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

Part 2:
Analysis of mesopores and macropores by gas adsorption

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

Partie 2: Analyse des mésopores et des macropores par adsorption de gaz

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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.

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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 15901-2 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 *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

Generally speaking, different types of pores can be pictured as apertures, channels or cavities within a solid body, or as the space (i.e. an interstice or a void) 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 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 (i.e. cavities with no access to an external surface) is not covered in this part of ISO 15901.

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 surface areas.

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

a) controlled drug release;

b) catalysis;

c) gas separation;

d) filtration including sterilization;

e) materials technology;

f) environmental protection and pollution control;

g) natural reservoir rocks;

h) building material properties;

i) polymer and ceramic industries.

It is well established that the performance of a porous solid (e.g. its strength, reactivity, permeability or 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 to find that the results obtained do not always concur, 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.

Commonly used methods are as follows.

— **Mercury porosimetry**, where the pores are filled with mercury under pressure. This method is suitable for many materials with pores in the approximate diameter rang of 0,003 µm to 400 µm, and especially in the range of 0,1 µm to 100 µm.

— **Mesopore and macropore analysis by gas adsorption**, where the pores are characterized by adsorbing a gas, such as nitrogen, at liquid nitrogen temperature. This method is used for pores in the approximate diameter range 0,002 µm to 0,1 µm (2 nm to 100 nm), and is an extension of the surface area estimation technique (see ISO 9277). (Discussion of other pore size distribution analysis techniques can be found in Recommendations for the Characterization of Porous Solids [1].)

- **Micropore analysis by gas adsorption**, where the pores are characterized by adsorbing a gas, such as nitrogen, at liquid nitrogen temperature. This method is used for pores in the approximate diameter range 0,000 4 µm to 0,002 µm (0,4 nm to 2 nm).

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

Part 2:
Analysis of mesopores and macropores by gas adsorption

1 Scope

This part of ISO 15901 describes a method for the evaluation of porosity and pore size distribution by gas adsorption. It is a comparative, rather than an absolute test. The method is limited to the determination of the quantity of a gas adsorbed per unit mass of sample at a controlled, constant temperature.

This part of ISO 15901 does not specify the use of a particular adsorptive gas, however nitrogen is the adsorptive gas most commonly used in such methods. Similarly, the temperature of liquid nitrogen is the analysis temperature most commonly used. Use is sometimes made of other adsorptive gases, including argon, carbon dioxide and krypton, and other analysis temperatures, including those of liquid argon and solid carbon dioxide. In the case of nitrogen adsorption at liquid nitrogen temperature, the basis of this method is to measure the quantity of nitrogen adsorbed at 77 K as a function of its relative pressure.

Traditionally, nitrogen adsorption is most appropriate for pores in the approximate range of widths 0,4 nm to 50 nm. Improvements in temperature control and pressure measurement now allow larger pore widths to be evaluated. This part of ISO 15901 describes the calculation of mesopore size distribution between 2 nm and 50 nm, and of macropore distribution up to 100 nm.

The method described in this part of ISO 15901 is suitable for a wide range of porous materials, even though the pore structure of certain materials is sometimes modified by pretreatment or cooling.

Two groups of procedures are specified to determine the amount of gas adsorbed:

- those which depend on the measurement of the amount of gas removed from the gas phase (i.e. gas volumetric methods), and
- those which involve the measurement of the uptake of the gas by the adsorbent (i.e. direct determination of increase in mass by gravimetric methods).

In practice, static or dynamic techniques can be used to determine the amount of gas adsorbed. To derive pore size distribution from the isotherm, it is necessary to apply one or more mathematical models, which entails simplifying certain basic assumptions.

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 8213, *Chemical products for industrial use — Sampling techniques — Solid chemical products in the form of particles varying from powders to coarse lumps*

ISO 9276-1, *Representation of results of particle size analysis — Part 1: Graphical representation*

ISO 9277:1995, *Determination of the specific surface area of solids by gas adsorption using the BET method*

3 Terms and definitions

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

3.1
adsorbate
adsorbed gas

3.2
amount adsorbed
n_a
number of moles of gas adsorbed at a given pressure p

3.3
adsorbent
solid material on which adsorption occurs

3.4
adsorption
enrichment of the adsorptive gas at the external and accessible internal surfaces of a solid material

3.5
adsorptive
gas or vapour to be adsorbed

3.6
blind pore
dead-end pore
open pore having a single connection with an external surface

3.7
equilibrium adsorption pressure
p
pressure of the adsorptive gas in equilibrium with the adsorbate

3.8
ink bottle pore
narrow necked open pore

3.9
interconnected pore
pore which communicates with one or more other pores

3.10
isotherm
relationship between the amount of gas adsorbed and the equilibrium pressure of the gas, at constant temperature

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
monolayer amount
n'_m
number of moles of the adsorbate that form a monomolecular layer over the surface of the adsorbent

3.15
monolayer capacity
V_m
volumetric equivalent of monolayer amount expressed as gas at standard conditions of temperature and pressure (STP)

3.16
open pore
cavity or channel with access to an external surface

3.17
porosity
open porosity
ratio of the volume of open pores and voids to the total volume occupied by the solid

3.18
relative pressure
ratio of the equilibrium adsorption pressure, p, to the saturation vapour pressure, p_0

3.19
right cylindrical pore
cylindrical pore perpendicular to the surface

3.20
saturation vapour pressure
vapour pressure of the bulk liquefied adsorptive gas at the temperature of adsorption

3.21
through pore
pore which passes all the way through the sample

3.22
volume adsorbed
volumetric equivalent of adsorbed amount expressed as gas at standard conditions of temperature and pressure (STP)

4 Symbols

Symbol	Quantity	SI Unit
A_{He}	slope of helium data regression from free space determination	$\mathrm{cm^3{\cdot}Pa^{-1}}$
a'_{p}	specific pore area	$\mathrm{m^2{\cdot}g^{-1}}$
B_{He}	intercept of helium data regression from free space determination	$\mathrm{cm^3}$
b	buoyancy	$\mathrm{g{\cdot}Pa^{-1}}$
C_{N}	non-ideal correction factor, equal to $0{,}464\mathrm{x}10^{-6}$ for nitrogen at 77,35 K	$\mathrm{Pa^{-1}}$
d_{p}	pore diameter	nm
m_{ss}	mass of the solid sample material	g
m_{a}	mass of gas adsorbed	g
m_{ai}^{*}	recorded mass on the balance of gas adsorbed of the ith dose	g
m_{ai}	correct mass of gas adsorbed at pressure p_i	g
n_{a}	amount of gas adsorbed	mol
n'_{a}	specific amount of gas adsorbed	$\mathrm{mol{\cdot}g^{-1}}$
n'_{m}	specific monolayer amount of gas	$\mathrm{mol{\cdot}g^{-1}}$
$n'_{\mathrm{a,x}}$	specific amount adsorbed at a particular relative pressure (x = 1, 2, 3)	$\mathrm{mol{\cdot}g^{-1}}$
p	pressure of the adsorptive gas in equilibrium with the adsorbate	Pa
p_{x}	adsorptive pressure, used to determine free space (x = 1, 2, 3)	Pa
p_{i}	adsorptive pressure of the ith dose	Pa
p_{man}	adsorptive pressure measured in the dosing manifold	Pa
p_0	saturation vapour pressure	Pa
p/p_0	relative pressure of the adsorptive gas (see Note 1)	1
p_{std}	standard pressure, equal to 101 325,02	Pa
R	ideal gas constant, equal to 8,314 510	$\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$
r_{K}	Kelvin radius	nm
t	statistical thickness of the adsorbed layers of gas (see Note 2)	nm
T_{amb}	ambient temperature	K
T_{b}	temperature of the cryogenic bath	K
T_{eq}	temperature of the dosing manifold when equilibrium of pressure has been achieved	K
T_{man}	temperature of the dosing manifold at time of the addition of the adsorptive dose	K
T_{std}	standard temperature, equal to 273,15	K
$V_{\mathrm{sh,b}}$	sample holder volume at cryogenic bath temperature	$\mathrm{cm^3}$
V_{d}	adsorptive volume of dose in sample holder	$\mathrm{cm^3}$

Symbol	Quantity	SI Unit
V_{di}	adsorptive volume of the ith dose placed in the sample holder	cm^3
$V_{fs,b}$	free space volume with sample holder immersed in cryogenic bath	cm^3
$V_{fs,amb}$	free space volume with sample holder at ambient temperature	cm^3
V'_{ai}	volume of gas adsorbed on the i^{th} dose at STP (273,15 K; 101 325 Pa)	$cm^3 \cdot g^{-1}$
V'_l	specific liquid equivalent of the volume of adsorbate condensed in pore capillaries	$cm^3 \cdot g^{-1}$
V_m	monolayer capacity of adsorbed gas	cm^3
V_{man}	volume of the dosing manifold	cm^3
$V_{m,l}$	molar volume of liquid condensate	$cm^3 \cdot mol^{-1}$
α_s	normalized adsorption (see Note 1)	1
ρ	density	$g \cdot cm^{-3}$
δ_a	thickness of one monolayer of adsorbate	nm
σ_l	surface tension of the liquid condensate	$J \cdot m^{-2}$

NOTE 1 According to ISO 31-0, the coherent SI unit for any quantity of dimension one (at present commonly determined “dimensionless”) is the unit one.

NOTE 2 While the symbol t is generally used to represent time, in the normal practice of pore size distribution analysis by gas adsorption, t is traditionally used to represent the statistical thickness of the adsorbed layers of gas, as indicated in the list above. Therefore all uses of the symbol t in this part of ISO 15901 refer to statistical thickness, and not to time.

5 Principles

5.1 General principles

The quantity of gas adsorbed on a surface is recorded as a function of the relative pressure of the adsorptive gas for a series of either increasing relative pressures on the adsorption portion of the isotherm, decreasing relative pressures on the desorption portion of the isotherm, or both. The relation, at constant temperature, between the amount adsorbed and the equilibrium relative pressure of the gas is known as the adsorption isotherm. The minimum pore size that can be investigated is limited by the size of the adsorptive molecule.

NOTE In the case of nitrogen, the minimum investigable pore size is approximately 0,5 nm.

The maximum pore width is limited by the practical difficulty of determining the amount of gas adsorbed at high relative pressure, p/p_0.

Comparative pore size distributions of less than 2 nm in width, called micropores, can be determined with nitrogen as the adsorptive gas, although other gases (e.g. argon) may provide more reliable results. Both nitrogen and argon have been used successfully for the determination of the mesopore size distribution.

The pore size distributions calculated respectively from the adsorption and desorption portions of the isotherm will not necessarily be the same.

Adsorption of gas into a porous solid takes place in accordance with a number of different mechanisms. For instance, in mesopores and macropores, multilayer adsorption onto the pore walls occurs initially. At higher relative pressures, capillary condensation takes place with the formation of a curved liquid-like meniscus. The computation of the mesopore size distribution is generally carried out using methods based upon the Kelvin equation.

When nitrogen is employed as the adsorptive gas at the temperature of liquid nitrogen, 77,35 K, the Kelvin equation may be expressed in the form:

$$r_\mathrm{K} = \frac{-2\sigma_\mathrm{l} V_\mathrm{m,l}}{R T_\mathrm{b} \ln\left(\frac{p}{p_0}\right)} = \frac{-0{,}953}{\ln\left(\frac{p}{p_0}\right)} \tag{1}$$

where

σ_l is the surface tension of the liquid condensate;

$V_\mathrm{m,l}$ is the molar volume of the liquid condensate;

R is the ideal gas constant;

T_b is the analysis temperature;

r_K is the radius of curvature of the adsorptive gas condensed in the pore;

p_0 is the saturation vapour pressure of nitrogen at the temperature of the liquid nitrogen;

p is the equilibrium pressure of the nitrogen adsorptive gas.

The numeric constants evaluate to a value of 0,953 nm for nitrogen at 77 K.

Since condensation is considered to occur only after an adsorbed layer has formed on the pore walls, it is necessary to make allowance for the thickness of this adsorbed film by means of an equation. In the case of cylindrical pores, this equation is:

$$d_\mathrm{p} = 2\left(r_\mathrm{K} + t\right) \tag{2}$$

where

d_p is the cylindrical pore diameter (in nm);

t is the thickness of the adsorbed layer (in nm).

Various methods exist for the evaluation of t as a function of relative pressure and for calculating pore size distribution [3] [4].

The Kelvin equation cannot be used for pores of less than approximately 2 nm diameter. This is because interactions with adjacent pore walls become significant and the adsorbate can no longer be considered liquid when it has bulk thermodynamic properties.

5.2 Choice of method

The required experimental data to establish a sorption isotherm may be obtained by volumetric or gravimetric methods, either in measurements at stepwise varied pressure and observation of the equilibrium volume of pressure or mass respectively, or by continuous varied pressure. Because sorption takes a long time in some parts of the isotherm, the stepwise static method is recommended to ensure the measurement of equilibrium values.

The volumetric method is based on calibration volumes and pressure measurements (see ISO 9277:1995, Figure 5). The volume of adsorbate is calculated as the difference between the gas admitted and the quantity of gas filling the dead volume (i.e. the free space in the sample container, including connections) by application of the general gas equation. The various volumes of the apparatus should be calibrated and their temperatures should be taken into account.