# INTERNATIONAL STANDARD

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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

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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see <a href="https://www.iso.org/directives">www.iso.org/directives</a>).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 24, *Particle characterization including sieving*, Subcommittee SC 4, *Particle characterization*.

This third edition cancels and replaces the second edition (ISO 9277:2010), which has been technically revised.

The main changes compared to the previous edition are as follows:

- the IUPAC classification of adsorption isotherms has been updated according to Reference [3];
- the description of dynamic vapour sorption (DVS) method in <u>6.3.6</u> has been added;
- <u>Annex A</u> has been revised;
- <u>Annex B</u> has been removed;
- the former Annex C (now <u>Annex B</u>) has been revised.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at <u>www.iso.org/members.html</u>.

## Introduction

Gas adsorption allows for assessing surface area of nonporous materials and porous materials with accessible porosity (which depends on the chosen adsorptive) via the Brunauer, Emmett and Teller (BET) theory<sup>[1],[2]</sup>. The BET theory is applicable only to adsorption isotherms of type II (disperse, nonporous or macroporous solids) and type IV (mesoporous solids) (see Figure 1, Type II and Type IVa isotherms). However, in the case of Type IVb isotherms, caution is required since pore condensation can occur at quite low  $p/p_0$  (see IUPAC recommendations<sup>[3]</sup>). The BET method cannot reliably be applied to solids which absorb the measuring gas. A strategy for BET area determination of microporous materials (type I isotherms) is described in <u>Annex B</u>.



#### Key

X relative pressure

Y amount adsorbed

SOURCE IUPAC Recommendations, 1994. Reproduced with the permission of the authors.<sup>[2]</sup>

#### Figure 1 — IUPAC (2015) classification of adsorption isotherms

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

## 1 Scope

This document specifies the determination of the overall specific external and internal surface area of either disperse (e.g. nano-powders) or porous, solids by measuring the amount of physically adsorbed gas according to the method of Brunauer, Emmett and Teller method,<sup>[1]</sup> based on the 2015 International Union for Pure and Applied Chemistry (IUPAC) recommendations<sup>[3]</sup>.

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

### 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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

#### <u>SO 9277:2022</u>

#### https://standards.iteh.ai/catalog/standards/sist/e184eb4e-ac7a-4781-9824

## 3 Terms and definitions 4e0a90829aed/iso-9277-2022

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

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at <u>https://www.electropedia.org/</u>

#### 3.1

#### adsorption

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

#### 3.2

#### physisorption

weak bonding of the *adsorbate* (3.2), reversible by small changes in pressure or temperature

**3.3 adsorbate** adsorbed gas

**3.4 adsorptive** gas or vapour to be adsorbed

**3.5 adsorbent** solid material on which *adsorption* (<u>3.1</u>) occurs

### 3.6

#### isotherm

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

#### 3.7

#### volume adsorbed

volumetric equivalent of *adsorbed amount* (3.8) expressed as gas at standard conditions of temperature and pressure (STP)

#### 3.8

#### adsorbed amount

number of moles of gas adsorbed at a given pressure and temperature

#### 3.9

#### monolayer capacity

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

#### 3.10

#### surface area

area of the external surface of a solid plus the internal surface of its accessible macro-, meso- and micropores (3.16)

#### 3.11

# specific surface area iTeh STANDARD PREVIEW

absolute surface area (3.10) of the sample divided by sample mass

#### 3.12

### molecular cross-sectional area

molecular area of the *adsorbate* (3.2), i.e. the area occupied by an adsorbate molecule in the complete monolayer

#### 3.13

nanopore

pore with width of about 100 nm or less

#### 3.14

#### macropore

pore with width greater than approximately 50 nm

#### 3.15

#### mesopore

pore with width between approximately 2 nm and 50 nm

#### 3.16

### micropore

pore with width of approximately 2 nm or less

#### 3.17

#### relative pressure

ratio of the equilibrium adsorption (3.1) pressure, p, to the saturation vapour pressure (3.18),  $p_{0}$ , at analysis temperature

#### 3.18

#### saturation vapour pressure

vapour pressure of the bulk liquefied adsorptive gas at the temperature of *adsorption* (3.1)

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

## 4 Symbols

<u>Table 1</u> presents the symbols used in this document, together with their common units derived from the SI. For comparison purposes, the lUPAC symbols are also given. All specific dimensions are related to sample mass in grams.

Symbol	Quantity	Unit			
a <sub>m</sub>	molecular cross-sectional area	nm <sup>2</sup>			
a <sub>s</sub>	specific surface area	$\mathrm{m}^2\mathrm{g}^{-1}$			
С	BET parameter <sup>a</sup>	1			
L	Avogadro constant ( $L = 6,022 \times 10^{23}$ )	mol <sup>-1</sup>			
m	mass of the solid sample	g			
m <sub>a</sub>	specific mass adsorbed <sup>a</sup>	1			
n <sub>a</sub>	specific amount adsorbed				
n <sub>m</sub>	specific monolayer capacity of adsorbate	mol g <sup>-1</sup>			
n <sub>m,mp</sub>	specific monolayer capacity derived from multipoint measurement	mol g <sup>-1</sup>			
n <sub>m,sp</sub>	specific monolayer capacity derived from single-point measurement	mol g <sup>-1</sup>			
р	pressure of the adsorptive in equilibrium with the adsorbate -ac 7a-4781-9824-	Ра			
$p_0$	saturation vapour pressure of the adsorptive	Ра			
$p/p_0$	relative pressure of the adsorptive <sup>a</sup>	1			
R	molar gas constant (= 8,314)	J mol <sup>-1</sup> K <sup>-1</sup>			
r <sub>s</sub>	radius of uniform nonporous spheres	nm			
t	time	min			
Т	temperature	К			
Va	specific volume adsorbed	$\mathrm{cm}^3\mathrm{g}^{-1}$			
V <sub>p,micro</sub>	specific micropore volume	$\mathrm{cm}^3\mathrm{g}^{-1}$			
ρ	(mass) density	g cm <sup>-3</sup>			
u <sub>c</sub>	combined standard uncertainty for the certified specific surface area of a BET reference material	m <sup>2</sup> g <sup>-1</sup>			
k	coverage factor for the combined standard uncertainty <sup>a</sup>	1			
U	expanded uncertainty ( $U = k u_c$ ) for the certified specific surface area of a BET reference material	$m^2 g^{-1}$			
<sup>a</sup> According to ISO 80000-1, the unit for any quantity of dimension one (at present commonly termed "dimensionless") is the unit one, symbol 1.					

Table	1	- Sy	<b>mbo</b>	ls
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## 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 Formula (1) (see 7.1). 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 — Schematic cross-section of a particle with surface detected by the adsorption method shown by dotted line

Nitrogen at its boiling point (about 77 K) was for many decades the adsorptive generally used for the determination of the specific surface area, mainly because liquid nitrogen was readily available and relatively strong attractive adsorptive-adsorbent interactions for many systems. However, due to nitrogen's quadrupole moment the orientation of a nitrogen molecule is affected by the surface chemistry of the adsorbent. This leads to uncertainties in the surface area determination by nitrogen in the order of approximately 20 % for some surfaces. However, argon at 87 K is a great alternative because argon does, contrary to the diatomic nitrogen molecule, not exhibit a quadrupole moment. Hence, argon adsorption is less sensitive to the surface chemistry leading to a much more reliable surface area determination for many adsorbent surfaces. If the sensitivity of the instrument when using argon or nitrogen is insufficient for low specific surface areas of about 1 m<sup>2</sup> g<sup>-1</sup> 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 K, the 'free 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 manometrically measure low uptakes of adsorptive with acceptable accuracy. Although at 77 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 (classified into micro-, meso-, macro- and nanopores) and different measuring temperatures. Moreover, it is well known from the concepts of fractal analysis 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 and/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 manometric (volumetric), by gravimetric or by the carrier gas method using continuous or discontinuous operation (see <u>6.3</u>).

## 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, nitrogen, argon). Degassing is complete when a steady value of the residual gas pressure, p, of its composition or of the sample mass is reached.



decomposition of the sample

### Figure 3 — Thermogravimetric control of degassing

Using the vacuum technique, isolate the heated sample container from the pump and trap (at time  $t_i$  in Figure 4). If the pressure is nearly constant 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.



#### Figure 4 — Pressure control of degassing

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.