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

**Part 2:
Analysis of mesopores and macropores
by gas adsorption**

*Distribution des dimensions des pores et porosité des matériaux solides
par porosimétrie au mercure et par adsorption de gaz —*

*Partie 2: Analyse des mésopores et des macropores par adsorption de
gaz*



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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 15901-2 was prepared by Technical Committee ISO/TC 24, *Sieves, sieving and other sizing methods*, Subcommittee SC 4, *Sizing by methods other than sieving*.

ISO 15901 consists of the following parts, under the general title *Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption*:

- *Part 1: Mercury porosimetry*
- *Part 2: Analysis of mesopores and macropores by gas adsorption*
- *Part 3: Analysis of micropores by gas adsorption*

Introduction

Generally speaking, different types of pores can be pictured as apertures, channels or cavities within a solid body, or as the space (i.e. an interstice or a void) between solid particles in a bed, compact or aggregate. Porosity is a term which is often used to indicate the porous nature of solid material and is more precisely defined as the ratio of the volume of accessible pores and voids to the total volume occupied by a given amount of the solid. In addition to the accessible pores, a solid can contain closed pores which are isolated from the external surface and into which fluids are not able to penetrate. The characterization of closed pores (i.e. cavities with no access to an external surface) is not covered in this part of ISO 15901.

Porous materials can take the form of fine or coarse powders, compacts, extrudates, sheets or monoliths. Their characterization usually involves the determination of the pore size distribution, as well as the total pore volume or porosity. For some purposes, it is also necessary to study the pore shape and interconnectivity, and to determine the internal and external surface areas.

Porous materials have great technological importance, for example in the context of the following:

- a) controlled drug release;
- b) catalysis;
- c) gas separation;
- d) filtration including sterilization;
- e) materials technology;
- f) environmental protection and pollution control;
- g) natural reservoir rocks;
- h) building material properties;
- i) polymer and ceramic industries.

It is well established that the performance of a porous solid (e.g. its strength, reactivity, permeability or adsorbent power) is dependent on its pore structure. Many different methods have been developed for the characterization of pore structure. In view of the complexity of most porous solids, it is not surprising to find that the results obtained do not always concur, and that no single technique can be relied upon to provide a complete picture of the pore structure. The choice of the most appropriate method depends on the application of the porous solid, its chemical and physical nature and the range of pore size.

Commonly used methods are as follows.

- **Mercury porosimetry**, where the pores are filled with mercury under pressure. This method is suitable for many materials with pores in the approximate diameter range of 0,003 μm to 400 μm , and especially in the range of 0,1 μm to 100 μm .
- **Mesopore and macropore analysis by gas adsorption**, where the pores are characterized by adsorbing a gas, such as nitrogen, at liquid nitrogen temperature. This method is used for pores in the approximate diameter range 0,002 μm to 0,1 μm (2 nm to 100 nm), and is an extension of the surface area estimation technique (see ISO 9277). (Discussion of other pore size distribution analysis techniques can be found in Recommendations for the Characterization of Porous Solids ^[1].)

- **Micropore analysis by gas adsorption**, where the pores are characterized by adsorbing a gas, such as nitrogen, at liquid nitrogen temperature. This method is used for pores in the approximate diameter range 0,000 4 μm to 0,002 μm (0,4 nm to 2 nm).

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

Part 2: Analysis of mesopores and macropores by gas adsorption

1 Scope

This part of ISO 15901 describes a method for the evaluation of porosity and pore size distribution by gas adsorption. It is a comparative, rather than an absolute test. The method is limited to the determination of the quantity of a gas adsorbed per unit mass of sample at a controlled, constant temperature.

This part of ISO 15901 does not specify the use of a particular adsorptive gas, however nitrogen is the adsorptive gas most commonly used in such methods. Similarly, the temperature of liquid nitrogen is the analysis temperature most commonly used. Use is sometimes made of other adsorptive gases, including argon, carbon dioxide and krypton, and other analysis temperatures, including those of liquid argon and solid carbon dioxide. In the case of nitrogen adsorption at liquid nitrogen temperature, the basis of this method is to measure the quantity of nitrogen adsorbed at 77 K as a function of its relative pressure.

Traditionally, nitrogen adsorption is most appropriate for pores in the approximate range of widths 0,4 nm to 50 nm. Improvements in temperature control and pressure measurement now allow larger pore widths to be evaluated. This part of ISO 15901 describes the calculation of mesopore size distribution between 2 nm and 50 nm, and of macropore distribution up to 100 nm.

The method described in this part of ISO 15901 is suitable for a wide range of porous materials, even though the pore structure of certain materials is sometimes modified by pretreatment or cooling.

Two groups of procedures are specified to determine the amount of gas adsorbed:

- those which depend on the measurement of the amount of gas removed from the gas phase (i.e. gas volumetric methods), and
- those which involve the measurement of the uptake of the gas by the adsorbent (i.e. direct determination of increase in mass by gravimetric methods).

In practice, static or dynamic techniques can be used to determine the amount of gas adsorbed. To derive pore size distribution from the isotherm, it is necessary to apply one or more mathematical models, which entails simplifying certain basic assumptions.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 8213, *Chemical products for industrial use — Sampling techniques — Solid chemical products in the form of particles varying from powders to coarse lumps*

ISO 9276-1, *Representation of results of particle size analysis — Part 1: Graphical representation*

ISO 9277:1995, *Determination of the specific surface area of solids by gas adsorption using the BET method*

3 Terms and definitions

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

- 3.1**
adsorbate
adsorbed gas
- 3.2**
amount adsorbed
 n_a
number of moles of gas adsorbed at a given pressure p
- 3.3**
adsorbent
solid material on which adsorption occurs
- 3.4**
adsorption
enrichment of the adsorptive gas at the external and accessible internal surfaces of a solid material
- 3.5**
adsorptive
gas or vapour to be adsorbed
- 3.6**
blind pore
dead-end pore
open pore having a single connection with an external surface
- 3.7**
equilibrium adsorption pressure
 p
pressure of the adsorptive gas in equilibrium with the adsorbate
- 3.8**
ink bottle pore
narrow necked open pore
- 3.9**
interconnected pore
pore which communicates with one or more other pores
- 3.10**
isotherm
relationship between the amount of gas adsorbed and the equilibrium pressure of the gas, at constant temperature
- 3.11**
macropore
pore of internal width greater than 50 nm

3.12**mesopore**

pore of internal width between 2 nm and 50 nm

3.13**micropore**

pore of internal width less than 2 nm which is accessible for a molecule to be adsorbed

3.14**monolayer amount**

n'_m

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

3.15**monolayer capacity**

V_m

volumetric equivalent of monolayer amount expressed as gas at standard conditions of temperature and pressure (STP)

3.16**open pore**

cavity or channel with access to an external surface

3.17**porosity**

open porosity

ratio of the volume of open pores and voids to the total volume occupied by the solid

3.18**relative pressure**

ratio of the equilibrium adsorption pressure, p , to the saturation vapour pressure, p_0

3.19**right cylindrical pore**

cylindrical pore perpendicular to the surface

3.20**saturation vapour pressure**

vapour pressure of the bulk liquefied adsorptive gas at the temperature of adsorption

3.21**through pore**

pore which passes all the way through the sample

3.22**volume adsorbed**

volumetric equivalent of adsorbed amount expressed as gas at standard conditions of temperature and pressure (STP)

4 Symbols

| Symbol | Quantity | SI Unit |
|-------------------|--|--|
| A_{He} | slope of helium data regression from free space determination | $\text{cm}^3 \cdot \text{Pa}^{-1}$ |
| a'_p | specific pore area | $\text{m}^2 \cdot \text{g}^{-1}$ |
| B_{He} | intercept of helium data regression from free space determination | cm^3 |
| b | buoyancy | $\text{g} \cdot \text{Pa}^{-1}$ |
| C_{N} | non-ideal correction factor, equal to $0,464 \times 10^{-6}$ for nitrogen at 77,35 K | Pa^{-1} |
| d_p | pore diameter | nm |
| m_{ss} | mass of the solid sample material | g |
| m_a | mass of gas adsorbed | g |
| m_{ai}^* | recorded mass on the balance of gas adsorbed of the i th dose | g |
| m_{ai} | correct mass of gas adsorbed at pressure p_i | g |
| n_a | amount of gas adsorbed | mol |
| n'_a | specific amount of gas adsorbed | $\text{mol} \cdot \text{g}^{-1}$ |
| n'_m | specific monolayer amount of gas | $\text{mol} \cdot \text{g}^{-1}$ |
| $n'_{a,x}$ | specific amount adsorbed at a particular relative pressure ($x = 1, 2, 3$) | $\text{mol} \cdot \text{g}^{-1}$ |
| p | pressure of the adsorptive gas in equilibrium with the adsorbate | Pa |
| p_x | adsorptive pressure, used to determine free space ($x = 1, 2, 3$) | Pa |
| p_i | adsorptive pressure of the i th dose | Pa |
| p_{man} | adsorptive pressure measured in the dosing manifold | Pa |
| p_0 | saturation vapour pressure | Pa |
| p/p_0 | relative pressure of the adsorptive gas (see Note 1) | 1 |
| p_{std} | standard pressure, equal to 101 325,02 | Pa |
| R | ideal gas constant, equal to 8,314 510 | $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ |
| r_K | Kelvin radius | nm |
| t | statistical thickness of the adsorbed layers of gas (see Note 2) | nm |
| T_{amb} | ambient temperature | K |
| T_b | temperature of the cryogenic bath | K |
| T_{eq} | temperature of the dosing manifold when equilibrium of pressure has been achieved | K |
| T_{man} | temperature of the dosing manifold at time of the addition of the adsorptive dose | K |
| T_{std} | standard temperature, equal to 273,15 | K |
| $V_{\text{sh},b}$ | sample holder volume at cryogenic bath temperature | cm^3 |
| V_d | adsorptive volume of dose in sample holder | cm^3 |

| Symbol | Quantity | SI Unit |
|--------------|---|-------------------------------------|
| V_{di} | adsorptive volume of the i th dose placed in the sample holder | cm^3 |
| $V_{fs,b}$ | free space volume with sample holder immersed in cryogenic bath | cm^3 |
| $V_{fs,amb}$ | free space volume with sample holder at ambient temperature | cm^3 |
| V'_{ai} | volume of gas adsorbed on the i th dose at STP (273,15 K; 101 325 Pa) | $\text{cm}^3 \cdot \text{g}^{-1}$ |
| V_l | specific liquid equivalent of the volume of adsorbate condensed in pore capillaries | $\text{cm}^3 \cdot \text{g}^{-1}$ |
| V_m | monolayer capacity of adsorbed gas | cm^3 |
| V_{man} | volume of the dosing manifold | cm^3 |
| $V_{m,l}$ | molar volume of liquid condensate | $\text{cm}^3 \cdot \text{mol}^{-1}$ |
| α_s | normalized adsorption (see Note 1) | 1 |
| ρ | density | $\text{g} \cdot \text{cm}^{-3}$ |
| δ_a | thickness of one monolayer of adsorbate | nm |
| σ_l | surface tension of the liquid condensate | $\text{J} \cdot \text{m}^{-2}$ |

NOTE 1 According to ISO 31-0, the coherent SI unit for any quantity of dimension one (at present commonly determined “dimensionless”) is the unit one.

NOTE 2 While the symbol t is generally used to represent time, in the normal practice of pore size distribution analysis by gas adsorption, t is traditionally used to represent the statistical thickness of the adsorbed layers of gas, as indicated in the list above. Therefore all uses of the symbol t in this part of ISO 15901 refer to statistical thickness, and not to time.

5 Principles

5.1 General principles

The quantity of gas adsorbed on a surface is recorded as a function of the relative pressure of the adsorptive gas for a series of either increasing relative pressures on the adsorption portion of the isotherm, decreasing relative pressures on the desorption portion of the isotherm, or both. The relation, at constant temperature, between the amount adsorbed and the equilibrium relative pressure of the gas is known as the adsorption isotherm. The minimum pore size that can be investigated is limited by the size of the adsorptive molecule.

NOTE In the case of nitrogen, the minimum investigable pore size is approximately 0,5 nm.

The maximum pore width is limited by the practical difficulty of determining the amount of gas adsorbed at high relative pressure, p/p_0 .

Comparative pore size distributions of less than 2 nm in width, called micropores, can be determined with nitrogen as the adsorptive gas, although other gases (e.g. argon) may provide more reliable results. Both nitrogen and argon have been used successfully for the determination of the mesopore size distribution.

The pore size distributions calculated respectively from the adsorption and desorption portions of the isotherm will not necessarily be the same.

Adsorption of gas into a porous solid takes place in accordance with 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. The computation of the mesopore size distribution is generally carried out using methods based upon the Kelvin equation.

When nitrogen is employed as the adsorptive gas at the temperature of liquid nitrogen, 77,35 K, the Kelvin equation may be expressed in the form:

$$r_K = \frac{-2\sigma_l V_{m,l}}{RT_b \ln\left(\frac{p}{p_0}\right)} = \frac{-0,953}{\ln\left(\frac{p}{p_0}\right)} \quad (1)$$

where

σ_l is the surface tension of the liquid condensate;

$V_{m,l}$ is the molar volume of the liquid condensate;

R is the ideal gas constant;

T_b is the analysis temperature;

r_K is the radius of curvature of the adsorptive gas condensed in the pore;

p_0 is the saturation vapour pressure of nitrogen at the temperature of the liquid nitrogen;

p is the equilibrium pressure of the nitrogen adsorptive gas.

The numeric constants evaluate to a value of 0,953 nm for nitrogen at 77 K.

Since condensation is considered to occur only after an adsorbed layer has formed on the pore walls, it is necessary to make allowance for the thickness of this adsorbed film by means of an equation. In the case of cylindrical pores, this equation is:

$$d_p = 2(r_K + t) \quad (2)$$

where

d_p is the cylindrical pore diameter (in nm);

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

Various methods exist for the evaluation of t as a function of relative pressure and for calculating pore size distribution [3] [4].

The Kelvin equation cannot be used for pores of less than approximately 2 nm diameter. This is because interactions with adjacent pore walls become significant and the adsorbate can no longer be considered liquid when it has bulk thermodynamic properties.

5.2 Choice of method

The required experimental data to establish a sorption isotherm may be obtained by volumetric or gravimetric methods, either in measurements at stepwise varied pressure and observation of the equilibrium volume of pressure or mass respectively, or by continuous varied pressure. Because sorption takes a long time in some parts of the isotherm, the stepwise static method is recommended to ensure the measurement of equilibrium values.

The volumetric method is based on calibration volumes and pressure measurements (see ISO 9277:1995, Figure 5). The volume of adsorbate is calculated as the difference between the gas admitted and the quantity of gas filling the dead volume (i.e. the free space in the sample container, including connections) by application of the general gas equation. The various volumes of the apparatus should be calibrated and their temperatures should be taken into account.

For gravimetric measurements, a sensitive microbalance and a pressure gauge are required (see ISO 9277:1995, Figure 6). The mass adsorbed is measured directly, but a pressure-dependent buoyancy correction is necessary. Equilibrium is observed by monitoring the mass indication. Because the sample is not in direct contact with the thermostat, it is necessary to ensure the correct temperature artificially.

6 Verification of apparatus performance

It is recommended that a certified reference material¹⁾, selected by the user, be tested on a regular basis in order to monitor instrument calibration and performance. In the case of specific surface area analysis, testing may be carried out on a local reference material which is traceable to a certified reference material.

7 Calibration

Calibration of individual components should be carried out in accordance with the manufacturer's recommendations. Generally speaking, calibration of pressure transducers and temperature sensors is accomplished with reference to standard pressure- and temperature-measuring devices which have calibrations traceable to national standards. Manifold volume calibration is achieved through appropriate pressure and temperature measures, using constant-temperature volumetric spaces or solids of known, traceable volume. Analysis tube calibration is generally achieved by the determining of free space, as described in 9.3.

8 Sample preparation

Sampling shall be carried out in accordance with ISO 8213. Before adsorption measurements are taken, it is necessary to remove physisorbed material from the surface of the adsorbent by "outgassing". In this process, it is essential to be able to obtain reproducible adsorption data whilst avoiding irreversible changes to the adsorbent surface. The outgassing technique should be selected in accordance with the adsorption system being studied, and the conditions should be controlled so that these objectives are achieved.

Several outgassing techniques exist. The commonest is exposure of the surface to high vacuum, usually at an elevated temperature. In some cases, flushing the adsorbent with an inert gas (which may be the adsorptive gas) at an elevated temperature is sufficient. With some microporous materials, one or more cycles of flushing with gas, followed by heating in vacuum, may be necessary before reproducible adsorption data can be obtained. Whatever technique is used, it is sometimes possible to reduce the outgassing time, especially for very damp materials, by a preliminary drying of the sample in an oven at a suitable temperature.

When vacuum conditions are used, outgassing to a residual pressure in the range of approximately 1,0 Pa to 0,01 Pa is usually sufficient for mesoporous materials, while a residual pressure of 0,01 Pa or lower is recommended for microporous materials. High vacuum conditions may cause surface changes with some adsorbents. As the rate of outgassing is heavily temperature dependent, the temperature should be the maximum compatible with minimal outgassing, whilst avoiding changes to the adsorbent (e.g. sintering, decomposition). Changes in the adsorbent may depend upon the heating rate used.

1) Certified reference materials are offered by a number of national standard bodies and are currently available from the following addresses:

Bundesanstalt für Materialforschung und -prüfung (BAM)
Division I. 1 Inorganic Chemical Analysis; Reference Materials
Branch Adlershof, Richard-Willstätter-Straße 11, D-12489 Berlin

Standard Reference Materials Program
National Institute of Standards and Technology (NIST)
100 Bureau Drive, Stop 2322
Gaithersburg, MD 20899-2322

This information is given for the convenience of users of this part of ISO 15901 and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

In order to optimize pretreatment, it is advisable to study the thermal behaviour of the material, e.g. by thermogravimetric analysis and differential scanning calorimetry, in order to determine the temperatures at which materials are evolved from the sample, together with any phase changes which could affect the history of the sample.

If this information is not available, temperature selection should be based on prior experience and general knowledge of the properties of the adsorbent, and trials should be conducted if necessary.

The progress of outgassing should be followed by a suitable monitoring variable. This may be the pressure in the system (commonly used for the vacuum technique), or the mass of the adsorbent (applicable to the gravimetric method). When the observed variable has reached a steady value, which may take 0,25 h or many more, depending on the sample, the completeness of outgassing should be checked, e.g. with vacuum techniques; which can be done by isolating the heated sample and checking that the pressure over the sample does not rise significantly over a period of a few minutes. A sample outgas rate of less than 0,7 Pa/min at ambient temperature is generally sufficient where nitrogen is to be used as the adsorptive gas.

In all cases, the outgassing conditions (e.g. temperatures, heating rates, duration, residual pressure) should be recorded.

9 Static volumetric method

9.1 Principle

In the static volumetric method, a known amount of gas is admitted to a sample bulb thermostatted at the adsorption temperature. Adsorption of the gas onto the sample occurs, and the pressure in the confined volume continues to fall until the adsorbate and the adsorptive gas are in equilibrium. The amount of adsorbate at the equilibrium pressure is the difference between the amount of gas admitted and the amount of adsorptive gas remaining in the gas phase. The pressure is measured, together with the temperatures and volumes of the system. The volumes are most easily determined by gas expansion of an inert gas such as helium.

9.2 Apparatus and materials

9.2.1 General

A static volumetric apparatus generally consists of a metal or glass manifold, which interconnects the sample tube, a saturation pressure probe, a pressure-measuring device, a vacuum source, and nitrogen and helium supplies. The volume of the manifold shall be calibrated. A means of recording the temperature of the manifold should be provided. Current commercial instrumentation offers two levels of vacuum systems and pressure resolution, both of which are suitable for the analyses discussed in this part of ISO 15901. The upper pore size limit of the technique is limited by the ability to measure adsorptive saturation pressure.

Sample tubes of various sizes may be used. Typical volumes range from 10 cm³ to 20 cm³. To minimize errors, the free space above the sample should be kept as small as possible and can, for example, be reduced by placing a glass rod in the neck of the sample tube.

9.2.2 Apparatus

9.2.2.1 Dewar flasks, of various sizes, and storage facilities for liquid nitrogen. A 20 litre to 40 litre storage vessel will generally be required.

9.2.2.2 Constant level device, to maintain the liquid nitrogen level around the sample tube at a minimum of 15 mm above the sample, and constant to within 1 mm. Minimizing volumes exposed to level change serves to minimize errors due to change.

9.2.2.3 Small electric heating mantle or furnace, to fit around the sample tube during outgassing. A maximum temperature of 350 °C is generally adequate.

9.2.2.4 Weighing balance, with a resolution of 1 mg or better.

9.2.3 Materials

9.2.3.1 Nitrogen or other suitable adsorptive gas (e.g. argon), dry, not less than 99,99 % purity.

9.2.3.2 Helium, not less than 99,99 % purity.

9.2.3.3 Liquid nitrogen or other means of temperature control (e.g. liquid argon), not less than 99 % purity.

9.3 Typical test procedure

9.3.1 General

The procedure described here assumes that manually-controlled apparatus is used. The use of automated apparatus based upon the same operating principles is acceptable.

9.3.2 Measuring mass of sample

Weigh the empty sample bulb, along with any stopper and void-space filling device. Weigh a representative test sample and place it in the sample bulb.

NOTE 1 To ensure accuracy, the sample is reweighed after analysis. If the mass is not equal to the initial mass after outgassing and prior to analysis, the calculations are based on the mass after analysis ("outgassed sample mass", see 9.3.8).

NOTE 2 For the measurement of nitrogen adsorption, it is preferable that the size of the sample be such that the total surface area lies between 5 m² and 200 m².

9.3.3 Outgassing

Connect the sample tube to the apparatus and outgas the sample (see Clause 7), first at room temperature and then, if necessary, while the sample is heated at a higher temperature for a sufficient duration. Outgas the powders carefully to avoid loss of sample. Evacuate the sample and the apparatus. Check the outgassing rate by isolating the sample from the vacuum system. Any significant increase in pressure indicates incomplete outgassing or a leak in the system (see ISO 9277:1995, Figure 4.).

NOTE 1 Sample outgassing can take place on another apparatus especially designed for that purpose. At the end of the outgassing process, the sample tube is filled to approximately atmospheric pressure with a dry inert gas, generally the adsorptive gas.

NOTE 2 For more precise measurement, helium can be introduced into the sample tube before immersion in the liquid nitrogen, thereby helping to maintain the outgassed condition of the sample. Given that some microporous materials retain helium strongly, it is important that, prior to analysis, all helium be evacuated completely, which can take many hours. Rather than helium, a non-adsorbing and non-reacting gas, e.g. the adsorptive gas, is introduced into the sample holder with the samples.

NOTE 3 When sealing valves are available, the sample can be transferred under vacuum.

9.3.4 Measuring free space

The free space shall be measured before or after the measurement of the adsorption isotherm. The calibration is done volumetrically, using helium at the measuring temperature. It should be noted that some materials may adsorb and/or absorb helium. In such cases, corrections can be made after measuring the sorption isotherm. If the measurement of the free space can be separated from the adsorption measurement, the use of helium can be avoided. The void volume of the empty sample cell is measured at ambient temperature using nitrogen. Subsequently, a blank experiment (with the empty sample cell) is performed under the same experimental conditions (temperature and relative pressure range) as the sorption measurements. The

required correction for the sample volume is made by entering the sample density or by pycnometric measurement with nitrogen at ambient temperature at the start of the sorption analysis (in which case the effects of nitrogen adsorption can be ignored). The need to determine free space may be avoided if difference measurements are used, i.e. by means of a reference and sample tube connected by a differential transducer. In this case, and in the case where variation in effective free space is known, a constant level device is not needed.

9.3.5 Measuring free space with helium

9.3.5.1 If free space determination is initiated before the sample is immersed into liquid nitrogen, use the following procedure.

Admit helium into the apparatus manifold to a pressure of between 7×10^4 Pa and $1,1 \times 10^5$ Pa. Record this pressure, p_1 , and then admit the helium into the sample tube. Record the new pressure, p_2 . Record the temperature of the manifold, T_{man} .

Immerse the sample bulb and saturation pressure probe in the liquid nitrogen. Record the new pressure of the helium, p_3 . Evacuate the sample and the apparatus. Maintain the level of liquid nitrogen at a constant level.

9.3.5.2 If free space determination is initiated after the sample is immersed into liquid nitrogen, use the following alternative procedure.

Connect the sample tube to the apparatus and outgas the sample, evacuating the sample and the apparatus. Determine saturation vapour pressure as described above. Ensure that the apparatus manifold is fully evacuated.

Admit helium into the apparatus manifold to a pressure of between $1,3 \times 10^4$ Pa and 4×10^4 Pa. Allow the helium to thermally equilibrate, then record the pressure, p_1 . Admit helium into the sample tube. Allow the helium to equilibrate such that a constant pressure is achieved. Record the new pressure, p_2 , and the apparatus manifold temperature. Close the sample and repeat the procedure, such that at least one additional helium sample pressure point is measured. Evacuate the helium from the apparatus and sample tube.

9.3.6 Measuring saturation pressure (p_0)

Stop evacuation and admit nitrogen into the saturation pressure tube whilst monitoring the pressure. Continue admitting nitrogen until the pressure is constant. Once the pressure reaches saturation, nitrogen will begin to condense in the saturation tube. Record the saturation vapour pressure of the nitrogen, p_0 . Close the saturation pressure valve. Re-evacuate the apparatus manifold. It is recommended that the saturation vapour pressure of nitrogen be recorded at least every 1 h to 2 h. An alternative way of obtaining the saturation pressure is to measure the temperature of the liquid nitrogen bath and to calculate the corresponding saturation pressure using a proper equation of state.

9.3.7 Measuring adsorption isotherm

To record the adsorption portion of the isotherm, the pressure of nitrogen over the sample is increased in a series of steps. Close off the vacuum system from the manifold and admit nitrogen into the manifold. Allow time for the nitrogen gas to thermally equilibrate with the manifold. Record the pressure in the manifold, p_{man} , and the temperature of the manifold, T_{man} . Allow nitrogen to expand into the sample tube. Allow enough time for the adsorption process to equilibrate, which is indicated by a constant pressure reading. Record this stable pressure, p (equilibrium pressure). Record the manifold temperature after equilibration, T_{eq} . Repeat this sequence of operations for subsequent steps, admitting nitrogen to the sample from the manifold in a series of doses, until the maximum required equilibrium pressure has been reached (generally at least $0,99 \times 10^6$ Pa, i.e. a relative pressure of at least 0,99). Care should be taken not to reach the saturation pressure of nitrogen over the sample while collecting the adsorption portion of the isotherm.

9.3.8 Measuring desorption isotherm

The desorption portion of the isotherm may then be recorded by decreasing the pressure of nitrogen over the sample in a series of steps. The procedure is identical to that for adsorption, except that for each step, instead of admitting nitrogen to the manifold, the pressure in the manifold should be reduced to below the pressure in the sample tube by using the vacuum system.

The number of steps, and therefore the dose pressures required, depend on the pore volume distribution of the sample and the number of isotherm points needed (at least 20 are recommended for each of the adsorption and the desorption portions of the curve). Since the pore volume of the sample is unknown before the analysis, the dose pressures are best determined on the basis of prior experience for the particular sample type.

CAUTION — Reduce the pressure in the sample tube by means of the vacuum system before lowering the Dewar flask of liquid nitrogen.

The outgassed sample mass should be measured either immediately after the outgassing or upon completion of the test. Before weighing, it is recommended that the sample be backfilled to atmospheric pressure with dry air or nitrogen, or kept under vacuum with appropriate buoyancy correction.

9.4 Calculations

9.4.1 Manifold volume

The volume of the manifold, V_{man} , should be determined when the apparatus is constructed or modified. This can be carried out by attaching a calibrated volume in place of the sample tube and expanding helium into it from the manifold, or by expanding helium into a chamber containing a known volume solid.

9.4.2 Free space

9.4.2.1 If free space determination is initiated prior to immersion of the sample into liquid nitrogen, use the following method of calculation.

First calculate the apparent volume of the free space at ambient temperature, $V_{\text{fs,amb}}$, using the expression:

$$\frac{p_1 V_{\text{man}}}{T_{\text{man}}} = p_2 \left(\frac{V_{\text{man}}}{T_{\text{man}}} + \frac{V_{\text{fs,amb}}}{T_{\text{std}}} \right) \quad (3)$$

where

V_{man} is the volume of the manifold;

T_{std} is standard temperature, 273,15 K.

Next calculate the apparent volume of the free space at liquid nitrogen temperature, $V_{\text{fs,b}}$, using the expression:

$$\frac{p_1 V_{\text{man}}}{T_{\text{man}}} = p_3 \left(\frac{V_{\text{man}}}{T_{\text{man}}} + \frac{V_{\text{fs,b}}}{T_{\text{std}}} \right) \quad (4)$$

The total volume of gas dosed into the sample tube after the i th dose, V_{di} , is given by:

$$V_{di} = V_{di-1} + \left(\frac{p_{\text{man}} V_{\text{man}}}{T_{\text{man}}} - \frac{p}{T_{\text{eq}}} V_{\text{man}} \right) \left(\frac{T_{\text{std}}}{p_{\text{std}}} \right) \quad (5)$$

where

V_{di-1} is the total volume of gas dosed into the sample tube before the i th dose (equal to zero for the calculation of the first dose of adsorptive gas);

p_{man} is the manifold pressure at the start of the i th dose cycle;

T_{man} is the manifold temperature at the start of the i th dose cycle;

p is the equilibrium pressure for the i th dose;

T_{eq} is the manifold temperature at the time equilibrium is attained;

T_{std} is standard temperature, 273,15 K;

p_{std} is standard pressure, $1,013\,25 \times 10^5$ Pa.

The volume sorbed on the i th dose is given by:

$$V'_{ai} = \frac{V_{di} - \left(\frac{p V_{\text{fs,b}}}{p_{\text{std}}} \right)}{m_{\text{ss}}} \quad (6)$$

where

$V_{\text{fs,b}}$ is the free space volume determined with the sample immersed in the liquid nitrogen;

m_{ss} is the mass of the solid sample.

In the above equation, if pressures are expressed in Pa, temperatures in K and the system volumes in cm^3 , then V'_{ai} is the volume, in cm^3 , which the adsorbed gas would occupy at one atmosphere pressure, p_{std} ($1,013\,25 \times 10^5$ Pa), at the normal freezing temperature of pure water, T_{std} (273,15 K). The isotherm is the cumulative volume adsorbed (generally expressed per gram of sample) as a function of relative pressure.

If it is necessary to correct the calculated volume adsorbed to compensate for the effect of non-ideal behaviour of the adsorptive gas contained within the volume of the sample holder at the temperature of the cryogenic bath, $V_{\text{sh,b}}$, this volume is given by:

$$V_{\text{sh,b}} = \frac{V_{\text{fs,b}} - V_{\text{fs,amb}}}{1 - \frac{T_{\text{b}}}{T_{\text{amb}}}} \quad (7)$$

where

$V_{\text{fs,b}}$ is the free space volume determined with the sample holder immersed in the cryogenic bath;

$V_{\text{fs,amb}}$ is the free space volume determined with the sample holder at ambient temperature;

T_{b} is the temperature of the cryogenic bath;

T_{amb} is the ambient temperature.

In this case, V'_{ai} is calculated from:

$$V'_{ai} = \frac{V_{di} - \left(\frac{pV_{fs,b}}{p_{std}} + \frac{V_{sh,b}C_N p^2}{p_{std}} \right)}{m_{ss}} \quad (8)$$

where

C_N is the non-ideal behaviour constant determined for the adsorptive gas, expressed per Pa of pressure. Currently C_N has the value of $0,464 \times 10^{-6} \text{ Pa}^{-1}$ for nitrogen at 77,35 K.

9.4.2.2 If free space determination is initiated after the sample is immersed into liquid nitrogen, use the following alternative method of calculation.

From the helium pressure data, a free space determination can be expressed by the linear relationship between the volume of helium dosed into the sample bulb and the resulting pressure at equilibrium. The volume dosed, V_{di} , is calculated by:

$$V_{di} = \left[\left(\frac{V_{man}(p_{mani} - p_i)}{T_{man}} \right) \frac{T_{std}}{p_{std}} \right] + V_{di-1} \quad (9)$$

where

V_{di-1} is the volume of gas dosed in the previous data point.

Linear regression of V_d versus p yields a slope and intercept that is used to correct nitrogen adsorption data for the sample free space volume.

For the nitrogen data, the volume adsorbed is determined by calculating the difference between the volume of gas dosed and the volume of gas remaining after the sample pressure has reached equilibrium. The above equation is used to determine the V_d . The nitrogen volume adsorbed is calculated by:

$$V'_{ai} = \frac{[V_{di} - (pA_{He} - B_{He})]}{m_{ss}} \quad (10)$$

where

A_{He} is the slope of the helium data regression;

B_{He} is the intercept of the helium data regression.

10 Flow volumetric method

10.1 Principle

The flow volumetric method is closely related to the static volumetric method, the difference being that gas is continuously admitted to the sample at a low rate rather than as a series of doses. The pressure is measured as a function of time and the flow rate is monitored carefully. The amount adsorbed can be determined by comparing the rate of pressure rise observed when the adsorptive gas is introduced to that observed when a non-adsorbing gas, such as helium, is used in a separate calibration. An alternative approach directly determines the quantity of gas adsorbed from the resulting pressure difference between two identical volumes of adsorptive gas. One volume is connected via a flow control valve to the sample tube, whilst the other volume is similarly connected to a balance tube without sample. Because gas is continuously introduced, the

analysis can, in some circumstances, be completed in a shorter space of time than when using a static volumetric method. However, it is important that the flow rate be maintained at a sufficiently low level to ensure that the adsorptive gas and adsorbate are close to equilibrium at all times.

10.2 Apparatus and materials

The apparatus and materials are similar to those used in the static volumetric method (see 9.2). The main difference is that a suitable flow-controlling device is used to introduce gas into the sample, rather than a simple on-off valve. Where the quantity of gas is determined from the difference between two identical volumes, differential pressure transducers are necessary and an additional empty sample (or balance) tube is positioned in the Dewar flask. There should be a separate device for controlling the flow of adsorptive gas into the balance tube.

10.3 Typical test procedure

Sample preparation is identical to the static volumetric method (see Clause 8). There are several variants of the test procedure for the flow volumetric method.

If the differential approach is used, adsorptive gas is introduced simultaneously into both the balance and sample tubes. The flow rates may be kept constant, in which case the volume of gas adsorbed is calculated from the difference in pressure between the sample and balance tubes. Alternatively, adsorptive gas may be delivered to the sample and balance tubes from two independent reservoirs of equal volume, and the flow rate varied in order to maintain a zero pressure difference between the two tubes. In this case, the volume of gas adsorbed is calculated from the difference in pressure between the two reservoirs.

In the non-differential approach, where a balance tube is not used, helium is initially introduced into the system to determine the pressure rise when no adsorption takes place. The sample is then re-evacuated and the adsorptive gas introduced. In this variant of the technique, the flow rate is generally maintained constant during the run.

With all flow volumetric techniques, care shall be taken to ensure that the flow rate of adsorptive gas does not exceed the rate of adsorption. Optimum experimental conditions need to be determined for each sample type and depend on the exact test procedure adopted.

EXAMPLE These conditions can be tested by carrying out the determination at a lower flow rate or with a longer total run time. If there is no significant difference in the isotherm, then the original conditions were acceptable.

It is recommended that a comparison be made with a static volumetric analysis when analyzing an unfamiliar sample type. As a guide, for a sample of total surface 20 m^2 , a typical flow rate is in the range $0,2 \text{ cm}^3/\text{min}$ to $0,4 \text{ cm}^3/\text{min}$ where gas is continuously introduced to the sample at a constant rate.

10.4 Calculations

The precise form of the calculation depends on the method and test procedure adopted.

11 Carrier gas method

11.1 Principle

In the carrier gas method, a range of mixtures of known concentrations of adsorptive gas in a non-adsorbing gas (such as helium) is admitted to the sample. As a result of adsorption on the sample, the concentration of adsorptive gas decreases. The decrease in concentration in comparison to that of the initial mixture generates a peak in the signal, recorded as a function of time by means of a gas detector, which is usually a thermal conductivity cell. After removal of the Dewar flask, a desorption peak is recorded. The sharper desorption peak can be better integrated, and is therefore preferred, when evaluating the adsorption isotherm. The sharpness of this peak relates to the speed at which the sample can be returned to ambient temperature. An ambient water bath or flow of ambient air can be used to assist the desorption process. Care is taken not to

disturb the signal by thermal diffusion. The detector is calibrated for each mixture of adsorptive gas and carrier, by injecting a known volume of pure adsorptive gas. The sample is kept at an ambient temperature to prevent adsorption of the injected adsorptive gas.

The desorption portion of the curve can be determined by saturating the sample with pure adsorptive gas, and then reducing the concentration of adsorptive gas in the mix to give the desired relative pressure. The volume sorbed is once again determined from the desorption signal obtained by removing the Dewar flask from the sample.

11.2 Apparatus and materials

The apparatus is similar to that defined in ISO 9277:1995, Figure 7.

11.3 Typical test procedure

Sample preparation is identical to the static volumetric method (see Clause 8). The sample is attached to the analysis port of the apparatus following preparation, as with the volumetric methods.

Void volume is not a factor in the carrier gas method, so measurement with helium is not needed.

For each selected point on the adsorption portion of the isotherm, a flow of the selected gas mixture is established over the sample at an ambient temperature. Once the detector signal and gas flow are constant, adjust the baseline detector signal offset to zero if necessary. A calibration injection of pure adsorptive gas may be needed to scale the detector signal to the lowing gas mixture. Calibrations may be determined in advance of a given analysis and applied to the present analysis without the necessity of a new calibration.

Raise a Dewar flask of cryogen up around the sample holder. The adsorptive concentration will decrease as gas adsorbs, causing an imbalance in the detector and a corresponding signal. When the signal returns to the stable base value, the adsorption process is complete. Integration of the difference between the signal and the base value will give a measure of the volume of gas adsorbed. Similarly, the volume adsorbed can be determined by desorbing the adsorbate and integrating the corresponding detector signal. Desorption is brought about by lowering the Dewar flask and returning the sample to ambient temperature.

Due to the fact that all gas available to desorb is present at the start of the desorption process, unlike in the adsorption process where the gas necessarily flows to the sample, the desorption peak is narrower than the adsorption peak and thus easier to integrate reliably. For this reason, it is better to use the integrated desorption peak rather than the integrated adsorption peak. It is helpful, however, to record the adsorption peak for comparison.

For each selected point on the desorption portion of the isotherm, a flow of the selected gas mixture is established over the sample at an ambient temperature. Make any necessary adjustment to the detector baseline offset and any necessary calibration adjustments. Next establish a flow of pure adsorptive gas over the sample. Raise the Dewar flask around the sample and allow time for saturation of the sample with pure adsorptive gas. With the Dewar flask around the sample, establish a gas mixture to give the desired relative pressure. Once the sorption process is finished, remove the Dewar flask and record the integrated desorption signal. Due to the nature of the desorption measurement, there is no corresponding adsorption peak as there is when recording the adsorption isotherm.

11.4 Calculations

The volume sorbed is calculated by integration of the desorption peak produced when returning the sample to ambient temperature. Nitrogen pressure is determined from the mole fraction of adsorptive gas in the mixture with carrier and ambient pressure. Saturation pressure is then used to calculate relative pressure in the usual manner.

Calculations of pore size distribution follow the same scheme as described for the volumetric method, once the isotherms are determined (see Clause 14).

12 Gravimetric method

12.1 Principle

In the gravimetric method, the amount of gas adsorbed is determined from the increase in mass of the sample. The adsorptive pressure is generally increased or decreased incrementally, as in the static volumetric method. The procedure does not require the calibration of instrument volume. A sensitive balance is required, and buoyancy corrections are applied.

12.2 Apparatus and materials

12.2.1 Apparatus

In the gravimetric method, the adsorbed mass is measured as a function of the gas pressure in the sample container using a microbalance (see ISO 9277:1995, Figure 6). Spring balances offer advantages with regard to vacuum application, electronic, compensating beam balances, on account of the larger relative resolution. A high-resolution pressure gage and a thermometer for the liquid nitrogen bath are required. Because the sample is not in contact with the thermostat, it is necessary to ensure that it is always at the measuring temperature, e.g. by means of radiation shields [5]. The apparatus should be equipped with a high vacuum aggregate. In the discontinuous procedure, the measuring gas is admitted or removed stepwise. The pressure should be kept constant until the mass reaches a constant value, and for that purpose a pressure control should be available.

12.2.2 Materials

12.2.2.1 Nitrogen, or other suitable adsorptive gas (e.g. argon), dry, not less than 99,99 % purity.

12.2.2.2 Liquid nitrogen, or other means of temperature control (e.g. liquid argon), not less than 99 % purity.

12.3 Typical test procedure

Before measuring the adsorption isotherm, the buoyancy of the balance and of the sample in the measuring gas at room temperature should be measured. By using an equal-arm instrument, the buoyancy of the balance is eliminated and that of the sample compensated for using compact counterweight of the same density as the sample [5].

After outgassing (see Clause 8), the sample is cooled to liquid nitrogen temperature by immersing the part of the vessel containing the sample bucket in a Dewar flask of liquid nitrogen (in the case of symmetric arrangements, this also includes the counterweight). The zero point of the isotherm should be measured at a vacuum lower than 10^{-2} Pa, because disturbances due to thermal gas flow exhibit a maximum at approximately 1 Pa. Adsorptive gas is then introduced. When the mass indication is constant, equilibrium has been reached and the mass (minus zero point) of the sample m_a and the pressure p are recorded. The adsorption portion of the isotherm should be determined by introducing nitrogen progressively to just below its saturation vapour pressure, and the desorption portion of the curve by stepwise decreasing the pressure. The temperature of the liquid nitrogen bath should be recorded.

12.4 Calculations

If a remaining buoyancy b has been observed, the mass values m_{ai} are calculated for each pressure p_i :

$$m_{ai} = m_{ai}^* + bp_i \quad (11)$$

The specific liquid volumes of the sorbate condensed in the pores is calculated using:

$$V'_l = \frac{m_{ai}}{\rho_{N_2}} = \frac{m_{ai}}{0,808\ 6} \quad (12)$$

where

ρ_{N_2} is the density of liquid nitrogen (in $\text{g}\cdot\text{cm}^{-3}$).

13 Types of isotherms

13.1 General

Figure 1 shows a classification of standard physisorption isotherms, as proposed by the International Union of Pure and Applied Chemistry (IUPAC) [3].

Type I isotherms are characterized by a rapid increase in the amount of gas adsorbed over the low relative pressure range. This is attributed to micropore filling. A subsequent horizontal or near horizontal plateau indicates that the micropores are filled and that little or no further adsorption takes place. There may be adsorbate condensation as the saturation pressure is approached. Microporous solids with relatively small external surfaces (e.g. activated carbons, molecular sieves zeolites and certain porous oxides) produce such isotherms.

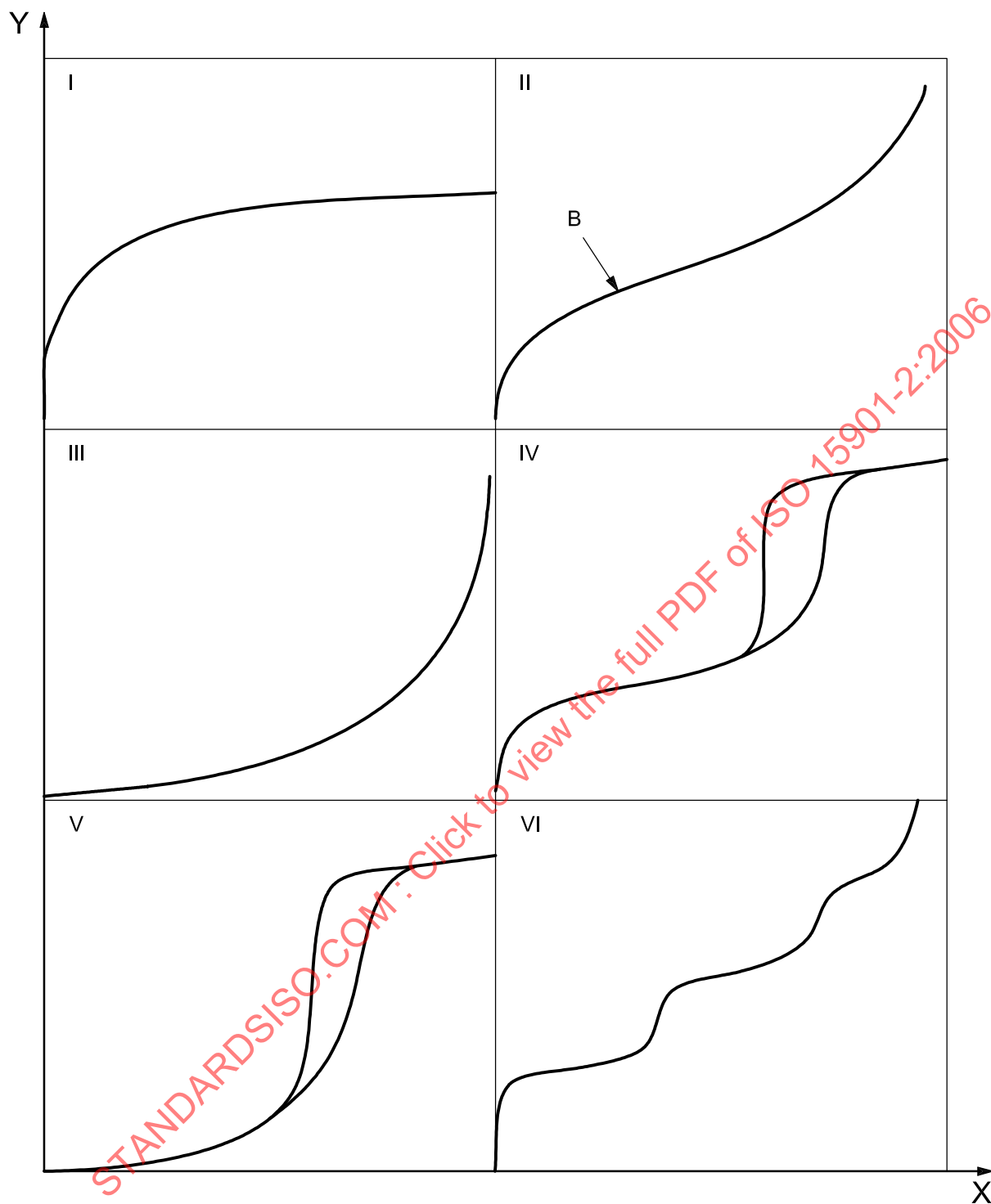
Type II isotherms are typically produced by solids which are non-porous or macroporous. Point B is often taken as indicative of the completion of the monolayer capacity.

Type III isotherms are distinguished by a convexity towards the relative pressure axis. These isotherms are found when weak gas-solid interactions occur on non-porous or macroporous solids, and are uncommon.

Type IV isotherms are found for mesoporous solids. A characteristic feature is that the adsorption portion of the isotherm is not the same as the desorption portion of the isotherm, and a hysteresis loop is observed. A plateau region is observed at higher p/p_0 values, which occasionally concludes with a final upward turn of the isotherm.

Type V isotherms are characterized by a convexity to the relative pressure axis. Unlike Type III isotherms, there occurs a point of inflection at higher relative pressures. Type V isotherms result from weak gas-solid interactions on microporous and mesoporous solids, and are relatively uncommon.

Type VI isotherms are notable for the step-like nature of the sorption process. The steps result from sequential multilayer adsorption or uniform non-porous surfaces. Such isotherms, in a well-defined form, are not given by nitrogen at liquid nitrogen temperature.



Key

B indication of completion of monolayer capacity

X p/p_0 , relative pressure

Y m_a , amount adsorbed

Figure 1 — Standard isotherm types (according to Reference [3])

It should be noted that not all experimental isotherms can be clearly assigned to one of the standard types (see Figure 1). Within these isotherm types, a variety of hysteresis loops has been found to exist. Although the effect of various factors on adsorption hysteresis is not fully understood, four characteristics exist and four characteristic types of hysteresis loops have been classified by the International Union of Pure and Applied Chemistry (IUPAC) [3], in accordance with the convention set out in 13.2.

13.2 Types of hysteresis loops

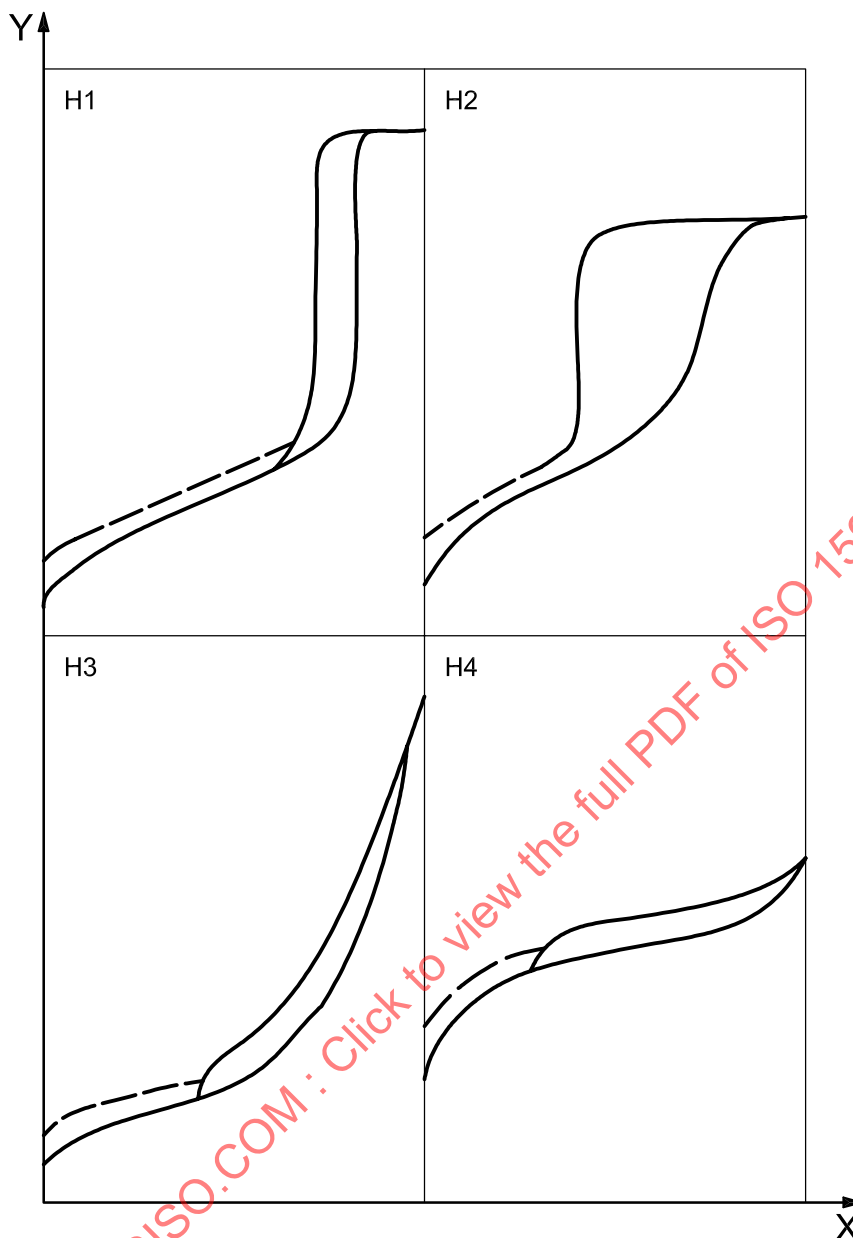
Figure 2 illustrates the standard types of hysteresis loop (according to Reference [3]).

Type H1 hysteresis loops are observed for mesoporous materials with relatively narrow distributions, and for agglomerates of spheroidal particles of fairly uniform size.

Type H2 hysteresis loops are given by some solids, such as certain silica gels, in which the pore size distribution and shape may not be well defined, e.g. wider distribution of pore sizes compared with H1 loop.

Type H3 hysteresis loops are exhibited by materials with plate-like particles (e.g. clays) or slit-shaped pores, and do not exhibit any limiting adsorption at higher relative pressures.

Type H4 hysteresis loops are seen with solids containing narrow, slit-shaped pores (e.g. active carbons), and also do not exhibit a limiting adsorption at higher relative pressures.



Key

X p/p_0 , relative pressure

Y m_a , amount adsorbed

Figure 2 — Standard types of hysteresis loop (according to Reference [3])

14 Calculation of pore size distribution

14.1 The use of reference isotherms

To assess whether microporosity, mesoporosity, or both are present in the test sample, it is necessary to first compare the experimental isotherm with a reference isotherm obtained on a non-porous solid. The reference isotherm may be calculated using a mathematical expression, but it is recommended that an experimentally determined reference isotherm be used where the adsorbent has similar chemical properties to the test sample (e.g. for highly siliceous zeolites, a non-porous silica should be used). The comparison between the experimental and reference isotherm may be carried out using several techniques, primarily the t -plot and α_s -plot methods.

The t -plot method is based on the t -curve, which is a plot of the amount of nitrogen adsorbed on the non-porous solid as a function of t , the statistical thickness of the adsorbed layer. t is calculated from the expression:

$$t = \frac{n_a \delta_a}{n'_m} \quad (13)$$

where

n is the amount of nitrogen adsorbed;

n'_m is the monolayer amount;

δ_a is the thickness of a single molecular layer, usually taken as 0,354 nm for nitrogen.

In the α_s -plot method, the amount of nitrogen adsorbed by the reference non-porous solid is normalized by using the amount adsorbed at some fixed relative pressure ($n'_{a,x}$), often taken as 0,4. The normalized adsorption α_s (equal to $n_a/n'_{a,x}$) is then plotted against p/p_0 to obtain a α_s -curve.

The t -plot or α_s -plot is constructed by plotting the amount of nitrogen adsorbed by the test sample against t , or α_s for the reference material, rather than p/p_0 , the conversion of p/p_0 to t or α_s being carried out by reference to the t -curve or α_s -curve. The shape of the plot depends on the nature of the porosity present in the test sample, as follows:

- if the t - or α_s -plot is linear and passes through the origin, the test sample is non-porous or macroporous;
- if the test sample contains mesopores, the plot shows an upward deviation at the relative pressure, corresponding to the onset of capillary condensation in the smallest mesopores;
- if the test sample contains micropores, the plot exhibits a downward deviation, because multilayers cannot fully develop within the constricted space inside micropores.

Some materials contain combinations of pores, which may result in a complex plot that is difficult to interpret. In such cases, caution is advised when analysing the isotherm.

14.2 Micropores

Although there is no single, widely-accepted method for the determination of micropore size distribution, a number of techniques are in use (see ISO 15901-3). Methods also exist to determine effective micropore volume.

14.3 Mesopores and macropores

14.3.1 General

Careful consideration is required of the conditions under which it is possible to calculate a pore size distribution in mesopores and macropores, from the experimental nitrogen adsorption data at 77 K. The calculation may be performed with most confidence when the experimental data indicate that:

- the pores are rigid and have sizes in a narrow, well-defined range (as evidenced by a Type H1 hysteresis loop);
- micropores or very large macropores are absent, or can be allowed for (as evidenced by a well-defined Type IV isotherm, or from the features of a t -plot or α_s -plot).

It is possible to use data from the adsorption or desorption branches of the isotherm. The choice is not easy and it may be helpful to summarise the main implications: the relatively simple pore structure of fairly uniform tubular pores would be expected to give a narrow Type H1 hysteresis loop, and in this case the desorption portion of the curve is generally used for the analysis. If a Type H2 loop is observed, this is indicative of the occurrence of connectivity, pore blocking and related percolation phenomenon, which implies that neither portion of the curve can be used with complete confidence because of the possibility of a combination of effects (i.e. both delayed condensation and network-percolation). The adsorption branch can be used for pore size analysis if a method is used that takes into account the effect of pore size on the delayed condensation phenomenon, especially in the range of the meta-stable state of the pore fluid. Furthermore, the adsorption portion of the curve enables a much more realistic pore size distribution curve to be obtained if the so-called “tensile strength effect” occurs during evaporation, which leads to a step down of the desorption portion of the curve at a certain p/p_0 , characteristic for each adsorptive gas and temperature (e.g. at 0,42 for N₂ at 77,35 K). In this case, a correct pore size distribution curve cannot be calculated from the desorption portion of the curve [3].

14.3.2 Determination of mesopore size distribution by the technique of Barrett, Joyner and Halenda

There are several variants of the algebraic procedure for deriving the pore size distribution from the adsorption isotherm. All assume that:

- the pores are rigid and of regular shape (e.g. cylindrical or slit-shaped);
- micropores are absent;
- the pore size distribution does not extend continuously above the largest pores measurable by this technique, which implies that all of the pores evaluated are filled at the highest relative pressure.

Barrett, Joyner and Halenda describe a commonly-used method [7]. The general procedure followed in the calculation is as follows.

- a) The data points are arranged in order of descending pressure, irrespective of whether the adsorption or desorption portion of the isotherm is used.
- b) The change in volume of nitrogen desorbed when moving to a lower pressure is considered to be made up of two contributions. These are:
 - 1) the removal of capillary condensate from pores in a size range calculated from the higher and lower pressures using the Kelvin equation, and
 - 2) the thinning of the multilayer film on the walls of pores which have previously been emptied of capillary condensate.
- c) To determine the actual pore size and volume, it is necessary to take into account that when capillary condensate is removed from a pore, a multiple layer film remains.

An example of mesopore size distribution calculation is given Annex A.

14.3.3 Determination of mesopore size distribution by density functional theory

The non-localize density function theory (NLDFT) and computer simulation methods have been developed into powerful methods for the description of sorption and phase behaviour of inhomogeneous fluids, confined to porous materials. These methods enable the calculation of equilibrium density profiles of a fluid adsorbed on surfaces and in pores, from which the adsorption isotherms, heats of adsorption and other thermodynamic quantities can be derived. Compared to the classical thermodynamic, macroscopic models, the NLDFT methods describe behaviour fluids confined in the pores on a molecular level. This enables molecular properties of gases to be related with 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.

In order to apply the theory practically for the calculation of pore size distributions from experimental adsorption isotherms, the theoretical model isotherms are calculated using methods of statistical mechanics. In essence, these isotherms are calculated by integrating the equilibrium density profiles 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.

For further information about NLDFT, see ISO 15901-3.

14.4 Representation of pore size distribution

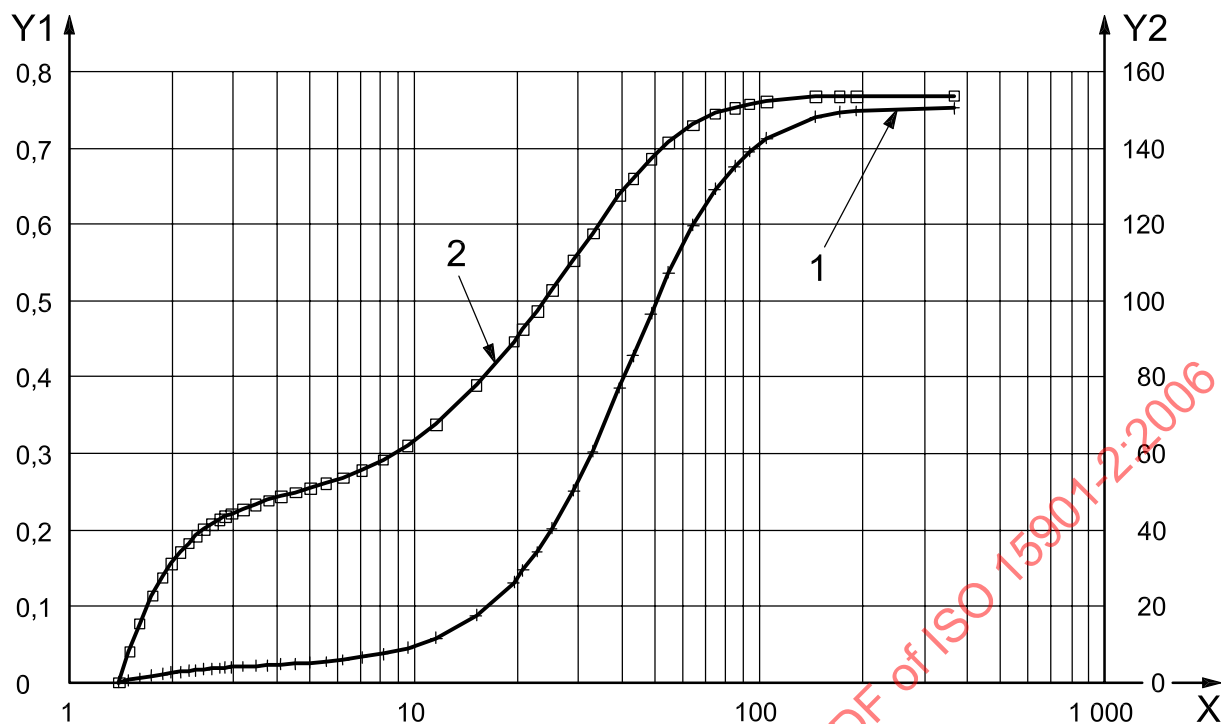
Calculated pore size distributions can be represented in a number of different ways. The most common are:

- cumulative pore volume, finer (or larger) than pore size;
- incremental pore volume versus pore size;
- differential pore volume versus pore size;
- log differential pore volume versus pore size.

For cumulative distributions, the total volume of pores either larger or smaller than the current pore size, for the specified pore size range, is plotted or reported in a table versus pore size. The cumulative pore volume versus pore width is included for an example analysis in Figure 3.

For incremental distributions, the absolute volume of pores determined between consecutive pore sizes is plotted, or reported in a table, versus the mid point of the pore size values that determine the current increment. For differential distributions, the incremental volume is divided by the difference between the upper and lower pore sizes that define the increment, to give the change in volume with change in diameter, and plotted, or reported in a table, again versus the mid point of the pore size values that define the increment. For log differential distributions, the incremental volume is divided by the difference in log of the upper and lower pore sizes that define the increment versus the midpoint of the pore size increment.

Pore size may be represented as width, diameter or radius. Additionally, pore area distribution may be calculated from the pore volume distribution, and represented as a cumulative, incremental, differential or log differential distribution. The cumulative pore volume may be presented as either that found in pores finer than the current pore width or that found in pores larger than the current pore width. Generally the BJH method is used to calculate the pore size distribution beginning at the largest pore width and progressing toward the smallest pore width. Figure 6 of Reference [6] shows the resulting cumulative pore volume larger than pore size. An example of cumulative pore and area finer than pore width is given in Figure 3 of this document.



Key

X pore width

Y1 cumulative pore volume

Y2 cumulative pore area

1 BJH desorption cumulative pore volume

2 desorption cumulative pore area

NOTE Figure 3 includes plots of the desorption cumulative pore volume, V_p , and pore surface area, a'_p , both versus pore diameter, d_p .

Figure 3 — Desorption cumulative pore volume and area for porous silica