



Designation: D4567 – 19

Standard Test Method for Single-Point Determination of Specific Surface Area of Catalysts and Catalyst Carriers Using Nitrogen Adsorption by Continuous Flow Method¹

This standard is issued under the fixed designation D4567; 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 m², 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 D3663) is preferred to the single-point method.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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 the user of this standard to consult and establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *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

D3663 Test Method for Surface Area of Catalysts and Catalyst Carriers

¹ This test method is under the jurisdiction of Committee D32 on Catalysts and is the direct responsibility of Subcommittee D32.01 on Physical-Chemical Properties.

Current edition approved July 1, 2019. Published August 2019. Originally approved in 1986. Last previous edition approved in 2013 as D4567 – 03(2013). DOI: 10.1520/D4567-19.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

D3766 Terminology Relating to Catalysts and Catalysis
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E456 Terminology Relating to Quality and Statistics
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions*—See Terminology D3766.

3.2 *Symbols*:

A_{cs} = cross-sectional area of nitrogen, 16.2×10^{-20} m².
 C_I = 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 cm³ atm/K mole.
 T_a = ambient temperature, K.
 V = volume of nitrogen adsorbed at ambient temperature and pressure, cm³.
 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.

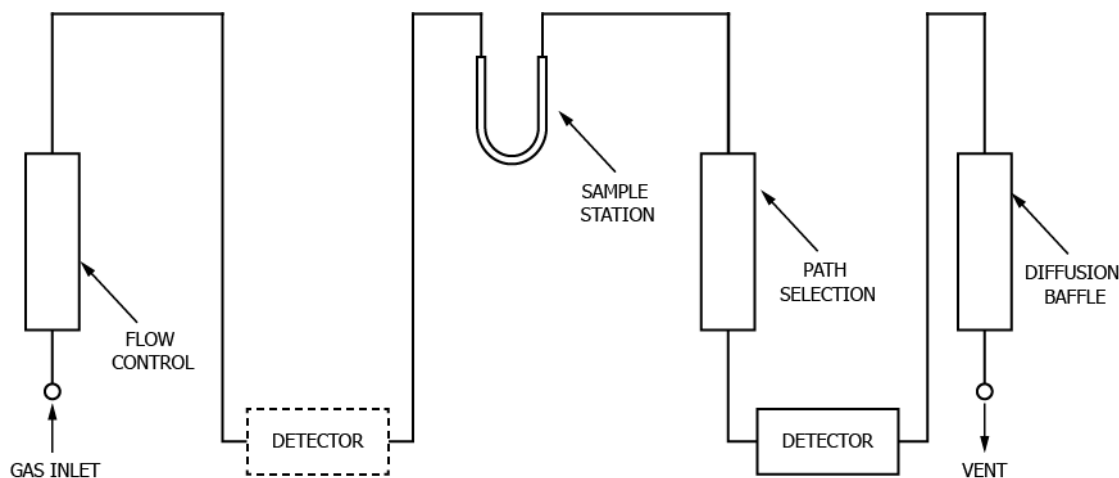


FIG. 1 Apparatus

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

6.1.1 *Flow Control*—A flow control system will be present after the gas inlet(s) to establish and control the flow of the analysis gas at the target concentration, eliminating fluctuations in the gas flow. The instrument can have a single gas inlet when working with pre-mixed gas or two gas inputs in the case the gas mixture is created in the instrument. The flow control system can consist of a combination of a pressure regulator, a regulating valve, and a volumetric flow meter or mass flow controller(s).

NOTE 1—In some systems, a flow meter may also be found after the sample cell to monitor the flow rate of the nitrogen-helium mixture.

6.1.2 *Thermal Conductivity Detector(s)*—The apparatus will contain at least one thermal conductivity detector situated after the path selector to sense changes in the gas mixture after flowing through the sample cell. Analyzers with mass flow controllers do not need a secondary reference detector before the sample station as the initial gas concentration is precisely known. In analyzers without mass flow control of the input gas, a reference detector to sense the nitrogen-helium gas mixture before the sample station is also necessary. When a two detector configuration is used, the detectors are initially balanced to allow the detection of changes in the nitrogen concentration.

NOTE 2—Some systems with a two detector configuration may include a Bridge Balance Meter, to display balance or imbalance between the two detectors or a Digital Integrator, to measure the imbalance between detectors and display the surface area of the sample, or both.

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

6.1.4 *Equilibration Paths*—The apparatus will have at least two equilibration paths, selected by a selector valve or a combination of valves, between the sample cell and the down stream detector. Two or more paths allow for temperature and pressure equilibration of a wide range of volumes of gases.

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

6.1.6 *Septum or Fixed Loop*, (not shown in Fig. 1) for injection of calibration gas. (Optional: only required on analyzers without precise mass flow control of input gas.)

6.1.7 *Degassing Station*, (not shown in Fig. 1) with heating mantle, for removal of adsorbed vapors from the sample. (The degassing station can either be integrated into the apparatus or part of an independent sample preparation device.)

6.1.8 *Cold Trap*, (not shown in Fig. 1) for removal of impurities in the gas mixture. (Optional: Cold trap is not required if gas purity meets noted specification.)

6.1.9 *Thermal Equilibration Tube*, (not shown in Fig. 1) to allow the flowing gas mixture to reach temperature and pressure equilibration before reaching the first detector, in two detector configuration systems, or the sample station.

NOTE 3—Instruments without a cold trap do not require a thermal equilibration tube.

6.2 *Dewar Flasks*.

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

6.4 *Gas-Tight Syringe or Gas Sampling Loop*, 1.00 cm³. (Optional: only required on analyzers without precise mass flow control of input gas.)

NOTE 4—Commercial instruments are available for determining single point BET area. These instruments typically conform to the schematic in Fig. 1, and the manufacturer's manual should be consulted for proper calibration and reporting of single point BET area.

7. Reagents

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