Designation: D4780 – 23

Standard Test Method for Determination of Low Surface Area of Catalysts and Catalyst Carriers by Multipoint Krypton Adsorption[1]

This standard is issued under the fixed designation D4780; 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 specific surface area of catalysts and catalyst carriers in the range from 0.05 m^2/g to 10 m^2/g. A volumetric measuring system is used to obtain at least three data points which fall within the linear *BET* region.

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

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3663 Test Method for Surface Area of Catalysts and Catalyst Carriers

D3766 Terminology Relating to Catalysts and Catalysis

E105 Guide for Probability Sampling of Materials

E122 Practice for Calculating Sample Size to Estimate, With Specified Precision, the Average for a Characteristic of a Lot or Process

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*—Consult Terminology D3766.

3.2 *Symbols:*

P_{H1} = initial helium pressure, torr.
P_{H2} = helium pressure after equilibration, torr.
T_{H1} = temperature of manifold at initial helium pressure, °C.
T_{H2} = temperature of manifold after equilibration, °C.
P_1 = initial Kr pressure, torr.
T'_1 = manifold temperature at initial Kr pressure, K.
T_1 = manifold temperature at initial Kr pressure, °C.
P_2 = Kr pressure after equilibration, torr.
T'_2 = manifold temperature at P_2, K.
T_2 = manifold temperature at P_2, °C.
$P_{o,N}$ = liquid nitrogen vapor pressure, torr.
$P_{o,krypton}$ = calculated krypton vapor pressure, torr.
$T's$ = liquid nitrogen temperature, K.
X = relative pressure, $P_2/P_{o,krypton}$.
V_d = volume of manifold, cm^3.
V_s = the apparent dead-space volume, cm^3.
W_s = weight of sample, g.
W_1 = tare weight of sample tube, g.
W_2 = weight of sample plus tare weight of tube, g.
V_{ds} = volume of krypton in the dead space, cm^3.
V_1 = See 12.3.5.
V_2 = See 12.3.6.
V_t = See 12.3.7.
V_a = See 12.3.9.
V_m = See 12.6.

4. Summary of Test Method

4.1 A catalyst or catalyst carrier sample is degassed by heating in vacuum to remove absorbed vapors from the surface. The quantity of krypton adsorbed at various low pressure levels is determined by measuring pressure differentials after introduction of a fixed volume of krypton to the sample at liquid nitrogen temperature. The specific surface area is then calculated from the sample weight and adsorption data using the *BET* equation.

5. Significance and Use

5.1 This test method has been found useful for the determination of the specific surface area of catalysts and catalyst carriers in the range from 0.05 m^2/g to 10 m^2/g for materials specification, manufacturing control, and research and development in the evaluation of catalysts. The determination of

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

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[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.

surface area of catalysts and catalyst carriers above 10 m^2/g is addressed in Test Method D3663 – Surface Area of Catalyst and Catalyst Carriers – and is appropriate for most samples with specific surface areas above 1 m^2/g.

6. Apparatus

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

6.1.1 *Vacuum System,* capable of attaining pressures below 10^{-4} torr (1 torr = 133.3 Pa). This will include a vacuum gage (not shown in Fig. 1). Access to the distribution manifold is through the valve *V*.

6.1.2 *Distribution Manifold,* having a volume between 5 cm^3 and 40 cm^3 (V_d) known to the nearest 0.01 cm^3. This volume is defined as the volume between the stopcocks or valves and it includes the volume within the pressure gage.

6.1.3 *Constant Volume Gages,* capable of measuring 1 torr to 10 torr to the nearest 0.001 torr and 0 torr to 1000 torr to the nearest torr (1 torr = 133.3 Pa).

6.1.4 *Valve* (*H*), from the helium supply to the distribution manifold.

6.1.5 *Valve* (*K*), from the krypton supply to the distribution manifold.

6.1.6 *Sample Tube(s),* with volume between 5 cm^3 and 25 cm^3, depending on the application. The sample tube(s) may be connected to the distribution manifold with standard taper joints, glass-to-glass seals, or compression fittings provided they are rated for vacuum service.

NOTE 1—Modern commercial instruments may employ sample tubes with volumes outside of this range, and may be capable of testing multiple samples simultaneously rather than separately as stated in 10.1.

6.1.7 *Dewar Flask(s)* for immersion of the sample tube(s) in liquid nitrogen. The nitrogen level should be fixed at a constant height by means of an automatic level controller or manually refilled to a predetermined mark on the sample tube(s) about 30 mm to 50 mm below the distribution manifold connectors.

6.1.8 *Thermometer* for measuring the temperature of the distribution manifold ($T_1(i)$ or $T_2(i)$) in degrees Celsius. (Alternatively, the distribution manifold may be thermostatted a few degrees above ambient to obviate the necessity of recording this temperature.)

6.1.9 *Heating Mantle(s) or Small Furnace(s)* for each sample tube to allow outgassing samples at elevated temperatures.

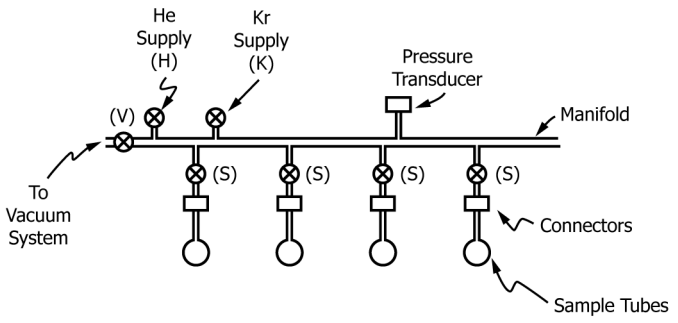

FIG. 1 Schematic Diagram of Surface Area Apparatus

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

6.1.11 *Thermometer* for measuring the temperature of the liquid nitrogen bath ($T_s(i)$) in kelvins. This will preferably be a nitrogen vapor-pressure-thermometer that gives $P_{o,N}(i)$ directly and has greater precision, or a resistance thermometer from which $P_{o,N}(i)$ values may be derived.

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

7.2 *Helium Gas,* at least 99.9 % pure.

7.3 *Krypton Gas,* at least 99.9 % pure.

7.4 *Liquid Nitrogen,* of such purity that the saturation vapor pressure $P_{o,N}$ is not more than 20 torr above barometric pressure. A fresh daily supply is recommended.

8. Sampling

8.1 A test sample shall be obtained from larger composites by riffling or splitting in accordance with subsection 5.12 of STP 447A[4], with the aim of obtaining a representative sample that represents shape and size distribution of the larger composite. Guide E105 can provide guidance on constructing a sampling plan with the representative sample can be determined by Practice E122.

9. Procedure—Sample Preparation and Degassing

9.1 Select a sample tube of the desired size. A 5 cm^3 tube is preferred for small samples to minimize dead space. However, larger tubes may be required for larger samples or for finely powdered samples, to avoid *elutriation of the powder* when degassing is started.

9.2 Evacuate the sample tube and then fill to atmospheric pressure with helium. This may be done on the surface area unit, or on a separate piece of equipment.

9.3 Remove the sample tube, cap, and weigh. Record the weight as W_1.

9.4 Place the sample, whose weight is known approximately, into the sample tube. If possible, choose the sample size to provide an estimated total surface area of 1 m^2 to 5 m^2.

[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 *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[4] Manual on Test Sieving Methods, ASTM STP 447A, ASTM International, 2005.