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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

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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).

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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·kg^{-1}	m^2·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
$V_{\mathrm{Hg,0}}$	initial intruded volume of mercury	m^3	cm^3, mm^3	
$V_{\mathrm{Hg,max}}$	total intruded volume of mercury	m^3	cm^3, mm^3	
V_{p}	specific pore volume	m^3 · kg^{-1}	mm^3·g^{-1} cm^3·g^{-1}	
γ	surface tension of mercury	N·m^{-1}	dyne·cm^{-1}	1 dyne·cm^{-1} = 10^{-3} N·m^{-1}
ρ_{Hg}	density of mercury	kg·m^{-3}	g·cm^{-3}	1 g·cm^{-3} = 10^3 kg·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	
$m_{SH+S+\mathrm{Hg}}$	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.