Standard Test Method for
Single-Point Determination of Specific Surface Area of Catalysts and Catalyst Carriers Using Nitrogen Adsorption by Continuous Flow Method[1]

This standard is issued under the fixed designation D 4567; 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 single-point determination of the surface area of catalysts and catalyst carriers that exhibit Type II or Type IV nitrogen adsorption isotherms using a nitrogen-helium flowing gas mixture. This test method is applicable for the determination of total surface areas from 0.1 to 300 m^2, where rapid surface area determinations are desired.

1.2 Because the single-point method uses an approximation of the BET equation, the multipoint BET method (Test Method D 3663) is preferred to the single-point method.

NOTE 1—This is particularly true when testing microporous materials.

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]
D 3663 Test Method for Surface Area of Catalysts
D 3766 Terminology Relating to Catalysts and Catalysis
E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E 456 Terminology Relating to Quality and Statistics
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions*—See Terminology D 3766.

3.2 *Symbols:*

A_{cs} = cross-sectional area of nitrogen, 16.2×10^{-20} m^2.
C_{I_T} = integrator counts.
$C_I^T a$ = integrator counts corrected for ambient temperature.
$C_I^P a$ = integrator counts corrected for ambient pressure.
N = Avogadro's number, 6.02×10^{23}, molecules/mole.
P = partial pressure of nitrogen, torr.
P_a = ambient pressure, torr.
P_o = saturated equilibrium vapor pressure of liquid nitrogen, torr.
R = gas constant, 82.1 cm^3 atm/K mole.
T_a = ambient temperature, K.
V = volume of nitrogen adsorbed at ambient temperature and pressure, cm^3.
W_1 = tare of sample cell, g.
W_2 = sample mass + tare of sample cell after analysis, g.
W_s = mass of sample, g.

4. Summary of Test Method

4.1 The sample is degassed by heating in a flow of inert gas to remove adsorbed vapors from the surface. The sample is then immersed in a liquid nitrogen bath causing adsorption of nitrogen from a flowing mixture of a fixed concentration of nitrogen in helium. When adsorption is complete, the sample is allowed to warm to room temperature causing desorption, which results in an increase in the nitrogen concentration in the flowing mixture. The quantity of nitrogen gas desorbed is determined by sensing the change in thermal conductivity.

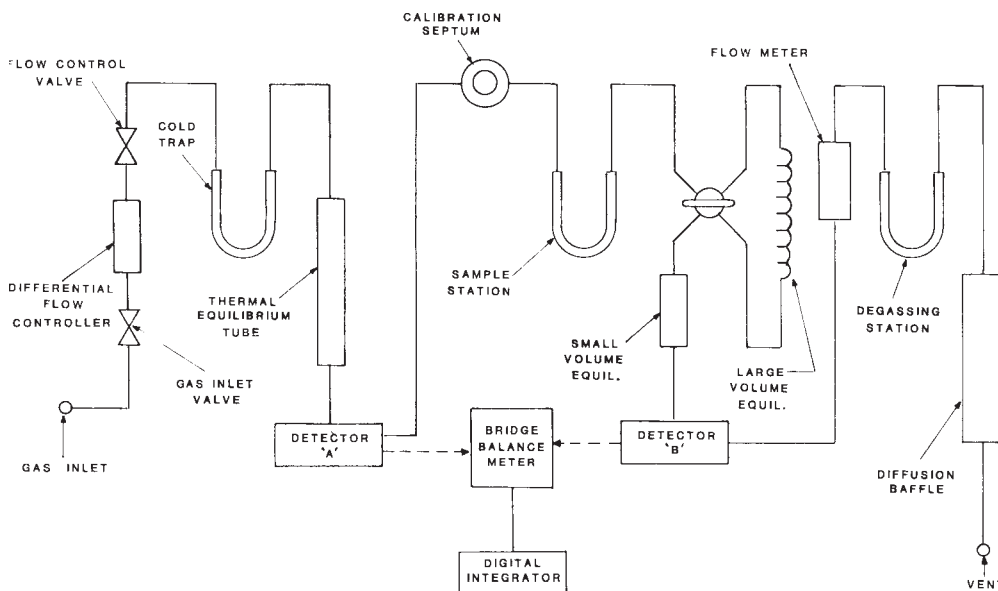4.2 Calculation of the surface area is based on a modified form of the BET equation.

FIG. 1 Apparatus

5. Significance and Use

5.1 This test method is useful for determining the specific surface area of catalysts and catalyst carriers for material specifications, manufacturing control, and research and development in the evaluation of catalysts.

6. Apparatus

6.1 A schematic diagram of the apparatus is shown in Fig. 1. The apparatus may be constructed of glass or metal tubing. It has the following features:

6.1.1 *Differential Flow Controller* from the gas inlet valve to a flow control valve to eliminate fluctuations in the gas flow.

6.1.2 *Two Thermal Conductivity Detectors*—A reference detector (*A*) to sense the nitrogen-helium gas mixture and a second detector (*B*) to sense changes in the gas mixture after flowing through the sample cell. The two detectors are initially balanced to allow the detection of changes in the nitrogen concentration.

6.1.3 *Flow-Through Sample Cells*, of various volumes and shapes depending on the application.

6.1.4 *Two Equilibration Tubes* selected by a selector valve, between the sample cell and detector (*B*). The small volume tube has a volume of approximately 20 cm³ and the large volume tube has a 100 cm³ capacity to allow for temperature and pressure equilibration of a wide range of volumes of gases.

6.1.5 *Flow Meter*, to monitor the flow rate of the nitrogen-helium mixture maintained at approximately 20 cm³/min.

6.1.6 *Diffusion Baffle*, to prevent air from diffusing back into the system during cooling of the sample.

6.1.7 *Bridge Balance Meter*, to display balance or imbalance between detectors *A* and *B*.

6.1.8 *Digital Integrator*, to measure the imbalance between detectors *A* and *B* and display the surface area of the sample.

6.1.9 *Septum or Fixed Loop*, for injection of calibration gas.

6.1.10 *Degassing Station*, for removal of adsorbed vapors from the sample.

6.1.11 *Cold Trap*, for removal of impurities in the gas mixture.

6.1.12 *Thermal Equilibration Tube*, to allow the flowing gas mixture to reach temperature and pressure equilibration before reaching detector (*A*).

6.2 *Heating Mantle*.

6.3 *Dewar Flasks*.

6.4 *Laboratory Balance* with 0.1 mg (10^{-7} kg) sensitivity.

6.5 *Gas-Tight Syringe or Gas Sampling Loop*, 1.00 cm³.

7. Reagents

7.1 *Liquid Nitrogen*, of such purity that the saturated equilibrium vapor pressure is not more than 20 torr above ambient pressure.

7.2 *Cylinder*, with pressure regulator, of high purity 30 mole % nitrogen in helium equivalent to a relative pressure of approximately 0.3, where the nitrogen concentration is known to within 0.1 mole %. Concentrations lower than 30 mole % should be used for materials containing micropores, for example, zeolites.

8. Calibration of the Apparatus

8.1 If the gas mixture contains impurities, place a Dewar flask containing liquid nitrogen around the cold trap.

8.2 Using a gas-tight syringe inject 1.00 cm³ (or some other known volume) of air or nitrogen into the calibration septum. The digital integrator should display 2.84 ± 0.03 counts (see 11.3) for a 1.00-cm³ injection (or a proportional number of counts for a different volume). If the counts are greater than 2.84, increase the gas flow through the flow control valve. If the counts are less than 2.84, decrease the gas flow and retest.

9. Preparation of Sample

9.1 Weigh to 0.0001 g a clean, dry empty sample cell. Record the mass, W_1.

9.2 Place the catalyst sample into the sample cell. Choose the sample size to provide an estimated surface area of 0.1 to 300 m^2.

9.3 Attach the sample cell to the degassing station.

9.4 Attach an empty cell to the sample station.

9.5 Open the gas inlet valve and adjust the flow control valve to allow a gas flow of approximately 20 cm^3/min. Observe the reading on the flow meter.

9.6 Install a heating mantle around the sample cell and raise the temperature to 300°C (573 K).

NOTE 2—Certain materials will decompose at 300°C (for example, alumina hydrates) or will sinter (for example, platinum black). Lower degassing temperatures are permitted for such materials. However, the degassing temperature should be specified when reporting the results.

9.7 Continue degassing at about 300°C (573 K) for a minimum of 1 h. Overnight degassing is permissible. If lower temperatures are used for degassing, longer times may be required.

9.8 Remove the heating mantle and allow the sample to cool.

9.9 Remove the sample cell from the degassing station, protecting the sample from exposure to atmospheric contaminants.

9.10 Remove the empty cell from the sample station.

10. Surface Area Determination

10.1 Attach the sample cell to the sample station.

10.2 Allow any air to be purged from the system by the flowing gas mixture. This condition can be ascertained by observing that the bridge balance meter indicates a balance.

10.3 To initiate adsorption, place a Dewar flask of liquid nitrogen around the sample cell so that the liquid level is approximately 2 to 3 cm from the top of the cell.

10.4 When adsorption is complete, as indicated by the bridge balance meter and digital integrator, remove the Dewar flask.

10.5 Clear the digital integrator.

10.6 Immerse the sample cell in a beaker of room temperature water until the gas flow returns to its original rate as indicated by the flow meter.

NOTE 3—If the flow meter does not return to its original value, obtained before the digital integrator starts to count, either remove some of the sample or use the large volume equilibration tube (see Fig. 1) and repeat steps 10.2-10.6.

10.7 When the counter stops counting, record the counter reading.

10.8 Remove the sample cell from the sample station, dry thoroughly and weigh. Record the mass, W_2.

11. Calculations

11.1 Calculate the total surface area of the sample from a modified form of the BET equation as follows:

$$\text{Total surface area} = (P_a V N A_{cs})/(RT_a)(1 - P/Po) \qquad (1)$$

11.2 Using 30 mole % nitrogen as the adsorbate in helium at an ambient temperature of 22°C (295 K) and a pressure of 1.0 atm (760 torr) and assuming that P_o is 775 torr,

$$\text{Total surface area} = 2.84\ V \qquad (2)$$

TABLE 1 Repeatability and Reproducibility

Test Result (Consensus), m^2/g	95% Repeatability Limit (Within Laboratory), m^2/g, (%)	95% Reproducibility Limit (Between Laboratories), m^2/g, (%)
10.33	0.17 (1.7)	1.82 (17.6)
153.2	2.66 (1.7)	22.24 (14.5)
277.6	4.49 (1.6)	46.61 (16.8)

11.3 Thus, 2.84 m^2 of surface area corresponds to 1.00 cm^3 of nitrogen adsorbed.

11.4 Calculate the mass of sample as follows:

$$W_S = W_2 - W_1 \qquad (3)$$

11.5 For ambient temperatures other than 295 K, multiply the integrator counts (C_I) by 295/T_a.

$$C_i^T a = C_I \times 295/Ta \qquad (4)$$

11.6 For ambient pressures other than 760 torr, multiply the integrator counts (C_I) by P_a/760.

$$C_I^P a = C_I \times P_a/760 \qquad (5)$$

11.7 For gas concentrations other than 30 mole %, multiply the integrator counts by $(1 - P/P_o)/0.706$. The partial pressure P of the gas is the product of the mole fraction and ambient pressure. P_o is assumed to be ambient pressure plus 15 torr.

11.8 Calculate the specific surface area as follows:

$$\text{Specific surface area} = C_I/W_S \qquad (6)$$

or if the corrections in 11.5, 11.6, or 11.7, or combination thereof, have been used:

$$\text{Specific surface area} = \frac{C_I}{W_S} \times \frac{295}{T_a} \times \frac{P_a}{760} \times \frac{1 - P/P_o}{0.706} \qquad (7)$$

12. Presentation of Data

12.1 Report the specific surface area in square metres per gram to three significant figures.

13. Precision and Bias [3]

13.1 *Test Program*—An interlaboratory study was conducted in which the named property was measured in three separate test materials in 22 separate laboratories. Practice E 691, modified for nonuniform data sets, was followed for the data reduction. Analysis details are in the research report.

13.2 *Precision*—Pairs of test results obtained by a procedure similar to that described in the study are expected to differ in absolute value by less than 2.772 S, where 2.772 S is the 95 % probability limit on the difference between two test results see Table 1, and S is the appropriate estimate of standard deviation. Definitions and usage are given in Terminology E 456 and Practice E 177, respectively.

13.3 *Bias*—The test method described is without known bias. Results from this single-point method are statistically comparable to those of the multipoint method based on three samples ranging in specific surface areas from 10 to 280 m^2/g.

NOTE 4—No microporous materials were tested in the interlaboratory study supporting this method. Microporous materials may produce different results.

14. Keywords

14.1 adsorption; catalyst carriers; catalysts; continuous flow; surface area