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

This standard is issued under the fixed designation C1274; 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 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)<sup>2</sup> 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<sub>2</sub>, 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<sup>2</sup> (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<sup>2</sup>/g and, as a

convention, many instruments (as well as certificates of reference materials) report surface area as m<sup>2</sup> g<sup>-1</sup>, instead of using SI units (m<sup>2</sup> kg<sup>-1</sup>).

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:<sup>3</sup>

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:<sup>4</sup>

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

<sup>1</sup> 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.

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<sup>2</sup> The boldface numbers in parenthesis refer to the list of references at the end of this standard.

<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.

<sup>4</sup> 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:<sup>5</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*—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<sup>3</sup> 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<sup>2</sup> g<sup>-1</sup>).

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

<sup>5</sup> *Compilation of ASTM Standard Terminology*, 8th ed, 1994.

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 <sup>2</sup>
Nitrogen	77.35	0.162 <sup>A</sup>
Argon	77.35	0.138 <sup>B</sup>
Argon	87.27	0.142
Krypton	77.35	0.202 <sup>C</sup>

<sup>A</sup> 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<sup>2</sup> 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<sup>2</sup> at 87.27 K) is less sensitive to differences in structure of the adsorbent surface.

<sup>B</sup> 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<sup>2</sup>, 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.

<sup>C</sup> 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<sup>-1</sup> 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<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, from a cylinder or other source of purified nitrogen.

8.3 *Ultra-High Purity Helium*, 99.99 mol %, 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, from a cylinder or other source of purified helium, if needed for determination of void space above sample.

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

8.5 *Liquid Argon*.

8.6 *Ultra-High Purity Argon*, 99.99 mol %, 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, from a cylinder or other source of purified argon.

8.7 *Ultra-High Purity Krypton*, 99.99 mol %, 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, from a cylinder or other source of purified argon.

8.8 *Comments on Proper Selection of Adsorbate:*

8.8.1 Nitrogen at its boiling point (about 77.35 K) is the most commonly used adsorptive for customary ceramic materials (customary cross-sectional area of 0.162 nm<sup>2</sup>). (See Table 1.)

8.8.2 In case of ceramic materials with very low specific surface, the sensitivity of the instrument when using nitrogen adsorption may be insufficient. Therefore, for the BET surface area analysis of ceramics with specific surface areas below 1 m<sup>2</sup> g<sup>-1</sup>, it is recommended to use krypton adsorption at liquid nitrogen temperature. Application of Kr at 77.35 K as adsorptive allows for volumetric measurement of very low uptakes with acceptable accuracy (as a consequence of the low *p*<sub>0</sub> of about 2.63 torr (360.63 Pa)) and for assessing specific surface areas down to at least 0.05 m<sup>2</sup>. For krypton at 77.35 K, the number of molecules trapped in the void volume of the sample cell is significantly reduced (to 1/300th) compared to the conditions of nitrogen adsorption at the same temperature.

8.8.3 The results of measurements with different adsorptives may deviate from each other because of different molecular areas, different accessibilities to pores, different measuring temperatures, and so forth.

9. Hazards

9.1 Precautions applying to the use of LN<sub>2</sub>, LAr, compressed gases, and specific properties of powder samples shall be observed.

10. Sampling, Test Specimens, and Test Units

10.1 The goal of powder sampling is to collect a small amount of powder from the bulk quantity such that this smaller fraction is representative of the characteristics of the entire bulk. No mandatory instructions are given. However, it is advisable to perform statistical sampling in accordance with ISO 8213:1986 since it is important that the aliquot being analyzed represent the larger bulk sample from which it is taken. Homogenize the bulk sample 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 aliquots and combining them improves the reliability of the sampling process. Rotating riffles that satisfy these requirements are commercially available.

10.2 Obtain enough powder samples to run one or more analyses in accordance with the equipment sample size recommendations.

11. Sample Preparation Procedure

11.1 Remove physically adsorbed impurities from the sample surface prior to the determination of an adsorption isotherm. This can be achieved at elevated temperatures under vacuum or by inert gas flow. It is crucial to outgas the sample under conditions (that is, time and temperature) which provide a clean sample surface at the beginning of the analysis while avoiding irreversible changes to the surface (solid sample shall not be altered). Most ceramic materials can be safely outgassed at relatively high temperatures (200 to 300 °C) in a few hours; however, outgassing overnight at temperatures around 150 °C is generally a safe way to achieve a clean sample surface and is commonly practiced (specific outgassing conditions recommended for selected ceramic materials are summarized in Table 2). Outgassing is complete when a steady value of the residual gas pressure, *p*<sub>out</sub> (recommended 1 Pa or lower ) of its composition, or when a steady sample mass, *m*, is reached.

11.2 If the ceramic material is wet (that is, when any moisture condensation is observed on the walls of the sample cell during sample outgassing), the sample requires pretreatment to remove excess moisture. Dry an aliquot of a ceramic sample at 90 to 110 °C for 1 to 2 h. If the ceramic material is known to be substantially free of moisture, or subsequent preparation steps are known to be adequate for moisture removal, then this step may be omitted.

11.3 The following examples and conditions shall be carefully considered for any unknown ceramic material:

11.3.1 In most cases, physisorbed water has to be removed from the adsorbent surfaces prior to the adsorption experiment. If the sample contains a large amount of water, either physisorbed on the surface, condensed in pores, or within its crystal structure, a special heating program is often needed that allows for a slow removal of most of the pre-adsorbed water at temperatures below 100 °C, accompanied by a stepwise increase in temperature until the final outgassing temperature is reached. This is done to avoid potential structural damage of the sample due to surface tension effects and hydrothermal

TABLE 2 Specific Examples of Outgassing Conditions (Under Vacuum) for Various Ceramic Materials

Ceramic Material	Outgassing Temperature <i>T</i> , °C	Outgassing Time <i>t</i> , Minimum, h
Silica	200 (or 150)	3 (or 12)
Quartz	200	3
Boehmite	105	1
Silica/alumina	300	3
Alumina	300	3
Silicon carbide	200	3
Silicon nitride	200	3
Kaolin (Kaolinite)	200	3
Titania	140	12
Glass fibers	120	24
Zirconium oxide	140	12

alteration. For outgassing of extremely sensitive samples and fine powders, so-called pressure-controlled heating under vacuum is recommended. This outgassing procedure consists of heating steps achieved by controlling the temperature rise based on the gas pressure evolved from a porous material under vacuum. When, during evacuation and heating, a fixed pressure limit (usually approximately 7 to 10 Pa) is overtaken due to species/moisture evolved from the sample surface, the temperature ramp is stopped (the temperature is kept constant while evacuation is continued). When the pressure falls back below the limit, the temperature ramp is continued, etc., until a desired dwell temperature is achieved.

11.3.2 Take particular care during outgassing of certain ceramic materials (such as green-bodies) that may contain organic binders or other additives (see also ISO 18757). In such cases, any decomposition during outgassing at elevated temperatures could adversely change the chemical or physical properties, or both, of the solid (such as altered adsorption interactions with the analysis gas, certain pores or cracks blocked and thus inaccessible, particles sintered, crystalline phase transition, etc.). Preliminary thermal gravimetric analysis can be used to determine a proper outgassing temperature. 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.

11.3.3 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.

11.4 The following steps outline a typical sample preparation procedure:

11.4.1 Weigh an empty sample cell to the nearest 0.1 mg and record the mass (to determine the optimal mass of sample for the adsorption measurement, see the recommendations given in the user manual of the adsorption apparatus used for the measurement).

11.4.2 Weigh the appropriate amount of sample into the sample cell, recording the mass to the nearest 0.1 mg.

11.4.3 *Vacuum Outgassing* (refer also to Test Method **D1993**, ISO 9277, and ISO 18757 for outgassing procedures):

11.4.3.1 With the apparatus at atmospheric pressure, place the sample cell containing the ceramic sample onto the outgassing apparatus.

11.4.3.2 Begin the outgassing procedure as appropriate for the apparatus.

11.4.3.3 Place a heating mantle or other source of heat around the sample cell and outgas (evacuate) the sample at temperature  $T$  for at least time  $t$  (see **Table 2** for recommended  $T$  and  $t$  values for selected ceramic materials) or longer, as required to obtain and hold a residual gas pressure  $p_{out}$  at least 1 Pa (or better) for at least 30 min.

11.4.3.4 Once the typical outgassing times have been determined, future samples can be outgassed on the basis of time alone, if desired, allowing a reasonable margin of excess time. Some samples will be found to require less than ½ h, especially if moisture exposure has been minimal. In these cases, the minimum time that gives a stable surface area may be used for outgassing.

NOTE 2—After outgassing, 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 conduction of the cooling bath.

11.4.3.5 After outgassing, the sample cell may be moved directly to the analyzer. Otherwise, remove the sample cell from the heat source and continue evacuation until it is ready for analysis.

11.4.3.6 Go directly to **11.4.5** and continue the remaining steps of the procedure.

11.4.4 *Flow Outgassing*:

11.4.4.1 Open the gas control valve and insert the delivery tube into the sample cell, and allow purging with either helium or nitrogen for a minimum of 1 min.

11.4.4.2 Place a heating mantle or other source of heat around the sample cell and outgas (purge) the sample at temperature  $T$  for at least time  $t$  (see **Table 2** for recommended  $T$  and  $t$  values for selected ceramic materials) or longer, to ensure that all traces of moisture condensing in the top of the sample cell are absent. The minimum degassing time that gives a stable surface area (that is, a surface area that does not increase with additional degassing) may be used for outgassing.

11.4.4.3 Once the typical outgassing times have been determined, future samples can be outgassed on the basis of time alone, if desired, allowing a reasonable margin of excess time. Some samples will be found to require less than ½ h, especially if moisture exposure has been minimal. In these cases, the minimum time that gives a stable surface area may be used for outgassing.

11.4.4.4 After outgassing, the sample cell may be moved directly to the analyzer. Otherwise, remove the sample cell from the heat source and continue the flow of purging gas until it is ready for analysis.

11.4.5 Determine the mass of the outgassed, dry sample (see **14.1**) and record it to the nearest 0.1 mg. Avoid inconsistent use of helium, as a buoyancy error of 1 mg/cm<sup>3</sup> of cell volume can occur. Sample mass determination may be done before or after adsorption measurement. As an alternative, the sample mass may be determined directly (after measurement only) by quantitatively pouring it from the sample cell into a tared weighing pan, if feasible.

11.4.6 Go directly to Section **13** and continue the remaining steps of the procedure.

## 12. Calibration and Standardization

12.1 To ensure proper working conditions and correct data evaluation, the apparatus performance shall be checked on a regular basis (for example, quarterly) using a certified reference material or a local reference material. The local reference material shall be traceable to a certified reference material.

12.1.1 *Manometric (Volumetric) Apparatus*—Refer to Test Method **D1993** and ISO 15901-2 for calibration procedures.

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

### 13. Measurement Procedure

13.1 *Manometric (Volumetric) Apparatus*—Refer to Test Method **D1993**, ISO 15901-2, and ISO 9277 for analysis procedures.

13.2 *Automated and Dynamic Flow Instruments*—Attach the properly prepared sample cell to analysis port in accordance with manufacturer's instructions. Include any required hardware.

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

13.3.1 *(Multipoint BET Analyses Only)*—Use a minimum of four data points evenly spaced in the 0.05 to 0.3 relative pressure ( $p/p_o$ ) range (in the linear BET transformation range of the isotherm characteristic of the sample). The sample mass shall refer to the weights of outgassed material.

13.3.2 *(Single-Point BET Analyses Only)*—Use highest relative pressure known to be in the linear BET transformation range of the isotherm. Commonly, the data point at relative pressure 0.3 is used. The sample mass shall refer to the weights of outgassed sample.

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

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

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

13.5 Refer to the user's manual or specific manufacturer's instructions for the multipoint gas adsorption analyzer to be used, and become thoroughly familiar with the procedures. Perform analysis in accordance with the instrument manufacturer's instructions using the specified conditions. There are numerous manometric (volumetric) instruments available that offer a variety of saturation vapor pressure ( $p_o$ ) measurement options and Dewar sizes.

13.6 Fill the Dewar with bath coolant and allow it to reach temperature equilibrium. Refill the Dewar between each analysis. The time required to reach equilibrium is dependent upon Dewar size and quality (see manufacturer's specifications).

13.7 Determine the void volume of the sample cell by measurement with helium or by calculation using an assumed sample density in  $\text{g cm}^{-3}$ .

13.8 Obtain data points. A data point consists of the relative pressure at equilibrium and the total amount of adsorbed gas (that is, volume in  $\text{cm}^3$  (STP), normalized by 1 g of sample) at that relative pressure.

13.9 The reproducibility of the results can be verified by repeated measurements using fresh samples for each run. The mean value with standard deviations shall be reported.

### 14. Calculation

NOTE 3—For details, refer to **Annex A1**.

#### 14.1 Sample Mass:

$$\text{sample mass (dried)} = (\text{mass of cell} + \text{sample}) - (\text{mass of cell}) \quad (1)$$

Record each mass to nearest 0.1 mg.

NOTE 4—Avoid inconsistent use of helium, as a buoyancy error of  $1 \text{ mg/cm}^3$  of cell volume can occur.

14.2 Most automated instruments will perform the following computations at the completion of the analysis. The user shall verify that the internal computations conform to the following method. For equations and detailed description of methods, see **4.6** and **Annex A1**.

14.3 *Specific Surface Area (Multipoint BET)*—(for equations, see **Annex A1**):

14.3.1 Construct a plot of  $[p/p_o]$  on the X-axis versus  $[(p/p_o) / V_a(1 - (p/p_o))]$  on the Y-axis, for data sets having  $p/p_o$  in the range from 0.05 to 0.30 (linear region of BET) in accordance with **Eq A1.1**.

14.3.2 Use a minimum of four data points that give the best straight line and calculate the slope  $a$  and y-intercept  $b$  of the BET plot (in accordance with **Eq A1.1** and **Eq A1.2**). The slope  $a$  and y-intercept  $b$  (where  $b \geq 0$ ) are used to calculate the monolayer capacity in accordance with **Eq A1.3**. 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, **Eq A1.1**, in **Annex A1**). Typically, the linear range includes relative pressures between 0.05 and 0.30 (**4**). It is the responsibility of the operator to ensure that these guidelines are appropriate for their samples.

14.3.3 The surface area is calculated from three or more points within the pressure range that yields the highest correlation coefficient and a positive y-intercept.

14.3.4 Calculate the specific surface area (SSA) in accordance with **Eq A1.7**. Report the result to the nearest  $0.1 \text{ m}^2 \text{ g}^{-1}$ .

14.3.5 The BET method is not applicable if there is a negative intercept (that is, negative  $C$ -constant), or a straight line is not obtained. In particular, a negative intercept may be indicative of the presence of micropores (see **Annex A2** for details).

### 15. Report

15.1 Report the following information:

15.1.1 Complete sample identification (for example, composition, trade name, source, lot number, production date, pretreatments, and nominal powder size).

15.1.2 *Equipment and Test Parameters*:

15.1.2.1 Type, make, and model number of the test equipment,

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

15.1.2.3 Mass of outgassed sample to the nearest 0.1 mg,

15.1.2.4 Adsorptive analysis gas composition, purity, and measurement temperature,

15.1.2.5 The measured free space in  $\text{cm}^3$ ,

15.1.2.6 The saturation pressure, and

15.1.2.7 Number of tests per sample.

15.1.3 *Test Results*:

15.1.3.1 BET specific surface area (SSA) ( $\text{m}^2 \text{ g}^{-1}$ ) reported to the nearest  $0.1 \text{ m}^2 \text{ g}^{-1}$  or three significant figures.

**TABLE 3 Precision for Single-Point and Multipoint BET Methods<sup>A</sup>**

Material	Number of Laboratories	Surface Area (average)	Precision					
			Single-Point BET Method			Multipoint BET Method		
			Repeatability Standard Deviation, $S_r$	Reproducibility Standard Deviation, $S_R$	Repeatability Limit	Reproducibility Limit	Repeatability, C.V.	Reproducibility, C.V.
AlN	6	2.82	0.09	0.12	0.24	0.24	3.1 %	4.3 %
Si <sub>3</sub> N <sub>4</sub> (SNT)	17	9.30	0.24	0.38	0.66	1.05	2.6 %	4.1 %
Si <sub>3</sub> N <sub>4</sub> (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 %
Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	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 × √2 × standard deviation.

Material	Number of Laboratories	Surface Area, avg	Precision					
			Single-Point BET Method			Multipoint BET Method		
			Repeatability Standard Deviation, $S_r$	Reproducibility Standard Deviation, $S_R$	Repeatability Limit	Reproducibility Limit	Repeatability, C.V.	Reproducibility, C.V.
AlN	6	2.83	0.15	0.22	0.42	0.62	5.3 %	7.9 %
Si <sub>3</sub> N <sub>4</sub> (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 %
Y <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	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 × √2 × standard deviation.

<sup>A</sup> From the IEA Annex II Subtask 6 on Development and Testing of Procedures for Characterization of Ceramic Powders (September 1993).

15.1.3.2 Collected isotherm point(s) as volume adsorbed, or desorbed, versus relative pressure; experimental procedure for adsorption isotherm determination (for example, volumetric, gravimetric).

15.1.3.3 *BET Evaluation Parameters*, multipoint or single-point determination (and possible corrections in accordance with A1.3.2.1), BET plot or range of linearity (relative pressure range used), linear regression values for the BET slope (*a*-intercept, *b*-slope,  $R^2$ ) correlation coefficient, monolayer capacity ( $n_m$ ) expressed in mol/g, molecular cross-sectional area ( $a_m$ ), and BET *C* parameter.

15.1.4 Certified or local reference material(s) used for validation of results. Refer to practices for validation and calibration of equipment.

NOTE 5—To ensure proper working conditions and correct data evaluation, the apparatus performance shall be monitored on a regular basis (for example, quarterly) using a certified reference material or a local reference material. The local reference material shall be traceable to a certified reference material.

## 16. Precision and Bias

16.1 *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 data 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 the single-point and multipoint BET methods 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. The specific precision data for this IEA study are listed in detail in Table 3.

16.2 *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 E177. Coefficient of variation (C.V.) is defined as the standard deviation divided by the mean value.

16.3 *Bias*—No justifiable statement can be made on the bias of the procedure in this test method because there has been no interlaboratory study with six or more participants testing a material with an accepted reference value.

## 17. Keywords

17.1 advanced ceramics; BET surface area; ceramics; krypton adsorption; multipoint surface area; nitrogen adsorption; outgassing; physical adsorption; single-point surface area; specific surface area; surface area

A1. STEP-BY-STEP BET SURFACE AREA CALCULATIONS

A1.1 Linear Form of the BET Equation

A1.1.1

$$\frac{p/p_0}{V_a [1 - (p/p_0)]} = \frac{1}{V_m \cdot C} + \frac{C - 1}{V_m \cdot C} \cdot p/p_0 \quad (A1.1)$$

where:

- $p$  = absolute (equilibrium) pressure, Pa,
- $p_0$  = saturation vapor pressure (of adsorbate), Pa,
- $p/p_0$  = relative pressure,
- $V_a$  = volume of gas adsorbed at  $p/p_0$ ,  $\text{cm}^3$  (STP)  $\text{g}^{-1}$ ,
- $V_m$  = monolayer capacity,  $\text{cm}^3$  (STP)  $\text{g}^{-1}$ , and
- $C$  = BET constant, which is correlated with the effective attractive interaction between adsorptive and adsorbent.

A1.2 Transformation of the Measured Physisorption Data Into the BET Plot

A1.2.1 To construct a multipoint BET graph based on physisorption data collected within a selected relative pressure range (typically 0.05 to 0.3), the expression  $[(p/p_0) / V_a(1 - (p/p_0))]$  is plotted versus  $[p/p_0]$ . When the BET theory assumptions hold, the plot should give a straight line:  $y = b + ax$ , with a positive intercept  $a$ . The slope and the intercept, respectively, are:

$$a = \frac{\Delta Y}{\Delta X} = \frac{C - 1}{V_m \cdot C} \text{ and } b = \frac{1}{V_m \cdot C} \quad (A1.2)$$

where both  $a$  and  $b$  may be determined by linear regression.

Fig. A1.1 shows an example of a BET plot for  $\text{N}_2$  (77.35 K) adsorption on a mesoporous  $\text{SiO}_2$  glass using the data collected within the classical BET relative pressure range. The plot gives the required straight line and positive intercept.

A1.3 Evaluation of the Monolayer Capacity

A1.3.1 Based on Eq A1.1 and A1.2, in case of multipoint BET analysis, the statistical monolayer capacity  $V_m$  is determined as:

$$V_m = \frac{1}{a + b} \quad (A1.3)$$

and the BET  $C$  constant parameter is determined as:

$$C = \frac{b}{a} + 1 \quad (A1.4)$$

For details on relevance of the BET  $C$  constant values, see Annex A2. When  $V_m$  has been determined for multipoint analysis ( $V_{m,mp}$ ), go directly to A1.4 and perform calculation of SSA.

A1.3.2 Single-point BET calculation is a simplified procedure requiring only the determination of a single point on the isotherm in the range of relative pressures between 0.2 and 0.3 (having established that the BET plot for the particular type of material gives a straight line). For  $C \gg 1$ , the ordinate intercept  $1 / (V_m C)$  of the BET plot is small and Eq A1.1 simplifies to:

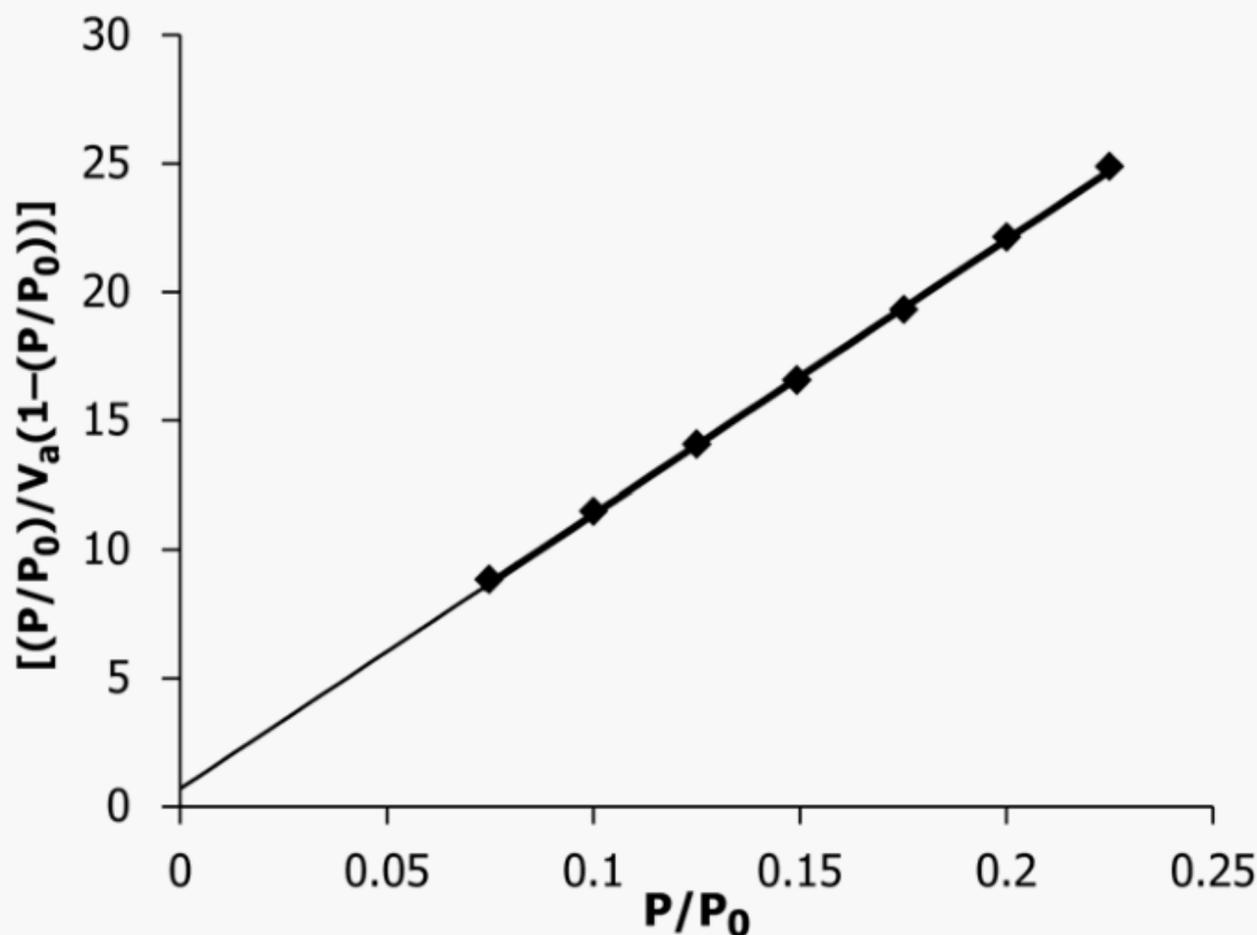


FIG. A1.1 BET Plot for  $\text{N}_2$  (77.35 K) on a Mesoporous  $\text{SiO}_2$  Glass

$$V_{m,sp} = V_a(1 - p/p_o) \quad (A1.5)$$

**A1.3.2.1 Correction of a Single-Point Monolayer Capacity**—The single-point monolayer capacity  $V_{m,sp}$  is less than or equal to monolayer capacity derived from a multipoint determination  $V_{m,mp}$ . For measurements on samples of similar materials the error in the single-point method can be corrected, for example, by performing a multipoint analysis first to determine (1) either the appropriate value of the intercept, which can then be used in subsequent single-point analyses, or (2) the appropriate value of the BET parameter  $C$ , which can then be used to correct the single-point monolayer capacity  $V_{m,sp}$  values using the following equation:

$$\frac{V_{m,mp} - V_{m,sp}}{V_{m,mp}} = \frac{1 - (p/p_o)}{1 + (p/p_o) \cdot (C - 1)} \quad (A1.6)$$

When  $V_m$  for single-point analysis ( $V_{m,sp}$ ) has been determined and corrected, go directly to **A1.4** and perform calculation of SSA.

#### A1.4 Calculation of SSA

**A1.4.1** The specific surface area (per unit mass of the dry sample) is calculated from the monolayer capacity (obtained by multipoint or single-point determination) by assessing a value for the average area occupied by each molecule adsorbed in the complete monolayer (per 1 g of adsorbent), in accordance with **Eq A1.7**:

$$a_s = n_m a_m L \quad (A1.7)$$

where:

- $a_s$  = specific surface area (SSA),  $m^2 g^{-1}$  (surface area/g of sample),
- $a_m$  = molecular effective cross-sectional area of adsorbate,  $m^2/(\text{adsorbed})$  molecule; for  $N_2$  at 77 K,  $a_m = 16.2 \times 10^{-20} m^2/\text{molecule}$  (see **Table 1**),
- $V_m$  = monolayer capacity,  $cm^3$  (STP)/g of sample (see **A1.4.1.1**),
- $n_m$  = monolayer capacity, number mol/g of sample (see **A1.4.1.1**),
- $w_m$  = monolayer capacity, g (of gas adsorbed)/g of sample (see **A1.4.1.1**),
- $M_V$  = molar volume (volume in  $cm^3$  occupied by 1 mol of gas at STP) =  $22414 cm^3$  (STP)/mol,
- $M_{ad}$  = molar mass of adsorbate, g/mol (see **Table 1**), and
- $L$  = Avogadro's number,  $6.02 \times 10^{23}$  molecules/mol.

**A1.4.1.1** Monolayer capacity can be expressed alternatively in terms of volume at STP, or weight, or number of moles, of a given adsorbate, per g of adsorbent:

$$n_m = \frac{V_m}{M_V} = \frac{w_m}{M_{ad}} \quad (A1.8)$$

## A2. COMMENTS ON APPLICABILITY OF THE BET METHOD FOR EVALUATION OF SSA OF MICROPOROUS CERAMIC MATERIALS (WITH PORES OF DIAMETERS BELOW 2 NM)

**A2.1** The BET equation is, in a strict sense, not applicable for microporous adsorbents (a critical appraisal of the BET method is given in various textbooks on porosity measurements **(4, 5)**). It is difficult to separate the processes of mono-multilayer adsorption from micropore filling, and the latter is usually completed at relative pressures below 0.1. It appears that in the presence of micropores, the linear (BET) range is significantly shifted to lower relative pressures. Therefore, the surface area obtained by applying the BET method on adsorption isotherms measured on microporous solids does not reflect the true internal surface area, but shall be considered as a kind of characteristic or equivalent BET area. In this case, it is of course obligatory to report the range of linearity for the BET plot. A quite convenient procedure on how to find the linear range of the BET plot for microporous materials based on two criteria **(6)** has been recently suggested: (1) the quantity of  $C$  parameter must be positive (that is, any negative intercept on the ordinate of the BET plot is an indication that one is outside the valid range of the BET

equation), and (2) the application of the BET equation shall be limited to the pressure range where the term  $V_a(p_o - p)$  or alternatively  $V_a(1 - p/p_o)$  continuously increases with increasing  $p/p_o$ . An example of this procedure is shown in **Fig. A2.1** for  $N_2$  (77.4 K) adsorption on a microporous silicon carbide derived carbon, where the relative pressure  $P/P_o$  is plotted against the term  $V_a(1 - p/p_o)$ . The upper limit of the linear BET range is then the maximum of this plot as given in criterion (2) above. In the case of this sample, the linear BET range is  $P/P_o = 0.03-0.081$ , well below the classical BET range. The correct, linear BET plot using the determined range is shown in **Fig. A2.2**. In contrast, if the classical range ( $P/P_o = 0.05-0.3$ ) is applied to the data, the resulting BET plot (**Fig. A2.3**) is nonlinear. Additionally, in this case, the BET plot intercept is negative, which would mean that the BET  $C$  constant is negative (that is, any negative intercept on the ordinate of the BET plot is an indication that one is outside the valid range of the BET equation).

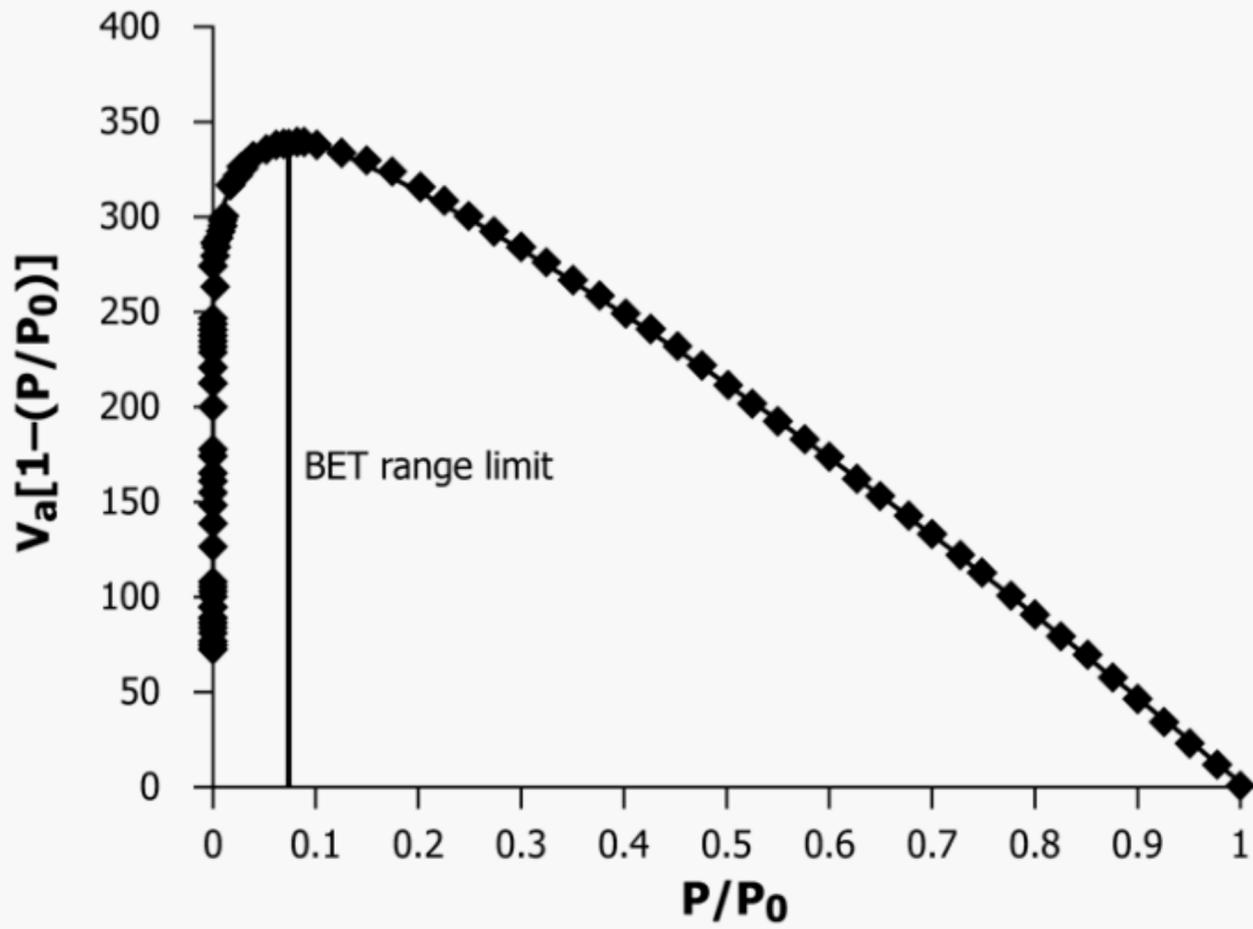


FIG. A2.1 Plot Used to Determine the Upper Limit (Graph Maximum) for the BET Range (N<sub>2</sub>/77.35 K Adsorption) in a Microporous Silicon Carbide Derived Carbon

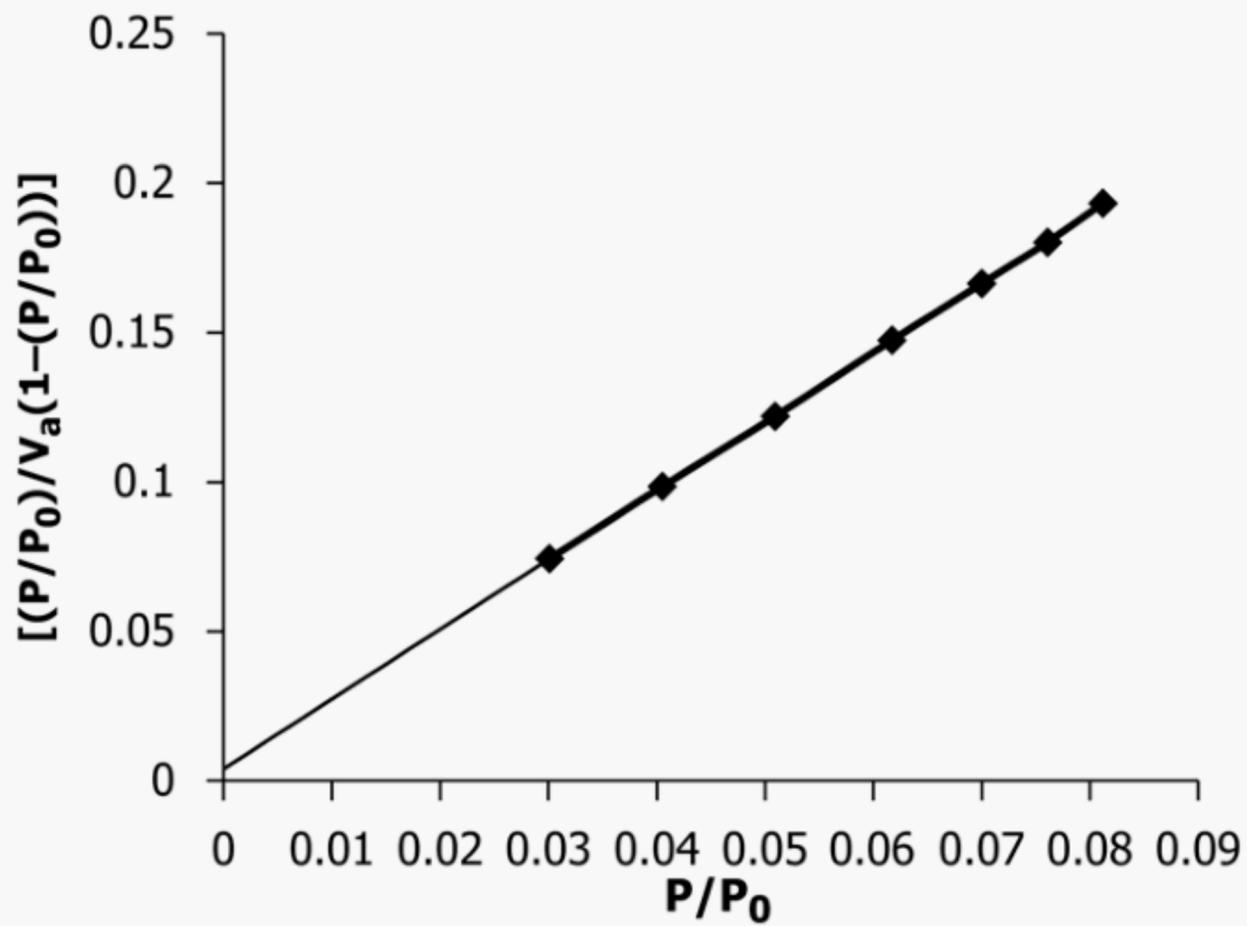


FIG. A2.2 BET Plot in the Relative Pressure Range Determined Using the Method Proposed in A2.1

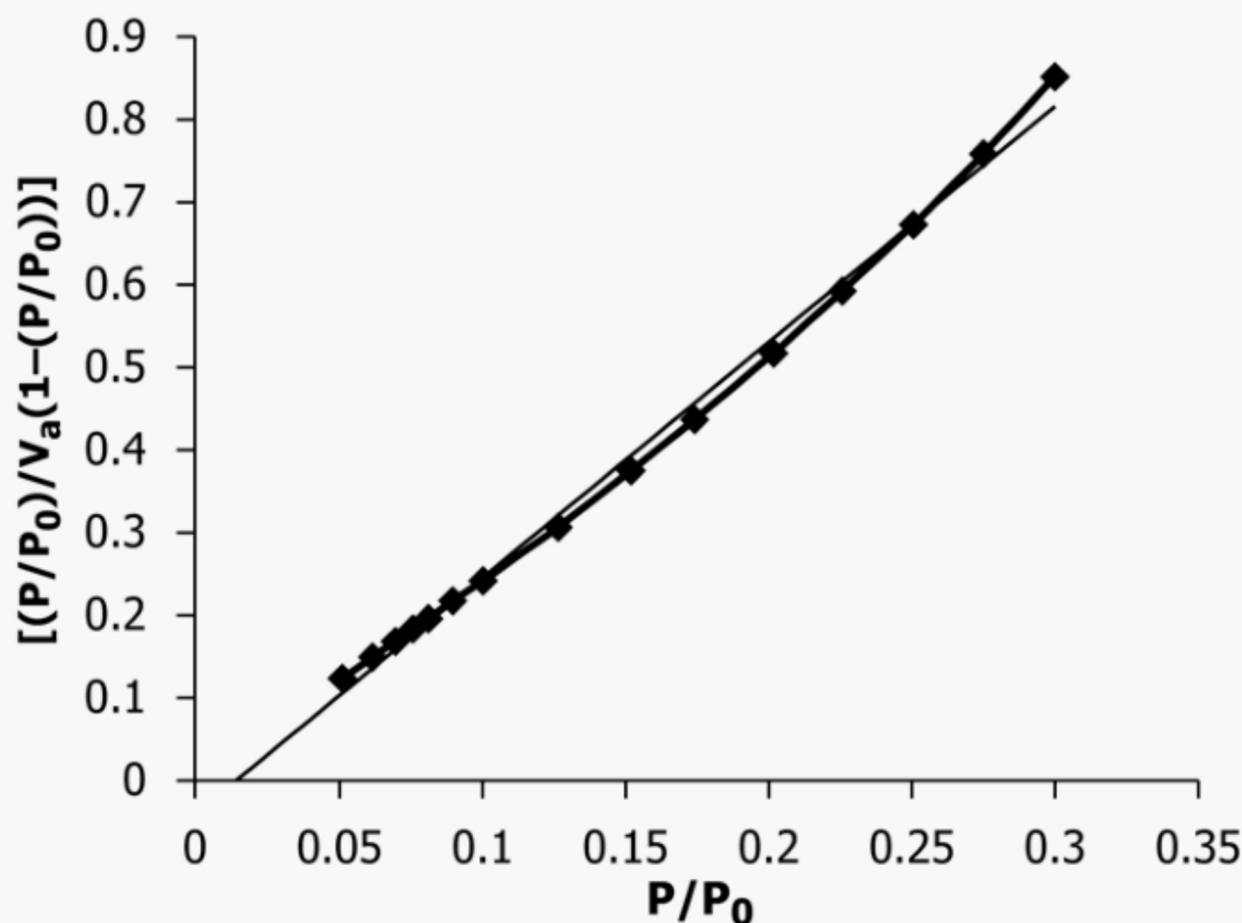


FIG. A2.3 BET Plot Using the Classical Relative Pressure Range

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