Designation: D 4820 – 99

Standard Test Methods for Carbon Black—Surface Area by Multipoint B.E.T. Nitrogen Adsorption[1]

This standard is issued under the fixed designation D 4820; 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 These test methods cover the determination of the nitrogen surface area of carbon blacks by the conventional Brunauer, Emmett, and Teller (B.E.T.) theory of multilayer gas adsorption behavior using multipoint determinations. These test methods specify 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 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, and means to deal with accidental mercury spills.)

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 3324 Practice for Carbon Black—Improving Test Reproducibility Using ASTM Reference Blacks[2]

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

3. Significance and Use

3.1 These test methods are used to measure the standard nitrogen surface area of carbon blacks by the Multipoint (B.E.T.) Method.

4. Sampling

4.1 Samples may be taken in accordance with Practice D 1799 and Practice D 1900.

Test Method A—Surface Area by Classical Glass Vacuum Apparatus

5. Summary of Test Method

5.1 The nitrogen surface area is measured by evaluating the amount of nitrogen absorbed, at liquid nitrogen temperature, by a carbon black standard (or other carbon black sample) at several (at least five) partial pressures of nitrogen.

6. Apparatus

6.1 *Classical Glass Vacuum Apparatus* or equivalent, constructed as shown in Fig. 1, including diffusion pump, manometer, and buret similar to the one illustrated in Fig. 1.

6.1.1 Equivalent apparatus must include: manometer, gas buret, gas storage vessels, diffusion and vacuum pumps, and sample cell (see Note 7).

6.2 *Oven*, vacuum-type, capable of temperature regulation to± 5°C at 200°C. Pressure should be less than 135 Pa (1 mmHg).

6.3 Sample cells which, when attached to the vacuum apparatus, will maintain pressure below 1.35 mPa (10 nm Hg).

6.4 *Dewar Flasks*, two each with volumes of 2 dm^3.

6.5 *Mechanical Vacuum Pump*.

6.6 *McCloud Gage*, or equivalent means to measure status of the vacuum.

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

6.8 Gas-tight glass stopcock assemblies as required for the apparatus.

6.9 Supply of small (30 cm^3) glass vials with caps for oven drying samples.

6.10 *Heating Mantle* or equivalent, capable of maintaining a temperature of 300 ± 10°C.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,

[1] This test method is under the jurisdiction of ASTM Committee D-24 on Carbon Blackand 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.

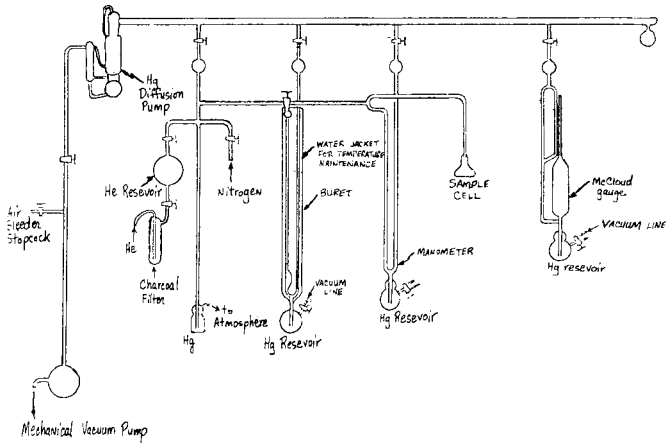

FIG. 1 Glass Vacuum Apparatus

where such specifications are available.[3] Other grades may be used, provided it is first ascertained that it is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean distilled water or water of equal purity.

7.3 *Liquid nitrogen*.

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

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

7.6 *Instrument grade mercury*.

7.7 High vacuum stopcock grease, Apiezon-type *N*.

8. Preparation of Apparatus

NOTE 1—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 1.35 mPa (10 nmHg) 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 cm^3 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 1.35 mPa (10 nmHg).

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

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

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

8.2.6 Transfer approximately 2 cm^3 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 cm^3 of instrument grade mercury. Record the mass of the mercury used to ±0.001 g, W_m.

8.2.11 Reinstall the sample cell containing the mercury onto the apparatus.

8.2.12 Re-evacuate the sample cell, manometer, and gas burette to a pressure below 1.35 mPa (10 nmHg).

8.2.13 Repeat 8.2.3-8.2.9.

8.3 *Buret Factor Calculations*:

8.3.1 For each set of data (see 8.2.9) determine the pressure change by measuring the difference in buret readings before and after helium dosing as follows:

$$P_{B1} = V_{B1} - V_{B2} \tag{1}$$

8.3.2 Determine the total buret pressure difference for each data set as follows:

$$P_{BT} = (V_{B1} - V_{B2})_1 + (V_{B1} - V_{B2})_2 + \ldots \tag{2}$$

8.3.3 Determine buret pressure to cell pressure ratio for each data set as follows:

$$A = \frac{P_{BT}}{P_c} \tag{3}$$

8.3.4 Determine the ratio of cell temperature to buret temperature for each data set as follows:

$$B = \frac{T_c}{T_B} \tag{4}$$

8.3.5 Determine the product of the temperature and pressure for each data set as follows:

$$C = A \times B \tag{5}$$

8.3.6 Determine the average *C* value for the empty sample cell (C_E) and the cell with the mercury (C_m).

8.3.7 Determine the volume of mercury used as follows:

$$V = W_m \div \text{density of mercury}$$

$$\text{density of mercury} = 13.5955\ \text{Mg/m}^3 \text{ at } 0°\text{C} \tag{6}$$

8.3.8 Determine the buret volume factor corrected to standard temperature and pressure (STP) as follows:

$$F_B = \frac{V}{C_E - C_m} \times \frac{273.15\ K}{101.32\ \text{kPa}} \tag{7}$$

9. Sample Preparation Procedure

9.1 Dry a portion of the standard reference black to be tested (such that the portion contains well in excess of 50 m^2 in surface area of the black) in a vacuum oven at 200°C and a pressure below 1.35 Pa (10 μmHg) for 1 h.

9.2 Weigh out a sample cell to the nearest 0.0001 g and record the mass.

9.3 Weigh into the cell a sample of the black to be tested, that has been dried as required in 9.1, so that the cell contains approximately 50 m^2 of surface area for the black.

9.3.1 If this is not a measurement of a standard reference

[3] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

black, and the type of black is unknown, assume a surface area of 75 m^2/g and weigh out approximately 0.5 g. Record the combined mass of the cell and black.

9.4 With apparatus at atmospheric pressure, seal the sample cell containing the carbon black onto the vacuum apparatus.

9.5 Turn on the mechanical vacuum pump. After pressure is reduced below 135 Pa (1 mmHg), proceed to 9.6.

9.6 Start up diffusion vacuum pump.

9.7 Place heating mantle around sample cell and de-gas the sample at 300 ± 10°C for 1 h or longer as required to obtain and hold a pressure less than 1.35 mPa (10 nmHg); record temperature and heating time. Periodically check the vacuum with the McCloud gage or similar instrument. A pressure less than 1.35 mPa (10 nmHg) should be maintained.

9.8 Remove heating mantle and allow the sample cell to cool to room temperature.

10. Calibration Procedure

NOTE 2—This procedure is designed to measure the dead volume (that is, helium factor) in the system using helium, as helium is not adsorbed onto the surface of the black at the temperature of liquid nitrogen.

10.1 When the sample has cooled, immerse the sample bulb to a depth of 10 cm in the liquid nitrogen contained in the Dewar flask.

NOTE 3—Since liquid nitrogen tends to evaporate rather rapidly, be sure to keep the level constant for the duration of the test.

10.2 Measure the helium factor of the sample cell system (that is, calibrate the system) using helium gas as follows:

10.2.1 Admit a dose of helium to the gas buret that is approximately 50 % of the volume of the buret.

10.2.2 Read and record gas buret volume (V_{B1}) and temperature (T_B).

10.2.3 Dose sample cell with approximately 2 cm^3 of helium. Read and record manometer pressure (P).

10.2.4 Read and record gas buret volume (V_{B2}), having dosed the sample with helium.

10.2.5 Repeat incremental dosing of sample cell with helium twice more; read and record buret volume, manometer pressure and buret temperature for each dosing.

10.2.6 Calculate helium factor in accordance with 12.2 in Section 12.

NOTE 4—When helium factors are calculated, the three results should not differ by more than ±4 $\mu m^3/Pa$ (± 0.0005 $cm^3/mmHg$). If their differences are more than this, repeat 10.2.1-10.2.5 to obtain factors that are within 4 $\mu m^3/Pa$ (0.0005 $cm^3/mmHg$) of each other.

10.3 While the cell is still immersed in liquid nitrogen, evacuate helium from the entire system. After approximately 15 min, read the vacuum with the McCloud or equivalent gage. When a pressure less than 1.35 mPa (10 nmHg) has been attained, begin measurement procedure.

11. Measurement Procedure

11.1 Fill the gas buret with nitrogen gas to approximately 75 % of its volume.

11.2 Dose the sample cell with an amount of nitrogen gas to give an approximate pressure reading of 4.7 kPa (35 mmHg). This value is just below the beginning of the linear region on the adsorption isotherm for carbon black. Read and record buret pressures (P_{B1}, P_{B2}), as done in 10.2, and temperature (T_B) along with the manometer pressure (P) for each dose.

11.3 Allow the pressure in the sample cell-manometer system to equilibrate for 0.5 h or more to obtain a constant pressure. Read and record manometer pressure (P).

11.4 For subsequent doses, introduce 1 to 1.5 cm^3 of nitrogen to the sample in successive doses. Obtain a minimum of five data sets in the pressure range of 6 kPa (45 mmHg) to 27 kPa (200 mmHg). In determining carbon black surface areas, it is not necessary to take readings at manometer pressures higher than 27 kPa (200 mmHg) since this value is beyond the linear region of the adsorption isotherm.

11.5 Obtain the saturation vapor pressure of liquid nitrogen (P_o) by accurately measuring the barometric pressure and adding 2 kPa (15 mmHg) to its value as follows:

$$P_o = \text{barometric pressure (kPa)} + 2\ \text{kPa} \quad (8)$$

NOTE 5—In principle, a more accurate means of measuring P_o is to immerse an identical, empty reference cell in a Dewar flask to a depth equivalent to the sample cell. Admit nitrogen gas into the reference cell to obtain equilibrium pressure (P_o), that is, approximately 103 kPa (775 mmHg).

11.6 With both vacuum pumps running, open the stopcocks so that the sample cell is open to the vacuum line. Remove the liquid nitrogen from around the sample cell, allowing adsorbed nitrogen to exhaust into the vacuum line.

11.7 Proceed to Section 12.

12. Calculation

12.1 *Sample Mass*:

$$\text{Mass of sample (dried)} = (\text{mass of cell} + \text{sample}) - (\text{mass of cell})$$
$$(\text{Record masses to} \pm 0.0001\ \text{g}) \quad (9)$$

12.2 *Helium Factor*— Calculate helium factor as follows:

$$\text{Helium factor} = \Sigma \frac{\left(\frac{V_B \times 273.15\ \text{K}}{101.32\ \text{kPa}} \times \frac{V_{B2} - V_{B1}}{T_B} \right)}{P} \Bigg/ n \quad (10)$$

where:

V_B = volume of buret (see Section 10),
T_B = temperature of buret in Kelvin (K = 273.15 + °C),
V_{B1} = initial volume in buret,
V_{B2} = final volume in buret,
P = pressure in manometer, and
n = number of data sets.

12.3 *Nitrogen Surface Area*:

12.3.1 Calculate volume of nitrogen admitted to the nearest ± 0.0001 cm^3 as follows:

$$V_{ADM} = F_B \times \frac{P_{B2} - P_{B1}}{T_B} \quad (11)$$

where:

V_{ADM} = volume of gas admitted at stp,
F_B = buret factor,
P_{B2} = final pressure in buret (read after 0.5 h equilibration),
P_{B1} = initial pressure in buret (read before each dose), and