Porosity and pore size distribution of materials

Part 4. Method of evaluation by liquid expulsion

ICS 17.040.20

BSi

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Contents

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 liquid expulsion. Other Parts of BS 7591 are as follows:

Part 1. *Method of evaluation by mercury porosimetry*

Part 2. *Method of evaluation by gas adsorption*

[1] Part 3. *Method of evaluation by challenge test*

This British Standard describes a method of evaluation only and should not be used or quoted as a specification defining limits of performance. Reference to this British Standard should indicate that the method of evaluation used is in accordance with BS 7591 : Part 4 : 1993.

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[1] In preparation

Method

Introduction

In general, different types of pores can 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 can contain closed pores which are isolated from the external surface and into which fluids are not able to penetrate. The characterization of closed or blind pores is not covered in this Part of this standard.

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 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 to find 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 0.04 μm (0.4 nm to 40 nm) and is an extension of the surface area estimation technique (see BS 4359 : Part 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 pore size characteristics (such as mean, maximum and the distribution of pore sizes) that allow the flow of liquid from one side of the wetted structure to the other. It is a comparative and usually non-destructive test. Pore size is commonly expressed as 'pore diameter'. The pore diameter is calculated from the applied gas pressure, which causes the liquid filled pores to be emptied, resulting in a flow of gas through the sample.

The method is suitable for the study of through-pore materials, such as filter paper, paper, polymer membrane filters and cloth. It enables pore sizes to be estimated within the general size range of about 50 μm down to about 0.05 μm.

The test involves the application of pressures up to 1 MPa[2] (150 psi). For most materials this pressure does not cause compaction or deformation of the material which would result in a change in the pore structure.

The technique should be considered to be comparative, as for most porous media a theory is not available to allow an absolute calculation of pore size.

It is the recommended method for the evaluation of filter papers (see BS 6410).

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.

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[2] 1 Pa = 1 N/m^2.

3 Definitions (see also figure 1)

For the purposes of this Part of BS 7591, the following definitions

3.1 blind pore (dead end pore)

An open pore having a single connection with an external surface.

3.2 bubble point

The pressure at which the first flow of gas through a wetted sample occurs; it is a measure of the largest pore in the sample.

3.3 closed pore

A cavity with no access to an external surface.

3.4 ink bottle pore

A narrow necked open pore.

3.5 interconnected pore

A pore which communicates with one or more other pores.

3.6 mean flow pore size

The average pore diameter corresponding to the point where 50 % of the 'dry' curve crosses the 'wet' curve in a plot of flow rate against applied pressure.

3.7 open pore

A cavity or channel with access to an external surface.

3.8 pore diameter

The diameter of a pore, assumed to be cylindrical, emptied of fluids at a given pressure, as calculated from a given equation (see clause **7**).

3.9 pore size distribution

The distribution of pore diameters in a porous body by the application of a given equation (see clause **7**, which assumes a cylindrical pore model).
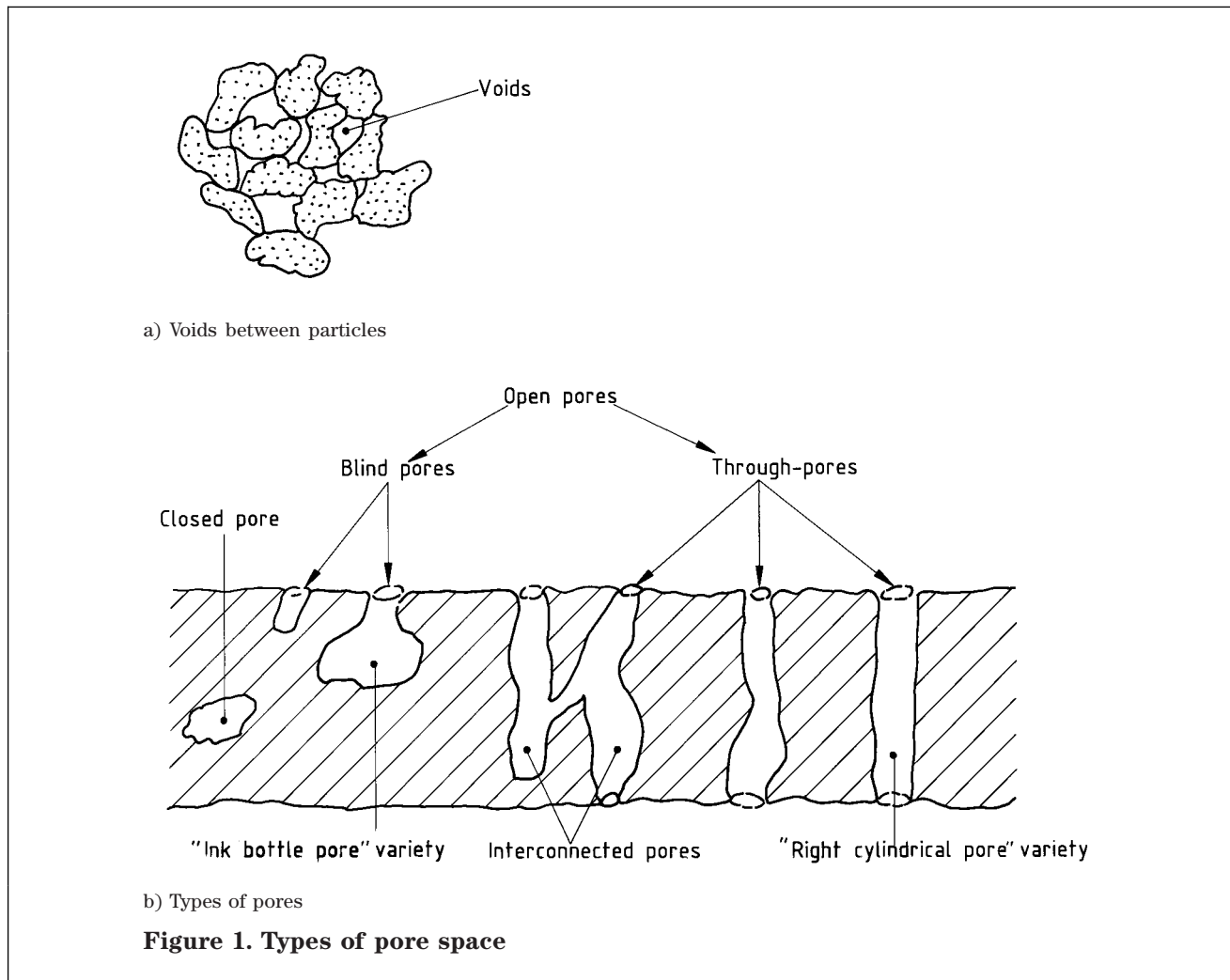

a) Voids between particles

b) Types of pores

Figure 1. Types of pore space

3.10 right cylindrical pore

A cylindrical open pore perpendicular to the surface of the porous body and which passes through the body from one side to the other.

3.11 through-pore

An open pore which passes through the sample from one side to the other.

3.12 void

The space between particles or fibres in a bed, i.e. inter-particle, or inter-fibre, pore.

4 Principle

If the through-pores within a material are filled with a liquid, i.e. wetted, the liquid can be expelled by applying a differential gas pressure across the wetted sample. Gas will flow through the wetted sample when the differential gas pressure exceeds the capillary attraction forces of the liquid contained in the largest pores. Progressively increasing the differential gas

pressure across the wetted sample will result in the smaller through-pores being emptied of their liquid, producing an increased gas flow. From a knowledge of the applied gas pressure and the resulting gas flow through the sample, once when wetted and once when dry, the pore distribution is calculated.

The technique is based on the relationship between pore diameter and applied pressure as described by the capillary rise equation (see **7.1**). There are several assumptions inherent in the calculations.

5 Apparatus

5.1 *Pore size apparatus*

NOTE 1. A schematic diagram of a simple form of manually controlled apparatus is shown in figure 2. This apparatus can be used to estimate pore size distribution by the liquid expulsion method as well as to obtain a reading of bubble point.

NOTE 2. The bubble point (or bubble pressure) test is used for instance to determine the equivalent pore size of fabrics (see BS 3321) or the largest pore size of filter papers (see BS 6410).
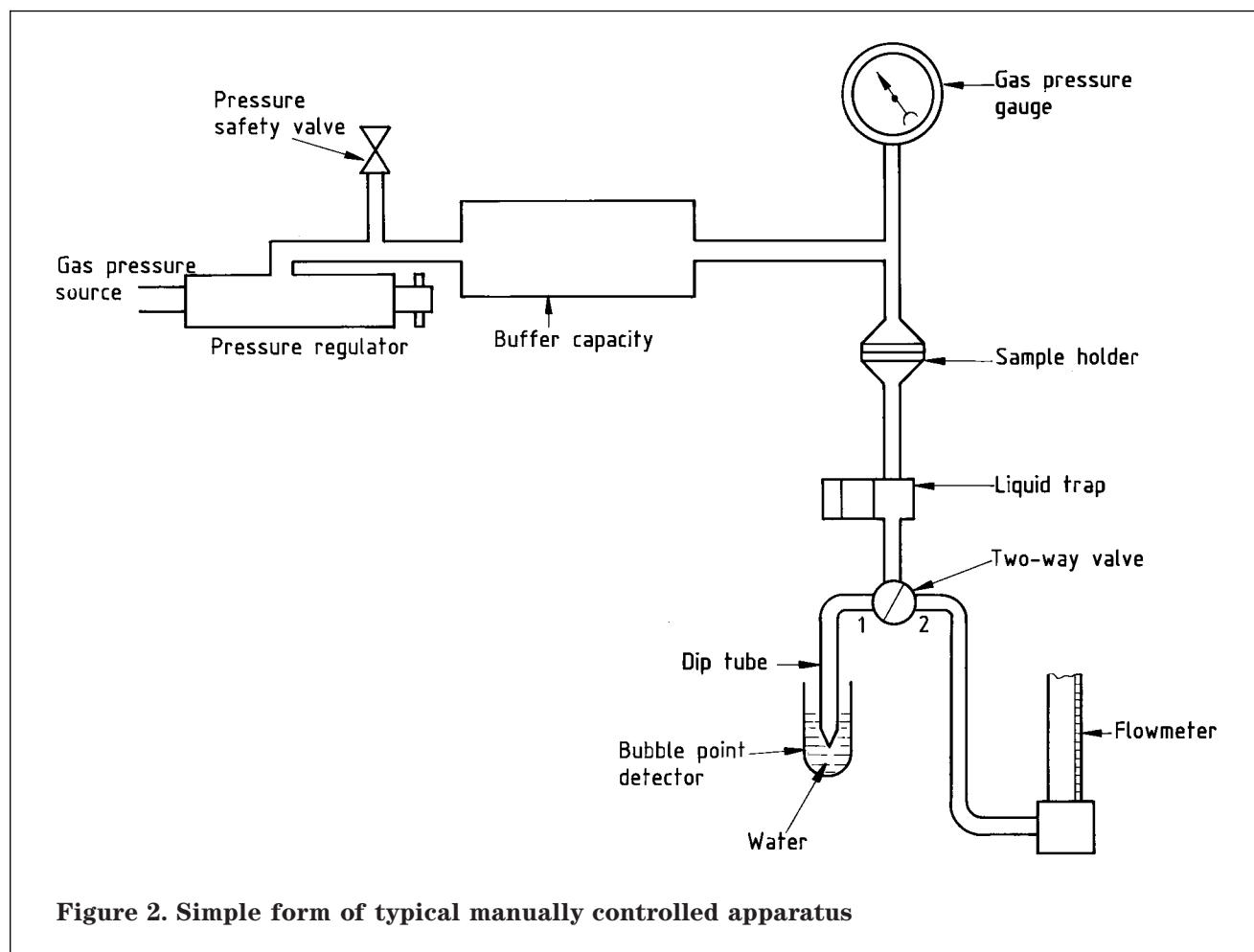

Figure 2. Simple form of typical manually controlled apparatus

5.1.1 *Gas pressure source*, for example compressed air, at up to about 0.6 MPa to 1.0 MPa (about 100 psi to 150 psi) available at a flow rate of up to about 100 l/min.

NOTE. There should be a buffer capacity between the compressor and the apparatus to minimize pressure fluctuations. When using high pressures, the operator should ensure adequate personal protection.

5.1.2 *Gas pressure gauge*, calibrated to the accuracy necessary for the test to be performed.

NOTE. An error of 1 % in pressure reading will calculate to a 1 % error in pore size.

5.1.3 *Sample holder*

NOTE. This typically holds a thin disc of sample material, usually supported downstream by a large pore structure, or mesh, which is too coarse to interfere with the pore sizes to be measured (see figure 3).

5.1.4 *Bubble point detector*, an optional device used to identify the onset of gas flow through the sample.

5.1.5 *Flowmeter*, for measuring the flow rate of gas through the specimen, calibrated to an accuracy of within ± 3 %.

5.1.6 *Liquid trap*, for collecting liquid expelled from the pores to prevent it interfering with the detection of the bubble point or gas flow.

5.1.7 *Two-way valve*, for diverting the gas flow to either:

a) the bubble point detector; or

b) the flowmeter.

5.2 *Vacuum vessel and pump*, comprising a glass beaker within a vacuum desiccator or bell jar and a pump capable of producing a vacuum of 0.7 kPa.

NOTE. The vacuum vessel is sometimes used for sample preparation.

Direction of gas flow
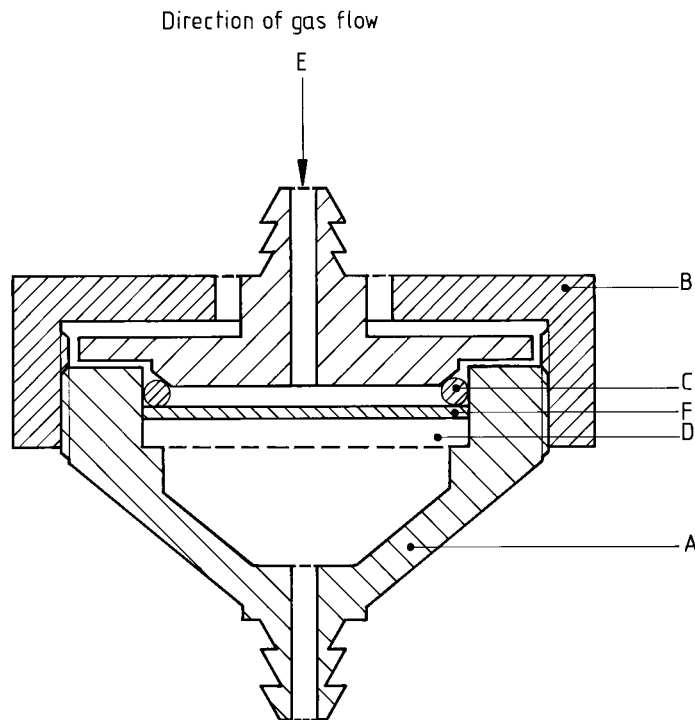
Key

A base

B locking ring

C 'O' ring seal

D support disc

E air inlet

F test sample

Figure 3. Typical sample holder

6 Procedure

6.1 Sampling

Take the sample intended for analysis (the test sample) representatively from the bulk material and ensure it is of an area appropriate to the range of the flowmeter.

NOTE. If the sample area is too large the flow of gas through the sample may be too large for the meter to measure. Highly permeable samples will need a smaller area; 20 mm to 50 mm is a typical diameter range for a sample of porous material.

6.2 Preparation of test samples

Test the sample either in the 'as received' condition, or after pre-treatment.

NOTE. Typical pre-treatments are given in a) and b).

a) *Pre-treatment for papers*

Test samples may be conditioned at a relative humidity of 50 % $\pm$ 2 % and a temperature of 23 °C $\pm$ 1 °C, in accordance with BS 3431 : 1973. An alternative pre-treatment may be by oven drying.

b) *Pre-treatment for resin treated papers*

The resin should be cured before commencing the test. Curing may be carried out by exposure to a high temperature for a period (e.g. 150 °C for 10 min), or to high humidity, or to ultraviolet light depending on the resin involved.

6.3 Choice of wetting liquid

Ensure that the liquid fully wets the sample, i.e. has a contact angle close to 0°, low surface tension and low volatility, and is not reactive with the sample.

NOTE. Water is not recommended; preferred is a fully fluorinated hydrocarbon liquid (i.e. a perfluorocarbon) or a high boiling point alkane, as they can be obtained as pure liquids whose surface tension is known and is not variable. Reference should be made to the supplier's literature regarding any health and safety instructions appropriate to the liquid used.

6.4 Pre-wetting of test sample

Fully immerse the test sample in the wetting liquid and degas in the vacuum vessel, if appropriate, for 2 min or until no more gas bubbles are released from the pores in the test sample. Do not use a vacuum vessel if obvious sample deterioration occurs, such as would occur with some fibrous filters.

6.5 Analysis of test sample

6.5.1 *General*

Seal the pre-wetted sample into the sample holder, and slowly increase the gas pressure by means of the pressure regulator. Direct the gas flow passing through the test sample either through the bubble point detector or through the flowmeter, depending on the measurement required.

6.5.2 *Bubble point analysis*

With the two-way valve opened to the bubble point detector, observe and record the pressure at which initial gas flow occurs, as indicated by the appearance of the first stream of bubbles.

6.5.3 *Pore size distribution analysis*

Turn the two-way valve to the flow meter and record the gas flow through the wetted test sample with increasing gas pressure.

NOTE 1. If the approximate largest and smallest pore sizes to be expected are known, the appropriate range of gas pressures to use can be calculated in advance from equations (1) or (2) of **7.1**.

Continue increasing the gas pressure until all of the pores are empty of wetting liquid; this may be seen as a straight line on the plot of flow against pressure (see figure 4).

NOTE 2. This procedure is known as the 'wet run'.

Reduce the gas gauge pressure to zero and re-commence the analysis with the now dried test sample still in its holder, again recording flow through the test sample against applied pressure.

NOTE 3. This procedure is known as the 'dry run'.

Continue recording data until the dry run plot overlays the wet run plot, until the maximum permissible pressure is reached.

NOTE 4. Carrying out the wet run first is advantageous, in terms of time taken, but only if the pores are within the measurement limit of the technique. If this is not the case, the dry run can be performed first, followed by the wet run.

Decrease the gas gauge pressure to zero and remove the sample.

NOTE 5. Where material compression occurs (possibly even from the clamping action of the holder), care should be taken when directly comparing results with less compressible material.

7 Calculation of results

7.1 Equation relating applied pressure to pore diameter

Relate applied pressure to pore diameter, assuming a cylindrical pore shape, by the capillary rise equation:

$$d = \frac{4\sigma \cos \theta}{p} \times 10^6 \qquad (1)$$

where

d is the pore diameter (µm);

σ is the surface tension (N/m) of the liquid;

θ is the contact angle in degrees between the liquid and the pore wall;

p is the pressure (Pa).

For liquids which are fully wetting (zero contact angle), such as perfluorocarbons, this equation simplifies to:
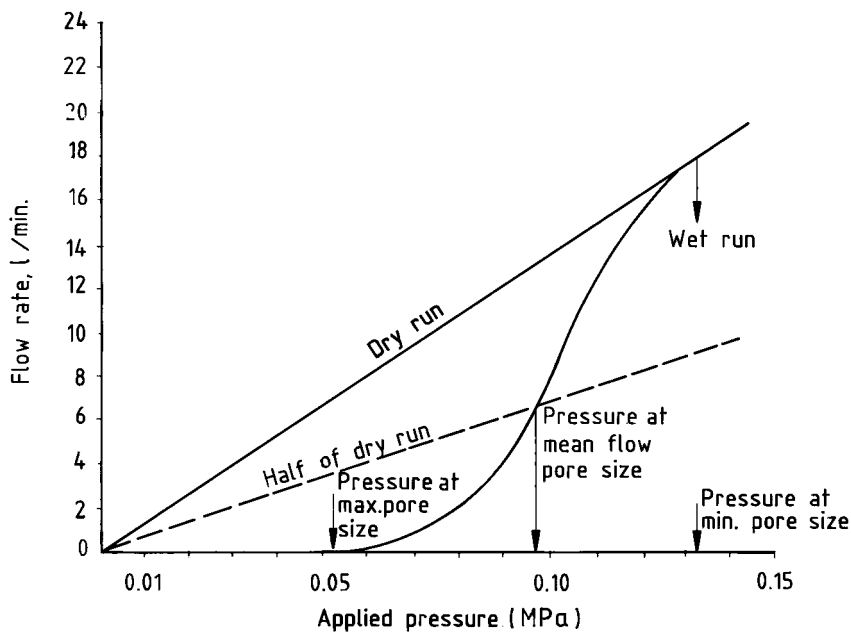
$$d = \frac{4\sigma}{p} \times 10^6 \qquad (2)$$

Figure 4. Typical plot of flow rate against applied pressure for wet and dry runs, performed on a single test sample
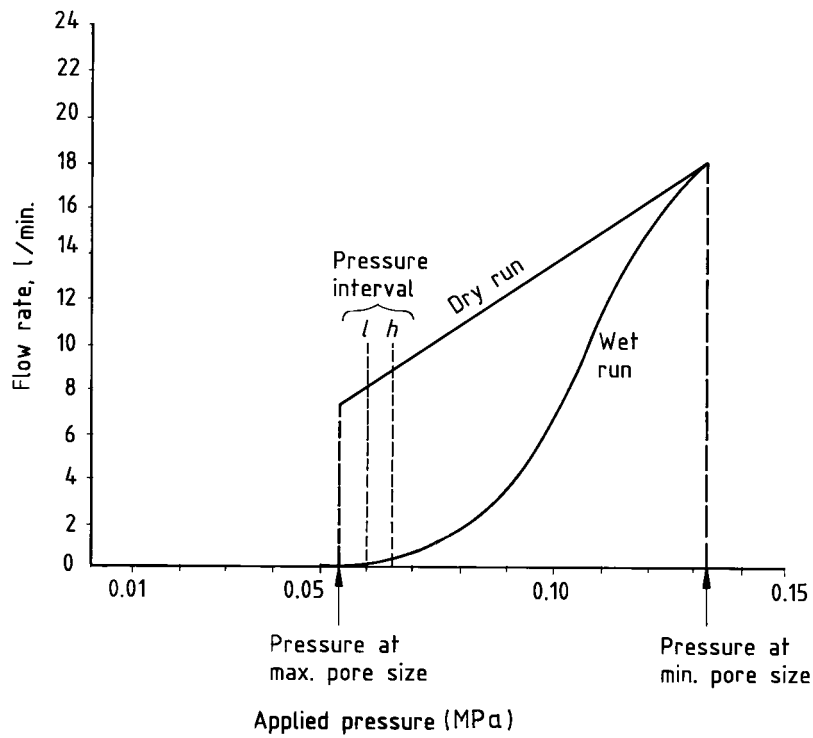

Figure 5. Example of plot of wet and dry runs from maximum to minimum pore sizes

7.2 Bubble point calculation

Calculate the pore size at the bubble point (largest pore size) using equations (1) or (2), as appropriate, from the recorded bubble point pressure (see **6.5.2**) and the surface tension and contact angle of the liquid.

NOTE. As this test is subjective, the result should be treated with some caution.

7.3 Maximum, minimum and mean flow pore size calculations

Plot the flow rate against applied pressure data for the wet and dry runs. Divide each dry flow value by two and plot against pressure on the same graph (see figure 4).

The point at which the wet run curve leaves the baseline approximates to the bubble point pressure. This corresponds to the initial gas flow, as detected by the flow sensor, and is denoted as the maximum pore diameter.

The point on the curve at which the dry run meets the wet run is at the minimum pore diameter.

The point of intersection of the half dry run plot with the wet run curve is at the mean flow pore diameter.

The maximum, minimum and mean flow pore sizes can be calculated from equation (1) or (2). An example of the calculations is given in annex A.

7.4 Pore size distribution calculation

From figure 5 select small intervals of pressure l to h between maximum and minimum pore sizes.

Calculate the percentage Q of pores between the pore diameters for any pressure interval l to h from flows at l and h as follows:

$$Q = \left(\frac{\text{wet flow } h}{\text{dry flow } h} - \frac{\text{wet flow } l}{\text{dry flow } l} \right) 100 \qquad (3)$$

The pore size distribution by flow is computed by accumulating values of Q from the maximum to the minimum pore sizes.

Example

Typical calculation, using data from figure 5, to determine the percentage of flow passing through a pore diameter range of 1.07 µm to 0.98 µm (e.g. 0.060 to 0.065 × 10^6 Pa) is given as follows:

$$Q = \left(\frac{0.4}{9.0} - \frac{0.2}{8.3} \right) 100$$
$$= \quad 2.0 \text{ \%}$$

Present the pore size distribution as shown in figures 6 and 7.

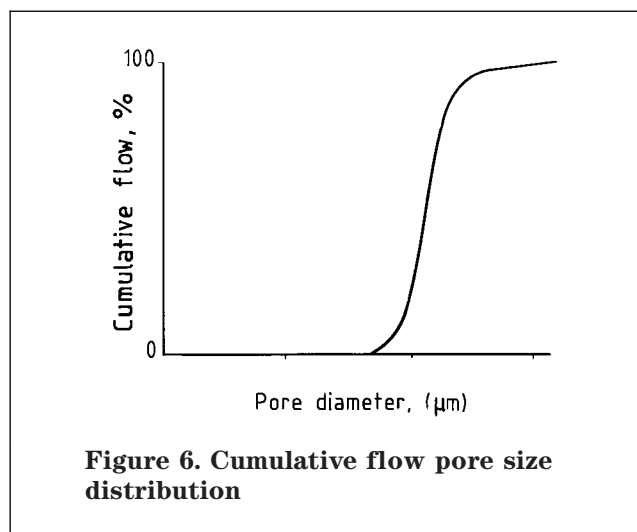NOTE. Commercially available automated instruments can provide these calculations automatically.

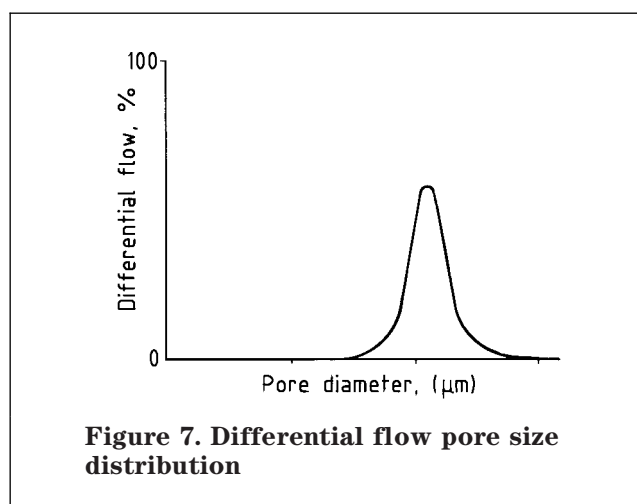**Figure 6. Cumulative flow pore size distribution**

Figure 7. Differential flow pore size distribution

8 Test report

A summary of the measurement conditions and constants used in the calculation shall be provided with each result as follows:

    a) analysis laboratory;

    b) sample identification;

    c) sample source;

    d) sample diameter;

    e) instrument used;

    f) pre-treatment conditions;

    g) contact angle of liquid;

    h) surface tension of liquid;

    i) operator's name;

    j) date of analysis.

NOTE. The results should be reported as, for instance, maximum pore diameter, minimum pore diameter, mean flow pore size and pore size distribution (cumulative and/or differential).

Annex

Annex A(informative)

Examples of the calculation of maximum, minimum and mean flow pore diameters

From the information given in figure 5 and using a typical perfluorocarbon fluid of surface tension 16×10^{-3} N/m to wet the pores fully, the maximum, minimum and mean flow pore diameters may be calculated from equation (4), as follows:

$$d = \frac{64\,000}{p} \qquad\qquad (4)$$

where

d is pore diameter (μm);

p is applied pressure (Pa).

Then

Maximum pore diameter $= \dfrac{64\,000}{0.052 \times 10^6} = 1.23$ μm diameter

Minimum pore diameter $= \dfrac{64\,000}{0.132 \times 10^6} = 0.48$ μm diameter

Mean flow pore diameter $= \dfrac{64\,000}{0.097 \times 10^6} = 0.66$ μm diameter

List of references (see clause 2)

Informative references

BSI standards publications

BRITISH STANDARDS INSTITUTION, London

BS 3321 : 1986	*Method for the measurement of the equivalent pore size of fabrics (bubble pressure test)*
BS 3431 : 1973	*Method for the conditioning of paper and board for testing*
BS 4359 :	*Determination of the specific surface area of powders*
BS 4359 : Part 1 : 1984	*Recommendation for gas adsorption (BET) methods*
BS 6410 : 1991	*Methods of test for filter papers*

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