INTERNATIONAL STANDARD

ISO 18757

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

Poudres céramiques — Détermination de l'aire massique (surface spécifique) par adsorption de gaz à l'aide de la méthode BET

Reference number
ISO 18757:2003(E)

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Foreword

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

INTERNATIONAL STANDARD **ISO 18757:2003(E)**

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

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 9277:1995, *Determination of the specific surface area of solids by gas adsorption using the BET method*

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.

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	nm^2	a_m
a_s	specific surface area	$\mathrm{m}^2\ \mathrm{g}^{-1}$	a_s
C	BET parameter	1 [a]	C
L	Avogadro constant ($= 6{,}022 \times 10^{23}$)	mol^{-1}	L
m	mass of the solid sample	g	m
m_a	specific mass of gas adsorbed	1 [a]	m [a]
n_a	specific amount of gas adsorbed	$\mathrm{mol\ g}^{-1}$	n [a]
n_m	specific monolayer capacity of adsorbate; amount of adsorbate needed to cover the surface with a complete monolayer of molecules	$\mathrm{mol\ g}^{-1}$	n_m, n_m [a]
$n_\mathrm{m,\ mp}$	specific monolayer capacity derived from multi-point measurement	$\mathrm{mol\ g}^{-1}$	—
$n_\mathrm{m,\ sp}$	specific monolayer capacity derived from single-point measurement	$\mathrm{mol\ g}^{-1}$	—
p	pressure of the adsorbate in equilibrium with the adsorbate	Pa	p
p_0	saturation vapour pressure of the adsorbate	Pa	p^0
t	time	s	t
T	temperature	K	T
V_a	specific volume adsorbed	$\mathrm{m}^3\ \mathrm{g}^{-1}$	V [a]

[a] 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.

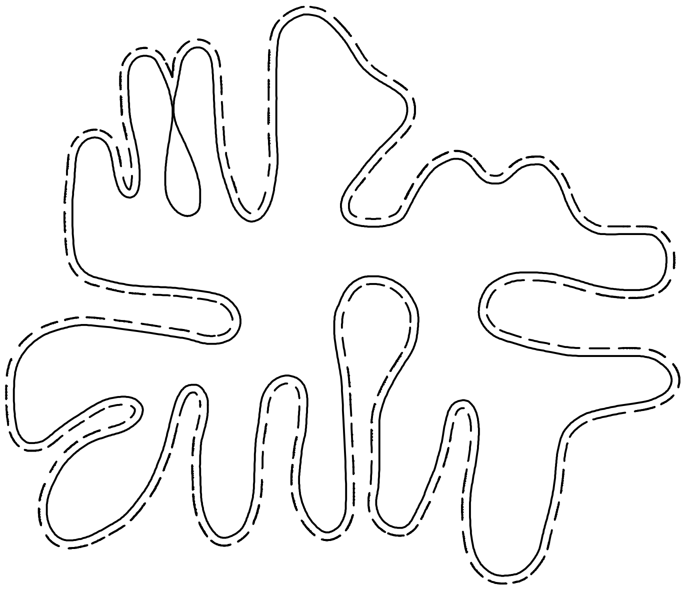
5 Principle

The method specified involves the determination of the amount of adsorbate 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:

$$\frac{p/p_0}{n_\mathrm{a}\left[1-(p/p_0)\right]} = \frac{1}{n_\mathrm{m,mp}C} + \frac{C-1}{n_\mathrm{m,mp}C} \times (p/p_0) \qquad (1)$$

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 m² to 5 m² 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

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].

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.

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_1, B_1, and C_1 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.

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^{-2} Pa·s^{-1} for a nitrogen adsorption analysis. Using krypton or argon as the analysis gas will require even tighter levels of about 10^{-4} Pa·s^{-1} since those gases are typically adsorbed at lower absolute pressures. In general, the leak-rate should be below 10^{-4} to 10^{-5} 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^{-3} 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.

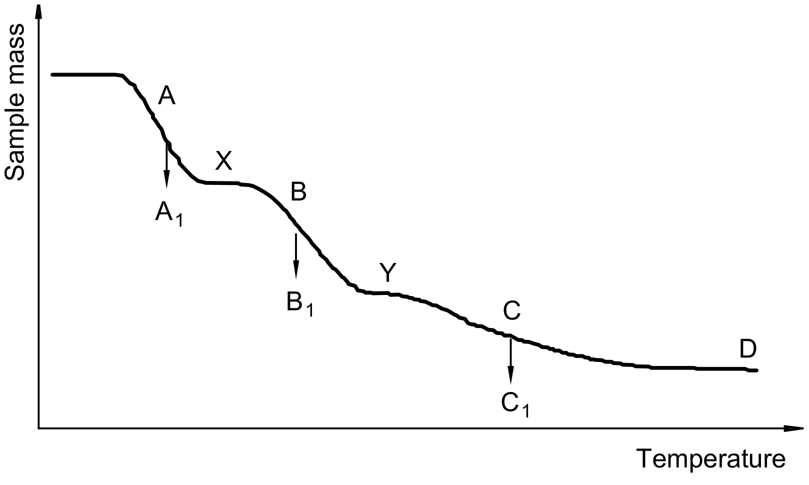


Figure 2 — Outgassing of sample at different temperatures

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^{-5} 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^{-4} resolution of full scale].

f) The following analysis gases are recommended for a total sample surface area of:

— Nitrogen	(volumetric technique)	5 m^2 to 100 m^2
	(carrier gas technique)	1 m^2 to 100 m^2
— Argon	(volumetric technique)	1 m^2 to 30 m^2
	(carrier gas technique)	0,2 m^2 to 5 m^2
— Krypton	(volumetric technique)	0,2 m^2 to 5 m^2
	(carrier gas technique)	0,02 m^2 to 0,5 m^2

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]:

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

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 N_2, He, Ne and Ar as a function of temperature according to Equation (2) (data are compiled from ref. [5])

Adsorbent	A	B	C	$D \times 10^3$	$E \times 10^6$
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	—

Table 3 — Saturation pressures N_2, Ar, and Kr (data are compiled from ref. [4], [5], [6])

	N_2 @ 77 K	Kr @ 77 K	Ar @ 77 K	Ar @ 87 K	
Molecular cross-sectional area nm^2	0,162	0,210 [a]	0,166 [a]	0,142 [a]	
Temperature K	Saturation pressure, p_0 Pa			Temperature K	p_0 Pa
75,40	80 019	210,38	19 344	81,27	53 329
75,85	84 595	234,11	20 868	83,50	66 661
76,35	89 911	263,18	22 675	85,10	79 994
76,90	96 048	298,78	24 811	86,51	93 326
77,15	98 941	316,24	25 836	87,28	101 325
77,35	101 303	330,91	26 680	87,77	106 658
77,55	103 707	346,11	27 547	88,91	119 990
77,85	107 395	370,10	28 891	89,97	133 323
78,35	113 760	413,30	31 250	91,85	159 987
78,85	120 407	460,90	33 766	94,27	199 984

[a] Other values for the cross sectional area of Kr or Ar have also been used, see ref. [4] for further details.

6.4 Evaluation of data

The general procedure of the data analysis is described in Clause 7 of ISO 9277:1995.

In addition, the following are special recommendations for the multi-point BET analysis of advanced ceramic materials:

a) A minimum of 4 valid data points shall fall within the relative pressure range between 0,05 and 0,30. Preferably the relative pressure of those data points shall be equally spaced within that range.

b) A minimum correlation coefficient of 0,999 is required for the BET analysis over that range. The exclusion of certain data points is possible according to the following principles.

   1) If a clear deviation from the linear relationship is observed below or above a certain relative pressure the corresponding data points can be omitted. A standard test for outliers may not be sufficient for this procedure since the fit through the data points will usually change gradually over the evaluation range. If an individual data point can be recognized as an outlier (more than 4 σ from the mean value), this is an indication that the measurement technique needs further refinement or that the available surface area of the sample is insufficient to produce reliable analysis data. As a guideline: once a correlation coefficient of $>$ 0,999 9 is achieved, any further elimination of data points will have only a very small effect on the calculated surface area values or the BET C-values.

   2) The upper limit of the BET range can also be determined by calculating the single point surface area values of each data point. If the single point surface area values indicate a maximum when plotted against the relative pressure of those data points, the latter maximum should be used as the upper limit of the BET multi-point calculation range.

   3) A third method involves the calculation of the BET surface area for various ranges within the measured data points. Using two consecutive data points for the BET calculation allows plotting the calculated value against the mean relative pressure of those two data points. Once the calculated BET surface area as determined from those two data points is plotted against the average relative pressure of the data points used in that calculation, one will quite often find a range where the data points are more constant or where the surface area actually goes through a minimum. The centre point of that range shall then be used and extended to each side by two or more relative pressure points (data points). The latter range shall now be used for the complete BET multi-point analysis.

7 Test report

The report on an analysis in accordance with this International Standard shall include the following items:

a) reference to this International Standard, i.e. ISO 18757;

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 outgassing conditions of the sample, e.g. temperature, residual pressure, partial pressures, duration of outgassing, flushing with adsorptive or helium, mass reduction;

e) mass of outgassed sample;

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 correction;

g) adsorptive (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 Kelvin (the approximate sample temperature is sufficient unless further details about the sample temperature are recorded during the analysis), saturation vapour pressure;

i) evaluation parameters: multi-point or single-point determination, BET plot or range of linearity, relative pressure used for the single point method, monolayer capacity, molecular cross-sectional area a_m;

   1) For multi point analysis:

   The relative pressure range as used in the BET graph for the actual analysis, the correlation coefficient for the linear fit in that range, and the C-value as calculated from the multi-point BET analysis.

   2) For single point analysis:

   Relative pressure at which the single point analysis was performed and any further corrections which might be included in the surface area calculation (e.g. knowing or assuming a specific C-value can be used to achieve a better fit between the single point and the multi point results, however, any correction like this has to be specifically mentioned in the report).

j) reference or standard material used to validate the technique;

k) specific surface area of the sample, a_s expressed in square meters per gram.

Annex A
(informative)

Sample preparation — Outgassing

Table A.1 — Specific examples of outgassing conditions for various materials

Material	Surface area m^2g^{-1}	Outgassing temperature	Time	Vacuum
γ-Alumina	50-300	200 °C	1 h (min)	$<$ 0,1 Pa
α-Alumina	0,1-25	200 °C	1 h (min)	$<$ 1 Pa
Bohemite	50-100	105 °C	1 h (min)	$<$ 1 Pa
Silica non-porous	10-100	160 °C	3 h	$<$ 1 Pa
Silica mesoporous	$>$ 200	200 °C	3 h	$<$ 0,1 Pa
Silica (mica)	0,1-10	200 °C	3 h	$<$ 0,1 Pa
Silica/alumina	$>$ 200	300 °C	3 h	$<$ 0,1 Pa
Quartz	0,1-10	200 °C	3 h	$<$ 1 Pa
Silicon carbide	1-30	200 °C	3 h	$<$ 1 Pa
Silicon nitride	1-30	200 °C	3 h	$<$ 1 Pa
Kaolin (Kaolinite)	10-100	200 °C	3 h	$<$ 0,1 Pa
Titania (rutile)	1-10	120 °C or 200 °C	24 h or 1 h	$<$ 1 Pa
Glass fibres	0,1-1	120 °C	24 h	$<$ 0,1 Pa

Annex B
(informative)

Reference materials

Table B.1 — List of available standard reference materials

		Surface area m^2g^{-1}	**Outgassing temperature**	**Time**	**Vacuum**
NIST Gaithersburg, MD 20899-0001, USA; (301) 975 6776, fax (301) 948 3730; e-mail: SRMINFO@enh.nist.gov					
RM 8570	Calcined kaolin	10,9 ± 0,50	300 °C	3 h	$<$ 0,1 Pa
RM 8571	Alumina	158	300 °C	3 h	$<$ 0,1 Pa
RM 8572	Silica-alumina	291	300 °C	3 h	$<$ 0,1 Pa
(SRM 1900)	Silicon nitride	2,85 ± 0,09	300 °C	3 h	$<$ 0,1 Pa
BAM Rudower Chaussée 5, 12489 Berlin; +49 30 6392 5830, +49 30 6392 5787; e-mail doris.wiedemann@mailgw3.bam-berlin.de					
CRM BAM-PM-101	Silica	0,177 ± 0,004			
CRM BAM-PM-102	α-Alumina	5,41 ± 0,04			
CRM BAM-PM-103	Alumina type 60	156,0 ± 1,3			
CRM BAM-PM-104	Alumina type 150	79,8 ± 0,4			
BCR Frédérique Siccardi; e-mail MRM Sales <bcr.sales@irmm.jrc.be>					
CRM 169	α-Alumina	0,104 ± 0,012	75 °C	12 h	$<$ 0,1 Pa
CRM 170	α-Alumina	1,05 ± 0,05	140 °C	12 h	$<$ 0,1 Pa
CRM 171	Alumina	2,95 ± 0,13	140 °C	12 h	$<$ 0,1 Pa
CRM 172	Natural quartz	2,56 ± 0,10	140 °C	12 h	$<$ 0,1 Pa
CRM 173	Rutile TiO_2	8,23 ± 0,21	140 °C	12 h	$<$ 0,1 Pa
CRM 175	Tungsten	0,181 ± 0,031	140 °C	12 h	$<$ 0,1 Pa

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