Designation: D 6556 – 03

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

This standard is issued under the fixed designation D 6556; 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 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[2]

D 1900 Practice for Carbon Black—Sampling Bulk Shipments[2]

D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries[2]

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.

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 Practice D 1799 and Practice D 1900.

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 minutes at the same conditions intended for degassing the sample. Weigh the empty sample cell to the nearest 0.1 mg and record the mass.

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[1] This test method is under the jurisdiction of ASTM Committee D24 on Carbon Black and is 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.

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 ± 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.

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 ± 10°C for ½ h or longer as required to obtain and hold a pressure less than 1.4 Pa (10 µm Hg).

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.

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.

9.2 Fill the Dewar with liquid nitrogen and allow it to reach temperature equilibrium, preferably 0.5 to 1 h.

9.3 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).

9.4 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.

9.5 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.

9.6 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.

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*:

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

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:

$$V_a = \frac{\textit{Volume of Nitrogen for each dosing in cm}^3}{\textit{sample mass in g}} \quad (2)$$

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[3] equation as follows:

$$\frac{P}{V_a\ (P_o - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \times \frac{P}{P_o} \quad (3)$$

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

[3] Brunauer, Emmett and Teller, Journal of the American Chemical Society, Volume 60, 1938, p. 309.

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:

$$\text{Surface area } (m^2/g) = Vm \times 4.35 \quad (4)$$

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.

where:

Vm = $\frac{1}{B + M}$

B = Y-axis intercept, $\pm 10^{-5}$,
M = slope of the straight line, $\pm 10^{-5}$, 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[4] 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* P/P_o *equally spaced in the range of 0.2 to 0.5.*

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

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:

$$STSA = M \times 15.47 \quad (5)$$

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 In instances where the V_a-t *plot yields a negative intercept, report the STSA value as being equivalent to the NSA value. This prevents STSA values from being higher than the NSA values, as this is a theoretical impossibility.*

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.

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

12. Precision and Bias

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

12.2 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 2 and Table 3.

12.3 *Nitrogen Surface Area (NSA)*

12.3.1 A Type 1 interlaboratory precision program was conducted. 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). The number of participating laboratories is listed in Table 2.

12.3.2 The results of the precision calculations for this test are given in Table 2. The materials arranged in ascending "mean level" order.

12.3.3 *Repeatability*—The **pooled relative** repeatability, (*r*), of the NSA test has been established as 1.87 %. Any other value in Table 2 may be used as an estimate of repeatability, as appropriate. The difference between two single test results (or determinations) found on identical test material under the repeatability conditions prescribed for this test will exceed the repeatability on an average of not more than once in 20 cases in the normal and correct operation of the method. Two single test results that differ by more than the appropriate value from Table 2 must be suspected of being from different populations and some appropriate action taken.

NOTE 2—Appropriate action may be an investigation of the test method procedure or apparatus for faulty operation or the declaration of a significant difference in the two materials, samples, etc., which generated the two test results.

12.3.4 *Reproducibility*—The **pooled relative** reproducibility, (*R*), of the NSA test has been established as 3.18 %. Any other value in Table 2 may be used as an estimate of reproducibility, as appropriate. The difference between two single and independent test results found by two operators working under the prescribed reproducibility conditions in different laboratories on identical test material will exceed the reproducibility on an average of not more than once in 20 cases in the normal and correct operation of the method. Two single test results produced in different laboratories that differ by more than the appropriate value from Table 2 must be suspected of being from different populations and some appropriate investigative or technical/commercial action taken.

12.3.5 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (true) test property value. Reference values do not exist for this test method since the value or level of the test property is exclusively defined by the test method. Bias, therefore, cannot be determined.

12.4 *Statistical Thickness Surface Area (STSA)*

12.4.1 A Type 1 interlaboratory precision program was conducted. 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). The number of participating laboratories is listed in Table 3.

12.4.2 The results of the precision calculations for this test are given in Table 3. The materials are arranged in ascending "mean level" order.

12.4.3 *Repeatability*—The **pooled relative** repeatability, *(r)*, of the STSA test has been established as 3.49 %. Any other value in Table 3 may be used as an estimate of repeatability, as appropriate. The difference between two single test results (or determinations) found on identical test material under the repeatability conditions prescribed for this test will exceed the repeatability on an average of not more than once in 20 cases in the normal and correct operation of the method. Two single test results that differ by more than the appropriate value from Table 3 must be suspected of being from different populations and some appropriate action taken.

NOTE 3—Appropriate action may be an investigation of the test method procedure or apparatus for faulty operation or the declaration of a significant difference in the two materials, samples, etc., which generated the two test results.

12.4.4 *Reproducibility*—The **pooled relative** reproducibility, *(R)*, of the STSA test has been established as 6.87 %. Any other value in Table 1 may be used as an estimate of reproducibility, as appropriate. The difference between two single and independent test results found by two operators working under the prescribed reproducibility conditions in

TABLE 2 Precision Parameters for Test Method D 6556, Carbon Black—NSA (Type 1 Precision)

Units	10^3 m^2/kg (m^2/g)						
Material	Number of Laboratories	Mean Level	*Sr*	*(r)*	*SR*	*(R)*
SRB D6 (N762)	19	30.6	0.25	2.33	0.41	3.82
SRB F6 (N683)	19	35.3	0.47	3.77	0.60	4.83
SRB E6 (N660)	19	36.0	0.40	3.16	0.48	3.77
SRB C6 (N326)	18	78.3	0.40	1.44	0.78	2.82
SRB B6 (N220)	19	110.0	0.53	1.37	0.94	2.42
SRB A6 (N134)	19	143.9	0.70	1.37	1.30	2.56
Average		72.4				
Pooled Values			0.48	1.87	0.81	3.18

TABLE 3 Precision Parameters for Test Method D 6556, Carbon Black—STSA (Type 1 Precision)

Units	10^3 m^2/kg (m^2/g)					
Material	Number of laboratories	Mean Level	*Sr*	*(r)*	*SR*	*(R)*
SRB D6 (N762)	16	29.6	0.45	4.32	0.76	7.29
SRB F6 (N683)	16	34.1	0.61	5.06	0.72	6.02
SRB E6 (N660)	16	35.1	0.77	6.24	0.78	6.27
SRB C6 (N326)	15	79.2	0.69	2.45	1.42	5.09
SRB B6 (N220)	16	105.4	0.96	2.59	1.86	5.00
SRB A6 (N134)	16	135.7	1.37	2.87	3.17	6.60
Average		69.8				
Pooled Values			0.86	3.49	1.70	6.87

different laboratories on identical test material will exceed the reproducibility on an average of not more than once in 20 cases in the normal and correct operation of the method. Two single test results produced in different laboratories that differ by more than the appropriate value from Table 3 must be suspected of being from different populations and some appropriate investigative or technical/commercial action taken.

12.5 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (true) test property value. Reference values do not exist for this test method since the value or level of the test property is exclusively defined by the test method. Bias, therefore, cannot be determined.

13. Keywords

13.1 Brunauer/Emmett/Teller; carbon black, B.E.T.; nitrogen adsorption; nitrogen surface area; statistical thickness surface area; surface area by multipoint B.E.T. method, external surface area