



Standard Test Method for Determination of Pore Volume and Pore Volume Distribution of Soil and Rock by Mercury Intrusion Porosimetry¹

This standard is issued under the fixed designation D 4404; 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—Keywords were added editorially in December 1998.

1. Scope

1.1 This test method covers the determination of the pore volume and the pore volume distributions of soil and rock by the mercury intrusion porosimetry method. The range of apparent diameters of pores for which this test method 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 μm and 2.5 nm (0.0025 μm). Larger pores must be measured by another method.

1.2 Mercury intrusion porosimetry is useful only for measuring pores open to the outside of a soil or rock fragment; mercury intrusion porosimetry will not give the volume of any pores completely enclosed by surrounding solids. This test method will give only the volume of intrudable pores that have an apparent diameter corresponding to a pressure within the pressurizing range of the testing instrument.

1.3 The intrusion process proceeds from the outside of a fragment toward its center. Comparatively large interior pores can exist that have smaller pores as the only means of access. Mercury intrusion porosimetry will incorrectly register the entire volume of these “ink-bottle” pores as having the apparent diameter of the smaller access pores. In a test sample, inter-fragment pores can exist in addition to intra-fragment pores (see Section 3 for definitions). The inter-fragment pores will vary in size and volume depending on the size and shape of the soil or rock fragments and on the manner in which the fragments are packed together. It is possible that some inter-fragment pores can have the same apparent diameter as some intra-fragment pores. When this occurs this test method cannot distinguish between them. Thus, the test method yields an intruded pore volume distribution that is in part dependent upon the packing of multifragment samples. However, most soils and rocks have intra-fragment pores much smaller than the inter-fragment pores. This situation leads to a bi-modal pore size distribution and the distinction between the two classes of pores can then be made (see Fig. 1 and Fig. 2).

1.4 Mercury intrusion may involve the application of high pressures to the sample. This may result in a temporary, or

permanent, or temporary and permanent alteration in the pore geometry. Generally, soils and rocks are composed of comparatively strong solids and are less subject to these alterations than certain other materials. However, the possibility remains that the use of this test method may alter the natural pore volume distribution that is being measured.

1.5 *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 consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precaution statements, see Section 8.

2. Referenced Documents

2.1 ASTM Standards:

C 699 Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of, and Physical Tests on, Beryllium Oxide Powder²

3. Terminology

3.1 Definitions:

3.1.1 *apparent pore diameter*—the diameter of a pore that is assumed to be cylindrical and that is intruded at a pressure, P , given by the equation in 4.1.

3.1.2 *inter-fragment pores*—those pores between fragments when they are packed together and that are intruded during the test.

3.1.3 *intra-fragment pores*—those pores lying within the exterior outlines of the individual soil and rock fragments.

3.1.4 *intruded pore volume*—the corrected volume of mercury intruded during the test.

4. Summary of Test Method

4.1 When a liquid does not wet a porous solid, it will not enter the pores in the solid by capillary action. The non-wetting liquid (mercury in this test method) can 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 given as follows:

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² *Annual Book of ASTM Standards*, Vol 12.01.

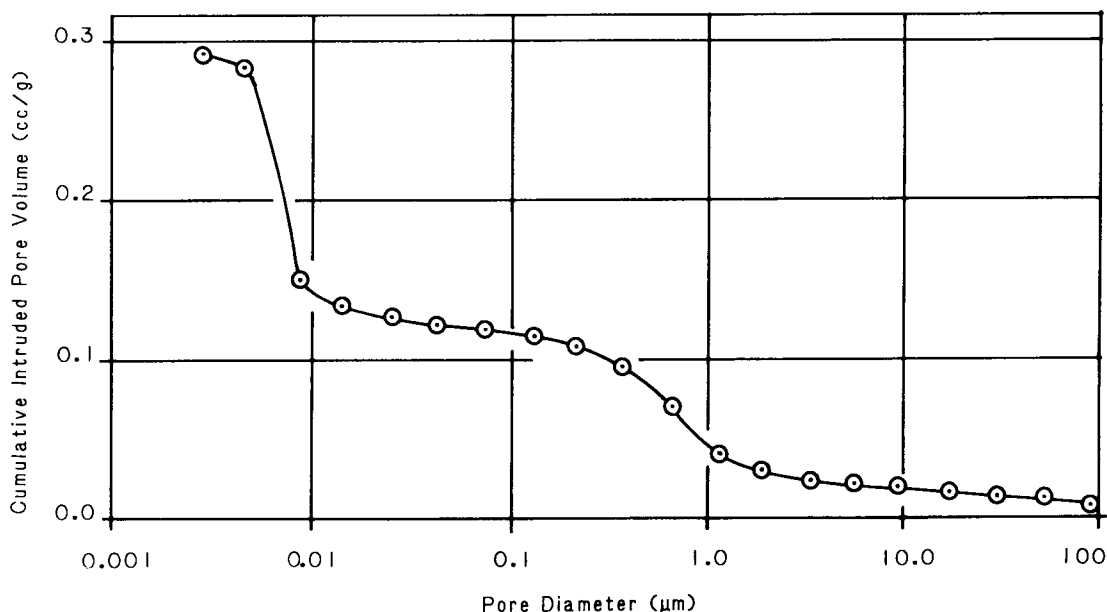


FIG. 1 Example of Cumulative Pore Volume Distribution Plot

$$d = -4\gamma(\cos\theta)/P \quad (1)$$

where:

d = apparent pore diameter being intruded,

γ = surface tension of the mercury,

θ = contact angle between the mercury and the pore wall,
and

P = absolute pressure causing the intrusion.

Any set of convenient and compatible units may be used.

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

5. Significance and Use

5.1 This test method is intended for use in determining the volume and the volume distribution of pores in soil and rock with respect to the apparent diameter of the entrances of the pores. In general, both the size and volume of the pores affects the soil or rock performance. Thus, the pore volume distribution is useful in understanding soil and rock performance and in identifying a material that can be expected to perform in a particular manner (1, 2).³

6. Apparatus

6.1 *Mercury Intrusion Porosimeter*— This shall be equipped with a sample holder capable of containing one or several soil or rock fragments. This sample 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 intruded mercury volumes to an accuracy of at least $\pm 1 \text{ mm}^3$ ($\pm 10^{-3} \text{ cm}^3$).

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

6.3 *Analytical Balance*, with an accuracy of at least $\pm 10^{-7} \text{ kg}$ ($\pm 0.1 \text{ mg}$).

7. Reagent

7.1 *Triple-Distilled Mercury*.

8. Safety Precautions

8.1 Mercury is a hazardous substance that can cause illness and death. Store mercury in closed containers to control its evaporation and use only in well ventilated rooms. Mercury can also be absorbed through the skin so avoid direct contact. Wash hands immediately after any operation involving mercury; the use of gloves is advocated. Exercise extreme care to avoid spilling mercury. Clean up any spills immediately using procedures recommended explicitly for mercury. Handle intruded samples with great care and dispose of in a safe and environmentally acceptable manner immediately after completion of the test.

9. Sampling, Test Specimens, and Test Units

9.1 The material from which the test sample is drawn shall be representative of the soil or rock. The test sample shall be as large as practicable considering the test apparatus.

NOTE 1—Sample size is limited by the pore-measuring capacity of the penetrometer, which is currently (1984) slightly more than 1 cm^3 . The small sample size may prevent the measurement of porosity represented by relatively large cracks and fissures in the material. Judgement is required in the application of these measurements to the characterization of the soil or rock masses.

10. Conditioning

10.1 The ideal preconditioning for the test specimen is an

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

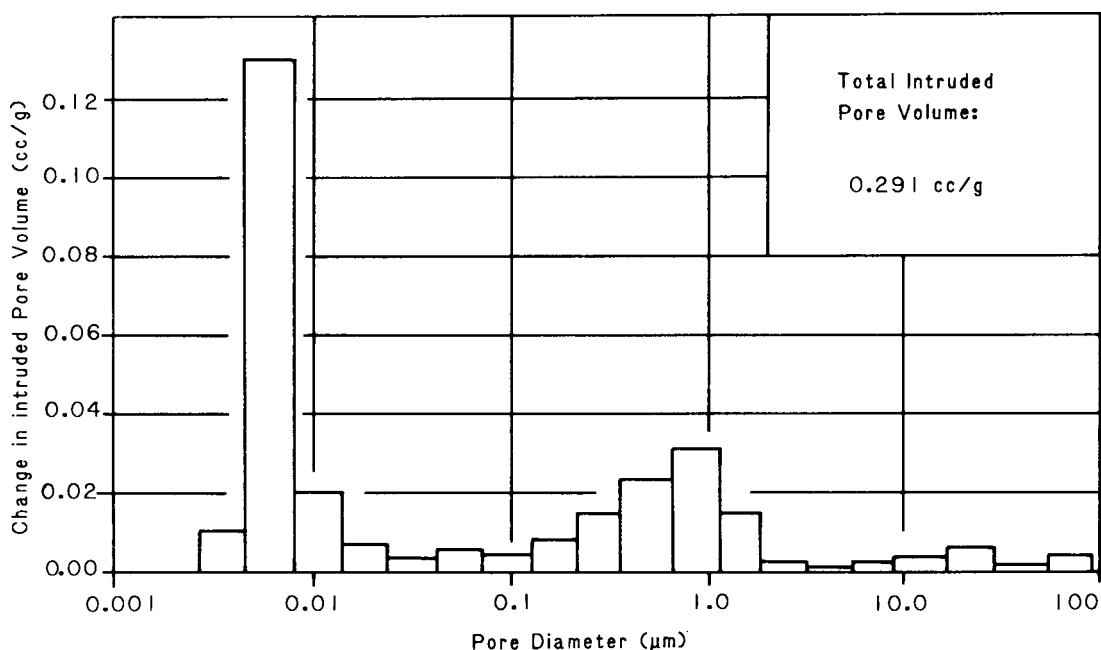


FIG. 2 Example of Differential Pore Volume Distribution Plot

outgassing or drying procedure that removes all foreign substances from the pores and pore walls of the soil or rock and does not alter the soil or rock in any way. If possible, the appropriate combination of temperature and pressure and the required time of conditioning shall be experimentally determined for the specific soil or rock under test. This outgassing or drying technique shall then be the one specified and used.

10.2 Where the procedure described in 10.1 is not practical, rock or coarse-grained soil without fines shall be outgassed in a vacuum at at least 1.3 Pa (10 μmHg) and at a temperature of 150°C for at least 24 h. Soil containing any plastic fines requires special drying procedures to avoid alteration of pore structure. Freeze drying has been successfully employed (3, 4) and is a simple procedure. Critical region drying may also be used (5), but is more complex and expensive than freeze drying.

11. Procedure

11.1 Outgas or dry the test specimen in accordance with 10.1 or 10.2.

11.2 Weigh the outgassed or dried specimen and record this weight.

11.3 Place the outgassed or dried material in the penetrometer.

NOTE 2—When performing the operation described in 11.2 and 11.3, the outgassed or dried material is exposed to the laboratory atmosphere and can reabsorb vapors. Thus, this operation should be carried 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 μmHg).

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

NOTE 3—The pressure required to fill the penetrometer with mercury is also capable of intruding sufficiently large pores of both the inter- and intra-fragment classes. Thus, the process can intrude some pores and the volume distribution of these pores cannot subsequently be determined. This fact should be recognized, and where possible, a filling pressure should be selected that will not intrude pores in the diameter range of 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 incrementally, 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, the pressure shall be maintained during the pause and not allowed to decrease.

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 may result in some of the pore volume being incorrectly assigned to smaller pore diameters. The extent to which this may be a problem can be assessed by conducting two tests, each at a different pressure increase rate, and comparing the results.

NOTE 6—Use of the equation in 4.1 requires the absolute pressure, P . With some instruments it may not be possible to read the absolute pressure directly. In this case the gage pressure shall be recorded at each step, and the absolute pressures subsequently calculated.

NOTE 7—The choice of pressure intervals at which data are to be recorded is left to the judgment of the operator. Normally, at least 10 to 15 intervals will be required to adequately define the pore volume distribution. In selecting these pressure intervals, a rough idea of the expected distribution is helpful, since the pressure interval can be larger in regions where little or no intrusion occurs and should be smaller in regions where a large volume of intrusion is expected. It is not necessary to continue the process up to the maximum pressurizing capability of the instrument if all

of the pores of interest in a particular test specimen 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 is required to obtain values to use in correcting intrusion data for compressibilities and temperature changes.

12.2 Select a nonporous material that has approximately the same compressibility and bulk volume as the soil or rock 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 steps used for the soil or rock tests to ensure that temperature changes due to pressuring are the same.

12.4 Results of the blank run are a series of measured volume changes that can also be expected to occur along with actual intrusion in a test on a material. Such blank run results are used to correct the intruded volumes as discussed in 13.3.2.

12.5 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, one of these effects will be dominant. Therefore, results of the blank test will be either an apparent intrusion (compressibility dominant) or an expulsion of mercury (heating dominant).

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

12.5.2 If the blank results show a mercury expulsion, they are to be added to the volumes in a test on the soil or rock.

13. Calculation

13.1 Intruding pressures must be expressed as absolute pressures before they can be used to compute the corresponding pore diameters. If the recorded values are gage pressures, they should be converted to absolute pressures in accordance with the manufacturer's instructions. If the instrument reads directly in absolute pressure, omit this step.

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

13.2.1 Where triple-distilled mercury is used, the surface tension can generally be relied upon to be that reported in handbooks, that is, 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 only as a linear term.

13.2.2 The contact angle enters the equation as a cosine function, 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; references to some of these measurements are given in Appendix X1. This appendix also lists references for several methods of contact-angle measurement that have been found useful. The ideal value for reducing the data is the one that has been determined for the material under test. If

direct measurement is impractical, the use of an assumed value is customary. If mercury intrusion is being used for the comparison of similar materials for quality control purposes, then an assumed value is satisfactory, however, when different materials are being compared, the assumption of a single value for the contact angle may lead to errors.

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

13.3.1 Low-pressure corrections account for the fact that part of the apparent intrusion recorded at the lowest pressures is actually the compression of the air trapped in the penetrometer when it was filled with mercury. This correction is important only when the distribution of large pores must be measured accurately. When large pores are not of interest (pores larger than about 50 μm diameter), the low pressure correction may be safely ignored.

13.3.2 High pressure corrections to the intruded volume readings represent the compressibility of the sample, penetrometer, and mercury, as well as temperature changes that occur as a result of pressurization. The value of this correction is experimentally determined with the blank intrusion test performed in Section 12. Values determined in the blank test are either added to or subtracted from the intrusion volumes 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 or drying procedure,

14.1.4 Contact angle used in calculations,

14.1.5 A table showing the corrected cumulative intrusion volumes on a per gram basis and the corresponding absolute intruding pressure (Note 8), and

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.

NOTE 8—The pore size distribution may also be expressed in terms of intruded volume per cubic centimetre of total sample volume, if this is a more convenient form for the results.

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 or change shall be on the ordinate, with an arithmetic or logarithmic scale as appropriate, and the apparent pore diameters shall be on the abscissa with a logarithmic scale.

14.2.1 A differential plot can lead to a distorted image of the pore size distribution unless care is exercised in the selection of the diameter points at which the slope or change in intrusion is calculated. It is recommended that pore diameters be selected

that are approximately equally spaced on the logarithmic diameter axis, and that these diameters be used consistently to avoid distortions in the appearance of the differential plot.

14.2.2 When a differential plot is presented, there shall be on the plot itself a statement of the cumulative total intruded pore volume. Typical examples of both cumulative and differential pore volume distribution plots are shown in Fig. 1 and Fig. 2. The intra-fragment pore concentration is shown to the left of the plot; the inter-fragment concentration is to the right.

15. Precision and Bias

15.1 Appendix A of Ref (3) shows examples of single-

laboratory variations for several compacted soils. No multi-laboratory comparisons are available, and statistical evaluations of variability are totally lacking.

16. Keywords

16.1 frequency distribution; hydraulic conductivity; mercury; permeability; pore distribution; pore volume; poresize; porosimetry; porosity; soil; soil physics; voids

APPENDIX

(Nonmandatory Information)

X1. DETERMINING 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 along 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 in question with the mercury used for the porosimetry experiment. Ref (6) gives a summary of a wide variety of experimental techniques for measuring contact angles.

X1.2 Some contact angles have been reported in the references. Some examples of contact angles are given in Table X1.1.

X1.3 If a published contact angle value is to be adopted, it is recommended that the reference be carefully studied to assess the validity of its use for reducing porosimetry data.

TABLE X1.1 Examples of Contact Angles

Material	Contact Angle, ^o	Reference
Alkali borosilicate glass	153	(7)
Quartz	132–147	(8)
Clay minerals	139–147	(9)
Aluminum oxide	127	(10)

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