

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

Part 3: Analysis of micropores by gas adsorption

ICS 19.120

National foreword

This British Standard is the UK implementation of ISO 15901-3:2007. Together with BS ISO 15901-2:2006, it supersedes BS 7591-2:1992 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee LBI/37, Sieves, screens and particle sizing.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

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This British Standard was published under the authority of the Standards Policy and Strategy Committee on 28 September 2007

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ISBN 978 0 580 55281 6

Amendments issued since publication

Amd. No.	Date	Comments

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



Reference number
ISO 15901-3:2007(E)

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Contents

Page

Foreword.....	iv
Introduction	v
1 Scope	1
2 Normative references	1
3 Terms and definitions.....	1
4 Symbols	3
5 Principles	5
5.1 General.....	5
5.2 Methods of measurement	6
6 Procedure of measurements	6
6.1 Sampling.....	6
6.2 Sample pre-treatment	6
6.3 Measurement.....	7
7 Verification of apparatus performance.....	7
8 Calibration	7
9 Evaluation of the micropore volume.....	7
9.1 General.....	7
9.2 Determination of the micropore volume according to Dubinin and Radushkevich	9
9.3 Micropore analysis by comparison of isotherms	10
9.4 Determination of micropore size distribution by the Horvath-Kawazoe (HK) and the Saito-Foley (SF) method.....	14
9.5 Determination of micropore size distribution by non-local density functional theory	15
10 Test report	19
Annex A (informative) Horvath-Kawazoe and Saito-Foley methods	20
Annex B (informative) NLDFT method	23
Bibliography	26

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.

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	$\text{J}\cdot\text{cm}^6$
K_{As}	Kirkwood-Mueller constant of adsorbent	$\text{J}\cdot\text{cm}^6$
a_s	specific surface area	$\text{m}^2\cdot\text{g}^{-1}$
$a_{s,\text{ref}}$	specific surface area of reference sample	$\text{m}^2\cdot\text{g}^{-1}$
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	$\text{m}\cdot\text{s}^{-1}$
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	$\text{J}\cdot\text{mol}^{-1}$
E_0	characteristic adsorption energy	$\text{J}\cdot\text{mol}^{-1}$
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 ($1,380\,650\,5 \times 10^{-23}$)	$\text{J}\cdot\text{K}^{-1}$
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}