INTERNATIONAL STANDARD

ISO 15901-1

First edition
2005-12-15

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

Part 1: Mercury porosimetry

Distribution des dimensions des pores et porosimétrie des matériaux solides par porosimétrie au mercure et par adsorption de gaz —

Partie 1: Porosimétrie au mercure

Reference number
ISO 15901-1:2005(E)

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Published in Switzerland

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 15901-1 was prepared by Technical Committee ISO/TC 24, *Sieves, sieving and other sizing methods*, Subcommittee SC 4, *Sizing by methods other than sieving*.

ISO 15901 consists of the following parts, under the general title *Evaluation of pore size distribution and porosimetry 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) can 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 is more precisely defined as the ratio of the volume of the accessible pores and voids to the total volume occupied by a given amount of the solid. In addition to the accessible pores, a solid can 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 can 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 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 properties;

— polymers and ceramic.

It is well established that the performance of a porous solid (e.g. its strength, reactivity, permeability of adsorbent power) 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 appropriate diameter of 0,003 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 (2,0 nm to 100 nm), and is an extension of the surface area estimation technique;

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 2,0 nm, and is an extension of the surface area estimation technique.

Evaluation of pore size distribution and porosimetry 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 in pores of 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 psia) corresponding to a minimum equivalent pore diameter of approximately 0,003 µm. The maximum diameter will be 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 interparticle and intraparticle porosity. In general, it cannot distinguish between these porosities where they co-exist.

The method is suitable for the study of most non-wettable, by mercury, porous materials. Samples that amalgamate with mercury, such as certain metals, e.g. gold, aluminium, reduced copper, reduced nickel and silver, can be unsuitable for this technique or can require a preliminary passivation. Under the applied pressure, some materials are deformed, compacted or destroyed, whereby open pores can be collapsed and closed pores opened. In some cases, it is possible to apply sample compressibility corrections and useful comparative data can still be obtained. For these reasons, the mercury porosimetry technique is considered to be comparative.

2 Normative references

The following referenced documents are indispensable for the application of this document. 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 8213, *Chemical products for industrial use — Sampling techniques — Solid chemical products in the form of particles varying from powders to coarse lumps*

M 024 4/85, Quecksilber und seine Verbindungen. Merkblatt der Berufsgenossenschaft der chemischen Industrie, Postfach 101480, D-69004 Heidelberg, Germany

3 Terms and definitions

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

3.1
bulk density
powder density under defined conditions

3.2
blind pore
dead-end-pore
open pore having a single connection with an external surface

3.3
closed pore
cavity not connected to the external surface

NOTE Closed pores are not covered in this International standard.

3.4
contact angle
angle that a non-wetting liquid makes with a solid material

3.5
external surface area
area of external surface including roughness but outside pores

3.6
ink bottle pore
narrow necked open pore

3.7
interconnected pore
pore which communicates with one or more other pores

3.8
internal surface area
area of internal pore walls

3.9
intraparticle porosity
ratio of the volume of open pores internal to the particle to the total volume occupied by the solid

3.10
interparticle porosity
ratio of the volume of space between particles in a powder to the apparent volume of the particles or powder

3.11
macropore
pore of internal width greater than 50 nm

3.12
mesopore
pore of internal width between 2 nm and 50 nm

3.13
micropore
pore of internal width less than 2 nm which is accessible for a molecule to be adsorbed

3.14
open pore
cavity or channel with access to an external surface

3.15
open porosity
ratio of the volume of open pores and voids to the total volume occupied by the solid

3.16
pore size
pore width (for example, the diameter of a cylindrical pore or the distance between the opposite walls of a slit) that is a representative value of various sizes of the vacant space inside a porous material

NOTE One of the methods to determine pore sizes is by mercury porosimetry.

3.17
pore volume
volume of pores determined by stated method

3.18
porosimeter
instrument for measuring porosity and pore size distribution

3.19
porosimetry
methods for the estimation of porosity and pore size distribution

3.20
porosity
ratio of total pore volume to apparent volume of particle or powder

3.21
porous solid
solid with cavities or channels which are deeper than they are wide

3.22
skeletal density
mass of a powder divided by the total volume of the sample, including closed pores but excluding open pores

3.23
apparent density
mass of a powder divided by the total volume of the sample, including closed and inaccessible pores, as determined by the stated method

3.24
powder density
mass of a powder divided by its apparent volume, which is taken to be the total volume of the solid material, open and closed pores and interstices

3.25
surface area
extent of available surface area as determined by given method under stated conditions

3.26
surface tension
force required to separate a film of liquid from either a solid material or a film of the same liquid

3.27
through pore
pore which passes all the way through the sample

3.28
total porosity
ratio of the volume of voids plus the volume of open and closed pores to the total volume occupied by the solid

3.29
true density
true particle density
mass of the particle divided by its volume, excluding open and closed pores

3.30
void
space between particles, i.e. an interparticle pore

4 Symbols

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

Symbol	Term	SI unit	Derived unit	Conversion factors for obsolete units
p	pressure	Pa	MPa, psia,	1 psia = 1 lb·in^{-2} = 6 894 Pa
			Torr, mm Hg	1 Torr = 1 mm Hg = 133,32 Pa
d_p	pore diameter	m	nm, µm, Å	1 nm = 10^{-9} m, 1 µm = 10^{-6} m, 1 Å = 10^{-10} m
t	time	s	h	1 h = 3 600 s
S	specific surface area	$m^2 kg^{-1}$	$m^2 g^{-1}$	—
V_{Hg}	intruded volume (of mercury)	m^3	cm^3, 10^3 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, 10^3 mm^3	—
$V_{Hg,max}$	final intruded volume of mercury	m^3	cm^3, 10^3 mm^3	—
V_p	specific pore volume	$m^3 \cdot kg^{-1}$	10^3 mm^3 g^{-1}	—
γ	surface tension of mercury	$N \cdot m^{-1}$	$dyne \cdot cm^{-1}$, $N \cdot m^{-1}$	$dyne \cdot cm^{-1} = N \cdot m^{-1}$
ρ	density of mercury = 13,534 at 25,0 °C	$kg \cdot m^{-3}$	$g \cdot cm^{-3}$, 10^3 $kg \cdot m^{-3}$	$10^3 kg \cdot m^{-3} = 1\ g \cdot cm^{-3}$
θ	contact angle of mercury at the sample, measured through the liquid phase	rad	°	1°= (π/180) rad

5 Principles

A non-wettable liquid can enter a porous system only when forced by pressure. The pore size distribution of a porous solid can be determined by forcing mercury into an evacuated sample under increasing pressure and measuring the volume of mercury intruded as a function of pressure. 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.

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, having a uniform bore capillary tube through which the sample can be evacuated and through which mercury can enter.

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 void volume of the sample. Since different materials exhibit a wide range of open porosities a number of sample holders with different diameter capillary tubes and sample volumes may be required. A special design of sample holder is often used with powdered samples to avoid loss of powder during evacuation.

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

The porosimeter may have several ports for high- and low-pressure operations, 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 vacuum pump, equipped with mercury retainer, to a residual pressure of 7 Pa or less 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, of analytical quality, with a purity of at least ratio of 99,4 mass %.

7 Procedures for calibration and performance

7.1 General

Sample preparation and the filling of the sample holder with mercury require 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 fills the pores in the sample. The volume of mercury displaced from a precision glass capillary tube is most commonly determined as a function of electrical capacity change.

7.2 Pressure signal calibration

Pressure is usually measured with electronic pressure transducers which will have been 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, traceable to an accredited organisation, 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, traceable to an accredited organisation, 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 3 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 or a local reference material, selected by the user, must be tested on a regular basis to monitor instrument calibration and performance. The local reference material must be traceable to a certified reference material. Certified reference materials are offered by a number of national standard bodies and are currently available from BAM [1)], in Germany, and NIST [2)], in the USA.

8 Procedures

8.1 Sampling

Sampling should be performed in accordance with ISO 3165. The sample for test should be representative of the bulk material and should be of an appropriate quantity. Particular precautions should be taken when its 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 subsampling methods are appropriate as follows.

a) From a block

Several pieces 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 then 125 µm. Polished test pieces should be washed to remove adhering particles, which can affect the sample mass and block its pores. The sample should be dried to constant mass. For materials subject to hydration, wash with a non-aqueous liquid.

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 can 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 can arise due to proximity between adjacent faces. This can be overcome by rolling steel wire gauze between the faces to keep the surfaces separate.

1) Bundesanstalt für Materialforschung und –prüfung (BAM) Division I. 1 Inorganic Chemical Analysis; Reference Materials Branch Adlershof, Richard-Willstätter-Straße 11, D-12489 Berlin.

2) Standard Reference Materials Program National Institute of Standards and Technology (NIST) 100 Bureau Drive, Stop 2322 Gaithersburg, MD 20899-2322.

8.1.2 Quantity of test sample

The quantity of test sample required is dependent upon its nature. The largest possible sample size commensurate with the size of cell 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 will usually be necessary to ascertain the optimum quantity of test sample. The test sample is placed preferably in a sample holder having a bulk sample volume between 1 cm^3 and 15 cm^3; also larger cells may be used.

8.2 Method

8.2.1 Sample pretreatment

Sample pretreatment is not required in mercury porosimetry and is often not used. However, pretreatment 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 can proceed more quickly for samples that have been pretreated 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 can be saturated with atmospheric vapours such as water. Thus, pretreatment removes adsorbed material that 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.

In order to optimize pretreatment, it is advisable to study the thermal behaviour of the material, e.g. by thermogravimetric analysis and differential scanning calorimetry, to determine the temperatures at which materials are evolved from the sample, together with any phase changes which could affect the history of the sample. In many cases, heating to 110 °C in a vacuum oven at 3 Pa ($2{,}5 \times 10^{-2}$ Torr) for 4 h will be suitable. However, care should be taken to ensure that the treatment does not affect the porous nature of the sample.

When a satisfactory pretreatment regime has been established, the sample can be out-gassed by heating and/or evacuation or by flowing inert gas. If the sample is in a form that allows amalgamation with, or wetting by, mercury, it can 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 to be used should be recorded after any pretreatment.

8.2.2 Filling of the sample holder

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

8.2.3 Evacuation

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 can tend to fluidize under vacuum with loss of sample into the vacuum system. This effect can be avoided by selection of sample holders designed specially 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[5]. The evacuation time is considerably reduced for pre-dried samples.

8.2.4 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 shall 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 it shall be taken into account when turning the sample holder in vertical position. A typical filling pressure would be less than 5 kPa.

8.2.5 Measurement

8.2.5.1 Low pressure

Admit unreacting dry gas (e.g. air, nitrogen or helium) into the evacuated measuring cell in a controlled manner to increase the pressure either in stages, continuously or by step-wise pressurization according to the proper equilibration conditions for mercury entering the pores and to a required precision corresponding to the particular pores sizes of interest. Pressure and corresponding volume of mercury intruded can be recorded either graphically or via a computer. When the maximum required pressure has been reached, reduce the pressure to ambient and transfer the sample holder to the high-pressure unit or phase.

8.2.5.2 High pressure

Transfer the sample holder to the high-pressure unit or phase (and mercury can be added if needed) so that it is possible to dispose to the total length of the capillary. 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 in stages, 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 the required precision corresponding to the particular pores sizes of interest. As a consequence, mercury is pressed into the pore system and the decreasing length of the mercury column is measured as a function of pressure. Pressure and corresponding volume of mercury intruded can be recorded either graphically or via a computer. If required, the pressure may be decreased either in stages, in a step-wise mode or continuously to determine the mercury extrusion curve. When the maximum required pressure has been reached, reduce the pressure, carefully, to atmospheric. Pressure may be reduced in a controlled manner which allows the recording of the volume extruded versus the decreasing pressure.

8.2.6 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 mass of the sample is advisable.

8.2.7 Blank and sample compression correction

8.2.7.1 General

The mercury, the sample and its holder, and other components of the volume detector system are compressed to different degrees under elevated pressures. Compressibility corrections can 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. It should be noted that sample expansion due to heating of the sample resulting from compression can offset some of the effects of sample compression.

8.2.7.2 Measurement of correction

A blank test is carried out without using a test sample, or preferably using a control sample which is non-porous but of similar size and heat capacity as the test sample, if available. The test is made under exactly the same conditions as are 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 that occurs within the system, from pressurization and depressurization, can result in density and volume changes.

Please note that tests carried out using an empty sample holder produce less than optimum results.

8.2.7.3 Applying the correction

The result of the test described above is a series of apparent volume changes. Subtract the apparent intrusions from the measured intrusions on the test sample. Then add the apparent extrusions to the measured intrusions on the test sample. When carrying out the correction measurement without test sample, the data should be corrected for the sample volume before blank subtractions or additions.

9 Evaluation

9.1 Calculation of the pore size distribution

The pressure exerted is inversely proportional to the clear width of the pore entrance. For pores of cylindrical shape, the Washburn equation [3] gives the relation between pressure and diameter, as given in Equation (1):

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

Using the Washburn equation, the pressure readings are converted to 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·m^{-1} and 0,490 N·m^{-1} are reported. If the value is unknown γ = 0,480 N·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 θ = 140° may be used.

The intruded volume related to sample mass as ordinate in dependence of the pressure exerted are corrected for hydrostatic pressure of mercury over the sample and is recorded by the instrument (Figure A.1). The pressure is converted to pore diameter by means of Equation (1). The relationship of the intruded volume related to sample mass as the ordinate versus the pore diameter as the abscissa is plotted to give the pore volume distribution (Figure A.2). The abscissa of pore diameter is scaled most suitably logarithmic.

Voids between aggregates of the dumped sample are recorded as pores. In case of intrusion into pores that have small connections to outside (ink bottle pores), intrusion pore size reflects pore size distribution of the necks and the total volume of all filled pores. Additionally, the calculated pore area is incorrect.

Curves obtained from decreasing pressure should not be used to establish a pore volume distribution, if part of the mercury intruded is retained by the pore system. The retention relation can be used only for a qualitative assessment of voids exhibiting small connections to outside (ink bottle pores).

9.2 Calculation of the specific pore volume

The maximum value of the pore size distribution as represented in Figures A.1 and A.2 gives the specific pore volume, V_{p}, in the meso- and macropore range. It includes interparticle porosity of the material, intraparticle porosity of the dumped sample and any volumetric change of the sample resulting from presentation.

9.3 Calculation of the specific surface area

Assuming pores of cylindrical shape, a surface distribution can be derived from the pore volume distribution. According to Rootare and Prenzlow [4], a specific surface area of the intruded pores can be calculated from the pressure/volume curve without using a pore model, whereby it is necessary that the material be free of ink bottle pores and not be deformed by the applied pressure, as given in Equation (2):

$$S = \frac{1}{\gamma \cos\theta} \int_{V_{Hg,0}}^{V_{Hg,max}} p \cdot \mathrm{d}V \qquad (2)$$

From the function $V = V(p)$ the integral may be calculated either graphically or by means of a numerical method.

Because the surface area of small pores less than the diameter calculated from maximum pressure (3 nm) is not measured (estimated smaller) and also the surface area of ink bottle pores is calculated as a cylindrical pore with the neck diameter (estimated larger), the results are not necessarily comparable with those derived from gas adsorption methods.

10 Reporting

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

a) laboratory, operator, date;

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

c) sample source;

d) mass, m, of outgassed sample, expressed in grams;

e) instrument and sample holder type used;

f) pretreatment;

g) outgassing conditions: temperature and evacuation pressure;

h) fill pressure;

i) stepwise or scanning methodology:

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

   2) if scanning, the scan speed is required;

j) corrected pressure and corrected volume intruded at each pressure stage;

k) sample holder calibration constant;

l) contact angle used, expressed in degrees;

m) surface tension value used, expressed in newton·metres;

n) mercury density and temperature;

o) specification whether the sample is a solid or a powder;

p) reproducibility for measurements using a fresh sample, standard deviation;

q) cumulative and differential pore volume distribution according to Figures A.2 and A.3 or in another format. Additionally, histograms and log differential distributions can be useful for some distributions with broad or multi-modal population;

r) specific intruded volume, expressed in cubic centimetres per gram;

s) specific surface area, S, expressed in square metres per gram, and calculated from specific intruded volume;

t) method of any blank correction applied;

Annex A
(informative)

Mercury porosimetry analysis results for alumina reference sample

A.1 Presentation of pore size distributions

Presentation of pore size distributions as

pressure: Intruded volume distribution,

pore: Intruded normalised volume distribution,

differential pore: Volume distribution.

Table A.1 — Experimental mercury intrusion data for an alumina sample (0,914 5 g) **— Tabular report**

Pressure MPa	**Pore diameter** nm	**Incremental pore volume** cm^3/g	**Cumulative pore volume** cm^3/g	**-dV/dD pore volume** $cm^3/(g \cdot nm)$	**% of total intrusion volume**
0,005 0	294 161,07	0,000 0	0,000 0	0,000	0,000 0
0,009 0	163 422,81	0,016 6	0,016 6	$1,270 \times 10^{-7}$	2,876 5
0,011 5	127 896,12	0,003 6	0,020 2	$1,013 \times 10^{-7}$	3,500 3
0,016 4	89 683,25	0,003 5	0,023 7	$9,159 \times 10^{-8}$	4,106 7
0,021 3	69 051,89	0,001 7	0,025 4	$8,240 \times 10^{-8}$	4,401 3
0,031 2	47 141,20	0,001 6	0,027 0	$7,302 \times 10^{-8}$	4,678 6
0,041 3	35 612,72	0,000 7	0,027 7	$6,072 \times 10^{-8}$	4,799 9
0,051 0	28 839,32	0,000 5	0,028 2	$7,382 \times 10^{-8}$	4,886 5
0,076 0	19 352,70	0,000 5	0,028 7	$5,271 \times 10^{-8}$	4,973 1
0,100 8	14 591,32	0,000 3	0,029 0	$6,301 \times 10^{-8}$	5,025 1
0,125 8	11 691,62	0,000 2	0,029 2	$6,897 \times 10^{-8}$	5,059 8
0,150 6	9 766,30	0,000 2	0,029 4	$1,039 \times 10^{-7}$	5,094 4
0,200 1	7 350,35	0,000 3	0,029 7	$1,242 \times 10^{-7}$	5,146 4
0,249 9	5 885,58	0,000 1	0,029 8	$6,827 \times 10^{-8}$	5,163 7
0,299 7	4 907,59	0,000 1	0,029 9	$1,023 \times 10^{-7}$	5,181 1
0,339 7	4 329,72	0,000 2	0,030 1	$3,461 \times 10^{-7}$	5,215 7
0,398 3	3 692,71	0,000 2	0,030 3	$3,140 \times 10^{-7}$	5,250 4
0,499 7	2 943,38	0,000 7	0,031 0	$9,342 \times 10^{-7}$	5,371 7
0,598 8	2 456,25	0,000 3	0,031 3	$6,159 \times 10^{-7}$	5,423 7
0,695 7	2 114,14	0,000 2	0,031 5	$5,846 \times 10^{-7}$	5,458 3
0,799 8	1 838,97	0,000 2	0,031 7	$7,268 \times 10^{-7}$	5,493 0
0,898 2	1 637,50	0,000 1	0,031 8	$4,964 \times 10^{-7}$	5,510 3
0,998 2	1 473,46	0,000 2	0,032 0	$1,219 \times 10^{-6}$	5,545 0
1,243 8	1 182,51	0,000 1	0,032 1	$3,437 \times 10^{-7}$	5,562 3

Table A.1 (*Continued*)

Pressure MPa	**Pore diameter** nm	**Incremental pore volume** cm^3/g	**Cumulative pore volume** cm^3/g	**-dV/dD pore volume** $cm^3/(g \cdot nm)$	**% of total intrusion volume**
1,493 7	984,67	0,000 2	0,032 3	$1{,}011 \times 10^{-6}$	5,597 0
1,748 5	841,18	0,000 3	0,032 6	$2{,}091 \times 10^{-6}$	5,648 9
2,016 5	729,39	0,000 1	0,032 7	$8{,}945 \times 10^{-7}$	5,666 3
2,509 9	586,00	0,000 1	0,032 8	$6{,}974 \times 10^{-7}$	5,683 6
3,014 1	487,97	0,000 2	0,033 0	$2{,}040 \times 10^{-6}$	5,718 2
3,544 7	414,93	0,000 1	0,033 1	$1{,}369 \times 10^{-6}$	5,735 6
4,041 6	363,92	0,000 2	0,033 3	$3{,}920 \times 10^{-6}$	5,770 2
4,501 7	326,72	0,000 2	0,033 5	$5{,}377 \times 10^{-6}$	5,804 9
5,022 1	292,87	0,000 2	0,033 7	$5{,}907 \times 10^{-6}$	5,839 5
5,497 6	267,54	0,002 0	0,035 7	$7{,}896 \times 10^{-5}$	6,186 1
5,728 5	256,75	0,006 5	0,042 2	$6{,}028 \times 10^{-4}$	7,312 4
5,982 7	245,84	0,044 0	0,086 2	$4{,}033 \times 10^{-3}$	14,936 8
6,215 4	236,64	0,085 0	0,171 2	$9{,}235 \times 10^{-3}$	29,665 6
6,374 7	230,73	0,078 2	0,249 4	$1{,}322 \times 10^{-2}$	43,216 1
6,460 9	227,65	0,046 9	0,296 3	$1{,}524 \times 10^{-2}$	51,342 9
6,603 5	222,73	0,053 1	0,349 4	$1{,}080 \times 10^{-2}$	60,544 1
6,713 8	219,07	0,035 7	0,385 1	$9{,}756 \times 10^{-3}$	66,730 2
6,814 5	215,83	0,027 4	0,412 5	$8{,}464 \times 10^{-3}$	71,478 1
6,982 0	210,66	0,030 1	0,442 6	$5{,}813 \times 10^{-3}$	76,693 8
7,230 5	203,42	0,038 3	0,480 9	$5{,}290 \times 10^{-3}$	83,330 4
7,550 1	194,81	0,030 1	0,511 0	$3{,}496 \times 10^{-3}$	88,546 2
8,042 9	182,87	0,026 8	0,537 8	$2{,}245 \times 10^{-3}$	93,190 1
8,598 6	171,05	0,015 3	0,553 1	$1{,}295 \times 10^{-3}$	95,841 3
9,116 8	161,33	0,007 5	0,560 6	$7{,}714 \times 10^{-4}$	97,140 9
10,119 5	145,34	0,007 8	0,568 4	$4{,}879 \times 10^{-4}$	98,492 5
12,734 0	115,50	0,006 0	0,574 4	$2{,}011 \times 10^{-4}$	99,532 1
15,267 3	96,34	0,001 5	0,575 9	$7{,}827 \times 10^{-5}$	99,792 1
17,648 9	83,34	0,000 7	0,576 6	$5{,}385 \times 10^{-5}$	99,913 4
20,194 4	72,83	0,000 1	0,576 7	$9{,}520 \times 10^{-6}$	99,930 7
25,168 5	58,44	0,000 3	0,577 0	$2{,}084 \times 10^{-5}$	99,982 7
30,273 3	48,58	0,000 1	0,577 1	$1{,}015 \times 10^{-5}$	100,000 0
34,918 3	42,12	0,000 0	0,577 1	0,000	100,000 0
39,835 5	36,92	0,000 0	0,577 1	0,000	100,000 0
44,769 9	32,85	0,000 0	0,577 1	0,000	100,000 0
49,787 5	29,54	0,000 0	0,577 1	0,000	100,000 0
54,729 2	26,87	0,000 0	0,577 1	0,000	100,000 0
60,089 7	24,48	0,000 0	0,577 1	0,000	100,000 0
69,870 2	21,05	0,000 0	0,577 1	0,000	100,000 0
79,866 3	18,42	0,000 0	0,577 1	0,000	100,000 0
89,703 2	16,40	0,000 0	0,577 1	0,000	100,000 0
99,731 1	14,75	0,000 0	0,577 1	0,000	100,000 0

Table A.1 (*Continued*)

Pressure MPa	**Pore diameter** nm	**Incremental pore volume** cm^3/g	**Cumulative pore volume** cm^3/g	-d*V*/d*D* **pore volume** $cm^3/(g \cdot nm)$	**% of total intrusion volume**
119,753 0	12,28	0,000 0	0,577 1	0,000	100,000 0
139,892 0	10,51	0,000 0	0,577 1	0,000	100,000 0
159,460 0	9,22	0,000 0	0,577 1	0,000	100,000 0
179,293 0	8,20	0,000 0	0,577 1	0,000	100,000 0
199,214 0	7,38	0,000 0	0,577 1	0,000	100,000 0
220,242 0	6,68	0,000 0	0,577 1	0,000	100,000 0
239,980 0	6,13	0,000 0	0,577 1	0,000	100,000 0
260,078 0	5,66	0,000 0	0,577 1	0,000	100,000 0
300,718 0	4,89	0,000 0	0,577 1	0,000	100,000 0
339,708 0	4,33	0,000 0	0,577 1	0,000	100,000 0
379,685 0	3,87	0,000 0	0,577 1	0,000	100,000 0
410,646 0	3,58	0,000 0	0,577 1	0,000	100,000 0

A.2 Intrusion data summary

Specific intruded volume: 0,577 1 cm^3/g

Specific pore volume: 0,545 0 cm^3/g

Specific surface area: 10,011 m^2/g

Median pore diameter: 228,2 nm

Average pore diameter: 230,6 nm

Contact angle: 140°

Mercury surface tension: 480 N/m

Mercury density: 13,532 5 g/cm^3

Notes on intrusion data summary calculations:

Interparticle filling and sample compression effects are included in the total intruded volume and result in over-estimation of the total pore volume and total pore area. Appropriate corrections should be made through blank corrections and subtraction of interparticle filling volume. Note the initial low-pressure step seen in Figure A.1 and final large pore diameter step in Figure A.2.

Median pore diameter is defined as that corresponding to the 50th percentile of pore volume. That is, 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. Average pore diameter is calculated using the total pore volume and total pore area according to the geometry of a cylinder, that is, the diameter is given by four times the ratio of pore volume to pore area.

Bulk and apparent density are calculated using sample mass and corresponding volumes. For bulk density, the volume is that of the sample plus pores not filled at the applied pressure of interest, generally that at the start of the analysis or filling of the sample holder with mercury. For apparent density, the volume is that of the