Designation: D6761 – 22

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

This standard is issued under the fixed designation D6761; 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 nm (4 Å).

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

1.3 **Warning—**Mercury has been designated by many regulatory agencies as a hazardous material that can cause central nervous system, kidney, and liver damage. Mercury, or its vapor, may be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Material Safety Data Sheet (MSDS) for details and EPA's website—http://www.epa.gov/mercury/faq.htm—for additional information. Users should be aware that selling mercury or mercury containing products, or both, into your state or country may be prohibited by law.

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 establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 8. Warning statements are given in 10.1.4, 10.1.7, and 10.1.11.

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]

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:*

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 0.4 nm (4 Å) diameter pore mouth).

3.1.3 Other definitions and terms used in this test method are defined in Terminology D3766.

3.2 *Symbols for Mercury Intrusion:*

W = mass of sample
W_c = mass of sealed empty sample cell
W'_C = mass of sealed sample cell filled with mercury
W_s = mass of sealed sample cell with sample
W'_S = mass 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
W_b = weight mercury reservoir after filling burette with sample
$W_{b'}$ = mass of mercury reservoir after filling burette without sample

[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.

Current edition approved April 1, 2022. Published April 2022. Originally approved in 2002. Last previous edition approved in 2017 as D6761 – 17. DOI: 10.1520/D6761-22.

[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.

3.3 *Symbols for Helium Pycnometry:*

V_C = volume of sample cell and associated tubing, cm^3
V_R = reference volume, cm^3
V_S^{He} = 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 = mass of sample + tare weight of sample cup, g
W_3 = mass of sample, g
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 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. This test method requires the use of mercury in order to perform the measurements.

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.

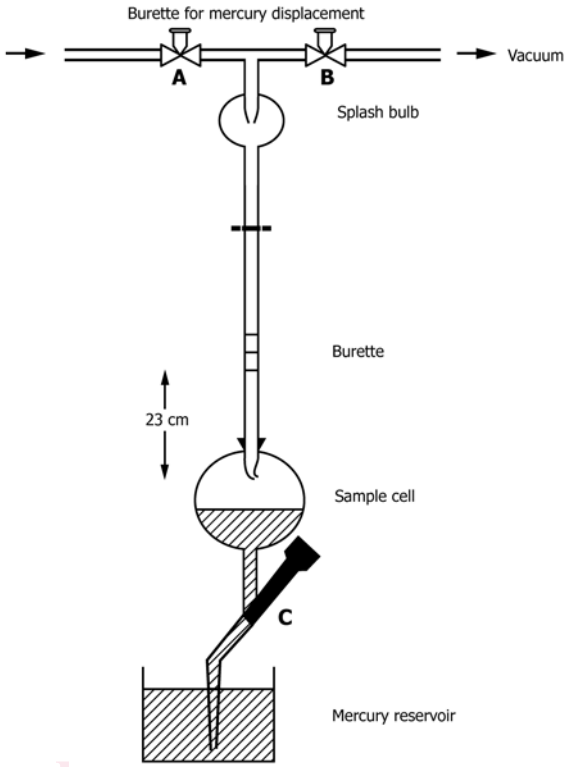

FIG. 1 Schematic Diagram of Burette

6.1.7 *Cold Trap,* or other method or device to prevent mercury vapor from being vented into the laboratory 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.

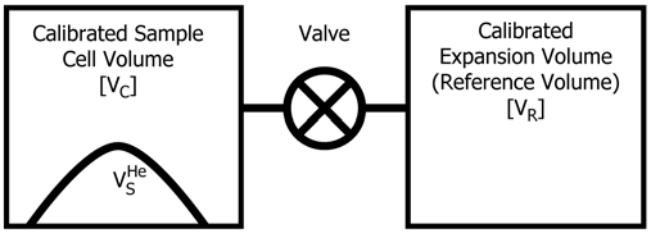

FIG. 2 Pycnometer Apparatus

6.2.6 *Cold Trap,* or other method or device to prevent mercury vapor from being vented into the laboratory through the vacuum pump 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:

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.

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

7. Reagents

7.1 *For Mercury Intrusion:*

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 a fume hood or 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.

8.1.5 Recycling of waste mercury is recommended and to be conducted in accordance with local government hazardous waste regulations. Disposal of waste mercury and mercury contaminated materials should be performed as mandated by local government hazardous waste regulations.

9. Sampling

9.1 A test sample shall be obtained from larger composites by riffling or splitting in accordance with STP 447A (paragraph 5.12),[3] with the aim of obtaining a representative sample that represents shape and size distribution of the larger composite.

10. Procedure

10.1 *For Mercury Intrusion Instruments:*

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

10.1.2 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.

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

10.1.4 When the low pressure port is again at atmospheric pressure, unseal the penetrometer and remove it 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 up, so mercury does not spill from the open stem end.)

10.1.5 Weigh the mercury-filled penetrometer using an analytical balance, and record this weight as (W'_C). Empty the penetrometer, dispose of the mercury in an approved container, and clean the penetrometer.

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

10.1.7 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.)

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

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

10.1.10 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.

10.1.11 When the low pressure run is complete, bring the low pressure chamber back to atmospheric pressure and follow

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