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Subcommittee on Characterization of Porous Solids

RECOMMENDATIONS FOR THE
CHARACTERIZATION OF POROUS SOLIDS

(Technical Report)

*Prepared for publication by the Subcommittee
on Characterization of Porous Solids, consisting of*

J. ROUQUEROL† (France, *Chairman*); D. AVNIR (Israel); C. W. FAIRBRIDGE (Canada);
D. H. EVERETT (UK); J. H. HAYNES (UK); N. PERNICONE (Italy); J. D. F. RAMSAY (UK; France);
K. S. W. SING (UK) and K. K. UNGER (FRG).

Recommendations for the characterization of porous solids

Abstract - These recommendations aim to be a tool for the selection and appraisal of the methods of characterization of porous solids, and to also give the warnings and guidelines on which the experts generally agree. For this purpose, they successively consider the description of a porous solid (definitions, terminology), the principal methods available (stereology, radiation scattering, pycnometry, adsorption, intrusion, suction, maximum buble pressure, fluid flow, immersion or adsorption calorimetry, thermoporometry, size exclusion chromatography, Xenon NMR and ultrasonic methods) and finally the general principles which are worth being followed in the selection of the appropriate method.

Contents

I. Introduction

Most materials are to some extent porous : indeed, it is quite difficult to find or prepare a truly non-porous solid. It is well known that physical properties such as density, thermal conductivity and strength are all dependent on the pore structure of a solid and that the control of porosity is of great industrial importance for example in the design of catalysts, industrial adsorbents, membranes and ceramics. Furthermore, porosity is one of the factors which influence the chemical reactivity of solids and the physical interaction of solids with gases and liquids.

The complexity and variety of porous materials has led to the application of **many experimental techniques for their characterization**. For example, a great deal of effort has been expended in the development and refinement of various methods for the determination of pore size distribution. Unfortunately, much of this work has been carried out on ill-defined materials, which may partly explain why there is a lack of general agreement on the advantages and disadvantages of the various procedures described in the literature.

The following recommendations are presented in order to clarify :
1- The terms used to describe real porous materials ;
2- The quantitative description of pore structure of different types. ;
3- The selection of appropriate experimental techniques for the characterization of porous materials ;
4- The appraisal and significance of experimental data.

Because many of the **major applications** and therefore **important methods** of characterization of porous solids **depend upon adsorption**, these recommendations are closely related to the former recommendations of Commission I-6 entitled "Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity" (Ref. 1) ; "Reporting data on adsorption from solution at the solid/solution interface" (Ref. 2) ; "Manual of symbols and terminology for physicochemical quantities and units. Appendix II. Part I : Definitions, Terminology and Symbols in Colloid and Surface Chemistry" (Ref. 3) ; and "Part II : Heterogeneous Catalysis" (Ref. 4), respectively. Also, these recommendations rely heavily on material presented during three IUPAC meetings specially organized for that purpose and whose proceedings are available in the three books "Characterization of porous solids" (Ref. 5 to 7). These books also provide an up-to-date source of references for most methods and aspects referred to in this document, so that, except for a very few special cases, it was not considered necessary to quote here other references than the basic ones mentioned above.

II. Description of a porous solid

1. General definitions and terminology

In this section, which is intended for convenient reference, a number of useful terms are listed and defined in a condensed way. They are introduced in a more detailed manner in the following sections.

Aggregate : loose, unconsolidated assemblage of particles.

Agglomerate : rigid, consolidated assemblage of particles.

Density :
"true" density : density of the material *excluding* pores and interparticle voids
"apparent" density : density of the material *including* closed and inaccessible pores
"bulk" density : density of the material *including* pores *and* interparticle voids.

Divided solid : solid made of more or less independent particles which may be in the form of a powder, aggregate or agglomerate.

Hydraulic radius : mean value for a porous solid, obtained through the relationship :
$$r_h = V_p / A$$
(r_h : hydraulic radius, V_p : pore volume determined at saturation, A : surface area, e.g. determined by the BET method).

Porous solid : a solid with pores, i.e. cavities, channels or interstices, which are deeper than they are wide.

Pore volume V_p : volume of the pores, as measured by a given method which must be stated, (together, for instance, with the nature of the probe-molecule, the wavelength of the radiation used or the ultimate intrusion pressure ...).

Pore size (generally, pore width) : the distance between two opposite walls of the pore (diameter of cylindrical pores, width of slit-shaped pores). Micro-, Meso- or Macropores : see end of section II5.

Pore size distribution : represented by the derivatives $\dfrac{dA_p}{dr_p}$ or $\dfrac{dV_p}{dr_p}$ as a function of r_p, where A_p, V_p and r_p are the wall area, volume and radius of the pores. The size in question is here the radius, which implies that the pores are known to be, or assumed to be, cylindrical. In other cases r_p should be replaced by the width.

Porosity ε : ratio of the total pore volume V_p to the apparent volume V of the particle or powder (excluding interparticle voids). In some cases one may distinguish between *open porosity* (i.e. the volume of pores accessible to a given probe molecule) and *closed porosity*. The methods used to measure pore volume and apparent volume should be stated.

Roughness (or rugosity) **factor** : ratio of the external surface area to the area of the geometrical envelope of the particles.

Surface area : extent of the total surface as determined by a given method under stated conditions. It is essential to state the method used.
External surface area of a powder : area of the external surface of the particles, taking into account their roughness, i.e. all cavities which are wider than deep, but not the surface of the pore walls.

Internal surface area of a powder : area of the pore walls, excluding the external surface area.

2. Qualitative description of a porous solid

Any solid material which contains cavities, channels or interstices may be regarded as porous, though in a particular context a more restrictive definition may be appropriate. Thus, in describing a porous solid, care must be exercised in the choice of terminology in order to avoid ambiguity. With the help of Fig. 1, we can for instance classify the pores according to their *availability to an external fluid*. From this viewpoint, a first category of pores are those totally isolated from their neighbours, as in region (a), which are described as *closed pores*. They influence such macroscopic properties as bulk density, mechanical strength and thermal conductivity, but are inactive in such processes as fluid flow and adsorption of gases. On the other hand, pores which have a continuous channel of communication with the external surface of the body, like (b) (c) (d) (e) and (f), are described as *open pores*. Some may be open only at one end (like b) and (f) ; they are then described as *blind* (i.e. *dead-end*, or *saccate*) pores. Others may be open at two ends (*through* pores), like around (e). Pores may also be classified according to *their shape* : they may be *cylindrical* (either open (c) or blind (f)), *ink-bottle* shaped (b),

funnel shaped (d) or *slit*-shaped. Close to, but different from porosity is the *roughness* of the external surface, represented around (g). To make the distinction, a convenient and simple convention is to consider that a rough surface is not porous unless it has irregularities that are deeper than they are wide.
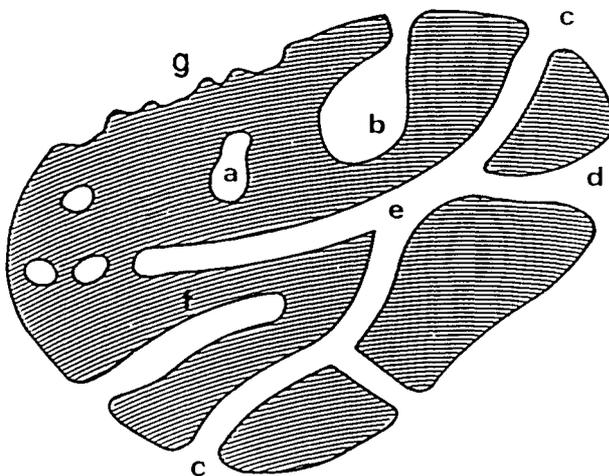
Fig.1 : Schematic cross-section of a porous solid

3. Origin of pore structures

Some porous materials are *consolidated*, existing as relatively rigid, macroscopic bodies whose dimensions exceed those of the pores by many orders of magnitude ; they may be called *agglomerates*. Others are *unconsolidated*, being nonrigid, more-or-less loosely packed assemblages of individual particles ; they may be called *aggregates*. The particles themselves may be nonporous (e.g. sand), and therefore surrounded by a network of *interparticle voids*, with properties dependent only on the size, shape and manner of packing of the constituent particles. In other cases (e.g. spraydried catalysts) the particles themselves may be significantly porous, and it may then be necessary to distinguish between *internal* (or *intraparticle*) *voids*, and *interparticle* voids. In general, internal pores will be smaller, both in size and in total volume, than the voids between particles ; nevertheless, they will often provide the dominant contribution to the surface area of the solid.

The distinction between consolidated and unconsolidated materials is not always clearcut. Indeed, the two forms are aften interconvertible for example, by grinding of the former, and by sintering of the latter.

Thus, **porous materials can be formed by several different routes.**
In a first case, pores are an inherent feature of particular *crystalline structures*, e.g. zeolites and some clay minerals. Such intracrystalline pores are generally of molecular dimensions, and form highly regular networks.

A second class of porous materials is formed by loose packing (*i.e. aggregation*) and subsequent consolidation (*i.e. agglomeration*) of *small particles* as for instance in some inorganic gels and in ceramics. These processes are *constitutive*, in that the final structure depends mainly on the original arrangement of the primary particles and on their size.

A third route is described as *subtractive*, in that *certain elements of an original structure are selectively removed* to create pores. Examples are the formation of porous metal oxides by thermal decomposition

of hydroxides, carbonates, nitrates, oxalates and of porous glasses by chemical etching of multiphase solids. Many porous organic polymer membranes are formed in this way. A more complex process, although related to the same mechanisms, is that of the activation of carbons.

Finally, the pore structure of plant and animal tissues, which is of literally vital importance and must fulfil stringent conditions, is determined by natural processes of cell division and selforganization, which are as yet imperfectly understood.

4. Quantitative description of pore structures

"Porosity" may be defined as the fraction ε of the apparent volume of the sample which is attributed to the pores detected by the method used : $\varepsilon = V_p/V$. The value of this fraction depends on the method used to determine the apparent volume V, which excludes interparticle voids (geometrical determination, fluid displacement) and on that used to assess the pore volume V_p (adsorption and capillary condensation, fluid displacement, ultrasonics etc ...). Some methods , indeed, have only access to "open pores" (i.e. the methods using a fluid) whereas others may also have access to "closed pores" (i.e. methods using a radiation). Moreover, for a given method, the value depends on the size of the molecular probe (fluid displacement, adsorption) or of the yardstick (stereology). Thus, a recorded value of porosity can be expected to reflect not only a physical property of the material, but also the experimental method used for its determination.

The pore volume V_p used in the above relationship may be either that of the open pores (leading to the "open porosity") or that of the closed pores (leading to the "closed porosity") or that of both types of pores together (leading to the "total porosity").

The "specific surface area" (a, a_p or s) **is defined as the accessible** (or detectable) **area of solid surface per unit mass of material.** It is similarly dependent on the method and experimental conditions employed, and on the size of the probe used (e.g. adsorbate molecular size, wavelength of radiation, etc ...). However, since the interpretation of such measurements usually relies on simplified models of the processes concerned, the recorded value may further depend on the validity of the assumptions inherent to the model.

The **"pore size"** is a property of major importance in practical applications of porous materials, but it is even less susceptible to precise definition. The problems already mentioned for the specific surface area are complicated by the fact that the pore shape is usually highly irregular and variable, leading to a variety of definitions of "the size". Moreover, pore systems usually consist of interconnected networks, and the recorded results will often depend on the sequence in which pores are encountered within the method used (e.g. mercury intrusion). For these reasons, quantitative descriptions of pore structure are often based on *model systems*.

5. Idealized systems : pore shape and size

For the sake of simplicity, the *shape* of pores, when known or assumed, is preferably described in terms of *cylinders* (which may be the case for activated oxides like alumina or magnesia), *prisms* (some fibrous zeolites), *cavities* and *windows* (other zeolites), *slits* (possible in clays and activated carbons), or *spheres* (although, most often, the pores are on the contrary, the *voids left between* solid spheres in contact with each other, as it happens with gels : silica gel, zirconia gel etc ...). The real description of many real porous solids is complicated by the existence of :
-- *different shapes* of pores in the same material
-- *connections* between pores, which may vary in size, shape and location
-- *a distribution in the size* of the pores.

To describe these complexities it was necessary to introduce descriptors based upon the concepts of *"connectivity"*, *"percolation"*, *"tortuosity"* and, more recently, *"fractal geometry"* which is referred to

in the next section.

In most uses of porous solids, the *size of pores* is a major parameter : hence the development of a number of methods whose aim is to carry out a "pore size analysis". Pore size has a precise meaning when the geometrical shape of the pores is well defined and known (e.g. cylindrical, slit-shaped etc ...). Nevertheless, the limiting size of a pore, for most phenomena in which porous solids are involved, is that of its *smallest dimension* which, in the absence of any further precision, is referred to as the *width* of the pore -(*i.e.* the width of a slit-shaped pore, the diameter of a cylindrical pore ...)-. To avoid a misleading change in scale when comparing cylindrical and slit-shaped pores, *one should use the diameter of a cylindrical pore (rather than its radius) as its "pore-width"*.

The following distinctions and definitions were adopted in previous IUPAC documents (Ref. 1 and 4) :
-- *Micropores* have widths smaller than 2 nm.
-- *Mesopores* have widths between 2 and 50 nm.
-- *Macropores* have widths larger than 50 nm.

6. Fractal analysis

Fractal geometry has emerged recently as an analytical tool which is suitable for the description of complex structures, such as those which are found in most porous objects. It is basically a multiple-resolution analysis which searches for simple scaling power laws of the type :

$$\text{amount of surface property} \propto \text{resolution of analysis}^D \qquad (1)$$

where D is the fractal dimension of the surface for which the property is relevant. "Amount of surface property" is, for instance, the monolayer value, the pore volume, or the intensity of scattered radiation. The corresponding change in resolution is then achieved by changing the size of the adsorbate, the pore radius, or by changing the angle of the scattered light. Obviously, the surface which scatters need not coincide with the surface accessible for adsorption or for pore-filling. Therefore D characterizes the *effective geometry* for a given process, and not necessarily *the* geometry. This conclusion of the fractal approach bears, in fact, on all methods used to characterize a porous solid.

An explicit example of eq. (1) is :

$$N_{\text{m}} = k\sigma^{-D_{\text{ads}}/2} \qquad (2)$$

where N_{m} is the number of molecules needed to form a monolayer coverage, σ is the cross-sectional area of the adsorptive molecule, k is a constant, and the subscript "ads" denotes that the D is the fractal dimension of the surface accessible for adsorption.

Also, the pore-volume distribution, $dV_{\text{p}}/dr_{\text{p}}$ vs r_{p}, of a solid whose surface is fractal, is given by :

$$\frac{dV_{\text{p}}}{dr_{\text{p}} } = k' \, r_{\text{p}}^{(2-D_{\text{ads}})} \qquad (3)$$

where k' is another constant.

In addition to adsorption, fractal analysis has been employed for virtually all experimental methods described in this report, and especially to small angle X-ray and neutron scatterings, image analysis , nmr , and flow. For each of these cases, eq. (1), suitably expressed and modified, has been used.

III. Principal methods available to characterize a porous solid

1. Stereology

Stereology is based on *direct observations of cross-sections of the solid.*
The first practical requirement is that a plane cross-section of the material under study can be prepared, in a suitable form for study by optical or electron microscopy. The contrast between matrix and pores may require enhancement, e.g. by impregnating the pores with a fluorescent resin, or by surface replication and shadowing. The resolution of the imaging determines the range of pore sizes accessible by this method. If the pore structure is suspected of being anisotropic, sections in a variety of non-parallel planes should be examined.

The second practical requirement is the collection of a statistically significant number of measurements of a variety of geometrical characteristics of the image. These may include :
a) the ratio of the fractional areas of pore and matrix in the total image
b) the distribution of lengths of randomly chosen straight lines which traverse a pore from one boundary with the matrix to another
c) the perpendicular distance between parallel tangents to the boundary of each pore, and
d) the number of times that an arbitrary line, of given length, terminates in pore or matrix, and the number of times that it crosses the pore-matrix interface.

In practical terms, such data can be acquired speedily and reliably by modern image-analysis techniques, and processed automatically to yield values of porosity, and measures of pore-size distribution, specific surface, and mean curvature of the solid surface. Qualitative impressions of the pore shape may also be gained.

A refinement of this technique employs serial sectioning, whereby a series of parallel planes, separated perpendicularly by a distance commensurate with the pore size, is examined sequentially. This can give information on the connectivity of the pore space, which would otherwise be lacking.

Because stereology is based on direct observations, it *can yield values of the pore structural parameters that are, in a sense, more realistic than those derived from less direct methods,* which require the use of idealised models for their interpretation. On the other hand, *such real values are of little use in predicting many of the practically important properties of porous media,* such as permeability. A further point is that the specific surface measured stereologically will generally be considerably lower than that deduced from gas adsorption, to an extent dependent on the resolution of the microscopic image (in the usual case when a molecular resolution is not reached). This is a consequence of the fractal nature of the solid surface.

2. Radiation scattering

2.1 *Basic principle*
Radiation scattering from solids can arise from variations of scattering length density (see below) which occur over distances exceeding the normal interatomic spacings. Such variations occur when solids contain pores, and details of the porosity and surface area can be obtained from measurements of the angular distribution of scattered intensity. The appropriate angular range (see below) where this information is contained is given by $d \sim \lambda/2\theta$ where d is the pore size, and λ the wavelength of radiation, which may be X-rays, neutrons or light.

In a scattering experiment a monochromatic beam of electromagnetic radiation (light, X-rays) or neutrons of wavelength λ_0 intensity I_0 and wavevector $\overline{k_0}$ on a sample, and the scattered intensity is measured as a function of angle, 2θ, to the incident direction (Fig.2).
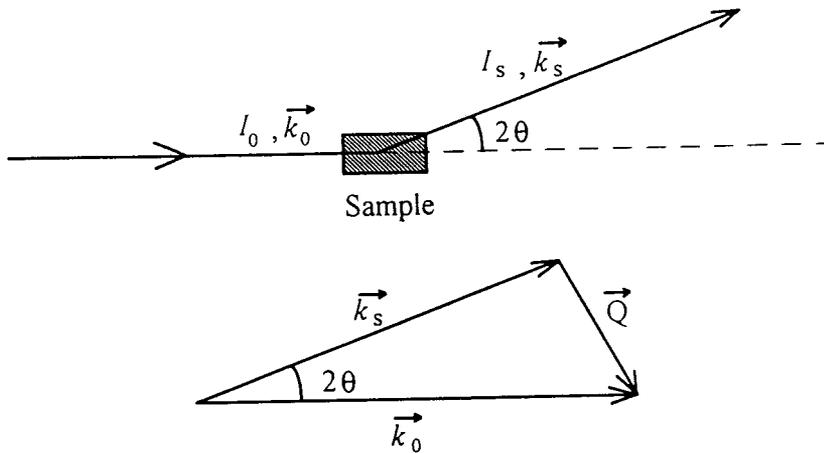
Fig.2 : Schematic representation of the incident and scattered beams

Typical wavelengths for different types of radiation and the corresponding spatial resolution of density fluctuations or inhomogeneities such as pores, which may be determined experimentally are given in Table I.

Table I

Type of radiation	Typical wavelength/nm	Inhomogeneity	Spatial resolution/nm
Light	400 - 600	refractive index	200 - 20 000
X-rays	0.1 - 0.4	electron density	5 - 50
neutrons	0.1 - 2.5	scattering length density	50 - 500

2.2 *Experimental method*

Both small angle X-ray and neutron scattering are established techniques and their experimental application is similar. However, limitations on sample size, thickness and containment are much more restricted with X-rays because of absorption of radiation. Instrumentally both require a source of radiation, a monochromator, collimation system, sample containment and a detection system.

The usual options available for both radiations are summarised below :

	X-rays	Neutrons
Source	X-ray generator, Synchrotron	Thermal reactor, pulse source
Monochromator	Crystal	Velocity selector
Collimation	Pin hole / slit	Circular diaphragm
Containment	Plastic film windows	Little restriction, eg silica or metal cells
Sample size	thin eg < 1mm	Typically 1-10mm thick
Detector	Photographic film linear or 2D-gas filled	High resolution 2-D multicell
Sample to detector distance	Generally < 2 m	Variable (~ 2 to 40 m)

2.3 *Scope of application*

Scattering techniques are non-destructive and have particular advantages in the characterisation of the surface and porous properties of materials containing either closed or molecular sized pores and where outgassing pretreatment may result in irreversible changes in microstructure. Measurements may be carried out, indeed, in the presence of a gas and there is no need to evacuate the sample. For these reasons, these techniques have been used to measure mean pore sizes covering a range from 1 to 1000 nm.

Important information on the contribution of porosity contained in closed and open pores can be derived from X-ray and neutron scattering. This is achieved by condensing probe molecules, having a similar scattering cross section to the solid, in the open pores.

3. Pycnometry

Fluid displacement measurements (pycnometry) lead to an estimate of the "apparent density" of a solid, defined as the ratio of its mass to the volume enclosed by an envelope of fluid surrounding the solid. Various criteria can be used for defining the envelope. In the limit, where the envelope follows the contours of the surface structure at an atomic level, then in the absence of internal closed pores the apparent density will be a close approximation to the density of bulk solid. In practice, the envelope may be defined in terms of increasingly fine-grained criteria. The apparent density will then be dependent on the scale on which the surface contours are followed ; porosity is thus a fractal property (see II,6).

Experimentally, the volume may be measured by fluid displacement. If a liquid does not wet the solid the surface of the liquid will follow only convex regions of the solid, and so will not penetrate the pore structure. (Measurements of mercury intrusion at higher pressures are dealt with in section III,5). On the other hand, a fluid that wets the surface will tend to penetrate all pores which are accessible to its molecules. Since probe molecules may be excluded from the finest pores, the pore volume obtained in this way may be expected to increase as the size of the probe molecule decreases.

It is often assumed that the density, ρ_t measured with helium gas (the so-called "true density") represents that of the bulk solid, ρ_s but this assumption is valid only if there is independent evidence that the gas is not adsorbed, and that the solid does not contain closed pores. The absence of adsorption may be checked by carrying out measurements in various pressure and temperature ranges. It is usually wise to make measurements at as high a temperature as convenient. The absence of closed pores may be inferred if $\rho_t = \rho_s$ where ρ_s is determined independently.

The measurement of apparent densities by liquid displacement also assumes that the density of the bulk liquid remains constant up to the solid surface. In practice the effects of adsorption are often small, but they can be detected by comparing the results of experiments using liquids of similar molar volume, but different chemical properties. It is also important to use an experimental technique in which both the solid and the liquid are thoroughly degassed before being brought into contact. Sufficient time must be allowed for equilibrium penetration to occur. Difficulties in arriving at well defined values arise if the solid swells in contact with the liquid (e.g. certain clays).

4. Adsorption from the gas phase

Gas adsorption measurements are widely used for the characterization of a variety of porous solids (e.g. oxides, carbons, zeolites and organic polymers). Of particular importance is the application of physisorption (physical adsorption) for the determination of the surface area and pore size distribution of catalysts, industrial adsorbents, pigments, fillers and other materials.

Nitrogen (at 77 K) is the recommended adsorptive for determining the *surface area* and *mesopore size distribution*, but it is necessary to employ a range of probe molecules to obtain a reliable assessment of the *micropore size distribution*. An alternative technique to gas adsorption (e.g. mercury porosimetry) must be used for *macropore size analysis*. For operational reasons, krypton adsorption (at 77 K) is usually adopted for the determination of relatively low specific surface areas (say, $< \sim 2$ m^{2}g^{-1}), but this technique cannot be employed for the study of porosity.

4.1 *Basic methodology*

Various procedures have been devised for determining the amount of gas adsorbed. Volumetric methods are generally employed for measuring nitrogen or krypton isotherms at temperatures ~ 77 K, but gravimetric techniques are especially useful for studying the adsorption of vapours at, or near, ambient temperature. The isotherm is usually constructed point-by-point by the admission and withdrawal of known amounts of gas, with adequate time allowed for equilibration at each point. Recently, automated techniques have been developed, which in some cases involve the slow continuous admission of the adsorptive and thus provide a measure of the adsorption under quasi-equilibrium conditions. Alternatively a carrier gas technique, along with conventional gas chromatographic equipment, may be employed -provided that the adsorption of the carrier gas is negligible under the conditions used. Prior to the determination of the isotherm, it is usual to remove all physisorbed material. The exact conditions required to attain a "clean" surface depend on the nature of the system. For the determination of the surface area and mesopore size distribution by nitrogen adsorption, outgassing to a residual pressure of $\sim 10^{-4}$ Torr is considered acceptable. Determination of the outgassed mass of the sample is one of the major sources of error (or at least of discrepancy between different experimenters). Inorganic oxides are usually outgassed at temperatures $\sim 150°$C whilst microporous carbons and zeolites require higher temperatures ($\sim 300°$C).

4.2 *Determination of surface area*

It is now standard practice to apply the Brunauer-Emmett-Teller (BET) method to derive the surface area from physisorption isotherm data. For this purpose it is convenient to apply the BET equation in the form

$$\frac{p}{n^a(p^0 - p)} = \frac{1}{n_m^a C} + \frac{(C-1)}{n_m^a C} \cdot \frac{p}{p^0}$$

where n^a is the amount adsorbed at the relative pressure p/p^0, n_m^a is the monolayer capacity and C is a constant, which is dependent on the isotherm shape.

According to the BET equation, a linear relation is given if $p/n^a(p^0-p)$ is plotted against p/p^0 (i.e. the BET plot). In this manner it is possible to obtain n_m^a, but the range of linearity of the BET plot is always restricted to a limited part of the isotherm -usually not above $p/p^0 \sim 0.3$.

The second stage in the application of the BET method is the calculation of the surface area, A (BET) -often termed the "BET area"- from n_m^a. This requires a knowledge of the average area, a_m (i.e. molecular cross-sectional area), occupied by each adsorbed molecule in the complete monolayer.
Thus,

$$A(\text{BET}) = n_m^a \cdot L \cdot a_m$$

where L is the Avogadro constant.

It is usually assumed that the BET nitrogen monolayer is close-packed, giving $a_m(N_2) = 0.162$ nm^2 at 77 K. However, it must be kept in mind that a constant value of $a_m(N_2)$ is unlikely and that caution needs to be exercised in dealing with surfaces which give rise to either especially strong or weak adsorbent-adsorbate interactions which are able to influence the packing.

It is now recognized that the underlying BET *theory* is unsound since it is based on an oversimplified extension of the Langmuir mechanism to multilayer adsorption. To obtain a reliable value of n_m^a it is necessary that the knee of the isotherm is fairly sharp (i.e. the BET constant C is not less than ~ 100). A very low value of C (< 20) is associated with an appreciable overlap of monolayer and multilayer adsorption and the application of the BET analysis is then of doubtful value.

In view of the complexity of physisorption, it has been found useful to apply an empirical procedure for isotherm analysis. This approach makes use of standard adsorption data obtained with non-porous reference materials and attempts to interpret the differences in isotherm shape in terms of the various mechanisms of physisorption. In favourable cases, it can provide an independent assessment of the total surface area of mesoporous or macroporous solids and the *external* area of microporous solids.

4.3 *Assessment of microporosity*
Physisorption in pores of molecular dimensions is associated with enhanced adsorbent-adsorbate interactions and takes place at very low p/p^o. In addition, there appears to be a cooperative micropore filling process which occurs at somewhat higher p/p^o -but still before the onset of capillary condensation. These micropore filling processes lead to a distortion of the isotherm shape in the monolayer range and in the absence of capillary condensation they are followed by multilayer adsorption on the relatively small *external* surface. The net result is the appearance of a classical "Langmuir" (or Type I) isotherm, which was formerly attributed to monolayer adsorption. It is now generally agreed that the values of surface area as derived by either the Langmuir or the BET analysis are incorrect.

If the plateau is virtually horizontal, the limiting uptake can be taken as a measure of the micropore capacity since multilayer adsorption on the external surface is negligible. If the isotherm has a finite slope in the multilayer region, the micropore capacity and external area can be evaluated provided that capillary condensation is absent or confined to high p/p^o.

To convert the micropore capacity into the micropore volume, it is usually assumed that the pores are filled with liquid adsorptive -as in the case of mesopore filling. However, this does not allow for the fact that the degree of molecular packing in small pores is affected by the pore size and shape. To allow for this complication, it is recommended that the term *apparent micropore volume* should be adopted and linked with the adsorption of a particular gas.

As indicated earlier, no reliable procedure has been developed for the computation of the micropore size distribution from a single isotherm. For this purpose it is necessary to employ a range of adsorptive molecules of different size (preferably globular) and take into account the different stages of micropore filling.

4.4 *Assessment of mesoporosity*
Capillary condensation of nitrogen leads to one of the major methods to characterize mesoporosity. With other methods also involving the curvature of a meniscus it is presented in the next section.

5. Methods depending on interfacial curvature

A liquid/gas or liquid/liquid interface contained within a pore will tend, at equilibrium, to assume a shape of uniform mean curvature (gravity effects being altogether negligible at this scale). The value of the mean curvature will depend on the relative wettability of the pore wall by each of the two fluids separated by the interface, and on the size and shape of the pore. In a uniform cylindrical pore of *radius r*, or in a parallel-sided slit of *width r*, the mean curvature C will be equal to $-2\cos\theta/r$, where θ is the contact angle (conventionally measured through the denser of the two fluids). In pores of less regular shape, the curvature cannot be calculated ; in pores of non-uniform cross-section, there may be regions where no stable positions of the interface exist. Nevertheless, C remains related, in principle at least, to the reciprocal of the "pore size".

Two equilibrium conditions can be stated for such an interface. For *hydrostatic* equilibrium, the product of the curvature C and the interfacial tension σ will equal the difference in hydrostatic pressure, ΔP, between the more and less dense fluids :

$$\Delta P = \sigma C \qquad\qquad (Laplace\ equation)$$

Moreover, if these two fluids are a pure liquid, of molar volume V_m^l, and its vapour, then under conditions of *diffusional* equilibrium the vapour pressure p at the temperature T will differ from the normal saturation vapour pressure p^o according to

$$\frac{RT}{V_m^l}\ln p / p^o = \sigma C \qquad\qquad (Kelvin\ equation)$$

where R is the universal gas constant. These two conditions are not independent, of course, but since hydrostatic equilibrium will usually be established many orders of magnitude more quickly than diffusional equilibrium, they may be treated as independent in practice.

Evidently, then, measurements of either p/p^o or of ΔP can be used to determine C and, thence, the pore radius r. These principles underlie the methods to be described hereafter.

5.1 *Capillary condensation method*
Physisorption by a mesoporous solid occurs in two stages : the initial part of the adsorption isotherm follows the same path as that given by the corresponding non-porous solid of the same surface area (i.e. monolayer-multilayer adsorption on the mesopore walls) ; secondly, the upward deviation at higher p/p^o is associated with the progressive filling of the mesopores by the process of capillary condensation. If the adsorbent contains no macropores, the isotherm reaches a plateau at high p/p^o, where the mesopore filling is complete. The total mesopore volume, V_p, can be derived from the amount of vapour adsorbed at the plateau (i.e. as $p/p^o \rightarrow 1$) by assuming that the pores have been filled with the condensed adsorptive in the normal liquid state. If the pore size distribution extends continuously into the macropore range, or if swelling of the adsorbent occurs, the plateau may be indistinct -or even non-existent- and in that case the assessment of total pore volume is questionable.

Mesopore size calculations are usually made with the aid of the Kelvin equation, which in its simplest form becomes

$$r_k = \frac{2\sigma^{lg}V_m^l}{RT\ln (p/p^o)}$$

and relates p/p^o, the relative pressure at which condensation occurs, to r_K, the radius of the equivalent hemispherical meniscus. σ^{lg} and V_m^l are respectively the surface tension and the molar volume of the liquid condensate.

If the radius of a cylindrical pore is r_p and a correction is made for the thickness, t, of a layer already adsorbed on the pore walls, then

$$r_p = r_K + t$$

Correspondingly, for a parallel-sided slit, the slit-width, d_p, is given by

$$d_p = r_K + 2t$$

Values of t are derived from adsorption data determined on an appropriate non-porous solid.

A number of different computational procedures have been proposed to obtain the mesopore size distribution from nitrogen adsorption data. All of them are more or less related to the well known "BJH" procedure (after Barrett, Joyner and Halenda). These procedures are based on the notional emptying of the mesopores by the step-wise reduction of p/p^o, allowance being made for the thinning of the multilayer in those pores already emptied of condensate. It is necessarily assumed that the meniscus curvature is controlled by the pore size and shape, that the pores are rigid and confined to the mesopore range and that there are no pore blocking effects. Furthermore, the derived pore size distribution is dependent on whether the adsorption or desorption branch of the hysteresis loop is used for the computation.

It is evident that the computation of mesopore size distribution is subject to a number of uncertainties and indeed the derived distribution may often give a misleading picture of the true pore structure. On the other hand, gas adsorption is one of the few non-destructive methods available for investigating mesoporosity and the various distinctive features of physisorption isotherms (including the types of hysteresis loops) have been found to be extremely useful for the characterization of industrial adsorbents and catalysts.

5.2 Intrusion methods

A *non-wetting liquid* $(\pi/2 < \theta \le \pi)$ requires a positive excess hydrostatic pressure ΔP to be applied to enable it to enter pores of radius r; ΔP will vary inversely with r. This principle is the basis of *mercury porosimetry*.

A weighed sample is enclosed in a stout metal bomb, and evacuated to remove air from the pores. Mercury is then admitted to fill the cell and surround the sample, and is subjected to progressively increasing pressures, applied hydraulically. At each pressure P, the corresponding volume V of mercury contained in the cell is measured. (Alternatively, V may be made the independent variable, yielding measurements of $P(V)$; many commercial instruments work in this way).

It is assumed that as the pressure is increased, mercury enters pores in decreasing order of size. Thus, if ΔV is the volume intruded between P and $P + \Delta P$, it will equal the volume of pores with radii between r and $r - \Delta r$, with

$$r = -\frac{2\sigma\cos\theta}{P}$$

In this way, a volumetric distribution of pore sizes is obtained.

This interpretation evidently depends on the validity of the geometrical and other assumptions involved. The radius r is to be regarded not as a literal pore dimension, but rather as the size of an equivalent cylindrical pore which would fill at a given pressure. A value of the factor $\sigma\cos\theta$ must be assumed; customarily, σ is taken to be 484 mN m^{-1}, the value for pure mercury, despite the likelihood of contamination by hydraulic fluid. The contact angle θ is usually assumed to be 141°, for no stronger reason than that of tradition. Most importantly, the presumption that the pores are invaded in decreasing order of size may be invalidated by network effects, which imply that the sequential filling of pores is dictated primarily by their mode of interconnection.

Experimentally, the pressure can be varied between 0.1 and 2000 bars, corresponding to *cylindrical pore radii between 75* μm *and 3.5* nm. (At high pressures, a blanck correction must be applied to compensate for the compressibility of mercury and for elastic distortion of the cell and other component parts). Adequate control of temperature is essential, since the pressure within a closed, liquid-filled cell will be strongly temperature-dependent. This is not usually provided for in commercial instruments, and absolute calibration of pressure and volume transducers is not normally available. At the high pressures employed, the *sample may be deformed elastically or even damaged irreversibly*. On reducing the pressure, a substantial volume of mercury may be retained in the pores. The method is therefore destructive.

Despite these potential drawbacks, *mercury porosimetry is very widely accepted as a standard measure*

of total pore volume and of pore size distribution, *in the macro- and mesopore ranges*. In those rare cases where there may be specific interaction between mercury and the material under examination, the method may be modified by substitution of another non-wetting fluid.

5.3 *Suction method*

When *a wetting liquid* ($0 \leq \theta < \pi/2$) is held within a porous solid, the Laplace equation predicts that it will experience a reduced hydrostatic pressure, inversely proportional to the radius of pores in which menisci are formed. This principle is the basis of *suction porosimetry*. In practice, water is often chosen as a suitable wetting liquid for most inorganic solids.

An initially saturated sample of a porous medium is placed on a permeable support, through which it maintains hydraulic contact with a reservoir of water. The hydrostatic pressure in the reservoir is progressively reduced, and the volume of water withdrawn from the sample is recorded. The resultant relationship between reduced pressure (suction) and equilibrium saturation is often known as the *moisture characteristic* of the porous solid, and is related to the pore size distribution in much the same way as is the mercury intrusion curve.

The lower limit of pore size accessible to this technique will be reached when vapour bubbles nucleate in the reservoir. For this reason, the liquid should be thoroughly outgassed. Suctions of several bars may then be achieved, corresponding to *pore radii as small as a few tenths of a micron*. Even this limit can be surpassed (i.e. smaller pores detected), in principle, by increasing the gas pressure above the sample, rather than reducing the liquid pressure beneath it.

Clearly, the pore size of the supporting plate must be smaller than that of the sample.

For solids not wetted by water, or for those that are appreciably water-soluble, other liquids (preferably of low volatility, such as silicone oils) may be used.

When the direction of pressure change is reversed, marked hysteresis is often found between drainage and rewetting. The pore size distribution is customarily derived from the drainage curve. This is *closely analogous to the mercury intrusion curve*, and where the two methods overlap they give reasonably concordant results. For the same reason, the suction method is open to the *same objections as mercury porosimetry, notably model-dependence and interference from network effects* (also found with the capillary condensation method).

5.4 *Maximum bubble pressure method*

This method is usually applied to thin samples of consolidated materials, e.g. paper, *membranes*, filter discs, etc ... The sample is mounted horizontally in a cell in such a way that its outer edge is sealed. It is then saturated with a wetting liquid (usually water) and a thin layer (2-3 mm) of liquid is allowed to remain on top of the sample. An increasing air pressure is then applied beneath the sample, until an air bubble is forced through the sample. This will occur at the largest through pore in the sample, whose size can then be calculated from the Laplace equation in the usual way.

Applied in this fashion, the method is chiefly useful for discovering imperfections in thin films. It can be extended, however, to give a distribution of pore sizes, by continuing to increase the gas pressure and measuring the increasing gas flow rate. It thus becomes a variant of the permeability method, in which the population of pores being sampled is determined by capillarity.

Clearly, the pressures attainable may be limited by the mechanical strength of the material ; *a lower limit of pore size of some microns is to be expected.*

6. Fluid flow

This method aims to derive the porous structure of a plug of material from its permeability to a fluid flow.

The steady state flux of a fluid through a porous material is sensitive to all structural aspects of the material. In its simplest application an elementary measurement of gas or liquid flux through a compact is all that is required, but a variety of extensions including the use of two component mixtures and non-steady state flow have been discussed in the literature.

In practice the interpretation of flux data can become complicated -even for the steady state- and is subject to uncertainties which render such procedures inadvisable as characterization methods without supplementation by other techniques.

The steady state volume flux J_v of an *incompressible fluid* through a porous medium of cross sectional area A_c, length l and porosity ε under a pressure differential Δp can be measured as a mean fluid velocity u in the porous medium, and can be also be expressed in terms of the mean velocity in the pores u_p,

$$J_v = A_c u = A_c \varepsilon \, u_p$$

In the classical Kozeny treatment, the Poiseuille equation links this experimental quantity to the hydraulic radius r_h, equal to ε/A, where A is the surface area per unit volume of porous medium, by

$$J_v = \frac{\beta_c \, \varepsilon \, r_h^2 \, \Delta p}{\eta \quad l} = \frac{\beta_c \, \varepsilon^3 \, \Delta p}{\eta \, A^2 \, l}$$

Here β_c is a factor dependent on pore structure. Kozeny assigned values of $\beta_c = 0.5$ for cylinders and 0.33 for slits, Carman divided these factors by τ^2, where τ is interpreted as a tortuosity factor to which he gave a value of 1.5.

Steady state gas flow is more complicated because compressibility and molecular effects, which predominate at low pressures, introduce a pressure dependence. By the same token however the interpretation is richer. A general equation, due to Weber, recognizes three components of the gas phase flux J due to Poiseuille flow, slip flow, and self diffusion respectively. The measured flux can be expressed in terms of the permeability (or mean diffusion coefficient) P_g by

$$J = A_c \, \varepsilon \, P_g \, \frac{\Delta p}{RTl}$$

and P_g can be expressed in terms of the three components by the equation

$$P_g = D_{gK} \left[\frac{3\pi}{32} \frac{\beta_p \, r_h}{\beta_K \, \lambda} + \frac{\pi}{4} \frac{2\beta_s \, r_h / \lambda}{(1 + 2\beta_s \, r_h / \lambda)} + \frac{1}{1 + 4\beta_K r_h / \lambda} \right]$$

Here the pressure dependence is expressed through the (hydraulic) Knudsen number, r_h/λ where λ is the mean free path and is given, according to simple kinetic theory, by

$$\frac{1}{\lambda} = \frac{p}{\eta} \left\{ \frac{2M}{RT} \right\}^{1/2}$$

The factor D_{gK} is the Knudsen diffusion coefficient

$$D_{gK} = \frac{4}{3} \beta_K r_h \left[\frac{8RT}{\pi M} \right]^{1/2}$$

Three new structure factors β_K, β_s, β_p, are introduced in these equations and are related to the ratios of the measured permeability components in real materials to the same component in a single circular capillary having the same hydraulic radius as the experimental material. Their geometry dependence is involved since it includes both cross-sectional shape and short tube effects.

In general P_g passes through a minimum with r_h/λ, becoming linear at high pressure and passing to the limit D_{gK} at low pressure. Short tube effects, which truncate long trajectories inside porous media, usually eliminate the minimum and simple linear behaviour is observed.

The interpretation of flux data must be further considered in heterogeneous media due to the effects of pore size distribution and pore connectivity. This is conveniently done in terms of the structure factors. Structure factors have been calculated for a wide range of network pore models and simple analytical equations are available for some of these. It should be noted that in most porous compacts pore properties are likely to vary with position on a macroscopic scale. Structure factors are modified by these variations which can also have profound effects on non-steady state flow.

The foregoing assumes that adsorption is negligible, although in practice adsorption can give rise to extra fluxes not accounted for in the simple kinetic theory treatments referred to above as well as to blocking effects which can modify the channel available for gas phase flow. Applications of flow methods should always be critically examined with this in mind.

7. Calorimetric methods

Brief accounts are given hereafter of a few calorimetric methods, quite different from each other, which provide an independent assessment of the surface area, microporosity or mesoporosity of a porous solid.

7.1 Immersion calorimetry

This method is based on the determination of the enthalpy change occurring on immersing a "dry" sample into a liquid. This enthalpy change is related to the extent of the solid *surface*, to the presence of *micropores* and to the chemical and structural *nature* of the surface.

To assess the overall *surface area*, in favourable cases one may simply determine the enthalpy of immersion of the outgassed solid into the liquid. For this purpose, the knowledge of the areal enthalpy of immersion of the solid is a prerequisite. This requires the measurement of the enthalpy of immersion of a non-microporous reference sample of known surface area and with similar nature of the surface and after outgassing under the same conditions. The immersion liquid is usually either water (for any hydrophilic solid, like mineral oxides) or an organic liquid (n-hexane, benzene, ...) for hydrophobic solids like carbons. Even for microporous solids, the enthalpy of immersion is approximately proportional to the extent of the surface area including the walls of the micropores (in contrast to the BET method). Another approach, which now determines the non-microporous part of the surface area, is a modified Harkins and Jura (HJ) procedure where the solid is precovered with ca. two layers of adsorbate prior to immersion, so that the micropores are filled and the chemical nature of the surface is screened. In this case there is no need for any calibration or reference experiment and only the surface tension of the liquid/vapour interface must be known.

To assess the area associated with *microporosity* one simply needs to take the difference between the overall surface area contribution and the "non-microporous" surface area. Information on the size of the micropores can be obtained from the kinetics and enthalpy of immersion into a set of liquids with increasing molecular size.

Immersion calorimetry has the advantage of being sensitive and accurate, but it requires the preparation of sealed thin-walled or brittle-ended glass bulbs enclosing the outgassed or pre-covered sample. Rather

specialised expertise is therefore involved.

7.2 *Gas adsorption calorimetry*
Adsorption calorimetry of argon and nitrogen also provides a means for detecting microporosity, which enhances the enthalpy of adsorption of both gases (as compared with a non-porous surface). In case the enhancement is appreciable with nitrogen but negligible with argon, this will usually mean that micropores smaller than 1 nm are absent and that the quadrupolar N_2 molecule is in specific interaction with chemical functions of the surface.

7.3 *Liquid adsorption calorimetry*
A liquid-flow microcalorimeter can be used to determine the enthalpy of displacement of, say, an alkane (e.g. n-heptane) by an alcohol (e.g. n-butanol). After pre-calibration with a similar sample of known surface area, one obtains a value for the surface area of the sample under study. This method does not assess the porosity proper (only the surface area) and has a limited accuracy but it is simple and convenient, specially when the sample must not be dried.

7.4 *Thermoporometry*
This is a method to assess the *mesoporosity*. It relies on the depression of the melting point of a condensed adsorbate, due to the presence of pores. The porous solid is usually first saturated with either water or benzene, frozen down to, say, 213 K and then studied on heating in a Differential Scanning Calorimetry (DSC) equipment up to the bulk 3D-melting point T_{fus}^b of the adsorbate. The melting temperature is depressed by ΔT in the mesopores, down to T_{fus}^p, which is pore-size dependent so that an appropriate analysis of the experimental DSC curve leads to a pore-size distribution curve. The adsorbate condensed out of the mesopores finally melts at the normal 3D-melting point and may be used for internal calibration.

For this method a low-temperature DSC must be used but has the advantage of providing the *internal size of the pores* (in the case of bottle-shaped pores) in the 1.5 to 150 nm range whereas the common capillary condensation method based on the N_2 desorption isotherm are expected to provide the sizes of the pore-openings (when they are smaller than the pore proper). Clearly, these two methods are complementary. Thermoporometry is well suited for studies of wet porous samples (which could not withstand being dried or evacuated) and to foresee, of course, the effect of frost ; whereas the accessibility of pores to gases or liquids is advantageously studied by the capillary condensation method.

8. Other methods

8.1 *Size exclusion chromatography (SEC)*
The porous material is packed into a column which is inserted into a high pressure liquid chromatography (HPCL) equipment. Solutions of polymers of known molecular mass and low polydispersity are successively injected and eluted. For each solution, the retention volume V_R is measured. Smaller probe molecules penetrate more pores (provided a smaller pore size is present in the material), have a longer path and therefore lead to a larger retention volume.

The assumptions in the calculation of the pore size distribution of the packing material are that the probe molecules are spheres and the pores are cylindrical in shape. It is further assumed that the polymer probe has zero enthalpy of transfer from the bulk solvent outside the particles to the solvent within the pores.

Unlike other methods, this approach requires no assumptions about the contact angle or surface tension.

The method is particular suitable for the assessment of meso- and macroporosity of swelling polymers.

8.2 *Xenon NMR*

This technique for characteristing porous media relies on changes in the *NMR chemical shift of a probe molecule that accesses an internal void*. The method has been developed with ^{129}Xe and depends on the structure and ease of diffusion of molecules in the pore structure. It has particular applications in the case of micropores e.g. with zeolites, and microporous silicas, aluminas, polymers ...

A contribution to the NMR chemical shift for xenon, adsorbed, say, in a zeolite, is due to xenon-wall interactions : it depends on the structure and *dimensions* of cages and channels and the ease of diffusion in the zeolite crystal.

This technique, which has probably scope for more development, is non-destructive and can provide microscopic information on pore networks. An understanding of the influence of the different contributions to the measured NMR shifts is required for the technique to be fully exploited. In this respect, measurements at below ambient temperatures and at progressive degrees of pore filling are informative.

8.3 *Ultrasonic method*

The attenuation and velocity of propagation of ultrasound in porous solids depends on pore size and porosity. The theory of the method is very complex and has been developed mainly for two phase (solid/void) systems. Thus ultrasonic techniques can be applied to assess the width of voids, d and porosity, ε, from variations in the ultrasonic velocity, v ,and attenuation, α_a. The method is appropriate when $\sigma d > 0.2$, where σ is the longitudinal wave number in the matrix given by :

$$\sigma = \frac{\omega}{v}$$

ω ($=2\pi v$) being the circular frequency of the sound wave of frequency v.

Typically, when $v > 10^7$Hz, the method is applicable for the non-destructive examination of voids in solids, where $d > 1\mu$m. The method is applicable to materials with porosities up to ~30%, such as solid foams, rocks and soils, but is also valuable in the detection and assessment of voids in ceramics, steels, alloys etc ...

IV Conclusions and Recommendations

Specific recommendations and indications on the limits of applicability of each method are given in the various sections of this document. In addition, we give hereafter a number of general remarks which summarize the philosophy of the Subcommittee :

1. The complexity of the porous texture of materials is such that *even on theoretical grounds the concepts which can be used to describe the texture usually entail the introduction of simplifying assumptions.*

2. No experimental method provides *the* absolute value of parameters such as porosity, surface area, pore-size, surface roughness : each gives a characteristic value which depends on the principles involved and the nature of the probe used (atom or molecule, radiation wavelength ...). One cannot speak of *the* surface area of an adsorbent but, instead, of its "*BET-nitrogen* surface area", "*equivalent* BET-nitrogen surface area", modified HJ-*calorimetric* surface area, *cumulative* water thermoporometry surface area etc ...

3./ The selection of a method of characterization must start from the material and from its intended use.

4. The method chosen must indeed assess a parameter *related as directly as possible* to phenomena involved in the application of the porous material. In this respect, it may often be advisable to select a method involving physical phenomena similar or close to those involved during the practical application (*i.e.* adsorption or capillary condensation methods if the porous substance is to be used as a dessicant, or a freezing point depression method if one is interested in the frost resistance of a construction material ...) so that the parameters determined are appropriate.

5. Rather than to "check the validity" of distinct methods, certified reference materials are needed to establish how these methods differ and, of course, to calibrate any individual equipment or technique.

6. As a consequence, *one must not look for a "perfect agreement" between parameters provided by different methods.* Such an agreement, when it occurs, is not necessarily a proof of the validity of the derived quantities.
Instead, one must be aware of the specific, limited and complementary significance of the information delivered by each method of characterization of a porous solid.

Acknowledgements

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