Designation: D 6761 – 02

Standard Test Method for Determination of the Total Pore Volume of Catalysts and Catalyst Carriers[1]

This standard is issued under the fixed designation D 6761; 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 total pore volume of catalysts and catalyst carriers, that is, the volume of pores having pore diameter between approximately 14 μm and 0.4 to 0.6 nm (4 to 6 Å).

1.2 This test method involves hazardous materials, operations and equipment. *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 to determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 8, 9.1.7, and 9.1.11.

2. Referenced Documents

2.1 *ASTM Standards:*

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 *particle volume*—the volume of a particle including pores into which mercury cannot penetrate at ambient pressure (smaller than approximately 14 μm diameter pore mouth).

3.1.2 *true volume*—the volume of a particle, including pores, into which helium cannot penetrate (smaller than about approximately 4 to 6 Å diameter pore mouth).

3.1.3 Other definitions and terms used in this test method are defined in Terminology D 3766.

3.2 *Symbols*:

3.2.1 *For Mercury Intrusion*:

W = weight of sample,
W_c = weight of sealed empty sample cell,
W'_C = weight of sealed sample cell filled with mercury,
W_s = weight of sealed sample cell with sample,
W'_S = weight of sealed sample cell with sample filled with mercury,
V^C_{Hg} = volume of mercury in empty sample cell (volume of sample cell),
V^S_{Hg} = volume of mercury in cell with sample,
V^{Hg}_S = sample volume, cm^3,
V_{Hg} = specific sample volume,
V_P = particle volume,
D_P = particle density,
W_b = weight mercury reservoir after filling buret with sample.

3.2.2 *For Helium Pycnometry*:

V_C = volume of sample cell and associated tubing, cm^3,
V_R = reference volume, cm^3,
V^{He}_S = sample volume, cm^3,
V_{Cyl} = volume of calibration cylinder, cm^3,
V_{STD} = volume of calibration standard, cm^3,
V_{He} = specific sample volume,
P'_1 = pressure in empty sample cell, psig or Pascals,
P'_2 = pressure in empty sample cell, after the reference volume has been included in the system, psig or Pascals,
P_1 = pressure in sample cell with sample or calibration standard before the reference volume has been included in the system, psig or Pascals,
P_2 = pressure with sample or calibration standard in the sample cell, after the reference volume has been included in the system, psig or Pascals,
W_1 = tare weight of sample cup, g,
W_2 = weight of sample + tare weight of sample cup, g,
W_3 = weight of sample, g,
D_t = true density,
$P.V.$ = pore volume.

4. Summary of Test Method

4.1 The total pore volume of a catalyst or catalyst carrier is determined as the difference between the particle volume and

[1] This test method is under the jurisdiction of ASTM Committee D32 on Catalysts and is the direct responsibility of Subcommittee D32.02 on Physical-Mechanical Properties.

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[2] *Annual Book of ASTM Standards*, Vol 05.05.

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

the true volume, measured by mercury intrusion and helium pycnometry, respectively. The particle volume is determined by mercury intrusion at ambient pressure and the true volume is determined by helium displacement at pressures above ambient.

5. Significance and Use

5.1 This test method provides for the measurement of volume of pores that are in the range of catalytic importance and possibly for adsorption processes.

6. Apparatus

6.1 *For Mercury Intrusion*:

6.1.1 *Chamber,* capable of holding the sample cell (commonly referred to as a penetrometer), which contains the sample. This chamber must be capable of being evacuated and contain enough mercury to fill the penetrometer.

6.1.2 *Glass Sample Cell (penetrometer),* having a wide base and narrow bore stem. If the sample is powder, the penetrometer should have a provision in the base to prevent fine particles from passing into the stem when the cell is evacuated. The penetrometer must have the capability of being sealed.

6.1.3 *Vacuum Pump,* capable of attaining pressures of less than 0.05 torr.

6.1.4 *Valve,* for choosing vacuum and vent, for evacuation of the sample cell and filling the sample cell, respectively.

6.1.5 *Valve,* for rapid evacuation or venting of the system.

6.1.6 *Valve,* for controlled evacuation or venting.

6.1.7 A method or device to prevent mercury vapor from being vented into the room through the vacuum pump and to prevent contaminants from entering the vacuum pump.

6.1.8 *Pressure-Measuring Device,* capable of reading in the range 0 to 1000 torr or higher.

6.1.9 *Balance,* measuring to the nearest 1 mg (±0.001 g).

6.2 *For Mercury Intrusion with a Burette*—A schematic diagram of the burette is shown in Fig. 1. It has the following features:

6.2.1 *Glass Sample Cell,* with a needle valve suitable for handling mercury. The tip, which is submerged in the mercury reservoir, should be narrow enough so as to prevent drops of mercury from becoming lost if the reservoir is removed for weighing.

6.2.2 *Burette,* a calibrated narrow bore tube ending in a curved tip in the sample cell to prevent fine particles from passing into the burette. There is a clear mark on the burette at 23 cm above the curved tip.

6.2.3 *Manifold,* with a splash bulb and appropriate needle valves for choosing either vacuum or vent.

6.2.4 *Mercury Reservoir with Lid,* capable of containing the amount of mercury necessary to fill the sample cell and burette while the tip of the sample cell valve is still submerged in mercury. A weighing bottle of 5 cm diameter and 3 cm height is suitable.

6.2.5 *Vacuum Pump,* capable of attaining pressures of 0.05 torr.

6.2.6 *Cold Trap,* to prevent mercury vapor from being vented into the laboratory and to prevent contaminants from entering the vacuum pump.

6.3 *For Helium Pycnometry*—A schematic diagram of the pycnometer apparatus is shown in Fig. 2. It should be constructed from metal and have the following features:

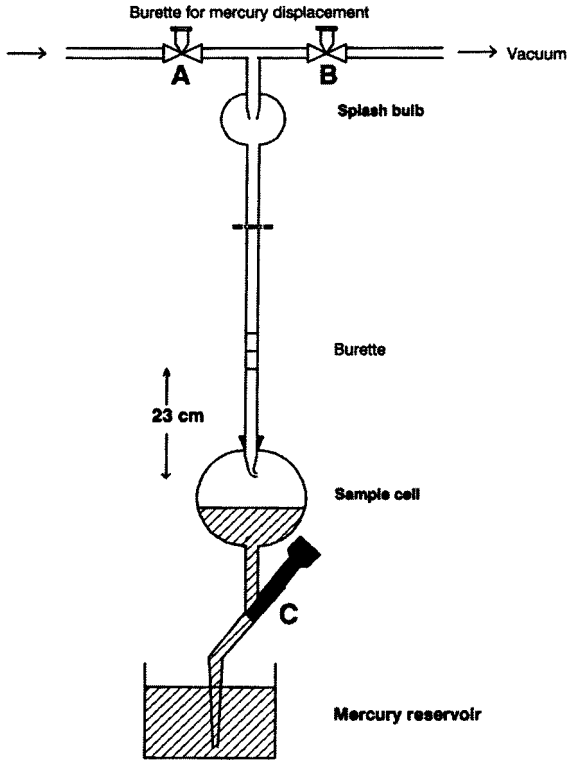

FIG. 1 Schematic Diagram of Burette

6.3.1 *Sample Cell,* having a volume suitable for the desired sample size and calibrated to the nearest 0.1 cm^3. This volume is indicated in Fig. 2.

6.3.2 *Reference Volume (V_R),* a precisely calibrated volume known to the nearest 0.02 cm^3.

6.3.3 *Pressure Transducer,* (0 to 25 psig or 0 to 172.3 kPa) with minimum volume displacement and linear within 0.1 %.

6.3.4 *Pressure Relief Valve,* set to 25 psig (172.3 kPa), to avoid overpressurization of the transducer.

6.3.5 *Filter,* to prevent powder from contaminating the pressure transducer.

6.3.6 *Input Flow Control Valves,* to control pressurization.

6.3.7 *Output Flow Control Valves,* to vent the gas.

6.3.8 *Valve,* to connect the reference volume to the sample cell.

6.3.9 *Non-Porous Calibration Standard,* (preferably stainless steel) of known volume which fills ¼ to ⅔ of the sample cup.

6.3.10 *Digital Meter,* for reading the pressure to 0.001 psig (6.89 Pa) from the transducer.

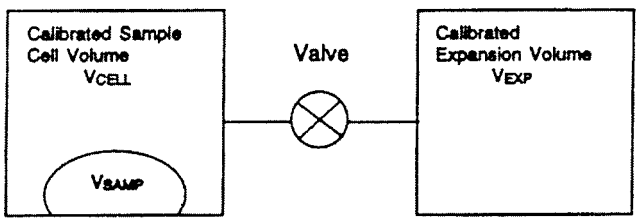

FIG. 2 Pycnometer Apparatus

6.3.11 *Sample Cell Cover,* with O-ring seal.

7. Reagents

7.1 *For Mercury Instrusion*:

7.1.1 *Mercury,* triply distilled.

7.2 *For Helium Pycnometry*:

7.2.1 *Helium Gas,* a cylinder of helium gas at least 99.9 % pure, with regulator.

8. Hazards

8.1 Samples that have been exposed to mercury are dangerous. Apply the precautions given by the following:

8.1.1 Mercury is a hazardous substance that can cause illness and death. Mercury can also be absorbed through the skin; avoid direct contact.

8.1.2 Always store in closed containers to control its evaporation, and use it only in well-ventilated rooms.

8.1.3 Wash hands immediately after any operation involving mercury.

8.1.4 Exercise extreme care to avoid spilling mercury. Clean up spills immediately using procedures recommended explicitly for mercury.

9. Procedure

9.1 *For Mercury Intrusion Instruments*:

9.1.1 Weigh the empty penetrometer with sealing device in place (W_C).

9.1.2 Place the empty penetrometer in the low pressure port of the instrument, seal it, and follow the manufacturer's recommendations for evacuating the penetrometer and subsequently filling it with mercury.

9.1.3 When the penetrometer is completely filled with mercury, follow the manufacturer's recommendations for bringing the low pressure port to atmospheric pressure.

9.1.4 When the low pressure port is again at atmospheric pressure, unseal the penetrometer and remove it from the low pressure port.

9.1.5 Weigh the mercury-filled penetrometer using an analytical balance, and record this weight as (W'_C).

9.1.6 Weigh the sample using an analytical balance. Record this as (W).

9.1.7 Hold the penetrometer with the stem down and carefully pour the sample into the bulb. (**Warning**—When pouring powders into the bulb, place your finger over the stem opening in the center of the bulb so that powder does not enter the stem. Large granules or chunks may be loaded with forceps. Touching such pieces with the fingers should be avoided as skin oils may be transferred that can slightly alter the results or create evacuation problems.)

9.1.8 Seal the penetrometer, being careful to avoid using excessive sealing grease.

9.1.9 Weigh the sealed penetrometer with the sample using an analytical balance. Record this weight as (W_s).

9.1.10 Place the penetrometer assembly with the sample in the low pressure port of the instrument, seal it, and follow the manufacturer's recommendations for evacuating the penetrometer and performing a low pressure analysis.

9.1.11 When the low pressure run is complete, bring the low pressure chamber back to atmospheric pressure and follow the manufacturer's recommendations for removing the penetrometer from the low pressure port. (**Warning**—As the penetrometer is removed from the low pressure port, be sure to tilt the bulb end of the penetrometer down and the stem end up, so mercury does not spill from the open stem end.)

9.1.12 Weigh the sealed penetrometer with sample and filled with mercury using an analytical balance. Record this weight as (W'_S).

9.2 *For Mercury Intrusion Using the Burette Method*:

9.2.1 Place a coolant (liquid nitrogen or dry ice-acetone mixture) around the cold trap.

9.2.2 Close the vent valve *(A)* and the sample cell valve *(C)*, and evacuate the burette by opening the vacuum valve *(B)*.

9.2.3 Slowly open the sample cell valve and allow mercury to fill the sample cell and the burette. Close the sample cell valve *(C)* when the mercury level is 1 to 2 cm above the 23 cm mark. Open the vent valve *(A)* to allow ambient pressure in the burette. Adjust the mercury level in the burette to the 23 cm mark by slowly draining mercury via the sample cell valve *(C)* into the mercury reservoir.

9.2.4 Place a lid on the mercury reservoir and weigh it using an analytical balance.

9.2.5 Drain the mercury from the burette and the sample cell into the mercury reservoir and close the sample cell valve *(C)*.

9.2.6 Weigh the catalyst sample using an analytical balance and record this weight as (W). Place this sample in the sample cell. Connect the sample cell to the burette and place the mercury reservoir under the sample cell with the tip of the sample cell valve *(C)* submerged in mercury.

9.2.7 Evacuate the burette and sample cell with sample by closing the vent valve *(A)* and slowly opening the vacuum valve *(B)* in order to prevent fine particles from entering into the burette.

9.2.8 Allow the sample to degas at 0.05 torr or lower for a minimum of 30 min before filling with mercury.

9.2.9 Repeat steps 9.2.2 through 9.2.4 giving the weight of the mercury reservoir (W_b).

9.2.10 Drain the mercury from the burette and the sample cell into the mercury reservoir, taking care that afterwards no particles of the sample are floating on the mercury in the reservoir.

9.3 *For Helium Pycnometry*:

9.3.1 *Calibration Procedure*—To determine the cell and reference volumes of the pycnometer.

9.3.1.1 Place an empty sample cup in the sample cell holder and seal according to the manufacturer's suggested procedure.

9.3.1.2 Open the output valves and zero the output display.

9.3.1.3 Turn the selector valve to exclude the reference volume.

9.3.1.4 Close the vent valve.

9.3.1.5 Open the input flow control valve and pressurize the sample cell to between 15 and 19 psig (103.4 and 130.9 kPa) using the input valve to control the rate of pressurization. When the desired pressure is reached, close the input valve to stop the flow of gas into the sample chamber.

9.3.1.6 Record the pressure on the digital display. This value is P'_1.

9.3.1.7 Turn the selector valve to include the reference volume.

9.3.1.8 Record the displayed pressure reading as P'_2.

9.3.1.9 Vent the pressure using the vent valve.

9.3.1.10 Place the calibration standard cylinder into the sample cup and repeat steps 9.3.1.2 through 9.3.1.9, recording the pressure in 9.3.1.6 as P_1 and the pressure in 9.3.1.8 as P_2.

9.3.1.11 Calculate the reference volume (V_R) and the cell volume (V_C) as follows:

$$V_R = \frac{V_{cyl}}{\frac{1}{(P'_1/P'_2)-1} - \frac{1}{(P_1/P_2)-1}} \quad (1)$$

$$V_c = \frac{V_R}{(P'_1/P'_2)-1} \quad (2)$$

9.3.2 *Sample Preparation Procedure*:

9.3.2.1 Weigh the empty sample cup and record as W_1.

9.3.2.2 Place enough sample in the sample cup to fill it to a minimum of ¼ capacity, place in the sample cell holder, and seal according to the manufacturer's directions.

9.3.2.3 Close the input valve and open the output valve.

9.3.2.4 Turn the selector valve to include V_R.

9.3.2.5 Completely open the output valve.

9.3.2.6 Open the input valve and adjust the input valve to give a slow flow of helium gas. This can be observed by bubbling the output from the vent into the breaker of water.

9.3.2.7 After purging the sample and tubing for a minimum of 15 min, close the input toggle valve.

9.3.3 *Sample Volume Determination Procedure*:

9.3.3.1 Repeat the procedure in steps 9.3.1.2 through 9.3.1.9. Record the pressure in 9.3.1.6 as P_1 and in 9.3.1.8 as P_2.

9.3.3.2 Remove the sample cup and weigh. Record this weight as W_2.

10. Calculation

10.1 *For Sample Volume by Mercury Intrusion*:

10.1.1 Calculate the weight of the sample, W, as follows:

$$W = W_S - W_C \quad (3)$$

10.1.2 Calculate the volume of the sample cell as follows:

$$V_{Hg}^C = \frac{W'_C - W_C}{Density\ of\ Hg} \quad (4)$$

10.1.3 Calculate the volume of the sample cell with the sample, as follows:

$$V_{Hg}^S = \frac{W'_S - W_S}{Density\ of\ Hg} \quad (5)$$

10.1.4 Calculate the volume of the sample, as follows:

$$V_S^{Hg} = V_{Hg}^C - V_{Hg}^S \quad (6)$$

10.1.5 Calculate the specific sample volume by mercury intrusion as follows:

$$V_{Hg} = \frac{V_S^{Hg}}{W} \quad (7)$$

10.1.6 Express the results as particle density D_P, as follows:

$$D_P = \frac{1}{V_{Hg}} \quad (8)$$

10.2 *For Sample Volume by Helium Pycnometry*:

10.2.1 Calculate the weight of the sample, W_3, as follows:

$$W_3 = W_2 - W_1 \quad (9)$$

10.2.2 Calculate the volume of the sample, V_S^{He}, as follows:

$$V_S^{He} = V_C + \frac{V_R}{1-(P_1/P_2)} \quad (10)$$

10.2.3 Calculate the specific sample volume by helium pycnometry as follows:

$$V_{He} = \frac{V_S^{He}}{W_3} \quad (11)$$

10.2.4 Express the results as the true density, D_t, as follows:

$$D_t = \frac{1}{V_{He}} \quad (12)$$

10.3 Calculate the pore volume as follows:

$$P.V. = \frac{1}{D_P} - \frac{1}{D_t} \quad (13)$$

11. Precision and Bias

11.1 *Test Program* —An interlaboratory study was conducted in which the named property was measured in three separate test materials in six separate laboratories. Practice E 691 was followed for the data reduction. Analysis details are in the Research Report.[4]

11.2 *Precision*—Pairs of test results obtained by the procedure described in the study are expected to differ in absolute value by less than 2.77 *S*, where 2.77 *S* is the 95 % probability interval limit on the difference between the two test results, and *S* is the appropriate estimate of the standard deviation (see Table 1). Definitions and usage are given in Terminology E 456 and Practice E 177, respectively.

11.3 *Bias*—The procedure in this test method has no known bias because the value is defined only in terms of this test method.

12. Keywords

12.1 helium pycnometry; mercury intrusion; particle volume; pore volume; true volume

[4] Supporting data are available from ASTM International Headquarters. Request Research Report RR:D32-1039.

TABLE 1 Precision Data

Test Result (consensus mean)	95 % Repeatability Interval (within laboratory)	95 % Reproducibility Interval (between laboratories)
0.3852 cc/g	0.008 cc/g (2.0 % of mean)	0.022 cc/g (5.7 % of mean)
0.6811 cc/g	0.016 cc/g (2.4 % of mean)	0.031 cc/g (4.6 % of mean)
0.8755 cc/g	0.015 cc/g (1.7 % of mean)	0.046 cc/g (5.3 % of mean)