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Evaluation of pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption —

Part 1:
Mercury porosimetry

Evaluation de la distribution de taille des pores et la porosité des matériaux solides par porosimétrie à mercure et l'adsorption des gaz —

Partie 1: Porosimétrie à mercure

Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

The committee responsible for this document is ISO/TC 24, *Particle characterization including sieving*, Subcommittee SC 4, *Particle characterization*.

This second edition cancels and replaces the first edition (ISO 15901-1:2005), which has been technically revised. It also incorporates the Corrigendum ISO 15901-1:2005/Cor 1:2007.

ISO 15901 consists of the following parts, under the general title *Evaluation of pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption*:

- *Part 1: Mercury porosimetry*
- *Part 2: Analysis of mesopores and macropores by gas adsorption*
- *Part 3: Analysis of micropores by gas adsorption*

Introduction

In general, different pores (micro-, meso-, and macropores) may be pictured as either apertures, channels or cavities within a solid body or as space (i.e. interstices or voids) between solid particles in a bed, compact or aggregate. Porosity is a term which is often used to indicate the porous nature of solid material and in this International Standard is more precisely defined as the ratio of the total pore volume of the accessible pores and voids to the volume of the particulate agglomerate. In addition to the accessible pores, a solid may contain closed pores which are isolated from the external surface and into which fluids are not able to penetrate. The characterization of closed pores is not covered in this International Standard.

Porous materials may take the form of fine or coarse powders, compacts, extrudates, sheets or monoliths. Their characterization usually involves the determination of the pore size distribution as well as the total accessible pore volume or porosity. For some purposes it is also necessary to study the pore shape and interconnectivity and to determine the internal and external specific surface area.

Porous materials have great technological importance, for example in the context of the following:

- controlled drug release;
- catalysis;
- gas separation;
- filtration including sterilization;
- materials technology;
- environmental protection and pollution control;
- natural reservoir rocks;
- building materials;
- polymers and ceramic.

It is well established that the performance of a porous solid (e.g. its strength, reactivity, permeability) is dependent on its pore structure. Many different methods have been developed for the characterization of pore structure. In view of the complexity of most porous solids, it is not surprising that the results obtained are not always in agreement and that no single technique can be relied upon to provide a complete picture of the pore structure. The choice of the most appropriate method depends on the application of the porous solid, its chemical and physical nature and the range of pore size.

The most commonly used methods are as follows:

a) Mercury porosimetry, where the pores are filled with mercury under pressure. This method is suitable for many materials with pores in the approximate diameter range of 0,004 µm to 400 µm.

b) Meso- and macropore analysis by gas adsorption, where the pores are characterized by adsorbing a gas, such as nitrogen at liquid nitrogen temperature. The method is used for pores in the approximate diameter range of 0,002 µm to 0,1 µm (2 nm to 100 nm).

c) Micropore analysis by gas adsorption, where the pores are characterized by adsorbing a gas, such as nitrogen at liquid nitrogen temperature. The method is used for pores in the approximate diameter range of 0,4 nm to 2 nm.

Evaluation of pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption —

Part 1:
Mercury porosimetry

WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. This International Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this International Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard describes a method for the evaluation of the pore size distribution and the specific surface area of pores in solids by mercury porosimetry according to the method of Ritter and Drake[1][2]. It is a comparative test, usually destructive due to mercury contamination, in which the volume of mercury penetrating a pore or void is determined as a function of an applied hydrostatic pressure, which can be related to a pore diameter.

Practical considerations presently limit the maximum applied absolute pressure to about 400 MPa (60 000 psi) corresponding to a minimum equivalent pore diameter of approximately 4 nm. The maximum diameter is limited for samples having a significant depth due to the difference in hydrostatic head of mercury from the top to the bottom of the sample. For the most purposes, this limit can be regarded as 400 µm. The measurements cover inter-particle and intra-particle porosity. In general, without additional information from other methods it is difficult to distinguish between these porosities where they co-exist. The method is suitable for the study of most porous materials non-wettable by mercury. Samples that amalgamate with mercury, such as certain metals, e.g. gold, aluminium, copper, nickel and silver, can be unsuitable with this technique or can require a preliminary passivation. Under the applied pressure some materials are deformed, compacted or destroyed, whereby open pores may be collapsed and closed pores opened. In some cases it may be possible to apply sample compressibility corrections and useful comparative data may still be obtainable. For these reasons, the mercury porosimetry technique is considered to be comparative.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3165, *Sampling of chemical products for industrial use — Safety in sampling*

ISO 14488, *Particulate materials* — Sampling and sample splitting for the determination of particulate properties

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
porosimeter
instrument for measuring pore volume and pore size distribution

3.2
porosimetry
methods for the estimation of pore volume, pore size distribution, and porosity

3.3
porous solid
solid with cavities or channels which are deeper than they are wide

3.4
powder
porous or nonporous solid composed of discrete particles with maximum dimension less than about 1 mm, powders with a particle size below about 1 µm are often referred to as fine powders

3.5
pore
cavity or channel which is deeper than it is wide, otherwise it is part of the material's roughness

3.6
void
interstice
space between particles, i.e. interparticle pore

3.7
macropore
pore of internal width greater than 50 nm

3.8
mesopore
pore of internal width between 2 nm and 50 nm

3.9
micropore
pore of internal width less than 2 nm

3.10
closed pore
pore totally enclosed by its walls and hence not interconnecting with other pores and not accessible to fluids

3.11
open pore
pore not totally enclosed by its walls and open to the surface either directly or by interconnecting with other pores and therefore accessible to fluid

3.12
ink bottle pore
narrow necked open pore

3.13
pore size
internal pore width (for example, the diameter of a cylindrical pore or the distance between the opposite walls of a slit) which is a representative value of various sizes of vacant space inside a porous material

3.14
pore volume
volume of open pores unless otherwise stated

3.15
pore diameter
diameter of a pore in a model in which the pores typically are assumed to be cylindrical in shape and which is calculated from data obtained by a specified procedure

3.16
median pore diameter
diameter that corresponds to the 50th percentile of pore volume, i.e. the diameter for which one half of the pore volume is found to be in larger pores and one half is found to be in smaller pores

3.17
modal pore diameter
mode
pore diameter of the maximum in a differential pore size distribution curve

3.18
hydraulic pore diameter
average pore diameter, calculated as the ratio of pore volume multiplied by four to pore area.

3.19
bulk volume
volume of powder or solids, including all pores (open and closed) and interstitial spaces between particles.

3.20
bulk density
ratio of sample mass to bulk volume

3.21
skeleton volume
volume of the sample including the volume of closed pores (if present) but excluding the volumes of open pores as well as that of void spaces between particles within the bulk sample

[SOURCE: ISO 12154]

3.22
skeleton density
ratio of sample mass to skeleton volume

3.23
apparent volume
total volume of the solid constituents of the sample including closed pores and pores inaccessible or not detectable by the stated method;

3.24
apparent density
ratio of sample mass to apparent volume

3.25
envelope volume
total volume of the particle, including closed and open pores, but excluding void space between the individual particles

3.26
envelope density
ratio of sample mass to envelope volume

3.27
porosity
ratio of the volume of the accessible pores and voids to the bulk volume occupied by an amount of the solid

3.28
interparticle porosity
ratio of the volume of void space between the individual particles to the bulk volume of the particles or powder

3.29
intraparticle porosity
ratio of the volume of open pores inside the individual particles of a particulate or divided solid sample to the bulk volume occupied by the sample

3.30
surface area
extent of accessible surface area as determined by a given method under stated conditions

3.31
surface tension
work required to increase a surface area divided by that area.

3.32
contact angle
angle at which a liquid/vapour interface meets the surface of a solid material

4 Symbols and abbreviated terms

For the purposes of this document, the following symbols apply.

Symbol	Term	SI unit	Derived and obsolete units	Conversion factors
P	pressure	Pa	MPa, psia, Torr, mmHg	1 MPa = 10^6 Pa 1 psi = 1 lb in^{-2} = 6 895 Pa 1 Torr = 1 mmHg = 133,32 Pa
d_p	pore diameter	m	nm, µm, Å	1nm = 10^{-9} m, 1µm = 10^{-6} m, 1 Å = 10^{-10} m
t	time	s	h	1 h = 3 600 s
S	specific surface area	$m^2 \cdot kg^{-1}$	$m^2 \cdot g^{-1}$	
V_{Hg}	intruded volume of mercury	m^3	cm^3, mm^3	10^3 mm^3 = 1 cm^3 = 10^{-6} m^3
$V_{Hg,0}$	initial intruded volume of mercury	m^3	cm^3, mm^3	
$V_{Hg,max}$	total intruded volume of mercury	m^3	cm^3, mm^3	
V_p	specific pore volume	$m^3 \cdot kg^{-1}$	$mm^3 \cdot g^{-1}$ $cm^3 \cdot g^{-1}$	
γ	surface tension of mercury	$N \cdot m^{-1}$	$dyne \cdot cm^{-1}$	1 $dyne \cdot cm^{-1}$ = 10^{-3} $N \cdot m^{-1}$
ρ_{Hg}	density of mercury	$kg \cdot m^{-3}$	$g \cdot cm^{-3}$	1 $g \cdot cm^{-3}$ = 10^3 $kg \cdot m^{-3}$
Θ	contact angle of mercury at the sample	rad	°	1° = (π/180) rad
m_S	mass of the test sample	kg	g	
m_{SH}	mass of empty sample holder	kg	g	
m_{SH+S}	mass of sample holder with sample	kg	g	
$m_{SH+S+Hg}$	mass of sample holder with sample and filled with mercury	kg	g	

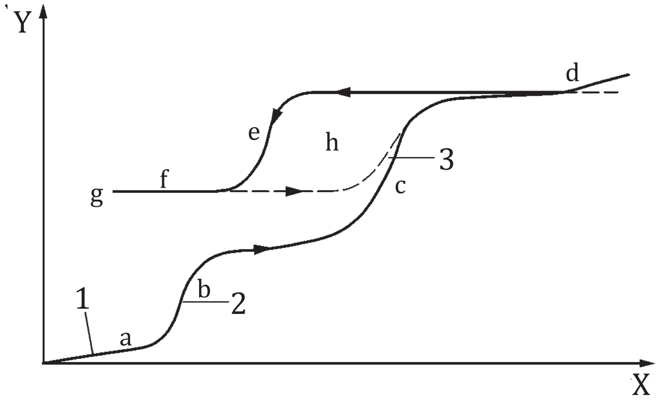
Symbol	Term	SI unit	Derived and obsolete units	Conversion factors
V_B	bulk volume	m^3	cm^3	
V_S	skeleton volume	m^3	cm^3	
V_{SH}	volume of sample holder	m^3	cm^3	
ρ_B	bulk density	$kg \cdot m^{-3}$	$g \cdot cm^{-3}$	
ρ_S	skeleton density	$kg \cdot m^{-3}$	$g \cdot cm^{-3}$	
ε	porosity	—		

5 Principles

Mercury porosimetry is a widely accepted method for pore size analysis of various materials such as pharmaceutical tablets, building materials, catalysts and their supports, mainly because it allows pore size/porosity analysis to be undertaken over a wide range of pore sizes from meso- to macropores with pore widths about 0,004 µm to about 400 µm[1]–[7]. In contrast to capillary condensation, where the pore fluid wets the pore walls (i.e. the contact angle is smaller than 90 degrees), mercury porosimetry describes a non-wetting situation (i.e. the contact angle is greater than 90 degrees) and therefore pressure must be applied to force mercury into the pores. Thus, a progressive increase in hydrostatic pressure is applied to enable the mercury to enter the pores in decreasing order of width. Accordingly, there is an inverse relationship between the applied pressure, p, and the pore diameter, d_p, which in the simplest case of cylindrical pores is given by the Washburn equation (see 9.1).

In the application of mercury porosimetry, the volume of mercury entering the pore structure is measured as the applied pressure is gradually increased. The value V_Hg at the applied pressure, p, gives the cumulative volume of all available pores of diameter equal to, or greater than, d_p. The determination may proceed either with the pressure being raised in a step-wise manner and the volume of mercury intruded measured after an interval of time when equilibrium has been achieved, or by raising the pressure in a continuous (progressive) manner.

Figure 1 shows two intrusion/extrusion cycles of mercury into a porous powder as a function of pressure. Region (a) corresponds to a re-arrangement of particles within the powder bed, followed by intrusion of the interparticle voids (b). Filling of intraparticle pores occurs in the region (c) and for some materials (reversible) compression is then possible at higher pressures (d). Hysteresis (h) is observed and extrusion (e) occurs at different pressures than for the intrusion. On completion of a first intrusion-extrusion cycle, usually some mercury is retained by the sample, thereby preventing the loop from closing (f). Intrusion-extrusion cycles after the first cycle continue to show hysteresis (g) but eventually the loop closes, showing that there is no further entrapment of mercury. On most samples, entrapment is not observed anymore after just the second cycle, which also indicates that hysteresis and entrapment are essentially of different origin.



Key

1 powder compression
2 interparticle filling
3 intraparticle filling
Y intruded mercury, V_{Hg}
X hydraulic pressure, lg p

Figure 1 — Characteristic features of mercury porosimetry curves

The hysteresis and entrapment phenomena is undoubtedly important in order to obtain a comprehensive pore size analysis. Mercury entrapment appears to be caused by the rupture of mercury bridges in pore constrictions during extrusion from ink-bottle pores. Different mechanisms have been proposed to explain intrusion/extrusion hysteresis [6]–[12]. The single pore mechanism implies that hysteresis can be understood as an intrinsic property of the intrusion/extrusion process due to nucleation barriers associated with the formation of a vapour-liquid interface during extrusion, or discussed in terms of differences in advancing and receding contact angles. In contrast, the network models take into account the ink-bottle and percolation effects in pore networks. It is now generally accepted that pore blocking effects, which can occur on the intrusion branch, are similar to the percolation effects involved in the desorption of gases from porous networks. Indeed, the shape of a mercury intrusion/extrusion hysteresis loop often agrees well with that of the corresponding gas adsorption loop[9][10]. Thus, mercury intrusion and the capillary evaporation appear to be based on similar mechanisms. The pore blocking/percolation effects are dominant in disordered pore networks, and a reliable pore size distribution can only be calculated from the intrusion branch by applying complex network models, based on percolation theory. The application of such models also allows one to obtain a limited amount of structural information from the intrusion/extrusion hysteresis loop [11][12].

6 Apparatus and material

WARNING — It is important that proper precautions for the protection of laboratory personnel are taken when mercury is used. Attention is drawn to the relevant regulations and guidance documents which appertain for the protection of personnel in each of the member countries.

6.1 Sample holder

The sample holder may consist of a vessel with a uniform bore capillary tube through which the sample can be evacuated and the vessel filled with mercury. The capillary tube is attached to a wider bore tube in which the test sample is located. If precise measurements are required, the internal volume of the capillary tube should be between 20 % and 90 % of the expected pore and interparticle volume of the sample. Since different materials exhibit a wide range of open porosities a number of sample vessel holders with different tube diameters and vessel volumes is required. A special design of sample holder is often used with powdered samples to avoid loss of powder during evacuation.

In order to evaluate the porosity and the bulk and skeleton densities, the volume of the sample holder, including the capillary tube, must be known.

6.2 Porosimeter

An instrument capable of carrying out the test at two sequential measurements, a low pressure test up to at least 0,2 MPa (30 psi) and a high-pressure test up to the maximum operating pressure of the porosimeter [circa 400 MPa (60 000 psi)].

The porosimeter may have several ports for high and low pressure operation, or the low pressure test may be carried out on a separate unit.

Prior to any porosimetry measurement it is necessary to evacuate the sample using a typical rotary vacuum pump, equipped with a mercury retainer and then to fill the sample holder with mercury to a given low pressure. A means of generating pressure is necessary to cause intrusion of mercury.

A means of detecting the change in the volume of mercury intruded to a resolution of 1 mm^3 or less is desirable. This is usually done by measuring the change in capacitance between the mercury column in the capillary tube and a metal sleeve around the outside of the sample holder.

6.3 Mercury

Mercury in analytical quality should be used for the measurements (at least a mass ratio of 99,5 % purity[17]).

7 Procedures for calibration and performance

7.1 General

Sample preparation and the filling of the sample holder with mercury require a vacuum, the level of which is usually recorded using a transducer. For the porosity evaluation, two signals are required to be measured in a porosimeter; the applied pressure and the corresponding volume change of mercury as it intrudes into the pores in the sample. The volume of mercury displaced from a precision glass capillary tube shall be preferably determined as a function of an electrical capacity change.

7.2 Pressure signal calibration

Pressure is usually measured with electronic pressure transducers which are factory calibrated. The accuracy of the pressure measurement should be within ±1 % of the full scale transducer reading or ±2 % of the actual reading, whichever is the lower. It is recommended that verification of calibration and traceability to an accredited organization, be regularly performed.

7.3 Volume signal calibration

The accuracy of the volume measurement should be within ±1 % of the total volume to be measured. It is recommended that verification of calibration, and traceability to an accredited organization, be regularly performed.

7.4 Vacuum transducer calibration

The accuracy of the indicated vacuum is generally not critical. The vacuum manifold system, without a sample, should be capable of achieving at least 7 Pa, and if possible it should be calibrated to within 1 Pa at this level.

7.5 Verification of porosimeter performance

It is recommended that a certified reference material selected by the user is tested on a regular basis to monitor instrument calibration and performance. If a non-certified reference material is used for this purpose, its values must be traceable to one of a certified reference material. Certified reference materials are offered by a number of national metrology institutes as well as by various private companies. Certified reference materials for mercury porosimetry are currently available from BAM1) in Germany, and NIST2) in the U.S.

8 Procedures

8.1 Sampling

Sampling should be performed in accordance with ISO 3165 and ISO 14488. The sample for test should be representative of the bulk material and should be of an appropriate quantity. Particular precautions should be taken when the test sample properties are directionally orientated. It is also recommended that a second sample is taken and held in reserve in case a repeated determination is necessary.

8.1.1 Obtaining a test sample

Since the material from which the sample for test is taken may be in a variety of forms, different sub-sampling methods are appropriate as follows.

a) From a block

Several pieces of about 1 cm^3 may be taken in order to represent different zones from within the block. The pieces may be cut with a saw or core drill or crushed. There is a possibility that saw or crushing marks can be interpreted as pores. If coarse pores are of particular interest, polish the surface of the pieces with a medium of 10 µm maximum particle size. If fine pores are of particular interest, test the sample in the as-sawn condition and ignore data from pore diameter greater than 125 µm.

b) From a powder

Powdery and granular material samples which are free-flowing should be subdivided by rotary sampling or chute riffling. Non-free-flowing powders may be sampled by coning and quartering. To help distinguish between inter- and intraparticle pores, it may be beneficial to sieve the sample to a particle size range which allows clearer distinction between the two, but it is important to establish that this does not make the sampling unrepresentative.

c) From a film or sheet

Film or sheet material may be sampled by either cutting a strip, or by stamping disks, to fit the appropriate sample holder. Difficulties in testing material in this form may arise due to proximity between adjacent faces. This can be overcome by rolling steel wire gauze between the faces to keep the surfaces separate.

8.1.2 Quantity of sample

The quantity of test sample required is dependent upon its nature. The largest possible sample size commensurate with the size of sample holder should be taken. However, the total pore volume should lie within the recommended measuring range of the capillary tube and the apparatus. In the case of unknown specimens, a preliminary test is usually necessary to ascertain the optimum quantity of test

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1) BAM Bundesanstalt für Materialforschung und –prüfung, Department I.6 Inorganic Reference Materials, Richard-Willstätter-Straße 11, D-12489 Berlin, Germany

2) Standard Reference Materials Program, National Institute of Standards and Technology (NIST), Office of Reference Materials, 100 Bureau Drive, Stop 2300 Gaithersburg, MD 20899 2300, USA

sample. The test sample is placed preferably in a sample holder having a volume between 1 cm^3 and 15 cm^3, but larger sample holders may be used.

8.2 Method

8.2.1 Sample pre-treatment

Sample pre-treatment outside the mercury porosimeter is not always required, but does frequently lead to more accurate and repeatable results, especially for samples which are highly hydrophilic or porous. Evacuation of atmospheric gases at the start of the analysis may proceed more quickly for samples that have been pre-treated due to less evaporation of adsorbed vapours during this evacuation. In addition, since sample mass is often determined before the sample is placed in the sample holder, pre-treated samples will yield more reliable masses than those which may be saturated with atmospheric vapours such as water. Thus pre-treatment will remove adsorbed material which can obscure its accessible porosity: this includes adsorbed water and other materials such as organic molecules used in the manufacture or operation of the porous solid.

When a satisfactory pre-treatment regime has been established, the sample can be out-gassed by heating and/or evacuation or by a flowing inert gas. If the sample is in a form which allows amalgamation with, or wetting by mercury, it may be possible to passivate the surface e.g. by producing a thin layer of oxide, or by coating with a polymer or stearate.

The mass of the test sample, m_S, used should be recorded after any pre-treatment.

8.2.2 Filling of the sample holder and evacuation

After sample pre-treatment, the sample should be transferred to a clean and dry sample holder. To minimize recontamination by, for example, resorption of water vapour, it may be prudent to effect the transfer in a purged glove box, and to dose the sample holder with nitrogen for final transfer to the porosimeter.

Determine the mass of the empty sample holder, m_{SH}, and after filling the sample holder with the sample determine the mass of the sample holder containing the sample, m_{SH+S}. The sample mass, m_S, is calculated by subtracting m_{SH} from m_{SH+S}.

The object of sample evacuation is to remove the majority of vapours and gases from the sample, prior to filling the sample holder with mercury.

Fine powders with relatively high surface area may tend to fluidize under vacuum with loss of sample into the vacuum system. This effect may be avoided by selection of sample holders designed especially for powders, and by controlling the rate of evacuation.

The evacuation vacuum, dependent upon the nature of the material, may be varied. Care should be taken to ensure that pore structure does not change due to evacuation as is possible for some materials[3]. The evacuation time is considerably reduced for pre-dried samples.

8.2.3 Filling the sample holder with mercury

A vacuum is required to ensure the transfer of mercury from the reservoir to the sample holder. If the mercury is de-aerated during filling, this maintains the sample vacuum and avoids air-bubble entrapment.

The hydrostatic pressure of the mercury over the sample under vacuum conditions must be recorded before starting the measurement to correct the applied pressure. In vertically filled sample holders the filling pressure consists of the applied pressure and the hydrostatic pressure. The hydrostatic pressure may be minimized by filling the sample holder in a horizontal position, but any hydrostatic pressure must be taken into account when turning the sample holder to a vertical position. A typical filling pressure should be less than 5 kPa.

8.2.4 Measurement

8.2.4.1 Low pressure

Admit non-reacting dry gas (e.g. air, nitrogen or helium) into the evacuated sample holder in a controlled manner to increase the pressure either in stages, continuously or by step-wise pressurization in order to obtain proper equilibration conditions for mercury to enter the pores and to achieve the required precision corresponding to the particular pore sizes of interest. Pressure and corresponding volume of mercury intruded are to be recorded. When the maximum required pressure has been reached reduce the pressure to ambient and transfer the sample holder to the high-pressure unit.

In order to evaluate the porosity and the bulk and skeleton densities determine the mass of the sample holder with sample and mercury, $m_{SH+S+\mathrm{Hg}}$

8.2.4.2 High pressure

Transfer the sample holder to the high-pressure unit. Increase the pressure in the system to the final pressure reached in the low pressure phase and record the intrusion volume at this pressure, since subsequent intrusion volume are calculated from this initial volume. Increase the pressure via the hydraulic fluid on the mercury either continuously (uninterrupted increase in both pressure and time), stepwise (uniform and regular increase in unit pressure-time interval), or in stages (non-uniform increase in either pressure or time over numbered intervals) according to the proper equilibration conditions for mercury entering the pores and to a required precision corresponding to the particular pores sizes of interest. As a consequence, mercury is pressed into the pore system and the intruded volume is measured as a function of pressure. When the maximum required pressure has been reached, reduce the pressure, carefully, to atmospheric. It is highly recommended to determine the mercury extrusion curve; an understanding and proper interpretation of the obtained hysteresis loop allows one to arrive at a more comprehensive pore size analysis. Analogous to the intrusion process, the pressure may be reduced in a controlled manner (either in stages, in a step-wise mode or continuously) which allows the recording of the volume extruded versus the decreasing pressure.

8.2.5 Completion of test

Before finally removing the sample holder from the porosimeter, ensure that the pressure in the apparatus has been returned to ambient. A visual check to ascertain that the mercury has penetrated the sample is advisable.

8.2.6 Blank and sample compression correction

8.2.6.1 General

The mercury, the sample and the sample holder, and other components of the volume detector system are compressed to different degrees under elevated pressures. Compressibility corrections may be justified where the porosity is low, the sample is relatively compressible, or where high precision is required. Changes in temperature due to pressurization affect the volume of mercury due to thermal expansion.

If necessary, a blank test is carried out, preferably using a control sample which is non-porous but of similar size and heat capacity as the test sample. The test is made under exactly the same conditions as those employed for the actual test sample or when using a blank sample holder. A correction for sample volume displacement should be used in order to minimize temperature effects due to pressurization. The heat transfer process which occurs within the system, from pressurization and depressurization, can result in density and volume changes.

8.2.6.2 Applying the correction

The result of the test described above is a series of apparent volume changes. Apparent intruded mercury volumes are to be subtracted from the measured intrusion volumes on a test sample. Apparent extruded mercury volumes are then added to the measured extrusion volumes on the test sample. When carrying out the correction measurement without a test sample, the data should be corrected for the sample volume before blank subtractions or additions.

Depending on details of the experimental set-up, additional corrections are necessary for hydrostatic pressure of mercury over the sample.

9 Evaluation

9.1 Determination of the pore size distribution

The pressure exerted is inversely proportional to the internal width of the pore entrance. For pores of cylindrical shape, the Washburn equation [see Formula (1)] gives the relation between pressure, p, and diameter, d_p[4]:

$$d_p = \frac{-4\gamma\cos\theta}{p} \tag{1}$$

Using the Washburn equation, the pressure readings are converted to the pore diameter.

The surface tension of mercury, γ, depends on the sample material and on temperature. Furthermore, for highly curved surfaces, it depends on the curvature. At room temperature, values between 0,470 $N{\cdot}m^{-1}$ and 0,490 $N{\cdot}m^{-1}$ are reported. If the value is unknown $\gamma = 0{,}480\ N{\cdot}m^{-1}$ should be used.

In most cases, for mercury the contact angle, θ, is between 125° and 150°. The contact angle should be determined using an appropriate instrument. If the value is unknown, $\theta = 140°$ may be used.

Graphical representation of the cumulative intruded specific volume (V_{Hg}/m_s) as the ordinate versus the pore diameter as the abscissa gives, when plotted, a pore volume distribution (Figure A.2). Because of the pore diameter size range, the most suitable scale for the pore diameter abscissa is logarithmic.

Interparticle volume may be recorded as pore volume together with the intruded mercury into intraparticle pores. This additional intrusion volume may produce an incorrect pore size distribution if not recognized.

In the case of intrusion into pores that have small connections to the outside (ink bottle pores), the intrusion pore size measured reflects the pore size distribution of the necks and total volume of all filled pores. Thus, the calculated pore area may be incorrect.

Curves obtained from decreasing pressure (extrusion curve) should not be used to establish a pore volume distribution. However, it is strongly recommended that the measurement should not be solely confined to the determination of an intrusion curve since it is possible to identify certain distinctive powder characteristics from features of the intrusion–extrusion behaviour. Reproducibility of the hysteresis loop in a second intrusion–extrusion cycle indicates that the structure of the sample was not irreversibly affected in the first cycle (i.e. there was no fracture of the material) and thus gives additional information about the texture of the material, i.e. characteristics of the pore network [11][12] .

9.2 Determination of the specific pore volume

The maximum value of the cumulative pore volume distribution as represented in Figure A.2 gives the apparent specific pore volume, V_p, in the meso- and macropore range because it includes interparticle porosity of the material, intraparticle porosity of the sample, and any volumetric change of the sample resulting from pressurization. Note that the pore volume of narrow mesopores (pore diameter smaller than 4 nm; assuming a mercury contact angle of 140°) and micropores cannot be assessed by mercury intrusion.

9.3 Determination of the specific surface area

Assuming pores of cylindrical shape from the pore volume distribution, a surface distribution may be derived. According to Rootare and Prenzlow[5], from the pressure/volume curve, a specific surface area of the intruded pores can be calculated without using a pore model, assuming the material is free of ink bottle pores and not deformed by applied pressure:

$$S = \frac{1}{\gamma \cos\theta} \int_{V_{\mathrm{Hg},0}}^{V_{\mathrm{Hg,max}}} p dV \tag{2}$$

The surface area calculated from Formula (2) may not be comparable with that derived from gas adsorption methods because pores smaller than 4 nm cannot be assessed (assuming a contact angle of 140°).

9.4 Determination of the bulk and skeleton densities

Mercury porosimetry measurements can also be used to obtain the bulk and skeleton density of the sample respectively. To determine these quantities the volume of mercury surrounding the sample in the completely filled sample holder, at the filling pressure, and also the mercury volume intruded into the pores at maximum pressure (prior to any deformation) are used.

9.4.1 Bulk density

The bulk volume of the sample, V_B, including voids and pores not filled at the lowest pressure, is found by subtracting the volume of mercury, V_{Hg}, occupying the space not filled by the sample from the volume of the empty sample holder, V_{SH}. The mercury volume is determined from the weight of the sample holder with the sample before and after filling with mercury and the density of mercury at the temperature of the measurement.

$$V_B = V_{SH} - V_{\mathrm{Hg}} \tag{3}$$

$$V_{\mathrm{Hg}} = (m_{SH+S+\mathrm{Hg}} - m_{SH+S})/\rho_{\mathrm{Hg}} \tag{4}$$

The bulk density is calculated by dividing the sample mass by the bulk volume.

$$\rho_B = m_S/V_B \tag{5}$$

9.4.2 Skeleton density

The skeleton volume of the sample, V_S, is found by subtracting the total volume of mercury filling the pores obtained at the high pressure test, $V_{\mathrm{Hg,max}}$, from the bulk volume of the sample, $V_{B.}$

$$V_S = V_B - V_{\mathrm{Hg,max}} \tag{6}$$

The skeleton density is calculated by dividing the sample mass by the skeleton volume.

$$\rho_S = m_S/V_S \tag{7}$$

NOTE Open pores with aperatures greater than 4 nm are not accessible to mercury porosimetry, and therefore, if such pores are present, a skeleton volume cannot be determined, but rather an apparent volume is assessed.

9.5 Determination of the porosity

From the bulk volume and the skeleton volume the porosity can be calculated.

$$\varepsilon = (V_B - V_S)/V_B \tag{8}$$

Closed pores and pores that are not filled at the highest intrusion pressure (e.g. smaller than about 4 nm), are not accounted for in the porosity determined by mercury porosimetry.

10 Reporting

A summary of the measurement conditions and constants used in the calculation should be recorded for each result as follows:

a) reference to this part of ISO 15901, i.e. ISO 15901-1, laboratory, operator, date;

b) sample identification (e.g. if known, chemical composition, purity, particle size distribution, density), method of sampling, sample division;

c) instrument and sample holder type used;

d) sample pre-treatment;

e) outgassing conditions (duration, temperature and evacuation pressure);

f) mass, m_S, of outgassed test sample;

g) specification whether the sample is a powder, a solid monolith or consists of crushed pieces of a monolith;

h) filling pressure;

i) stepwise or continuous methodology:

   1) if stepwise, the equilibrium time of rate of change pressurization is required; and

   2) if continuous, then the pressurization rate is required;

j) pressure and volume intruded at each pressure value;

k) contact angle used;

l) surface tension value used;

m) mercury density and temperature;

n) tabular report consisting of: pressure, pore diameter, specific intrusion volume, log differential pore volume, percentage of total intrusion volume, surface area, median, modal and hydraulic pore diameters, bulk and skeleton density, porosity;

o) cumulative and log differential pore volume distribution according to Figures A.2 and A.3 or in any other format. Additionally, differential distributions can be useful for some distributions with narrow or monomodal population;

p) specific pore volume $V_\mathrm{p} = V_\mathrm{Hg,max}/m_S$;

q) method of blank correction, if applied.

Annex A
(informative)

Mercury porosimetry analysis results

A.1 Presentation of pore size distributions (Example)

Presentation of pore size distributions are as follows:

- tabular report (consisting of: pressure, pore diameter, specific intrusion volume, differential pore volume, log differential pore volume, percentage of total intrusion volume, surface area);
- intrusion data summary;
- cumulative pore volume distribution (graph);
- log differential pore volume distribution.

A.2 Intrusion data summary (Example)

Total Intruded Volume:

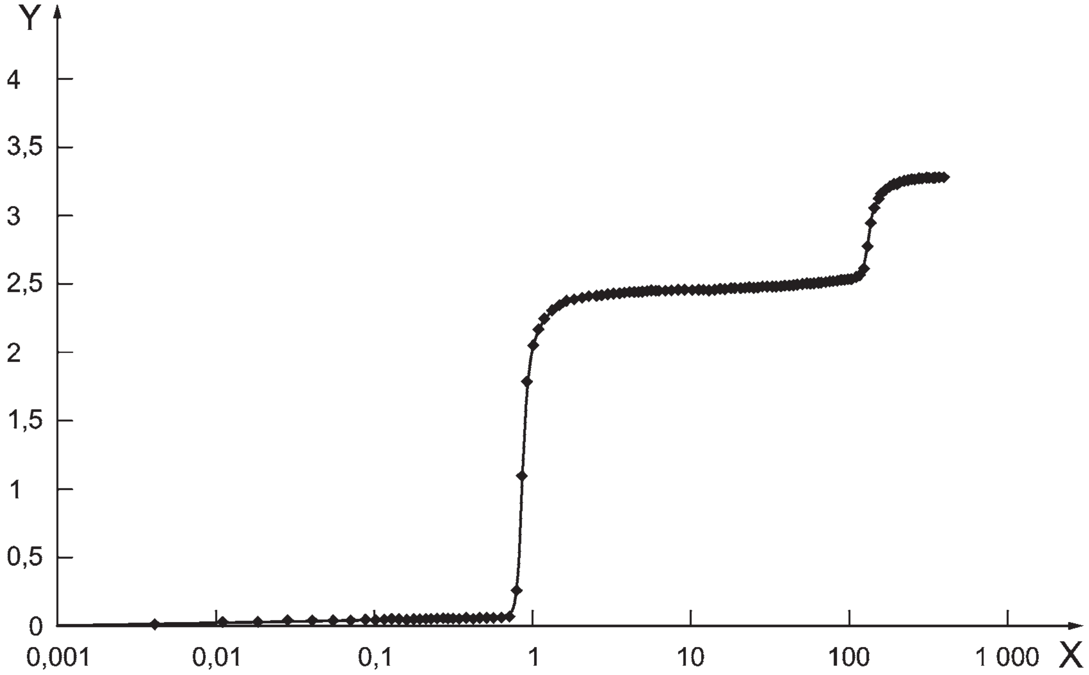
Modal Pore Diameter:

Median Pore Diameter:

Mean Pore Diameter:

Specific Surface Area:

Bulk and Skeleton Density:

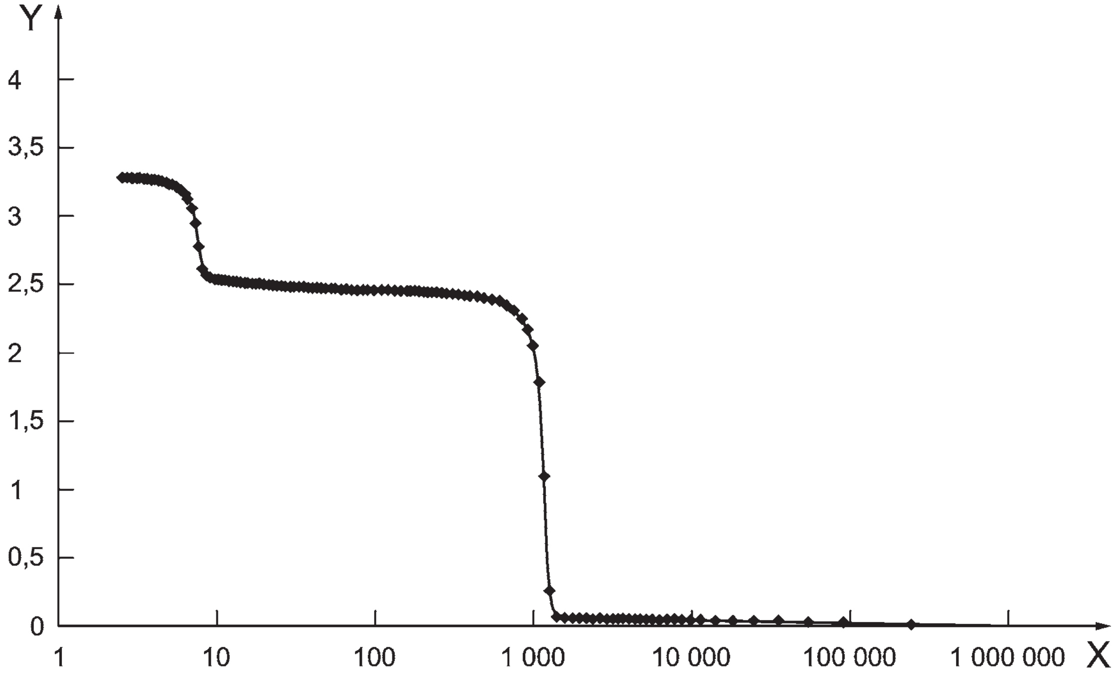


Key

X pressure, in MPa

Y cumulative intruded volume, in cm^3/g

Figure A.1 — Intruded volume versus pressure

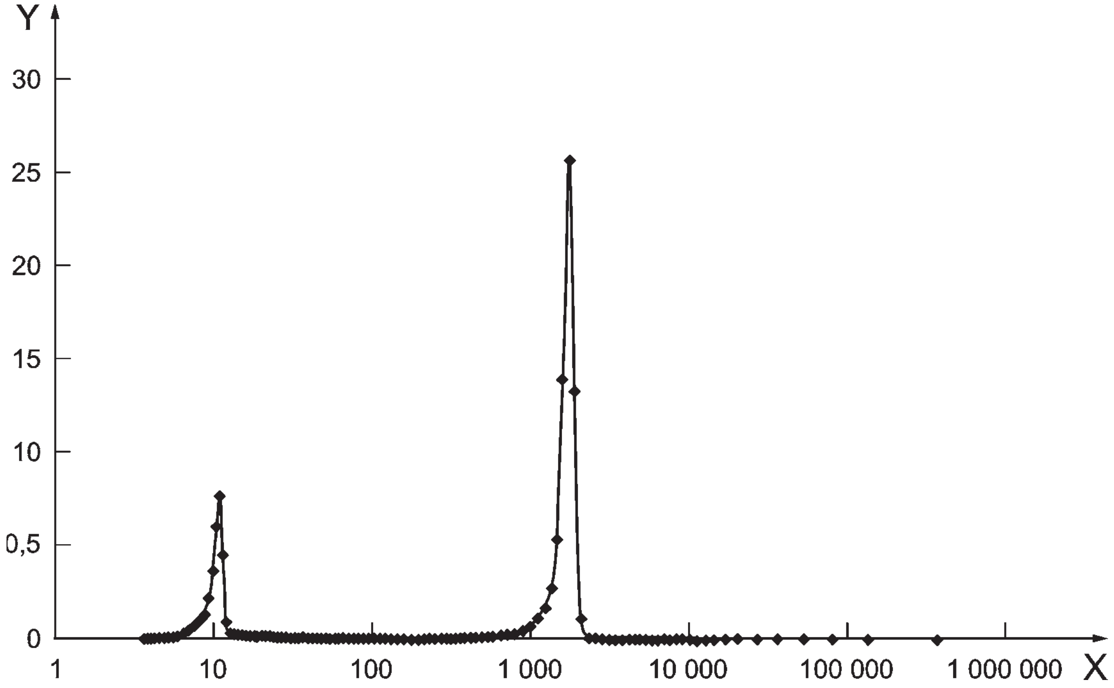


Key

X pore diameter, in nm

Y cumulative intruded volume, in cm^3/g

Figure A.2 — Pore Volume versus pore diameter



Key

X pore diameter, in nm

Y cumulative intruded volume, in cm^3/g

NOTE Although the units of the log differential pore volume axis are expressed in cm^3/g, they are not to be used for pore volume calculation.

Figure A.3 — Log Differential pore volume versus pore diameter

Annex B
(informative)

Recommendations for the safe handling of mercury

Mercury should be handled with the same care that any other laboratory chemical is given. It is strongly recommended to check and conform to specific regulations and recommendations for the use of mercury for each country. For instance, in the U.S., the current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for mercury vapour is 0,1 mg/m^3 of air. In addition, the National Institute for Occupational Safety and Health (NIOSH) has established in 2004 a recommended exposure limit (REL) for mercury vapour of 0,05 mg/m^3 as a time-weighted average (TWA) for up to a 10-hour workday and a 40-hour workweek[13][14][15]. But it should be stressed that these exposure limits and regulations may be different for every country. Safe working conditions are quite easy to maintain if a few simple guidelines are followed[15].

a) If at all possible, any operation with mercury should be performed in a separate room with proper ventilation and no “lab-traffic”. It is of advantage to place the mercury porosimeter in an environment in which atmospheric conditions can be easily controlled and extreme temperatures can be avoided. The use of a so-called “Tacky Mat” placed outside the Mercury Test area, on which mercury porosimeter users must step with both feet when exiting the Mercury Test area, is also recommended. In case it is not possible to operate the mercury porosimeter in a separate room, one should at least make sure that the laboratory has

   1) a good ventilation system to avoid concentration of harmful gases and vapours,

   2) an uncarpeted laboratory floor,

   3) the porosimeter positioned inside a tray of suitable dimensions, and

   4) the porosimeter positioned under a fume hood, if required by local rules.

b) The operator should wear PVC or latex gloves and protection glasses.

c) Always work with mercury over a spill tray. Keep all containers with mercury sealed when not in use. Waste mercury in any work area must be in spill trays covered with oil.

d) Ensure that containers of mercury are securely capped when not actually being poured from or into. Handle containers of mercury, including sample cells, in a well-ventilated area.

e) Use the mercury vapour traps supplied on the equipment and never override or disable any safety device.

f) Mercury porosimeter measurement cells should be cleaned in a fume hood. Use a large vessel for sample holder handling. The vessel should be placed inside the fume hood and all the operations of opening and emptying the sample holder containing mercury and all the operations related to mercury handling should be carried out inside the vessel. This is necessary to contain mercury in case of accidental spilling. Samples after mercury porosimetry tests are contaminated and therefore cannot be simply disposed. Separate the samples from the used mercury and keep the samples inside the container. The mercury still contained in the pores can be recovered and recycled along with the other used mercury.

g) It is not only from an environmental standpoint that it is important to stress that used mercury should be recycled. It can be sent to an appropriate institution or company which specializes in the recycling of mercury. Re-distilled (i.e. triple distilled) mercury can be used again in mercury porosimetry applications.

Under normal operation conditions, the above stated recommended exposure limits should never be reached. However, it is advisable to periodically check the actual concentration, for instance by monitor badges which are worn by the operator. This test should be performed at least annually, but always after a spill has occurred. All mercury spills should be cleaned immediately and thoroughly by mechanical, chemical, or other appropriate means (there are special mercury neutralizing chemicals available, e.g. glycerine and zinc based substances). Anyone dealing with the clean-up should wear a respirator and protective clothing to prevent any skin contact with mercury.

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