

Porosity and pore size distribution of materials —

Part 2: Method of evaluation by gas adsorption

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- British Coal Corporation
- British Laboratory Ware Association
- Coated Abrasives Manufacturers' Association
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Foreword

This Part of BS 7591 has been prepared under the direction of the General Mechanical Engineering Standards Policy Committee and is one of a series which describes recommended methods for the evaluation of porosity and pore size distribution.

This Part of BS 7591 describes the evaluation of porosity by gas adsorption. Other Parts of BS 7591 are as follows:

- *Part 1: Method of evaluation by mercury porosimetry;*
- *Part 3: Method of evaluation by challenge test¹⁾;*
- *Part 4: Method of evaluation by liquid expulsion¹⁾.*

The symbols and units used in this Part of BS 7591 do not necessarily conform to BS 5775, but are those widely used in the industry.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 16, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

¹⁾ In preparation.

Introduction

In general, different types of pores may be pictured as either 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. 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. a cavity with no access to an external surface, is not covered in this Part of this 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 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, for example in the context of:

- controlled drug release;
- catalysis;
- gas separation;
- filtration including sterilization;
- materials technology;
- environmental protection and pollution control;
- natural reservoir rocks.

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 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 material, its chemical and physical nature and the range of pore size.

The most 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 range of 0.003 μm to 400 μm , and especially in the range 0.1 μm to 100 μm .

Gas adsorption, where the pores are characterized by adsorbing a gas, such as nitrogen, at liquid nitrogen temperature. This method is most appropriate for pores in the approximate diameter range of 0.0004 μm to 0.05 μm (0.4 nm to 50 nm), and is an extension of the surface area estimation technique (see BS 4359-1).

Challenge test, where the effective size of the through-pores in a structure is estimated by the passage of test particles or molecules of different sizes. This method is often used for pores in the approximate diameter range of 0.005 μm to 100 μm .

Liquid expulsion, where the through-pores in a structure are characterized by the pressure required to empty them of a wetting fluid. This method is normally used for pores in the approximate diameter range of 0.05 μm to 50 μm .

1 Scope

This Part of BS 7591 describes the evaluation of porosity and pore size distribution by gas adsorption, which should be regarded as a comparative, rather than an absolute, test. The method is limited to the determination of the quantity of nitrogen adsorbed per unit mass of sample at the temperature of liquid nitrogen. The basis of the method is to measure the amount of nitrogen adsorbed at 77 K as a function of its relative pressure. Nitrogen adsorption is most appropriate for pores in the approximate range of widths 0.4 nm to 50 nm. Under certain circumstances larger pore widths may be evaluated. This standard describes the determination of micropore volume below 2 nm and the calculation of mesopore size distribution between 2 nm and 50 nm. Other gases, or organic vapours, may be used for the determination of micropore distributions but such approaches are not described in this standard.

The method described is suitable for a wide range of porous materials. It should be noted that the pore structure of some materials may be modified by pretreatment or cooling.

The procedures which have been devised for the determination of the amount of gas adsorbed may be divided into two groups:

- a) those which depend on the measurement of the amount of gas removed from the gas phase (i.e. gas volumetric methods); and
- b) 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 may be used to determine the amount of gas adsorbed. To derive the pore size distribution from the isotherm it is necessary to apply a mathematical model and this always entails the introduction of certain simplifying assumptions.

2 Informative references

This Part of BS 7591 refers to other publications that provide information or guidance. Editions of these publications current at the time of issue of this standard are listed on the inside back cover, but reference should be made to the latest editions.

3 Definitions (see also Figure 1)

For the purposes of this Part of BS 7591 the following definitions apply.

3.1

adsorbate

the adsorbed gas

3.2

adsorbed amount (n)

the number of moles of the gas adsorbed at a given pressure p

3.3

adsorbent

the solid material on which adsorption occurs

3.4

adsorptive

the gas or vapour to be adsorbed

3.5

blind pore (dead end pore)

a pore with a single connection with an external surface

3.6

equilibrium adsorption pressure (p)

the pressure of the gas in equilibrium with the adsorbate

3.7

ink bottle pore

a narrow necked open pore

3.8

interconnected pore

a pore which communicates with one or more other pores

3.9

isotherm

the relation, at constant temperature, between the amount adsorbed and the equilibrium pressure of the gas

3.10

macropore

a pore with width greater than about 50 nm

3.11

mesopore

a pore with width between approximately 2 nm and 50 nm

3.12

micropore

a pore with width of about 2 nm or less

3.13

monolayer amount (n_m)

the number of moles of the adsorbate that forms a monomolecular layer over the surface of the adsorbent

3.14

open pore

a cavity or channel with access to an external surface

3.15

porosity (open porosity)

the ratio of the volume of accessible pores and voids to the total volume occupied by a given amount of the solid

3.16

relative pressure

the ratio of the equilibrium adsorption pressure, p , to the saturation vapour pressure, p°

3.17

right cylindrical pore

a cylindrical pore perpendicular to the surface

3.18

saturation vapour pressure (p°)

the vapour pressure of the bulk liquified adsorbate at the temperature of adsorption

3.19

through pore

a pore which passes all the way through the sample

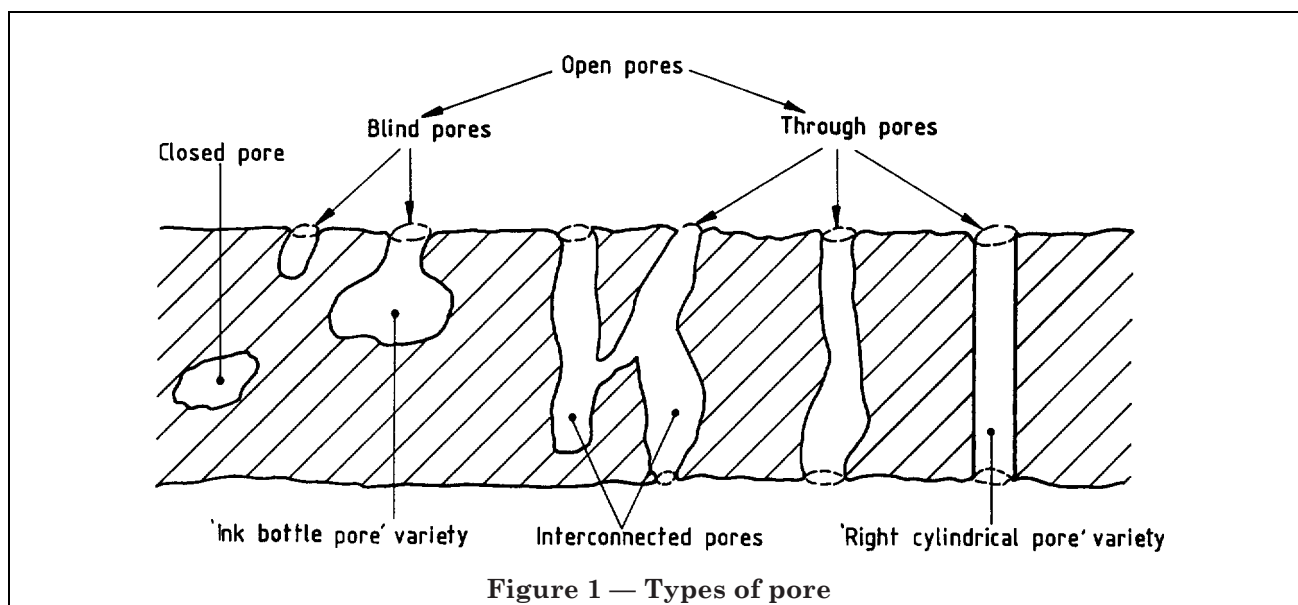


Figure 1 — Types of pore

4 Principles

4.1 General principle

The quantity of nitrogen adsorbed on a surface is recorded as a function of the relative pressure of nitrogen for a series of either increasing relative pressures on the adsorption branch of the isotherm or decreasing pressures on the desorption branch of the isotherm. 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 which can be investigated is limited by the size of the adsorptive molecule, e.g. about 0.4 nm in the case of nitrogen. The maximum pore size is limited by the practical difficulty of determining the amount of gas adsorbed at high relative pressure; in the case of nitrogen about 50 nm. Pore size distributions less than 2 nm width, micropores, are not reliably determined with nitrogen as the only adsorptive.

The pore size distribution calculated from the adsorption and desorption branches of the isotherm will not be in agreement (see 11.3). It is recommended that the analysis is carried out using the adsorption branch of the isotherm.

Adsorption of nitrogen in a porous solid takes place according to a number of different mechanisms. For instance, in mesopores 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 on the Kelvin equation.

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

$$r_k = 0.4078 / \log (p^\circ/p)$$

where

r_k is the radius of curvature of the adsorptive condensed in the pore (in nm);

p° is the saturation pressure of nitrogen at the temperature of the liquid nitrogen (in mmHg);

NOTE 1 mmHg = 133.322 Pa.

p is the equilibrium pressure of the nitrogen adsorptive (in mmHg).

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 using an equation which in the case of cylindrical pores is:

$$d_p = 2(r_k + t)$$

where

d_p is the cylindrical pore diameter (in nm);

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

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

The Kelvin equation cannot be used for pores of less than 2 nm diameter. This is because interactions with adjacent pore walls become significant and the pore can no longer be considered as filled with a condensed liquid having bulk thermodynamic properties.