Final Report: Interlaboratory Study for the Measurement of BET-Specific Surface Area Using an Industrially Relevant TiO₂ Nanopowder

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1. Overview

This report summarizes the findings of an interlaboratory study (ILS) conducted in 2009-2010 under the auspices of the Versailles Project on Advanced Materials and Standards (VAMAS) Technical Working Area (TWA) 34 (Nanoparticle Populations).[1] The stated objective of this ILS was to assess the "real world" measurement precision and between-laboratory variation for determination of the surface area of an industrially relevant metal-oxide nanomaterial in powder form. The test material, nanocrystalline titanium dioxide, also serves as the source material for production of a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM 1898).

Within the context of toxicological, exposure, and environmental fate assessment of engineered nanomaterials (ENMs), it is now widely acknowledged that accurate and precise physicochemical characterization is a requirement in order to establish meaningful causal relationships between material properties and observed biological or environmental effects; such studies are seriously compromised by the lack of reliable physicochemical data. Scientifically credible and rigorously evaluated reference materials, in conjunction with interlaboratory comparisons, will play an important role in enabling such assessments by providing confidence in measurement data.

An important metric used in exposure studies, and relevant to environmental, health and safety assessments in general, is the particle surface area. Surface area is typically reported on a unit mass basis and referred to as the specific surface area (SSA); in exposure studies the *total* surface area may be reported, but it is determined using the same measurement approaches. SSA can be determined by different methods, and is generally considered to be a method-specific value. The most widely used method for determining SSA is based on isothermal gas sorption coupled with the Brunauer-Emmett-Teller (BET) isotherm analysis. The linear form of the BET equation is shown below:

$$\frac{p}{n^a \left(p^o - p \right)} = \frac{1}{n_m^a C} + \frac{\left(C - 1 \right)}{n_m^a C} \times \frac{p}{p^o}$$

where p and p^0 are the equilibrium and saturation pressure of the adsorbate gas (most commonly N₂), n^a is the quantity of adsorbed gas at equilibrium pressure (typically in cm³/g at standard

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[1] http://www.vamas.org/twa34/index.html

temperature and pressure, STP), n_m^a is the monolayer adsorption quantity (also at STP), and C is the "BET constant" (related to the heat of adsorption). Measurements are taken under isotherm conditions (77 K for N_2) at different p/p_0 values. The left side quantity of this equation is plotted against p/p_0 and the monolayer adsorption and constant C are obtained from the slope and intercept (which must be positive). By convention, only results obtained within the p/p_0 range between 0.05 and 0.3 (considered the linear range) are used for determination of the SSA. Then,

$$\text{SSA}_{\text{BET}} = \frac{n_m^a N a}{V_m}$$

where N is Avogadro's number, a_m is the effective cross-sectional area of an adsorbed molecule (taken by convention as 0.162 nm^2 for N_2), and V_m is the molar volume of the gas at STP (in cm^3).

The test protocol developed for this ILS (see Appendix A) is generally compliant with ISO 9277:1995 (Determination of the specific surface area of solids by gas adsorption using the BET method), ASTM C1274-00(2006) (Standard test method for advanced ceramic specific surface area by physical adsorption), and IUPAC recommendations[2] for the characterization of porous solids. The test material, protocol, and material safety data sheet were provided to all participating laboratories. Additionally, a spreadsheet template was provided to facilitate reporting of measurement results, instrumentation, protocol deviations, and analyst comments.

A total of 20 laboratories participated in the ILS, which included an international sampling of government, academic, and commercial organizations (see full listing below) representing a range of competence levels and instrumentation (both commercial and custom built). With two exceptions, all laboratories employed the static volumetric gas sorption method; one laboratory used the gravimetric gas sorption method and another used a dynamic gas sorption method. There is insufficient representation from gravimetric and dynamic methods to draw any conclusions regarding systematic differences in the reported results compared with the more commonly used static volumetric approach. As per the protocol, all participants used N_2 at 77 K as the adsorbate. The results of a single laboratory were excluded from global averaging after a quality check, using a widely available certified reference material, confirmed that their instrument was not operating at the required performance level. This laboratory is identified or referred to as an outlier in subsequent discussions.

2. Summary of Results

Figure 1 shows a summary of the multi-point BET laboratory means and standard deviations based on three replicate analyses. Several laboratories reported more than three replicates, in which case, a random number generator was used to select three values for averaging purposes. The global mean of laboratory means is shown as a solid line with the 95 % confidence intervals

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[2] *Pure Appl Chem*, **66**, 1739-58 (1994)

shown as dashed lines.[3] The global mean of means (54.7 m^2/g ± 1.2 m^2/g) was determined after exclusion of results from laboratory 18, which was determined to be an outlier. The removal of laboratory 18 was based on a follow-up quality check using a certified reference material. Both the reference and the test material results were substantially low, and the laboratory independently confirmed that the instrument was not functioning properly at the time of analysis.
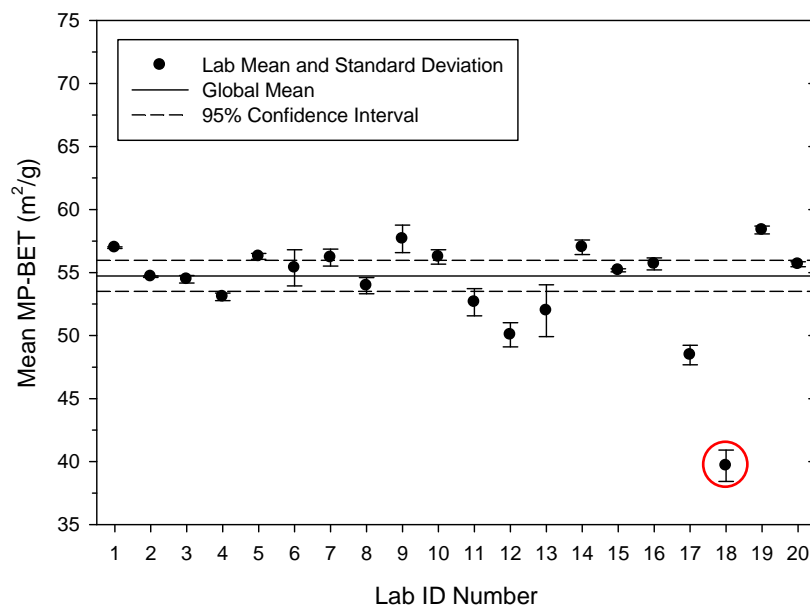

Figure 1. Mean multipoint (MP) BET results for all reporting laboratories. Solid line represents the global mean-of-means with the outlier (circled in red) removed (54.7 m^2/g) and dashed lines show the 95 % confidence intervals (± 1.2 m^2/g). Laboratory ID numbers were randomly assigned.

As can be seen in Figure 1, most laboratories fall within or close to the 95 % confidence intervals. The most commonly reported deviation from the protocol involved the use of a test mass outside the prescribed range (0.5 g to 0.6 g). Figure 2 therefore shows the mean multi-point results as a function of the mean test mass reported by each laboratory. A majority of laboratories used a test mass close to or within the prescribed range, but a substantial fraction deviated (mostly on the low side). Several laboratories reported using lower test masses due to size limitations of their sample bulb. Regardless, there is no obvious dependence on test mass apparent in Figure 2. In fact, based on these results and on robustness tests carried out at NIST prior to the ILS, it appears that a lower mass (between 0.1 g and 0.5 g) does not substantially alter the measured results. It is worth noting that one of the most significant contributions to variability is due to gravimetric errors; these errors are most likely to arise from incomplete degassing or weighing errors due to powder handling (e.g., static electricity can hinder accurate weighing and transfer of fine powders like SRM 1898). Such errors will tend to be independent of the nominal mass used in the analysis. On the other hand, errors resulting from an improperly calibrated balance, used to determine sample mass, or due to subtraction of the mass associated with the sample holder, should decrease with increasing test mass. Also of note, there is no clear

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[3] A 95 % confidence interval is approximated here by multiplying the standard error ($s/\sqrt{n}$, where s is the sample standard deviation and n is the number of samples) of the laboratory means by a coverage factor $k \approx 2$.

dependence of the results on the instrument manufacturer (see Figure 3). A total of 17 different instrument models from seven different manufacturers were used in this study. The single very low value associated with manufacturer ID = 1 is the previously identified outlier, which was traced to a transient (i.e., correctable) performance issue and does not reflect on the instrument or manufacturer. It does, however, reflect on the importance of using reference materials to verify performance of gas sorption analyzers.

Figure 2. Mean laboratory multi-point results as a function of the mean test mass used for the measurement. The hatch marked area indicates the mass range specified in the protocol. The previously identified outlier is excluded from this graph.

Figure 3. Mean laboratory multi-point results plotted versus instrument manufacturer. The manufacturer ID was randomly assigned. All instruments were commercially available except for one custom built system. The previously identified outlier is excluded from this graph.

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The one obvious correlation evident from the reported results is a roughly inverse relationship between the calculated multi-point SSA and the *C* value obtained from the BET fit as shown in Figure 4 (the previously identified outlier is excluded). The *C* value is an indication of the strength of interaction between the adsorbent and adsorbate, and is related to the heat of adsorption. The majority of SSA values that fall within the 95 % confidence interval in Figure 4 exhibit *C* values between roughly 80 and 100; reported mean *C* values did not exceed 140, although a few individual replicates did exceed this value.
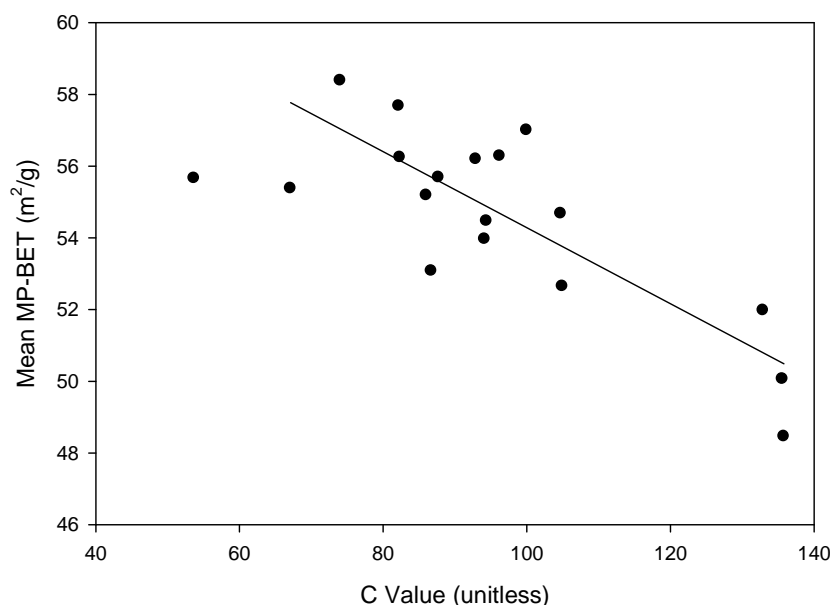
Figure 4. Correlation between laboratory mean multi-point SSA and the resulting *C* value obtained from the fit to the linear form of the BET equation.

Figure 5 shows a set of representative isotherms for measurements in which the test sample mass was similar and within the prescribed range. The linearity exhibited over the relative pressure range from 0.05 to 0.3 confirms the general appropriateness of using the BET model. Most of the laboratories reported p/p_0 ranges corresponding to the prescribed range (0.05 to 0.3); three laboratories reported a truncated range that ended near $p/p_0 = 0.2$, but the corresponding SSA results were close to the global mean and the calculated *C* values fell between about 80 and 100. It is also evident that the *C* values are subject to greater variation than are the corresponding BET SSA values.
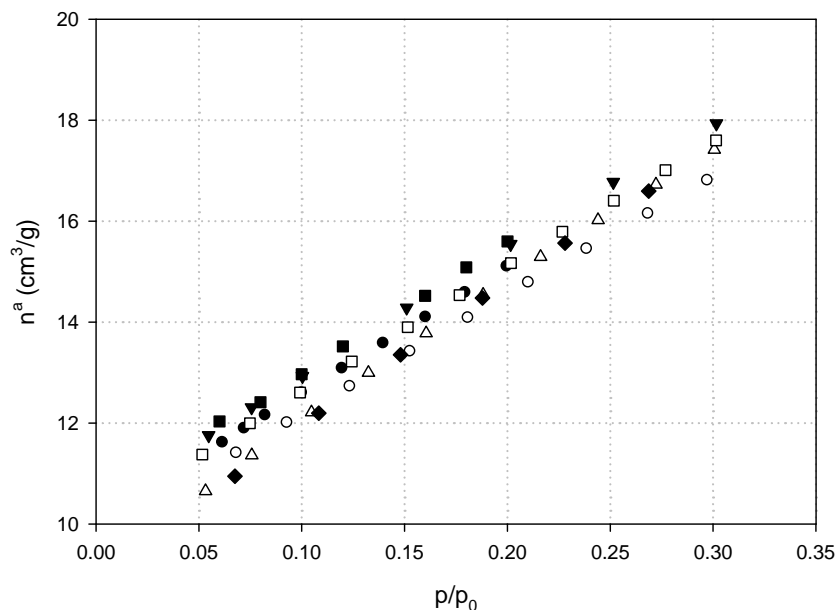
Figure 5. Representative isotherms selected from several reporting laboratories in which the test mass was in the prescribed range.

When presented with the choice between novice, intermediate or expert levels of competence, the majority of analysts identified themselves as intermediate. Only one analyst/laboratory identified itself as novice, and there was no clear pattern relating self identified competence level with the reported values. In fact, excluding the outlier, spreads for the intermediate and expert levels were nearly identical.

Figure 6 shows the laboratory means calculated using the single point BET method. Of the 20 participating laboratories, 16 reported a single point value. Apparently, some commercial instruments do not support single point analysis (a special form of the BET equation that requires a single data point, and requires certain assumptions). Additionally, the outlier (laboratory 18) has been excluded from Figure 6. The overall spread (95 % confidence interval = 1.0 m^2/g) is slightly smaller compared with the multi-point results, and the global mean of laboratory means (53.1 m^2/g) is also lower than the corresponding multi-point value by approximately 2.9 %; it is well established that the calculated single point value will typically be smaller than the multi-point value for the same material under the same measurement conditions.[4] The difference between the two values depends on the inherent C value and the relative pressure used for the single point measurement.

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[4] ISO 9277:1995, Determination of the specific surface area of solids by gas adsorption using the BET method.
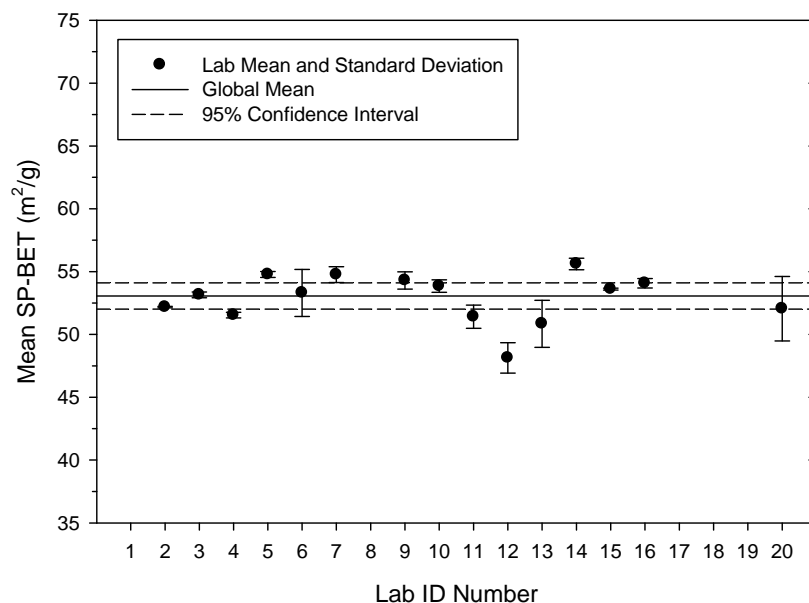
Figure 6. Mean laboratory single point (SP) BET results for each reporting laboratory, shown on same scale as Figure 1.

3. Comments, Test Deviations and other Considerations

The two most commonly reported deviations from the protocol involved use of a test mass outside the prescribed range and variations in the degas routine due to the lack of a programmable degas device. As stated previously, there does not appear to be any substantial problem associated with using lower test mass (within the range reported in this study). It is worth noting that a wide range of "sample bulbs" are available from different instrument manufacturers, and some laboratories appear to use only a single bulb type/size; in some cases this may limit the powder mass that can be easily accommodated depending on the volume/mass ratio of the test material (i.e., unconsolidated fine powders, such as SRM 1898, tend to occupy more space than, say, pelleted materials or coarser powders). Similarly, variations in the degas routine do not appear to have caused any substantial variations in the reported results. Here, based on robustness tests conducted at NIST and on published guidance (e.g., IUPAC recommendations), the most critical aspect is attaining the target degas temperature and holding that temperature for a sufficient period of time. Differences in the ramp routine employed to reach the target temperature are most likely not as important, and thus did not appear to impact the current study.

Surprisingly, only one laboratory reported any difficulty arising from the effects of static electricity on handling of the test powder; based on experiments conducted at NIST, such problems were anticipated and would be commonly encountered for other industrial fine powders. It is not clear if most laboratories used anti-static devices (as recommended in the protocol) as this was not generally reported, or if the local environmental conditions (primarily humidity) were such that static electricity was mitigated. It is certainly possible that some of the

observed variation can be traced to gravimetric or other effects arising from statically charged powder; however, this cannot be determined based on the ILS results.

Additionally, some laboratories may have used He to backfill the sample tube after degassing, rather than the recommended N_2. This can contribute a gravimetric error (underestimate bias) as a result of the difference in density between He and air, which leads to an overestimatation of the SSA. The magnitude of this error depends on the void space in the sample tube (i.e., sample tube volume minus the volume displaced by the sample), and can be substantial (of order 2 % to 5 %). Yet the effect can be minimized by using a smaller sample tube or by inserting a fill rod. Only one laboratory specifically stated that they used He as a backfill gas, but the reported SSA replicate values for this laboratory were well within the 95 % confidence intervals around the global mean. This laboratory also indicated that they were not equipped to seal their sample tube following degassing and backfilling, so it is entirely possible that some of the light He rapidly escaped and was replaced by air, thereby mitigating the effect; they also report using a fill rod, which would further reduce the impact of using He.

A final consideration worthy of comment is the prescribed degas dwell time (2 h). One analyst commented that, after 2 h of degassing at the target temperature, an increase in pressure was observed when the test sample was isolated from vacuum, suggesting incomplete degassing; they also report that at room temperature the pressure was stable. Robustness tests conducted at NIST prior to the ILS indicated that dwell times longer than 2 h did not impact the measured SSA. In fact, the SSA was roughly constant after about 1.5 h. The shorter dwell time was chosen primarily for convenience, but since the ILS has shown that the capacity to follow a specific ramp protocol may vary widely, using a longer dwell time may serve to lessen any potential effects due to variations in the ramp profile.

4. Participating Laboratories

Participating laboratories are listed below in alphabetical order, with the principal or initial contact identified in parentheses. VAMAS member laboratories are identified with a superscript V. Commercial instrument manufacturers are identified with a superscript M.

AAIPharma, USA (Bob Whittle)
BEL Japan Inc., Japan (Masayuki Yoshida) [M]
Delta Analytical Instruments, Inc., USA (Michael Riley)
Dupont, USA (Rick Maynard)
Environmental Protection Agency, National Risk Management Research Laboratory, USA (Chris Impellitteri)
Federal Institute for Materials Research and Testing (BAM), Germany (Peter Klobes) [V]
Food and Drug Administration, National Center for Toxicological Research, Center for Phototoxicology, USA (Paul Howard)
Hiden Isochema, UK (Mark Roper) [M]
Horiba Instruments Inc., USA (Amy Hou) [M]
Industrial Technology Research Institute, Center for Measurement Standards, Taiwan – measurements conducted at Particulate Technology Laboratory, TLIRI, National Taiwan University (Ta-Chang Yu) [V]
Korea Research Institute of Standards and Science, Republic of Korea (Byung Il Choi) [V]
Micromeritics Instrument Corporation, USA (Jeff Kenvin) [M]
National Institute for Occupational Safety and Health, USA (Aleksandr Stefaniak)
National Institute for Occupational Safety and Health, USA (Mike Keane)
National Institute of Standards and Technology, Engineering Laboratory, USA (Chiara F. Ferraris/Max Peltz)
National Physical Laboratory, UK (Richard Gilham) [V]
Quantachrome Corporation, USA (Riaz Ahmad) [M]
University of Cincinnatti, USA (Hafiz Salih)
University of Iowa, Department of Chemistry, USA (Vicki H. Grassian)
University of Massachusetts - Lowell, USA (Dan Schmidt)

4. Acknowledgements

Appendix A: Study Protocol

PLEASE READ ENTIRE DOCUMENT BEFORE BEGINNING TESTS

Safety Precautions and Material Handling

Please exercise caution in handling the test material. Refer to the enclosed MSDS sheet for further information on control techniques to reduce exposure. Note that this material has a low bulk density and easily forms an aerosolized dust when disturbed. Use of a properly working HEPA-filtered balance enclosure or vented hood may be appropriate for sample transfer and weighing operations. Work incrementally with small volumes of material in order to minimize potential exposure. After completion of analysis, used test material should be disposed of following your organization's recommendations or policies regarding disposal of inorganic nonreactive nanomaterials. Use personal protective equipment that is appropriate for work involving a powdered ultrafine material (e.g., lab coat, gloves, eye protection such as safety glasses/goggles). Consult the NIOSH Respirator Selection Logic (NIOSH 2004) for guidance on respirator selection.

1. Apparatus

The procedure is written for static volumetric (manometric) or gravimetric gas sorption instruments using N_2 as the adsorbate at liquid nitrogen temperature. Use of a dynamic flow type instrument or use of an adsorbate other than N_2 is permissible for this study, but it is the participant's responsibility to implement the procedure correctly and to fully report any deviations from the protocol. The procedure also assumes that the analyst is competent using the test instrument and is knowledgeable with respect to general gas sorption methodology including the manufacturer recommended procedures for determination of the BET specific surface area (BET-SSA).

2. Reagents and Materials Required

Nitrogen, helium or other gases used in the analysis should be ultra-high purity grade (99.99+ %). Standard glass sample tubes, fill rods and other measurement hardware typically used for gas sorption analysis of powdered solids. Analytical balance capable of 0.1 mg precision. Equipment capable of maintaining a sample degas temperature of 200 ºC.

3. Test Material

You have been provided with a single bottle containing approximately 5 grams of nanocrystalline titanium dioxide (TiO_2) powder test material; material removed from the bottle should be used only once, and then disposed of following each analysis. There is sufficient test material for 10 or more independent analyses.

4. Calibration of Measurement Apparatus

Follow the manufacturer's instructions for calibration and operational verification of your test instrument. No special procedures are required.

5. Test Procedure

The test procedure described below is generally compliant with ISO 9277:1995 (Determination of the specific surface area of solids by gas adsorption using the BET method), ASTM C1274-00(2006) (Standard test method for advanced ceramic specific surface area by physical adsorption), and IUPAC recommendations for the characterization of porous solids (Pure & Appl. Chem., Vol. 66, pp. 1739-58, 1994).

5.1 Sampling and Loading of Test Material

Prior to opening, gently roll and invert the bottle several times to ensure good mixing of the test material. If you have an anti-static device, apply it to your sample tube and the sample bottle before removing test material; this will reduce static dispersal of the powder.

Select a clean dry sample tube appropriate for powdered solids; the sample tube should be rinsed with laboratory alcohol and dried at (100 to 110) ºC for at least 2 hours. Use a fill rod (volume displacement device), if available, to reduce the free space. **Determine to 0.1 mg precision** the combined mass of the sample tube, fill rod and stopper (or seal frit or other tube sealing device appropriate for your sample tube). This is the empty tube mass.

Weigh out between 0.5 and 0.6 grams of test material onto a clean weighing paper or weighing boat; the exact mass is not critical. Transfer the test material to the pre-weighed sample tube. Depending on the size and geometry of your sample tube, it may be possible to use a funnel or it may be necessary to add the test material incrementally using a small spatula or spoon. Powder has a tendency to adhere to the sample tube inner wall because of static electricity. Use a pipe cleaner or employ an anti-static device to ensure that powder does not adhere to the wall above the liquid N_2 level. Add the fill rod (if using one) and seal the tube. Transfer the tube to the degas port of your instrument.

5.2 Degassing the Test Sample

The test material should be degassed <u>under vacuum</u> by raising the temperature from ambient to 200 ºC within approximately 60 min, then holding at **200 ºC for 2 hours**. Afterwards, the sample should be allowed to cool slowly back to ambient [Note: if degassing is programmable on your instrument, the temperature should first be raised to 110 ºC at a rate no faster than 10 ºC/min and held there for 10 min, before continuing to the target degas temperature at a rate no faster than 10 ºC/min]. The sample tube should be backfilled with N_2 gas after completion of the degas procedure [Note: <u>do not</u> backfill with He, as this will cause a significant tare weight error].

After cooling to ambient, remove the sample tube and immediately seal tube with stopper if not using a built-in sealing device (e.g., seal frit), then determine the post-degas mass to 0.1 mg. Subtract the mass of the empty tube determined before degassing; the difference is the test sample mass. Record this value.

5.3 Analysis

Attach the sample tube containing the degassed test material to the analysis port of your instrument according to the manufacturer's instructions. **Select at least 4 analysis points** (no more than 10) in the relative pressure (p/p^o) range between 0.05 and 0.3; the points should be evenly spaced within this range. Measurements should be taken at each point after equilibrium is established.

Input the degassed sample mass calculated above. Use a value of 0.162 nm^2 for the molecular cross-sectional area of N_2 at 77.3K. For other parameters and settings, use the instrument manufacturer's recommended values for routine BET-SSA analysis.

To ensure integrity of the sample cell and port seal prior to initiating measurements, the analysis protocol should include a leak test performed after pulling a vacuum and sealing the sample tube.

5.4 Calculation and Reporting

Results should be analyzed using the linear BET equation:

$$\frac{p}{n^a\left(p^o-p\right)}=\frac{1}{n^a_m C}+\frac{(C-1)}{n^a_m C}\times\frac{p}{p^o}$$

where n^a is the amount adsorbed at the relative pressure p/p^o, n^a_m is the monolayer capacity and C is a constant dependent on the isotherm shape and strength of the adsorbate-sorbent interaction. This analysis is typically accomplished automatically on commercial instruments.

Use the accompanying Excel file to report your results. The following data should be reported:

1. calculated multipoint and single point BET-SSA values in m^2/g
2. calculated C value
3. r^2 (correlation coefficient) from the linear fit to the BET equation
4. "raw" adsorption isotherm data: n^a, amount of gas adsorbed (in units of moles/g or cm^3/g at standard temperature and pressure) versus p/p^o
5. sample mass (grams) after degassing, to 0.1 mg precision

Report analysis results for at least **3 replicate measurements** performed on separate samplings of the test material (i.e., do not reanalyze the same sample of test material, but use fresh samples independently degassed and analyzed).

Additionally, please report the following information using the Excel reporting file:

❖ Organization
❖ Name of analyst
❖ Level of analyst expertise
❖ Date(s) of analysis
❖ Instrument make and model
❖ Deviations from standard protocol
❖ Problems encountered with the test material or procedure; other comments

The specific identity of reporting laboratories will be known only to the study organizers. Each organization will be acknowledged generically, but assigned an identification number for publication of results. The laboratory ID will provide anonymity, but allow each participant to compare their results within the context of all reported results. The IDs will be assigned only after the study is completed and the results are released.

Results should be sent electronically to: <u>vince.hackley@nist.gov</u> using the Excel reporting form.

Questions or problems should be directed to the email address above, or you may call Vince Hackley at (301) 975-5790.