



# Standard Test Method for Advanced Ceramic Specific Surface Area by Physical Adsorption<sup>1</sup>

This standard is issued under the fixed designation C 1274; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers determination of surface area of advanced ceramic materials. This test method specifies general procedures that are applicable to many commercial physical adsorption instruments. This test method provides specific sample outgassing procedures for listed materials, including silicon carbide, silicon nitride, and zirconium oxide. It includes additional general outgassing instructions for other advanced ceramic materials. The multipoint equation of Brunauer, Emmett and Teller<sup>2</sup> (BET) along with the single point approximation of the BET equation form the basis for all calculations.

1.2 This test method does not include all existing procedures appropriate for outgassing advanced ceramic materials. The included procedures provided acceptable results for samples analyzed during round robin testing. The investigator must determine the appropriateness of listed procedures.

1.3 This test method uses SI units as standard. State all numerical values in terms of SI units unless specific instrumentation software reports surface area using alternate units. In this case, present both reported and equivalent SI units in the final written report. Many instruments report surface area as  $\text{m}^2/\text{g}$ , instead of using correct SI units ( $\text{m}^2/\text{kg}$ ).

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 and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>3</sup>

D 1993 Test Method for Precipitated Silica—Surface Area by Multipoint BET Nitrogen Adsorption

<sup>1</sup> This specification is under the jurisdiction of ASTM Committee C28 on Advanced Ceramics and is the direct responsibility of Subcommittee C28.03 on Physical Properties and Performance.

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<sup>2</sup> Brunauer, S., Emmett, P. H., and Teller, E., *J. Am. Chem. Soc.* 60, 1938, pp. 309–319.

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

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

## 3. Terminology

### 3.1 Definitions:<sup>4</sup>

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

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

3.1.5 *aliquant*, *n*—a representative portion of a whole that divides the whole leaving a remainder.

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

3.1.7 *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.

3.1.8 *surface area*, *n*—the total area of the surface of a powder or solid including both external and accessible internal surfaces (from voids, cracks, open porosity, and fissures). The area may be calculated by the BET (Brunauer, Emmett, and Teller<sup>2</sup>) equation from gas adsorption data obtained under specific conditions. It is useful to express this value as the specific surface area, for example, surface area per unit weight of sample ( $\text{m}^2/\text{g}$ ).

3.1.9 *surface area (BET)*, *n*—the total surface area of a solid calculated by the BET (Brunauer, Emmett, Teller<sup>2</sup>) equation, from nitrogen adsorption or desorption data obtained under specific conditions.

3.1.10 *surface area, specific*, *n*—the area, per unit mass of a granular or powdered or formed porous solid, of all external plus internal surfaces that are accessible to a penetrating gas or liquid.

## 4. Summary of Test Method

4.1 An appropriate sized sample (to provide at least the minimum surface area required for reliable results for the

<sup>4</sup> *Compilation of ASTM Standard Terminology*, 8th ed, 1994.

instrument or apparatus used) is outgassed under appropriate conditions prior to analysis.

4.2 (*Multipoint BET Analyses Only*)— 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 0.999 (preferably 0.9999) or greater for the linear relationship used in the BET graph ( $\frac{1}{\text{adsorbed volume} * (1/\text{relative pressure} - 1)}$ ). Typically, the linear range includes relative pressures between 0.05 and 0.30, however, microporous materials usually require use of a range of lower relative pressures, such as 0.01 to 0.10.

4.3 (*Single Point BET Analyses Only*)— 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. (It may be necessary to perform a multipoint analysis of the material first to determine the optimum single point relative pressure.)

4.4 The sample is accurately weighed (to at least 1% of the sample mass) after analysis. It is important to use an analytical balance to determine the sample weight. The physical adsorption instrument or apparatus measures the total amount of gas adsorbed onto, or desorbed from, the sample under analysis. The sample weight is then used to normalize the measured results. Any error in the sample weight will be propagated into the final BET surface area.

4.5 Calculations are based on the BET equation, as required by the instrument being used for the determination. The cross sectional area for the adsorbate is taken to be 0.162 nm<sup>2</sup> if nitrogen is used as the adsorptive. Use the appropriate value recommended by the instrument manufacturer for adsorptives other than nitrogen. Report this cross sectional area with the BET surface area results.

## 5. Significance and Use

5.1 Both suppliers and users of advanced ceramics can benefit from knowledge of the surface area of these materials. Results of many intermediate and final processing steps are controlled by, or related to, specific surface area of the advanced ceramic.

## 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, prevent 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 outgassing is performed by evacuating or flushing the sample. Outgassing can be accelerated by using elevated temperatures, provided no irreversible sample changes occur. Typical minimum vacuum levels attained are 10<sup>-1</sup> Pa. Typical flushing gases are helium, nitrogen, or a mixture of the two. Outgassing is complete when duplicate surface area analyses produce results within expected instrument repeatability limits, when a constant residual vapor

pressure is maintained upon isolation from the vacuum source, or when flushing gas composition is unaffected while passing over the sample.

## 7. Apparatus

7.1 *Classical Vacuum Apparatus*—Refer to Test Method D 1993 for apparatus description.

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 which measure physical adsorption based on the dynamic flow method.

## 8. Reagents and Materials

8.1 *Liquid Nitrogen*.

8.2 *Nitrogen*, 99.99 mole percent, with the sum of O<sub>2</sub>, Ar, CO<sub>2</sub>, hydrocarbons (as CH<sub>4</sub>), and H<sub>2</sub>O totaling less than 10 ppm, dry and oil-free, cylinder, or other source of purified nitrogen.

8.3 *Helium*, 99.99 mole percent, with the sum of N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub>, hydrocarbons (as CH<sub>4</sub>), and H<sub>2</sub>O totaling less than 10 ppm, dry and oil-free, cylinder, or other source of purified helium, if needed for determination of void space above sample.

8.4 *Blended Nitrogen and Helium*, dry and oil-free, cylinder, or other source of blended gases. The actual composition of the blend must be known. For use with dynamic flow instruments only.

## 9. Sampling, Test Specimens, and Test Units

9.1 No specific instructions are given. However, it is important that the aliquant being analyzed represent the larger bulk sample from which it is taken. The bulk sample should be homogenized before any sampling takes place. Best results are obtained when a flowing bulk material is temporarily diverted into a collector for an appropriate time. It is better to sample the entire flow for a short time than to sample a portion of the flow for a longer time. Collecting several small aliquants and combining them improves the reliability of the sampling process. Rotating riffles are available that satisfy these requirements.

## 10. Calibration and Standardization

10.1 *Classical Vacuum Apparatus*—Refer to Test Method D 1993 for calibration procedures.

10.2 *Automated and Dynamic Flow Instruments*—Follow manufacturer's instructions for calibration and operational verification of the instrument.

## 11. Outgassing

11.1 *Classical Vacuum Apparatus*—Refer to Test Method D 1993 for outgassing procedures.

11.2 *Automated and Dynamic Flow Instruments*:

11.2.1 Weigh (to the nearest 0.1 mg) clean, empty sample tube, along with stopper or seal. Record the empty tube weight.

**TABLE 1 Precision for Single Point and Multipoint BET Methods**

Material	Number of Laboratories	Surface Area (average)	Precision Single Point BET Method		Repeatability Limit	Reproducibility Limit	Repeatability C.V.	Reproducibility C.V.
			Repeatability Standard Deviation $S_r$	Reproducibility Standard Deviation $S_R$				
A1N	6	2.82	0.09	0.12	0.24	0.24	3.1 %	4.3 %
Si3N4 (SNT)	17	9.30	0.24	0.38	0.66	1.05	2.6 %	4.1 %
Si3N4 (SNR)	6	12.55	0.79	0.86	2.18	2.38	6.3 %	6.8 %
SiC	16	13.27	0.25	0.67	0.69	1.86	1.9 %	5.1 %
Y2O3-ZrO2	9	17.72	0.34	0.89	0.95	2.47	1.9 %	5.0 %

This table was calculated using the relationship: limit =  $1.96 \times \sqrt{2} \times$  standard deviation

Material	Number of Laboratories	Surface Area (average)	Precision Multi Point BET Method		Repeatability Limit	Reproducibility Limit	Repeatability C.V.	Reproducibility C.V.
			Repeatability Standard Deviation $S_r$	Reproducibility Standard Deviation $S_R$				
A1N	6	2.83	0.15	0.22	0.42	0.62	5.3 %	7.9 %
Si3N4 (SNT)	11	10.06	0.41	1.11	1.15	3.06	4.1 %	11.0 %
SiC	10	14.22	0.28	1.50	0.77	4.16	2.0 %	10.6 %
Y2O3-ZrO2	6	18.46	0.43	1.72	1.19	4.76	2.3 %	9.3 %

This table was calculated using the relationship: limit =  $1.96 \times \sqrt{2} \times$  standard deviation

11.2.2 Add representative sample to empty sample tube. Sample quantity should be sufficient to satisfy minimum surface area as required by manufacturer.

11.2.3 Attach prepared sample tube to outgassing port of instrument. Secure heating mantle or oven around sample tube at the time appropriate for sample.

11.2.4 Initiate outgassing program according to manufacturer's instructions. Program mantle or oven for initial outgassing temperature. Increase temperature as appropriate for the sample. Allow sample to continue to outgas until prescribed vacuum level or detector signal is achieved and/or for prescribed outgassing time. Be aware that heating of the sample without a sufficient vacuum can lead to hydrothermal conditions, which then could result in changes in the sample. Thus, it is recommended to assure a vacuum of 1 Pa or better at all times during the heat-out. Outgassing without those vacuum conditions can be used once an initial test on similar samples has confirmed that no changes in the sample surface area occur. This is especially important when the flow gas (He) technique is used for the out-gassing process.

NOTE 1—Specific outgassing information will be added after round robin test samples are selected.

11.2.5 Remove heating mantle or oven from sample tube. Allow sample tube to cool to ambient temperature. Remove and seal sample tube according to manufacturer's instructions.

11.2.6 Weigh sample tube (to the nearest 0.1 mg) to obtain sample and tube weight. Record weight. Subtract empty sample tube weight determined in 11.2 to obtain outgassed sample weight. Record calculated weight.

## 12. Procedure

12.1 *Classical Vacuum Apparatus*—Refer to Test Method D 1993 for analysis procedures.

12.2 *Automated and Dynamic Flow Instruments*—Attach appropriately prepared sample holder to analysis port according to manufacturer's instructions. Include any required hardware.

12.3 (*Automated Instruments Only*)—Select, or input, desired analysis and report parameters.

12.3.1 (*Multipoint BET Analyses Only*)— Use at least four analysis points in the linear BET transformation range of the isotherm characteristic of the sample. If necessary, input the outgassed sample weight. (The final weight should be determined and entered after the analysis.)

12.3.2 (*Single Point BET Analyses Only*)— Use highest relative pressure known to be in the linear BET transformation range of the isotherm. If necessary, input the outgassed sample weight. (The final weight should be determined and entered after the analysis.)

12.4 (*Dynamic Flow Instruments Only*)— Collect data points as volume of gas desorbed versus relative pressure:

12.4.1 (*Multipoint BET Analyses Only*)— Use at least four analysis points in the linear BET transformation range of the isotherm characteristic of the sample.

12.4.2 (*Single Point BET Analyses Only*)— Use highest relative pressure known to be in the linear BET transformation range of the isotherm.

12.5 Perform analysis using the specified conditions according to instrument manufacturer's instructions.

12.6 When the analysis has finished and the sample has warmed to room temperature, remove and seal the sample tube. Dry tube and weigh (to the nearest 0.1 mg). Record the final tube and sample weight. Subtract the empty tube weight recorded in 11.2 to obtain the final sample weight. Record final sample weight.

12.7 (*Automated Instruments Only*)—Edit the file containing sample information to include the final sample weight. Generate final sample report.

## 13. Calculation

13.1 *Classical Vacuum Apparatus*—Refer to Test Method D 1993 for calculations.

13.2 *Automated and Dynamic Flow Instruments*:

13.2.1 (*Automated Instruments Only*)—Software automatically calculates results for the chosen reports using the final weight input in 12.7.

13.2.2 (*Dynamic Flow Instruments Only*)— Follow manufacturer’s instructions for multipoint, or single point, calculations. Use the final sample weight determined in 12.6 when calculating the specific surface area.

## 14. Report

14.1 Report the following information:

14.1.1 Complete sample identification,

14.1.2 Collected isotherm point(s) as volume adsorbed, or desorbed, versus relative pressure. Note whether adsorption or desorption isotherm is used. Note any units used other than standard,

14.1.3 Analysis gas used (with cross sectional area if other than nitrogen, for which 0.162 nm<sup>2</sup> should be used),

14.1.4 BET specific surface area, note any units used other than standard,

14.1.5 Final sample weight, note any units used other than standard, and

14.1.6 Sample outgassing method, including total time and outgassing temperature(s).

## 15. Precision and Bias

15.1 *Interlaboratory Test Program*—The IEA Annex II Subtask 6 on Development and Testing of Procedures for

Characterization of Ceramic Powders (September 1993) studied various characterization techniques. Single Point and Multipoint nitrogen gas adsorption were used to determine the specific surface area of the samples. Generally, each laboratory tested four samples of several different ceramic powders. For all the powders tested, the specific surface areas determined by Single Point and Multipoint BET method show agreement between the methods, with the Single Point data slightly lower than those of Multipoint. The between-laboratory coefficient of variation (C.V) is less than 7% for the Single Point data and less than 11% for the Multipoint data.

15.2 *Definitions and Standard Deviations*—The terms repeatability standard deviation,  $s_r$ , repeatability limit, reproducibility standard deviation,  $s_R$ , and reproducibility limit are used as specified in Practice E 177. Coefficient of variation (C.V.) is defined as the standard deviation listed in the table divided by the mean value.

15.3 *Bias*—No justifiable statement can be made on the bias of the procedure in this test method for measuring Advanced Ceramic Specific Surface Area by Physical adsorption because there has been no interlaboratory study with six or more participants testing a material with an accepted reference value.

## 16. Keywords

16.1 advanced ceramics; BET surface area; ceramics; multipoint surface area; outgassing; physical adsorption; single point surface area; specific surface area; surface area

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