Designation: C1274 – 12 (Reapproved 2020)

Standard Test Method for
Advanced Ceramic Specific Surface Area by Physical Adsorption[1]

1. Scope

1.1 This test method covers the determination of the surface area of advanced ceramic materials (in a solid form) based on multilayer physisorption of gas in accordance with the method of Brunauer, Emmett, and Teller (BET) **(1)**[2] and based on IUPAC Recommendations (1984 and 1994) **(2, 3)**. This test method specifies general procedures that are applicable to many commercial physical adsorption instruments. This test method provides specific sample outgassing procedures for selected common ceramic materials, including: amorphous and crystalline silicas, TiO_2, kaolin, silicon nitride, silicon carbide, zirconium oxide, etc. The multipoint BET **(1)** equation along with the single-point approximation of the BET equation are the basis for all calculations. This test method is appropriate for measuring surface areas of advanced ceramic powders down to at least 0.05 m^2 (if in addition to nitrogen, krypton at 77.35 K is utilized as an adsorptive).

1.2 This test method does not include all existing procedures appropriate for outgassing of advanced ceramic materials. However, it provides a comprehensive summary of procedures recommended in the literature for selected types of ceramic materials. The investigator shall determine the appropriateness of listed procedures.

1.3 The values stated in SI units are to be regarded as standard. State all numerical values in terms of SI units unless specific instrumentation software reports surface area using alternate units. In this case, provide both reported and equivalent SI units in the final written report. It is commonly accepted and customary (in physical adsorption and related fields) to report the (specific) surface area of solids as m^2/g and, as a convention, many instruments (as well as certificates of reference materials) report surface area as $m^2\ g^{-1}$, instead of using SI units ($m^2\ kg^{-1}$).

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1993 Test Method for Precipitated Silica-Surface Area by Multipoint BET Nitrogen Adsorption

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

2.2 *ISO Standards:*[4]

ISO 9277 Determination of Specific Surface Area of Solids by Gas Adsorption Using the BET Method

ISO 15901-2:2006 Pore Size Distribution and Porosity of Solid Materials by Mercury Porosimetry and Gas Adsorption, Part 2—Analysis of Mesopores and Macropores by Gas Adsorption

ISO 8213:1986 Chemical Products for Industrial Use—Sampling Techniques—Solid Chemical Products in the Form of Particles Varying from Powders to Coarse Lumps

---

[1] This test method is under the jurisdiction of ASTM Committee C28 on Advanced Ceramics and is the direct responsibility of Subcommittee C28.03 on Physical Properties and Non-Destructive Evaluation.

Current edition approved April 1, 2020. Published April 2020. Originally approved in 1994. Last previous edition approved in 2012 as C1274 – 12. DOI: 10.1520/C1274-12R20.

[2] The boldface numbers in parenthesis refer to the list of references at the end of this standard.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, Case postale 56, CH-1211, Geneva 20, Switzerland, http://www.iso.ch.

ISO 18757 Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics)—Determination of Specific Surface Area of Ceramic Powders by Gas Adsorption Using the BET Method

3. Terminology

3.1 *Definitions:*[5]

3.1.1 *adsorbate, n*—material that has been retained by the process of adsorption.

3.1.2 *adsorbent, n*—any solid having the ability to concentrate significant quantities of other substances on its surface.

3.1.3 *adsorption, n*—process in which molecules are concentrated on a surface by chemical or physical forces, or both.

3.1.4 *adsorption isotherm, n*—relation between the quantity of adsorbate and the equilibrium (relative) pressure of the adsorptive, at constant temperature.

3.1.4.1 *Discussion*—Typically, the amount adsorbed is presented on an isotherm as volume in cm^3 STP (standard temperature and pressure, that is, 273.15 K and 101325.02 Pa) normalized per mass of sample.

3.1.5 *adsorptive, n*—any substance available for adsorption.

3.1.6 *aliquot, n*—a representative portion of a whole that divides the whole, leaving a remainder.

3.1.7 *molecular cross-sectional area, n*—molecular area of the adsorbate, that is, the area occupied by an adsorbate molecule in the completed closed-packed monolayer.

3.1.8 *monolayer capacity, n*—amount of the adsorbate (expressed as number of moles, volume at STP, or weight) that forms a closed-packed (complete) monomolecular layer over the surface of the adsorbent.

3.1.9 *outgassing, n*—evolution of gas from a material under a vacuum or inert gas flow at or above ambient temperature.

3.1.10 *physical adsorption (van der Waals adsorption), n*—the binding of an adsorbate to the surface of a solid by forces whose energy levels approximate those of condensation.

3.1.11 *relative pressure, n*—ratio of the equilibrium adsorption pressure, p, to the saturation vapor pressure, p_0.

3.1.12 *saturation vapor pressure, n*—vapor pressure of the bulk liquefied adsorbate at the temperature of adsorption.

3.1.13 *surface area, n*—total surface area of the surface of a powder or solid, including both external and accessible internal surfaces (from voids, cracks, open porosity, and fissures).

3.1.13.1 *Discussion*—The surface area may be calculated by the BET equation (1) from gas adsorption data obtained under specific conditions. It is useful to express this value as the specific surface area (see 3.1.13), that is, surface area per unit mass of sample ($m^2 g^{-1}$).

3.1.14 *surface area (BET), n*—total surface area of a solid calculated by the BET equation (1) from gas adsorption or desorption data obtained under specific conditions.

3.1.15 *surface area, specific (SSA), n*—area per unit mass of a granular or powdered or formed porous solid of all external and internal surfaces that are accessible to a penetrating gas or liquid.

4. Summary of Test Method

4.1 An appropriately sized (to provide at least the minimum surface area required for reliable results, refer to requirements provided by the manufacturer of the instrument or apparatus being used) aliquot of sample is outgassed under appropriate conditions prior to analysis. For details on outgassing methods and examples of specific outgassing conditions recommended for selected ceramic materials, see Section 11.

4.2 The adsorptive gas is admitted to a sample container held at a constant temperature. The amounts adsorbed are measured in equilibrium with the adsorptive gas pressure, p, and plotted against the relative pressure, p/p_0 (where p_0 is the saturation vapor pressure), to give an adsorption isotherm. Adsorption isotherms may be obtained by volumetric (manometric) measurements or by the carrier gas flow measurements (flow volumetric method) and gravimetric techniques. This test method employs volumetric and flow volumetric methods.

4.3 *(Multipoint BET Analyses Only)*—The volume of gas adsorbed, or desorbed, is determined for a minimum of four relative pressures within the linear BET transformation range of the physical adsorption, or desorption, isotherm characteristic of the advanced ceramic. The linear range is that which results in a least-square correlation coefficient of 0.995 (preferably 0.999) or greater for the linear relationship (see linear form of BET equation, in Annex A1). Typically, the linear range includes relative pressures between 0.05 and 0.30 (4, 5). However, microporous materials usually require use of a range of lower relative pressures (often a linear BET range can be found in the relative pressure range from 0.01 to 0.1 (5, 6)). For details, see Annex A2.

4.4 *(Single-Point BET Analyses Only)*—The volume of gas adsorbed, or desorbed, is determined at the highest known relative pressure within the linear BET transformation range of the physical adsorption, or desorption, isotherm. Typically, a relative pressure of 0.30 is used. However, it may be necessary to perform a multipoint analysis of the material first to determine the optimum single-point relative pressure.

4.5 The physical adsorption instrument or apparatus measures the total amount of gas adsorbed onto, or desorbed from, the sample under analysis. The sample mass is then used to normalize the measured results. Therefore, it is important to use an analytical balance to determine the sample weight. The mass of dry and outgassed sample, recorded to the nearest 0.1 mg, shall be used. Any error in the sample weight will be propagated into the final BET surface area result.

4.6 Typical steps involved in the evaluation of the BET surface area (see Annex A1 for calculation details):

4.6.1 Transformation of a physisorption isotherm into the BET plot;

4.6.2 An assessment of the monolayer capacity (multipoint or single-point method). (See Eq A1.1-A1.6 in Annex A1.); and

NOTE 1—Monolayer capacity can be expressed alternatively in terms of STP volume (V_m), weight (w_m), or number of moles (n_m) of adsorbate in a complete monolayer per 1 g of sample.

4.6.3 Calculation of the specific surface area (SSA), a_s (see Eq A1.7 in Annex A1), which requires knowledge of the monolayer capacity as well as the effective molecular cross-sectional area of the adsorbate. Recommended customary values for molecules of N_2 at 77.35 K, Ar at 87.27 K, and Kr at 77.35 K, are provided in Table 1.

5. Significance and Use

5.1 Advanced ceramic powders and porous ceramic bodies often have a very fine particulate morphology and structure that are marked by high surface-to-volume (S-V) ratios. These ceramics with high S-V ratios commonly exhibit enhanced chemical reactivity and lower sintering temperatures. Results of many intermediate and final ceramic processing steps are controlled by, or related to, the specific surface area of the advanced ceramic. The functionality of ceramic adsorbents, separation filters and membranes, catalysts, chromatographic carriers, coatings, and pigments often depends on the amount and distribution of the porosity and its resulting effect on the specific surface area.

5.2 This test method determines the specific surface area of advanced ceramic powders and porous bodies. Both suppliers and users of advanced ceramics can use knowledge of the surface area of these ceramics for material development and comparison, product characterization, design data, quality control, and engineering/ production specifications.

TABLE 1 Cross-Sectional Areas of Selected Commonly Used Adsorptives

Adsorptive	Temperature, K	Recommended Value of Cross-Sectional Area, nm^2
Nitrogen	77.35	0.162[A]
Argon	77.35	0.138[B]
Argon	87.27	0.142
Krypton	77.35	0.202[C]

[A] Very often the orientation of the adsorbed N_2 molecules (having quadruple moment) can be affected by specific interactions with polar groups on the surface of adsorbent (i.e. in case of highly polar surfaces, such as with hydroxylated oxide surface groups (7-9)). This can lead to a significant reduction in the effective cross-sectional area. If the standard value for N_2 molecule (0.162 nm^2 at 77.35 K) is used, the BET surface area of hydroxylated silica surfaces can be overestimated by 20 %. Therefore, in case of ceramics with surfaces of high polarity, argon (which is a chemically inert monoatomic gas) adsorption at 87.3 K is an alternative adsorptive recommended for surface area determination, since the cross-sectional area of argon (0.142 nm^2 at 87.27 K) is less sensitive to differences in structure of the adsorbent surface.

[B] The use of argon at 77.35 K (which is approximately 6.5 K below the triple point of bulk argon) is considered to be less reliable than nitrogen, because at 77.35 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 77.35 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.

[C] The use of krypton at 77.35 K allows to manometrically measure very low uptakes with acceptable accuracy. However, similar to argon at 77.35 K, krypton at 77.35 K is significantly below the triple point temperature of bulk krypton (approximately 38.5 K), and the structure of the krypton monolayer may be strongly affected by the surface chemistry of the adsorbent. This will directly influence the effective krypton cross-sectional area. The value given in the table can be considered to be a customary value.

6. Interferences

6.1 This test method can be used to determine the internal and external surface of a powder or solid only after these surfaces have been cleaned of any physically adsorbed molecules. Such adsorbed species, for example water or volatile organic compounds, affect physical adsorption of the gas probe molecules used to measure surface area. Therefore, it is necessary to remove these adsorbed contaminants prior to surface area analysis. Generally, such a procedure is performed by evacuating or purging the sample with inert gas. Outgassing can be accelerated by using elevated temperatures, provided no irreversible sample changes occur. Typical minimum vacuum levels attained are 10^{-1} Pa. Commonly used purging gases are helium, nitrogen, or a mixture of the two. The outgassing procedure is optimal or complete, or both when: (*1*) duplicate surface area analyses produce results within expected instrument repeatability limits, (*2*) constant residual vapor pressure is maintained upon isolation from the vacuum source, or (*3*) purging gas composition is unaffected while passing over the sample.

6.2 The outgassing procedures and temperatures shall not produce any changes in composition, phase, or surface morphology of the powder specimens. The outgas temperature limits are determined by the stability limits of the powder samples.

7. Apparatus

7.1 *Manometric (Volumetric) Apparatus*—See Test Method D1993 and ISO 15901-2 for description of technology.

7.2 *Automated and Dynamic Flow Instruments*—Commercial instruments are available from several manufacturers for the measurement of specific surface area by physical adsorption. Some are automated versions of the classical vacuum apparatus. Others may use a gravimetric technique to determine the amount of adsorbed gas on the sample surface. Additionally, commercial instruments are available that measure physical adsorption based on the dynamic flow method.

7.3 *Sample Cells,* that when attached to the adsorption apparatus will maintain isolation from the atmosphere equivalent to a specified (helium) leak rate determined by the manufacturer of the instrument.

7.4 *Heating Mantle or Equivalent,* capable of maintaining a temperature in range from 100 to 300 ± 10 °C.

7.5 *Analytical Balance,* with 0.1 mg sensitivity.

7.6 *Oven (Optional),* gravity convection, capable of maintaining a temperature of 115 ± 10 °C.

8. Reagents and Materials

8.1 *Liquid Nitrogen.*

8.2 *Ultra-High Purity Nitrogen,* 99.99 mol %, with the sum of O_2, Ar, CO_2, hydrocarbons (as CH_4), and H_2O totaling less than 10 ppm, dry and oil-free, from a cylinder or other source of purified nitrogen.

8.3 *Ultra-High Purity Helium,* 99.99 mol %, with the sum of N_2, O_2, Ar, CO_2, hydrocarbons (as CH_4), and H_2O totaling