BS ISO 15901-2:2022

BSI Standards Publication

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

Part 2: Analysis of nanopores by gas adsorption

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National foreword

This British Standard is the UK implementation of ISO 15901-2:2022. It supersedes BS ISO 15901-3:2007 and BS ISO 15901-2:2006, which are withdrawn.

The UK participation in its preparation was entrusted to Technical Committee LBI/37, Particle characterization including sieving.

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

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Published by BSI Standards Limited 2022

ISBN 978 0 539 12743 0

ICS 19.120

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This British Standard was published under the authority of the Standards Policy and Strategy Committee on 28 February 2022.

Amendments/corrigenda issued since publication

Date	Text affected

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INTERNATIONAL STANDARD

ISO 15901-2

Second edition
2022-01

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

Part 2: Analysis of nanopores 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 nanopores par adsorption de gaz

Reference number
ISO 15901-2:2022(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.

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 of the voluntary nature of standards, 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 www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 24, *Particle characterization including sieving*, Subcommittee SC 4, *Particle characterization*.

This second edition cancels and replaces ISO 15901-2:2006 and ISO 15901-3:2007, which have been technically revised. It also incorporates the Technical Corrigendum ISO 15901-2:2006/Cor.1:2007.

The main changes compared to the previous edition are as follows:

— the analysis of nanopores by gas adsorption which combines the characterization of both micro- and mesopores is now addressed;

— the classification of adsorption isotherms and hysteresis loops has been updated.

A list of all parts in the ISO 15901 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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Introduction

In general, different types of pores may be pictured as apertures, channels, or cavities within a solid body or as the 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 accessible pores and voids to the total volume occupied by a given amount of the solid. According to the 2015 IUPAC recommendations[1], nanopores are defined as pores with internal widths of equal or less than 100 nm and are divided into several subgroups dependent on their pore width:

— pores with width greater than about 50 nm are called macropore*s*;

— pores of widths between 2 nm and 50 nm are called mesopores;

— pores with width of about 2 nm and less are called micropore*s;*

Further, IUPAC suggested a subclassification of micropores into supermicropores (pore width 0,7 nm to 2 nm), and ultramicropores (pore width < 0,7 nm). 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, i.e. cavities with no access to an external surface, is not covered in this document.

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 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 area.

Porous materials have great technological importance, e.g. 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. 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.

Different methods for the characterization of nanopores 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. Among these, mercury porosimetry (see ISO 15901-1) and gas adsorption are popular ones because by combining both it is possible to assess a wide range of pore sizes from below 0,5 nm up to 400 µm. While mercury porosimetry is the standard technique for macropore analysis, gas adsorption techniques allow to assess pores up to approximately 100 nm. In this case, physical adsorption can be conveniently used, is not destructive, and is not that cost intensive as compared to some of the above-mentioned methods. Particularly, with regard to the

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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.

The measuring techniques of the method described in this document are similar to those described in ISO 9277 for the measurement of gas adsorption at low temperature. However, in order to assess the full range of pore sizes including microporosity, adsorption experiments have to be performed over a wide range of pressures from the ultralow pressure range (e.g. turbomolecular pump vacuum) up to atmospheric pressure (0,1 MPa).

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

Part 2: Analysis of nanopores by gas adsorption

1 Scope

This document describes a method for the evaluation of porosity and pore size distribution by physical adsorption (or physisorption). The method is limited to the determination of the quantity of a gas adsorbed per unit mass of sample as a function of pressure at a controlled, constant temperature[1]-[9]. Commonly used adsorptive gases for physical adsorption characterization include nitrogen, argon, krypton at the temperatures of liquid nitrogen and argon (77 K and 87 K respectively) as well as CO_2 (at 273 K). Traditionally, nitrogen and argon adsorption at 77 K and 87 K, respectively, allows one to assess pores in the approximate range of widths 0,45 nm to 50 nm, although improvements in temperature control and pressure measurement allow larger pore widths to be evaluated. CO_2 adsorption at 273 K – 293 K can be applied for the microporous carbon materials exhibiting ultramicropores. Krypton adsorption at 77 K and 87 K is used to determine the surface area or porosity of materials with small surface area or for the analysis of thin porous films.

The method described is suitable for a wide range of porous materials. This document focuses on the determination of pore size distribution from as low as 0,4 nm up to approximately 100 nm. The determination of surface area is described in ISO 9277. The procedures which have been devised for the determination of the amount of gas adsorbed may be divided into two groups:

— those which depend on the measurement of the amount of gas removed from the gas phase, i.e. manometric (volumetric) methods;

— 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. However, the static manometric method is generally considered the most suitable technique for undertaking physisorption measurements with nitrogen, argon and krypton at cryogenic temperatures (i.e. 77 K and 87 K, the boiling temperature of nitrogen and argon, respectively) with the goal of obtaining pore volume and pore size information. This document focuses only on the application of the manometric method.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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, *Determination of the specific surface area of solids by gas adsorption — BET method*

ISO 14488, *Particulate materials — Sampling and sample splitting for the determination of particulate properties*

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3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

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
amount 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
amount of the adsorbate that forms 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
nanopore
pore with width of 100 nm or less

3.11
macropore
pore with width greater than about 50 nm

3.12
mesopore
pore with width between approximately 2 nm and 50 nm

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3.13
micropore
pore with width of about 2 nm or less

3.14
supermicropore
pore with width between approximately 0,7 nm and 2 nm

3.15
ultramicropore
pore with width of approximately < 0,7 nm

3.16
physisorption
weak bonding of the adsorbate, reversible by small changes in pressure or temperature

3.17
pore size
pore width, i.e. diameter of cylindrical pore or distance between opposite walls of slit

3.18
pore volume
volume of pores as determined by stated method

3.19
relative pressure
ratio of the equilibrium adsorption pressure, p, to the saturation vapour pressure, p_0, at analysis temperature

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

3.21
volume adsorbed
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	Description	Unit
A_a	Kirkwood-Mueller constant of adsorptive	$J \cdot cm^6$
A_s	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
α_s	normalized adsorption	1[a]
α_{s*}	polarizability of adsorbent	cm^3
c	speed of light	$m \cdot s^{-1}$
d_a	diameter of an adsorptive molecule	nm
d_{HS}	diameter of hard spheres	nm

[a] According to ISO 80000-1, the coherent SI unit for any quantity of dimension one (at present commonly determined "dimensionless") is the unit one, symbol 1.

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Symbol	Description	Unit
d_p	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
ε_{ff}/k_B	well depth parameter of gas-gas Lennard Jones potential	K
ε_{sf}/k_B	well depth parameter of gas-solid Lennard Jones potential	K
k_B	Boltzmann constant ($1{,}381 \times 10^{-23}$)	$J\,K^{-1}$
l	nuclei-nuclei pore width	nm
$m_a{}^*$	mass adsorbed	g
m_e	mass of an electron	kg
N_A	Avogadro's constant ($6{,}022 \times 10^{23}$)	mol^{-1}
N_a	number of atoms per unit area (m^2) of monolayer	m^{-2}
N_s	number of atoms per unit area (m^2) of adsorbent	m^{-2}
n_a	specific amount adsorbed	$mol \cdot g^{-1}$
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[a]
R	ideal gas constant (8,314)	$J mol^{-1} K^{-1}$
ρ_g	gas density	$g \cdot cm^{-3}$
$\rho_{g,STP}$	gas density at STP (273,15 K; 101,3 kPa)	$g \cdot cm^{-3}$
ρ_l	liquid density	$g \cdot cm^{-3}$
σ	distance between two molecules at zero interaction energy	nm
σ_{ff}	distance parameter of gas-gas Lennard Jones potential	nm
σ_{sf}	distance parameter of gas-solid Lennard Jones potential	nm
T	temperature	K
T_{cr}	critical temperature	K
t	statistical layer thickness	nm
V_a	specific volume of the adsorbate	$cm^3 \cdot g^{-1}$
V_g	specific adsorbed gas volume at STP (273,15 K; 101,3 kPa)	$cm^3 \cdot g^{-1}$
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

[a] According to ISO 80000-1, the coherent SI unit for any quantity of dimension one (at present commonly determined "dimensionless") is the unit one, symbol 1.

5 Principles

5.1 General

Physisorption is a general phenomenon and occurs whenever an adsorbable gas (the adsorptive) is brought into contact with the surface of a solid (the adsorbent). The forces involved are the van der Waals forces. Physisorption in porous materials is governed by the interplay between the strength of fluid-wall and fluid-fluid interactions as well as the effects of confined pore space on the state of fluids in narrow pores. The effect of pore width on the interaction potential is demonstrated schematically in Figure 1[8].

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