# INTERNATIONAL STANDARD

First edition 2003-12-01

## Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of specific surface area of ceramic powders by gas adsorption using the BET method

iTeh ST Poudres céramiques — Détermination de l'aire massique (surface spécifique) par adsorption de gaz à l'aide de la méthode BET (standards.iteh.ai)

ISO 18757:2003 https://standards.iteh.ai/catalog/standards/sist/6ad05397-23a3-4256-8aa0-6f9375fd2994/iso-18757-2003



Reference number ISO 18757:2003(E)

#### PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

# iTeh STANDARD PREVIEW (standards.iteh.ai)

<u>ISO 18757:2003</u> https://standards.iteh.ai/catalog/standards/sist/6ad05397-23a3-4256-8aa0-6f9375fd2994/iso-18757-2003

© ISO 2003

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office Case postale 56 • CH-1211 Geneva 20 Tel. + 41 22 749 01 11 Fax + 41 22 749 09 47 E-mail copyright@iso.org Web www.iso.org

Published in Switzerland

## Contents

#### Page

1	Scope	1			
2	Normative references	1			
3	Terms and definitions	1			
4	Symbols and abbreviated terms	2			
5	Principle	2			
6	Procedure	3			
6.1	General procedure	3			
6.2	Sample preparation	3			
6.3	Experimental conditions	5			
6.4	Evaluation of data	6			
7	Test report	7			
Ann	Annex A (informative) Sample preparation — Outgassing				
Ann	Annex B (informative) Reference materials				
Bibli	Bibliography				

# (standards.iteh.ai)

<u>ISO 18757:2003</u> https://standards.iteh.ai/catalog/standards/sist/6ad05397-23a3-4256-8aa0-6f9375fd2994/iso-18757-2003

## 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 18757 was prepared by Technical Committee ISO/TC 206, *Fine ceramics*.

## iTeh STANDARD PREVIEW (standards.iteh.ai)

<u>ISO 18757:2003</u> https://standards.iteh.ai/catalog/standards/sist/6ad05397-23a3-4256-8aa0-6f9375fd2994/iso-18757-2003

# Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of specific surface area of ceramic powders by gas adsorption using the BET method

#### 1 Scope

This International Standard provides guidelines for the determination of the total specific external and internal surface area of disperse or porous (pore diameter > 2 nm) fine ceramic materials by measuring the amount of physically adsorbed gas according to the method of Brunauer, Emmet and Teller (BET method) [1]. General guidelines of the method are described in ISO 9277. This International Standard only focuses on specific details relevant to fine ceramic materials. It should further be noted that the BET method cannot be applied to type I isotherms (microporous materials or chemisorption behaviour) or when the solid absorbs the measuring gas.

NOTE For further details on those subjects please see IUPAC references [2], [3] or the textbook by Gregg and Sing [4].

#### 2 Normative references II en STANDARD PREVIEW

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 18757:2003

ISO 9277:1995, Determination of the specific surface area of solids by gas adsorption using the BET method 6f9375fd2994/iso-18757-2003

#### 3 Terms and definitions

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

#### 3.1

#### adsorption

enrichment of the adsorbate 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

#### adsorbate

measuring gas to be adsorbed

#### 3.4

#### adsorbent

solid, which adsorbs the measuring gas

#### 3.5

#### surface area

area of external surface of a fine ceramic powder plus the internal surface of its accessible macro- and mesopores

#### 3.6

#### adsorption isotherm

relation between the quantity of adsorbate and the equilibrium pressure of the adsorbate at constant temperature

#### 4 Symbols and abbreviated terms

Table 1 presents the symbols used in this International Standard, together with their SI units. For comparison purposes, the IUPAC [3] symbols are also given. All specific dimensions are related to sample mass, in grams.

ISO symbol	Parameter	SI unit	IUPAC symbol
$a_{\sf m}$	molecular cross-sectional area occupied by an adsorbed molecule in a complete monolayer	nm²	$a_{\sf m}$
$a_{s}$	specific surface area	$m^2 g^{-1}$	$a_{s}$
C	BET parameter	1 <sup>a</sup>	C
L	Avogadro constant (= $6,022 \times 10^{23}$ )	mol <sup>-1</sup>	L
m	mass of the solid sample	g	m
$m_{a}$	specific mass of gas adsorbed	1 <sup>a</sup>	m <sup>a</sup>
$n_{a}$	specific amount of gas adsorbed TANDARD PREVIEW	$r \mod g^{-1}$	n a
$n_{\sf m}$	specific monolayer capacity of adsorbate; amount of adsorbate needed to cover the surface with a complete monolayer of molecules since a	mol $g^{-1}$	$n_{ m m}$ , $n_{ m m}$ a
$n_{\sf m,\ \sf mp}$	specific monolayer capacity derived from multi-point measurement	mol $g^{-1}$	_
$n_{\sf m,sp}$	specific monolayer capacity derived from single-point measurement	mol $g^{-1}$	—
p	pressure of the adsorbate in equilibrium with the adsorbate ad 05397-23a3-4256-8	aa0- Pa	p
$p_0$	saturation vapour pressure of the adsorbate	Pa	$p^0$
t	time	S	t
Т	temperature	K	Т
$V_{a}$	specific volume adsorbed	$m^{3} g^{-1}$	V <sup>a</sup>
<sup>a</sup> According to one, symbol 1.	ISO 31-0, the coherent SI unit for any quantity of dimension one (at present commonly term	ed "dimensionle	ess") is the unit

Table 1 — Symbols

### 5 Principle

The method specified involves the determination of the amount of adsorbate required to cover the external and accessible internal pore surface of a solid with a complete monolayer of adsorbate (see Figure 1).

This monolayer capacity can be calculated from the adsorption isotherm using the BET equation:

$$\frac{p/p_0}{n_a \left[1 - (p/p_0)\right]} = \frac{1}{n_{m,mp}C} + \frac{C - 1}{n_{m,mp}C} \times (p/p_0)$$
(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 K) is the most frequently used adsorbate. Krypton or argon at liquid nitrogen temperature are two other gases that are frequently used. The latter two gases offer an improved sensitivity for the analysis of low surface-area samples (less than about  $1 \text{ m}^2$  to  $5 \text{ m}^2$  total surface area of the sample). Results of measurements with different adsorbates may deviate from each other because of different molecular cross sectional areas, different accessibility to pores and different measuring temperatures.



NOTE The dotted line shows the first adsorbate layer on the surface (See ISO 9277).

#### Figure 1 — Particle with surface (solid line) detected by the adsorption method

## **iTeh STANDARD PREVIEW**

The adsorbate gas is admitted to the sample container, which is held at a constant temperature. The amounts adsorbed are measured in equilibrium with the adsorbate gas pressure, p, and plotted against the relative pressure,  $p/p_0$ , to give an adsorption isotherm. Adsorption isotherms may be obtained by volumetric or gravimetric measurement or by the carrier gas method using a continuous or discontinuous operational mode. Further details are described in corresponding references [2], [3], 7-23a3-4256-8aa0-

6f9375fd2994/iso-18757-2003

#### 6 Procedure

#### 6.1 General procedure

General sample preparation procedures and a description of the different measurement techniques are provided in 6.2 and 6.3 of ISO 9277:1995. Specific conditions and examples for fine ceramic materials are described in 6.2 to 6.4 below.

#### 6.2 Sample preparation

The sample preparation method is one of the most crucial steps during the surface area analysis procedure. The sample has to be outgassed (also commonly termed "degassed") under conditions, which will not alter the solid sample, but which provide a "clean" sample surface at the beginning of the analysis. Moisture might be adsorbed in pores or the surface might be contaminated with other residues from the previous treatment/preparation of the sample. Most ceramic materials can be outgassed at higher temperatures (150 °C to 300 °C) without irreversible changes of the surface. It is strongly recommended to evacuate the sample to a pressure of < 1 Pa (preferably < 0,1 Pa) prior to and during the entire heat treatment. Outgassing for 8 h is usually sufficient to achieve a clean sample surface and 0,5 h to 3 h is commonly practical. However, the following examples and conditions should be carefully considered for any unknown material.

a) If the sample contains a large amount of water, either physisorbed on the surface, condensed in pores or within its crystal structure, and if the temperature is raised too quickly and without keeping a sufficient vacuum (< 1 Pa to 2 Pa) near the sample, hydrothermal conditions occur. These frequently result in physical changes of the solid structure, e.g. small cracks or pores are closed whereas small particles or bumps of the surface disappear, resulting in a lower value of the measured surface area of the sample.</p>

- b) Ceramic green-bodies or powders may contain organic binders or other additives, which may decompose at elevated temperatures. First of all the decomposition results in a weight loss of the sample and secondly some burn-out residue may be left behind at the surface of the solid, which consequently changes the surface chemical properties and the adsorption behaviour of the analysis gas. As a result of this, the surface area of the sample can increase or decrease depending on how the residue effects the sample surface. It can block certain pores or cracks and thus reduce the accessible surface area or it may form a porous residue layer by itself and thus increase the measured surface area. Preliminary thermal gravimetric analysis can be used to determine a proper outgassing temperature. Figure 2 gives a schematic example. The preparation of various test samples at the indicated temperatures A, B, C and D can be used to find the suitable outgassing conditions. The points indicated as A<sub>1</sub>, B<sub>1</sub>, and C<sub>1</sub> indicate the sample after a specific isothermal hold, e.g. for 1 h, at the indicated temperature. On the other hand it is recommended to use outgassing temperatures for a specific sample which lie on the flat plateau part (see points X, Y or Z as shown in Figure 2), since variations in the sample preparation will be minimized in this way. In order to better understand the changes during the outgassing process, it is recommended to determine the decomposition products with the help of a mass spectrometer. In general the surface area of a sample goes through a maximum as a function of temperature and it is recommended to use the highest value as the true surface area of the sample. However, it should be noted that depending on the nature of the sample, higher outgassing temperatures could also lead to irreversible physical changes of the solid; e.g, a glass powder or fibre sample may have microcracks on the surface, which can close at higher temperatures, or carbonates may decompose and very small crystallites form, which now have a higher surface area compared to the original sample.
- c) In situations where the sample shows an unexpectedly high weight loss during outgassing, the sample shall be checked carefully after the analysis, by other techniques like X-ray diffraction or electron microscopy besides a chemical analysis of its composition and the previously mentioned mass spectrometry during the outgassing process. **iTeh STANDARD PREVIEW**
- d) Outgassing of the sample at elevated temperatures by flushing with helium or the adsorbate gas is only acceptable if prior tests under vacuum conditions have confirmed the validity of the flushing-gas method for similar samples.
- e) After cooling the sample back to room temperature a complete and successful outgassing can also be checked through a "leak-test". One can assume that the sample surface is sufficiently clean if the leak test of the sample volume does not show an increased leak rate compared to the empty system. As a general recommendation, the leak-rate should not surpass a value of 10<sup>-2</sup> Pa·s<sup>-1</sup> for a nitrogen adsorption analysis. Using krypton or argon as the analysis gas will require even tighter levels of about 10<sup>-4</sup> Pa·s<sup>-1</sup> since those gases are typically adsorbed at lower absolute pressures. In general, the leak-rate should be below 10<sup>-4</sup> to 10<sup>-5</sup> times the first reported pressure point per second. In the case of the carrier gas method a leak-test as described above cannot be performed.
- f) In addition one should consider that it takes longer (10 min to 30 min) for the sample to reach the cooling bath temperature at low gas pressures, e.g. at 10<sup>-3</sup> Pa, due to lower thermal conductivity values under low absolute pressure conditions. This is especially important when a gravimetric analysis technique is applied, since the sample has no thermal contact to the wall of the sample cell and correspondingly the cooling bath.



Temperature

Figure 2 — Outgassing of sample at different temperatures

#### 6.3 Experimental conditions

The following conditions use the recommendations given in ISO 9277 with slight modifications.

- a) The temperature of the sample/cooling bath and/or  $p_0$  should be monitored during the analysis. It is recommended to measure this at least once during the analysis or every two hours in case of longer analysis times.
- b) The purity of the adsorbate should be at least 99,99 %. Any helium used to calibrate volumes or as a carrier gas should have a purity of > 99,999 %.
- c) The sample mass should be recorded to 1 %, preferably 0,1 %, accuracy. The sample mass after outgassing shall be used.
- d) The saturation pressure of the adsorbate can be determined directly by condensing the analysis gas into a second sample tube. The latter sample tube should be in close proximity to the analysed sample (same height in the cooling bath and less than 10 mm horizontal distance between sample tube and the saturation pressure tube).
- e) A high resolution pressure transducer (resolution at least 10<sup>-5</sup> of full scale) should be used. For krypton or argon measurements at liquid nitrogen temperature (approximately 77 K) a suitable low-pressure transducer is recommended [e.g. a 10 torr (1 333 Pa) transducer with at least 10<sup>-4</sup> resolution of full scale].
- f) The following analysis gases are recommended for a total sample surface area of:

— Nitrogen	(volumetric technique) 5 m <sup>2</sup> to 100 m <sup>2</sup> (carrier gas technique) 1 m <sup>2</sup> to 100 m <sup>2</sup> PREVIEW
— Argon	(volumetric technique) (1m² to 30 m² eh.ai) (carrier gas technique) 0,2 m² to 5 m²
— Krypton	(volumetric technique) 0,2 m <sup>2</sup> to 5 m <sup>2</sup> https://standards.teb.a/catalog/standards/sist/6ad95397-23a3-4256-8aa0- (carrier gas technique) 75 0,02 m <sup>2</sup> to 0.5 m <sup>2</sup> 0,2 m <sup>2</sup> to 0.5 m <sup></sup>

g) For krypton or argon adsorption at liquid nitrogen temperature (approximately 77 K) the saturation pressure should be calculated assuming a supercooled liquid/gas transition. Nitrogen can be used in those cases in the following way. When the nitrogen saturation pressure is determined, the pressure is then converted into the corresponding temperature, and the latter temperature is again converted into the equivalent krypton or argon saturation pressures. Tables 2 and 3 list corresponding pressure-temperature relations for nitrogen, argon and krypton. Alternatively the following formula could be used for the conversion process (pressure is given in mm Hg and covers the range from the triple point to the critical point; 1 mm Hg = 133,32 Pa) [5]:

$$\log p_0 = A + \frac{B}{T} + C \log T + DT + ET^2 \tag{2}$$

h) Single point BET analysis: the volume of gas adsorbed, or desorbed, is usually determined at a relative pressure of  $p/p_0 = 0.3$ . However, in the case where the BET-graph shows a strong deviation from linearity in that range, the highest known relative pressure within the linear BET transformation range (multi-point BET graph) of the physical adsorption, or desorption, isotherm shall be used. (It may be necessary to perform a multi-point analysis on the same type of material first in order to determine the optimum single point relative pressure.)

# Table 2 — Saturation pressures N2, He, Ne and Ar as a function of temperature according to Equation (2) (data are compiled from ref. <sup>[5]</sup>)

Adsorbent	A	В	С	$D \times 10^3$	$E  imes 10^6$
Nitrogen	21,623	-455,57	-7,510 7	17,214	—
Helium	2,382 6	-2,832 3	4,199 2	506,18	38 084,1
Neon	1,469 1	-70,075	3,060 7	-14,362	—
Argon	24,018	-542,78	-8,443	16,824	—