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Standard Test Method for Determining Pore Volume Distribution of Catalysts and Catalyst Carriers by Mercury Intrusion Porosimetry¹

This standard is issued under the fixed designation D4284; 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.

^{ε1} NOTE—Editorial corrections made throughout in February 2017.

1. Scope

1.1 This test method covers the determination of the pore volume distributions of catalysts and catalyst carriers by the method of mercury intrusion porosimetry. The range of apparent diameters of pores for which it is applicable is fixed by the operant pressure range of the testing instrument. This range is typically between apparent pore entrance diameters of about 100 and 0.003 μm (3 nm).

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 **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 and/or mercury containing products into your state or country may be prohibited by law.

1.4 *This standard does not purport to address all of the safety problems, 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.* Specific hazard information is given in Section 8.

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. Referenced Documents

2.1 *ASTM Standards*:²

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 of Terms Specific to This Standard:*

3.1.1 *apparent pore diameter*—the diameter of a pore, assumed to be cylindrical, that is intruded at a pressure, P , and is calculated with Eq 1.

3.1.2 *interparticle pores*—those pores that occur between particles when they are packed together and that are intruded during the test.

3.1.3 *intraparticle pores*—those pores lying within the envelopes of the individual catalyst particles and that are intruded during the test.

3.1.4 *intruded pore volume*—the volume of mercury that is intruding into the pores during the test after this volume has been corrected, if necessary, per 13.3.2.

4. Summary of Test Method

4.1 When a liquid does not wet a porous solid it will not voluntarily enter the pores in the solid by capillary attraction. The nonwetting liquid (mercury in this test method) must be forced into the pores by the application of external pressure. The size of the pores that are intruded is inversely proportional to the applied pressure. When a cylindrical pore model is assumed, the relationship between pressure and size is:

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.

$$d = \frac{-4\gamma(\cos \theta)}{P} \quad (1)$$

where:

- d = apparent diameter of the pore being intruded,
- γ = surface tension of the mercury,
- θ = contact angle between the mercury and the solid, and
- P = absolute pressure causing the intrusion.

4.2 The volume of the intruded pores is determined by measuring the volume of mercury that is forced into them at various pressures. The single determination of a pore size distribution plot involves increasing the pressure, either continuously or step-wise, and recording the measured intruded volume.

5. Significance and Use

5.1 This test method is intended to determine the volume distribution of pores in catalysts and catalyst carriers with respect to the apparent diameter of the entrances to the pores. In general, both the size and volume of pores in a catalyst affect its performance. Thus, the pore volume distribution is useful in understanding a catalyst's performance and in specifying a catalyst that can be expected to perform in a desired manner.

6. Limitations

6.1 Mercury intrusion porosimetry, in common with many other test methods, is only capable of sensing pores that are open to the outside of a catalyst or catalyst carrier particle, and will not determine the volume of any pores that are completely enclosed by surrounding solid. Also, the test method will only determine the volume of intrudable pores that have an apparent diameter corresponding to a pressure within the pressuring range of the testing instrument.

6.2 The intrusion process proceeds from the outside of a particle toward its center. Comparatively large, interior pores can exist that have smaller pores as the only means of access. The test method will incorrectly register the entire volume of these "ink-bottle" pores as having the apparent diameter of the smaller access pores.

6.3 In the penetrometer, interparticle pores can be created in addition to the intraparticle pores. (See Section 3 for terminology.) These interparticle pores will vary in size and volume depending on the size and shape of the catalyst particles and on the manner in which the particles are packed together in the test chamber. It is possible that some of the interparticle pores will have the same apparent diameter as some of the intraparticle pores. When this occurs, the test method cannot distinguish between them. Thus, the test method can yield an intruded pore volume distribution that is, in part, dependent upon the packing of multi-particle samples. However, many catalysts have intraparticle pores that are much smaller than the interparticle pores. This situation leads to a bimodal pore size distribution and the distinction between the two classes of pores can frequently be made.

6.4 Mercury intrusion can involve the application of high pressures on the sample. This may result in a temporary, or permanent, alteration in the pore geometry. Generally, catalysts and catalyst carriers are made from comparatively strong solids

and are less subject to these alterations than some other materials. However, the possibility remains that the use of the test method may alter the natural pore volume distribution that it seeks to measure.

7. Apparatus

7.1 *Mercury Intrusion Porosimeter*, equipped with a sample holder capable of containing one or several catalyst or catalyst carrier particles. This holder is frequently called a penetrometer. The porosimeter shall have a means of surrounding the test specimen with mercury at a low pressure, a pressure generator to cause intrusion, pressure transducers capable of measuring the intruding pressure with an accuracy of at least $\pm 1\%$ throughout the range of pressures over which the pores of interest are being intruded, and a means of measuring the intruded mercury volumes with an accuracy of at least $\pm 1 \text{ mm}^3$ ($\pm 10^{-3} \text{ cm}^3$).

7.2 *Vacuum Pump*, if not part of the porosimeter, to evacuate the sample holder.

7.3 *Analytical Balance* capable of measuring the sample's mass with an accuracy of at least $\pm 0.1\%$. This usually means that the balance must be sensitive to $\pm 10^{-7} \text{ kg}$ ($\pm 0.1 \text{ mg}$).

7.4 *Mercury*, with a purity equal to, or better than, double distilled.

8. Hazards

8.1 Samples that have been exposed to mercury are dangerous. Apply the precautions that follow:

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 any 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 The sample from which test material will be drawn shall be representative of the catalyst or the catalyst carrier. The actual amount of sample used in a test will depend on the sensitivity of the porosimeter and the porosity of the sample.

10. Conditioning

10.1 The ideal preconditioning for the test specimen is an outgassing procedure that removes all foreign substances from the pores and pore walls of the catalyst, but does not alter the solid catalyst in any way. If possible, the appropriate combination of heat and vacuum and the required time of conditioning shall be experimentally determined for the specific catalyst

or catalyst carrier under test. This outgassing technique shall then be the one specified and used.

10.2 Where the procedure described in 10.1 is not practical, outgas the sample in a vacuum of at least 1.3 Pa (10 μ m Hg) at a temperature of 150°C for at least 8 h.

NOTE 1—The procedure in 10.2 is unlikely to alter the pore structure of a catalyst but it can severely change the pore structure of many other materials.

11. Procedure

11.1 Outgas the test sample in accordance with 10.1 or 10.2.

11.2 Weigh the outgassed specimen and record this weight.

11.3 Place the outgassed catalyst in the penetrometer in accordance with the manufacturer's instructions.

NOTE 2—Since, when performing the operations described in 11.2 and 11.3, the outgassed catalyst is exposed to the laboratory atmosphere and can reabsorb vapors, carry these operations out as rapidly as possible.

11.4 Place the penetrometer containing the sample in the appropriate chamber of the porosimeter, following the manufacturer's instructions, and evacuate to a pressure of at least 1.3 Pa (10 μ m Hg).

11.5 Fill the penetrometer with mercury, in accordance with the manufacturer's instructions, by pressuring to some suitably low pressure.

NOTE 3—The pressure required to fill the penetrometer with mercury is also capable of filling sufficiently large pores of both the inter- and intra-particle classes. Thus, the filling process can fill some pores with mercury and the volume distribution of these pores cannot subsequently be determined. This fact should be recognized and, where possible, select a filling pressure that will not intrude pores in the diameter range of subsequent interest.

11.6 Place the filled penetrometer in the pressure vessel of the porosimeter and prepare the instrument for pressurization and intrusion readings in accordance with the manufacturer's instructions.

11.7 Raise the pressure, either continuously or step-wise, and record both the absolute pressure and the volume of intruded mercury until the maximum pressure of interest is reached.

NOTE 4—When raising the pressure incrementally, minimize the pressure drop during the pause. Certain modern instruments allow for an automatic repressurization to the target pressure when the pressure decreases. When samples with relatively narrow pore size distribution are analyzed, the extent of depressurization and repressurization may affect test method precision and the measured pore volume.

NOTE 5—When testing some materials, the time required to achieve intrusion equilibrium will not be the same at all pressures. Often, the equilibrium time is appreciably longer at pressures that cause an abrupt and large increase in intruded volume. Failure to record the equilibrium intrusion will result in some of the pore volume being incorrectly ascribed to smaller pore diameters. Assess the extent to which this may be a problem by conducting two tests, each at a different pressuring rate, and compare the results. Measure recorded intrusion values at, essentially, equilibrium.

NOTE 6—Use of Eq 1 requires the absolute pressure, P . With some instruments, it may not be possible to read the absolute pressure directly. In this case, record the gage pressures and calculate the absolute pressures subsequently.

NOTE 7—If incremental pressure steps are used, the choice of pressure intervals at which data are to be recorded will be specified by those

directing the test, or left to the judgement of the operator. A minimum of 10 to 15 data points will be required to define the pore volume distribution. Frequently, 25 or more points are found to be helpful. In selecting these pressure points, a rough idea of the expected distribution is helpful, since the pressure intervals can be larger in regions where little or no intrusion occurs. The intervals should be smaller in regions where a large volume of intrusion occurs abruptly.

NOTE 8—It is not necessary to continue the process up to the maximum pressuring capability of the instrument if all of the pores of interest in a particular test have been intruded at a lesser pressure.

11.8 Upon completion of the pressuring cycle, reduce the pressure and disassemble and clean the instrument in accordance with the manufacturer's instructions.

12. Blank Test for Corrections

12.1 An intrusion test on a nonporous sample may be required to obtain values to use in correcting intrusion data for compressibilities and temperature changes.

12.2 Select a nonporous material for this test that has approximately the same compressibility and bulk volume as the catalyst or catalyst carrier sample that is to be tested.

12.3 Test the nonporous sample in exactly the same manner as outlined in Section 11. Raise the pressure in the same manner as used for the catalyst tests to ensure that temperature changes due to pressuring are the same.

12.4 The results of this blank test are a series of measured volume changes that can also be expected to occur, along with actual pore intrusion, during a test on a catalyst or catalyst carrier. They are used to correct the intruded volumes as discussed in 13.3.2.

12.5 The compressibilities of the various components in the system augment the measured intrusion values while the pressure-induced heating and consequent expansion of the system reduces the measured volumes. In a particular instrument, either one of these effects may be dominant. Hence, the results of the blank test may be either an apparent intrusion (compressibility dominant) or an expulsion of mercury (heating dominant).

12.5.1 If the blank results show apparent intrusion, they are to be subtracted from the values measured in the test on the catalyst.

12.5.2 If the blank results show a mercury expulsion, they are to be added to the volumes measured on the catalyst or catalyst carrier.

13. Calculations

13.1 Express the intruding pressures as absolute pressures prior to computing the corresponding pore diameters. If the recorded values are gage pressures, they must be converted to absolute pressures in accordance with the instrument manufacturer's instructions. If the instrument reads directly in absolute pressure, omit this step.

13.2 The absolute pressures are next converted to apparent intruded pore diameters with the equation in 4.1. This step requires that the surface tension and contact angle be known.

13.2.1 When double-distilled mercury is used, the value of the surface tension can generally be relied upon to be that reported in handbooks, for example, 0.484 N/m (484 d/cm) at

25°C. Small deviations from this value are not significant as the surface tension enters the equation as a linear term.

13.2.2 The contact angle enters the equation as its cosine, and it is more important to know the value of the angle accurately for the material under test. The contact angle of mercury has been measured on a variety of solids by several different techniques, and references to some of these measurements are given in [Appendix X1](#) which also lists references for several methods of contact angle measurement that have been found useful (1-6).³ The ideal value for reducing the data is one that has been determined for the particular material under test. If this is impractical, the use of an assumed value is necessary. If mercury intrusion is being used for the comparison of similar materials for quality control purposes, then an assumed, or agreed upon, value is satisfactory. But, when different materials are being compared, the assumption of a single value for the contact angle can lead to errors.

13.3 The next step in the calculations is the correction of the intruded volume readings. The corrections fall into two categories: low-pressure corrections and high-pressure corrections.

13.3.1 A low-pressure correction, that accounts for the compression of air trapped during filling, can be applied as discussed in Ref (4). However, this correction should not be necessary if mercury filling is carried out as required in 11.4.

13.3.2 The high-pressure correction to the intruded volume readings represents a composite of several phenomena, for example, the compression of the sample, penetrometer, and mercury, and the temperature changes that occur as a result of pressurization. Experimentally determine the value of this correction with the blank intrusion test performed in Section 12. Either add or subtract the values found in the blank test to correct the intrusion volumes as discussed in 12.5.

13.4 The final calculation is the conversion of the corrected intruded volumes to a unit mass basis. Divide each corrected intrusion value by the sample mass.

14. Report

14.1 The report shall include the following specific information:

14.1.1 Sample description.

14.1.2 Sample mass.

14.1.3 Sample outgassing procedure.

14.1.4 Contact angle and surface tension values used in calculations.

14.1.5 A table or graph (depending on whether step-wise or continuous pressuring was used) showing the corrected cumulative intrusion volumes on a per gram basis and the corresponding absolute intruding pressures.

14.1.6 A graphical, cumulative pore volume distribution having the intruded volumes per gram on the ordinate with an arithmetic scale and the apparent pore diameters on the abscissa with a logarithmic scale. This cumulative distribution will appear as a smooth line if continuous pressuring was used

and should show the data points if step-wise intrusion pressuring was used. Typical examples of both types of cumulative plots are shown in [Appendix X2](#).

14.2 The report may also include a differential plot of the distribution. This plot may have either the slope of the cumulative plot, taken at various points, or the incremental increase in intrusion between various points plotted against the apparent pore diameters. The slope of change shall be on the ordinate with an arithmetic or logarithmic scale, as appropriate, and the apparent pore diameters on the abscissa with a logarithmic scale. When a differential plot is presented, there shall be, on the plot itself, a statement of the cumulative, total intruded pore volume.

15. Precision and Bias⁴

15.1 This test method will, in the general case, measure both inter- and intraparticle pore volumes. The volume of interparticle pores will depend on the arrangement of the particles in the penetrometer and may vary widely from test to test. Thus, no statement as to the precision of measuring interparticle pore volumes with this test method is possible. However, when the intraparticle pore volume can clearly be distinguished, a precision statement on the measurement of this volume is possible.

15.2 *Interlaboratory Test Program*—An interlaboratory study was run in which randomly drawn samples of three representative alumina supports were analyzed for pore volume distribution in each of 13 laboratories. One sample was further crushed to 10 to 20 mesh size and also analyzed as a fourth sample. Each laboratory performed three replicate analyses on each of the four materials. Practice E691 was followed for the design and analysis of the data. Analysis details are in the research report.

15.3 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 2.77 S, where 2.77 S is the 95 % probability limit on the difference between two test results, and S is the appropriate estimate of standard deviation. Definitions and usage are given in Terminology E456 and Practice E177 respectively.

15.3.1 Material B possessed a bimodal distribution of pore sizes with distinct distribution of pores above and below 100 nanometres. Hence, in addition to the statistical results for the four samples, results are also presented for “Material B >100 nanometres” and Material B <100 nanometres. The following results were obtained for total pore volume measurements:

Material	Test Result (Consensus), cc/g	95 % Repeatability Limit (Within Laboratory), cc/g (%)	95 % Reproducibility Limit (Between Laboratories), cc/g (%)
A	0.6629	0.0222 (3.3)	0.0637 (9.6)
B	0.3834	0.0102 (2.7)	0.0249 (6.5)
C	0.8626	0.0233 (2.7)	0.0687 (8.0)
D	0.6628	0.0216 (3.3)	0.0571 (8.6)
B >100 nm	0.1275	0.0078 (6.1)	0.0122 (9.6)
B <100 nm	0.2546	0.0064 (2.5)	0.0211 (8.3)

³ The boldface numbers in parentheses refer to the list of references at the end of this standard.

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D32-1032.

The following results were obtained for the measurement of median pore diameter (that is, in nanometres):

Material	Test Result (Consensus) nanometres (nm)	95 % Repeatability Limit (Within Laboratory) nm (%)	95 % Reproducibility Limit (Between Laboratories) nm (%)
A	6.99	0.16 (2.2)	0.96 (14)
B	15.2	2.04 (13)	2.79 (18)
C	13.2	0.60 (4.5)	0.94 (7.2)
D	7.09	0.11 (1.6)	0.74 (10)
B >100 nm	531	88.6 (17)	418 (79)
B <100 nm	9.2	0.16 (1.7)	0.45 (4.9)

15.4 The dispersion of the pore volume distribution was estimated for Material A from the raw data obtained from all the laboratories. In this study the dispersion was defined as the

pore size range, in nanometres, with logarithmic upper and lower limits about the mean pore diameter which included 95 % of the total pore volume of the distribution. Material A had the pore volume and pore characteristics as reported in 15.3. Details of the calculations are described in the research report. For Material A the following results were obtained for dispersion at 95 % pore volume:

Test Result (Consensus) Dispersion nm	95 % Repeatability Limit (Within Laboratory) nm (%)	95 % Reproducibility Limit (Between Laboratory) nm (%)
3.29	0.29 (8.8)	1.34 (41)

15.5 *Bias*—No estimate of the bias of the test method is possible.

APPENDIXES

(Nonmandatory Information)

X1. CONTACT ANGLES

X1.1 The contact angle between mercury and the wall of a pore in a solid depends upon many factors. Among these are: the nature of the solid, the cleanliness of the pore wall, the

roughness of the pore wall, whether the mercury is advancing or retreating on the solid surface and, the purity of the mercury. For these reasons, the operant contact angle for a particular material will generally be different from that for another material. Thus, the best contact angle to use in reducing the porosimetry data is one that has been measured on the material under test, with the mercury that is to be used for the porosimetry experiment. Ref (1) gives a summary of a wide variety of experimental techniques for measuring contact angles. Some contact angles have been reported in the literature and a few are given below. If a published contact angle is to be adopted, it is recommended that the reference be studied carefully to assess the validity of its use for reducing porosimetry data.

TABLE X1.1 Contact Angles

Material	Contact Angle, °	Reference
Titanium Oxide	160	2
Titanium Oxide	141	6
Alkali Borosilicate Glass	153	2
Tungsten Carbide	121	2
Quartz	132–147	3
Clay Minerals	139–147	4
Aluminum Oxide	127	5
Zinc Oxide	141	6
Carbon	155	6

X2. EXAMPLES OF CUMULATIVE PORE VOLUME DISTRIBUTIONS

X2.1 See Fig. X2.1 and Fig. X2.2.

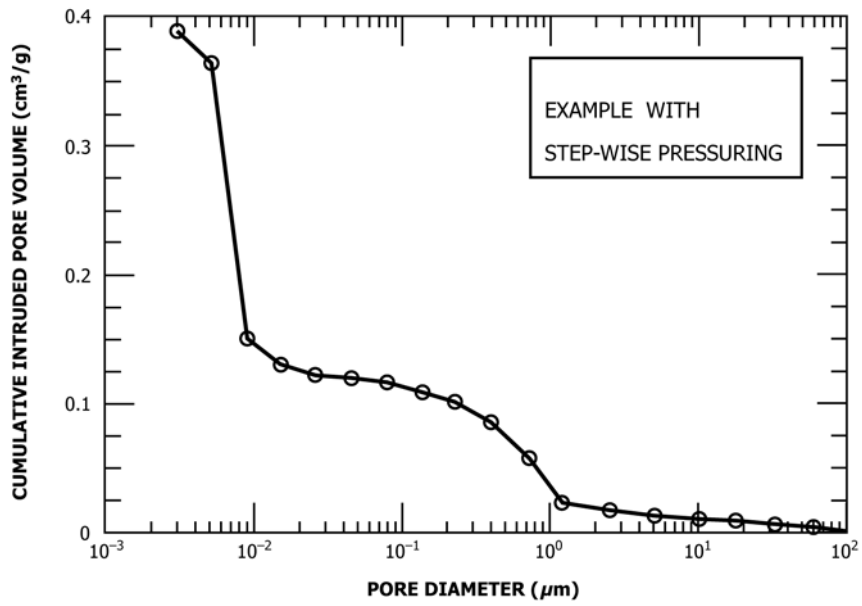


FIG. X2.1 Example with Step-Wise Pressuring

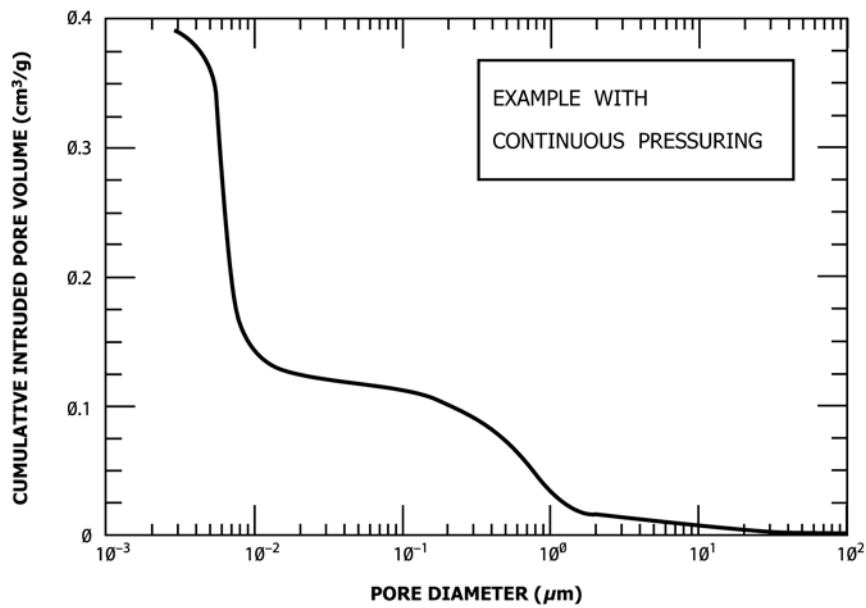


FIG. X2.2 Example with Continuous Pressuring



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