Designation: D6556 – 21

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

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D3765 Test Method for Carbon Black—CTAB (Cetyltrimethylammonium Bromide) Surface Area (Withdrawn 2007)[3]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4.2 CTAB Surface Area (formerly Test Method D3765) has been withdrawn.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.

$$CTAB = STSA * 1.0170 + 2.6434 \qquad (1)$$

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 ± 10°C.

5.5 *Oven, Gravity Convection,* capable of maintaining a temperature of 125 ± 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, through the sample bed, and allow purging with 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 ± 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) shall be the minimum time used for degassing. Failure to do so will lead to underreporting of the NSA and STSA values for the sample under test.

NOTE 2—For carbon blacks at their moisture pickup equilibrium, like standard reference blacks that have been exposed to atmospheric conditions, longer degassing times likely will be required in order to achieve stable results. It has been found that for SRB-8B, SRB-8C, and SRB-9C, 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. Again, failure to fully degas the carbon black will result in underreporting of NSA and STSA values.

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 shall be the minimum time used for degassing. It will be necessary to determine these minimum times for each grade of carbon black.

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 ± 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 shall be the minimum time used for degassing (see Note 2). It will be necessary to determine these minimum times for each grade of carbon black.

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. Follow all manufacturer's specific recommendations for free space and P_o measurement options to obtain reliable NSA and STSA values.

9.2 Fill the Dewar with liquid nitrogen (LN2) and allow it to reach temperature equilibrium. The Dewar shall be refilled approximately once per hour or between each analysis. The time required to reach equilibrium is dependent upon Dewar size and quality. Consult the manufacturer's recommendations for Dewar equilibration times and conditions.

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 equilibrium 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. Consult the manufacturer's recommendations for Dewar cleaning.

9.3 Following is a list of P_o measurement options, listed in decreasing order of reliability of P_o values. Follow all manufacturer's recommendations for determination of P_o values that are to be used for NSA and STSA calculations.

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 analysis, 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 analysis, 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 initiat-

ing 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.

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. For calculated sample free space, the free space of the empty sample cells must be known, generally from an analysis with empty sample cells. The free space for each cell must be determined for some cell designs. Follow all manufacturer's recommendations for obtaining optimum free space values, whether measured directly over the sample, or calculated using the free space volume of the sample cells, along with the sample mass and density. Follow all manufacturer's recommendations for maintaining stable, and perhaps minimized, free space values, for example, by using filler rods.

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, particularly when backfilling at the end of degassing or an analysis, 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:*

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

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:

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

10.4 *Nitrogen Surface Area:*

TABLE 1 Example of NSA Data Analysis

N121[A]				
	Raw Data		Calculation	
P/Po	Vol. Ads., cm^3/g	Rel. Press. Range	Correlation Coefficient	NSA, m^2/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., cm^3/g	Rel. Press. Range	Correlation Coefficient	NSA, m^2/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., cm^3/g	Rel. Press. Range	Correlation Coefficient	NSA, m^2/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.

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:

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

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 mono-molecular 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, along with a positive y-intercept, 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 An alternative interpretation of the proper relative pressure range for NSA calculations is to use 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:

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

where:

$V m$ = $\frac{1}{B + M}$

B = Y-axis intercept,
M = slope of the straight line, and
4.35 = area occupied by 1 cm^3 of nitrogen =
$$\frac{(6.02 \times 10^{23})(16.2 \times 10^{-20})}{22400}$$

6.02×10^{23} = Avogadro's number,
16.2×10^{-20} = area of nitrogen molecule in m^2, and
22400 = number of cm^3 occupied by one mole of gas at STP.

10.5 *Statistical Thickness Surface Area:*

10.5.1 Determine the STSA[5] of the black using a plot of the volume of nitrogen gas adsorbed per gram of sample at STP (V_a) versus the statistical layer thickness (t).

10.5.2 Prepare the V_a-t plot by plotting t (nm) on the X axis versus V_a (dm^3/kg at STP) on the Y axis, for data sets having a minimum of 4 points collected at equally spaced P/P_o values in the range of 0.2 to 0.5. Do not change the range of points used to calculate STSA values.

where:

t = statistical layer thickness of carbon black = $0.088(P/P_o)^2 + 0.645 \ (P/P_o) + 0.298$

NOTE 5—The carbon black thickness model was developed using an N762 carbon black in the P/Po range of 0.2 to 0.5. T values calculated outside of this range are invalid and will result in erroneous STSA values.

10.5.3 Determine the slope of the V_a-t plot using standard linear regression.

10.5.4 Calculate the STSA to the nearest 0.1 m^2/g as follows:

$$STSA = M \times 15.47 \qquad (6)$$

where:

M = slope of the V_a-t plot, and
15.47 = a constant for the conversion of nitrogen gas to liquid volume, and conversion of units to m^2/g.

10.5.5 STSA is based on a thickness model developed using an N762 carbon black. This carbon black was chosen because of its low surface area and low structure level. This universal model does not perfectly apply to all carbon blacks; consequently, while it is theoretically impossible for external surface area to be higher than total surface area, in practice there are instances where STSA is higher than NSA. For analyses that yield STSA values that are higher than NSA, the measured STSA value should be reported.

11. Report

11.1 Report the following information:

11.1.1 Proper sample identification,

11.1.2 Number of data points and relative pressures used to obtain both NSA and STSA,

11.1.3 The sample mass to the nearest 0.1 mg, and

11.1.4 The NSA or STSA, or both, of the sample reported to the nearest 0.1 m^2/g.

12. Precision and Bias

12.1 These precision statements have been prepared in accordance with Practice D4483-99. Refer to this practice for terminology and other statistical details.

12.2 *Nitrogen Surface Area (NSA):*

12.2.1 A Type 1 interlaboratory 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 material on each of two days (total of four tests). A test result is the value obtained

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

[5] Magee, R. W., *Rubber Chemistry and Technology*, Vol. 68, No. 4, 1995, p. 590.