is recommended that the P_o value be determined prior to initiating NSA/STSA analyses. A P_o value of 1.3 to 2.6 kPa (10 to 20 mm Hg) above atmospheric pressure and two consecutive P_o values that differ by no more that 0.13 kPa (1 mm Hg) over a 10-min time period are indications of a stable Dewar. Experience will teach the operator about expected differences in P_o and atmospheric pressure in their laboratory.

TABLE 1 Example of NSA Data Analysis

N121[A]				
Raw Data		Calculation		
P/Po	Vol. Ads., cm³/g	Rel. Press. Range	Correlation Coefficient	NSA, m²/g
0.0500	26.716	. . .	. . .	. . .
0.1000	29.753	. . .	. . .	. . .
0.1500	32.313	0.05–0.15	0.999981	123.9
0.2000	34.692	0.05–0.20	0.999992	124.0
0.2500	37.110	0.05–0.25	0.999990	123.6
0.3000	39.641	0.05–0.30	0.999935	122.8
N326[B]				
Raw Data		Calculation		
P/Po	Vol. Ads., cm³/g	Rel. Press. Range	Correlation Coefficient	NSA, m²/g
0.0500	16.675	. . .	. . .	. . .
0.1000	18.318	. . .	. . .	. . .
0.1500	19.859	0.05–0.15	0.999960	75.6
0.2000	21.426	0.05–0.20	0.999948	76.3
0.2500	23.035	0.05–0.25	0.999964	76.6
0.3000	24.751	0.05–0.30	0.999979	76.6
N683[B]				
Raw Data		Calculation		
P/Po	Vol. Ads., cm³/g	Rel. Press. Range	Correlation Coefficient	NSA, m²/g
0.0500	8.194	. . .	. . .	. . .
0.1000	9.113	. . .	. . .	. . .
0.1500	9.945	0.05–0.15	0.999939	38.2
0.2000	10.739	0.05–0.20	0.999950	38.5
0.2500	11.543	0.05–0.25	0.999972	38.6
0.3000	12.364	0.05–0.30	0.999973	38.4

[A] The most accurate NSA is measured between 0.05 and 0.20 relative pressure.
[B] The most accurate NSA is measured between 0.05 and 0.30 relative pressure.

NOTE 4—A minimum wait time of 10 min is recommended between P_o measurements, as immersing the P_o cell into the LN2 disrupts the temperature equilibration. P_o measurements taken at short intervals will result in erroneously high and unstable values.

9.5 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.

9.6 Obtain a minimum of five data points evenly spaced in the 0.1 to 0.5 relative pressure (P/P_o) range. For some tread carbon blacks, particularly N100 and N200 series, it is necessary to measure two additional data points, 0.05 and 0.075, in order to increase the accuracy of the NSA measurement. 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.

9.7 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.

10. Calculation

10.1 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.

10.2 *Sample Mass:*

$$\text{sample mass (dried)} = (\text{mass of cell} + \text{sample}) - (\text{mass of cell}) \tag{2}$$

Record masses to nearest 0.1 mg.

10.3 *Volume of Nitrogen Adsorbed:*
10.3.1 Calculate total volume of nitrogen adsorbed per gram of sample to the nearest 0.0001 cm^3/g as follows:

$$V_a = \frac{\textit{Volume of Nitrogen for each dosing in cm}^3}{\textit{sample mass in g}} \tag{3}$$

10.4 *Nitrogen Surface Area:*
10.4.1 Determine the nitrogen surface area (NSA) using a B.E.T. plot from the Brunauer, Emmett, and Teller[4] equation as follows:

$$\frac{P}{V_a(P_o - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \times \frac{P}{P_o} \tag{4}$$

where:
P = manometer pressure in kPa,
P_o = saturation vapor pressure of nitrogen in kPa,
V_m = volume of nitrogen per gram that covers one monomolecular layer in standard cm^3/g, and
C = B.E.T. constant. Its numerical value depends on the heat of adsorption of the monomolecular layer.

10.4.2 Plot P/P_o on the X-axis versus $\frac{P}{V_a(P_o - P)}$ on the Y-axis, for data sets having P/P_o in the range of 0.05 to 0.30 (linear region of B.E.T. equation).

10.4.3 The data points (three or more) that give the best straight line are used to calculate the slope and y-intercept. The slope and y-intercept are used to calculate the surface area. For examples of how to select the proper relative pressure range, see Table 1.

10.4.4 As an alternative, the interpretation of the proper relative pressure can generally be simplified by specifying the following pressure ranges for the various carbon black types:

	BET Range
N300 and Carcass Grades	0.1–0.3
N100 and N200	0.05–0.2
Carbon Blacks > 130 m^2/g	0.05–0.1

It is the responsibility of the operator to assure that these guidelines are appropriate for their samples.

10.4.5 A B.E.T. plot that yields a negative y-intercept could be indicative of the presence of micropores (<2 nm diameter), but other factors can produce a negative y-intercept. The surface area is calculated from three or more points within the pressure range that yields the highest correlation coefficient and a positive y-intercept.

10.4.6 Calculate the nitrogen surface area to the nearest 0.1 m^2/g as follows:

$$\text{Surface area } (\text{m}^2/\text{g}) = Vm \times 4.35 \tag{5}$$

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