

# INTERNATIONAL STANDARD

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## **Determination of the specific surface area of solids by gas adsorption using the BET method**

*Détermination de l'aire massique (surface spécifique) des solides par  
adsorption de gaz à l'aide de la méthode BET*



Reference number  
ISO 9277:1995(E)

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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.

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.

International Standard ISO 9277 was prepared by Technical Committee ISO/TC 24, *Sieves, sieving and other sizing methods*, Subcommittee SC 4, *Sizing by methods other than sieving*.

Annexes A and B of this International Standard are for information only.

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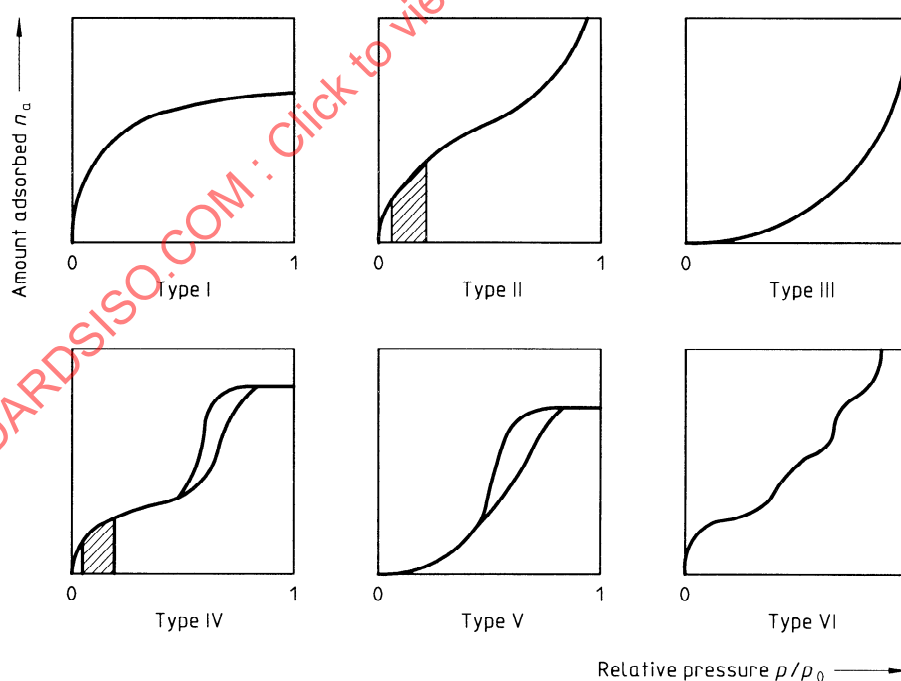
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# Determination of the specific surface area of solids by gas adsorption using the BET method

## 1 Scope

This International Standard specifies the determination of the total<sup>1)</sup> specific external and internal surface area of disperse or porous solids by measuring the amount of physically adsorbed gas according to the method of Brunauer, Emmett and Teller (BET method) [1], based on the 1984 IUPAC Recommendations [2].

The BET method is applicable only to adsorption isotherms of type II (disperse, nonporous or macroporous solids) and type IV (mesoporous solids, pore diameter between 2 nm and 50 nm) (see figure 1). Inaccessible pores are not detected. The BET method cannot reliably be applied to type I isotherms or to solids which absorb the measuring gas.



**Figure 1 — IUPAC classification of adsorption isotherms (typical BET range is indicated in types II and IV by the hatched area)**

1) For solids exhibiting a chemically heterogeneous surface, e.g. metal-carrying catalysts, the BET method gives the total surface area, whereas the metallic portion of the surface area may be measured by chemisorption methods.

## 2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 8213:1986, *Chemical products for industrial use — Sampling techniques — Solid chemical products in the form of particles varying from powders to coarse lumps*.

## 3 Definitions

For the purposes of this International Standard the following definitions apply.

**3.1 adsorption:** Enrichment of the adsorptive at the external and accessible internal surfaces of a solid.

**3.2 physisorption:** Weak bonding of the adsorbate, reversible by small changes in pressure or temperature.

**3.3 adsorptive:** Measuring gas to be adsorbed.

**3.4 adsorbent:** Solid which adsorbs the measuring gas.

**3.5 adsorbate:** Enriched adsorptive at the surface of the adsorbent.

**3.6 surface area:** Area of the external surface of a solid plus the internal surface of its accessible macro- and mesopores.

**3.7 adsorption isotherm:** Relation between the quantity of adsorbate and the equilibrium pressure of the adsorptive at constant temperature.

## 4 Symbols and units

Table 1 presents the symbols used in this International Standard, together with their SI units. For comparison purposes, the IUPAC [2] symbols are also given. All specific dimensions are related to sample mass in grams.

Table 1 — Symbols

| ISO symbol | Parameter                                                                                                                        | SI unit                                              | IUPAC symbol |
|------------|----------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------|--------------|
| $a_m$      | molecular cross-sectional area occupied by an adsorbed molecule in a complete monolayer                                          | $\text{nm}^2$                                        | $a_m$        |
| $a_s$      | specific surface area                                                                                                            | $\text{m}^2 \text{g}^{-1}$                           | $a_s$        |
| $C$        | BET parameter                                                                                                                    | 1 1)                                                 | $C$          |
| $L$        | Avogadro constant ( $= 6,022 \times 10^{23}$ )                                                                                   | $\text{mol}^{-1}$                                    | $L$          |
| $m$        | mass of the solid sample                                                                                                         | g                                                    | $m$          |
| $m_a$      | specific mass adsorbed                                                                                                           | 1 1)                                                 | $m^a$        |
| $n_a$      | specific amount adsorbed                                                                                                         | $\text{mol} \cdot \text{g}^{-1}$                     | $n^a$        |
| $n_m$      | specific monolayer capacity of adsorbate; amount of adsorbate needed to cover the surface with a complete monolayer of molecules | $\text{mol} \cdot \text{g}^{-1}$                     | $n_m, n_m^a$ |
| $n_{m,mp}$ | specific monolayer capacity derived from multipoint measurement                                                                  | $\text{mol} \cdot \text{g}^{-1}$                     | —            |
| $n_{m,sp}$ | specific monolayer capacity derived from single-point measurement                                                                | $\text{mol} \cdot \text{g}^{-1}$                     | —            |
| $p$        | pressure of the adsorptive in equilibrium with the adsorbate                                                                     | Pa                                                   | $p$          |
| $p_0$      | saturation vapour pressure of the adsorptive                                                                                     | Pa                                                   | $p^0$        |
| $p/p_0$    | relative pressure of the adsorptive                                                                                              | 1 1)                                                 | $p/p^0$      |
| $R$        | molar gas constant ( $= 8,314$ )                                                                                                 | $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ | $R$          |
| $t$        | time                                                                                                                             | min                                                  | $t$          |

| ISO symbol                                                                                                                                               | Parameter                | SI unit                           | IUPAC symbol |
|----------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------|-----------------------------------|--------------|
| $T$                                                                                                                                                      | temperature              | K                                 | $T$          |
| $V_a$                                                                                                                                                    | specific volume adsorbed | $\text{mm}^3 \cdot \text{g}^{-1}$ | $V^a$        |
| 1) According to ISO 31-0, the coherent SI unit for any quantity of dimension one (at present commonly termed "dimensionless") is the unit one, symbol 1. |                          |                                   |              |

## 5 Principle

The method specified involves the determination of the amount of adsorbate or adsorptive gas required to cover the external and the accessible internal pore surfaces of a solid (see figure 2) with a complete monolayer of adsorbate. This monolayer capacity can be calculated from the adsorption isotherm using the BET equation (1) (see 6.1). Any gas may be used, provided it is physically adsorbed by weak bonds at the surface of the solid (van der Waals forces), and can be desorbed by a decrease in pressure at the same temperature.



**Figure 2 — Particle with surface detected by the adsorption method shown by dotted line**

Nitrogen at its boiling point (about 77 K) is usually the most suitable adsorptive. If the sensitivity of the instrument when using nitrogen is insufficient for low surface areas, adsorptives of heavier molecules or of vapour pressure lower than nitrogen, e.g. krypton, may be used. The results of measurements with different adsorptives may deviate from each other because of different molecular areas, different accessibilities to pores and different measuring temperatures.

The adsorptive gas is admitted to the sample container which is held at a constant temperature. The amounts adsorbed are measured in equilibrium with the adsorptive gas pressure  $p$  and plotted against relative pressure,  $p/p_0$ , to give an adsorption isotherm. Adsorption isotherms may be obtained by volumetric, gravimetric, calorimetric or spectroscopic measurement or by the carrier gas method using continuous or discontinuous operation.

## 6 Procedure

### 6.1 Sample preparation

Sampling shall be carried out in accordance with ISO 8213. Prior to the determination of an adsorption isotherm, remove physically adsorbed material from the sample surface by degassing, while avoiding irreversible changes to the surface. Ascertain the maximum temperature at which the sample is not affected by thermogravimetric analysis (see figure 3) or by trial experiments using different degassing conditions of time and temperature. When vacuum conditions are used, degassing to a residual pressure of approximately 1 Pa or better is usually sufficient. Degassing of the sample can also be performed at elevated temperature by flushing with helium or with the adsorptive. Degassing is complete when a steady value of the residual gas pressure  $p$ , of its composition or of the sample mass  $m$  is reached.

Using the vacuum technique, isolate the heated sample container from the pump and trap (at time  $t_a$  in figure 4). If the pressure does not rise significantly over a period of 15 min to 30 min, degassing is complete. This procedure also establishes the absence of leaks. The specific surface area should be related to the mass of the degassed sample.

After degassing, the sample container is cooled to the measuring temperature. It should be noted that, at low gas pressures, the temperature of the sample needs some time to equilibrate due to the reduced thermal conduction of the cooling bath.

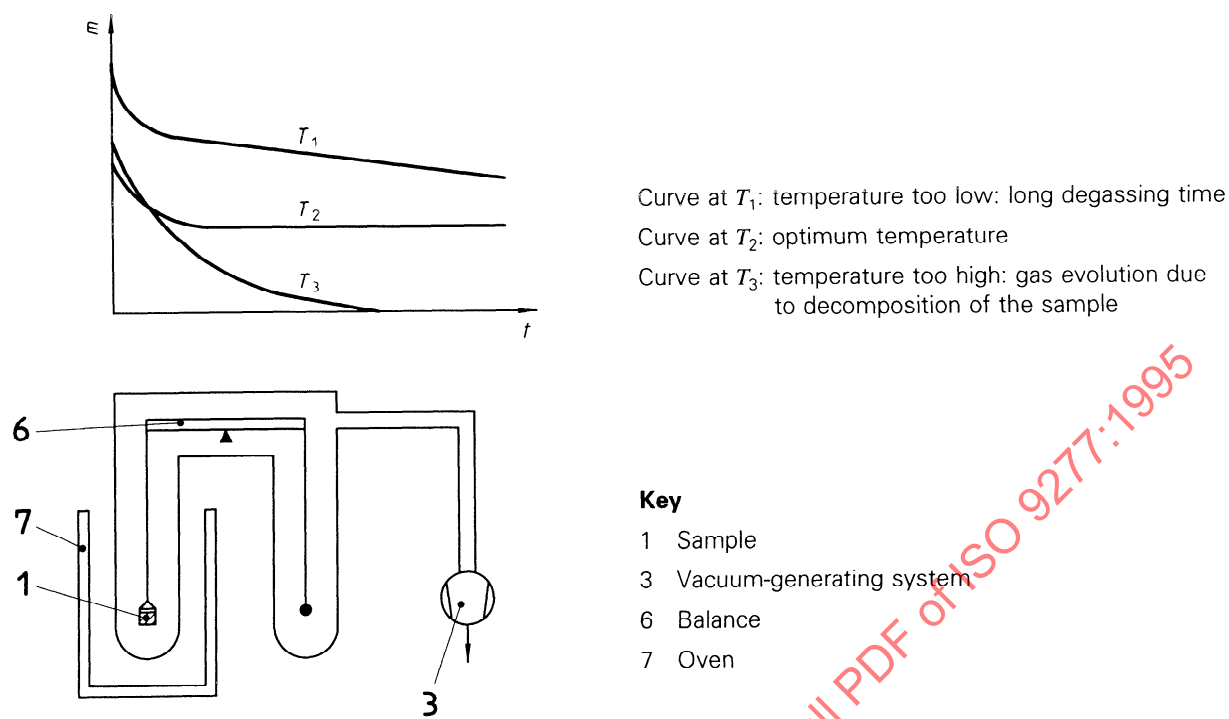


Figure 3 — Thermogravimetric control of degassing

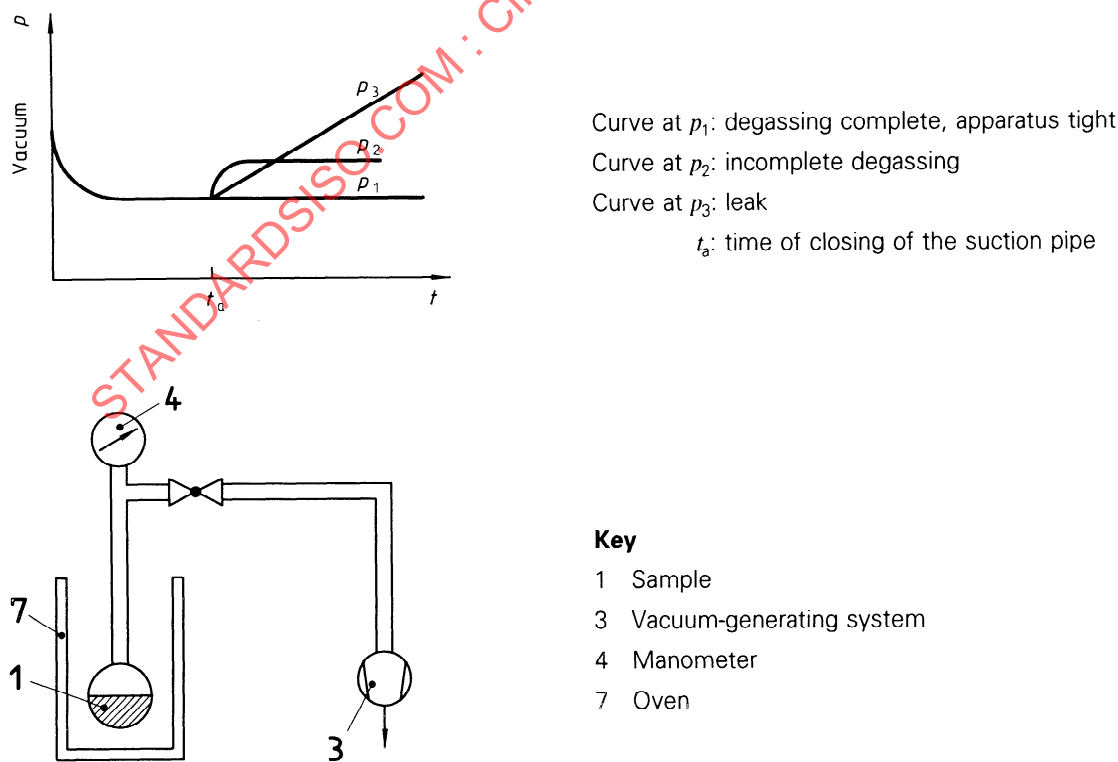


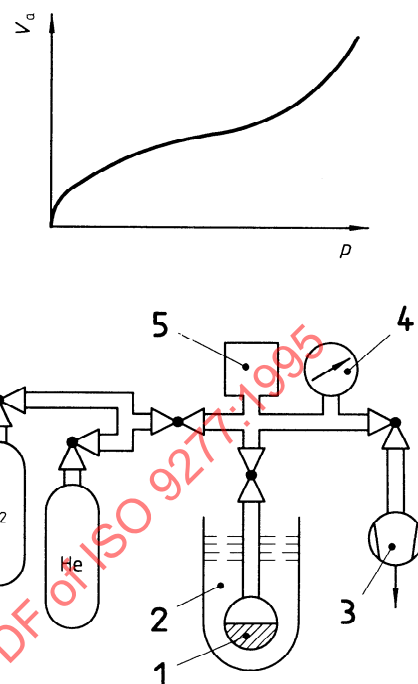
Figure 4 — Pressure control of degassing

## 6.2 Experimental conditions

The precision of the measurement depends on the control of the following conditions.

- The temperature of the adsorptive should be monitored during the analysis.
- The purity of the adsorptive and any helium used to calibrate volumes or as a carrier gas should be at least 99,99 %. If necessary, the gases should be dried and cleaned, e.g. oxygen removed from nitrogen.
- The saturation pressure  $p_0$  of the adsorptive at the measuring temperature can either be determined directly using a nitrogen vapour pressure thermometer, or it can be monitored and determined by measurement of the thermostat bath temperature.
- The validity of the result depends on careful sampling and sample preparation.

In the discontinuous static procedure, at least four points within the relative pressure range for which the BET equation is valid (typically 0,05 to 0,3) should be measured in equilibrium. For continuous measurements, the deviation from equilibrium must be controlled either by occasional interruption of the gas flow or by control measurements using the discontinuous method.



### Key

- Sample
- Dewar vessel with liquid nitrogen
- Vacuum-generating system
- Manometer
- Calibrated volume (gas burette)

Figure 5 — Volumetric method

## 6.3 Methods of measurement

### 6.3.1 Volumetric method

In order to determine the adsorption isotherm volumetrically by the discontinuous method, known amounts of adsorptive are admitted stepwise into the sample container (see figure 5). At each step, adsorption of the gas by the sample occurs and the pressure in the confined volume falls until the adsorbate and the adsorptive are in equilibrium. The adsorbed volume may be compensated by the introduction of calibrated increments of gas so that the pressure remains constant. The amount of gas adsorbed is the difference between the amount of gas admitted and the amount of gas filling the dead volume (free space in the sample container, including connections), which is determined by application of the general gas equation. The various volumes of the apparatus and their temperatures should be taken into account.

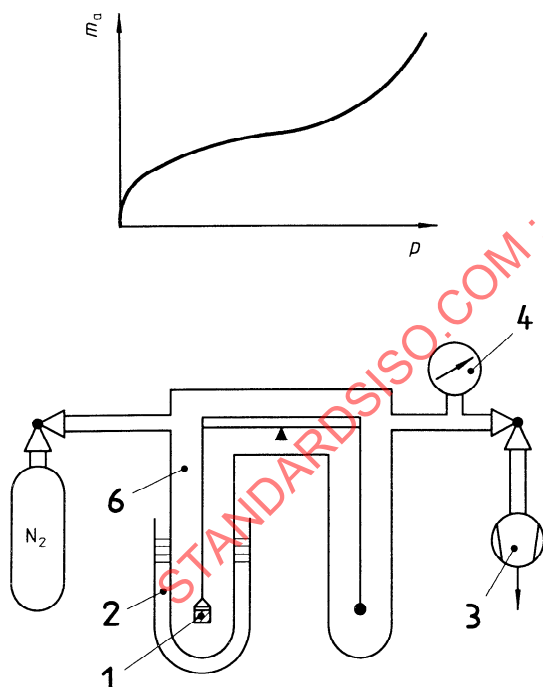
The dead volume must be determined before or after the measurement of the adsorption isotherm. The calibration is done volumetrically using helium at the measuring temperature. It should be noted that some materials may absorb helium. In this case, corrections can be made after measuring the helium isotherms. During sample measurement and determination of the dead volume, it is recommended that the liquid level in the cooling bath be maintained, unless otherwise compensated, at least 50 mm above the sample and constant to within 1 mm. The determination of the dead volume may be avoided using difference measurements, i.e. by means of reference and sample tubes connected by a differential transducer.

In the continuous volumetric measurement, the amount of admitted adsorptive may be calculated from the pressure difference and the duration of the gas flow through a calibrated capillary or metering valve.

### 6.3.2 Gravimetric method

In the continuous gravimetric method, the mass of gas adsorbed is measured as a function of the gas pressure in the sample container using a microbalance (see figure 6). Before measurement of the adsorption isotherm, the buoyancy of the balance and of the sample in the adsorptive 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 a compact counterweight of the same density as the sample. Because the sample is not in contact with the thermostat, it is necessary to ensure that it is always at the measuring temperature. The sample temperature should be monitored.

The zero point of the isotherm should be measured at a vacuum better than  $10^{-2}$  Pa because disturbances due to thermal gas flow exhibit a maximum at about 1 Pa.



#### Key

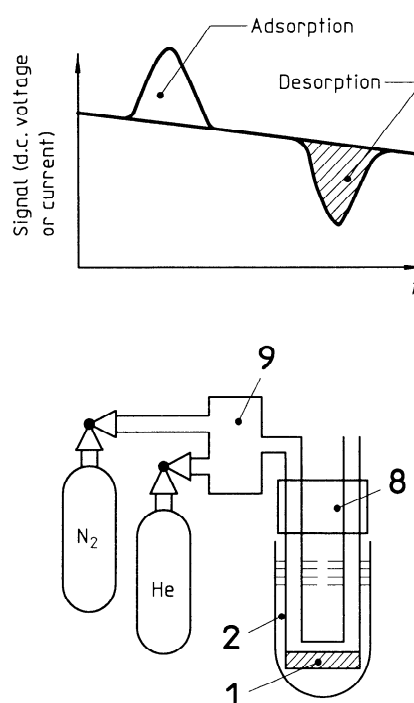
- 1 Sample
- 2 Dewar vessel with liquid nitrogen
- 3 Vacuum-generating system
- 4 Manometer
- 6 Balance

Figure 6 — Gravimetric method

In the discontinuous gravimetric procedure, the adsorptive is admitted stepwise and the pressure is kept constant until the sample mass reaches a constant value.

### 6.3.3 Carrier gas method

In the carrier gas method, a range of mixtures of known concentrations of adsorptive in a non-adsorbable gas (helium) is admitted to the sample (see figure 7). As a result of adsorption on the sample, the concentration of adsorptive 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, usually a thermal conductivity cell. After removal of the cooling bath, a desorption peak is recorded. The sharper desorption peak can be better integrated and is preferred for the adsorption isotherm evaluation. Care must be taken that the signal is not disturbed by thermal diffusion. It is necessary to calibrate the detector by injecting a known volume of pure adsorptive. The sample and calibration peaks should be of similar size [3].



#### Key

- 1 Sample
- 2 Dewar vessel with liquid nitrogen
- 8 Heat conductivity detector
- 9 Gas mixer

Figure 7 — Carrier gas method

## 7 Evaluation of adsorption data

### 7.1 General

The amount of gas adsorbed  $n_a$ , preferably expressed in moles per gram, is plotted as ordinate against the respective relative pressure  $p/p_0$  as abscissa to give the adsorption isotherm. The monolayer capacity  $n_m$  is calculated using the BET equation<sup>2)</sup> (1):

$$\frac{p/p_0}{n_a[1 - (p/p_0)]} = \frac{1}{n_m C} + \frac{C - 1}{n_m C} \cdot \frac{p}{p_0} \quad \dots (1)$$

### 7.2 Multipoint determination

In the BET diagram,  $(p/p_0)/n_a[1 - (p/p_0)]$  is plotted as ordinate against  $p/p_0$  as abscissa (see figure 8). The plot should give a straight line  $y = a + bx$  within the relative pressure range 0,05 to 0,3. The intercept  $a$  must be positive. The slope  $b = \Delta y/\Delta x = (C - 1)/(n_m C)$  and the intercept  $a = (1/n_m C)$  may be

determined graphically or by linear regression. From this the monolayer capacity

$$n_m = \frac{1}{a + b} \quad \dots (2)$$

and the BET parameter

$$C = \frac{b}{a} + 1 \quad \dots (3)$$

can be derived.

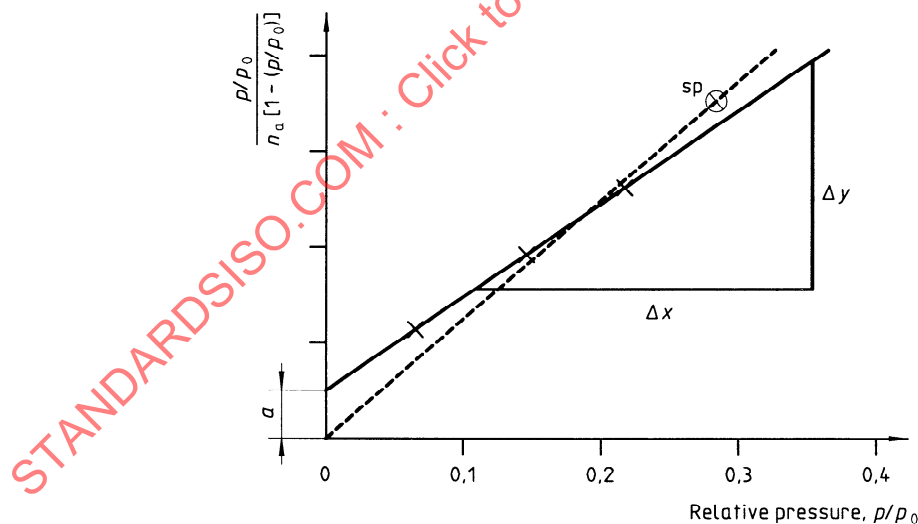
The specific surface area per unit mass of the sample,  $a_s$ , is calculated from the monolayer capacity by assessing a value for the average area occupied by each molecule in the complete monolayer:

$$a_s = n_m a_m L \quad \dots (4)$$

A molecular cross-sectional area  $a_m = 0,162 \text{ nm}^2$  is recommended for nitrogen at 77 K. Equation (4) then becomes:

$$a_s = 9,76 \times 10^4 n_m \quad \dots (5)$$

expressed in square metres per gram.



NOTE — Dashed line = single-point method, with measuring point sp.

Figure 8 — BET plot

2) A modified equation includes, besides the  $C$ -value, an additional parameter limiting the number of layers on the surface<sup>[4]</sup>. Although the two-parameter BET equation as recommended by IUPAC allows for an unlimited number of adsorbed layers<sup>[5]</sup>, it gives comparable results for mesoporous material.

Generally accepted values for the molecular cross-sectional area are:

- 0,166 nm<sup>2</sup> for argon at 77 K and
- 0,202 nm<sup>2</sup> for krypton at 77 K,

although uncertainty exists for these values [6].

Values for the molecular area of other adsorbates can be found in the literature [7 and 8]. For some materials and adsorbates, the range of linearity in the BET plot occurs at lower relative pressures. Linearity of the BET plot alone is not proof of the validity of the measurement; moreover, the range of linearity must be exhibited at  $n_a/n_m \approx 1$ . The BET method is not applicable if a straight line is not obtained or if there is a negative intercept. In the range  $100 < C < 200$ , completion of the monolayer becomes clearly evidenced by the appearance of a bend in the vicinity of  $p/p_0 \approx 0,1$  and the BET method fits well.

$C$ -values above 200 may be indicative of the presence of micropores. The  $C$ -value gives an indication of the force of the adsorbent-adsorbate interaction but cannot be used to calculate quantitatively the adsorption enthalpy. An estimation of the errors resulting from uncertainties in the measured values or in the linear regression does not include all the fundamental sources of error. Rather, the reproducibility of the results should be verified by repeated measurements using fresh samples for each run, and the mean value with standard deviations reported.

### 7.3 Single-point determination

Having established that the BET plot for the particular type of material gives a straight line, it is possible to use a simplified procedure requiring only the determination of a single point on the isotherm in the range of relative pressures between 0,2 and 0,3. For  $C \gg 1$ , the ordinate intercept  $1/(n_m C)$  of the BET plot is small and equation (1) simplifies to:

$$n_{m,sp} = n_a \left( 1 - \frac{p}{p_0} \right) \quad \dots (6)$$

The monolayer capacity  $n_{m,sp}$  is less than or equal to  $n_{m,mp}$  derived from a multipoint determination. For measurements on samples of similar materials the error in the single-point method can be corrected for by performing a multipoint analysis first to determine:

- either the appropriate value of the intercept, which can then be used in subsequent single-point analyses;

- or the appropriate value of the BET parameter  $C$ , which can then be used to correct the single-point  $n_{m,sp}$  values using the equation:

$$\frac{n_{m,mp} - n_{m,sp}}{n_{m,mp}} = \frac{1 - (p/p_0)}{1 + (p/p_0)(C - 1)} \quad \dots (7)$$

## 8 Test report

A report of the determination of the specific surface area of a solid by gas adsorption using the BET method shall include the following information:

- a) a reference to this International Standard;
- b) laboratory, type of equipment, operator, date of determination;
- c) characterization of the sample, e.g. source, chemical composition, purity, method of sampling, sample division;
- d) pretreatment and degassing conditions, e.g. temperature, residual pressure, partial pressures, duration of degassing, flushing with adsorbate or helium, mass reduction;
- e) mass of degassed sample, in grams;
- f) experimental procedure for adsorption isotherm determination, e.g. volumetric, gravimetric, chromatographic, static or continuous gas admission, single-point determination, calibration of dead volume or buoyancy;
- g) adsorbate (chemical nature, purity, moisture content);
- h) adsorption isotherm ( $n_a$ , expressed in moles per gram, plotted against relative pressure,  $p/p_0$ ), sample temperature in kelvins, saturation vapour pressure, expressed in pascals;
- i) evaluation parameters: multipoint or single-point determination, BET plot or range of linearity, monolayer capacity  $n_m$  expressed in moles per gram,  $C$  value, molecular cross-sectional area  $a_m$  expressed in square nanometres;
- j) specific surface area,  $a_s$ , expressed in square metres per gram;
- k) reference material(s) used for validation of results.