Adsorption 11: 61–66, 2005

Gas Adsorption Data Uncertainty and Propagation Analyses

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Abstract. Experimental uncertainties inherent to manometric gas adsorption techniques are identified, analysed, calculated and discussed. Contributions of these uncertainties to the amount of nitrogen adsorbed and to the BET specific surface area of a carbon black standard were evaluated. Inaccurate liquid nitrogen level control affects the equilibrium pressure and hence the amount of gas adsorbed. The sources of greatest (controllable) uncertainty are liquid nitrogen level control, sample preparation conditions and sample mass measurement.

Keywords: adsorption, BET specific surface area, experimental uncertainty

1. Introduction

The manometric gas adsorption technique is the most often used experimental procedure for the characterization of powdered adsorbents. Such measurements lead to the evaluation of the amount of gas adsorbed, Brunauer-Emmet-Teller (BET) specific surface area (SSA), pore volume and pore size distribution (PSD). Every experimental result is characterized by its experimental uncertainty, i.e. the range of possible variation of the actual measured parameter. If an experimental method incorporates measurement and control of several parameters, then uncertainties and inaccuracy in their control contribute to the final calculated results. Thus, researchers working in the area of characterization of porous materials should appreciate the necessity for the following actions: the determination of all experimental parameters, a detailed analysis of uncertainties associated with them, and understanding and evaluation of how these uncertainties propagate into the final results.

Sources of uncertainties in manometric adsorption include the dosing and sampling volumes, temperature control of these volumes, dosing, equilibrium, and barometric pressure measurements, liquid nitrogen level-control, and sample mass measurements; data processing errors derive from ignoring thermal transpiration effects and non-ideal gas behavior (Badalyan and Pendleton, 2003). In addition to these sources of uncertainties, we will discuss the influence of departure from the ideal gas behavior on the amount of gas adsorbed, and on subsequent calculations and results. Although the second virial coefficient can account for low pressure non-ideal gas behaviour, at supercritical pressures the relatively dense continuous phase requires the inclusion of the third virial coefficient, or the use of another equation of state. The virial equation of state (VEoS) truncated after the third virial coefficient gives an accuracy of compressibility values to within 10^{-4} at temperatures $>T_c$ for densities up to about 0.17 ρ_c (Trusler, 2000). This limit is not unique; Badalyan reported an average error of 0.18% in density data for n-octane using the third virial coefficient to densities up to 0.3 ρ_c at both sub- and supercritical temperatures (Badalyan, 1987). At higher densities, cubic equations of state (CEoS) or multiparameter equations of state (MPEoS) are usually employed.

The Peng-Robinson (PREoS) (Fitzgerald et al., 2003) or the Soave-Redlich-Kwong (SRKEoS) (Zhou et al., 2002) CEoS and the Bender (BEoS) (Herbst and Harting, 2002; Puziy et al., 2003; Ustinov and Do, 2003) or Benedict-Webb-Rubin (BWREoS) MPEoS are the most widely used EoS' to evaluate supercritical gas phase density. In each case, these authors did

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not evaluate the effect of the errors in adsorbate density determination on the amount of gas adsorbed. The effect can be easily estimated by comparison of values for the amount of gas adsorbed calculated using reliable density data with those calculated via adsorbate density data calculated according to the chosen EoS.

Previously, we showed how the quoted reproducibility of BET SSA results between different laboratories is overestimated due to a lack of experimental uncertainty considerations between different equipment and calibration procedures (Badalyan and Pendleton, 2003). Here, we revisit the various sources of experimental uncertainties and discuss their contributions to a combined experimental uncertainty in BET SSA evaluation during manometric gas adsorption measurements, and comment on their implications for supercritical gas adsorption analyses.

2. Sources of Uncertainties and Their Evaluation

2.1. Volume Calibration

The calibration of the various physical volumes in any manometric gas adsorption apparatus must be made by a direct method whenever possible usually by filling a compartment with a degassed fluid at a known temperature at atmospheric pressure. In most cases one may employ water and appropriate reference density data (Lide and Kehiaian, 1999). The accuracy of this procedure depends on the extent of degassing, mass measurement reproducibility, and on the temperature control and its measurement of the environment in which the volume determination is made. For most equipment, this volume (plus water) and isolation valve exceeds 500 g; since the standard uncertainty for most balances in this range $< \pm 0.005$ g, and considering the combined standard uncertainty (CSU) u_c (water density), the relative combined standard uncertainty, (RCSU) u_c (vol)/vol $\approx 0.16\%$. When making several parameter measurements (for example, volume for this case), it is very important to acknowledge that the sample standard uncertainty (SSU) for a parameter may be greater or less than the CSU, which is usually calculated using the law of propagation of uncertainties (Taylor, 1982). It is advised to use the greater of these uncertainties.

Another source of uncertainties is due to the determination of the dosing volume since it is usually not possible to apply the above direct method. The most frequently applied method involves helium expansion from a known physical volume to an unknown one at isothermal conditions, for example at room temperature. Reliable helium density data (McCarty and Arp, 1990) should be used for dosing volume calculations. Ultra-high purity gas should be employed. A volumetric EoS or interpolated density data may be used to solve the mass balance leading to the unknown volume determination. At normal temperatures the ideal gas EoS is suitable to define expansion volumes: the agreement between dosing volume calculations via the ideal gas EoS, the VEoS and interpolated density (from NIST tables) is within 0.006%. However, the value of the RCSU (dosing volume), obtained using material balance equation for various gas expansions and equation for uncertainty propagation, is much greater at 0.22% (Badalyan and Pendleton, 2003). Provided the dosing and measuring manifolds are maintained at the calibration temperature, thermal expansion contributions can be neglected. If large temperature differences exist they should be considered.

2.2. Dead-Volume Evaluation

Some researchers perform dead-volume measurements with helium gas at cryogenic temperatures, some at room temperatures, others more recently suggest at temperatures as high as 400°C (Malbrunot et al., 1997). The former approach is suitable for non-microporous adsorbents, the second and third for microporous materials wherein helium adsorption is purported to occur at cryogenic temperatures (Malbrunot et al., 1997; Rouquerol et al., 1999). Rouquerol suggests that the first approach is more accurate, provided that the temperature gradients can be reproduced. In the case of a glass tube adsorbent cell, the low thermal conductivity of Pyrex glass promotes this gradient reproduction without the introduction of a significant error. However, in the case of a stainless steel sampling cell, which may also be used for low pressure measurements as well as for high-pressure gas adsorption, such reproducibility is more difficult to achieve. Therefore, it becomes important to account for the temperature gradient from cryogenic to room temperatures along the sampling tube when calculating the amount of gas adsorbed. Our calculations were based on dividing this transition part of the stainless steel sample cell into 15 isochoric intervals, and calculating the amount of gas in each interval using either the VEoS (for low pressure nitrogen adsorption during calibrating nitrogen adsorption measurements at 77 K) or interpolated density data for high pressure adsorption (Badalyan and Pendleton, 2004). To demonstrate the impact of this temperature gradient on the BET SSA, we obtained 110.49 m^2/g, when taking into account the temperature gradient along the sampling tube, and 106.80 m^2/g, when not doing so. The difference between them is about 2.81%, which is much greater than the RCSU value of $\approx$0.63% reported earlier, but is consistent with the expanded uncertainty quoted for this material and other NIST standard surface areas (Badalyan and Pendleton, 2003). It is equally important to note that the former SSA value agrees within 0.16% of our previously reported area of 110.31 m^2/g.

It is also important to appreciate that since this volume is used in all subsequent amount adsorbed calculations, very careful consideration should be given to the precision of the liquid nitrogen level control during data collection.

2.3. *Liquid Nitrogen Level Control*

Liquid nitrogen level control has a direct impact on $u(P_e)$ and on the $u_c(n_i)/n_i$ (Badalyan and Pendleton, 2003). Previously (Badalyan et al., 2001) we reported a liquid nitrogen level control device capable of maintaining level control with SU of $< \pm 0.2$ mm around the sampling tube. Figure 1 shows how our recent modifications to this device (Badalyan and Pendleton, 2003) have reduced this uncertainty to $< \pm 0.06$ mm.

Allowing the liquid nitrogen level to fluctuate by $5\times$ the normal sensitivity of ± 0.2 mm during adsorption/desorption measurements generates a relative error in P_e/P_0 in the range -0.42% to $0.52\% \approx 10\ u_c(P_e)$ and the volume of gaseous nitrogen adsorbed varies between -8.53 to $+5.94\%$, as summarized in Tables 1 and 2. Of course, the magnitude of these errors is a function of the apparatus and the included dosing and expansion volumes. An examination of the data in Tables 1 and 2 indicate the sensitivity to precise liquid nitrogen level control.

2.4. *Calculation the Amount of Gas Adsorbed*

The calculation of the amount of a gas adsorbed is usually achieved via a material balance analysis of the amount of gas present in the various parts of the apparatus before and after equilibration. The amount present is usually determined from gas phase density evaluations, either via a precise volumetric EoS or via (P, ρ, T) tables. When adsorption experiments are carried out at sub-atmospheric pressures and cryogenic temperatures, the use of the ideal gas EoS (IGEoS) gives erroneous results. We have found that the VEoS including the thermal dependence of the second virial coefficient

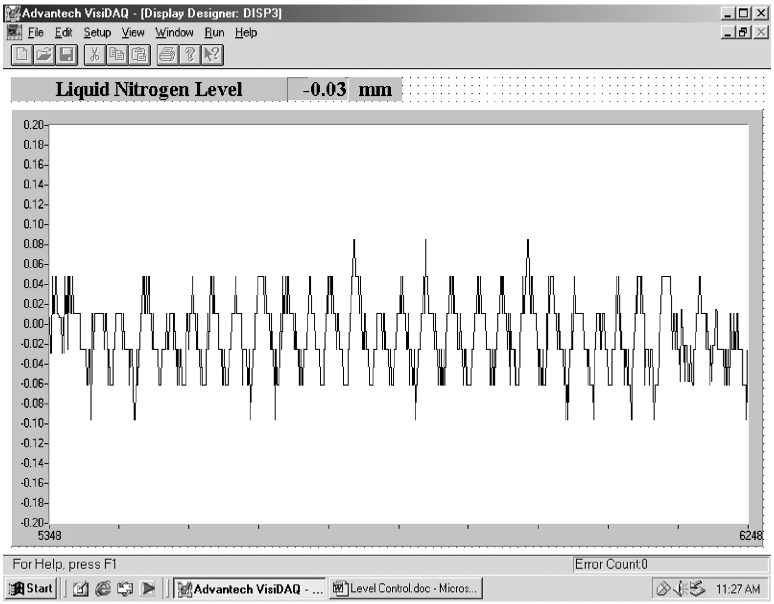

Figure 1. Typical liquid nitrogen level control.

Table 1. Influence of liquid nitrogen level control on pressure measurement precision.

P_e at $L = 0$ (Torr)	P_e at $L = -1$ mm (Torr)	Error (%)	P_e at $L = +1$ mm (Torr)	Error (%)
44.804	45.036	0.52	44.617	−0.42
201.30	202.00	0.35	201.01	−0.14
398.96	399.90	0.24	398.30	−0.17
592.27	593.16	0.15	591.53	−0.13

Table 2. Influence of liquid nitrogen level control on amount of nitrogen adsorbed.

V_{ads} at $L = 0$, cm^3 (STP)/g	V_{ads} at $L = -1$ mm, cm^3 (STP)/g	Error (%)	V_{ads} at $L = +1$ mm, cm^3 (STP)/g	Error (%)
23.47288	22.61072	−3.67	24.16780	2.96
30.61655	28.00546	−8.53	31.69827	3.53
41.62508	38.10121	−8.47	44.09923	5.94
56.22882	52.87503	−5.96	59.01730	4.96

(Badalyan and Pendleton, 2003) adequately accommodates the departure from ideal gas behaviour. A thermal relationship of the second virial coefficient for nitrogen is available from Dymond and Smith (1980) or from the IUPAC Tables (Angus et al., 1979). Provided all gas pressures are <1 atm, inclusion of the third virial coefficient makes negligible contributions. Application of the VEoS gives $0.28\% < u_c(V_{\text{ads}})/V_{\text{ads}} < 0.93\%$ over the pressure range $7.0 \times 10^{-7} P_0 < P < 0.98\ P_0$; this increase in RCSU reflects the cumulative nature of the experimental uncertainty, which, of course, has a far-reaching effect on mesopore analyses. Figure 2 shows how $u_c(V_{\text{ads}})$ varies with relative pressure during the adsorption and desorption branches of the isotherm.

When carrying out gas adsorption experiments from low-to-high pressures, one should, if possible, employ a single EoS. The VEoS truncated even after the third virial coefficient does not provide accurate density data. One may resort to CEoS', e.g. PREoS or SRKEoS, or more computationally complex MPEoS', e.g. BWREoS or BEoS, or Lee-Kesler corresponding states tables. Daubert et al. (1978) suggest that the PREoS is superior to the SRKEoS in the vicinity of the critical point, while Assael (1996) points out that Lee-Kesler corresponding states tables give more accurate results compared with the PREoS, however the computer time needed for these calculations is ten times that for PREoS. Jacobsen et al. (2000) warn that although BWREoS gives results sufficiently accurate for technical purposes for the gas and for supercritical states with low to moderate densities, they should not be used for scientific purposes when highly accurate density data are needed.

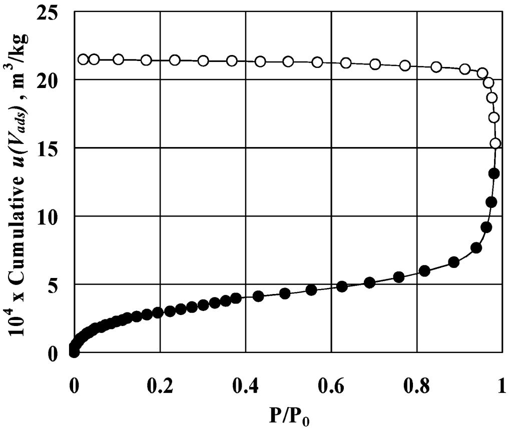

Figure 2. Cumulative CSU for the nitrogen amount adsorbed: ● adsorption; ○ desorption.

When calculations are made in real-time during low-to-high pressure adsorption experiments, data acquisition and subsequent calculations need to be performed quickly with minimal error in the final results. The PREoS leads to large uncertainty at high pressures; MPEoS' are computationally too cumbersome. We suggest one employs simple cubic interpolation techniques of density data, for example, Span et al. (2000), leading to errors within 0.05–0.10% of the reported data.

2.5. *Calculation of BET SSA*

Aside from its well-known limitations, the BET equation remains the foundation of material specific surface area analysis. Here, we analyse its structure for the correct evaluation of the uncertainty in BET SSA. Standard reference suppliers provide sample preparation conditions and data analysis specifications; for the reference carbon black analysed herein, we calculate the BET SSA in the range $0.04P_0$–$0.2P_0$. The BET SSA is a function of the average area occupied by an adsorbed molecule in the statistical monolayer, the molar volume, and the monolayer equivalent amount of the gas adsorbed via the "slope" and "intercept" of the linearised BET equation. The first two terms can be regarded as constants with fixed uncertainty. To calculate the $u_c(V_{\text{ads}}^m)$ one need to determine $u_c(x_i)$ and $u_c(y_i)$ where $x_i = P_{e_i}/P_0$, and $y_i = (P_{e_i}/P_0)/\lfloor V_{\text{ads}}(1 - P_{e_i}/P_0)\rfloor$. Analysis of these uncertainties reveals that $u_c(x_i) \ll u_c(y_i)$ requiring a weighted least squares analysis to give u_c (slope) and u_c (intercept) (Taylor, 1982). Using a weighting function in the form of $w_i = 1/[u_c(y_i)]^2$ leads to $u_c(y) = \sqrt{\sum_{i=1}^{n} (y_i - a - bx_i)^2/(n-2)}$ and slope, $a = 39.041$, and intercept $b = 0.276$, $R^2 = 0.9996$. Consequently, we find $u_c(V_{\text{ads}}^m) = 1.59 \times 10^{-4}$ $\text{m}^3(STP)/\text{kg}$ with $u_c(S_{\text{BET}}) \times 100\%/S_{\text{BET}} = 0.63\%$ (Badalyan and Pendleton, 2003).

2.6. Other Sources of Uncertainties

Uncertainty in the calculation of the SSA is also the result of contributions from a series of other uncertainty sources. Sample mass measurement errors make a significant impact on *all* data calculations. Additionally, a decrease in mass resolution from $\pm 5 \times 10^{-5}$ g to $\pm 5 \times 10^{-4}$ g causes $u_c(V_{\text{ads}})/V_{\text{ads}}$ to increase ten fold, now varying from 2.78 to 9.86% over the relative pressure range from 7×10^{-4} to 0.98. For a similar standard u_c(mass) applied to the BET specific surface area analysis, the final area RCSU increases from 0.63 to 6.19%. Therefore, whenever possible, one should measure the adsorbent mass when it is evacuated and contained in the sampling cell with an isolation valve using an analytical balance capable of accommodating the cell etc. with minimum uncertainty.

Thermal transpiration effects should always be considered at low pressures and when significant temperature differences exist between the pressure gauge and the sample cell. Takaishi and Sensui's thermal transpiration expression (Takaishi and Sensui, 1963) reduces an error from about 42.21% at an equilibrium pressure of 6×10^{-4} Torr to about 0.003% at an equilibrium pressure of 2.3691 Torr. These results show that if the first experimental equilibrium pressure is about 2 Torr, then one may neglect the thermal transpiration correction without introducing a significant error. Of course, these values are specific to each experimental apparatus, especially since the effect is also a function of a sample cell tube diameter. Calculation of the $u_c(V_{\text{ads}})$ should include uncertainty from the transpiration expression.

Most commercial and other adsorption units are constructed from 316 stainless steel. Over the temperature range 273–373 K, the change in manifold RCSU is 0.005%, which is significantly less than the RCSU of the dosing volume and may be neglected.

3. Conclusions

The principal contribution to the uncertainty in BET SSA evaluations are uncertainty in: outgassing sample mass, dead-volume determination, and liquid nitrogen level control. The contribution of thermal transpiration suggests that although it is only applied at low pressures, it impacts on the uncertainty of subsequent amounts of gas adsorbed due to the cumulative nature of the uncertainty propagation.

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