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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

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Foreword

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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.

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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.

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

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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]

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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]

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3.7
volume adsorbed
volumetric equivalent of adsorbed amount expressed as gas at standard conditions of temperature and pressure (STP)

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[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

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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

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

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

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[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.

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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	$mol\ g^{-1}$
$n_{m,mp}$	specific monolayer amount derived from multipoint measurement	$mol\ g^{-1}$
$n_{m,sp}$	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	$cm^3\ g^{-1}$
$V_{p,micro}$	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 ($= k\ u_c$) 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.

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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.

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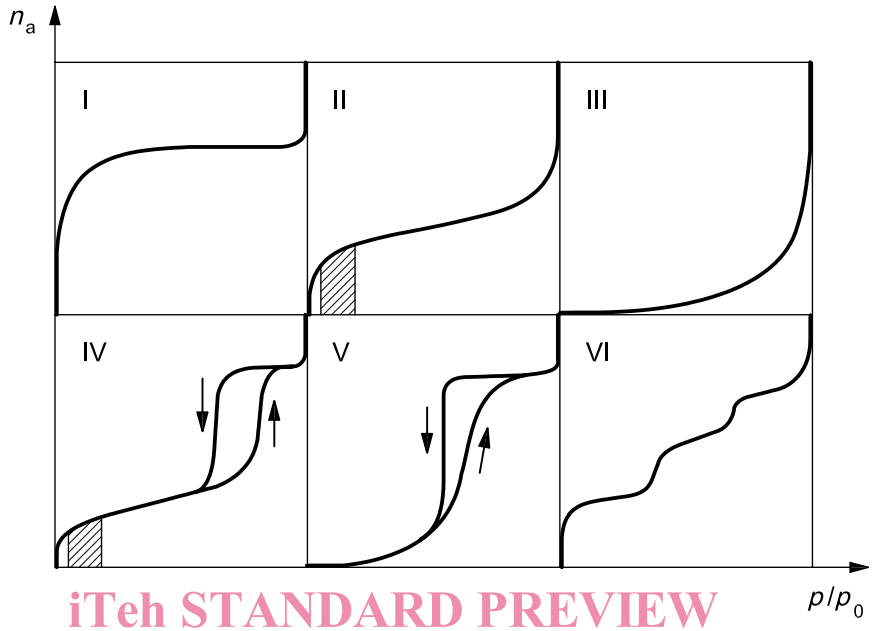
Nitrogen at its boiling point (about 77,3 K) is usually the most suitable adsorptive. Very often, argon at liquid argon temperature (i.e. 87,27 K) is a good alternative adsorptive for specific surface area determination (especially in the case of graphitized carbon and hydroxylated oxide surfaces, see 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.



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Key

n_a specific amount absorbed

p/p_0 relative pressure

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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

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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.

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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.

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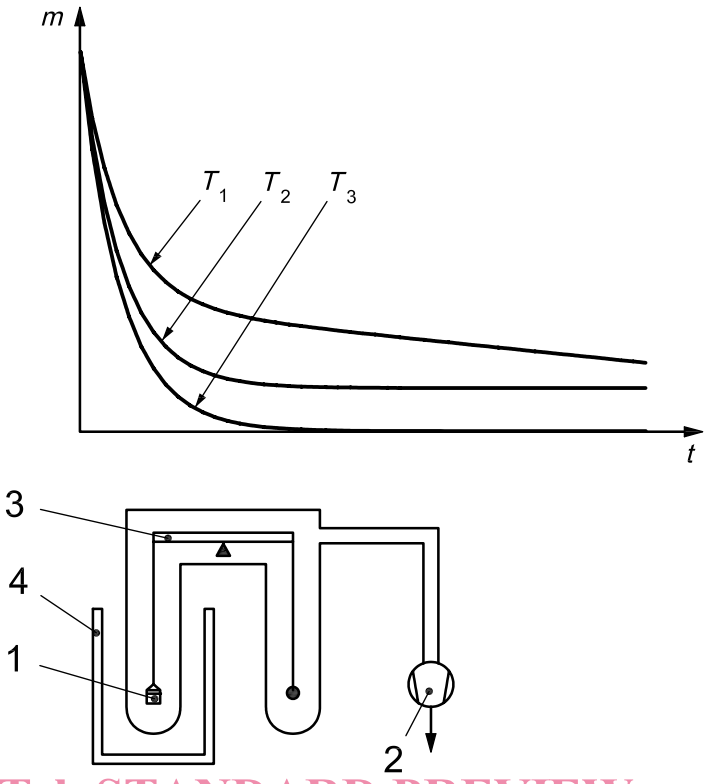

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Key

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		

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Figure 3 — Thermogravimetric control of degassing

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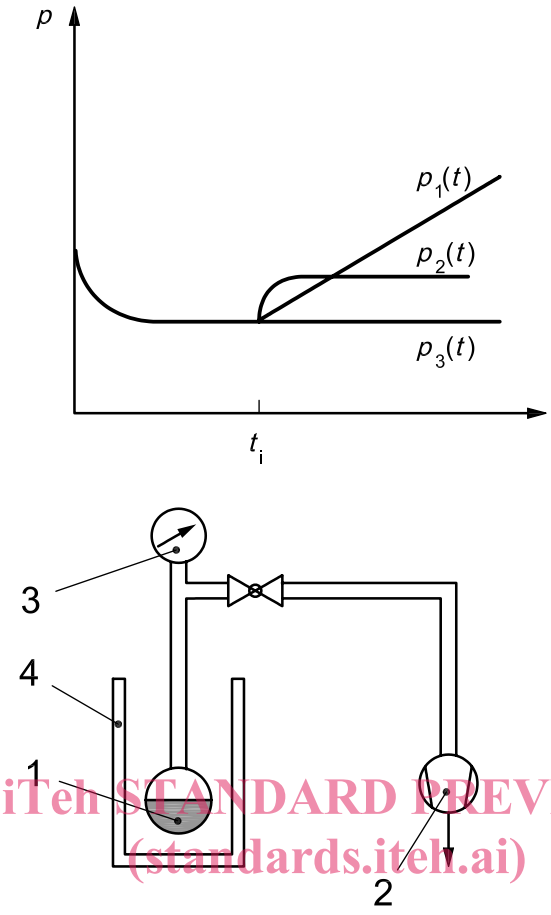

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Key

p	pressure	1	sample
t_i	time of sample isolation	2	vacuum-generating system
$p_1(t)$	degassing complete, apparatus tight	3	manometer
$p_2(t)$	incomplete degassing	4	oven
$p_3(t)$	leak		

Figure 4 — Pressure control of degassing

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