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Standard Guide for Evaluation of Nuclear Graphite Surface Area and Porosity by Gas Adsorption Measurements¹

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1. Scope

1.1 The purpose of this Guide is to provide methodologic information specific to highly graphitized, low surface area materials used in the nuclear industry. It applies to nitrogen adsorption measurements at 77 K for the characterization of graphite pore structure, such as: (1) specific surface area; (2) cumulative volume of open pores (for pore sizes less than about 300 nm); and (3) distribution of pore volumes as a function of pore sizes (for pore sizes less than about 30 nm). These properties are related to graphite's reactivity in oxidative environments, graphite's ability to retain fission products, and gas transport through graphite's pore system.

1.2 Characterization of surface area (also known as the Brunauer-Emmett-Teller "BET" method) and porosity in nuclear graphite by gas adsorption is challenged by nuclear graphite's low specific surface area, weak adsorption interactions, and energetic and structural heterogeneity of surface sites in gas-accessible pores. This guide provides recommendations and practical information related to the nitrogen adsorption method, including guidance on specimen preparation, selection of experimental conditions, data processing, and interpretation of results.

1.3 Other porosity characterization methods used for nuclear graphite, such as krypton adsorption at 77 K, argon adsorption at either 77 K or 87 K, helium pycnometry (Test Method B923), and mercury intrusion porosimetry, are not in the scope of this guide.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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 This guide is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.F0 on Manufactured Carbon and Graphite Products.

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1.6 *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:²

C1274 Test Method for Advanced Ceramic Specific Surface Area by Physical Adsorption

D3663 Test Method for Surface Area of Catalysts and Catalyst Carriers

D4641 Practice for Calculation of Pore Size Distributions of Catalysts and Catalyst Carriers from Nitrogen Desorption Isotherms

D4222 Test Method for Determination of Nitrogen Adsorption and Desorption Isotherms of Catalysts and Catalyst Carriers by Static Volumetric Measurements

D6556 Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption

D6761 Test Method for Determination of the Total Pore Volume of Catalysts and Catalyst Carriers

B923 Test Method for Metal Powder Skeletal Density by Helium or Nitrogen Pycnometry

2.2 ISO Standards:³

ISO 9227 Determination of the specific surface area of solids by gas adsorption – BET method (Second edition)

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *adsorbate, n*—the material retained by adsorption at the interface between a solid and a gas or liquid.

3.1.2 *adsorbent, n*—a solid material able to concentrate measurable quantities of other substances on its accessible surface, either external or in pores.

² 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.

³ Available from International Organization for Standardization (ISO), ISO Central Secretariat, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <http://www.iso.org>.

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

3.1.4 *adsorption isotherm, n*—a collection of numerical values showing the relationship between mass-normalized adsorbed amounts and the corresponding equilibrium pressures (or relative pressures) of the adsorptive at constant temperature. It is the primary experimental result of adsorption measurements and can be provided either in tabular form or graphical representation. Adsorption and desorption isotherms are collected sequentially by gradually increasing and decreasing, respectively, the target pressures at which data points are collected.

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

3.1.6 *BET surface area (S_{BET})*—the common name for SSA values calculated using the Brunauer – Emmett – Teller (BET) equation.⁴

3.1.7 *dead volume, n*—the void volume around the adsorbent in the measurement cell and in the connecting tubes. The precision of dead space calibration is limited by the equipment's performance and does not depend on the sample's surface area. Errors in calculation of the dead space volume affect the accuracy of gas adsorption results, especially for samples with low surface area.⁵

3.1.8 *distribution of pore volumes as a function of pore sizes (or pore size distribution, PSD), n*—a collection of numerical values of mass-normalized pore volumes accessible to gas and their corresponding pore sizes. It is calculated from adsorption isotherms through model-dependent algorithms and can be provided either in tabular form or graphical representation.

3.1.9 *macropores, n*—according to IUPAC nomenclature,⁶ pores with characteristic size larger than 50 nm. In nuclear graphite, the class of macropores includes large pores and cracks, gas evolution pores, fissures, etc. Gas adsorption methods are limited to pores less than about 300 nm, where condensation of nitrogen at 77 K leads to measurable pore filling. The volume of mesopores larger than about 300 nm cannot be measured with adequate precision by gas adsorption but can still be analyzed by mercury intrusion porosimetry.

3.1.10 *mesopores, n*—according to IUPAC nomenclature,⁶ pores with characteristic size (width for slit-shaped pores in graphite, diameter for cylindrical pores) between 2 nm and 50 nm. In nuclear graphite, the class of mesopores includes the smallest cracks, thermal shrinkage pores, and Mrozowski cracks.

3.1.11 *micropores, n*—according to IUPAC nomenclature,⁶ pores with characteristic size (width for slit-shaped pores in graphite) less than 2 nm. Micropores are not usually present in nuclear graphite.

3.1.12 *molecular cross-sectional area*—the area occupied by one single adsorbed molecule at the calculated completion of the first monolayer uptake.

3.1.13 *monolayer capacity (V_m), n*—the calculated amount of adsorbate, expressed as the number of moles, weight, or volume at standard temperature and pressure (STP), that would be needed to form a monomolecular adsorbed layer extending over the entire gas-accessible surface of the adsorbent.

3.1.14 *nitrogen surface area (NSA), n*—another name for SSA values measured using nitrogen as the adsorptive gas.

3.1.15 *relative pressure (P/P_0)*—the ratio between equilibrium pressure (P) and saturation vapor pressure (P_0) of the adsorptive at the ambient pressure and cold bath temperature of the measurement.

3.1.16 *saturation vapor pressure*—vapor pressure (P_0) of bulk adsorptive liquefied at the conditions of the measurements. Its value depends on the local atmospheric pressure and the temperature of the cold bath used for temperature control.

3.1.17 *specific surface area (SSA), n*—the total mass-normalized area of a solid, including both external and accessible internal surfaces (from pores, cracks, fissures, voids, etc.).

3.1.18 *specific total volume of open pores (total pore volume), n*—the total mass-normalized volume of gas-accessible pores in porous graphite. It is calculated from the maximum amount of adsorbate condensed in open pores just below the saturation pressure at measurement conditions. Pore openings larger than about 300 nm are generally too large for nitrogen condensation to occur with enough measurable resolution at 77 K.

3.1.19 *volume adsorbed (V_a), n*—the amount adsorbed, calculated at standard temperature and pressure (STP), at each equilibrium relative pressure (P/P_0) value during adsorption or desorption.

4. Summary of Guide

4.1 In volumetric (manometric) adsorption methods a previously outgassed specimen weighed with 0.1 mg precision is introduced in the measurement cell and evacuated. As part of the initial routine of commercial instruments, the dead volume is measured by helium expansion.

4.2 After immersion of the specimen in a cold temperature bath and evacuation, a known amount of the adsorptive gas is introduced in the measurement cell. As adsorption proceeds, the pressure in the cell drops until a constant (equilibrium) pressure is achieved. The amount adsorbed is calculated from the difference between the amount of gas introduced and the amount remaining in the dead space volume.

4.3 All pressure readings should be made at equilibrium conditions and constant temperature.

⁴ Brunauer, S., Emmett, P. H., Teller, E., "Adsorption of gases in multimolecular layers," *Journal of the American Chemical Society*, Vol 60, 1938, pp. 309–319.

⁵ Do, D. D., Do, H. D., Nicholson, D., "A computer appraisal of BET theory, BET surface area and the calculation of surface excess for gas adsorption on a graphite surface," *Chemical Engineering Science*, Vol 65, 2010, pp. 3331–3340.

⁶ Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez-Reinos, F., Rouquerol, J., Sing, K. S. W., "Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)," *Pure and Applied Chemistry*, Vol 87, 2015, pp. 1051–1069; DOI 10.1515/pac-2014-1117.

4.4 The amounts adsorbed must be normalized by the mass of the adsorbent in its outgassed condition. Any error in the sample weight is propagated in the final BET surface area results.

4.5 BET surface area measurements can use just a few data points equally spaced between $0.05 < P/P_0 < 0.30$ (Test Methods C1274, D6556, D3663, and ISO 9227). However, using a limited number of data points may lead to an erroneous selection of the linear range of the BET equation, and hence to inaccurate SSA values for weakly adsorbing nuclear graphite materials. For accurate SSA results it is always recommended to collect a larger number of data points over a broader P/P_0 range. See practical and methodological considerations in Section 7.

4.6 If full adsorption (and desorption) isotherms over the entire range of relative pressures ($0 < P/P_0 < 1$) are available (Test Method D4222), they can be used to obtain more information on graphite porosity (total pore volume and pore size distribution). See discussion in Section 8.

4.7 Fig. 1 shows a representative nitrogen adsorption-desorption isotherm for a medium grained nuclear graphite. Based on shape, the isotherm belongs to type II according to the International Union of Pure and Applied Chemistry (IUPAC) classification.⁶ Type II isotherms characterize adsorbents which allow continuous monolayer - multilayer transitions and unrestricted development of multilayers.

4.8 In the example shown in Fig. 1, the desorption curve does not overlap the adsorption curve. This effect (hysteresis) is observed with most nuclear graphites and is ascribed to the presence of large pores (mesopores) where condensation and evaporation of the adsorbate occur at different pressures.

4.9 Nuclear graphite is usually free of micropores (width < 2 nm), which would cause a strong initial rise of isotherms at very low pressures ($P/P_0 < 0.001$). High resolution adsorption isotherms on well outgassed nuclear graphites may show an initial isotherm rise starting from very low pressures. This feature is attributed to strong 2D adsorption on atomically ordered basal planes of graphitic crystallites due to their higher adsorption energy and accessibility. A subtle change of slope near $P/P_0 = 0.01$ indicates a structural reorganization in the first monolayer on basal plane sites (see inset in Fig. 1). Adsorption continues at higher pressures on the remaining, energetically non-uniform and atomically disordered graphite prismatic surfaces, and on other types of defective sites. On these surfaces statistical multilayer growth may commence long before the first monolayer is complete. This complicates the

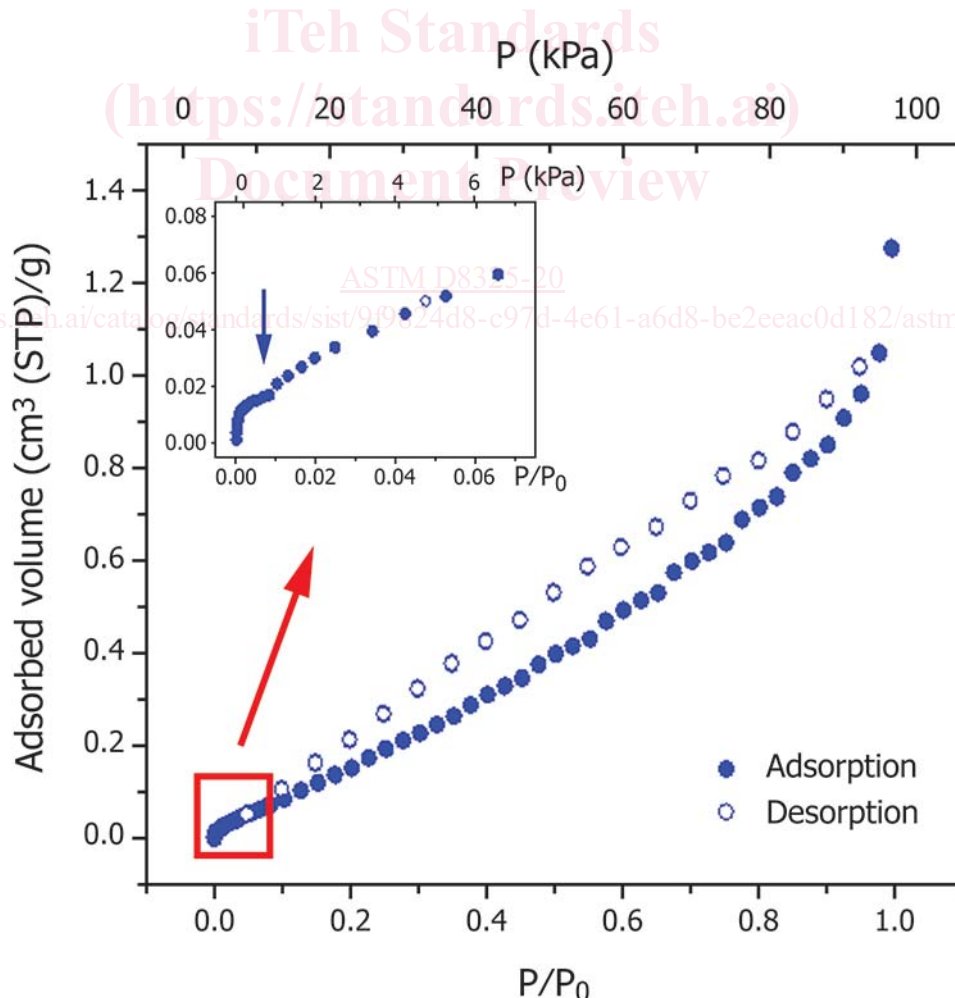


FIG. 1 Nitrogen Adsorption – Desorption Isotherm at 77 K on a Typical Medium Grained Nuclear Graphite

correct determination of $(P/P_0)_m$, the relative pressure corresponding to the completion of a monolayer.

4.10 Adsorption through statistical growth of multilayers continues as described by the BET theory up to about $0.35 P/P_0$ or higher (a deviation from the classical BET range). Capillary condensation in mesopores (2 nm to 50 nm in width), if present, may cause differences between adsorption and desorption branches, as noted before (see Fig. 1). Finally, a sudden rise in the isotherm curve as P/P_0 approaches 1 is generally associated with the condensation of nitrogen in macropores (large cracks, voids, fissures, etc., with sizes > 50 nm).

4.11 Apparatus:

4.11.1 Automated volumetric adsorption analyzers available commercially are preferred, as they ensure repeatability and reproducibility of measurements and unassisted operation over long periods of time. They also come equipped with data analysis software.

4.11.2 The user should check the operation manual and other specific instructions for the specific gas adsorption analyzer to be used and should understand and become familiar with its recommended sample preparation and data collection procedures.

4.11.3 Each commercial adsorption analyzer may come with its own series of options regarding the size of the coolant Dewar vessel, measurement methods to assess saturation vapor pressure (P_0), sample outgassing protocols, and data collection conditions. Follow the manufacturers' recommendations unless indicated otherwise below.

4.11.4 The time needed for collecting only multiple data points for BET surface area measurements may be about 2 h to 3 h.

4.11.5 The time needed for collecting full adsorption-desorption isotherms may be 24 h or longer. Using a large size Dewar bath (2 L or larger) is recommended in this case.

4.11.6 Among the various options for P_0 measurement, continuous measurement (at each new relative pressure condition) is the best practice. Other options, such as single P_0 per analysis, daily P_0 measurements, or user entered P_0 values should be avoided unless there is a distinct need for using them.

5. Practical Recommendations on Procedure

5.1 Sample Preparation:

5.1.1 The weight of the dry sample, free of adsorbed contaminants, must be known with a 0.1 mg precision. The use of a suitable analytical balance is required. Although the weight can be measured either before or after analysis, weighing the sample after drying and outgassing, but before running the analysis run, is recommended.

5.1.2 Use as large a graphite sample size as the measurement cell can accommodate. To minimize the dead space volume, use a suitable glass rod or glass balls.

5.1.3 Using highly accurate adsorption equipment and carefully chosen measurement conditions it is possible to assess the surface area of materials as low as 0.5 m^2 to $1 \text{ m}^2/\text{g}$ using nitrogen (or argon) as the adsorptive.⁶ For routine analysis some commercial instrument manufacturers recommend adjusting the sample size as to always have about 5 m^2 of

adsorbing surface in the cell, but not less than 20 mg. With rigid shapes of low surface area nuclear graphite, this condition may be difficult to meet because of the limited capacity of typical sample cells. Breaking graphite specimens into smaller pieces may help in fitting more low surface area material in the sample cell. However, crushing graphite into fine powder or small chunks should be avoided because mechanical actions may distort the structure and create larger internal surfaces than those present in the original graphite.

5.1.4 Outgas graphite prior to its analysis to remove from it any moisture and pre-adsorbed organic vapors. Either inert gas flow or vacuum outgassing at $300 \text{ }^\circ\text{C}$ to $350 \text{ }^\circ\text{C}$ can be used. A lower temperature must be used if graphite properties may change at the recommended degassing temperature (for example, for graphite irradiated at a lower temperature). Outgassed samples should be able to reach and hold a pressure of about 1.4 Pa ($10 \text{ } \mu\text{m Hg}$). Some commercial adsorption analyzers offer the option of defining acceptance conditions for the outgassing step, based on rates of rise in background pressure.

5.2 Reagents:

5.2.1 Ultra-high purity, oil-free adsorbate gases (N_2 , He and optionally Kr or Ar) with less than 10 ppmv total sum of impurities supplied from a cylinder.

5.2.2 Liquid nitrogen bath, preferably fresh. Impurities in liquid nitrogen (water, dissolved oxygen) raise the bath temperature and can thus lead to slow rises in saturation pressure P_0 which may affect the isotherm data unless continuous P_0 measurements are made during the analyses.

6. Measurement Procedure

6.1 The operator should select the table of relative pressures (P/P_0) according to the particular purpose of the intended analysis. The following recommendations are provided as a guidance but are not mandatory.

6.1.1 Although a minimum of five P/P_0 points might be enough for BET surface area measurements of most materials, for accurate surface characterization of nuclear graphite it is recommended to collect more data points. The linearization range of the BET equation is often found to be $0.05 < P/P_0 < 0.30$,⁶ but practice has shown that this range often needs to be extended up to 0.35 (or even beyond) for some weakly adsorbing materials, such as nuclear graphite. See practical recommendations for the consistent selection of P/P_0 linearization range in 7.1.9.

6.1.2 The use of the single-point BET method, although faster and repeatable, is not recommended because this method is based on an assumption that may lead to errors in BET surface area estimates of ~2 % to 4 % or more.⁷

6.1.3 Detailed analysis of surface and pore structure of nuclear graphite by gas adsorption is better performed from full adsorption-desorption isotherms with a total of 100 to 120 data points. Starting at pressures in the range of $10^{-5} P/P_0$ allows the detection of the strongest adsorption sites within the basal plane surfaces of graphite crystallites.

⁷ Rouquerol, J., Rouquerol, F., Sing, K. S. W., Llewellyn, P., Maurin, G., "Adsorption by powders and porous solids: Principles, methodology and applications," *Academic Press*, 2nd Edition, 2014.

6.1.4 Equilibration times at each relative pressure should be long enough to enable the access of slowly diffusing adsorbate through graphite pores to the whole volume of the solid material. The recommended equilibration time is 4 min to 5 min per point if the goal is measuring only BET surface area, and the solid graphite sample is not larger than about 1.0 g to 1.2 g. Longer equilibration times are needed for more detailed adsorption isotherm analyses or for larger volume solid graphite samples.

6.1.5 Adsorption equilibrium conditions after each pressure increment should be defined based on minimum tolerance of pressure variations during operator-selected equilibration times.

7. Methodological Recommendations on Data Processing

7.1 BET Equation:

7.1.1 In the BET method the specific surface area is calculated from the equivalent monolayer capacity, which is obtained by linearization of the following equation (the BET equation):

$$\frac{P/P_0}{V_a[1 - (P/P_0)]} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} (P/P_0) \quad (1)$$

where:

- P = equilibrium pressure (absolute) in Pa or Torr units,
- P_0 = saturation pressure (absolute) of adsorbate in Pa or Torr units,
- V_a = adsorbed volume at each relative pressure P/P_0 in cm^3 (STP) g^{-1} ,
- V_m = equivalent monolayer capacity in cm^3 (STP) g^{-1} , and
- C = BET constant, exponentially related to the enthalpy of adsorption in the first adsorbed layer.

7.1.2 The plot of $(P/P_0)/[V_a(1 - (P/P_0))]$ versus P/P_0 should yield a straight line with slope $s = (C - 1)/(V_m C)$ and intercept $i = 1/(V_m C)$. An example is shown in Fig. 2.

7.1.3 The monolayer capacity V_m and the C constant of the BET equation are calculated from the slope and intercept:

$$V_m = (s + i)^{-1} \quad (2)$$

$$C = (s / i) + 1 \quad (3)$$

7.1.4 The specific surface area is calculated from the following equation:

$$S_{BET} = SSA = \frac{V_m N_A a_m}{M_v} \quad (4)$$

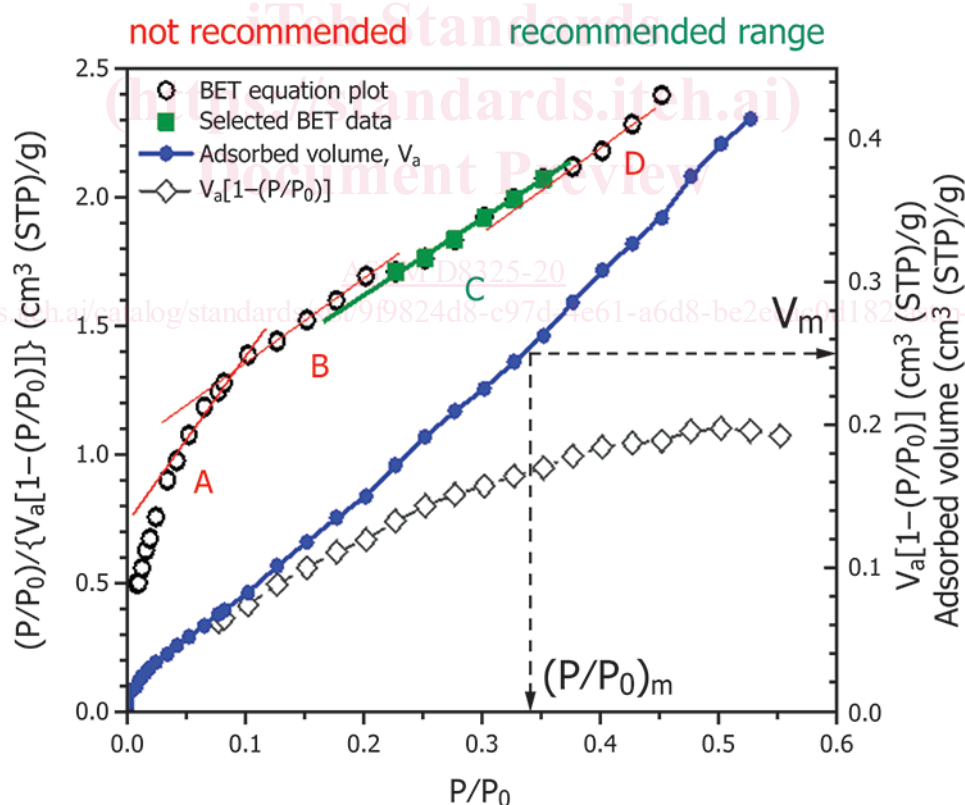


FIG. 2 Exemplification of the Recommended Procedure for Selection of the Proper Range of P/P_0 Data Points used for Linearization of BET Plots and Calculation of BET Surface Area