INTERNATIONAL STANDARD

ISO
15901-3

First edition
2007-04-15

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

Part 3:
Analysis of micropores by gas adsorption

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

Partie 3: Analyse des micropores par adsorption de gaz

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 15901-3:2007
https://standards.iteh.ai/catalog/standards/sist/d61fc435-f1bd-4d7f-8871-
fa6edfb627f3/iso-15901-3-2007

COPYRIGHT PROTECTED DOCUMENT

Contents

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 15901-3 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

According to the IUPAC Recommendations, 1984 [42], micropores are defined as pores with internal widths of less than 2 nm. Different methods for the characterization of micropores are available, including spectroscopy, electron and tunnel microscopy and sorption methods. 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. With regard to the application of microporous material as specific sorbents, molecular sieves and carriers for catalysts and biological active material, the field-proven methods of gas sorption are of special value. On account of the fractality of dispersed and porous materials, the results of adsorption measurements depend on the size of the gas molecules used (effective diameter and space required at the surface). Furthermore, micropores might not be accessible for larger molecules and, thus, exclusion effects can be observed.

The measuring techniques of the methods described in the present standard are similar to those of ISO 15901-2 and ISO 9277 for the measurement of gas adsorption at low temperature. From the measured isotherm, however, the very first part (i.e. relative pressures $< 10^{-1}$) is evaluated and thus the evaluation method is different.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

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

Part 3:
Analysis of micropores by gas adsorption

1 Scope

This part of ISO 15901 describes methods for the evaluation of the volume of micropores (pores of internal width less than 2 nm) and the specific surface area of microporous material by low-temperature adsorption of gases [1],[2],[3],[4],[5],[6],[7]. These are comparative, non-destructive tests. The methods use physisorbing gases that can penetrate into the pores under investigation. The method is applicable to isotherms of type I, II, IV or VI of the IUPAC classification (see ISO 15901-2:—, Figure 1, and ISO 9277).

The methods in this part of ISO 15901 are not applicable when chemisorption or absorption takes place.

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*

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

ISO 15901-2:—, *Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption — Part 2: Analysis of mesopores and macropores by gas adsorption*

3 Terms and definitions

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

3.1
adsorbate
adsorbed gas

3.2
adsorption
enrichment of the adsorptive at the external and accessible internal surfaces of a solid

3.3
adsorptive
gas or vapour to be adsorbed

3.4
adsorbent
solid material on which adsorption occurs

3.5
adsorption isotherm
relationship between the amount of gas adsorbed and the equilibrium pressure of the gas at constant temperature

3.6
adsorbed amount
number of moles of gas adsorbed at a given pressure, p, and temperature, T

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

3.8
monolayer amount
number of moles of the adsorbate that form a monomolecular layer over the surface of the adsorbent

3.9
monolayer capacity
volumetric equivalent of monolayer amount expressed as gas at standard conditions of temperature and pressure (STP)

3.10
macropore
pore with width greater than about 50 nm

3.11
mesopore
pore with width between approximately 2 nm and 50 nm

3.12
micropore
pore with width of about 2 nm or less

3.13
physisorption
weak bonding of the adsorbate, reversible by small changes in pressure or temperature

3.14
pore size
pore width, i.e. diameter of cylindrical pore or distance between opposite walls of slit

3.15
relative pressure
ratio of the equilibrium adsorption pressure, p, to the saturation vapour pressure, p_0, at analysis temperature

3.16
saturation vapour pressure
vapour pressure of the bulk liquefied adsorptive at the temperature of adsorption

3.17
volume absorbed
volumetric equivalent of the amount adsorbed, expressed as gas at standard conditions of temperature and pressure (STP), or expressed as the adsorbed liquid volume of the adsorbate

4 Symbols

For the purposes of this document, the following symbols apply, together with their units. All specific dimensions are related to sample mass, in grams.

Symbol	Term	Unit
K_{Aa}	Kirkwood-Mueller constant of adsorptive	$J \cdot cm^6$
K_{As}	Kirkwood-Mueller constant of adsorbent	$J \cdot cm^6$
a_s	specific surface area	$m^2 \cdot g^{-1}$
$a_{s,ref}$	specific surface area of reference sample	$m^2 \cdot g^{-1}$
α_a	polarizability of adsorptive	cm^3
a_m	molecular cross-sectional area	nm^2
α_s	normalized adsorption (see Note 1)	1
$\alpha_{(s*)}$	polarizability of adsorbent	cm^3
β	affinity coefficient	1
c	speed of light	$m \cdot s^{-1}$
d_a	diameter of an adsorptive molecule	nm
d_{HS}	diameter of hard spheres	nm
d_p	effective pore diameter (cylindrical pore)	nm
d_s	diameter of an adsorbent molecule	nm
d_0	$d_0 = (d_s + d_a)/2$, distance between adsorptive and adsorbent molecules	nm
E	adsorption potential	$J \cdot mol^{-1}$
E_0	characteristic adsorption energy	$J \cdot mol^{-1}$
ε_{ff}	well depth parameter of the gas-gas Lennard Jones potential	K
ε_{sf}	well depth parameter of the gas-solid Lennard Jones potential	K
k_B	Boltzmann constant ($1,380\ 650\ 5 \times 10^{-23}$)	$J\ K^{-1}$
l	nuclei-nuclei pore width	nm
m_a	mass adsorbed	g
m_e	mass of an electron	kg
m_s	sample mass	g
N_A	Avogadro's constant ($6,022\ 1415 \times 10^{23}$)	mol^{-1}
N_a	number of atoms per unit area (square metre) of monolayer	m^{-2}

Symbol	Term	Unit
N_s	number of atoms per unit area (square metre) of adsorbent	m^{-2}
n_a	specific amount adsorbed	$mol \cdot g^{-1}$
n_m	monolayer capacity	$cm^3 \cdot g^{-1}$
p	pressure of the adsorptive in equilibrium with the adsorbate	Pa
p_0	saturation vapour pressure of the adsorptive	Pa
p/p_0	relative pressure of the adsorptive	1
R	ideal gas constant (8,314 472)	$Jmol^{-1}K^{-1}$
ρ_g	gas density	$g \cdot cm^{-3}$
$\rho_{g,STP}$	gas density at STP (273,15 K; 101 325,02 Pa)	$g \cdot cm^{-3}$
ρ_l	liquid density	$g \cdot cm^{-3}$
σ	distance between two molecules at zero interaction energy	nm
σ_{ff}	distance parameter of the gas-gas Lennard Jones potential	nm
σ_{sf}	distance parameter of the gas-solid Lennard Jones potential	nm
T	temperature	K
T_{cr}	critical temperature	K
t	statistical layer thickness (see Note 2)	nm
V_a	specific adsorbed liquid volume of the adsorbate	$cm^3 \cdot g^{-1}$
V_g	specific adsorbed gas volume at STP (273,15 K; 101 325,02 Pa)	$cm^3 \cdot g^{-1}$
V_{micro}	micropore volume	$cm^3 \cdot g^{-1}$
W	pore width (slit pore)	nm
χ_a	diamagnetic susceptibility of adsorptive	cm^3
χ_s	diamagnetic susceptibility of adsorbent	cm^3

NOTE 1   According to ISO 31-0 [43], the coherent SI unit for any quantity of dimension one (at present commonly referred to as "dimensionless") is the unit one, symbol 1.

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 liquid-like adsorbate layer. Therefore, all uses of the symbol t in this standard will refer to the statistical thickness and not time.

For gravimetric measurements, the mass adsorbed is measured directly (see ISO 9277:1995, Figure 6), but a pressure-dependent buoyancy correction is necessary. Equilibrium is observed by monitoring the mass indication. In the region between about 0,1 Pa to 100 Pa, thermal gas flow can seriously disturb the measurements. Because the sample is not in direct contact with the thermostat, it is necessary to ensure the correct temperature experimentally.

5 Principles

5.1 General

The methods described in this part of ISO 15901-3 are based on the measurement of the adsorption and desorption of gases at a constant low temperature and the evaluation of the initial part of the isotherm. Gases used are those which are bound by physisorption at the solid surface, in particular N_2 at 77,4 K, Ar at 77,4 K or 87,3 K, and CO_2 at 195 K or 273,15 K. Because of the different size of the gas molecules, and hence, different accessibility of the pores, and also because of the different measuring temperatures, different results can be obtained. In micropores, the potential of interactions of the opposite pore walls are overlapping and, hence, physisorption is stronger than in wide pores or at the external surface [8] (see Figure 1). As a consequence, micropores are filled at very low relative pressure (< 0,01). A significant portion of the micropores is indicated by a large and steep increase of the isotherm near its origin and subsequent bending to a plateau. Micropores are characterized by the micropore volume and the micropore distribution. Because the pore size is similar to the molecule diameter, the choice of the gas is decisive.
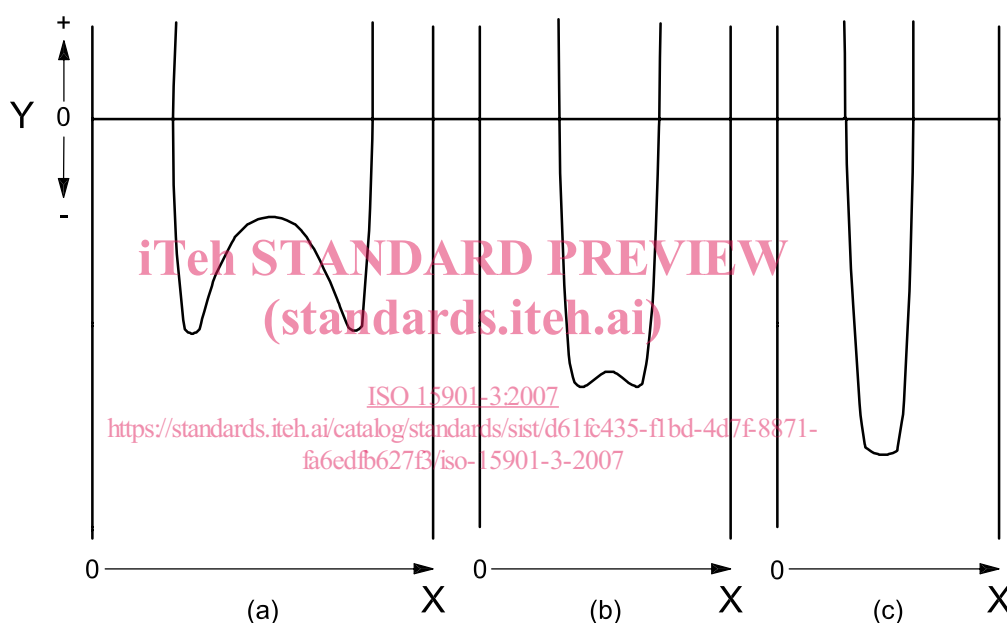
Key

X   distance between pore walls

Y   potential energy

Figure 1 — Three examples of the enhancement of interaction potential between a fluid and the surface in infinitely long, slit-like micropores as a function of the pore width (after Everett and Powl [8])

The pore size and volume analysis of microporous materials, such as zeolites, carbon molecular sieves, etc., is difficult, because the filling of pores of dimension 0,5 nm to 1 nm occurs at relative pressures of 10^{-7} to 10^{-5} where the rate of diffusion and adsorption equilibration is very slow. Argon at 87,3 K fills micropores of dimension 0,5 nm to 1 nm at appreciably higher relative pressures compared to nitrogen (at 77,4 K). Both the higher pore-filling pressure and higher temperature help to accelerate diffusion and equilibration processes compared to nitrogen adsorption. Hence, it is of advantage to analyse microporous materials by using argon as the adsorptive at liquid-argon temperature (87,3 K). However, as in the case of nitrogen adsorption at 77,4 K, the absolute pressures required to fill the most narrow micropores with argon are still very low. Associated with the low pressures required, is (as indicated above) the well known problem of diffusion restrictions, which prevent nitrogen molecules and also argon molecules from entering the narrowest micropores (as present in activated-carbon fibres, carbon molecular sieves, etc.). This can lead to erroneous adsorption isotherms, underestimated pore volumes, etc. A possibility to overcome these problems (at least for microporous carbons) is the use of CO_2 as the adsorptive at 273,15 K. The saturation pressure at this

temperature is about 3,48 MPa, i.e. in order to achieve the small relative pressures required to monitor the micropore filling, a turbomolecular pump-level vacuum is not necessary. With CO_2 adsorption up to 101 325 Pa (1 atm), one can detect pores from the narrowest micropores up to about 1,5 nm. At these relatively high temperatures and pressures, significant diffusion limitations no longer exist, which leads to the situation that equilibrium is achieved much faster relative to low-temperature nitrogen and argon experiments.

5.2 Methods of measurement

The experimental data required to establish an adsorption/desorption (sorption) isotherm may be obtained by volumetric (manometric) or gravimetric methods, by measurements either at stepwise, varied pressure with observation of the equilibrium value of pressure or mass, respectively, or at a continuously varied pressure. Because adsorption/desorption equilibrium can take a long time, the stepwise static method is recommended to ensure the measurement of equilibrium values.

The volumetric method is based on calibrated volumes and pressure measurements (see ISO 9277:1995, Figure 5). The amount of adsorbate is calculated as the difference between the gas admitted and the quantity of gas filling the dead volume (free space in the sample container including connections) by application of the general gas equation. Equilibrium is observed by monitoring the pressure in the free space. It is necessary to take special care in the pressure measurements for micropores as physical adsorption occurs at relative pressures substantially lower than in the case of sorption phenomena in mesopores and can span a broad spectrum of pressures (up to seven orders of magnitude in pressure). Consequently, more than one pressure transducer is necessary to measure the equilibrium pressure with sufficient accuracy. In order to study the adsorption of gases like nitrogen and argon (at their boiling temperatures) within a relative pressure range of $10^{-7} \leqslant p/p_0 \leqslant 1$ with sufficiently high accuracy, it is desirable to use a combination of different transducers with maximum ranges of 0,133 kPa (1 Torr [1]), 1,33 kPa (10 Torr) and 133 kPa (1 000 Torr). In addition, one has to assure that the sample cell and the manifold can be evacuated to pressures as low as possible, which requires a proper high-vacuum pumping system. The desired low pressure can be achieved by using a turbomolecular pump. For gas pressures below about 13 Pa (i.e. $p/p_0 < 10^{-5}$ for nitrogen and argon adsorption at 77 K and 87 K, respectively), it is necessary to take into account the pressure differences along the capillary of the sample bulb on account of the Knudsen effect (i.e. the thermal transpiration correction).

For gravimetric measurements, the mass adsorbed is measured directly (see ISO 9277:1995, Figure 6), but a pressure-dependent buoyancy correction is necessary. Equilibrium is observed by monitoring the mass indication. In the region between about 0,1 Pa and 100 Pa, thermal gas flow can seriously disturb the measurements. Because the sample is not in direct contact with the thermostat, it is necessary to ensure the correct temperature experimentally.

6 Procedure of measurements

6.1 Sampling

Sampling shall be performed in accordance with ISO 3165 and ISO 8213. The sample for test shall be representative of the bulk material and should be of an appropriate quantity. Repeated measurements using a second sample are recommended.

6.2 Sample pretreatment

The sample should be degassed in vacuum better than 1 Pa at elevated temperature to remove physisorbed material. During this process, irreversible changes of the surface structure (revealed, for example, by a colour change) should be avoided. The highest temperature that can be applied is favourably determined by means of thermogravimetry (see ISO 9277:1995, Figure 3). Otherwise, repeated measurements should be carried out by variying the time and the temperature (see ISO 9277:1995, Figure 4). Also, the temperatures at which materials are evolved from the sample can be determined by means of differential scanning calorimetry and the gas can be analysed.

---

1) Torr is a deprecated unit.