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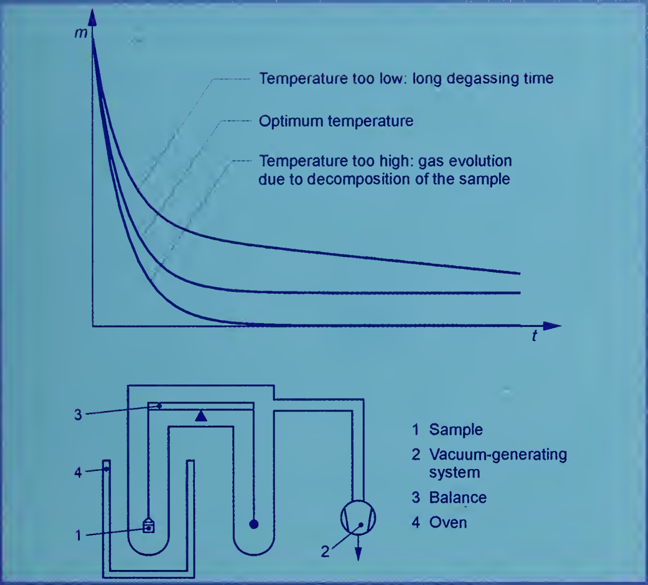
Porosity and Specific Surface Area Measurements for Solid Materials



Peter Klobes, Klaus Meyer
and Ronald G. Munro

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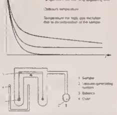

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Porosity and Specific Surface Area Measurements for Solid Materials

Peter Klobes and Klaus Meyer
Bundesanstalt für Materialforschung und -prüfung (BAM)

Ronald G. Munro
Materials Science and Engineering Laboratory,
National Institute of Standards and Technology

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Foreword

NIST SRM 1917 / CRM BAM-P127 (Mercury Porosimetry Standard), consisting of pellets of Al_2O_3 with a diameter of about 1 mm, was certified in August 2002 as a nanoporous reference material for mercury porosimetry. This reference material was the first jointly produced SRM/CRM of NIST and BAM. To complement this international reference material, NIST and BAM extended their collaboration to develop the present Guide addressing the broader metrological aspects of porosity and specific surface area measurements. The Guide examines the practical issues that need to be considered when conducting a measurement or analysis by one of the more commonly used porosimetry techniques, especially the gas adsorption and mercury intrusion methods. The Guide is written for persons who are not necessarily experts in the field, but who do have some basic knowledge and familiarity of the issues involved. Wherever appropriate, references to pertinent national and international standards and other comprehensive sources of information are noted.

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Disclaimer

Certain commercial equipment, instruments, or materials may be identified in this paper in order to specify an experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by either the National Institute of Standards and Technology or the Bundesanstalt für Materialforschung und -prüfung, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

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1. Introduction

Properties such as specific surface area, pore size, and pore size distribution are important material characteristics in many processing applications, including those for catalysts, sintered materials, pharmaceutical products, and chromatographic carriers. Improper pore and surface area analyses contribute to poor product quality, high rejection rates, and economic losses. Consequently, materials suppliers and manufacturers increasingly are using measurements of porosity and specific surface area as an integral part of their quality assurance programs (Gorman 2001).

1.1 Scope of the Present Guide

The motivation for this guide stems from a joint program between the Bundesanstalt für Materialforschung und -prüfung (BAM, Germany) and the National Institute of Standards and Technology (NIST, United States) to develop and provide jointly certified reference materials (NIST SRM 1917 / CRM BAM-P127). The present effort addresses issues and concerns pertaining to the measurement of specific surface area and porosity for porous or highly dispersed (particulate) materials, such as powders and compacts, which are characterized by a large surface to volume ratio.

In recent years, special interest has been focused on the ability to make meaningful comparisons among test results obtained by different individuals or groups and at different times and locations (Malghan *et al.* 1995). The need for consistency in these measured values has created a particular demand for the calibration of the equipment used for testing and analysis. Concurrently, the need for consistency also has created a need to understand and recognize the limits of applicability of alternative measurement devices and methods (see, for example, early round robin results, Munro *et al.* 1995). The use of certified reference materials has evolved as an essential aspect of the approach used to address both of these major concerns.

The present guide is by no means an exhaustive and comprehensive text on pore analysis. Rather, this volume attempts to convey the practical issues that need to be considered when conducting a measurement or analysis by one of the more commonly used porosimetry techniques, especially the gas adsorption and mercury intrusion methods. The guide is written for persons who are not necessarily experts in the field, but who do have some basic knowledge and familiarity of the issues involved. Wherever appropriate, references to pertinent national and international standards and other comprehensive sources of information have been included. Much of the basis for the text presented here stems from studies conducted at BAM, NIST, and other major facilities and from the broad experience gained over many years of participation in round robin tests and standards development efforts worldwide.

1.2 The Nature of Porous Solids

Particles in finely divided powders contain many unsaturated bonds at the surfaces of the particles. Due to this fact, some of these particles may bond together weakly to form a loosely coherent secondary particle, generally called an aggregate (Everett 1972; Everett 1986; Haber *et al.* 1991; Hackley *et al.* 2001). If the particles are joined more rigidly, as may occur under the influence of mechanical pressure and elevated temperature, these assemblages of particles are called agglomerates. Some of the possible cavities that may form in aggregates of spherical and plate-like particles are illustrated schematically in Figure 1.1.

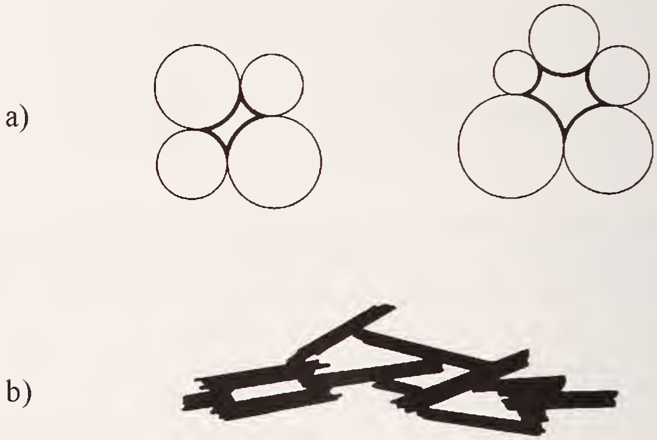


Figure 1.1. *Pores in different aggregates (Gregg 1982): a) spherical particles; b) plate like particles.*

Porous and finely divided solids formed in this manner are distinguished by large surface to volume ratios. These materials often exhibit enhanced chemical reactivity, higher adsorption capacity, and lower sintering temperature. In many practical applications exploiting this large ratio, the size of the accessible surface is as important as the chemical composition. For example, certain natural minerals, such as zeolites, have well defined characteristic cavities with pore sizes on the order of atomic dimensions. Their large specific surface areas allow them to possess not only a higher adsorption capacity, but also an enhanced functionality with respect to the separation of gases.

These materials are especially important in areas such as the chemical industry, materials engineering, ceramics production, and environmental engineering. Examples of their applications include the development and production of:

- catalysts
- adsorbents
- pigments
- pharmaceutical products
- chromatographic carriers
- sintered materials
- building materials
- ceramics
- filters

Significantly, every application appears to have an optimum specific pore size distribution.

A further consideration for porous materials is the fractal nature of the microstructure of the material. This issue is discussed in Chapter 2, Section 4. In essence, measurements of surface features depend on the size of the "gauge" that is used to probe the surface. Consequently, results derived from different studies will be comparable only if the same gauge is used. For comparability, therefore, it is necessary to adhere strictly to a regulated procedure which may include the standardization of instruments, detailed measurement procedures (including such considerations as sample pretreatment, temperature and duration of heating, and degassing), and the use of certified reference materials for the calibration of the instruments.

1.3 Important Characteristics

The size and morphological structure of a grain can have a significant influence on the processing of raw materials and on the effectiveness of their use. Such is the case, for example, for materials used as adsorbents, membranes, and catalysts. Consequently, numerous measurement procedures have been developed to characterize powders and porous solids with respect to these features (Sing *et al.* 1985; Rouquerol *et al.* 1994). Among the most commonly determined characteristics are the particle size distribution, the specific surface area (area per unit mass), the specific pore volume (pore volume per unit mass), and the pore size distribution. Additionally, several types of density measurements have been used as auxiliary information, especially for powders (for example, tap density and envelope density).

Rather generally, these characteristics are derived quantities; *i.e.*, they are calculated from the measured results of other quantities. Often the relevant measurements involve assumptions regarding both the quantities that are being measured and the validity of the measurement procedures for the given material. As such, the end results often are strongly dependent on the selected measurement and analysis methods. This issue is discussed in Chapter 3. We make the observation here to emphasize that the values derived from these methods must be considered comparative or relative values. Indeed, quantities determined in this manner are known formally as procedural quantities (Munro 2003). Such quantities do not have the theoretical basis to allow their values to be calculated independently of the associated measurement procedure.

2. Porous and Highly Dispersed Solids

The use of porous materials has evolved over a long period of time and in a wide variety of industries. In each application area, there have been efforts to characterize and describe the materials in ways that are meaningful to that area. As a result, different terminologies have evolved from different areas to describe the same features. Likewise, different measurement procedures have evolved to quantify what should be the same characteristic. A comprehensive discussion of the appropriate nomenclature is given in earlier volumes of the NIST Recommended Practice Guides (Hackley *et al.* 2001; see also Jillavenkatesa *et al.* 2001). This issue also has been addressed by the International Union of Pure and Applied Chemistry (IUPAC). In the interest of clarity and consistency, certain selected terms important to porous and dispersed materials are reviewed in this chapter, and a succinct glossary of terms is given in Appendix 4.

2.1 General Definitions and Terminology

Several definitions and terms used for the characterization of porous or dispersed solids warrant discussion because of their special relevance or their potential for confusion. The primary focus here is on sorption and intrusion properties.

2.1.1 Physical Adsorption (physisorption)

The physical adsorption of gases is an important part of several measurement techniques used for determining specific properties of porous solids. Adsorption, in general, occurs whenever a substance (the adsorptive, such as an adsorbable gas) accumulates at an interface or in an interfacial region. If the adsorption process involves only the weaker intermolecular forces that result from van der Waals interactions or hydrogen bonding and if there is no significant change in the electronic orbital states of the interacting species, then the process is called physical adsorption. The term physical adsorption is often contracted to physisorption. At constant temperature, the relation between the amount of substance adsorbed and the equilibrium pressure of the gas is known as the adsorption isotherm.

> Physisorption should not be confused with chemical adsorption (chemisorption). Chemical adsorption is an adsorption process in which significant chemical bonds are formed at the interface or in the interfacial region. These bonds change the electronic orbital states of the interacting species and may affect measurable properties. A significant heat of adsorption also may result from chemical adsorption.

To form a clear picture of physical adsorption, it is convenient to regard the interfacial layer as comprising two regions: the surface layer of the adsorbent (often called the adsorbent surface) and the space adjacent to the surface (the adsorption space) in which enrichment of the adsorptive can occur. The adsorptive in the adsorption space is considered to be in a fluid phase. To distinguish the adsorptive in the fluid phase from the adsorptive material already adsorbed onto the surface, the material adsorbed onto the surface is known as the adsorbate.

It is sometimes useful to make a further distinction between external and internal regions of the adsorbent surface, especially when discussing porous adsorbents of high surface area. The envelope surrounding the discrete particles or agglomerates of the adsorbent usually is regarded as the external surface. However, it is difficult to define such surfaces precisely because the surfaces rarely are smooth on an atomic scale. A suggested alternative convention is to assume that the external surface includes all the prominences and any surface cracks that are wider than they are deep. With that convention, the internal surface of the adsorbent then consists of the cracks, pores, and cavities that are deeper than they are wide and that are accessible to the adsorptive. The latter restriction is a procedural condition that results in a demarcation between internal and external surfaces that depends, in practice, on the method of assessment and the nature of the pore size distribution. Pores and cracks smaller in dimension than the absorptive may be, in effect, inaccessible.

The notion of external surface may also be used to define a measure of surface roughness. If the nominal external envelope of the solid has a well defined geometric shape, then the ratio of the area of the external adsorbent surface to the area of the geometric shape may be taken as the roughness factor for that surface.

2.1.2 Sorption

If molecules of the adsorptive penetrate the surface layer and enter into the structure of the bulk solid, a different term, absorption, is used. However, in some circumstances, it may be difficult, impossible, or even irrelevant to distinguish between adsorption and absorption. It then becomes convenient to use a more general term, sorption, that embraces both phenomena. In this case, the generalized terms sorbent, sorbate, and sorptive also may be used.

2.1.3 Desorption

The counterpart of adsorption is called desorption. Desorption denotes the process in which the amount of adsorbed material decreases. The terms adsorption and desorption often are used adjectivally to indicate the measurement direction from which experimentally determined adsorption values have been approached, e. g. the adsorption curve (or point) may be distinguished from the desorption curve (or point). If the adsorption and desorption curves do not coincide, then the process is said to exhibit adsorption hysteresis.

2.1.4 Multilayer Adsorption

When an adsorbate begins to form on a nascent surface, it is possible for each molecule to adsorb directly onto the surface. More precisely, each molecule occupies a position of closest approach to the adsorbent. In this state, the adsorbate is said to form a monolayer. If adsorption persists in excess of monolayer adsorption, we may visualize additional layers of adsorbate forming on top of the initial monolayer, each new layer being more remote from the substrate than the preceding layer. Adsorption that progresses beyond monolayer adsorption is called multilayer adsorption. For a given state of multilayer adsorption, there may be more pore space available than is occupied by the adsorbate. If gas phase molecules from the absorptive enter and occupy this residual pore space, a process called micropore filling is said to occur. If, instead, a condensate separated from the gas phase by menisci forms in the residual pore space, the special term capillary condensation is used. The presence of capillary condensation often contributes to the occurrence of adsorption hysteresis.

2.1.5 Monolayer Capacity

The amount of adsorbate needed to cover the surface of the adsorbent with a monolayer of molecules is called the monolayer capacity and is denoted here by the symbol n_m. (We follow the convention here that quantities relating to a monolayer of adsorbate are denoted by the subscript m.) The total surface coverage then can be described with respect to a monolayer of adsorbate. For both monolayer and multilayer adsorption, the surface coverage (θ) is defined as the ratio of the amount of adsorbed substance to the monolayer capacity.

2.2 Qualitative Description of a Porous Solid

Any solid material that contains cavities, channels, or interstices may be regarded as porous, but some care must be exercised in the choice of terminology to avoid ambiguity. To aid in the classification of porous materials, distinctions may be made with respect to the types of pores in the material and with respect to the nature of the constitution of the material.

2.2.1 Pore Types

With reference to Figure 2.1, we can classify pores according to how accessible they are to an external fluid. In this context, one category (closed pores) consists of pores that are inaccessible to an external fluid and totally isolated from their neighbors, as in region (a). Closed pores influence macroscopic properties such as bulk density, elasticity, mechanical strength, and thermal conductivity, but they are inactive in processes such as fluid flow and adsorption of gases. On the other hand, pores that have a navigable channel of communication with the external surface of the body (like b, c, d, e, and f) are described as open pores. Open pores are further classified into "through pores" and "blind pores." Through pores have an open channel that begins at one location on the surface, extends into the particle, and re-emerges on the surface at a different location (like the pore channels c-e-c and c-e-d). Blind pores (also called dead-end or saccate pores) are open to the surface only at one end (like b and f). A special distinction is made for blind pores like those in region of g of Figure 2.1. While these small surface irregularities are technically blind pores, it is often more useful and convenient to consider them separately as part of a distinct attribute, called surface roughness. A simple

Figure 2.1. *Schematic cross section of a porous solid (Rouquerol 1994).*

convention often used is to assume that surface irregularities are counted as pores only if they are deeper than they are wide.

Pores may be classified further according to their shape. Common shape terms include cylindrical (open c or blind f), ink-bottle (b), funnel (d), and slit shapes.

2.2.2 Pore Classes

Some materials are consolidated; *i.e.*, distinguishable microscopic particles are bound together in some manner to form a relatively rigid, macroscopic body whose dimensions exceed those of the pores by many orders of magnitude. The constituent particles themselves may be nonporous (*e.g.* sand), but the macroscopic body will still have a porosity consisting of the surrounding network of interparticle voids. In this case, the properties of the macroscopic body can be expected to be dependent primarily on the size, shape, and manner of packing of the constituent particles.

Other distinctions arise if the constituent particles themselves have a significant porosity. In such cases (*e.g.* spray-dried catalysts), it may then be necessary to distinguish between internal (or intraparticle) voids, and interparticle voids. In general, internal pores will be smaller than the voids between particles, both in size and in total volume; nevertheless, they often will provide the dominant contribution to the surface area of the solid. Which void type dominates depends on the volume/surface area ratio.

There are three special classes of pores that are expressly distinguished (Meyer 1994). The first class involves pores that are an inherent feature of a particular crystalline structure, such as occurs, for example, in zeolites and some clay minerals. Being inherent to the crystal structure, these intracrystalline pores are generally of molecular dimensions and form highly regular networks.

The second class of porous materials is distinguished by its sequential method of processing. The material is formed in two nominal steps, first by loose packing (*i.e.* aggregation) and then by consolidation (*i.e.* agglomeration) of the small particles into a macroscopic solid. Some inorganic gels and ceramics are formed in this manner. The final details of the resulting structure depend on the original arrangement of the primary particles and on their sizes and orientations.

The third distinguished class may be described as "subtractive" because certain elements of an original structure are selectively removed to create pores. Examples include porous metal oxides formed by the thermal decomposition of hydroxides, carbonates, nitrates, and oxalates and porous glasses formed by the chemical etching of multiphase solids. Many porous organic polymer membranes are formed in this way.

2.3 Quantitative Descriptions of Pore Structures

Porosity (more precisely, the volume fraction of porosity) may be defined operationally as the fraction, ε, of the apparent specific volume of the sample that is attributed to the pores: $\varepsilon = V_p/V$. The value of this fraction clearly depends on the method used to determine the apparent specific volume, V, which excludes interparticle voids (geometrical determination, fluid displacement), and on the method used to assess the specific pore volume V_p (adsorption and capillary condensation, fluid displacement, ultrasonics *etc*...). Some methods only have access to open pores (*e.g.*, those methods using a fluid), whereas other methods may access both open and closed pores (*e.g.*, methods using adsorption or scattering of electromagnetic radiation). Moreover, for a given method, the value determined experimentally depends on the size of the molecular probe (fluid displacement, adsorption) or of the gauge (stereology). Thus, a measured value of porosity is a reflection of both the physical state of the material and the experimental method used for its determination. To distinguish these three cases, it should be noted whether the specific pore volume, V_p, is due to the open pores (leading to the "open porosity"), the closed pores (leading to the "closed porosity"), or both types of pores together (leading to the "total porosity").

2.3.1 Specific Surface Area

The "specific surface area" (A) is defined as the area of solid surface per unit mass of material. In practice, what is actually determined is the accessible (or detectable) area of solid surface per unit mass of material. This distinction is important because the value determined in a measurement is dependent on the method, the experimental conditions employed, and the size of the probe (*e. g.*, the molecular size of the adsorbate or the wavelength of a radiation probe). More significantly, the specific surface area is usually deduced from measured quantities that must be interpreted using simplified models of the measurement process. Consequently, the recorded value depends inherently on the validity of the assumptions used in the model.

2.3.2 Pore Size

"Pore size," like specific surface area, it is not amenable to a precise definition. The problems already mentioned for the specific surface area are complicated further 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. As a result, the detected pore volume may depend on the sequence in which pores are encountered by the probe substance. Consequently, quantitative descriptions of pore structure usually are based on model systems.

To make the analysis tractable, systems with idealized pore shapes and sizes often are used. In practice, the shapes of pores, whether known or assumed, are preferably described in terms of a small number of shapes: cylinders (which may be appropriate 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. (We note, however, that when spherical shapes are considered, the pores are more likely to be the voids left between solid spheres in contact with each other, as happens with gels such as silica gel and zirconia gel during gelation).

The limiting feature of a pore, for most applications, is the size of the smallest dimension of the assumed pore shape. In the absence of greater precision, the smallest dimension is referred to as the width of the pore, *i.e.*, the width of a slit-shaped pore and the diameter of a cylindrical pore. (To avoid a misleading change in scale when comparing cylindrical and slit-shaped pores, the convention is to use the diameter of a cylindrical pore, rather than its radius, as its "pore width".) To facilitate discussions of pore sizes, the following conventions are recommended by IUPAC (McNaught 1997):

- Micropores: widths < 2 nm
- Mesopores: 2 nm < widths < 50 nm
- Macropores: widths > 50 nm

2.4 The Fractal Character of Porous Structures

The dependence of microstructural characteristics on the characteristic length scale of the measurement method hinders comparisons among results obtained by different methods. With rough surfaces, for example, the measured specific surface area increases as the probe is changed from hydrocarbons to small nitrogen molecules because there is an increasingly better covering of the surface as the effective radius of the probe molecule decreases.

In the mid 1980s, the insight that irregular physical structures are described only very inadequately by Euclidean geometry led to the introduction of Mandelbrot's concept of fractal geometry (Mandelbrot 1975). The important characteristic of the fractal model in porous materials is that it allows for a characteristic quantity that is independent of length scales.

The basic property of fractal objects is their so-called self-similarity (also called dilation invariance or scale invariance). Regardless of the scale of observation, one sees similar structures. Mathematically, scale invariance is a special symmetry property. The mathematical description of self-similarity leads to a non-integer, *i.e.* "fractal," dimension that is characteristic of the system.

Applying that concept to specific surface area (A), for example, A can be expressed as a limit derived from the use of probe molecules of different sizes.

$$A = \lim_{\substack{n \to \infty \\ \sigma \to 0}} n\sigma^{D/2}$$

where n = number of molecules in the monolayer, σ = area occupied by the molecules, and the exponent D is the fractal dimension.

The fractal dimension for an ideally flat surface is 2, and for the three-dimensional body (volume structure), it is 3. As the roughness of a flat surface increases, the portion of the surface extending into the 3rd dimension acquires a greater significance. Hence, one expects the fractal dimension of a porous material to be between 2 and 3. Mathematical fractals are defined constructively, therefore, self-similarity is found at all length scales. Physical fractal objects possess only limited regions of scale invariance; the interval is bounded from below by the order of magnitude of atoms, and from above by the respective macroscopic size of the object.

In recent years, numerous articles have been devoted to multilayer absorption (Pfeifer, Wu *et al.* 1989) and to finding correlations between the fractal dimension D and the characteristic properties of irregular or rugged solid adsorbents (*e.g.* catalysts), and also of macromolecules and colloid aggregates. Furthermore, there have been fractal descriptions of mass transport (diffusion, Knudsen flow) through the micro- and mesopore system of porous solids as well as of surface diffusion. Other work has centered on the fractal treatment of chaotic reactions, percolation, and aggregation (Pfeifer, Obert *et al.* 1989).

Experimentally, the fractal dimension D can be determined from the slope of a number of doubly logarithmic plots (log-log plots), of which we quote some examples:

a) Monolayer adsorption of molecules of different size;
number (n) of molecules in the monolayer versus the area (σ) occupied
$\sigma \log n = (D/2)\log \sigma + C$

b) Determination of pores by N_2 multilayer adsorption/desorption;
pore volume distribution (dV/dr) versus pore radius (r)
$\log(-dV/dr) = (2 - D)\log r + C$

c) Mercury porosimetry
First derivative of the pore volume with respect to the Hg intrusion pressure (dV/dP_{HHg}) versus P_{Hg}
$\log(dV/P_{Hg}) = (D - 4)\log P_{Hg} + C$

d) Plot of the BET specific surface area (S_{BET}) of sieve fractions versus the mean particle diameter (d)
$\log S_{BET} = (D - 3)\log d + C$

(The quantities C are additive constants and do not influence the slope).

A quasi-model-free thermodynamic method for calculating fractal dimensions directly from experimental adsorption and mercury intrusion data has been proposed by (Neimark 1990).

Fractal dimensions can also be determined by diffraction and scattering experiments (*e.g.* small angle x-ray scattering). In addition, image processing is applied in characterizing rocks and building materials.

The common feature of all these methods is that the intervals of self-similarity are given by the linear sections of the log-log plots; sometimes, several linear regions with different slopes may occur, indicating structural changes in the transition from one interval to the next. Figure 2.2 shows the experimental determination of the fractal dimension of a silica gel surface. The minimum condition for a well-defined fractal dimension to exist is (Pfeifer 1984)

$r_{max}/r_{min} > 2^{1/D}$,

with r_{max} and r_{min} being, respectively, the upper and lower bounds of the fractal region on the length scale.

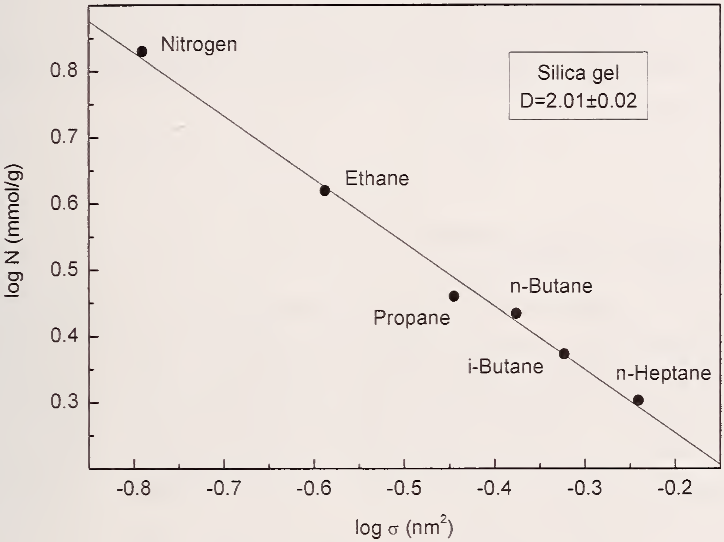


Figure 2.2. *Determination of the fractal dimension frm the monolayer adsorption capacity for different test molecules (Noack).*

At the time of the pioneering articles on the application of fractal concepts to problems of microstructure, it was hoped and assumed that the fractal dimension would be a universal characteristic parameter for porous solids. However, these great expectations have not been completely fulfilled, principally for two reasons. First, the accuracy of the experimental data used for calculating the fractal dimension is often very limited. Therefore, in many cases one cannot rely upon the fractal dimension as being a universal characteristic quantity for the texture of solids. Second, some scientists have expressed doubts concerning the applicability of the fractal concept in today's solid state research, at least in the broad way it was used in the past. Conner and Bennett (Conner 1993), using the Menger sponge as a model fractal, proposed that real catalysts (as used in industry) have pore systems without any fractal character, because the condition of self-similarity is not fulfilled and probably cannot be realised for practical purposes. According to Conner and Bennett, one can construct model systems without self-similarity and therefore without fractal properties, the log-log plots of which yield exact straight lines. A conclusion from this work would be that some former results in the fractal dimension of pore systems should be examined critically. Surfaces of real solids, on the other hand, can possess a fractal character, and for those materials, fractal concepts can be very useful for understanding the phenomena of surface roughness.

Even if the fractal concept is not relevant for all parameters of the void structure of solids (a matter of the description), we are still confronted with the problems of scale and method dependence and the impossibility of obtaining 'absolute' results.

3. Pore Analysis Instruments

Several methods have been developed for determining the surface area and the pore size distribution in porous systems. The operations of these different methods generally are based on different physical principles. It should be expected, therefore, that they effectively represent probes of different sizes and, hence, that the pore size ranges in which they are most reliable are necessarily different. Figure 3.1 compares the ranges of validity of a selection of

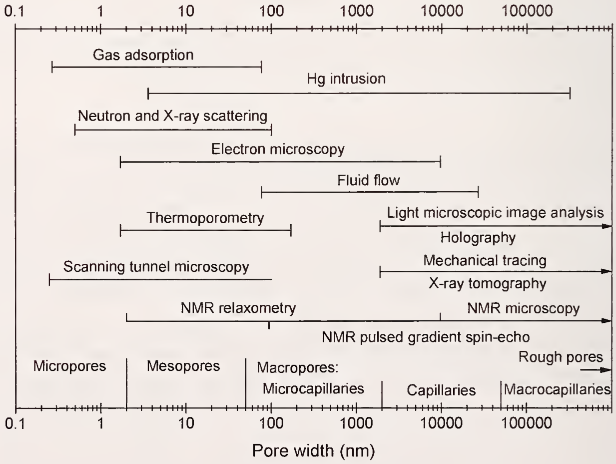


Figure 3.1. Measuring ranges of methods for pore size determination (after Meyer 1997)

methods commonly used for pore characterization, and Tables 3.1 and 3.2 describe some of the advantages and disadvantages of these methods.

Table 3.1. *Methods for the determination of total porosity (after Mikhail and Robens 1983)*

Procedure	Range of pore sizes	Assumption	Advantages	Disadvantages
Calculation of apparent density	Total		Easy calculation from commonly known property	
Small angle X-ray scattering	0.5 nm ≤ d ≤ 100 nm		Short time method	Special facilities
Small angle neutron scattering	0.5 nm ≤ d ≤ 100 nm		Short time method	Special facilities, limited to nuclear centers
Quantitative image analysis	d ≥ 20 nm	Spherical pores	Large pores can be measured, optical checking is possible, also microporosity can be measured by analysing TEM photography	Limitation to large pores, significant errors in coarse grain materials, area information, for spatial information large mathematical effort
Image analysis system	d ≥ 20 nm		Size measurements of pores of irregular shapes, application on ceramographic sections, figures, microphotos, view graphs	Subjective measurement, area information

The practical significance of using methods with different detection limits is illustrated quite graphically in Figure 3.2. The figure shows results from Dullien and Dhawan who investigated the pore volume distribution of a sandstone sample. They used both mercury porosimetry and optical microscope image analysis on a two-dimensional slice of the same sample. Apparently, the narrow distribution resulting from mercury porosimetry was determined mainly by the diameter of the pore opening, obviously quite narrow in this sample. In contrast, the image analysis examined pores that had been cut open when the specimen was sectioned for analysis. Apparently, the wide and flat distribution function resulted from the size of the cut single pores.

Table 3.2. *Methods for the determination of open porosity (Mikhail and Robens 1983)*

Procedure	Range of pore sizes	Assumption	Advantages	Disadvantages
Xylene and water impregnation	d > 100 nm		Simple method, short time	No pore size distribution, specimens with small diameter
Liquid metal impregnation			True pore network	No measurable pore size distribution, carbon burn-off
Air/He penetration	A few nanometers depending upon gas applied		Very short time method, about 1 min, good reproducibility, no influence on sample	No pore size distribution
N_2 adsorption	d < 50 nm		Correlation with BET surface area	Complicated evaluation program
Mercury intrusion	4 nm < d ≤ 60 µm	Cylindrical pores	Much in use, comparable data, extended range of pore sizes	Danger of breaking pore walls, large pores are filled at atmospheric pressure

Evidently, some care must be exercised when selecting a method. The following observations have been offered by IUPAC (Rouquerol *et al.* 1994).

- 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.

- No experimental method provides the absolute value of parameters such as porosity, surface area, pore size, and surface roughness. Each gives a characteristic value that 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.

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

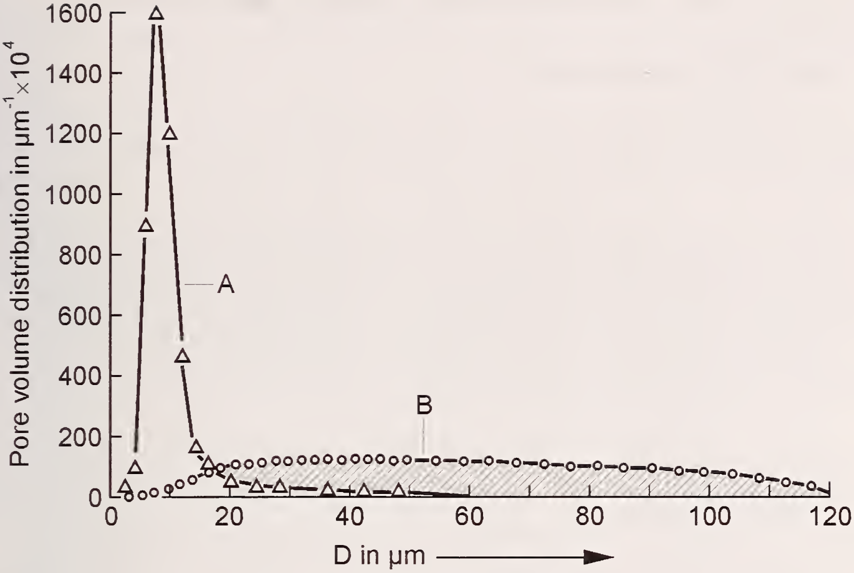


Figure 3.2. Comparison of pore volume size distributions for Clear Creek sandstone: curve (A) form mercury porosity; curve (B) from photomicrography (sphere model) (Dullien 1975).

- 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 method if the porous substance is to be used as a desiccant, or a freezing point depression method if one is interested in the frost resistance of a construction material...) so that parameters determined are appropriate.

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

- 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.

4. General Procedures for Powder Sampling and Preparation

4.1 Sampling Alternatives

The goal of powder sampling is to collect a small amount of powder from the bulk quantity such that this smaller fraction is representative of the characteristics of the entire bulk. Statistical sampling techniques (ISO 2859) have been developed to help ensure that a representative sampling is obtained. Statistical sampling requires the inspection of only a fraction of the bulk (thereby greatly reducing the amount of time and effort spent in sampling) and provides the advantage of calculating the level of certainty of detecting mistakes, upon applying a particular level of inspection.

After the primary samples have been drawn from the bulk, they need to be further sub-divided to provide a specimen quantity appropriate to use in the laboratory. The most important techniques for dividing bulk samples into laboratory samples are described in the following subsections (Allen 1981; Jillavenkatesa 2001).

4.1.1 Cone and Quartering

This method requires that the powder be poured into a cone shaped heap on a flat surface. The heap is flattened by a spatula and divided into 4 identical volumes. One of these smaller volumes is taken and the procedure repeated to produce 1/16 of the original material. This process is repeated until the sample size desired for the measurement is obtained.

4.1.2 Table Sampling

Table sampling involves powder flow along an inclined table with obstacles to divert and control the powder flow. The sample is introduced through a feeder at the top of an inclined plane from where the powder travels downward on the table plane. Guides in the shape of triangular prisms are placed in rows perpendicular to the direction of powder flow. The interaction of the powder with these guides causes the stream of powder to be divided into different fractions.

4.1.3 Spin Riffling (Van der Veen 1993)

A spinning (rotating) riffler is a rotary sample divider and causes division of the sample powders into a series of bottles mounted on a circular holder. The sample is introduced into the mass flow hopper while ensuring that the powder does not form a heap. The material flows from the hopper to a vibratory chute. The powder travels along the chute to the receivers (glass containers), which are rotating in a circular motion at a constant speed. This causes the containers to be filled uniformly. One can say that a spin riffler has a high reliability in comparison with other techniques. Because of the low relative standard deviation compared to other techniques, this cross riffling method is often applied to the production of reference materials.

Reference materials (RMs) of any type must be homogeneous with respect to the certified properties such that the between-sample variation in the properties of the RM artifacts is as low as possible. The minimization of the between-sample variation can be carried out by riffling using a rotating sample divider (8 ports) applying the cross-riffling scheme (see below) according to Van der Veen (1993). Referring to Figure 4.1, the first step of this procedure is a riffling step into 8 subsamples. After this step, each of these subsamples is riffled again, yielding 64 small subsamples. Using a recombination of these 64 samples, 8 new larger samples are formed. Then, 8 additional rifflings are performed to yield a new set of 64 small subsamples. In this manner, it may be expected that most of the inhomogeneity that may have remained after the first riffling (samples 1 trough 8) will have been removed. As was shown by Van der Veen (1993), the advantage of this riffling procedure is that even if the first 8 samples are not very representative for the batch, the samples A to H will be. To investigate the resulting homogeneity of the material, it is necessary to separate measurement uncertainty from heterogeneity of the samples. If multiple measurements on the same specimen are possible (in the case of nondestructive investigation methods), this may be achieved by averaging the results. Averaging allows the effect of measurement uncertainty to be minimized.

4.2 Steps in a Sampling Procedure

In general, a sampling procedure involves the selection of techniques that work best for the given powder system and must consider the nature of the powder and whether granules or larger solid pieces will be used to determine the specific surface area and the pore characteristics. The sampling procedure, therefore, must take into consideration the powder characteristics, the size of the bulk material, and the number of laboratory specimens to be prepared. Homogeneity testing is a critical component of any sampling procedure because it identifies inconsistencies between sub-samples and thus helps to ensure that the sub-samples are representative of the bulk sample. Figure 4.2 shows a general flowchart of the steps in a typical sampling procedure.

1	2	3	4	5	6	7	8		
⇓	⇓	⇓	⇓	⇓	⇓	⇓	⇓		
1-8	2-7	3-6	4-5	5-4	6-3	7-2	8-1	⇒	H
1-7	2-6	3-5	4-4	5-3	6-2	7-1	8-8	⇒	G
1-6	2-5	3-4	4-3	5-2	6-1	7-8	8-7	⇒	F
1-5	2-4	3-3	4-2	5-1	6-8	7-7	8-6	⇒	E
1-4	2-3	3-2	4-1	5-8	6-7	7-6	8-5	⇒	D
1-3	2-2	3-1	4-8	5-7	6-6	7-5	8-4	⇒	C
1-2	2-1	3-8	4-7	5-6	6-5	7-4	8-3	⇒	B
1-1	2-8	3-7	4-6	5-5	6-4	7-3	8-2	⇒	A

Figure 4.1. *Recombination table of the cross riffling scheme.*

4.3 Special Preparation Steps

Measurements using either the gas adsorption method or mercury intrusion method require additional preparations to ensure proper results.

4.3.1 Gas Adsorption Method

Prior to the measurement of an adsorption isotherm, all the physisorbed species should be removed from the surface of the adsorbent. This may be achieved by outgassing, a procedure involving exposure of the surface to a high vacuum at elevated temperatures, or by flushing the adsorbent with a inert gas, typically with helium or nitrogen, which subsequently may be the adsorbent.

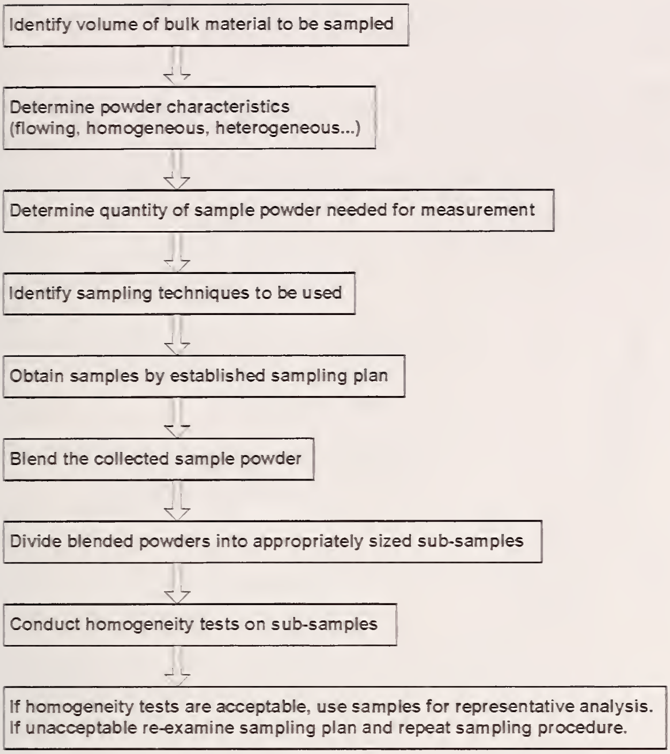


Figure 4.2. *Flowchart indicating steps in a typical sampling procedure.*

To obtain reproducible isotherms (ISO 9277), it is necessary to control the outgassing conditions such as temperature level, outgassing time, change in pressure over the adsorbent, and the residual pressure. Some samples require careful attention when heat is applied due to the possibility of thermal damage. In some cases, for example for zeolites, it is necessary to hold the temperature under 100 °C for an extended period to allow all water to be removed. With these microporous samples, reproducible isotherms are only obtained after one or more adsorption - desorption cycles. The rate of desorption is strongly temperature dependent, and to minimize the outgassing time, the temperature should be the maximum consistent with the avoidance of changes in the nature of the adsorbent and with the achievement of reproducible isotherms. Outgassing at a high temperature or under ultrahigh vacuum conditions, as well as flushing with certain gases may lead to changes in the surface composition, *e.g.* through decomposition of hydroxides or carbonates, formation of surface defects, or irreversible changes of the structure. The maximum temperature at which the sample is not affected may be determined by thermogravimetric analysis (Figure 4.3a) or by trial experiments using different degassing conditions of time and temperature.

The real sample mass can only be determined after degassing since the adsorbent contaminants can contribute significantly to the apparent initial mass of the sample. Furthermore, the sample must be protected from exposure to the atmosphere after degassing.

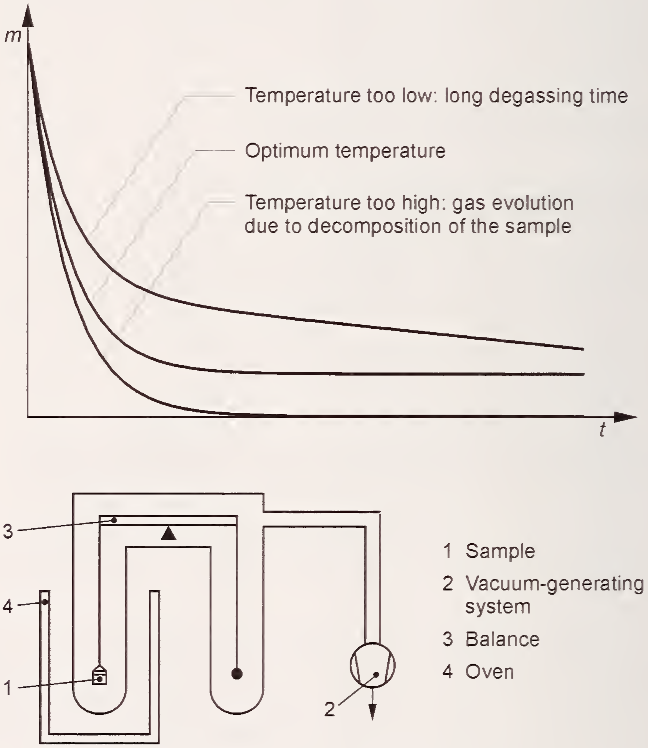
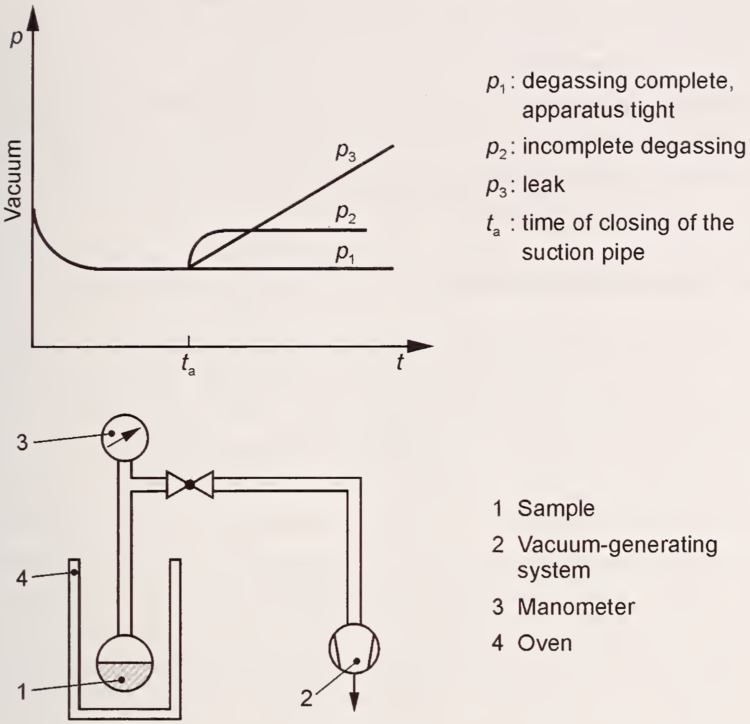


Figure 4.3a. Thermogravimetric control of degassing.

When vacuum conditions are used, the heated sample container must be isolated from the pump and trap. When the vacuum line is closed, such as at time t_a in Figure 4.3b, the extent of degassing is indicated by the gas pressure. If the pressure does not rise significantly over a period of 15 min to 30 min, degassing is complete. An increase in pressure to a higher steady value indicates that further degassing is needed. A rising pressure that does not stabilize indicates a leak in the vacuum line. When degassing is complete, the specimen is ready for measurement.



p_1 : degassing complete, apparatus tight
p_2: incomplete degassing
p_3: leak
t_a : time of closing of the suction pipe

1 Sample
2 Vacuum-generating system
3 Manometer
4 Oven

Figure 4.3b. *Pressure control of degassing.*

4.3.2 Mercury Intrusion Method

The additional preparation of the samples for investigation by the mercury intrusion method is not as specific as in the case of gas adsorption. Samples with high specific surface area may require pretreatment by heat and vacuum to remove vapors, typically water vapor, which occupies small pores and prevents the intrusion of mercury. If the sample is heat sensitive, then drying in a desiccator is required. Entrapment of small quantities of gas with the sample in the penetrometer gives no obvious manifestations to the analytical results.

5. Specific Surface Area and Pore Analysis by Gas Adsorption

Gas adsorption measurements are widely used for the characterization of a variety of porous solids. Of particular importance is the application of physisorption (physical adsorption) for the determination of the surface area and pore size distribution. 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 is mercury porosimetry 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 ($< 2\ m^2g^{-1}$), but this technique cannot be employed for the study of porosity.

5.1 Principle of Measurement

Various procedures have been devised for determining the amount of gas adsorbed. Volumetric methods are generally employed for measuring nitrogen or krypton isotherms at cryogenic temperatures, 77 K, but gravimetric techniques are especially useful for studying the adsorption of vapors 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. Automated techniques have been developed, which involve the slow continuous admission of the adsorptive and thus provide a measure of the adsorption under quasi-equilibrium conditions. 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 about 13 mPa (10^{-4} torr) is considered to be acceptable. Determination of the outgassed mass of the sample is one of the major sources of measurement uncertainty and contributes to the discrepancy between different experiments. Inorganic oxides are usually outgassed at temperatures from about 120 °C to 150 °C while microporous carbons and zeolites require higher temperatures (about 300 °C).

Argon at its boiling point (87 K) is the adsorptive most commonly used in connection with the micropore size analysis by means of the gas adsorption method. For the evaluation of the measured isotherm, it is necessary to chose among several evaluation procedures that differ according to the qualitative nature of the isotherm. Six classes of isotherms, Figure 5.1, are usually distinguished (Sing 1985).

Type I isotherms are observed for microporous solids having relatively small external surfaces (*e.g.* activated carbons, molecular sieve zeolites, and certain porous oxides). The limiting uptake is governed by the accessible micropore volume rather than by the internal surface area.

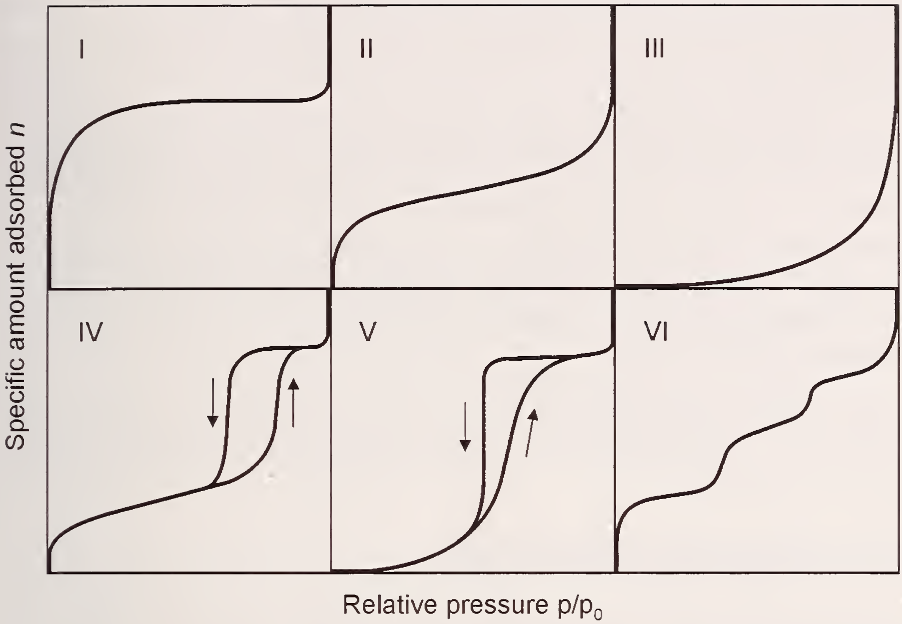


Figure 5.1. *Classification of isotherm types (Sing 1985)*

Type II isotherm is the normal form obtained with a non-porous or macroporous adsorbent. The type II isotherm represents unrestricted monolayer-multilayer adsorption.

Type III isotherms are convex to the p/p_0 axis over its entire range. This type is not common, but there are a number of systems (*e.g.* nitrogen on polyethylene) which exhibit isotherms with gradual curvature. In such cases, the adsorbate-adsorbate interactions play an important role.

Type IV isotherms are distinguished by two characteristic features. This type of isotherm exhibits a hysteresis loop, which is associated with capillary condensation taking place in mesopores, and has a limiting uptake over a range of high p/p_0. The initial part of the type IV isotherm is attributed to a monolayer-multilayer adsorption since it follows the same path as the corresponding part of a type II isotherm obtained with the given adsorptive on the same surface area of the adsorbent in a non-porous form. Type IV isotherms are characteristic of many mesoporous industrial adsorbents.

Type V isotherms are uncommon. They are related to the Type III isotherm in that the adsorbent-adsorbate interaction is weak, and they also exhibit hysteresis as in Type IV.

Type VI isotherms exhibit stepwise multilayer adsorption on a uniform non-porous surface. The sharpness of the steps depends on the system and the temperature. The step-height represents the monolayer capacity for each adsorbed layer and, in the simplest case, remains nearly constant for two or three adsorbed layers. Among the best examples of Type VI isotherms are those obtained with argon or krypton on graphitized carbon blacks at liquid nitrogen temperature.

Further subdivisions of the types I, II, III, and IV have been developed for some applications (Rouquerol *et al.* 1999), but those finer subdivisions will not be discussed here.

5.2 Determination of Surface Area

It is 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

$$\frac{p}{n_a(p_0 - p)} = \frac{1}{n_m C} + \frac{(C-1)}{n_m C} \cdot \frac{p}{p_0}$$

where n_a is the amount adsorbed at the relative pressure p/p_0, n_m is the monolayer capacity, and C is a constant that 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, but the range of linearity of the BET plot is always restricted to a limited part of the isotherm – usually not above $p/p_0 \approx 0.3$.

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 $n^a{}_m$. 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,

$$A_{(BET)} = n_m \cdot L \cdot a_m$$

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 that give rise to either especially strong or weak adsorbent-adsorbate interactions which are able to influence the packing.

A concern that must be recognized is that the theory underlying the BET method is based on an oversimplified extension of the Langmuir mechanism to multilayer adsorption. To obtain a reliable value of n_m it is necessary that the knee of the isotherm be fairly sharp (*i.e.* the BET constant C is not less than about 100). A very low value of C (< 20) is associated with an appreciable overlap of monolayer and multilayer adsorption; for that case, the application of the BET analysis is 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.

5.3 Mesoporosity and the Kelvin Equation

Adsorption of gas into a porous solid takes place according to a number of different mechanisms. For instance, in mesopores and macropores, 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.

In the gas adsorption measurements, the quantity of gas adsorbed on a surface is recorded as a function of the relative pressure of the adsorptive. Measurements at a series of increasing relative pressures yield the adsorption branch of the isotherm, while measurements at a series of decreasing relative pressures determine the desorption branch of the isotherm. The pore size distribution can be calculated either from the adsorption or the desorption branches of the isotherm (or both), but results from the two branches will not necessarily be in agreement. It is usually recommended that the analysis be carried out using the adsorption branch of the isotherm.

The computation of the mesopore size distribution is generally carried out using methods based on the Kelvin equation.

The minimum pore size that can be investigated is limited by the size of the adsorptive molecule, 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, the maximum size is about 300 nm. Using nitrogen as the adsorptive, comparative pore size distributions can be determined for micropores having widths less than 2 nm. However other gases, such as argon, may provide more reliable results.

$$r_k = \frac{2V_m \sigma \cos\vartheta}{RT \ln \frac{p}{p_o}}$$

where:

r_k = radius of curvature of the adsorptive condensed in the pore

p_o = saturation vapor pressure of nitrogen at the temperature of the liquid nitrogen

p = equilibrium pressure of the nitrogen adsorptive

σ = surface tension

V_m = molar gas volume of an ideal gas

ϑ = contact angle

For nitrogen at the boiling temperature, the Kelvin equation may be expressed in the form:

$$r_k = \frac{-0.953 \text{ nm}}{\ln \frac{p}{p_o}}$$

Since condensation is considered to occur after an adsorbed layer has formed on the pore walls, it is necessary to make allowance for the thickness of this adsorbed film. In the case of cylindrical pores (Barrett 1951; ASTM 4641-94 e1), the allowance is made using:

$$r_p = r_k + t_a$$

where:

r_p = cylindrical pore radius
t_a = thickness of the adsorbed film

Various methods exist for the evaluation of t_a as a function of relative pressure and for calculating the pore size distribution. One of the most frequently used equations is that of de Boer (de Boer 1965).

$$t_a = 0.1\ \text{nm} \cdot \sqrt{\frac{13.99}{0.034 - 0.4343 \cdot ln\frac{p}{p_o}}}$$

The required experimental data may be obtained in principle by volumetric, gravimetric, or continuous flow methods. All of these methods can provide data of comparable precision and reliability provided that the apparatus is correctly calibrated and that care is taken to ensure that the system is at equilibrium. However, for adsorption of nitrogen at liquid nitrogen temperature, the static volumetric method is recommended because:

a) The sample is in direct contact with the wall of the sample holder and therefore quickly reaches thermal equilibrium with the liquid nitrogen cryostat; and

b) by monitoring the pressure in the system, it is straightforward to determine when equilibrium between the adsorbate and adsorptive has been reached.

Finally, we note that the Kelvin equation cannot be used for pores less than about 2 nm diameter. This limitation occurs because interactions with adjacent pore walls become significant and the adsorbate can no longer be considered a liquid having bulk thermodynamic properties.

5.4 Microporosity

According to the IUPAC Recommendations (Sing 1985), micropores are defined as pores with internal width less than 2 nm. They are characterized by the micropore volume and the micropore distribution. Different methods for the characterization of micropores are available. Among the most important methods are sorption methods. The field-proven methods of gas sorption are of special interest with respect to the use of microporous material as specific sorbents, molecular sieves, and carriers for catalysts. In this approach, of course, the results of the adsorption measurements depend on the size of the adsorptive gas molecules because some micropores may not be accessible to larger molecules. Thus, exclusion effects may be observed.

In this section, methods for the evaluation of the volume of micropores and the specific surface area of microporous material by low-temperature adsorption gases are described. The methods use physisorbing gases which can penetrate into the pores under investigation. The methods are not applicable when chemisorption or absorption takes place.

The primary methods are described in the standards DIN 66135 and ISO 15901-3. These methods are based on the measurement of the adsorption of gases at constant low temperature and the evaluation of the initial part of the isotherm. The gases used are bound by physisorption at the solid surface, in particular N_2 at 77 K, Ar at 77 K or 87 K, or CO_2 at 195 K. It should be noted that these gas molecules have different sizes and the measurement temperatures are different. Consequently, they are not expected to yield the same values.

In micropores, the interaction potentials from opposite pore walls are overlapping and, hence, physisorption is stronger than in wide pores or at the external surface. As a consequence, micropores are filled readily at very low relative pressure. The filling of a significant portion of micropores is indicated by a large and steep increase of the isotherm near its origin and subsequent bending to a flat level.

In general, adsorption in micropores at low relative and absolute pressure proceeds slowly. To determine a suitable pore size distribution in the micropore range, many points with small increments of relative pressure should be measured. For that purpose, the apparatus must be completely leak-free, and wide connection tubes should allow for a rapid pressure adjustment.

The specific liquid volume V_a of the adsorbate condensed in the pores at the measuring temperature is calculated using

$$V_a = V_g \frac{\rho_g}{\rho_l} \qquad (5.1)$$

If the density ρ_g of the gas at pressure P_{App} and temperature T_{App} in the gas dosing supply is unknown, the standard density $\rho_{g,STP}$ (Table 5.1) should be used, applying the general gas equation:

$$V_a = V_{a,App}\frac{P_{App}}{P_{STP}}\cdot\frac{T_{STP}}{T_{App}}\cdot\frac{\rho_{g,STP}}{\rho_1} \tag{5.2}$$

where

V_a = specific volume of the adsorbate

V_g = specific volume of the gas

ρ_l = density of the liquefied adsorptive at measuring temperature

$\rho_{g,STP}$ = gas density at STP

STP = standard temperature and pressure, specified as:

P_{STP} = 101325 Pa

T_{STP} = 273.15 K

Table 5.1. *Recommended values for the calculation of liquid volumes(ISO 15901-3)*

Gas	$\rho_{g,STP}$ mg/cm^3	Measuring temperature K	ρ_l g/cm^3	$\rho_{g,STP} / \rho_l$ 1
N_2	1.2504	77	0.8086	$1.546 \cdot 10^{-3}$
Ar	1.7840	77	1.47	$1.21 \cdot 10^{-3}$
Ar	1.7840	87	1.40	$1.27 \cdot 10^{-3}$
CO_2	1.9770	195	1.2778	$1.547 \cdot 10^{-3}$

5.4.1 Micropore Volume from the Langmuir Isotherm

Adsorption measurements of highly microporous materials result in a Langmuir-type isotherm (type I of the IUPAC classification) if the external surface and the volume of mesopores are negligible (Figure 5.2). The plateau corresponds to the micropore quantity. The micropore volume can be calculated by use of Eq. (5.1) or (5.2). If macropores are also present, a steep increase near $p/p_o \approx 1$ may be observed. In general, the surface area of the macropores can be neglected. For a better resolution of the steep initial part of the curve, the isotherm of a microporous material, $V_a=f(p/po)$ or

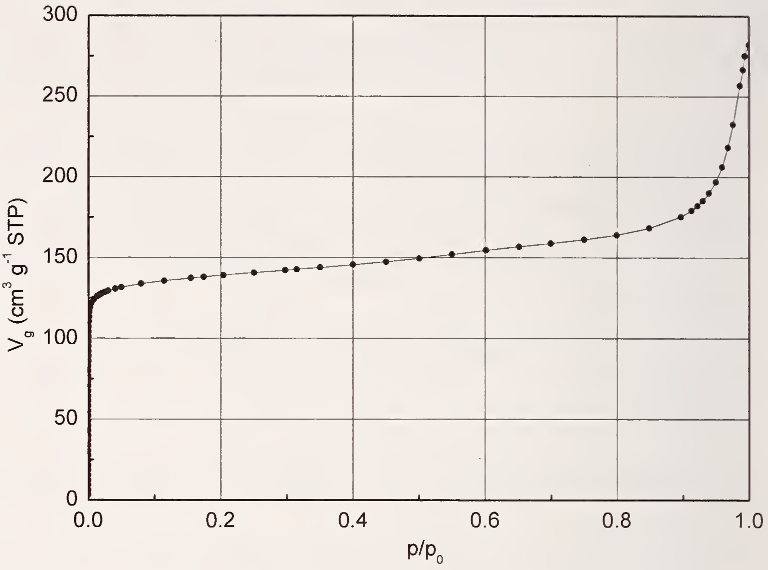


Figure 5.2. *Linear isotherm plot of Ar on zeolite at 87.3 K*

$m_a=f(p/p_o)$, is favorably represented on a logarithmic scale of the relative pressure (Figure 5.3).

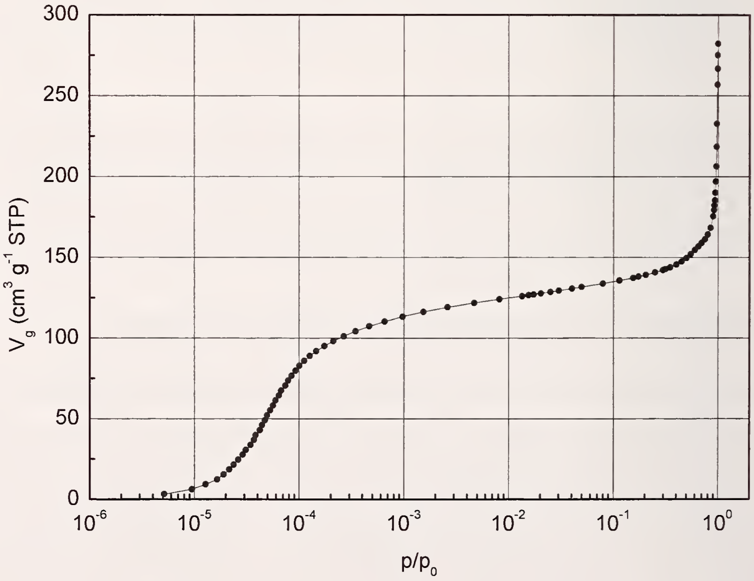


Figure 5.3. *Logarithmic isotherm plot of Ar on zeolite at 87.3 K*

5.4.2 Dubinin-Radushkevich Method

The method originally developed to investigate the microporosity of activated carbons (Dubinin 1955) can be used for any microporous material. Adsorption isotherms of pure gases on microporous sorbents can be described by means of Polanyi's potential theory. Each gas/sorbent system is characterized by an adsorption potential E which is influenced in particular by the chemical properties of the sorbent. The volume V_a filled at a given relative pressure p/p_o as a part of the total micropore volume V_{micro} is a function of the adsorption potential E:

$$V_a = f(E) \tag{5.3}$$

According to Dubinin, the adsorption potential equals the work required to bring an adsorbed molecule into the gas phase. For $T < T_{cr}$, Polanyi's potential yields

$$E = RT\,ln\frac{p_o}{p} \tag{5.4}$$

For the characteristic function (Dubinin 1969), the empirical relation can be expressed as

$$V_a = V_{micro}\,exp\left[-\left\{\left(\frac{RT}{\beta E_o}\right)ln\frac{p}{p_0}\right\}^2\right] \tag{5.5}$$

The characteristic adsorption energy E_o characterizes the pore distribution, while the affinity coefficient β unites all the curves for each gas on the same adsorbent to one characteristic curve. The Dubinin isotherm then can be written in logarithmic form to give a straight line:

$$log_{10} V_a = log_{10} V_{micro} - D\left[log_{10}\frac{p_o}{p}\right]^2 \tag{5.6}$$

$$\text{with } D = \frac{1}{\log_{10}(e)}\left(\frac{RT}{\beta E_0}\right)^2 \tag{5.7}$$

To evaluate the data, the region of relative pressure $10^{-4} < p/p_0 < 0.1$ is usually preferred. The data are registered in a diagram $log_{10}V_a$ versus $\left[log_{10}\frac{p_0}{p}\right]^2$ (Figure 5.4). The slope of the regression line gives the parameter D. The total micropore volume V_{micro} can be calculated from the ordinate intercept.

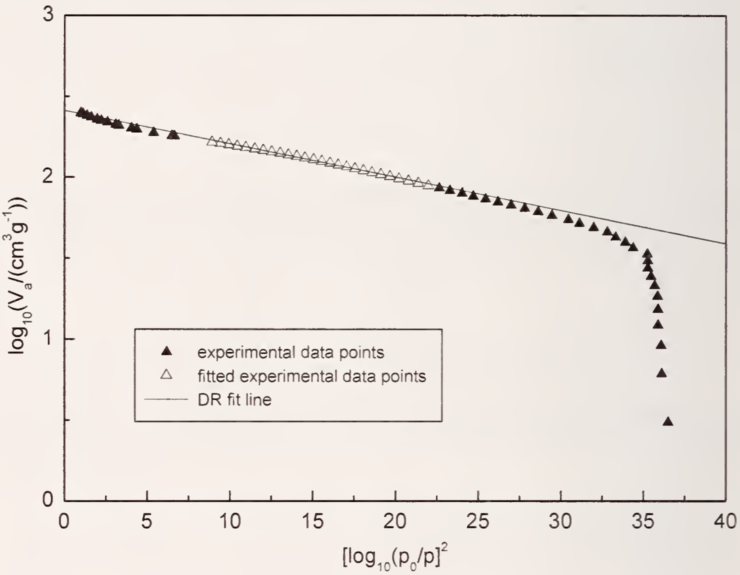


Figure 5.4. Dubinin-Radushkevich DR-plot of an adsorption isotherm of N2 at 77 K on activated carbon (Dubinin 1947)

5.4.3 Horvath-Kawazoe (HK) and Saito-Foley (SF) Methods

Horvath and Kawazoe (HK) (Horvath 1983; Horvath 1998) described a semi-empirical, analytical method for the calculation of effective pore size distributions from nitrogen adsorption isotherms in microporous materials. The original HK approach is based on the work of Everett and Powl (Everett 1976) and considers a fluid (nitrogen) confined to a slit-pore, such as can be found in some carbon molecular sieves and active carbons. Everett and Powl calculated the potential energy profiles for noble gas atoms adsorbed in a slit between two graphitized carbon layer planes. The adsorbed fluid is considered as a bulk fluid influenced by a mean potential field that is characteristic of the adsorbent-adsorbate interaction. The term *mean field* indicates that the potential interactions between an adsorbate molecule and the adsorbent, which may exhibit a strong spatial dependence, are replaced by an average, uniform potential field. Horvath and Kawazoe found by using thermodynamic arguments, that this average potential can be related to the free energy change of adsorption, yielding a relation between filling pressure and the effective pore width $d_p = l - d_s$, where d_s is the diameter of an adsorbent molecule, and the separation between nuclei of the two layers is l.

$$ln\left(\frac{p}{p_0}\right) = \frac{N_A}{RT} \cdot \frac{N_s A_s + N_a A_a}{\sigma^4 (l - 2d_0)} \cdot f_{HK}(\sigma, l, d_0) \tag{5.8}$$

with

$$f_{HK}(\sigma, l, d_0) = \frac{\sigma^4}{3(l-d_0)^3} - \frac{\sigma^{10}}{9(l-d_0)^9} - \frac{\sigma^4}{3(d_0)^3} + \frac{\sigma^{10}}{9(d_0)^9} \tag{5.9}$$

The parameters d_0, σ, A_s and A_a can be calculated using the following equations:

$$d_0 = \frac{d_a + d_s}{2} \tag{5.10}$$

$$\sigma = \left(\frac{2}{5}\right)^{\frac{1}{6}} \cdot d_0 \tag{5.11}$$

$$A_s = \frac{6 m_e c^2 \alpha_s \alpha_a}{\dfrac{\alpha_s}{\chi_s} + \dfrac{\alpha_a}{\chi_a}} \tag{5.12}$$

$$A_a = \frac{3}{2} m_e c^2 \alpha_a \chi_a \tag{5.13}$$

where m_e = mass of electron
c = speed of light in vacuum
α = polarizability
χ = magnetic susceptibility

According to equation (5.8), the filling of micropores of a given size and shape takes place at a characteristic relative pressure. This characteristic pressure is directly related to the adsorbent / adsorbate interaction energy. Saito and Foley extended the HK method to calculate effective pore size distributions from argon adsorption isotherms at 87 K in zeolites (Saito 1991; Saito 1995). Like HK, Saito and Foley (SF) based their method on the Everett and Powl potential equation (Everett 1976), but for a cylindrical pore geometry. Following the logic of the HK derivation, Saito and Foley derived an equation similar to the HK equation which related the micropore filling pressure to the (effective) pore diameter $d_p = l - d_s$.

$$\ln\left(\frac{p}{p_0}\right) = \frac{3}{4} \cdot \frac{\pi N_A}{RT} \cdot \frac{N_s A_s + N_a A_a}{d_0^4} \cdot f_{SF}(l, d_0) \tag{5.14}$$

with

$$f_{SF}(l, d_0) = \sum_{k=0}^{\infty} \left[\frac{1}{1+k} \cdot \left(1 - \frac{2d_0}{l}\right)^{2k} \cdot \left\{ \frac{21}{32} \alpha_k \left(\frac{2d_0}{l}\right)^{10} - \beta_k \left(\frac{2d_0}{l}\right)^{4} \right\} \right] \tag{5.15}$$

The parameters As and Aa can be calculated according to the equations (5.12) and (5.13).

Parameters α_k and β_k are constants defined as :

$$\alpha_k = \left(\frac{-4.5 - k}{k}\right)^2 \cdot \alpha_{k-1} \quad \text{and} \quad \beta_k = \left(\frac{-1.5 - k}{k}\right)^2 \cdot \beta_{k-1} \tag{5.16}$$

with $\alpha_0 = \beta_0 = 1$. N_s is the number of atoms per unit area of pore wall. N_a is the number of atoms per unit area of a monolayer.

To perform the HK and SF calculations the values for the adsorbent parameters α_s, χ_s, d_s, N_s as well as of the adsorptive parameters α_a, χ_a, d_a and N_a need to be known. The results are very sensitive with respect to the choice of these constants. Examples for adsorptive and adsorbent model parameters for application in connection with the Horvath-Kawazoe and Saito-Foley method are given in Tables 5.2 and 5.3. The constants were taken from the original papers of Horvath and Kawazoe (Horvath1983) and Saito and Foley(Saito 1991 and 1995). Please note that other values for these parameters can be found in the literature. Hence, to present meaningful

Table 5.2. Adsorbent Parameters (according to DIN 66135-4)

Parameter	Symbol	Graphite (a) and (b)	Zeolithe (c) and (d)	Unit
Polarizability	α_s	1.02	2.50	[10^{-24} cm^3]
Magnetic susceptibility	χ_s	13.5	1.30	[10^{-29} cm^3]
Surface density (atoms per m^2 of pore wall)	N_s	3.84	1.31	[10^{19} m^{-2}]
Diameter	d_s	0.34	0.28	[nm]

Table 5.3. Adsorbent Parameters (according to DIN 66135-4)

Parameter	Symbol	Graphite (a) and (b)	Zeolithe (c) and (d)	Unit
Polarizability	α_a	1.46	1.63	[10^{-24} cm^3]
Magnetic susceptibility	χ_a	2.00	3.25	[10^{-29} cm^3]
Surface density (atoms per m^2 of monolayer)	N_a	6.70	8.52	[10^{18} m^{-2}]
Diameter	d_a	0.30	0.34	[nm]

(a) Horvath 1983, (b) Horvath 1998, (c) Saito 1991, (d) Saito 1995 results, it is crucial that the adsorbent and adsorptive parameters employed in the HK and SF calculations always be stated in the analysis report.

Examples of results obtained by these methods and the constants from Tables 5.2 and 5.3 are given in Tables 5.4 and 5.5.

Table 5.4. *Relation between the micropore diameter and the relative pressure for nitrogen at 77.35 K in a carbon slit pore according to the Horvath-Kawazoe approach (DIN 66135-4) using the materials constants in Tables. 5.2 and 5.3.*

d_p [nm]	0.4	0.5	0.6	0.7	0.8	1.0	1.2	1.4	1.7	2.0
p/p_0	$1.8 \cdot 10^{-7}$	$1.2 \cdot 10^{-6}$	$1.7 \cdot 10^{-4}$	$9.6 \cdot 10^{-4}$	$3.2 \cdot 10^{-3}$	$1.4 \cdot 10^{-2}$	$3.5 \cdot 10^{-2}$	$6.3 \cdot 10^{-2}$	$1.1 \cdot 10^{-1}$	$1.6 \cdot 10^{-1}$

Table 5.5. *Relation between the micropore diameter and the relative pressure for argon at 87.27 K in a cylindrical zeolite pore according to the Saito-Foley approach (DIN 66135-4) using the materials constants in Tables. 5.2 and 5.3.*

d_p [nm]	0.4	0.5	0.6	0.7	0.8	1.0	1.2	1.4	1.7	2.0
p/p_0	$5.7 \cdot 10^{-7}$	$9.8 \cdot 10^{-6}$	$1.4 \cdot 10^{-4}$	$8.7 \cdot 10^{-4}$	$3.1 \cdot 10^{-3}$	$1.5 \cdot 10^{-2}$	$3.9 \cdot 10^{-2}$	$7.2 \cdot 10^{-2}$	$1.3 \cdot 10^{-1}$	$1.9 \cdot 10^{-1}$

5.4.4 Non-Local Density Functional Theory (NLDFT)

Two important methods have been developed to describe the sorption and phase behavior of inhomogeneous fluids confined to porous materials:computer simulation and density functional theory (DFT). DFT is a computational method that treats the intrinsic free energy of a system as a functional of the particle distribution function (Evans 1992). These methods can be used to calculate equilibrium density profiles of a fluid adsorbed on surfaces and in pores from which the adsorption/desorption isotherms, heats of adsorption, and other thermodynamic quantities can be derived. Pioneering studies on the application of the DFT and molecular modeling by computer simulation to study the adsorption and phase behavior of fluids in pores were performed by Tarazona and Evans (Tarazona 1984; Tarazona 1985). Seaton *et al.* (Seaton 1989) were the first to apply the DFT to the calculation of the pore size distribution (PSD) in both the meso-and micropore range. In that first attempt to perform the PSD analysis based on statistical mechanical results, the so-called local version of DFT was used. Although the local DFT provides qualitatively reasonable description of adsorption in the pores, it is quantitatively inaccurate especially in the range of small pores (*i.e.*, micropores).

A significant improvement in accuracy was obtained with the Non-Local Density Functional Theory (NLDFT) which was first used for the pore size analysis of microporous carbons in 1993 by Lastoskie *et al.* (Lastoskie 1993). Since then, the NLDFT has been applied frequently to the pore size analysis of microporous and mesoporous materials (Olivier 1995; Ravikovitch 1997; Ravikovitch 2001).

The NLDFT method is commercially available for many adsorbent/adsorptive systems. Unlike classical thermodynamic macroscopic models, the NLDFT methods describe the behavior of fluids confined in the pores on a molecular level which allows molecular properties of gases to be related to their adsorption properties in pores of different sizes. It follows that pore size characterization methods based on the NLDFT approach are applicable to the whole range of micropores and mesopores.

Under experimental equilibrium conditions, the adsorbed fluid in a pore is in equilibrium with a bulk gas phase. For such a system the grand canonical ensemble provides the appropriate description of the thermodynamics. The local density $\rho(r)$ of the pore fluid is therefore determined by minimizing the corresponding grand potential $\Omega[\rho(r)]$. Once $\rho(r)$ is known, other thermodynamic properties, such as the adsorption isotherm, heat of adsorption, free energies, phase transitions, etc. can be calculated. The grand potential function $\Omega[\rho(r)]$ is given by the following term:

$$\Omega[\rho(r)] = F[\rho(r)] - \int dr\rho(r)(\mu - V_{ext}(r))$$

where $F[\rho(r)]$ is the free energy functional in the absence of any external field and $V_{ext}(r)$ is the potential imposed by the walls, *i.e.*, $F[\rho(r)]$ depends of course on all the interactions.

To apply the theory practically to the calculation of the pore size distributions from experimental adsorption isotherms, the theoretical model isotherms are calculated using methods of statistical mechanics. In essence, those isotherms are calculated by integrating the equilibrium density profiles, $\rho(r)$, of the fluid in the model pores. A set of isotherms calculated for a set of pore sizes in a given range for a given adsorbate constitutes the model database. Such a set of isotherms called a kernel can be regarded as a theoretical reference for a given adsorption system and as such can be used to calculate pore size distributions from adsorption isotherms measured for the corresponding systems. It is important to realize that the numerical values of a given kernel depend on a number of factors such as the assumed geometrical pore model, values of the gas-gas and gas-solid interaction parameters, and other model assumptions. It is general practice to adjust interaction parameters (fluid-fluid and fluid-solid) in such a way that the model would correctly reproduce fluid bulk properties (*e.g.*, bulk liquid-gas equilibrium densities and pressures, liquid-gas interfacial tensions) as well as standard adsorption isotherms on well-defined non-porous adsorbents. The calculation of pore size distribution is based on a solution of the Adsorption Integral Equation (AIE), which correlates the kernel of theoretical adsorption/desorption isotherms with the experimental sorption isotherm:

$$N(p/p_0) = \int_{W_{Min}}^{W_{MAX}} N(p/p_0, W) f(W) dW$$

where

$N(p/p_0)$ = experimental adsorption isotherm data

W = pore width

$N(p/p_0, W)$ = isotherm on a single pore of width W

$f(W)$ = pore size distribution function

The AIE equation reflects the assumption that the total isotherm consists of a number of individual "single pore" isotherms multiplied by their relative distribution, $f(W)$, over a range of pore sizes. The set of $N(p/p_0, W)$ isotherms (kernel) for a given system (adsorptive/adsorbent) can be obtained by either Density Functional Theory or by Monte Carlo computer simulation. The pore size distribution is then derived by solving the AIE equation numerically. In general, the solution of the AIE represents an ill-posed problem, which requires some degree of regularization. The existing regularization algorithms (Lawson 1995; Provencher 1982; Wahba 1977) allow meaningful and stable solutions of this equation.

6. Pore Analysis by Mercury Intrusion Techniques (Mercury Porosimetry)

Mercury porosimetry is a very widely accepted method for determining total volume and pore size distribution in the meso- and macropore ranges.

6.1 Principle of Measurement

This method is based on the fact that a non-wetting liquid (*i.e.*, the contact angle, ϑ, between the liquid and the pore wall is such that $\pi / 2 < \vartheta \leq \pi$) requires that a positive excess hydrostatic pressure ΔP be applied to enable it to enter pores of radius r. ΔP varies inversely with r. The behavior of a non-wetting liquid in a porous sample was first described by E. W. Washburn (Washburn 1921), and the governing basic equation bears his name. The equation is directly applicable with mercury, the only known liquid really suitable for porosity measurements.

Mercury does not wet most substances and will not penetrate pores by capillary action. Liquid mercury has a high surface tension, *i.e.*, molecular forces in its surface film tend to contract its volume into a form with the least surface area. Consequently, entry of mercury into pores requires applying pressure in inverse proportion to the opening size.

To measure the pore volume or the pore size distribution, a weighed sample is enclosed in a stout bomb (penetrometer) and evacuated to remove air from the pores. Mercury is than admitted to fill the cell and surround the sample and is subjected to progressively higher pressures applied hydraulically. At each pressure P, the corresponding volume V of mercury contained in the cell is measured.

6.2 Calculation of the Pore Size Distribution

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 - Δr, with

$$r = \frac{2\sigma \cos\vartheta}{P} \qquad \text{(Washburn equation)}$$

In this way, a volumetric distribution of pore sizes is obtained (Washburn 1921).

Caveat: 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.

Washburn was the first to point out the fact that surface tension opposes the entrance into a small pore of any liquid having an angle of contact larger than 90°. Years later, Ritter and Drake (Ritter 1945) developed the method and apparatus for measuring the penetration of mercury into pores.

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 that would be filled at the given pressure.

Assuming that the pores are cylinders of different diameters is, of course, an oversimplification, but it is the best representation available except in the case of materials composed of stacked, thin sheets where slit-like openings predominate.

A value of the factor $\sigma \cos \vartheta$ must be assumed; customarily, σ is taken to be the value for pure mercury, 484 mN m^{-1}, despite the likelihood of contamination by hydraulic fluid. For many porous materials, the contact angle ϑ is about 140°, but its exact value depends on the material to be tested and must be known or measured prior to the analysis. Figure 6.1 shows the relative deviation in the calculated pore diameter as a function of the mercury contact angle. If the value of the contact angle is unknown, 140° is often assumed

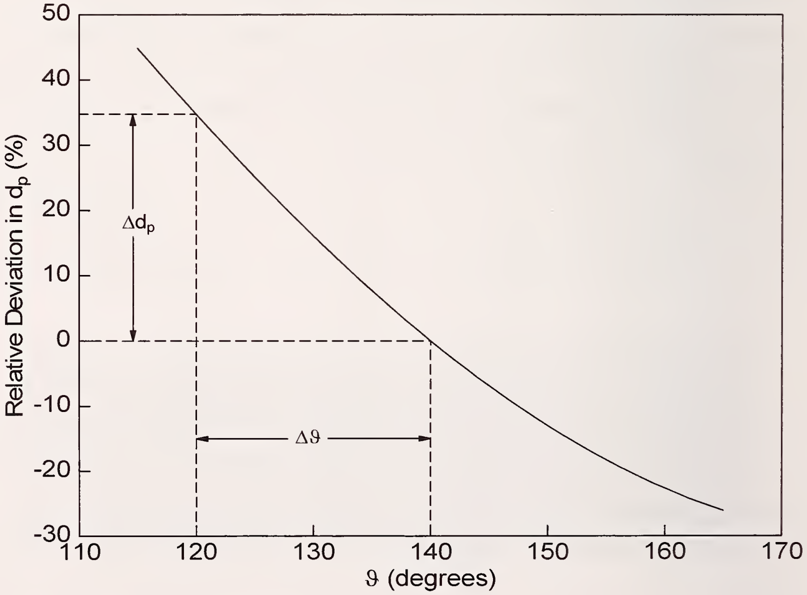


Figure 6.1. *Relative deviation in the calculated pore diameter d_p as a function of the mercury contact angle ϑ (reference value 140°).*

(DIN 66131).
For most metal oxides including, Al_2O_3 and SiO_2, as well as for supported catalysts, the contact angle (Groen 2002) is close to the presumed $\vartheta = 140°$. However, in zeolites the contact angle ranges from 127° to 140°, and assuming 140° in those cases may lead to erroneous interpretation.

The zeolite framework type seems to be the most important variable influencing the interaction between mercury and the zeolite. The most striking results are found for cement-like materials and carbonaceous materials, which show a relatively low (≤ 130°) and high (≥ 150°) contact angle, respectively.
Table 6.1 shows the measured mercury contact angles on some important

Table 6.1. *Average contact angles of some materials, as measured with the advancing angle and static angle method (Groen 2002).*
(n.d. = not determined)

	Method	
	Advancing angle	**Static angle**
Material	ϑ ± std. dev.	ϑ ± std. dev.
α-Al_2O_3	138 ± 0.2	137 ± 0.3
Al_2O_3	141 ± 0.2	141 ± 0.7
Amorphous SiO_2	141 ± 0.2	140 ± 0.9
TiO_2	n.d.	140 ± 0.3
1 wt.% Pt/Al_2O_3	142 ± 0.4	143 ± 0.8
5 wt.% Pt/Al_2O_3	136 ± 0.4	138 ± 0.3
16 wt.% Ni/Al_2O_3	139 ± 0.2	139 ± 1.3
H-ZSM-5 Si/Al=15	138 ± 0.8	n.d.
Na-ZSM-5 Si/Al=40	140 ± 0.7	140 ± 0.7
H-beta Si/Al=12.5	128 ± 0.4	n.d.
H-beta Si/Al=150	127 ± 0.2	n.d.
Na-Y Si/Al=2.5	132 ± 0.2	n.d.
H-USY Si/Al=16	138 ± 0.5	n.d.
Cement *enci* (low lime content)	128 ± 0.9	129 ± 0.7
Cement *tras* (high lime content)	129 ± 0.4	n.d.
Novacarb mesoporous carbon	150 ± 0.4	151 ± 0.7
Activated carbon	155 ± 0.4	155 ± 0.6
Norit	163 ± 1.1	n.d.

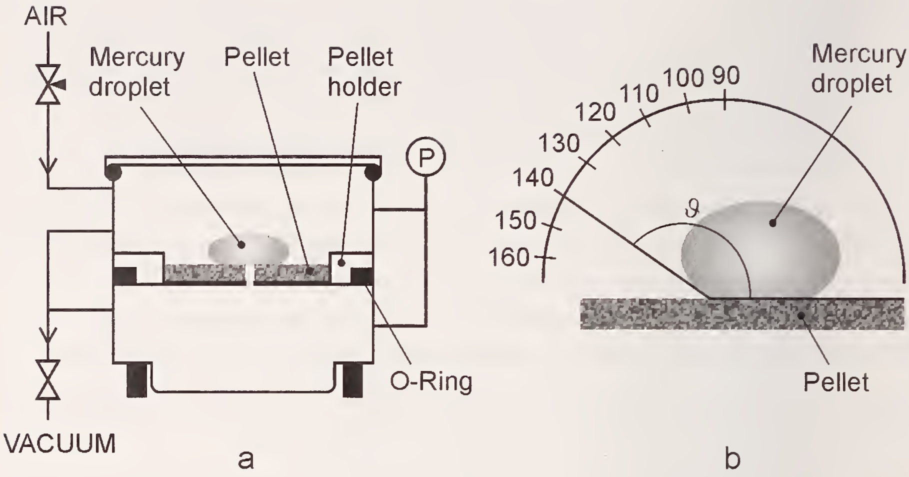


Figure 6.2. *Schematic representation of the (a) advancing angle and (b) static angle method for determination of the contact angle (Groen 2002).*

classes of porous materials.
In Table 6.1, values for ϑ and its standard deviation (std.dev.) are based on three replicate measurements.

Experimentally, the pressure can be varied between 10 kPa and 400 MPa (0.1 bar and 4 kbar), corresponding to cylindrical pore radii between 75 μm and 1.8 nm. (At high pressures, a blank 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 therefore is destructive. Figure 6.3 shows a typical intrusion/extrusion curve (volume vs. pressure curve) of a porous glass with a hysteresis loop that is typical for cylindrical pores.

The accuracy of pore diameter measurements by mercury porosimetry when the pores are right circular cylinders is exceptionally good, agreeing to at least 0.008 μm openings. However, true circular cross-section pores or pores of any regular geometry rarely are encountered in real materials. To the contrary, shapes of typical pores are slits, cracks, fissures, or highly irregular interstitial

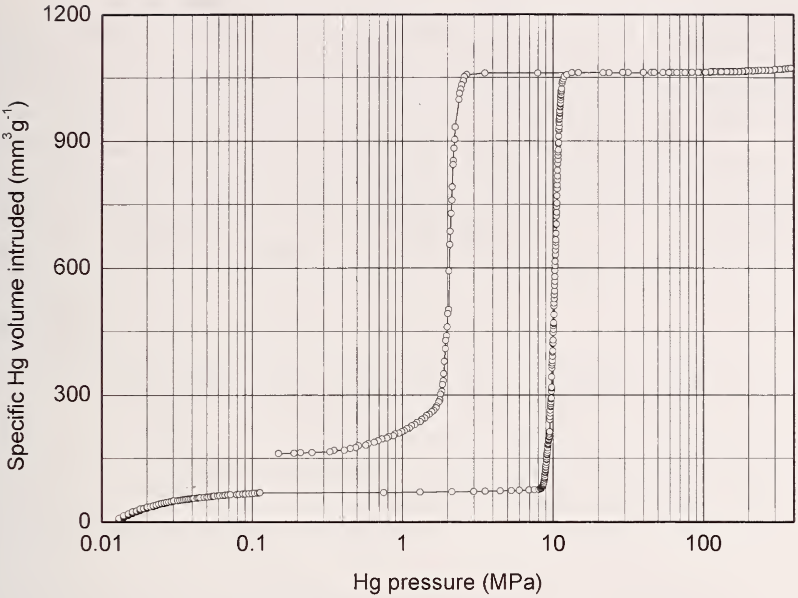


Figure 6.3. *Intrusion/extrusion curve (volume vs. pressure curve) of a porous glass.*

voids between particles. In order for the mathematics of pore characterization to be manageable, it is convenient to treat the filling of these complex pores as if they were right circular cylinders. This means that pore data from mercury porosimetry should be understood and used as equivalent cylindrical dimensions, just as the particle size determined by sedimentation of nonspherical particles is an equivalent spherical diameter. How pore shape alters basic pressure-volume curves is illustrated in Figure 6.4.

6.3 Calculation of the Specific Surface Area

Assuming pores of cylindrical shape, a surface distribution may be derived from the pore volume distribution. An estimate of the total surface area can be made from the pressure/volume curve (Rootare 1967) without using a pore

$$A = \frac{1}{\gamma \cos\vartheta} \int_{V_{Hg,0}}^{V_{Hg,\max}} p\,dV$$

model, but the material must be free of ink bottle pores:

From the function V = V(p) the integral may be calculated either graphically or by means of a numerical method.

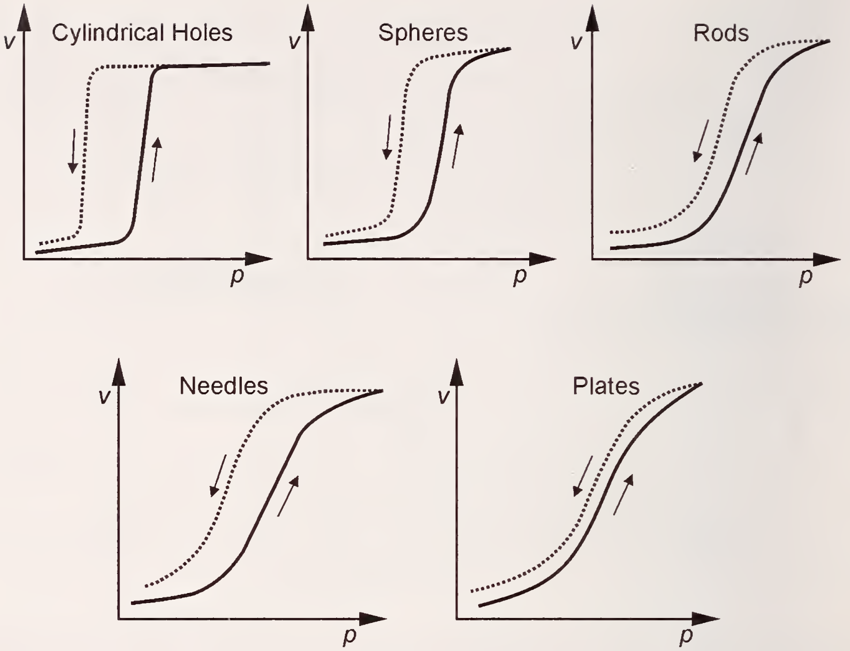


Figure 6.4. *Characteristic hysteresis loops for cylindrical holes and for pores formed within aggregates (Webb 1997).*

Because the surface of small pores is not measured, the results are not always comparable with those derived from adsorption methods such as the BET method. The recommended range (Rootare 1967) for the linear relation of specific surface area measured by the BET and Hg porosimetry method is approximately from 10 m^2/g to 100 m^2/g.

7. Conclusion

The present Guide addresses a full range of metrological issues pertaining to methods commonly used to determine quantitative measures of porosity and specific surface area in solid materials. These methods represent the best standard methods currently applied worldwide to meet today's demands for accuracy and reliability. In the natural course of evolving technology, some methods cited in this Guide as being in various stages of development have undoubtedly progressed to more advanced stages or have become approved standard test methods. New methods, motivated by emerging technologies in nanomaterials and multilayer film structures, already are on the horizon or under development. Many of the issues that will need to be addressed in those new and innovative methods are fundamentally the same as those discussed in the present Guide. Thus, the lessons learned here may also be of value and service to the next generation of porosity and specific surface area metrologies, and the Guide as a whole may serve as a substantial building block for the evolution of those measurement sciences.

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Appendix 1: SRM/CRMs Worldwide

Table A1.1. Producers / distributors of porous reference materials

Institution	Address	Web site	E-Mail
BAM	Bundesanstalt für Materialforschung und -prüfung (BAM) Richard-Willstätter-Str. 11 D-12489 Berlin Germany Tel: +49-30-8104-2061 Fax: +49-30-8104-1117	www.bam.de/service/	sales.crm@bam.de
IRMM	Institute for Reference Materials and Measurements Reference Materials Unit attn. BCR Sales Retieseweg B-2440 Geel Belgium Tel: +32(0)14 571-704 Fax: +32(0)14 590-406	www.irmm.jrc.be/	bcr.sales@irmm.jrc.be
LGC	LGC Promochem Queens Rd TEDDINGTON Middlesex TW11 0LY United Kingdom Tel: +44 (0)20 8943 7000 Fax: +44 (0)20 8943 2767	www.lgcpromochem.com/	uk@lgcpromochem.com
NIST	National Institute of Standards and Technology (NIST) Gaithersburg, MD 20899-0001, USA Tel: +1 301 975-6776 Fax: +1 301 948-3730	www.nist.gov/srm/	srminfo@nist.gov

Table A1.2. *Certified reference materials for porosity properties*

Material	SRM/CRM Number	Producer or Distributor	Method	Specific Surface Area*)	Mean Pore Diameter	Pore Volume
				m^2g^{-1}	nm	cm^3g^{-1}
Silica	BAM-PM-101	BAM	Kr ads.	0.177		
Alpha-Alumina	BAM-PM-102	BAM	N_2 ads.	5.41		
Alumina	BAM-PM-103	BAM	N_2 ads.	156.0	6.36	0.250
Alumina	BAM-PM-104	BAM	N_2 ads.	79.8	10.62	0.210
Zeolite (Faujasite)	BAM-P107	BAM	N_2 ads.		0.86	0.217
Alpha-Alumina	BAM-PM-120	BAM	Hg poros.		228.0	0.548
Porous glass	BAM-PM-121	BAM	Hg poros.		15.1	0.624
Porous glass	BAM-PM-122	BAM	Hg poros.		139.0	0.924
Alumina ceramics	BAM-P123	BAM	Hg poros.		3050	0.0995
Alumina ceramics	BAM-P125	BAM	Hg poros.		5800	0.2079
Alumina	BAM-P127 / NIST SRM 1917	BAM & NIST	Hg poros.		24.15	0.638
Alpha-Alumina	BCR-169	IRMM	N_2 ads.	0.104		
Alpha-Alumina	BCR-170	IRMM	N_2 ads.	1.05		
Alumina	BCR-171	IRMM	N_2 ads.	2.95		
Quartz	BCR-172	IRMM	N_2 ads.	2.56		
Titania-Rutile	BCR-173	IRMM	N_2 ads.	8.23		
Tungsten	BCR-175	IRMM	N_2 ads.	0.181		
Carbon black	LGC2101	LGC	N_2 ads.	10.5		
Carbon black	LGC2102	LGC	N_2 ads.	69		
Silica (nonporous)	LGC2103	LGC	N_2 ads.	142		
Silica (mesoporous)	LGC2104	LGC	N_2 ads.	247		
Portland-cement	SRM 114p	NIST		0.2086 (*) 0.3774 (**)		
Silica/Alumina	SRM 1897	NIST	N_2 ads.	258.32		
Silicon nitride	SRM 1899	NIST	N_2 ads.	10.52		
Silicon nitride	SRM 1900	NIST	N_2 ads.	2.85		
Alumina	SRM 1917 / CRM BAM-P127	NIST & BAM	Hg poros.		24.15	0.638
Silica/Alumina	SRM 1918	NIST	Hg poros.		8.847	0.547

*) Specific surface areas are measured using the N_2 or Kr BET method at 77 K, except those marked by (*) with the permeation method and (**) using the Wagner turbidimeter.

Appendix 2: Additional Illustrative Case Study Results

This appendix contains four additional case studies that may be of interest to the reader.
Appendix 2.1 CRM BAM-P107 (a microporous CRM)
Appendix 2.2 CRM BAM-PM-103 (a mesoporous CRM)
Appendix 2.3 CRM BAM-P123 (a macroporous CRM)
Appendix 2.4 CRM BAM-PM-122 (Hg Porosimetry)

Appendix 2.1 CRM BAM-P107 (a microporous CRM)

Microporous zeolite (faujasite type) is a crystalline material with a well defined and regular pore network. This material was certified by using DIN 66135-4 (Saito/Foley model for cylindrical pore geometry) for nitrogen adsorption. Certified values were reported for the micropore width and the micropore volume.

Table A2.1.1. *Certified values for the microporous CRM BAM-P107 for nitrogen adsorption*

Property	Unit	N	$\bar{\bar{x}}$	s	$s/\sqrt{N}$	$t_{n-1;0.975}, s/\sqrt{N}$
Specific Micropore Volume	cm^{3}g^{-1}	3	0.217	0.003	0.001	0.002
Median Pore Width	cm	1	0.86	0.03	0.01	0.02

N = number of laboratories (outlier free)
$\bar{\bar{x}}$ = average of averages (certified value)
s = standard deviation of laboratory averages
$s/\sqrt{N}$ = standard deviation of average of laboratory means, standard uncertainty of the certified value
$t_{n-1;0.975}, s/\sqrt{N}$ = half width of the confidence interval. The confidence interval covers the true value (with certainty of 95 %).

The nitrogen isotherm for BAM-P107 is shown in Figure A2.1.1.

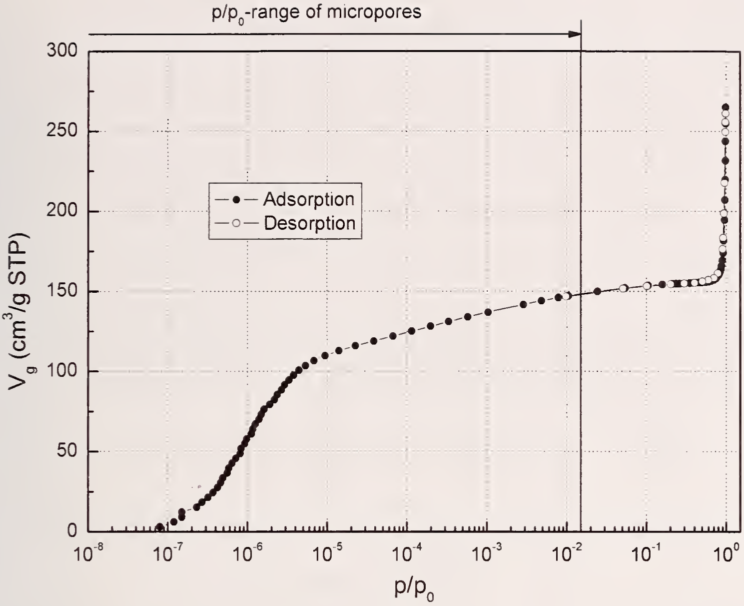


Figure A2.1.1. The nitrogen (N_2) Isotherm for CRM BAM-P107

Appendix 2.2: CRM BAM-PM-103 (a mesoporous CRM)

This CRM is a porous and highly dispersed material for which interlaboratory testing and statistical evaluation were used for the certification. The certified values are given in Table A2.2.1. The manufacturer's designation for this material was alumina type 60 (a mixture of transition aluminas). Figure A2.2.1 shows the N2 isotherm (type IV according to the IUPAC classification), and Figure A2.2.2 shows the pore size distribution as calculated by means of the BJH method. Figure A2.2.3 illustrates the statistical evaluation.

Table A2.2.1. Mesoporous CRM BAM-PM-103 certified values for the gas adsorption method

Material	Certified property (mean of laboratory means ± s)*		
	Specific Surface Area Method: BET (DIN 66131)	Specific Pore Volume Method: BJH (DIN 66134)	Hydraulic Pore Radius ($2V/A_{BET}$) Method: BJH (DIN 66134)
CRM BAM-PM-103 Alumina type 60 Adsorptive: nitrogen at 77 K	156.0 ± 7.2 m^2/g	0.250 ± 0.008 cm^3/g	3.18 ± 0.08nm

(*s: standard deviation of laboratory means)

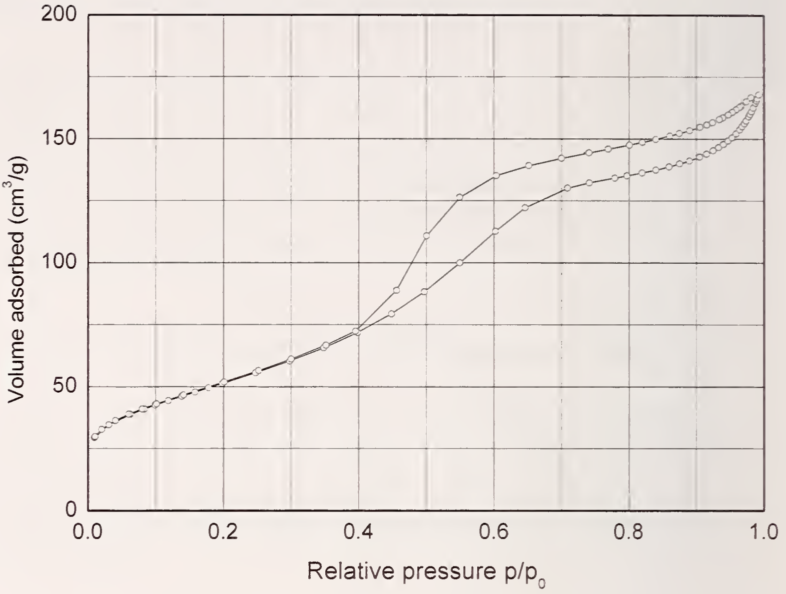


Figure A2.2.1. Adsorption isotherm of nitrogen at 77 K on BAM-PM-103 (alumina type 60).

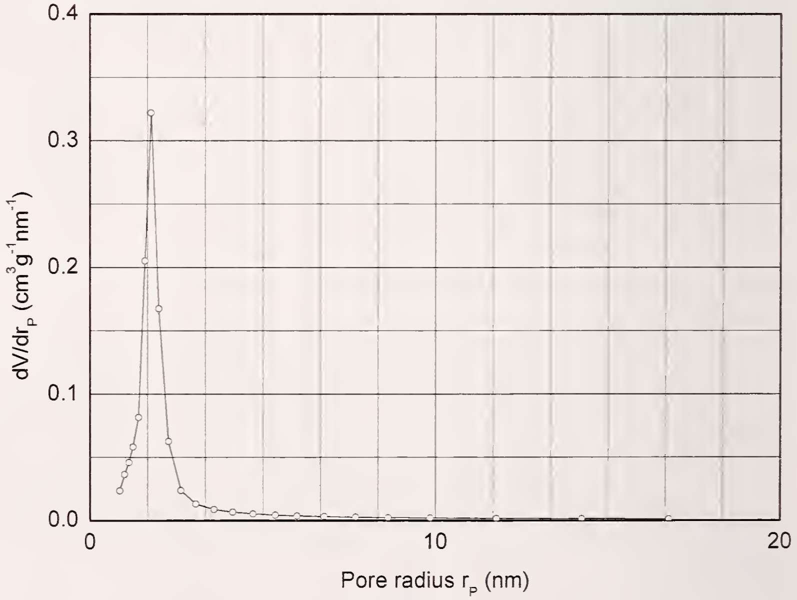


Figure A2.2.2. Pore size distribution of BAM-PM-103 (alumina type 60).

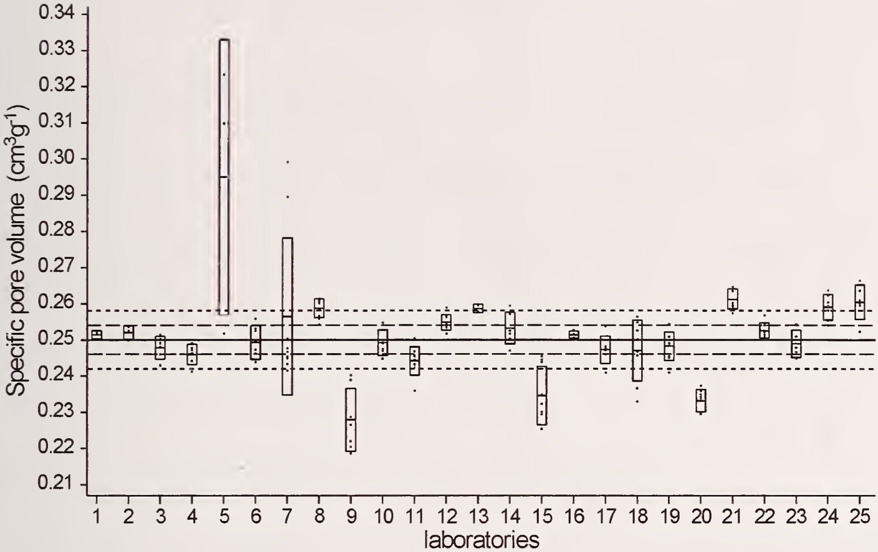


Figure A2.2.3. *Interlaboratory study: Specific pore volume (adsorption) of CRM BAM-PM-103 (alumina type 60), the wide-dashed line corresponds to the mean of means (certified value) with standard deviation (narrow-dashed lines); laboratory mean values with standard deviation, individual values (single points), and standard deviation of means are also given; laboratory number 5 is an outlier.*

Appendix 2.3 CRM BAM-P123 (a macroporous CRM)

CRM BAM-P123 was the first macroporous material certified for the relatively low intrusion pressure region of mercury porosimetry. The material (α-alumina) was certified by an interlaboratory comparison (26 laboratories from 4 European countries) using mercury porosimetry according to DIN 66133. The pores of the material were verified by imaging analysis and investigated by scanning electron microscopy.

Statistical data analysis was done for a designed experiment using 9 observed pressure-volume curves of the filter tube pieces per laboratory. The participating laboratories were qualified by means of a proficiency test using standardized pressure-volume (p-V) curves.

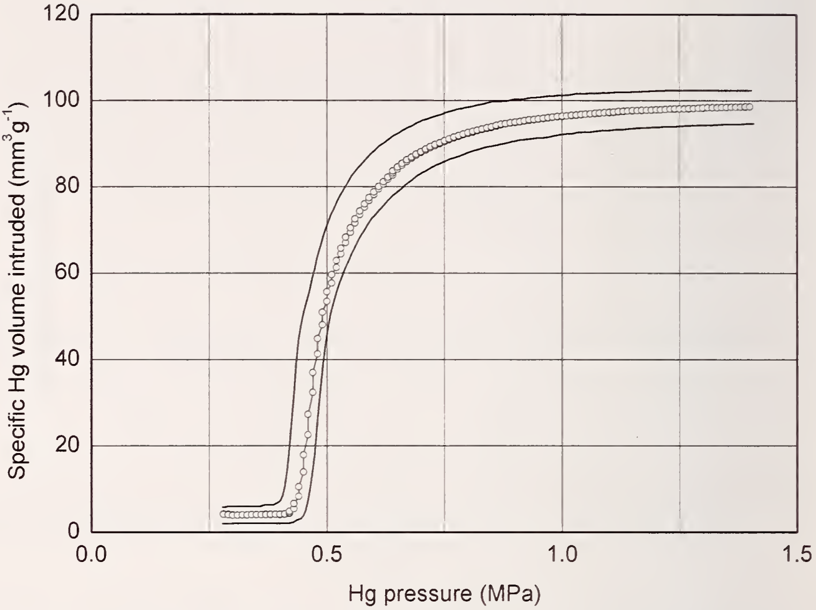


Figure A2.3.1. *Reference curve with simultaneous prediction bands at significance level 0.95 for the material CRM BAM-P123.*

In contrast to powders, there is no possibility of homogenizing compact samples. Therefore, the statistical analysis of the interlaboratory study included main steps:

- Evaluating the characteristics of the individual p-V curves by statistical considerations and standardizing the curves using those characteristics;
- Analyzing the variance of the curve characteristics and the standardized curves; and
- Constructing an average reference intrusion curve (certified p-V curve) with simultaneous confidence bands and prediction bands using the variance analytical results for the curve characteristics and the standardized curves.

Table A2.3.1. Certified single values of BAM-P123.

Quantity	Certified values	0.90 Confidence Interval	0.95 Confidence Interval	0.99 Confidence Interval	Unit
$V_{p,\ 1.4\ MPa}$	99.5	96.6 - 102.4	96.0 - 103.0	94.9 - 104.1	mm^3g^{-1}
p_{50}	0.483	0.463 - 0.503	0.459 - 0.507	0.451 - 0.515	MPa
d_{50}	3.05	2.92 - 3.18	2.89 - 3.21	2.85 - 3.25	μm

$V_{p,\ 1.4\ MPa}$ = Specific pore volume at 1.4 MPa

Appendix 2.4 CRM BAM-PM-122 (Hg Porosimetry)

CRMs for the high pressure range (from 0.1 MPa to 400 MPa) of the mercury intrusion method need to have a sharp and narrow pore size distribution, a graduation of the pore volumes and pore sizes of the CRMs, and a simple handling of the materials.

For this CRM, a new certification philosophy was used. Instead of certifying only single values of certain properties, such as the mean pore width or the pore volume, the whole mercury intrusion curve (pore volume as a function of intrusion pressure) was certified. This procedure resulted in a number of advantages for the user, including the availability a large number of certified data points in the typical working range of mercury porosimeters (0.1 MPa to 400 MPa), the possibility of assessing the pressure transducer performance over a wide range of pressure, volume calibration of the porosimeter, and the suitability of the CRM for 200 MPa instruments as well as for 400 MPa instruments. The interlaboratory tests (DIN 66133) were carried out with 25 participating laboratories. To provide a strict comparison of the statistical treatment of the results of each laboratory, a fixed grid of data points, regularly spaced on the logarithmic pressure scale, was used. Therefore, all of the experimental mercury intrusion curves were transformed into this standard grid of data points using a simple linear data interpolation. After calculating the mean mercury intrusion curve for each laboratory, the mean (non-weighted) curve of laboratory mean curves and the standard deviation at each data point leading to the uncertainty interval (Figures A2.4.1 and A2.4.2) were calculated. Since the materials consisted of micro-beads, mercury porosimetry measured some interparticle (intergranular) volume in addition to the real intraparticle pores. Because of its more or less random character, the intergranular volume could not be certified and had to be subtracted from the intrusion curve at the beginning of the data evaluation. All calculations were carried out on the basis of the Washburn equation (Washburn 1921) using values of 140° for the angle of contact of mercury and 0.480 N/m for its surface tension.

The resulting certified mercury intrusion curve is shown in Figures A2.4.1 and A2.4.2. The sharp pore size distribution of CRM BAM-PM-122 is seen in Figure A2.4.3.

Table A2.4.1. *Selected properties of CRM BAM-PM-122 for mercury porosimetry (DIN 66133).*

	Material	Specific Pore Volume at 395 MPa (mm^3/g)	Median Pore Width (nm)	Specific Surface Area (not certified) (m^2/g)
CRM BAM-PM-122	porous glass beads II	924.4 ± 17.2	139.0 ± 3.7	26.6

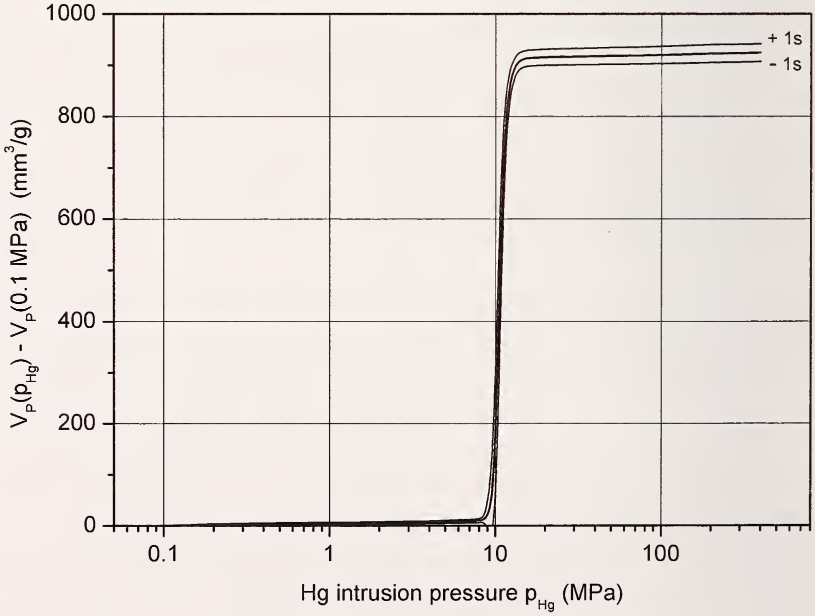


Figure A2.4.1. *Certified mercury intrusion curve for CRM BAM-PM-122 with uncertainty intervals (logarithmic pressure axis).*

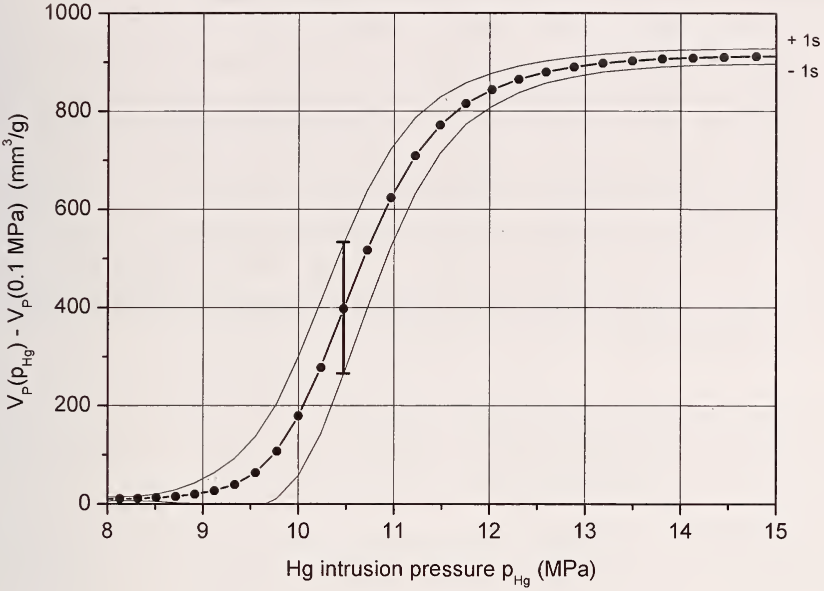


Figure A.2.4.2. *Certified mercury intrusion curve for CRM BAM-PM-122 with uncertainty intervals in the range between 8 MPa and 15 MPa (linear pressure axis).*

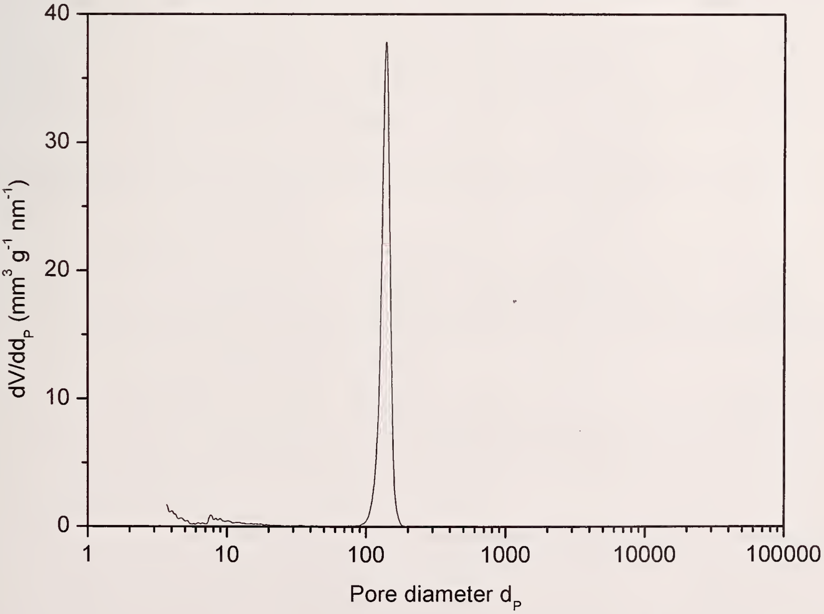


Figure A2.4.3. *Sharp pore size distribution for CRM BAM-PM-122 (not certified).*

Appendix 3: Relevant Measurement Standards

Many national and international standards setting bodies have included norms on the characterization of porous solids as part of their measurement standards and procedures. Some of these norms are generic and only describe the methods to be used to obtain certain typical parameters characterizing the pore properties. Other norms are more specific and apply to specific classes of materials, such as catalysts, ceramics, pigments, cements, and many more. Table A3.1 lists several major institutions and their internet addresses. A listing of the most relevant standards from these organizations is given in the following subsections:

Appendix 3.1 AFNOR Standards
Appendix 3.2 ASTM Standards
Appendix 3.3 British Standards
Appendix 3.4 CEN Standards
Appendix 3.5 DIN Standards
Appendix 3.6 ISO Standards

Table A3.1. *Selected national and international institutes that have issued test methods for the characterization of porous solids.*

Abbreviation	Institution	Web address
AFNOR	Association Française de Normalisation	http://www.afnor.fr/
ASTM	American Society for Testing Materials	http://www.astm.org/
BSI	British Standards Institution	http://bsonline.techindex.co.uk/
CEN	Comité Européenne de Normalisation	http://www.cenorm.be/
DIN	Deutsches Institut für Normung	http://www2.din.de/
ISO	International Organization for Standardization	http://www.iso.ch

Appendix 3.1 AFNOR Standards

X-11-620 (1994) Détermination de la surface spécifique des solides par adsorption de gaz á l'aide de la méthode BET

X-11-621 (1975) Détermination de l'aire massique (surface spécifique) des poudres par adsorption de gaz - Méthode B.E.T: Mésure volumétrique par adsorption d'azote à basse temperature

Appendix 3.2 ASTM Standards

D 1993-03	Standard Test Method for Precipitated Silicia Surface Area by Multipoint BET Nitrogen Adsorption
D2873-94(1999)e1	Standard Test Method for Interior Porosity of (PolyVinyl Chloride) (PVC) Resins by Mercury Intrusion Porosimetry
D4365-95(2001)	Standard Test Method for Determining Micropore Volume and Zeolite Area of a Catalyst
D4404-84(1998)e1	Standard Test Method for Determination of Pore Volume and Pore Volume Distribution of Soil and Rock by Mercury Intrusion Porosimetry
D4641-94(1999)e1	Standard Practice for Calculation of Pore Size Distributions of Catalysts from Nitrogen Desorption Isotherms
D3663-99	Standard Test Method for Surface Area of Catalysts and Catalyst Carriers
D3766-86(2002)	Standard Terminology Relating to Catalysts and Catalysis
D3906-03	Standard Test Method for Determination of Relative X-ray Diffraction Intensities of Faujasite-Type Zeolite-ontaining Materials
D3942-03	Standard Test Method for Determination of the Unit Cell Dimension of a Faujasite-Type Zeolite
D4222-98	Standard Test Method for Determination of Nitrogen Adsorption and Desorption Isotherms of Catalysts by Static Volumetric Measurements

D4284-03	Standard Test Method for Determining Pore Volume Distribution of Catalysts by Mercury Intrusion Porosimetry
D4365-95(2001)	Standard Test Method for Determining Micropore Volume and Zeolite Area of a Catalyst
D4404-84(1998)e1	Standard Test Method for Determination of Pore Volume and Pore Volume Distribution of Soil and Rock by Mercury Intrusion Porosimetry
D4567-99	Standard Test Method for Single-Point Determination of Specific Surface Area of Catalysts and Catalyst Carriers Using Nitrogen Adsorption by Continuous Flow Method
D4641-94(1999)e1	Standard Practice for Calculation of Pore Size Distributions of Catalysts from Nitrogen Desorption Isotherms
D4780-95(2001)	Standard Test Method for Determination of Low Surface Area of Catalysts by Multipoint Krypton Adsorption
D5604-96(2001)	Standard Test Methods for Precipitated Silica-Surface Area by Single Point B.E.T. Nitrogen Adsorption
D5900-98(2002)	Standard Specification for Physical and Chemical Properties of Industry Reference Materials (IRM)
D6556-02a	Standard Test Method for Carbon Black-Total and External Surface Area by Nitrogen Adsorption
C1274-00	Standard Test Method for Advanced Ceramic Specific Surface Area by Physical Adsorption
C493-98	Standard Test Method for Bulk Density and Porosity of Granular Refractory Materials by Mercury Displacement

Appendix 3.3 British Standards

BS 7591	Porosity and pore size distribution of materials
BS 7591-1:1992	Method of evaluation by mercury porosimetry

BS 7591-2:1992	Method of evaluation by gas adsorption
BS 7591-4:1993	Method of evaluation by liquid expulsion
BS 4359	Determination of the specific surface of powders
BS 4359-1:1996	BET method of gas adsorption for solids (including porous materials)
BS 4359-2:1982	Recommended air permeability methods
BS 4359-4:1995	Recommendations for methods of determination of metal surface area using gas adsorption techniques

Appendix 3.4 CEN Standards

EN 623-2 (1993)	Determination of density and porosity
EN 725-6 (1996)	Determination of specific surface area
EN 725-7 (1995)	Determination of absolute density
EN 725-8 (pr)	Determination of tamped bulk density
EN 725-9 (pr)	Determination of untamped bulk density

Appendix 3.5 DIN Standards

DIN 66131 (1993) Bestimmung der spezifischen Oberfläche von Feststoffen durch Gasadsorption nach Brunauer, Emmett und Teller (BET) (Determination of specific surface area of solids by gas adsorption using the method of Brunauer, Emmett and Teller (BET))

DIN 66132 (1975) Bestimmung der spezifischen Oberfläche von Feststoffen durch Stickstoffadsorption; Einpunkt-Differenzverfahren nach Haul und Dümbgen (Determination of specific surface area of solids by adsorption of nitrogen; single-point differential method according to Haul and Dümbgen)

DIN 66133 (1993) Bestimmung der Porenvolumenverteilung und der spezifischen Oberfläche von Feststoffen durch Quecksilberintrusion (Determination of pore volume distribution and specific surface area of solids by mercury intrusion)

DIN 66134 (1997) Bestimmung der Porengrößenverteilung und der spezifischen Oberfläche mesoporöser Feststoffe durch Stickstoffsorption; Verfahren nach Barrett, Joyner und Halender (BJH) (Determination of the pore size distribution and specific surface area of mesoporous solids by means of nitrogen sorption - Method of Barrett, Joyner and Halender (BJH))

DIN 66135 (2001/2002) Mikroporenanalyse mittels Gasadsorption (Micropore analysis by gas adsorption)
66135-1: Grundlagen und Messverfahren (Fundamentals and Testing procedure)
66135-2: Auswerteverfahren - Isothermenvergleichsverfahren (Evaluation by isotherms comparison)
66135-3: Bestimmung des Mikroporenvolumens nach Dubinin und Radushkev (Determination of the micropore volume according to Dubinin and Radushkevich)
66135-4: Bestimmung de Porenverteilung nach Horvath-Kavazoe und Saito-Foley (Determination of pore size distribution according to Horvath and Kavazoe and Saito-Foley)

E DIN 66136 (2003-03) Bestimmung des Dispersionsgrades von Metallen durch Chemisorption (Determination of the degree of dispersion of metals using chemisorption)
66136-1: Grundlagen (Principles)
66136-2: Volumetrisches Verfahren (Volumetric method)
66136-3: Strömungsverfahren (Flow method)

DIN 66137 (2002) Bestimmung der Dichte fester Körper (Determination of solid state density)
66137-1: Grundlagen (Principles)
66137-2: Gaspyknometrie (Gas pycnometry)
66137-3: Gasauftriebsverfahren (Gas bouancy method)

E DIN 66138 (2002) Messung der Sorption von Wasserdampf und anderen Dämpfen an Feststoffen durch Wägung (Measurement of sorption of water vapour and other vapours on solids by weighting)
66138-1: Messung des Feuchtegehalts (Measurement of the quantity of moisture)
66138-2: Messung der Wasserdampfsorptionsisotherme (Measurement of the water vapour sorption isotherm)

DIN/ISO 9277(2003) Bestimmung der spezifischen Oberfläche von Feststoffen durch Gasadsorption nach dem BET-Verfahren (Determination of the specific surface area by gas adsorption using the BET-method)

Appendix 3.6 ISO Standards (International Organization for Standardization, Geneva)

ISO/IEC Guide 2, *Standardization and Related Activities - General Vocabulary* (1996).

ISO Guide 30, *Terms and Definitions Used in Connection with Reference Materials* (2000).

ISO Guide 31, *Contents of Certificates of Reference Materials* (1996).

ISO Guide 32, *Calibration of Chemical Analysis and Use of Certified Reference Materials* (1997).

ISO Guide 33, *Uses of Certified Reference Materials* (1989).

ISO Guide 34, *Quality System Requirements for Reference Materials Producers* (1996).

ISO Guide 35, *Certification of Reference Materials - General and Statistical Principles* (1989).

ISO 2859-0, *Sampling Procedures for Inspection by Attributes -Part 0: Introduction to the ISO 2859 Attribute Sampling System* (1995).

ISO 8785, Geometrical Product Specification (GPS) – Surface imperfections – Terms, definitions and parameters (1998).

ISO 9000, *Qualitiy Management Systems-Fundamentals and Vocabulary* (2000).

ISO 9277, *Determination of the Specific Surface Area of Solids by Gas Adsorption Using the BET Method* (1995).

ISO/WD 14488, *Particle Size Analysis: Sample preparation-Sample splitting* (1999).

ISO/DIS 15901-1, *Evaluation of Pore Size Distribution and Porosity of Materials by Mercury Porosimetry and Gas Adsorption - Part 1: Mercury Porosimetry* (2004).

ISO/DIS 15901-2, *Evaluation of Pore Size Distribution and Porosity of Materials by Mercury Porosimetry and Gas Adsorption - Part 2: Analysis of Mesopores and Macropores by Gas Sorption* (2004).

ISO/CD 15901-3, *Evaluation of Pore Size Distribution and Porosity of Materials by Mercury Porosimetry and Gas Adsorption - Part 3: Analysis of Micropores by Gas Adsorption* (2004).

Appendix 4: Glossary

For comprehensive collection of metrological terms defined by international agreement see the *Vocabulaire International des Terms Fondamentaux and Généraux de Métrologie (BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, and OIML, 1993*), often referred to simply as the VIM. Terms related to the analytical characterization of porous solids are given here for ease of reference. (See also NIST Recommended Practice Guides SP 960-1 and SP 960-3 for additional related terms).

acceptance number: in acceptance sampling, the maximum number of non-conforming items in a sample that allows the conclusion that the lot conforms to the specification

acceptance sampling: sampling done to provide specimens for acceptance testing

acceptance testing: testing performed to decide if a material meets acceptance criteria

accepted reference value: a value that serves as an agreed upon reference for comparison, and which is derived as (1) a theoretical or established value, based on scientific principles, (2) an assigned or certified value, based on experimental work of some national or international organization, or (3) a consensus or certified value, based on collaborative experimental work under the auspices of a scientific or engineering group

accuracy (of a test method): closeness of the agreement between the true value (or an accepted standard value) of the property being tested and the average of many observations made according to the test method

accuracy (of measurement): closeness of the agreement between the result of a measurement and the value of the measurand

adsorbate: a molecular species that adheres to, or is adsorbed in, a surface layer of a solid substance; a substance that is adsorbed at the interface, or into the interfacial region, of a substrate material or adsorbent

adsorbed amount *(n)*: the number of moles of an adsorbed gas (which may depend on pressure and temperature)

adsorbent: the solid material or substrate on which adsorption occurs

adsorptive: the gas or vapor to be adsorbed

adsorption: the process by which a substance is accumulated at an interface or in an interfacial region. (Should not be confused with absorption which refers to accumulation inside a material)

agglomerate: rigid, consolidated assemblage of particles; an aggregate held together by physical or electrostatic forces

agglomeration: formation of aggregates *via* physical (van der Waals, hydrophobic) or electrostatic forces; the resulting structure is called an agglomerate

aggregate: a cohesive mass consisting of particulate sub-units; a loose, unconsolidated assemblage of particles

apparent density: the mass of a unit volume of powder, usually expressed as grams per cubic centimeter, determined by a specific method; density of a material, including closed and inaccessible pores, as determined by a stated method

average: for a series of observations, the total divided by the number of observations

batch: a definite quantity of some product or material produced under conditions that are considered uniform (ASTM 456-96)

bias: in statistics, a constant or systematic error in test results (ASTM 456-96)

blind pore (dead end pore): a pore with a single connection with an external surface

bulk density: the mass per unit volume of a powder under nonstandard conditions, for example, in a shipping container (not to be confused with apparent density); includes closed and interparticle voids

bulk sample: one or more portions which (1) are taken from material that does not consist of separately identifiable units and (2) can be identified after sampling as separate or composed units (ASTM 456-96)

cage: intracystalline pore with windows allowing no passage of molecules bigger than a molecule of water (H_2O)

calibrant: a reference material used for a calibration (ASTM E 135-04)

calibrate: to determine and record the relationship between a set of standard units of measure and the output of an instrument or test procedure (ASTM 456-96)

calibration: (1) the act or process of calibrating; the recorded relationship resulting from calibrating, (2) the determination of a bias conversion factor of an analytical process, under specified conditions, in order to obtain meaningful results

cavity: an intracrystalline pore of finite extent and having at least one window bigger than a water molecule

certificate of traceability: document stating the purpose, protocols, and measurement pathways that support claims by a Traceable Reference Material to have values traceable to specific standards or stated references; the document references specific reports of analysis

certified reference material: reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty as a stated level of confidence (VIM, 1993)

certified value: a value reported on an SRM/CRM certificate or report of analysis for which all known or suspected sources of bias have been fully investigated or included in an uncertainty statement or analysis.
(NIST SP 260-136)

channel: an intercrystalline pore allowing passage of molecules from one distinguishable region to another.

closed pore: a pore not connected to the surface; a contiguous volume enclosed by a solid substance

equilibrium adsorption pressure: the pressure of a substance in the gas state in equilibrium with that substance in the adsorbate state

external surface area: area of 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; the area of the smallest outermost surface forming a boundary of a volume occupied by a solid substance

heterogeneous material: material in which sub-samples of the material will have significantly different values of the characteristics under consideration, compared to the mean values of the characteristics for the whole material

homogeneous material: material in which sub-samples of the material do not have significantly different values of the characteristics under consideration from the mean value of the characteristics for the whole material

hydraulic radius: mean value of the ratio, $r_h = V_p / A$, for a porous solid, where

r_h = hydraulic radius,
V_p = pore volume determined at saturation, and
A = surface area (*e.g.* determined by the BET method)

increment: in sampling, a portion of material removed from a lot by a single operation

information value: a value that will be of interest and use to the user of a reference material, but for which insufficient information is available to assess the uncertainty associated with the value. (NIST SP 260 -136)

ink bottle pore: a narrow necked open pore

interconnected pore: pore that communicates with other pores

interlaboratory test comparison: organization, performance, and evaluation of tests on the same or similar items or materials by two or more laboratories in accordance with predetermined conditions(ISO Guide 2)

interlaboratory testing: the evaluation of a test method in more than one laboratory by analyzing data obtained from one or more materials that are as homogeneous as practical (ASTM 456-96)

internal surface area: area of the pore walls, excluding the external surface area

isotherm: in adsorption, the relation, at constant temperature, between the amount adsorbed and the equilibrium pressure of the gas

laboratory sample: a portion of material taken to represent the lot sample, or the original material, and used in the laboratory as a source of test specimens

laboratory sampling unit: a portion of material taken to represent one of the lot sampling units or the original material and used in the laboratory as a source of test specimens

macropore: pore of internal width greater than 50 nm

measurand: a quantity subject to measurement

measurement value: the numerical result of quantifying a particular property or dimension

mesopore: pore of internal width between 2 nm and 50 nm

micropore: pore of internal width less than 2 nm

monolayer amount (n_m): the number of moles of the adsorbate that forms a monomolecular layer over the surface of the adsorbent

open pore: a cavity or channel with access to an external surface

physisorption (as distinct from chemisorption): a general phenomenon, which occurs whenever an adsorbable gas (the adsorptive) is brought into contact with the surface of a solid (the adsorbent)

pore size: generally, pore width; diameter or distance between opposite walls of the pore; diameter of cylindrical pores; width of slit shaped pores; see also micro-, meso-, and macropores

pore size distribution: represented by the derivatives $\frac{dA_p}{dr_p}$ or $\frac{dV_p}{dr_p}$ as a function of r_p; where A_p, V_p and r_p are the wall area, volume and radius of the pores; for cylindrical pores, r_p is the pore radius; for other pore shapes, $2\ r_p$ should be replaced by the width.

pore volume: volume of pores as determined by stated method (together, for instance, with the nature of the probe molecule, the wavelength of the radiation used, the ultimate intrusion pressure, etc.)

porosity: 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.

porous solid: solid with pores, cavities, or channels that are deeper than they are wide

precision: the degree of agreement within a set of observations or test results obtained as directed in a test method

precision (single operator, within-laboratory): the precision of a set of statistically independent observations all obtained as directed in the method and obtained over the shortest practical time interval in one laboratory by a single operator using one apparatus and randomly draw specimens from one sample of the material being tested (ASTM 456-96)

precision (multiple operators, within-laboratory): the precision of a set of statistically independent test results all obtained in one laboratory using a single sample of material and with each test result obtained by a different operator, with each operator using one apparatus to obtain the same number of observations by testing randomly drawn specimens over the shortest practical time interval (ASTM 456-96)

precision (multiple operators, between-laboratory): the multi-laboratory, single-sample, single-operator-apparatus-day (within-laboratory) precision of a method; the precision of a set of statistically independent test results all of which are obtained by testing the same sample of material and each of which is obtained in a different laboratory by one operator using one apparatus to obtain the same number of observations by testing randomly drawn specimens over the shortest practical time interval (ASTM 456-96)

reference material: a material or substance one or more of whose property values are sufficiently homogeneous, stable, and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials (VIM 1993)

reference standard: a reference material, generally of the highest metrological quality available, from which measurements are derived

reference value: a best estimate value of the true value provided on a certificate, certificate analysis, or report of analysis where all known or suspected sources of bias have not been fully investigated (NIST SP 260-136)

relative pressure: the ratio (p/p_0) of the equilibrium adsorption pressure, p, to the saturation vapor pressure, p_0

right cylindrical pore: a cylindrical pore perpendicular to the surface

repeatability: a measure of precision and expressed as a standard deviation; the precision of successive measurements of the same sample, or the closeness of the agreement among the results of successive measurements of the same measurand, carried out under the following conditions of measurement (called repeatability conditions): the measuring instrument, the method of measurement, time, conditions of use, observer, and location.

reproducibility (of results of measurements): closeness of the agreement between the results of measurements of the same measurand carried out under changed conditions of measurement. A valid statement of reproducibility requires specification of the conditions changed. The changed conditions may include principle of measurement, method of measurement, observer, measuring instrument, reference standard, location, conditions of use, and time. Repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results. Results usually are understood to be corrected results.

riffler: a device for dividing a stream of particles into representative samples

roughness factor: ratio of the external surface area to the area of the geometrical envelope of the particles

sample: a portion of a material intended to be representative of the whole (ASTM 135-98); a portion of a lot of materials which is taken for testing or for record purposes; a group of specimens used, or observations made, which provide information that can be used for making statistical inferences about the population(s) from which the specimens were drawn

sample division: the process in sample preparation where the mass of the sample is decreased by partition or extraction without change in particle size (ISO/WD 14488-1999)

sampling plan: a procedure for obtaining a sample

sampling unit: an identifiable, discrete unit or subunit of material that could be taken as part of a sample

saturation vapor pressure: the vapor pressure of the bulk liquified adsorbate at the temperature of adsorption

specification: a precise statement of a set of requirements to be satisfied by a material, product, system, or service that indicates the procedures for determining whether each of the requirements is satisfied

specimen: a specific portion of a material or laboratory sample upon which a test is performed or which is selected for that purpose

standard deviation, s: *of a sample*, a measure of the dispersion of variates observed in a sample expressed as the positive square root of the sample variance

Standard Reference Material® (SRM®): a CRM issued by NIST that also meets additional NIST-specified certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of material. (NIST SP 260-136)

standardization: correlation of an instrument response to a standard of known accuracy

surface area: extent of total surface area, as determined by a given method under stated conditions. It is essential to state the method used!

systematic sampling: the process of selecting units in a sample in accordance with a specific order or location in time or space, or both

test method: a definitive procedure for the identification, measurement, and evaluation of one or more qualities, characteristics, or properties of a material, product, system, or service that produces a test result

test result: a value obtained by applying a given test method, expressed as a single determination or a specified combination of a number of determinations

test sample: the sample prepared from the laboratory sample from which the test portions are withdrawn

through pore: a pore which passes all the way through the sample

tortuosity: the path available for diffusion through a porous bed in relation to the shortest distance across the bed

total porosity: ratio of volume of pores and voids to overall volume

traceability: the property of a result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties (VIM, 1993); the ability to trace the history, application or location of an item or activity and like items or activities by means of recorded identification. (ANSI/ASQC A3-1987, A)

NIST Traceable Reference Material™ (NTRM™): a commercially-produced reference material with a well-defined traceability linkage to existing NIST standards for measurements. (NIST SP 260-136)

true density: the mass of a particle divided by its volume excluding pores and interparticle voids

uncertainty: an indication of the variability associated with a measured value that takes into account two major components of error: (1) bias and (2) the random error attributed to the imprecision of the measurement process (ASTM 456-96)

validation: proof, with reference materials or materials traceable to them, that a method is acceptable for all elements in its scope (ASTM 135-98)

void: space between particles

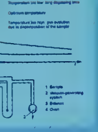
Appendix 5 : Abbreviations

A5.1 Organizations

AFNOR: Association Française de Normalisation
ASTM: American Society for Testing Materials
BAM: Bundesanstalt für Materialforschung und -prüfung, Germany
BIPM: Bureau International des Poids et Mesures
BSI: British Standards Institution
CEN: Comité Européenne de Normalisation
DIN: Deutsches Institut für Normung
IEC: International Electrotechnical Commission
IFCC: International Federation of Clinical Chemistry
ISO: International Organization for Standardization
IUPAC: International Union of Pure and Applied Chemistry
IUPAP: International Union of Pure and Applied Physics
NIST: National Institute of Standards and Technology, USA
OIML: Organisation Internationale de Métrologie Légale

A5.2 Scientific items

BET method: Method of Brunauer, Emmett, and Teller
BJH method: Method of Barrett, Joyner, and Halenda
CRM: Certified Reference Material
DFT: Density Functional Theory
DR method: Method of Dubinin-Radushkevich
HK method: Method of Horvath-Kavazoe
RM: Reference Material
SF method: Method of Saito-Foley
SRM®: Standard Reference Material (NIST)
STP: Standard Temperature (273.15 K) and Pressure (101.325 kPa)
VIM: *Vocabulaire International des Terms Fondamentaux and Généraux de Métrologie* (issued jointly by BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, and OIML)



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