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

Détermination de l'aire massique (surface spécifique) des solides par adsorption de gaz — Méthode BET

Reference number
ISO 9277:2010(E)

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Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
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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 9277 was prepared by Technical Committee ISO/TC 24, *Particle characterization including sieving*, Subcommittee SC 4, *Particle characterization*.

This second edition cancels and replaces the first edition (ISO 9277:1995), which has been technically revised.

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

1 Scope

This International Standard specifies the determination of the overall (see Note) specific external and internal surface area of disperse (e.g. nano-powders) or porous solids by measuring the amount of physically adsorbed gas according to the Brunauer, Emmett and Teller (BET) method (see Reference [1]). It takes account of the International Union for Pure and Applied Chemistry (IUPAC) recommendations of 1984 and 1994 (see References [7][8]).

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

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). Inaccessible pores are not detected. The BET method cannot reliably be applied to solids which absorb the measuring gas.

A strategy for specific surface area determination of microporous materials (type I isotherms) is described in Annex C.

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 14488, *Particulate materials — Sampling and sample splitting for the determination of particulate properties*

3 Terms and definitions

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

3.1
adsorption
enrichment of the adsorptive gas at the external and accessible internal surfaces of a solid material

[ISO 15901-2:2006[2], 3.4]

3.2
physisorption
weak bonding of the adsorbate, reversible by small changes in pressure or temperature

[ISO 15901-3:2007[3], 3.13]

3.3

adsorbate

adsorbed gas

[ISO 15901-2:2006[2], 3.1]

3.4

adsorptive

gas or vapour to be adsorbed

[ISO 15901-2:2006[2], 3.5]

3.5

adsorbent

solid material on which adsorption occurs

[ISO 15901-2:2006[2], 3.3]

3.6

isotherm

relationship between the amount of gas adsorbed and the equilibrium pressure of the gas, at constant temperature

[ISO 15901-2:2006[2], 3.10]

3.7

volume adsorbed

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

[ISO 15901-2:2006[2], 3.22]

3.8

adsorbed amount

quantity of gas adsorbed at a given pressure and temperature

NOTE 1 Adsorbed amount is expressed in moles.

NOTE 2 Adapted from ISO 15901-3:2007[3], 3.6.

3.9

monolayer amount

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

[ISO 15901-3:2006[3], 3.8]

3.10

surface area

extent of available surface area as determined by a given method under stated conditions

[ISO 15901-1:2006[1], 3.25]

NOTE For the purposes of this International Standard, the area includes the external surface of a solid plus the internal surface of its accessible macro-, meso- and micropores.

3.11

specific surface area

absolute surface area of the sample divided by sample mass

3.12
molecular cross-sectional area
molecular area of the adsorbate, i.e. the area occupied by an adsorbate molecule in the complete monolayer

3.13
macropore
pore with width greater than approximately 50 nm

NOTE Adapted from ISO 15901-3:2007[3], 3.10.

3.14
mesopore
pore with width between approximately 2 nm and 50 nm

[ISO 15901-3:2007[3], 3.11]

3.15
micropore
pore with width of approximately 2 nm or less

NOTE Adapted from ISO 15901-3:2007[3], 3.12.

3.16
relative pressure
ratio of the equilibrium adsorption pressure, p, to the saturation vapour pressure, p_0, at analysis temperature

[ISO 15901-3:2007[3], 3.15]

3.17
equilibrium adsorption pressure
pressure of the adsorptive gas in equilibrium with the adsorbate

[ISO 15901-2:2006[2], 3.7]

3.18
saturation vapour pressure
vapour pressure of the bulk liquefied adsorptive gas at the temperature of adsorption

[ISO 15901-2:2006[2], 3.20]

3.19
free space
head space
dead space
dead volume
volume of the sample holder not occupied by the sample

4 Symbols and abbreviated terms

Table 1 presents the symbols used in this International Standard, together with their common units derived from the SI. For comparison purposes, the IUPAC symbols (see References [7][8]) are also given. These may differ from the symbols generally used in International Standards. All specific dimensions are related to sample mass in grams.

Table 1 — Symbols

IUPAC symbol	Quantity	Unit
a_m	molecular cross-sectional area	nm^2
a_s	specific surface area	m^2 g^{-1}
C	BET parameter	1[a]
L	Avogadro constant ($= 6{,}022 \times 10^{23}$)	mol^{-1}
m	mass of the solid sample	g
m_a	specific mass adsorbed	1[a]
n_a	specific amount adsorbed	mol g^{-1}
n_m	specific monolayer amount of adsorbate	mol g^{-1}
$n_\mathrm{m,mp}$	specific monolayer amount derived from multipoint measurement	mol g^{-1}
$n_\mathrm{m,sp}$	specific monolayer amount derived from single-point measurement	mol g^{-1}
p	pressure of the adsorptive in equilibrium with the adsorbate	Pa
p_0	saturation vapour pressure of the adsorptive	Pa
p/p_0	relative pressure of the adsorptive	1[a]
R	molar gas constant ($= 8{,}314$)	J mol^{-1} K^{-1}
r_s	radius of uniform nonporous spheres	nm
t	time	min
T	temperature	K
V_a	specific volume adsorbed	cm^3 g^{-1}
$V_\mathrm{p,micro}$	specific micropore volume	cm^3 g^{-1}
ρ	(mass) density	g cm^{-3}
u_c	combined standard uncertainty for the certified specific surface area of a BET reference material	m^2 g^{-1}
k	coverage factor for the combined standard uncertainty	1[a]
U	expanded uncertainty ($= k\, u_\mathrm{c}$) for the certified specific surface area of a BET reference material	m^2 g^{-1}

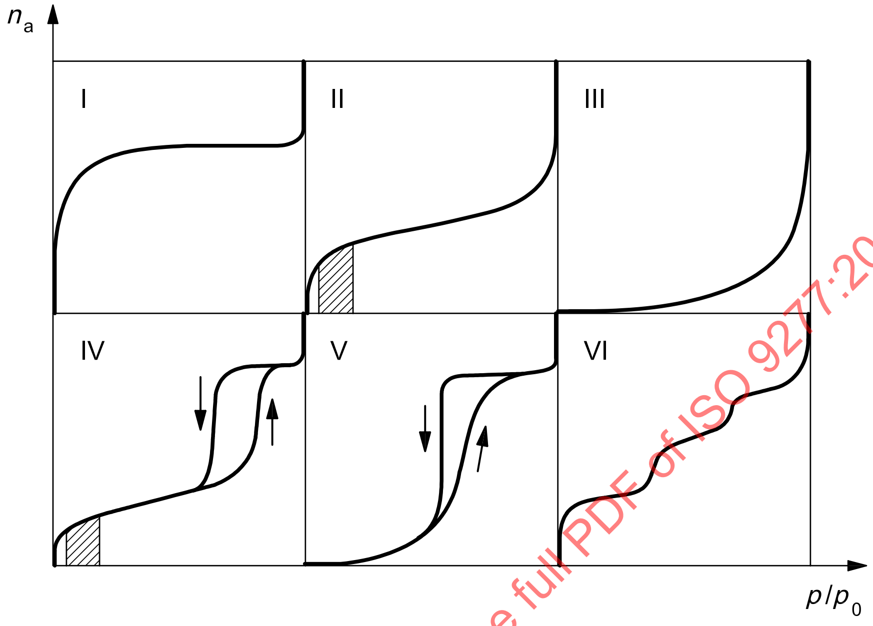
[a] According to ISO 80000-1:2009[4], 3.8, Note 3, the unit for any quantity of dimension one (at present commonly termed "dimensionless") is the unit one, symbol 1.

5 Principle

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 solids which absorb the measuring gas. A strategy for specific surface area determination of microporous materials (type I isotherms) is described in Annex C.

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 amount can be calculated from the adsorption isotherm using the BET equation [see Equation (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.

Nitrogen at its boiling point (about 77,3 K) is usually the most suitable adsorptive. Very often, argon at liquid argon temperature (i.e. 87,27 K) is a good alternative adsorptive for specific surface area determination (especially in the case of graphitized carbon and hydroxylated oxide surfaces, see Table A.1, footnote a) because it is a chemically inert monoatomic gas with a symmetrical electron shell configuration quite different from that of nitrogen, although the polarizabilities of argon and nitrogen are remarkably similar.



Key

n_a specific amount absorbed

p/p_0 relative pressure

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

Figure 2 — Schematic cross-section of a particle with surface detected by the adsorption method shown by dotted line

If the sensitivity of the instrument when using nitrogen is insufficient for low specific surface areas of about 1 $m^2 g^{-1}$ or lower, the application of krypton adsorption at liquid nitrogen temperature for the specific surface area analysis is recommended. As a consequence of the low p_0 of about 0,35 kPa for krypton at 77,3 K, the “dead space” correction (see 3.19) for unadsorbed gas is significantly reduced (to 1/300th) compared to the conditions of nitrogen adsorption at the same temperature and it becomes possible to volumetrically measure low uptakes of adsorptive with acceptable accuracy. Although at 77,3 K krypton is about 38,5 K below its triple point temperature, there is some evidence from microcalorimetry and neutron diffraction studies that in the BET region the adsorbate may well be in a liquid-like state and therefore the value of the supercooled liquid is recommended as the effective p_0 for the construction of the BET plot.

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. Moreover, it is well known from the concepts of fractal analysis (Reference [8]) that experimental results for the quantities of length and area in the case of irregular complex structures, such as those which are found in most porous or highly dispersed objects, are not absolute, but depend on the measurement scale, i.e. the "yardstick" used. This means that less area is available for larger adsorbate molecules.

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 (see 6.3).

6 Procedure

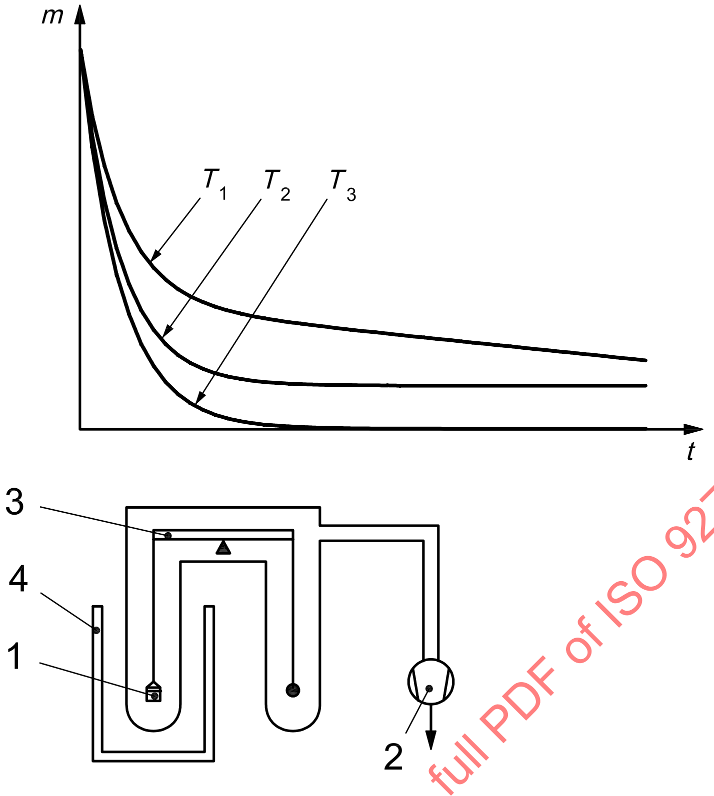
6.1 Sample preparation

Sampling shall be carried out in accordance with ISO 8213 and ISO 14488. 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), by spectroscopic methods, 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 an inert gas (e.g. helium). Degassing is complete when a steady value of the residual gas pressure p, of its composition or of the sample mass 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 is nearly constant over a period of 15 min to 30 min, degassing is complete. Almost invariant pressure also confirms 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 conductivity within the sample cell.

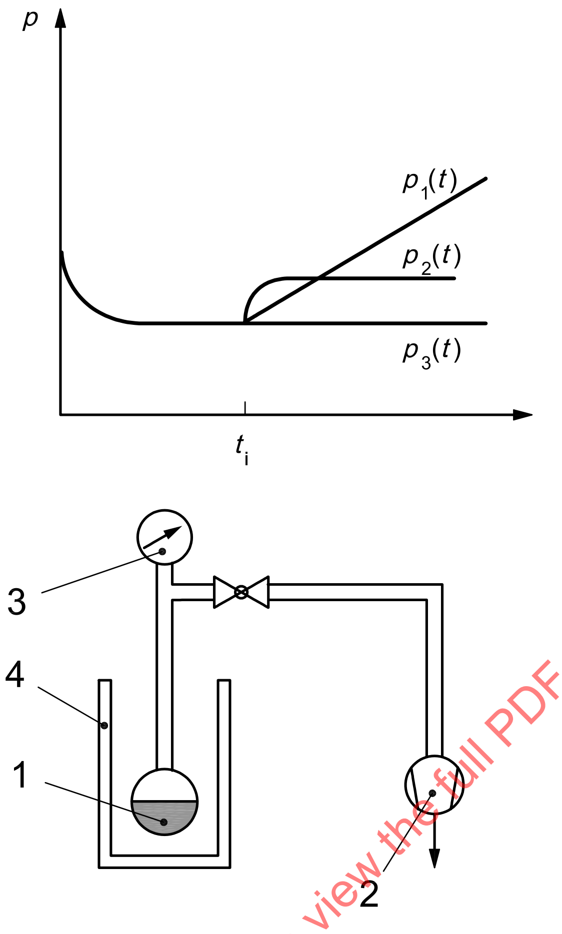
For sensitive samples, a pressure-controlled heating (see Figure 5) is recommended. This procedure consists in varying the heating rate in relationship to the gas pressure evolved from a porous material during the degassing under vacuum conditions. When a fixed pressure limit, p_L (usually around 7 Pa to 10 Pa), is surpassed due to the desorbed material from the sample surface, the temperature increase is stopped and the temperature is kept constant until the pressure falls below the limit. At that point the system continues the temperature ramp. This procedure is particularly suitable for avoiding structural changes in microporous materials, when fast heating rates can damage fragile structures due to a vigorous vapour release. In addition, the method is very safe in preventing sample elutriation when water or other vapours are released from the pores in very fine powder materials.



Key

m	sample mass	1	sample
t	degassing time	2	vacuum-generating system
T_1	temperature too low: long degassing time	3	balance
T_2	optimum temperature	4	oven
T_3	temperature too high: gas evolution due to decomposition of the sample		

Figure 3 — Thermogravimetric control of degassing

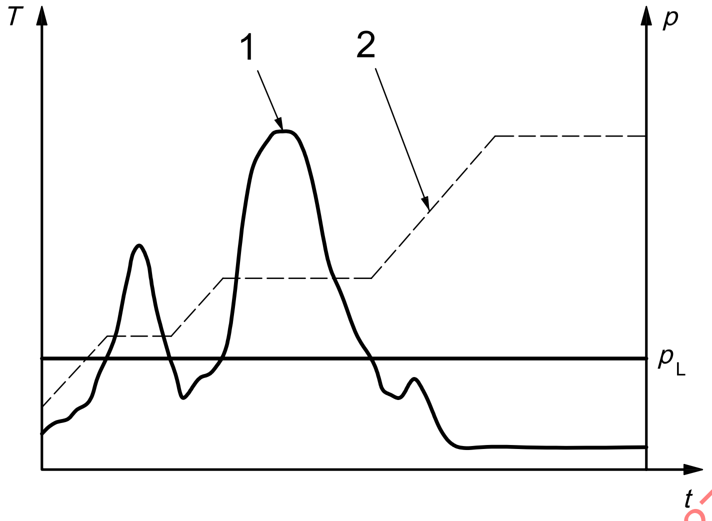


Key

p	pressure
t_i	time of sample isolation
$p_1(t)$	degassing complete, apparatus tight
$p_2(t)$	incomplete degassing
$p_3(t)$	leak

1	sample
2	vacuum-generating system
3	manometer
4	oven

Figure 4 — Pressure control of degassing



Key

p	pressure	1	pressure curve
T	temperature	2	temperature curve
t	time		
p_L	fixed pressure limit		

Figure 5 — Pressure-controlled heating

6.2 Experimental conditions

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

a) The temperature or the p_0 value of the adsorptive should be monitored during the analysis.

b) The purity of the adsorptive and any helium used to calibrate volumes or as a carrier gas should be at least 99,99 % volume fraction. If necessary, the gases should be dried and cleaned, e.g. oxygen removed from nitrogen.

c) The saturation vapour 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.

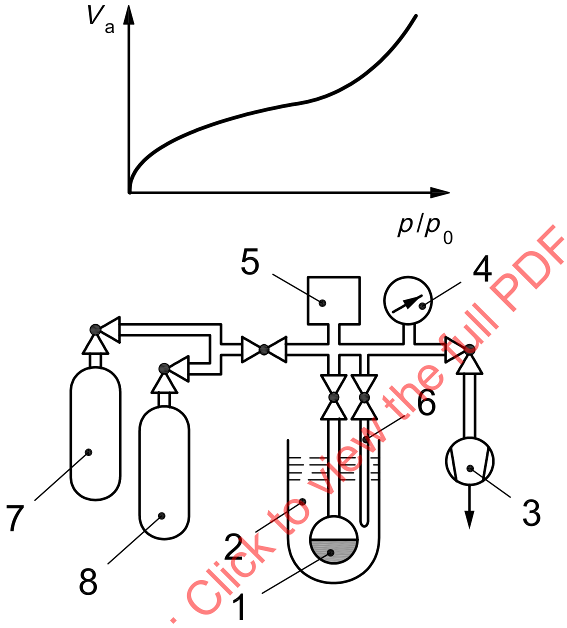
d) The validity of the result depends on careful sampling and sample preparation.

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, control the deviation from equilibrium either by occasional interruption of the gas flow or by control measurements using the discontinuous method.

6.3 Measuring methods for the assessment of the amount of adsorbed gas

6.3.1 Static volumetric method

In the static volumetric method, a known amount of gas is admitted to a sample bulb thermostated at the adsorption temperature (see Figure 6). Adsorption of the gas on to the sample occurs, and the pressure in the confined volume continues to fall until the adsorbate and the adsorptive 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 remaining in the gas phase. Measurement of the pressure is required together with temperatures and volumes of the system. The volumes are most easily determined by gas expansion of an inert gas such as helium. Determine the dead volume before or after the measurement of the adsorption isotherm. The calibration of the volumes of the system is done volumetrically using helium at the measuring temperature. It should be noted that some materials may adsorb or absorb helium. In this case, corrections can be made after measuring the adsorption isotherm. If the measurement of the dead volume 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 adsorption analysis (when nitrogen adsorption effects can be neglected). The determination of the dead volume may be avoided using difference measurements, i.e. by means of a reference and sample tube connected by a differential transducer. 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 15 mm above the sample and constant to within 1 mm.



Key

V_a specific volume absorbed
p/p_0 relative pressure of the adsorptive
1 sample
2 Dewar vessel with cooling bath
3 vacuum-generating system
4 manometer
5 calibrated volume (gas burette)
6 saturation pressure tube
7 adsorptive
8 gas for dead space measurement (e.g. He)

Figure 6 — Volumetric method

6.3.2 Flow volumetric method

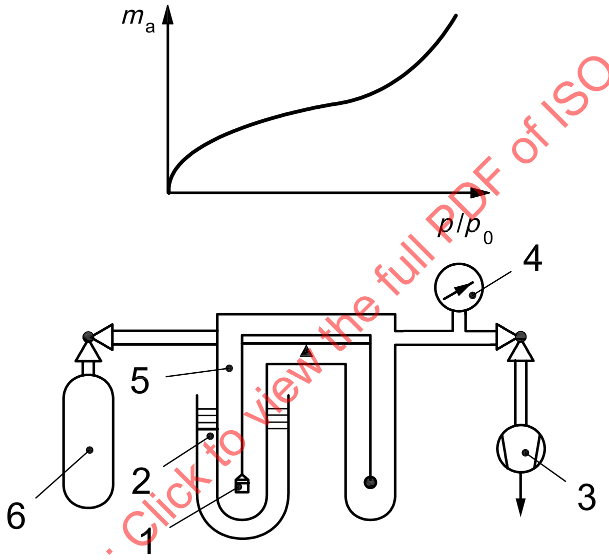
The flow volumetric method is similar to the static volumetric method, the difference is that gas is continuously fed to the sample at a relatively low flow rate rather than in a series of batch doses. By this method, the change in cell pressure is continuously measured at a controlled flow rate. The adsorbed amount is determined by comparing the rate of pressure rise with the adsorptive gas to that with a non-adsorbing gas such as helium used for calibration. An alternative approach which directly determines the quantity of gas adsorbed is to measure the pressure difference between the reference and sample tubes at the same volume of adsorptive gas fed. 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, under some circumstances, be completed in a shorter period of time than using a static volumetric method. However, special care has to be taken to ensure that the flow rate is low enough so that the adsorptive and adsorbate are close to equilibrium at all times. Determination of the dead volume and control of the liquid level in the cooling bath are recommended using the same requirements as described in 6.3.1.

6.3.3 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 7). 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.

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



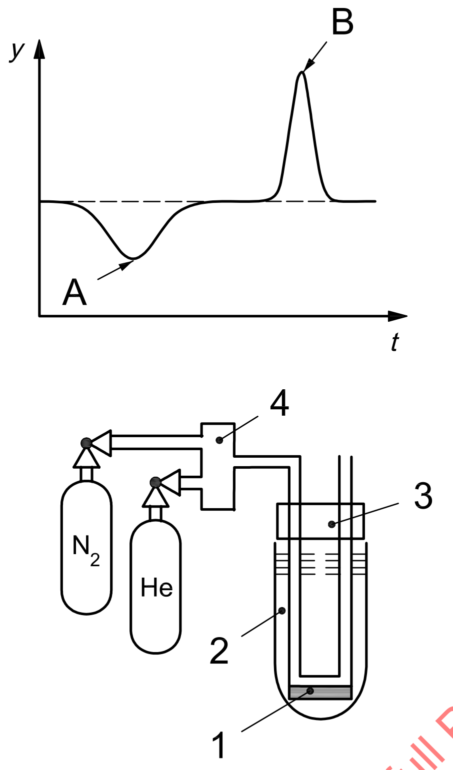
Key

m_a	specific mass absorbed
p/p_0	relative pressure of the adsorptive
1	sample
2	cooling bath
3	vacuum-generating system
4	manometer
5	balance
6	adsorptive

Figure 7 — Gravimetric method

6.3.4 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 8). 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 evaluation of the gas amount initially adsorbed. Take care 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 (see Reference [9]).



Key

y	detector signal	1	sample
t	time	2	Dewar vessel with cooling bath
A	adsorption trough	3	heat conductivity detector
B	desorption peak	4	gas mixer

Figure 8 — 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 on the ordinate against the corresponding relative pressure, p/p_0, on the abscissa to give the adsorption isotherm. The monolayer amount, n_m, is calculated using the BET equation:

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

NOTE A modified equation includes, besides the BET parameter, C, an additional parameter limiting the number of layers on the surface (Reference [10]). Although the two-parameter BET equation as recommended by IUPAC allows for an unlimited number of adsorbed layers (Reference [11]), it gives comparable results for mesoporous material.

7.2 Multipoint determination

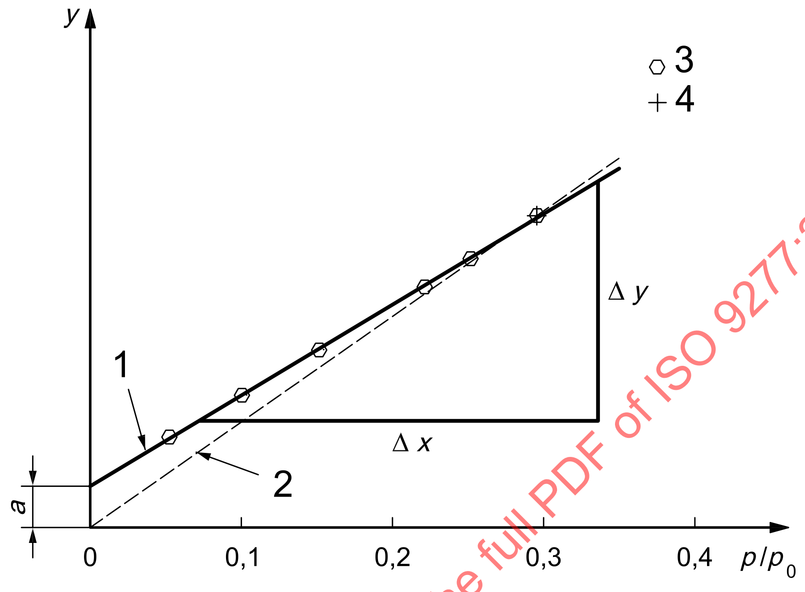
In the BET diagram, $(p/p_0)/[n_a(1-p/p_0)]$ is plotted on the ordinate against p/p_0 on the abscissa (see Figure 9). The plot should give a straight line $y = a + bx$ within the relative pressure range 0,05 to 0,3. It is a requirement that the intercept a be positive. The slope $b = \Delta y/\Delta x = (C-1)/(n_m C)$ and the intercept $a = 1/(n_m C)$ may be determined by linear regression. From this the monolayer amount

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

and the BET parameter

$$C = \frac{b}{a} + 1 \tag{3}$$

can be derived.



Key

$y = (p/p_0)/[n_a(1 - p/p_0)]$	left hand side of the BET equation	1	multipoint BET fit
p/p_0	relative pressure of the adsorptive	2	single point BET line
a	intercept on the ordinate	3	experimental data points
Δx	change in the abscissa (slope calculation)	4	data point selected for single point calculation
Δy	change in the ordinate (slope calculation)		

Figure 9 — BET plot

The specific surface area per mass of the sample, a_s, expressed in square metres per gram, is calculated from the monolayer amount by assessing a value for the average area occupied by each molecule in the complete monolayer:

$$a_s = n_m a_m L \tag{4}$$

A molecular cross-sectional area $a_m = 0{,}162\ \text{nm}^2$ is recommended for nitrogen at 77,3 K. Equation (4) then becomes

$$a_s = 9{,}76 \times 10^4\, n_m \tag{5}$$

where n_m is expressed in moles per gram.

For nonporous spheres, the specific surface area per mass of the sample, a_s is given by:

$$a_s = \frac{3}{\rho r_s} \tag{6}$$

where

r_s is the uniform radius of the spheres;

ρ is density.

Values for the molecular cross-sectional area of other adsorbates can be found in the literature (References [12] to [16]). Generally accepted values for the molecular cross-sectional area are shown in Annex A.

For some materials (mainly microporous adsorbents, see Annex C) and adsorptives, 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, it is a requirement that the range of linearity 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.

Values of C 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 $C >> 1$, the ordinate intercept $1/(n_m C)$ of the BET plot is small and Equation (1) simplifies to:

$$n_{m,sp} = n_a \left(1 - \frac{p}{p_0}\right) \qquad (7)$$

The monolayer amount $n_{m,sp}$ 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 Equation (8):

$$\frac{n_{m,mp} - n_{m,sp}}{n_{m,mp}} = \frac{1-(p/p_0)}{1+(p/p_0)(C-1)} \qquad (8)$$

8 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard (ISO 9277:2010);

b) laboratory, type of equipment, operator, date of determination;

c) sample identification (characterization of the sample), e.g. source, chemical class of the material, purity, method of sampling, sample division;

d) pretreatment and degassing conditions, e.g. degassing in a vacuum or in inert gas flow, temperature and duration of degassing;

e) mass of degassed sample;

f) experimental procedure for adsorption isotherm determination, e.g. volumetric, gravimetric, static or continuous gas admission, single-point determination, calibration of dead volume or buoyancy;

g) adsorptive (chemical nature, purity);

h) adsorption isotherm (n_a, plotted against relative pressure, p/p_0), measurement temperature;

i) evaluation parameters: multipoint or single-point determination, BET plot or range of linearity, monolayer amount n_m, BET parameter C, molecular cross-sectional area used;

j) specific surface area;

k) certified or local reference material(s) used for performance testing of the instrument and validation of results.

9 Use of reference materials

To ensure proper working conditions and correct data evaluation, the apparatus performance should be monitored periodically using a certified reference material or a quality control material. The quality control material, which can be an in-house produced secondary reference material, should be verified against a certified reference material. A number of national or international institutes or organizations offer certified reference materials, and currently useful certified reference materials for the BET method are listed in Annex B.

Annex A
(informative)

Cross-sectional areas of some frequently used adsorptives

Table A.1 — Cross-sectional areas

Adsorptive	Temperature K	Recommended value nm^2
Nitrogen	77,35	0,162[a]
Argon	77,35	0,138[b]
Argon	87,27	0,142
Krypton	77,35	0,202
Xenon	77,35	0,168
Carbon dioxide	195	0,195
Carbon dioxide	273,15	0,210
Oxygen	77,35	0,141
Water	298,15	0,125
n-Butane	273,15	0,444
n-Heptane	298,15	0,631
n-Octane	298,15	0,646
Benzene	293,15	0,430

[a] In the case of graphitized carbon and hydroxylated oxide surfaces, the orientation of the nitrogen quadrupole is dependent on the surface density of hydroxyl groups, because the nitrogen molecules tend to interact vertically with surface hydroxyl groups. This leads to a reduced value for the cross-sectional area of nitrogen. It is recommended to use Ar at the temperature of liquid Ar (87,3 K) for the determination of the BET area of such surfaces.

[b] Contrary to argon adsorption at 87,3 K, the use of argon at 77,3 K (which is about 6,5 K below the triple point of bulk argon) is considered to be less reliable than the adsorption of nitrogen. At 77,3 K, all nitrogen isotherms on nonporous adsorbents are type II, whereas some argon 77,3 K isotherms are type II and others are type VI. These and other differences indicate that at 77,3 K, the structure of the argon monolayer may be highly dependent on the surface chemistry of the adsorbent. The cross-sectional area for argon at 77,3 K is not well defined. The value of 0,138 nm^2, as given in the table is based on the assumption of a closed-packed liquid monolayer, and can also be considered to be the customary value. However, one can also find the use of 0,166 nm^2 in the literature.

Annex B
(informative)

Certified reference materials for the BET method

Certified reference materials are currently available from BAM[1] in Germany, IRMM[1] in Belgium, NIST[1] in the USA, and APPIE[1] in Japan (See Table B.1 and Reference [17]). Other and new certified reference materials can be searched for in COMAR, the international database for certified reference materials (www.comar.bam.de).

Bundesanstalt für Materialforschung und –prüfung (BAM)
Department I. Analytical Chemistry; Reference Materials
Richard-Willstätter-Straße 11,
D-12489 BERLIN
Germany
http://www.bam.de/

European Commission — Joint Research Centre
Institute for Reference Materials and Measurements (IRMM)
Reference Materials Unit, attn. reference materials sales
Retieseweg 111,
B-2440 GEEL
Belgium
http://irmm.jrc.ec.europa.eu/html/homepage.htm

Standard Reference Materials Program
National Institute of Standards and Technology (NIST)
100 Bureau Drive, Stop 2322
GAITHERSBURG
MD 20899-2322
USA
http://www.nist.gov/

The Association of Powder Process Industry and Engineering Japan (APPIE Japan)
No.5 Kyoto Bldg., 181 Kitamachi
Karasuma-dori, Rokujo-agaru, Shimogyo-ku
KYOTO 600-8176
Japan
http://www.appie.or.jp/english/

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[1] Example of a supplier offering certified reference materials commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of the products offered.

Table B.1 — Certified BET reference materials

Material	SRM/CRM No.	Producer or distributor	Method	Specific surface area m^2 g^{-1}	Uncertainty of the certified value
Silica	BAM-PM-101	BAM	Kr ads.	0,177	0,008[a]
Alpha-alumina	BAM-PM-102	BAM	N_2 ads.	5,41	0,09[a]
Alumina	BAM-PM-103	BAM	N_2 ads.	156,0	2,7[a]
Alumina	BAM-PM-104	BAM	N_2 ads.	79,8	0,8[a]
Porous glass	BAM-P105	BAM	N_2 ads.	198,5	1,6[b]
Activated carbon	BAM-P108	BAM	N_2 ads.	550	5[b]
Alpha-alumina	BCR-169	IRMM	N_2 ads.	0,104	0,012[a]
Alpha-alumina	BCR-170	IRMM	N_2 ads.	1,05	0,05[a]
Alumina	BCR-171	IRMM	N_2 ads.	2,95	0,13[a]
Quartz	BCR-172	IRMM	N_2 ads.	2,56	0,10[a]
Titanium dioxide	BCR-173	IRMM	N_2 ads.	8,23	0,21[a]
Tungsten	BCR-175	IRMM	N_2 ads.	0,18	0,04[a]
Silica/alumina	SRM 1897	NIST	N_2 ads.	258,32	5,29[b]
Silicon nitride	SRM 1899	NIST	N_2 ads.	10,52	0,19[b]
Silicon nitride	SRM 1900	NIST	N_2 ads.	2,85	0,09[b]
Titanium dioxide	SAP11-05 Class 1	APPIE	N_2 ads.	8,88	0,55[b]
Carbon black	SAP11-05 Class 2	APPIE	N_2 ads.	23,8	1,10[b]
Carbon black	SAP11-05 Class 3	APPIE	N_2 ads.	111,7	8,62[b]

[a] 95 % confidence interval of mean of the laboratory means from certification interlaboratory testing in m^2 g^{-1}.

[b] Expanded uncertainty $U = k\, u_c$ (with coverage factor $k = 2$ corresponding to a level of confidence of approximately 95 %) in m^2 g^{-1} where u_c is a combined standard uncertainty for the average, calculated according to ISO/IEC Guide 98-3[5].

Annex C
(informative)

Surface area of microporous materials

Specific surface area is a crucial parameter for optimizing the use not only of meso- and macroporous but also of microporous materials in many applications. However, due to the complex nature of porous materials, no single experimental technique can be expected to provide an evaluation of the “absolute” surface area. Surface area values are procedurally defined and should always be related to the method, conditions and probe molecules used in the experimental work. Despite the well-known limitations, the Brunauer-Emmett-Teller (BET) method of 1938 (see Reference [6]) continues to be widely used for the evaluation of specific surface areas of porous materials.

As pointed out in Clause 7, usually two stages are involved in the evaluation of the BET specific surface area. First, it is necessary to transform a physisorption isotherm into the BET plot and from it to derive the value of the BET monolayer amount, n_m. The second stage is the calculation of the specific surface area a_s, which requires knowledge of the molecular cross-sectional area.

In Reference [6], it was found that type II nitrogen isotherms on various adsorbents gave linear BET plots over the approximate p/p_0 range from 0,05 to 0,35.

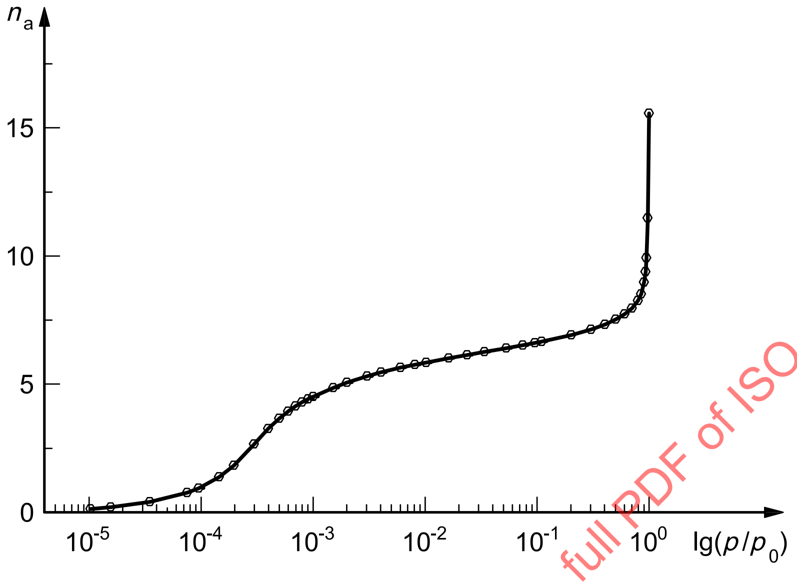
In addition to problems arising from the chemical and geometrical heterogeneity of the surface, the kind of porosity (i.e. existence of macro-, meso- or micropores) plays an important role for the applicability of the BET equation. The BET equation is applicable for specific surface area analysis of nonporous, macro- and mesoporous materials consisting of pores of wide pore diameter, but is in a strict sense not applicable in the case of microporous adsorbents (a critical appraisal of the BET method is given in various textbooks on porosity measurements, see References [13] to [16]). It is difficult to separate the processes of mono-multilayer adsorption from micropore filling, and micropore filling is usually completed at relative pressures below 0,1. It appears that in the presence of micropores, the linear (BET) range is significantly shifted to lower relative pressures. The application of the BET method is also problematic for estimating the specific surface area of mesoporous molecular sieves of pore widths less than about 4 nm, because pore condensation is observed at pressures very close to the pressure range where monolayer-multilayer formation on the pore walls occur. This may lead to a significant overestimation of the monolayer amount in case of BET analysis. Another problem is associated with the size and shape of adsorptive molecule, i.e. the effective yardstick used to assess the surface area. In case of adsorbents with very narrow cylindrical micropores (about 0,5 nm to 0,7 nm pore channels) the area covered by the adsorptive (usually nitrogen or argon) is significantly smaller than the total area available. This is due to the extreme curvature of the pore channels and the relatively large size of the probe molecule (problems related with the correct assessment of the specific surface area of zeolite particles have been recently discussed in Reference [18]). However, in broader super-micropores (>0,7 nm), a number of molecules located in the center of the pores do not touch the surface, i.e. this leads to an overestimation of the specific surface area.

Therefore, the specific surface area obtained by applying the BET method on adsorption isotherms from microporous solids does not reflect the true internal surface area, but should be considered as a kind of characteristic or equivalent BET area. In this case, it is obligatory to report the range of linearity for the BET plot. There is, of course, the question of how to find the linear range of the BET plot for microporous materials in a way that it reduces any subjectivity in the assessment of the monolayer amount. Reference [19] suggests a procedure which is mainly based on two criteria:

a) C shall be positive (i.e. any negative intercept on the ordinate of the BET plot is an indication that one is outside the valid range of the BET equation);

b) the application of the BET equation should be limited to the pressure range where the term $n_a(p_0 - p)$ or alternatively $n_a(1 - p/p_0)$ continuously increases with p/p_0.

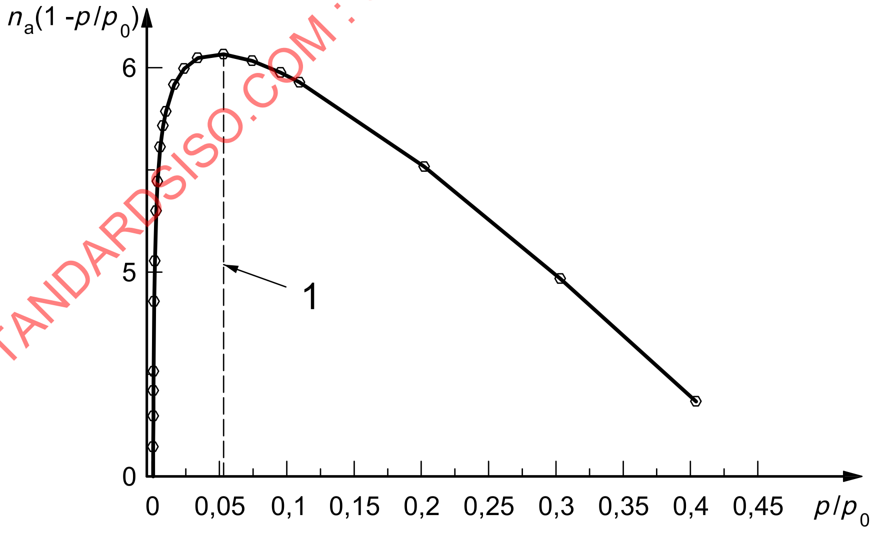
An example where this procedure was applied in order to determine the linear BET range for the argon adsorption isotherm at 87,3 K on a faujasite zeolite (adsorption isotherm data from Figure C.1) is shown in Figure C.2. It is clearly visible that based on this criterion all data points above a relative pressure of 0,053 have to be eliminated for application of the BET calculation. The resulting plot is shown in Figure C.3, i.e. the BET equation is applied to relative pressures below about 0,053 down to 0,01, and a linear plot with positive C constant is obtained.



Key

n_a	specific amount absorbed
p/p_0	relative pressure of the adsorptive

Figure C.1 — Semilogarithmic plot of the argon adsorption isotherm at 87,3 K on a faujasite-type zeolite



Key

$n_a(1 - p/p_0)$	denominator on the left hand side of the BET equation
p/p_0	relative pressure of the adsorptive
1	BET range limit

Figure C.2 — Plot of the term $n_a(1 - p/p_0)$ vs. p/p_0 for the argon isotherm shown in Figure C.1