Designation: D 4780 – 95 (Reapproved 2001)

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

This standard is issued under the fixed designation D 4780; 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 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 *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:*

D 3663 Test Method for Surface Area of Catalysts[2]

D 3766 Terminology Relating to Catalysts and Catalysis[2]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[3]

E 456 Terminology Relating to Quality and Statistics[3]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]

3. Terminology

3.1 *Definitions:*

3.1.1 Consult Terminology D 3766.

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 11.3.5.
V_2 = See 11.3.6.
V_t = See 11.3.7.
V_a = See 11.3.9.
V_m = See 11.6.

4. Summary of Test Method

4.1 A catalyst 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 to 10 m^2/g for materials specification, manufacturing control, and research and development in the evaluation of catalysts. The determination of surface area of catalysts and catalyst carriers above 10 m^2/g is addressed in Test Method D 3663.

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[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] *Annual Book of ASTM Standards*, Vol 05.03.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

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 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 to 10 torr to the nearest 0.001 torr and 0 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.

NOTE 1—Modern commercial instruments may employ simple tubes with volumes outside of this range, and may be capable of testing multiple samples simultaneously rather than separately as stated in 9.1.

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 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.

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 $P_{o,N}$ directly and has greater precision, or a resistance thermometer from which $P_{o,N}$ values may be derived.

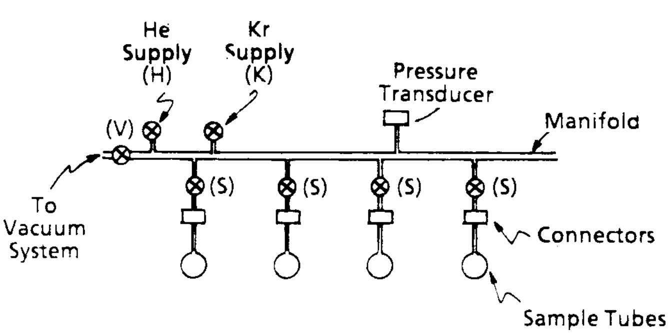

FIG. 1 Schematic Diagram of Surface Area Apparatus

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.[4] 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. Procedure—Sample Preparation and Degassing

8.1 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 *boiling* when degassing is started.

8.2 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.

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

8.4 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 to 5 m_2.

8.5 Attach the sample tube to the apparatus. If other samples are to be run, attach them at this time to the other ports.

8.6 Open the *S* valves where there are samples.

8.7 Slowly open the *V* valve, monitoring the rate of pressure decrease to avoid too high a rate, which might lead to excessive fluidization of powdered samples.

8.7.1 If a diffusion pump is used, it may be necessary to close the *V* valve system periodically to protect the diffusion pump fluid from exposure to pressures above 0.1 torr for periods of more than 30 s. Close the valve off for 2 min.

8.8 Install a heating mantle or furnace around each sample and raise the temperature to about 300°C (573 K). (**Warning**—Take special precautions if the moisture content exceeds approximately 5 % to avoid "bumping'' of powdered catalyst, and to avoid surface area loss by self-steaming. It is recommended that the heating rate not exceed 100 K/h under these circumstances.)

8.9 Continue degassing at about 300°C (573 K) for a minimum of 3 h, at a pressure not to exceed 10^{-3} torr. Overnight degassing is permissible.

NOTE 2—Certain materials decompose or sinter at 300°C. Lower

[4] *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.

degassing temperatures are permissible for such materials; however, the degassing temperature should be specified when reporting the results.

8.10 Remove the heating mantles, and allow the samples to cool.

8.11 Close the *S* valves.

8.12 It is permissible to exercise the option of preliminary degassing on an external unit. In such a case, follow the procedures of 8.5-8.11 and then repeat on the adsorption unit, except that the degassing on the adsorption unit can be at room temperature and need not exceed 1 h.

8.13 If it is desired to weigh the sample after preliminary degassing on an external unit, back-fill with helium to slightly above atmospheric pressure. Close the *S* valve.

8.13.1 Detach the sample tube from the apparatus, recap with the stopper used previously, and weigh. Record the weight as W_2.

8.13.2 Reattach the sample tube to the apparatus. Remove the backfilled gas by evacuation to less than 10^{-3} torr at room temperature. This should normally take 5 to 10 min.

9. Procedure—Dead-Space Determination

9.1 From this point on, each sample being tested for krypton adsorption shall be run on an individual basis. Thus, 9.1-10.12 shall be carried out separately for each tube in test.

9.2 The dead-space is the void volume of the charged sample tube, including the volume within the *S* valve, when the tube is immersed in liquid nitrogen to the proper depth.

9.3 Place a Dewar flask of liquid nitrogen around the sample and adjust the liquid level to a fixed point on the sample tube. Maintain this level through the test.

9.4 Zero the pressure gage, if needed.

9.5 Admit the helium gas into the system to a pressure of 600 to 900 torr by carefully opening the *H* valve. Record this pressure, P_{H1}, *and the manifold temperature,* T_{H1}.

9.6 Open the *S* valve to admit helium to the sample.

9.7 After about 5 min of equilibration, readjust the liquid nitrogen level (if needed), and record the pressure, P_{H2} *and manifold temperature,* T_{H2}.

9.8 Repeat 9.5-9.7 for each sample cell attached to the manifold.

9.9 Open all *S* valves, then slowly open the *V* valve to remove the helium gas.

9.10 Close the *S* valve when a pressure below 10^{-3} torr has been attained. This should normally take 5 to 10 min.

10. Procedure—Krypton Adsorption

10.1 Close the *V* valve.

10.2 Admit krypton gas by opening the K valve and record pressure as $P_1(1)$ *and temperature as* $T_1(1)$. *(It is desirable to choose* $P_1(1)$ *such that* $P_2(1)/P_o(1)$ *is about 0.05.)*

10.3 Open the *S* valve to admit krypton to the sample.

10.4 Allow sufficient time for equilibration, readjusting the liquid nitrogen level periodically if needed. Equilibrium shall be considered as attained when the pressure changes by no more than 0.001 torr in 5 min.

10.5 Record the equilibrium pressure, $P_2(1)$, and manifold temperature, $T_2(1)$.

10.6 Record the liquid nitrogen temperature $T'_s(1)$ or the nitrogen vapor pressure $P_{o,N}(1)$.

10.7 Close the *S* valve.

10.8 Repeat 10.2-10.7 until there are at least three points in the linear BET region ($P_2/P_{o,krypton}$ = 0.05 to 0.30). Designate the pressures, manifold temperatures, liquid nitrogen bath temperatures or nitrogen vapor pressures as $P_1(i)$, $P_2(i)$, $T_1(i)$, $T_2(i)$, $T'_s(i)$, and $P_{o,N}(i)$ respectively for each i'th iteration (i = 2 to n, where n is the total number of points).

NOTE 3—The quantity of krypton gas admitted at each adsorption point in step 10.2 depends on the manifold volume, possible dosing system, dead space, and sample surface area. It is recommended that small krypton doses be used initially to ensure that at least three equilibration points are obtained in the linear BET region.

10.9 Open the *S* valve, slowly open the *V* valve, remove the Dewar flask, and allow the sample tube to warm to room temperature.

10.10 When frost has disappeared from the sample tube, wipe it dry.

10.11 Backfill the sample tube with helium to atmospheric pressure or slightly above. Close the *S* valve.

10.12 Detach the sample tube from the apparatus, recap with the stopper used previously, and weigh. Record the weight as W_2. If the sample was previously weighed following degassing, this step may be omitted.

11. Calculation

11.1 Calculate the weight of sample W_s follows:

$$W_s = W_2 - W_1 \quad (1)$$

11.2 Calculate the dead space V_s as follows:

$$V_s = \frac{T'_s V_d}{P_{H2}} \times \left[\frac{P_{H1}}{T_{H1} + 273.2} - \frac{P_{H2}}{T_{H2} + 273.2}\right] \quad (2)$$

11.3 For each point, i = 1,2 ..., n, calculate the following:

11.3.1 If $P_{o,N}(i)$ is not measured directly, the values of $T'_s(i)$ can be converted to $P_{o,N}(i)$ by the following equation for $76 \leq T'_s(i) \leq 80$:

$$\text{In } P_{o,N}(i)/2549.78) = [Ax + Bx\ 3/2 + Cx^3 + Dx^6]/(1-x) \quad (3)$$

where:

X = $(1-T_s/126.2)$,
A = −6.09676,
B = 1.1367,
C = −1.04072, and
D = 1.93306 (**1**).[5]

11.3.2 Saturation vapor pressure of krypton $P_{o,krypton}(i)$:

$$P_{o,krypton}(i) = \exp[1.919 \text{ In } P_{o,N}(i) - 11.82] \quad (4)$$

NOTE 4—The above calculation of $P_{o,krypton}(i)$ is based on the use of the Clausius-Clapeyron equation to extrapolate the vapor pressure of liquid krypton to liquid nitrogen temperature (**2, 3**). Other methods have been reported in the literature or are used on commercially available instrumentation. These methods are acceptable, but should be identified in the report.

11.3.3 $X(i)$ = *relative pressure* = $P_2(i)/P_{o,krypton}(i)$

11.3.4 Manifold temperature in:

$$T'_1(i) = T_1(i) + 273.2 \quad (5)$$

[5] The boldface number in parentheses refers to the list of references at the end of this test method.

$$T'_2(i) = T_2(i) + 273.2$$

11.3.5 The krypton volume in the manifold (and dosing system) before equilibration (cm^3 STP):

$$V_1(i) = V_d \times \frac{P_1(i)}{T_1(i)} \times \frac{273.2}{760} \quad (6)$$

11.3.6 The krypton volume in the manifold (and dosing system) after equilibration (cm^3 STP):

$$V_2(i) = V_d \times \frac{P_2(i)}{T_2(i)} \times \frac{273.2}{760} \quad (7)$$

See 6.1.2 for V_d.

11.3.7 Total inventory of krypton in the system (cm^3 STP):

$$V_t(i) = V_t(i-1) + V_1(i) - V_2(i-1) \quad (8)$$

$$V_t(0) = 0$$

11.3.8 Volume of krypton in the dead space (cm^3 STP):

$$V_{ds}(i) = \frac{273.2\ V_s}{760\ T'_s} \times P_2(i) \quad (9)$$

See 11.2 for V_s.

11.3.9 The quantity of gas adsorbed (cm^3 STP/g):

$$V_a(i) = \frac{V_t(i) - V_2(i) - V_{ds}(i)}{W_s} \quad (10)$$

11.3.10 The BET function:

$$\text{BET}(i) = \frac{X(i)}{V_a(i)} \times \frac{1}{[1 - X(i)]} \quad (11)$$

11.4 Construct the BET plot, by plotting *X(i)* as the abscissae, BET(*i*) as the ordinates.

11.5 Using a straightedge, draw a line through the linear region. Determine the slope SL and intercept I of the line.

NOTE 5—The best fit line is preferably established by least squares calculation after inspection reveals which points to choose to define the line. Points within the apparently linear region should not deviate from the line by more than 1 % of the ordinate values.

11.6 Calculate V_m, the volume of adsorbate required to complete one statistical monolayer (cm^3 STP/g):

$$V_m = 1/(SL + I) \quad (12)$$

11.7 Specific surface area (m^2/g) = 5.64 × V_m. This assumes a value of 0.210 nm^2 for the cross sectional area of a krypton molecule at liquid nitrogen temperature.

NOTE 6—A value of 0.210 nm^2 for the cross-sectional area of a krypton molecule has been found to give similar specific surface areas for an oxidic material of approximately 10 m^2/g when measured by nitrogen and krypton adsorption (**4**). Other values between 0.14 and 0.24 nm^2 have been suggested in the literature (**5, 6**), with 0.192 nm^2 often cited as an average. Values other than 0.210 nm^2 which may be used with specific samples should be reported with the calculated specific surface area.

12. Report

12.1 Report the specific surface area to three significant figures or the nearest 0.01 m^2/g, whichever is greater.

12.2 The report shall include pretreatment, outgassing temperatures, and the assumed value of the cross-sectional area of the krypton molecule. The method of calculation of the krypton saturation vapor pressure $P_{o,krypton}$ shall also be specified if different from 11.3.2.

13. Precision and Bias [6]

13.1 *Test Program*—An interlaboratory study was conducted in which the named property was measured in two separate test materials in eight separate laboratories. Practice E 691, modified for non-uniform 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* s the 95 % probability interval limit on the difference between two test results, and *S* is the appropriate estimate of standard deviation. Definitions and usage are given in Practices E 456 and E 177, respectively.

Test Material	Test Result (Consensus Mean) m^2/g	95 % Repeatability Interval (Within Laboratory) m^2/g (mean %)	95 % Reproducibility Interval (Between Laboratories) m^2/g (mean %)
RRM02 Alumina	2.172	0.066 (3.1)	0.137 (6.3)
EA5151 Alumina	0.541	0.026 (4.8)	0.037 (6.8)

13.3 *Bias*—This test method is without known bias.

[6] Supporting data are available from ASTM International Headquarters. Request RR: D32-1025.

REFERENCES

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(**3**) Ziegler, W. T., and Mullins, J. C., Calculations of the Vapor Pressure and Heats of Vaporization and Sublimation of Liquids and Solids, Especially Below One Atmosphere. IV. Nitrogen and Fluorine, Report No. A-663, Georgia Institute of Technology, Atlanta, April, 1963.

(**4**) McClellan, A. L., and Harnsberger, H. F., J. Colloid Inter Sci., Vol 23, No. 577, 1967.

(**5**) Gregg, S. J., and Sing, K. S. W., *Adsorption, Surface Area and Porosity*, 2nd Ed., Academic Press, New York, NY, 1982.

(**6**) Lowell, S., and Shields, J. E., *Powder Surface Area and Porosity*, 3rd Ed., Chapman and Hall, New York, NY, 1991.