Evaluating the experimental uncertainty in gas and vapor sorption/adsorption measurements: fundamental considerations and experimental design implications

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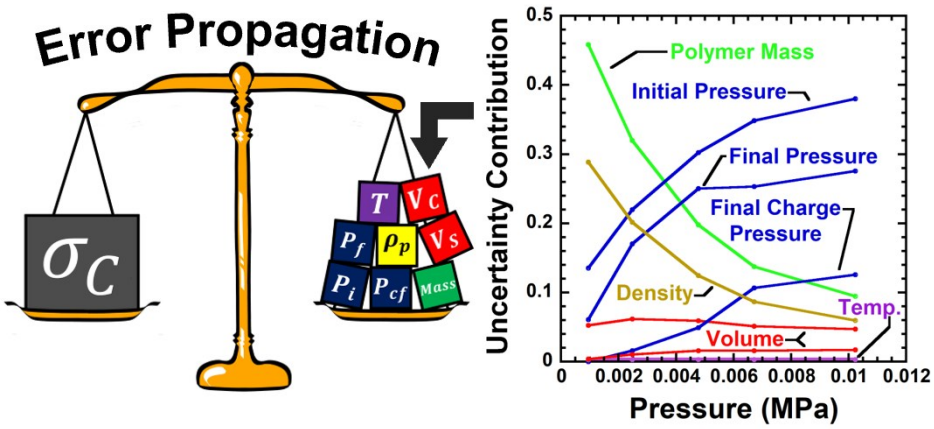

Abstract

High quality, accurate and reliable sorption and adsorption data provide the basis for designing large scale, energy efficient membrane/adsorption processes for gas and liquid separations and evaluate their techno-economic feasibility. As highlighted by Prof. David Sholl during his plenary lecture at the 2020 NAMS (*North American Membrane Society*) conference, the lack of uncertainty associated to published sorption/adsorption data represents one of the major roadblocks to progress in separation technologies. In this study, a standard methodology to estimate the uncertainty associated to sorption/adsorption measurements is proposed. A systematic analysis of the experimental uncertainty of gas and vapor sorption/adsorption measurement in polymers using the barometric method is performed in a variety of operative conditions, to individuate which factors contribute the most to the overall uncertainty under different experimental operation modes. This effort should push researchers in the field to adopt a standardized method to estimate the experimental uncertainty, which is expected to make experimental data coming from different laboratories in the world easier to compare.

Finally, the validity of the linear error propagation method, generally used to evaluate the uncertainty of sorption/adsorption data, is demonstrated by a *vis-à-vis* comparison with the Monte Carlo statistical method. Fundamental aspects and practical implications are highlighted and discussed.

1. Introduction

As worldwide energy demand increases, a more rational use of natural resources has become necessary. As 15% of the world's energy consumption is due to chemical separations[1], membrane technologies, used as both stand-alone and integrated processes, provide a viable pathway towards energy-efficient separations[1-3]. Although energy-efficient and eco-friendly separations are possible, the perceived risk in implementing them must be minimal. The availability of high quality, accurate, and reliable transport data (e.g., sorption and adsorption isotherms, permeability and selectivity data) is one of the major roadblocks to the design of new processes and to the evaluation of their technical and economic feasibility[1, 4-7].

More generally, the need for accurate and reproducible data is a major issue in several other areas of science[5-6, 8-11]: for example, in drug discovery, attempts to reproduce 53 landmark papers' data were successful in only 11% of the cases[12]. A major issue is the availability of uncertainty associated with published experimental data[6, 10, 13]. Often, membrane- and sorbent-related papers do not report details about how the experimental uncertainty was estimated, which prejudices the quality and usability of the reported data[13-14]. A critical issue is the lack of a standard, universally adopted method to estimate the experimental uncertainty, which often makes experimental data coming from different laboratories around the world difficult to compare[6, 10, 13-14].

The scope of this study is to provide a unifying approach to calculate the experimental uncertainty associated with gas and vapor sorption/adsorption measurements in polymers using the barometric (i.e., pressure decay) method. This is of major interest in membrane science, as well as related fields, such as batteries, gas storage, adsorption and controlled drug release. This

need has been highlighted by Prof. David Sholl at Georgia Institute of Technology during his plenary lecture at the 2020 NAMS (*North American Membrane Society*) conference.

Ideally, experimental uncertainty should be calculated by comparing a series of repeated measurements, which encompasses the effects of both systematic and random errors. In practice, there exist multiple impracticalities that prohibit this approach. For example, running enough sorption tests to satisfy statistical requirements would be extremely time consuming. Moreover, the cost of materials, whose availability is often limited to a few milligrams, can be prohibitive if repeated experiments are needed. To overcome these issues, the experimental uncertainty can be estimated in a predictive fashion using the so called error propagation methods, that is, using the experimental uncertainty associated to relevant parameters that affect the experiment[15-16]. In this paper, we propose a general, unifying methodology to evaluate the uncertainty associated to gas and vapor sorption/adsorption measurements in polymers using the barometric technique, which is expected to make experimental data from different laboratories easier to compare.

2. Validity and limitations of the proposed approach

The generalized analysis presented in this study refers to sorption/adsorption measurements via the pressure decay method, which is used in several laboratories around the world to measure gas and vapor sorption/adsorption isotherms in polymers and porous materials[17-19].

2.1 Vapor sorption measurements. The experimental setup generally consists of a sampling chamber, which contains a known mass of polymer, and a charge chamber, which houses a pressure transducer[20-22]. The two chambers are connected through a valve. The charge chamber is also connected to both a vacuum line and vapor generator (cf. Fig. 1A)

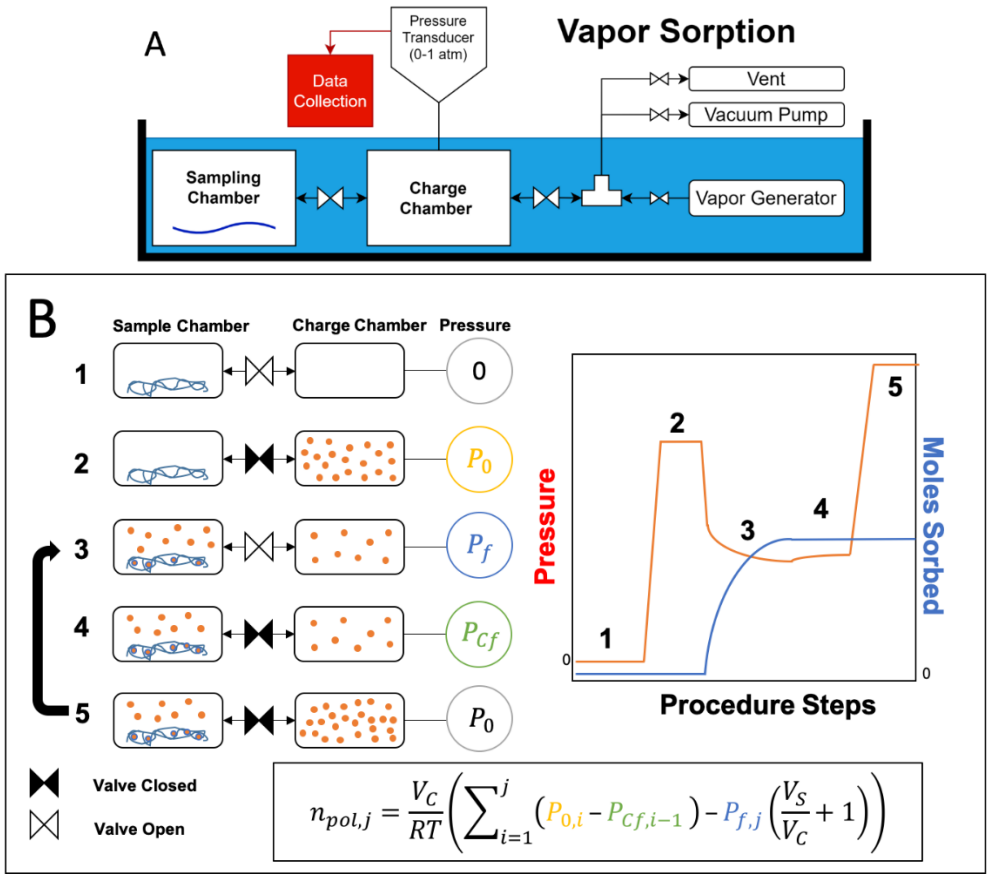

Figure 1. *A) Schematic of the constant volume pressure decay apparatus used to measure vapor sorption/adsorption in polymers and porous materials. B) Schematic of a typical vapor sorption measurement using the differential method.*

The entire apparatus is submerged in a water bath to maintain the temperature to the desired value. First, a full vacuum is pulled throughout the system to remove air and any trace of solvent or humidity trapped in the polymer (cf. Fig. 1B, *1)*). Then, the valve between the two chambers is closed and the charge chamber is filled with vapor and a few minutes are allowed for the pressure reading to stabilize (cf. Fig. 1B, *2)*). The sorption experiment starts by opening the valve separating the two compartments. The single transducer now reads the pressure of the combined sampling and charge chamber volume. A step pressure decrease is observed, due to vapor expansion, followed by a slower exponential decay resulting from vapor being sorbed in the polymer sample (cf. Fig. 1B, *3)*). Equilibrium is reached when pressure attains a constant value for several hours.

Further measurements are taken in a stepwise fashion, by closing the valve to the sampling chamber (cf. Fig. 1B, *4)*), adding more vapor to the charge chamber (cf. Fig. 1B, *5)*) and repeating the procedure described above. Vacuum is not pulled in between steps, making the analysis in this report specific to the *differential* sorption method.

The number of moles of vapor sorbed in the polymer at any equilibrium pressure was determined from the penetrant mass balance (cf. Fig. 1B). Specifically, the number of moles of vapor sorbed in the polymer at the end of any sorption step is equal to the initial number of moles of vapor fed to the system minus the number of moles in the external, contiguous vapor phase when sorption equilibrium is reached. Since vapor sorption experiments are run using the differential mode, the penetrant mass balance must take into account that some vapor will be left in the sampling chamber when closing the valve in between differential steps. Finally, the number of moles of vapor sorbed in the polymer during the previous step must be added.

To get the number of moles from pressure data, an equation of state must be used. The ideal gas equation of state is normally applied to run these calculations, based on the low-pressure operating conditions that usually accompany vapor sorption experiments ($\ll$ 500 Torr)[20-23]. The reliability of this method has been proved by elaborating the pressure data using the ideal gas equation of state and a generalized (i.e., Peng-Robinson[24]) equation of state, which provided the same results. Replacing the ideal gas equation of state into the penetrant mass balance, provides the following expression for the number of moles of vapor sorbed in the polymer at any given step *j*:

$$n_{pol,j} = \frac{V_C}{RT}\left(\sum_{i=1}^{j}\left(P_{0,i} - P_{Cf,i-1}\right) - P_{f,j}\left(\frac{V_S}{V_C} + 1\right)\right) \qquad \text{(Eq. 1)}$$

where V_S is the sampling chamber volume, V_C is the charge chamber volume, T is the absolute temperature and R is the universal gas constant. The volumes V_S and V_C are accurately measured using the Burnett method[25]. The subscripts "c" and "s" refer to the charge and sorption chamber, respectively, while "0" and "f" stand for initial and final, respectively. P_0, P_{Cf}, and P_f refer to the initial charge, final charge, and final overall pressures, respectively. Finally, the vapor concentration in the polymer at step j, $C_{pol,j}$, that is, the ratio between the number of moles of vapor sorbed by the polymer to the polymer volume, is calculated as follows:

$$C_{pol,j} = \frac{(n_{pol,j})\rho_{pol}}{m_{pol,dry}} \qquad \text{(Eq. 2)}$$

where ρ_{pol} is the polymer density and $m_{pol,dry}$ is the mass of the dry polymer sample.

The technical features of the vapor sorption apparatus considered in this study are shown in Table 1. As a case study, in this paper we consider methanol vapor sorption data at multiple temperatures in a Celazole® polybenzimidazole (PBI), reported previously by Bye et al.[20] and Loianno et al[21].

Table 1. *Technical details of the vapor sorption apparatus considered in this study.*

	Experimental range/value	*Uncertainty*	*Source*
Pressure sensor (MKS PDR2000 dual-capacitance manometer)	*0-500 Torr*	*0.25% of the reading*	*manufacturer*
Temperature controller (Techne TU-20HT immersion circulator)	*-20 to 120°C*	*± 0.5°C*	*manufacturer*
Charge chamber volume	*29.4778 cm³*	*± 0.098 cm³*	*Burnett method*
Sampling chamber volume	*7.63068 cm³*	*± 0.023 cm³*	*Burnett method*
Polymer mass (measured using a Mettler-Toledo ME54T3 analytical balance, weighing capacity = 52 g)	*0.005 to 0.01 g*	*± 0.0005 g*	*manufacturer*
Celazole® polybenzimidazole (PBI) density (measured with an Archimede's balance)	*1.27 g/cm³*	*± 0.014 g/cm³*	*[26]*

2.2 Gas sorption measurements. The setup used to measure gas sorption is similar to that used for vapor sorption measurements, but with two key differences. First, during the sorption process the valve between the charge and sampling chambers is closed, which means that an additional pressure transducer must be added to the sampling chamber (cf., Fig. 2A)[22].

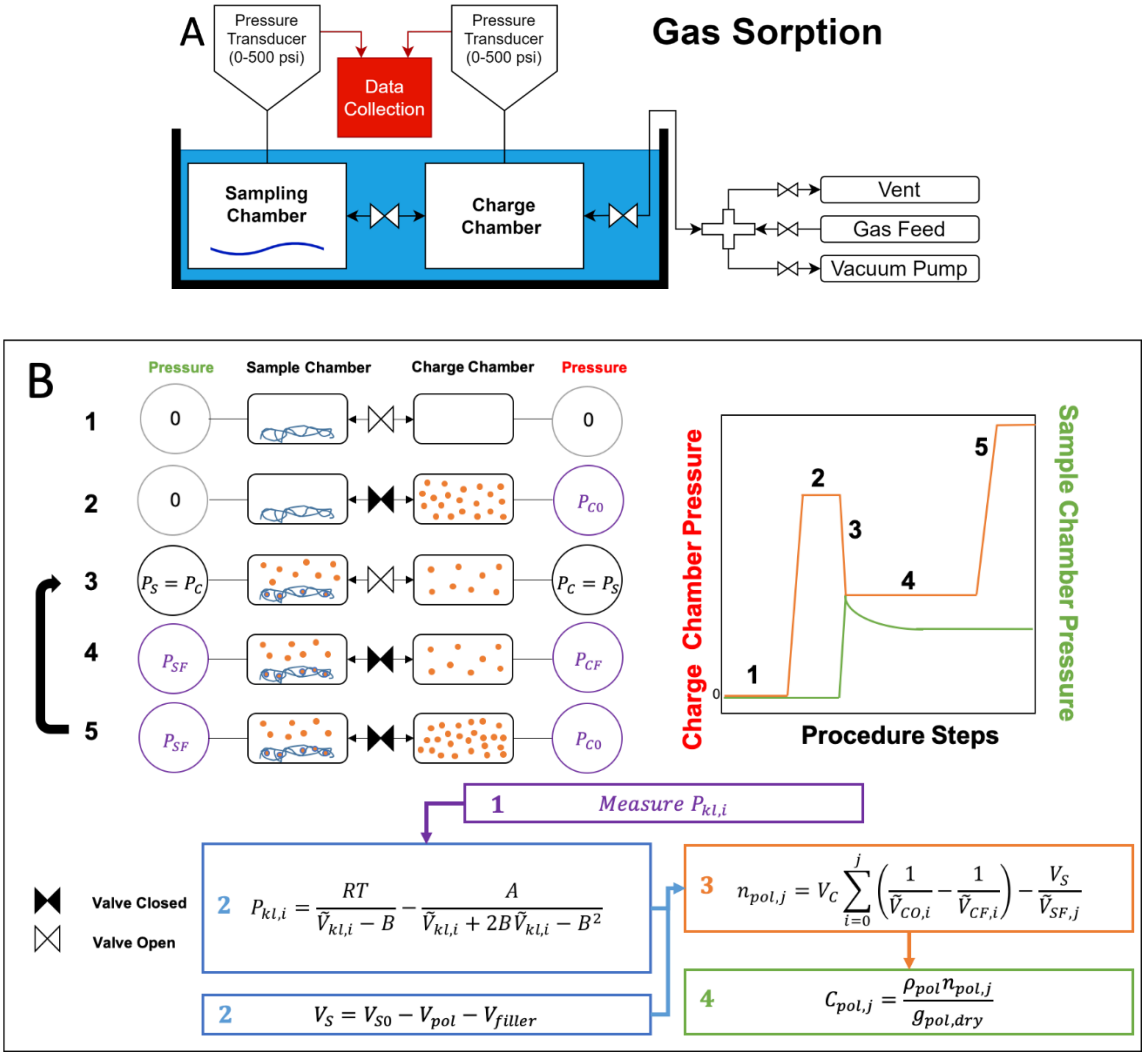

Figure 2. *A) Schematic of the constant volume pressure decay apparatus used to measure gas sorption/ adsorption in polymers and porous materials. B) Schematic of a typical gas sorption measurement using the differential method. Numbers denote step order for calculating concentration from pressure measurements.* V_{filler} *accounts for any other material (e.g., stainless steel beads) possibly used to reduce the total sampling chamber volume,* V_{S0}.

This choice helps minimize the effective volume of the chamber, enhance the signal-to-noise ratio and make sorption measurements more accurate. The penetrant mass balance discussed for the vapor sorption apparatus was adjusted to reflect the procedure for gas sorption. The moles of gas sorbed by the polymer at any given step j (cf. Fig. 2) is

$$n_{pol,j} = V_C \sum_{i=0}^{j} \left(\frac{1}{\tilde{V}_{C0,i}} - \frac{1}{\tilde{V}_{Cf,i}} \right) - \frac{V_S}{\tilde{V}_{Sf,j}} \quad \text{(Eq. 3)}$$

where V_S is the sampling chamber volume and V_C is the charge chamber volume. The balance is completed by applying an equation of state to solve for the gas molar volume ($\tilde{V}_{kl}$), where *k* refers to either the charge chamber (*c*) or the sample chamber (*s*) and *l* refers to either the initial (*0*) or final (*f*) states, as indicated in the mole balance. Since gas sorption measurements are run at high pressures, the ideal gas equation of state is no longer viable, therefore the Peng-Robinson or any other generalized equation of state must be used to convert the experimentally measured pressure data into number of moles[24]:

$$P_{kl} = \frac{RT}{\tilde{V}_{kl} - B} - \frac{A}{\tilde{V}_{kl}+2B\tilde{V}_{kl}-B^2} \quad \text{(Eq. 4)}$$

where P_{kl} is the pressure (in the volume *k* at state *l)* used to solve for the corresponding molar volumes $\left(\tilde{V}_{kl}\right)$. *A* and *B* are the Peng-Robinson parameters, which are related to penetrant critical properties as follows[27]:

$$A = \frac{0.457535(RT_C)^2}{P_C}\left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)\left(1 - \sqrt{\frac{T}{T_C}}\right)\right] \quad \text{(Eq. 5)}$$

$$B = \frac{0.077796(RT_C)}{P_C} \quad \text{(Eq. 6)}$$

where T_C, P_C and ω are the penetrant critical temperature, critical pressure and Pitzer acentric factor, respectively[27]. Finally, Eq. 2 is used to calculate the gas concentration in the polymer. The calculation pathway is shown in Fig. 2B.

To further improve the accuracy, the volume occupied by the polymer sample was subtracted from the volume of the sorption chamber.

The technical features of the gas sorption apparatus considered in this study are shown in Table 2. As a case study, in this paper we consider CO_2 sorption data at multiple temperatures in a thermally rearranged polybenzoxazole bearing triptycene groups (TPBO-0.25), reported previously by Loianno et al[22] and Box et al[28]. We stress the fact that although the methodology devised in this work to estimate the experimental uncertainty is of general validity in the case of pressure-decay based sorption/adsorption experiments, the results shown specifically reflect the features of the experimental setup used in our laboratory.

Table 2. *Technical details of the gas sorption system considered in this study.*

Gas Sorption Apparatus	*Experimental range/value*	*Uncertainty*	*Source*
Pressure sensors (Honeywell Super TJE)	*0 to 500 psi*	*0.5% of the reading*	*manufacturer*
Temperature (Techne TU-20HT immersion circulator)	*-20 to 120°C*	*± 0.5°C*	*manufacturer*
Charge chamber volume	*18.442 cm³*	*± 0.04*	*Burnett method*
Sampling chamber volume	*15.707 cm³*	*± 0.06*	*Burnett method*
TPBO mass (measured using a Mettler-Toledo ME54T3 analytical balance, weighing capacity = 52 g)	*0.1 to 0.5 g*	*± 0.0005 g*	*manufacturer*
TPBO density (measured using an Archimede's balance)	*1.393 g/ml*	*± 0.002 g/ml*	*22*
CO_2 Pitzer acentric factor (ω)	*0.228*	*± 0.006*	*29-31*
CO_2 critical pressure	*72.86 atm*	*± 0.127 atm*	*29, 31*
CO_2 critical temperature	*304.13 K*	*± 0.092 K*	*29, 31*

Finally, the effect of polymer swelling is neglected in the subsequent analysis. A detailed quantitative discussion of the effect of polymer swelling on sorption uncertainty is provided in section 1, Supporting Information.

3. Theoretical background

3.1 Error Propagation Theory. Error propagation provides the effect of experimental variables' uncertainties on the overall uncertainty of the final experimental output[15]. This uncertainty may be expressed in a number of ways, for example, absolute error, relative error or, most commonly, in terms of the standard deviation, σ. In this study, two methods will be considered to calculate the standard deviation of concentration in sorption and adsorption measurements. The first is the linear error propagation method[15] (LEP), which makes some assumptions about variable correlation but requires very little computational power. Depending on the difficulty of equations, the number of inputs and their degree of correlation, LEP may not be analytically viable. The second method is a statistical technique, namely the Monte Carlo error propagation method[32] (MCEP), which estimates the uncertainty through a series of repeated calculations of a given output upon randomly changing the inputs within their limits of precision. The output distribution provides an estimate of the output uncertainty. The MCEP method, though easy to implement, may still prove difficult to apply in practice due to its computational demands. In this study we use the two methods and verify whether or not they provide the same results. This comparison will help select situations where one method may be more appropriate than the other. The quantitative bases of the two methods, including their underlying assumptions, are shortly summarized hereafter.

3.2 Linear Error Propagation (LEP). Linear error propagation is based on the linear characteristics of the gradient of some functions. Given a linear or non-linear function f of the variables x_i, the standard deviation of f, σ_f, is given by[15-16, 33]:

$$\sigma_f^2 = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i}\sigma_{x_i}\right)^2 + \sum_{i=1}^{n} \sum_{j \neq i}^{n} \left(\frac{\partial f}{\partial x_i}\right)\left(\frac{\partial f}{\partial x_j}\right)\sigma_{ij}^2 \qquad \text{(Eq. 7)}$$

where σ_{x_i} is the standard deviation of variable i, $\frac{\partial f}{\partial x_i}$ is the first order partial derivative with respect to variable i, and σ_{ij}^2 is the covariance between two variables. Covariance is a measure of the dependence of one measured variable on the measurement of another and is quantified by the right-hand term in Eq. 6. If we forego the effects of covariance (i.e., the rightmost term in Eq. 6) on all of the measurements used to calculate f, that is, if we consider all measured inputs x_i in $f(x_1, x_2, \ldots x_n)$ to be independent of one another, then the propagated uncertainty of f is given by:

$$\sigma_f^2 = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i}\sigma_{x_i}\right)^2 \qquad \text{(Eq. 8)}$$

Within the linear error propagation method, the uncertainty associated to a given function f is proportional to the input (i.e., independent variables) uncertainty. Consequently, for non-linear functions, linear error propagation remains accurate only for small measurement errors.

Complications in linear error propagation calculations can result from the use of iterative functions. When two functions that share an independent measurement, i.e., $f(x, y)$ and $g(x, z)$, are used as intermediate steps, they become functionally correlated such that a change in the independent variable x will now affect both f and g. If the uncertainties of f and g are then accidentally treated as independent quantities in subsequent calculations, the propagated error will not be accounted for accurately. Therefore, the uncertainty of penetrant concentration of a single sorption step cannot be taken as independent of previous steps. Unfortunately, many independently measured variables are shared among subsequent differential sorption steps, such as temperature, polymer density, and chamber volumes. Therefore, a pitfall of linear error propagation when applied specifically to a constant volume-variable pressure sorption apparatus

is to do the work for the first step and reuse this calculated uncertainty in the next ones, without handling the resulting functional correlation. In this work, we account for and quantify this effect, as well as verify the uncertainty results through Monte Carlo methods[33].

3.3 Monte Carlo Error Propagation. Monte Carlo method (MCEP) propagates errors through a function by simulating repeated experiments. Simulations are carried out by randomly altering the original independent experimental measurements within their Gaussian distributions and repeating the calculations with those values (cf., Fig. 3). Obviously, the overarching hypothesis underlying this method is that the measured variables exhibit a Gaussian distribution, which is true in most cases. Once a sufficient number of simulations have been run, the standard deviation of the resulting collection of outputs is obtained. Consequently, this method of propagating error does not make any assumptions regarding a linear error response, and inherently accounts for functional correlation. Since millions of simulations need to be run, this method is very demanding from the computational point of view, as it requires enough iterations to reach a stable, near constant value (c.f., Fig. S2, section 2, Supporting Information). The example discussed in Fig. S2, Supporting Information, demonstrates how MCEP results compare to LEP results.

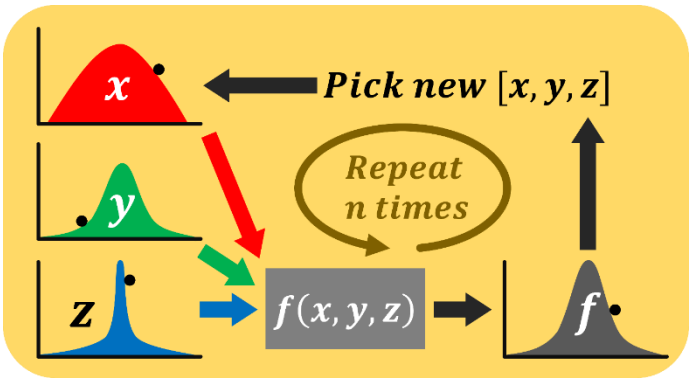

Figure 3. *Schematic of the Monte Carlo Error Propagation (MCEP) method.*

3.4 Uncertainty Contributions. When evaluating the uncertainty of a function that depends on multiple variables, it may be important, for practical reasons, to quantify the contribution of each variable to the overall output uncertainty. This information can be useful, for example, to identify the major source of uncertainty and optimize the design of an experimental apparatus and collect experimental data exhibiting the highest possible accuracy. Likewise, given a set of experimental sorption data, it may be relevant to know how much of the associated uncertainty is due to a specific input variable. In this study, we provide two similar definitions for the contribution each experimental variable makes to the overall uncertainty of the final sorption data, one for linear error propagation, and one for Monte Carlo error propagation. This definition for the LEP method starts from Eq. 7, which, after some algebra, provides the following expression to evaluate the fractional contribution of each independent variable to the overall variance:

$$\sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_i}\frac{\sigma_{x_i}}{\sigma_f}\right)^2 = 1 \qquad \text{(Eq. 9)}$$

where the contribution associated with each variable is $\left(\frac{\partial f}{\partial x_i}\frac{\sigma_{x_i}}{\sigma_f}\right)^2$.

A similar, considerably simpler process can be applied to evaluate the individual variable contribution to the overall uncertainty using the Monte Carlo method. To do this, we used a

sensitivity analysis in which we run Monte Carlo simulations while restricting all uncertain variables to their nominal values, except for a single measurement or groups of measurements. The result of these simulations is a modified uncertainty, σ'_{F_i}, which quantifies the contribution of each variable *i*. This process is repeated for all variables of interest and the corresponding uncertainties are the given contributions for that measurement or measurement group. If the uncertainty due to all variables being used in the MCEP simulation is σ_F, we can define the uncertainty contribution as the fractional variance in a similar way to LEP, that is, $\left(\frac{\sigma'_F}{\sigma_F}\right)^2$. For example, for both LEP and MCEP methods, the contribution of a measured pressure to the moles of penetrant sorbed by the polymer during a given sorption step depends on the pressure measurements in previous steps, therefore, to assess the contribution of the pressure transducer's uncertainty, we consider them as a single contribution.

If non-linear error responses in MCEP are insignificant, and functional covariance is accounted for, then the contributions resulting from this analysis should align completely with the contributions defined by LEP, i.e., the total uncertainty of the calculated result is sufficiently approximated by the sum of the individual, independently simulated contributions to uncertainty.

4. Results and Discussion

The uncertainty associated to a variety of experimental gas and vapor sorption data collected in this laboratory was calculated using the LEP and MCEP methods. We will consider first vapor sorption data collected using the procedure shown in Fig. 1 (cf. section 4.1), and then gas sorption

data collected using the procedure shown in Fig. 2 (cf. section 4.2). Obviously, the procedure described hereafter applies also for adsorption measurements in porous materials.

4.1 Case Study 1: methanol vapor sorption in Celazole® polybenzimidazole. Methanol vapor sorption isotherms in Celazole® polybenzimidazole (PBI) at 25, 35, and 45°C, in units of cm^3(STP)/cm^3(polymer), are shown in Fig. 4 A-B-C, respectively, as a function of vapor partial pressure[20-21]. The uncertainty calculated via the linear error propagation method (i.e., error bars) is compared directly with the uncertainty calculated via the Monte Carlo method. A generalized analytical expression for the concentration uncertainty, using LEP, can be found in Section 3, Supporting Information.

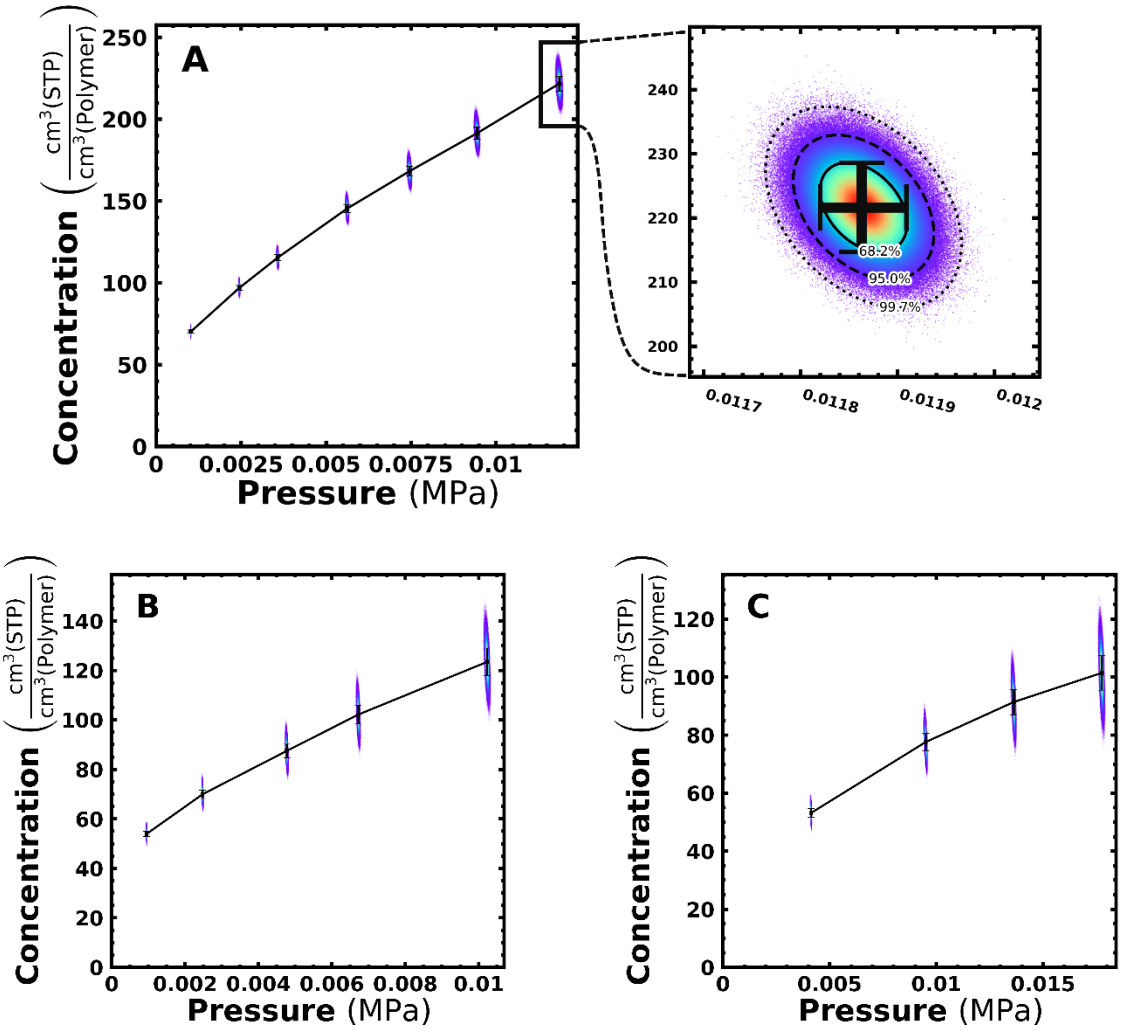

Figure 4. *Experimental methanol vapor sorption isotherms in Celazole® PBI at A) 25°C, B) 35°C, and C) 45°C as a function of pressure. Error bars are calculated via linear error propagation and are superimposed over a corresponding Monte Carlo error propagation (1,000,000 iterations). Lines are drawn to guide the eye. Experimental data are from ref.*[20-21].

At first glance, uncertainty values from the Monte Carlo method may appear larger relative to that calculated via the linear error propagation. This stems from the MCEP method providing a full Gaussian distribution of possible values in both the X and Y directions, rather than the single standard deviation that is shown by a single error bar, which is what LEP directly provides. Error bars residing within one standard deviation align between the two methods, which can be verified by the comparison shown later.

The differential method used to run sorption measurements experiences a growing coefficient of variation with increasing penetrant partial pressure. The coefficient of variation, which is defined as $CV = \frac{\sigma}{\mu} \times 100\%$, where μ is the mean value of the measurement and σ is its standard deviation (c.f., Section 4 of the Supporting Information), is a measure of how "spread out" the possible values of the measurement are from the average value. This growth in CV is essentially due to the impact of the uncertainty of the moles of penetrant sorbed by the polymer during previous steps. For example, for the methanol vapor isotherm in *Celazole*® PBI at 25°C, the CV of the concentration at the first sorption step, at 0.00102 MPa, is 1.44% (cf., Fig. 4A and S3A). At step 7 (i.e., the last step in that isotherm at 0.012 MPa), the CV is 2.07%, which indicates that CV increases with the total number of sorption steps (cf., Fig. 4A and S3A). Growth notwithstanding, it is unclear whether other factors may impact the CV significantly, such as the polymer mass and density. However, some variables can be ruled out as significant contributors to error, such as temperature. For example, the uncertainty of vapor sorption isotherms increase with increasing pressure without following a specific trend with temperature for both CV (25°C < 45°C < 35°C) and overall error (45°C < 25°C < 35°C) (cf., Figs. S3A-B). The sensitivity of the concentration to polymer mass (and other variables) will be further explored during the analysis of variable error contributions (cf. section 4.4). Overall, the uncertainty of vapor sorption data spans from 2.07% (at 25°C, 0.012 MPa) to 5.85% (at 45°C, 0.018 MPa).

4.2 Case Study 2: gas sorption in a triptycene-based polybenzoxazole (TPBO). The uncertainty of CO_2 sorption isotherms in a triptycene-containing polybenzoxazole (TPBO-0.25) at 5, 20, 35, and 50°C with pressures ranging from 0 up to around 3.5MPa is shown in Fig. 5 [22]. The total uncertainty

spans from 5.7% (at 5°C, 2.62 MPa) to 9.6% (at 35°C, 3.23 MPa) of the total concentration value. The uncertainty analysis accounts for all variables listed in Table 2.

In the case of gas sorption, at a given temperature, CV increases with increasing pressure and, at any given pressure, it increases with increasing temperature (cf., Fig. S4A). However, the absolute error appears independent of temperature (cf., Fig. S4B). Specifically, at pressures up to 1 MPa, the CV associated to CO_2 sorption in TPBO-0.25 varies from 2.3% to 4.0% (73% increase) between the 5 and 50°C isotherms respectively, while the uncertainty changes from ± 2.81 to ± 2.65 cm^3(STP)/cm^3(pol) (i.e., 6% decrease). The change in CV with temperature becomes smaller at higher pressures. At 2.5 MPa and in the same temperature range as before, CV changes from 5.5% to 7.6% (40% increase) while the uncertainty changes from ± 9.31 cm^3(STP)/cm^3(pol) to ± 7.17 cm^3(STP)/cm^3(pol) (i.e., 23% decrease). The increase in CV with temperature is not due to a change in absolute uncertainty, but rather to the fact that sorption decreases by about 50% with increasing temperature, due to negative sorption enthalpy[22]. This result suggests that changing temperature, at least at moderate pressures, does not have a large impact on the uncertainty.

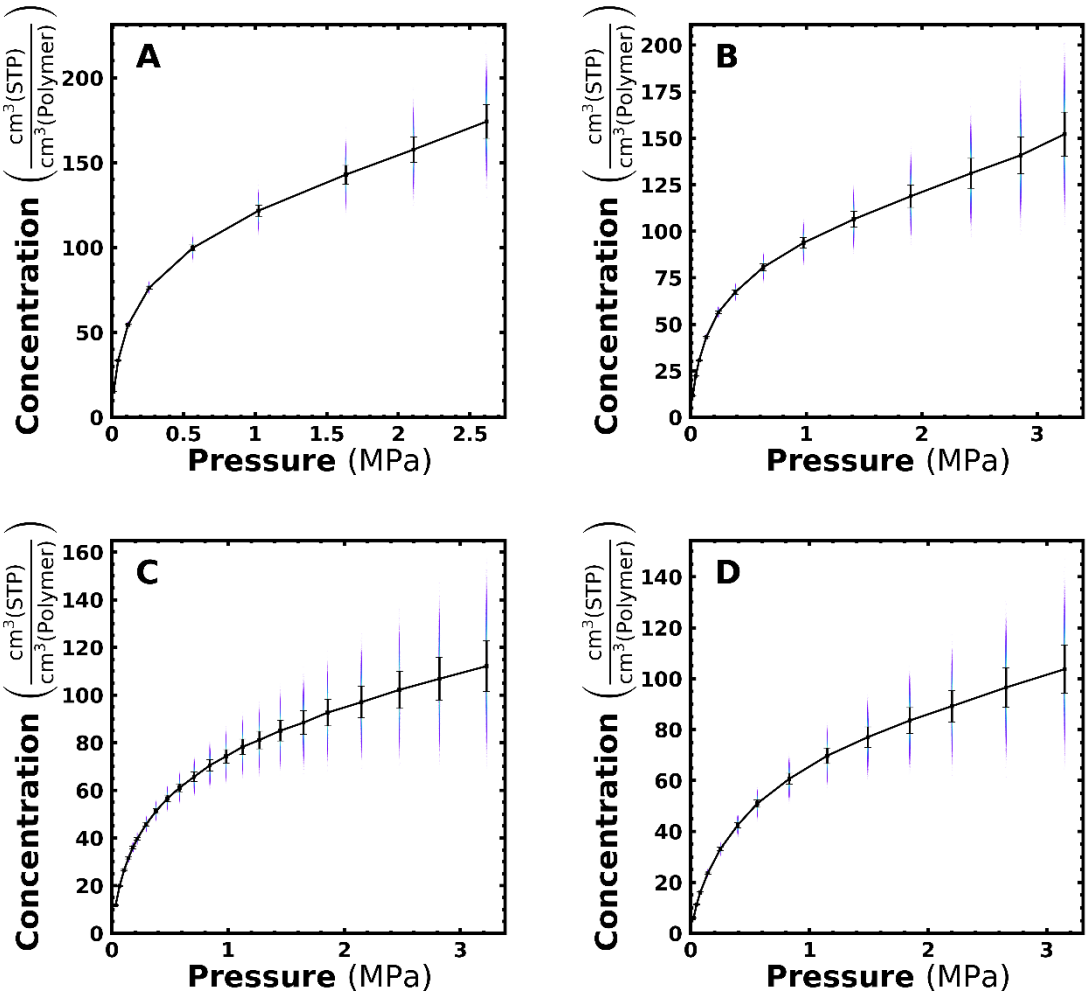

Figure 5. *Experimental CO_2 sorption isotherms in TPBO-0.25 at A) 5°C, B) 20°C, C) 35°C, and D) 50°C as a function of pressure. Error bars are calculated via linear error propagation, and are superimposed over the corresponding Monte Carlo error propagation (100,000 iterations). Lines are drawn to guide the eye. Experimental data are from ref.[22].*

4.3 Comparison between the MCEP and LEP methods. Monte Carlo error propagation, when performed with a sufficient number of iterations, is both more robust to large measurement errors and more precise compared to linear error propagation, at the cost of being relatively computationally expensive. This is even more true in cases where cubic equations of state must be solved multiple times per iteration, as in the case of gas sorption measurements. Specifically, in this work, performing the Monte Carlo analyses on a single six core processor required about

eight seconds per step per million iterations for vapor sorption calculations, and 400 seconds per step per million iterations for gas sorption calculations. The reason for this discrepancy between the computational cost of the two setups is primarily due to the equations of state used (i.e., Peng-Robinson for gas sorption and ideal gas for vapor sorption). Propagating error linearly, in contrast, is near-instantaneous for both vapor and gas sorption measurements (i.e., a few microseconds using the same processor) once derivatives have been calculated. Therefore, it is necessary to evaluate if linear error propagation can accurately approximate the MCEP methods in an effort to avoid time-intensive calculations. To do this, uncertainty associated to vapor and gas sorption data were propagated using the Monte Carlo method in several independent runs, that is, by increasing the number of iterations by an order of magnitude in each run. The Monte Carlo results were then compared to the outcomes of linear error propagation.

Figs. 6A-B show the percent difference between Monte Carlo and linear error propagation for every step in the vapor and gas sorption isotherm, respectively. Interestingly, the percent difference between MCEP and LEP methods in the vapor sorption apparatus approaches 0.05% at around 1M iterations and does not appear to decrease further (cf. Fig. 6A). In contrast, the gas sorption apparatus was limited by the amount of time the computation could be run and did not approach a constant value, but instead had a percent difference of around 0.1% at 1M iterations (cf. Fig. 6B). If a sufficient number of Monte Carlo iterations have been run, the average percent difference should become constant with additional iterations.

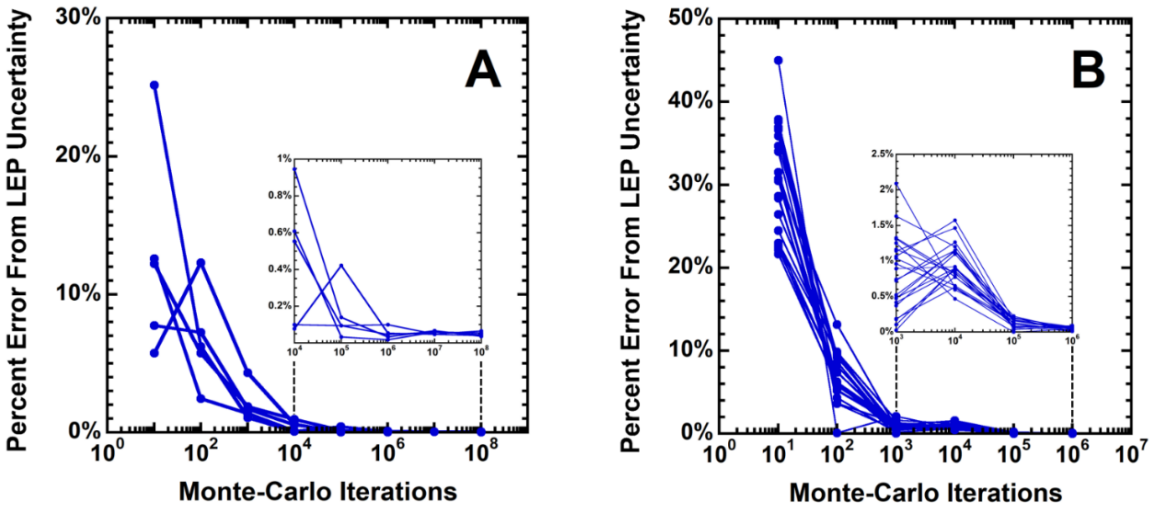

Figure 6. *Percent difference between Monte Carlo and linear error propagation for every step in the isotherm. A) Methanol in PBI at 35°C and B) CO_2 in TPBO-0.25 at 35°C. Each line represents a different pressure step.*

Since the linear error propagation library used in this work accounts for functional correlation, the 0.05% difference between the Monte Carlo and linear methods seen in the vapor sorption apparatus can be attributed to the nonlinear uncertainty response which LEP does not account for, but MCEP does. Therefore, when measuring gas and vapor sorption/adsorption in polymers with the barometric (i.e., pressure decay) method, linear error propagation can be safely used, at least for typical experimental conditions.

If Monte Carlo error propagation is the only method available due to cumbersome derivative calculations, or if error propagation software is not available, Figs. 6 provide useful guidelines for determining how many iterations are necessary to achieve equivalent results to that of LEP, or at least an acceptable approximate thereof.

4.4 Contribution of individual experimental variables to gas/vapor sorption uncertainty from LEP. In this section, the contribution of the individual experimental variable to the overall uncertainty

associated to gas and vapor sorption data, defined by Eq. 9, will be assessed. This information (cf., Figs. 7 and 8) may be helpful to optimize the design of an experimental apparatus, as well as to devise the best standard operating procedure to generate the highest quality data possible.

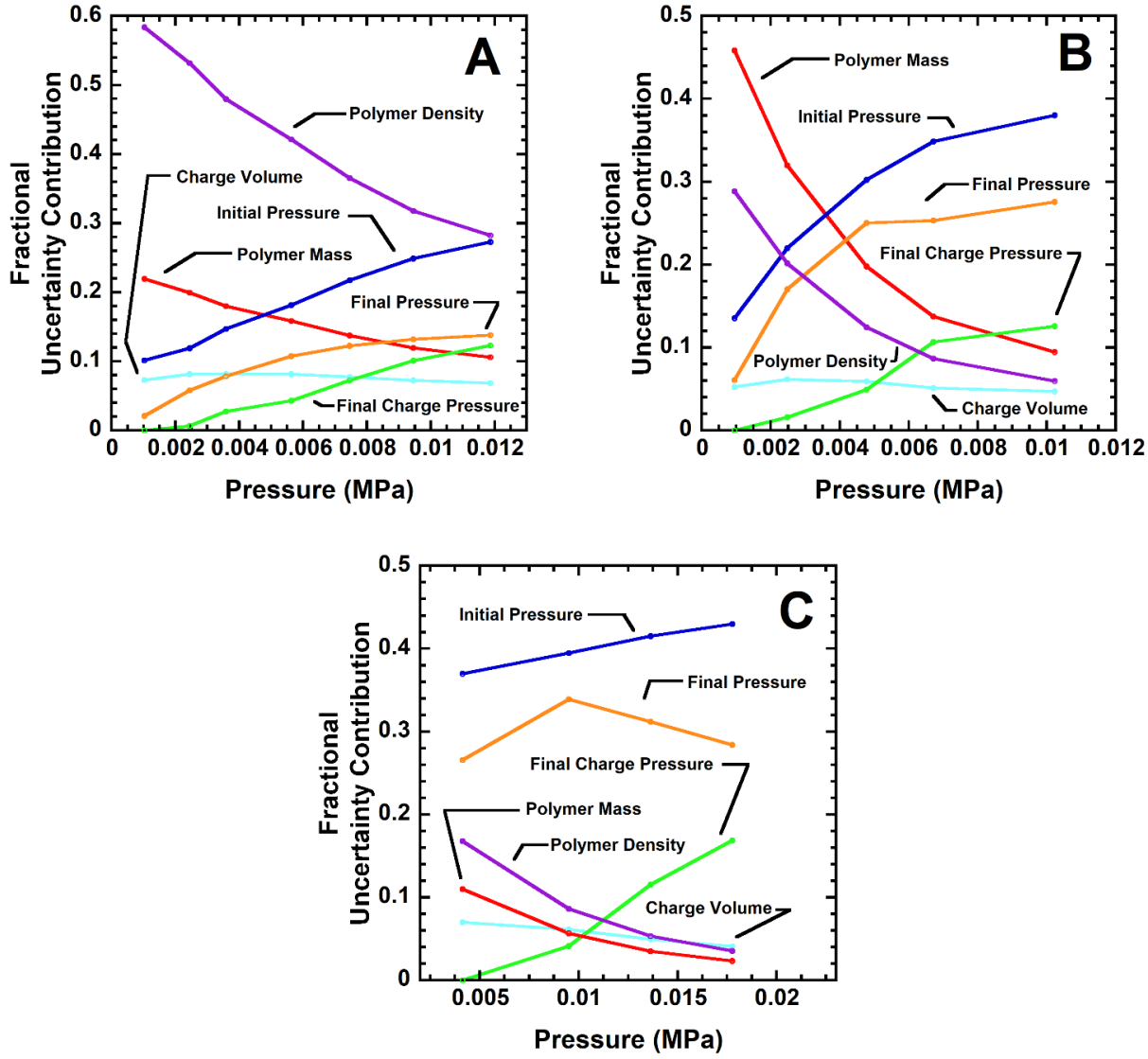

Figure 7. *Individual linear error propagation uncertainty contributions to experimental methanol sorption isotherms in PBI at A) 25°C, B) 35°C, and C) 45°C. Contributions of temperature and sample chamber volume are negligible and, for this reason, they are not shown.*

Using the LEP uncertainty contribution analysis, it can be shown that, at least when the apparatus available in our laboratory is used (cf. Fig. 1A), vapor sorption experiments acquire most of their

error from polymer density, polymer mass, and initial pressure measurement (c.f., Fig. 1B, *2)*), that is, the pressure in the charge chamber before each step begins. Initially, the polymer density is the dominating contributor to error (cf. Fig. 7A-B-C).

However, as the isotherm progresses and the number of pressure measurements used in the isotherm increases, polymer density and mass quickly stop contributing to the total error as much as other variables, such as the initial pressure (cf. Fig.1B step 2). This is a direct result of the way pressure measurements affect subsequent steps in the isotherm. Indeed, while polymer density and mass are used once at the end of each sorption step's calculation and are not re-used or re-measured between steps, the initial pressure of previous steps affect subsequent steps and its contribution propagates throughout them, allowing even small initial contributions to error to become much more significant after multiple sorption steps have been completed. This is consistent with the behavior of the other pressure measurements (such as final charge pressure), whose contribution to the total uncertainty increases as additional sorption steps are run.

Other variables, such as the volume of the charge chamber, contribute a near-constant amount to the overall uncertainty, but decrease in their fractional contribution as other variables increase in their own contributions. Interestingly, the contribution of the dry polymer density and mass initially appear less relevant at 45°C compared to the 25°C and 35°C isotherms. This cannot be due to the density and mass values used in the experiments, as the sample masses increase in the order 35°C (0.0036g) < 45°C (0.0056g) < 25°C (0.0074g) and density is assumed constant throughout all isotherms, although this does justify the small increase in polymer mass contribution from the 25°C to 35°C isotherms. One main difference in the 45°C isotherm is the pressure for the first sorption step (i.e., 0.00413 MPa), which is roughly 4 times larger than the

step 1 pressures observed in the 25°C (i.e., 0.00102 MPa) and 35°C (i.e., 0.000951 MPa) isotherms, as well as the higher average pressure step size, which is around twice as large for the 45°C isotherm ($\Delta P = 0.00454$ MPa per step) as compared to the 35°C and 25°C isotherms ($\Delta P = 0.00232$ MPa and 0.00207 MPa per step, respectively). This is also reflected in the high initial pressure contributions in the 45°C isotherm, step 1, as compared to the step 1 contributions in the 35°C and 25°C isotherms. Obviously, this is consequence of the methanol vapor pressure being an increasing function of temperature (methanol activity is evaluated as P/P^*, where P is the equilibrium final pressure and P^* is the methanol vapor pressure at the experimental temperature). Finally, as expected, the final charge pressure, that is, the final pressure in the charge chamber at the end of the sorption measurement, does not contribute to the first step, as it is only used to calculate moles of gas sorbed during the next steps.

In striking contrast, uncertainty in gas sorption experiments is dominated by the chamber volumes (c.f., Fig. 8). The sampling and charging chamber volumes collectively account for at least 80% of the total isotherm uncertainty at any step for all gas sorption isotherms.

The pressure transducer's contributions do not increase enough with increasing pressure, despite appearing to follow a similar trend as in the vapor sorption apparatus. These results are essentially due to the comparatively small pressure differences observed between the beginning and end of sorption steps in the gas apparatus compared to the vapor apparatus. Therefore, small uncertainty in the sampling chamber volume will vastly alter the number of moles calculated by the Peng-Robinson equation of state, that is, the molar balance used to generate sorption data.

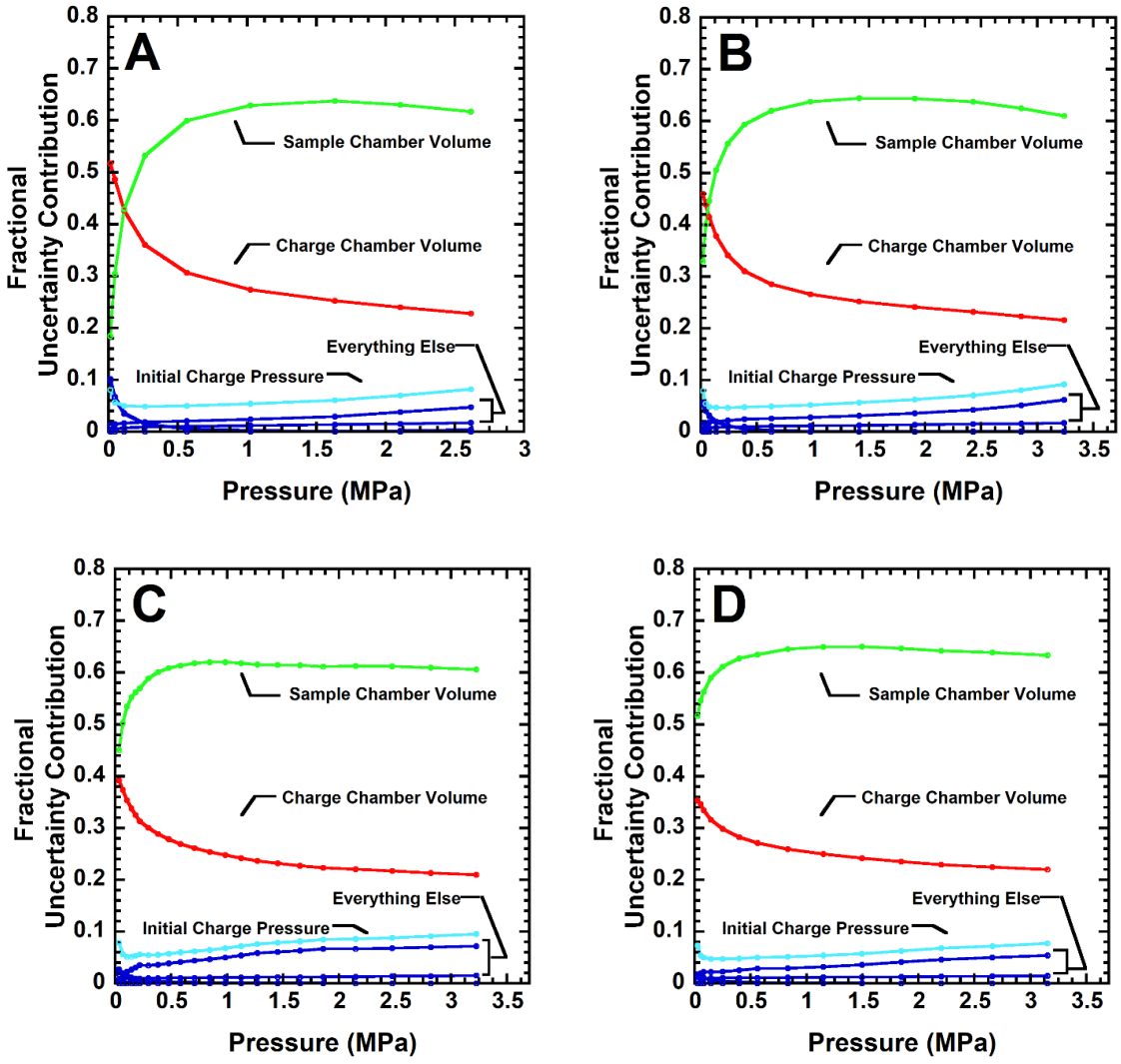

Figure 8. *Individual linear error propagation uncertainty contributions to experimental CO_2 sorption isotherms in TPBO-0.25 at A) 5°C, B) 20°C, C) 35°C, and D) 50°C. Dark blue plots denote contributions that provide a negligible contribution to the overall uncertainty, including final charge pressure, Pitzer acentric factor, penetrant critical temperature, penetrant critical pressure, polymer density, polymer mass, and final sample chamber pressure.*

Therefore, while in the vapor sorption apparatus the sampling chamber volume does not have a significant effect on the total uncertainty and thus isn't included in the contribution plot, it is the leading contributor to uncertainty in gas sorption measurements. This is due to two key design aspects that distinguish how sorption is measured in the two apparatuses. In the vapor sorption

apparatus, the valve between the sampling and charge chambers is left open during the experiment, leading to the charge chamber accounting for most of the observed volume during pressure decay. Moreover, for the apparatus used in this laboratory, the sampling chamber volume is nearly one-fourth that of the charge chamber (cf., Table 1). In contrast, the valve between the charge and sampling chambers is closed during gas sorption measurements. Moreover, the volumes of the charge and sampling chambers are comparable in the latter case (cf., Table 2).

As mentioned previously, in the gas sorption apparatus, chamber volume uncertainties contribute significantly to the overall uncertainty of concentration. Unlike other contributors to concentration error, which are either inherent to the devices being used (e.g., pressure transducers, temperature controllers), the materials involved in the experiment (e.g., polymer density), or measured constants (e.g., gas critical properties, gas molecular weight), the accuracy of the chamber volumes is controllable in that it can be improved by the operator. Indeed, while the accuracy of the pressure transducer or temperature controller is given by the factory which produced it, the volumes are measured by the operator through subsequent gas expansions (i.e., the Burnett method[25]), therefore more accurate measurements will lead to more accurate estimate of the volumes. If the chamber volumes used in the calculation of CO_2 sorption in TPBO-0.25 at 35°C were to be made twice as accurate (that is, the uncertainties were cut in half), the overall uncertainty of concentration would improve by 40.6% on average for all steps in the isotherm, and would reduce the percent uncertainty contribution of both chamber volumes by 24.8% (at step 4, lowest change) to 35.5% (at step 22, highest change), with an average reduction of 29% (c.f., Fig. 9). This sensitivity analysis shows the efficacy of improving the accuracy of volumes

calibration, especially when considering that an improvement to these values can be useful even if done after sorption experiments have been completed, as the pressure data collected during the experiment remain valid if volumes are re-calibrated to gain higher accuracy. In Fig. 9, the contributions of the single experimental variable to the overall uncertainty of CO_2 sorption data in TPBO-0.25 at 35°C is compared by assuming the actual uncertainty of the volumes (continuous lines) and by halving it (dashed lines), while keeping all other uncertainties unchanged.

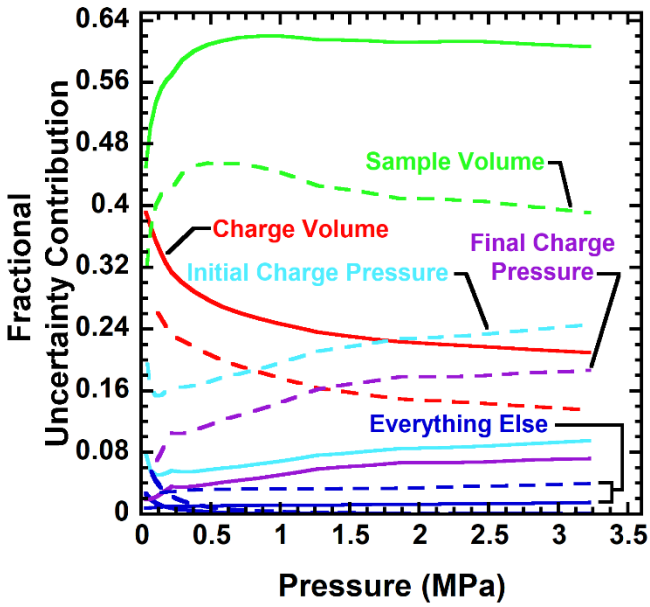

Figure 9. *Fractional uncertainty contributions of CO_2 sorption in TPBO-0.25 at 35°C using the true chamber volumes uncertainty (continuous lines, $\sigma_{V_{Charge}}$ = 0.04 cm³, $\sigma_{V_{Sampling}}$ = 0.06 cm³) and the halved chamber volumes uncertainties, (dashed lines, $\sigma_{V_{Charge}}$ = 0.02 cm³, $\sigma_{V_{Sampling}}$ = 0.03 cm³), while all other uncertainties remained constant. Lines are drawn to guide the eye. The chamber volumes are* $V_C = 18.442\ cm^3$ *and* $V_S = 15.707\ cm^3$.

Finally, to validate the legitimacy that MCEP and LEP can both be used to calculate the uncertainty, the convergence of uncertainty values must extend into the single variable contributions. This aspect is discussed in section 4.5.

4.5 Contribution of individual experimental variables to gas/vapor sorption uncertainty from MCEP. Uncertainty contributions from both LEP and MCEP methods matched for all variables involved in the calculation. The convergence of both methods for two significantly contributing variables are shown in Figs. 10, where the uncertainty contribution of the charge chamber volume in the gas sorption experiment, and the uncertainty contribution of polymer mass in the vapor sorption experiment is compared between the two methods. Specifically, in Figs. 10, the percentage departure of MCEP from LEP is shown as a function of the number of Monte Carlo iterations. The percent difference between the variable's contribution obtained through each method reached near or below 1% after 10^5 iterations.

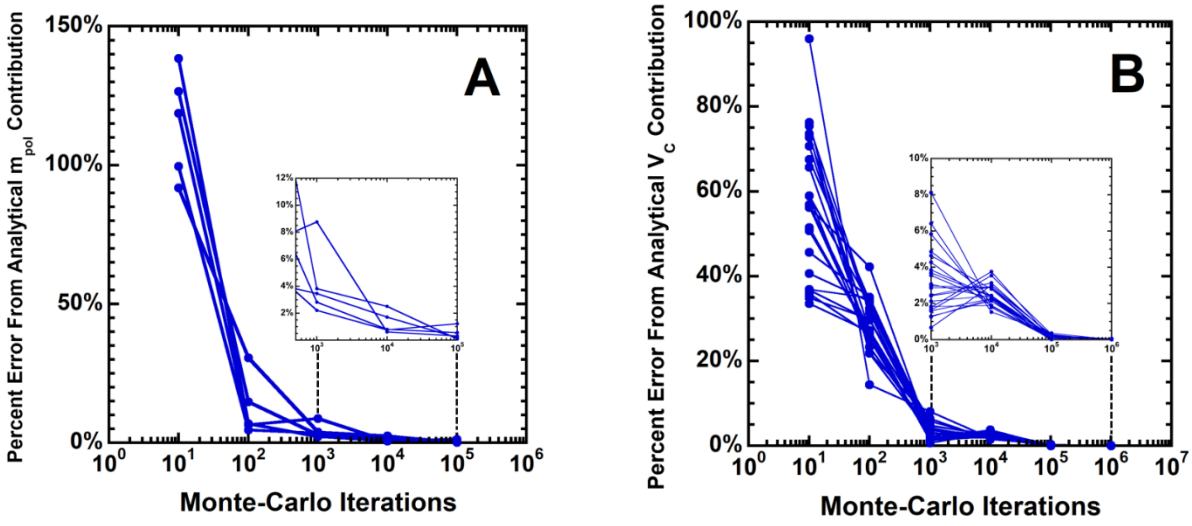

Figure 10. *Percentage deviation of MCEP method from LEP method in evaluating the contribution of a single experimental variable to the sorption experimental uncertainty as a function of the number of Monte Carlo iterations. A) Contribution of polymer mass to uncertainty of methanol vapor sorption in PBI at 35°C. B) Contribution of the charge chamber volume to uncertainty of CO_2 sorption in TPBO-0.25 at 35°C. The insert is shown to confirm that the two methods converge to the same result.*

As a result, each contribution to uncertainty as evaluated from the linear error propagation method is effectively equivalent to the Monte Carlo method and can be used in place of it without compromising contribution accuracy.

The analysis provided in this study confirms that not only the LEP and MCEP total uncertainties match for all cases discussed, but individual uncertainty contributions from both methods also match, validating the use of results from either method in optimizing the accuracy of sorption experiments.

A summary of the uncertainties estimated with the Monte Carlo method is shown in the Supporting Information, Fig. S5 (CO_2 sorption data in TPBO-0.25) and Fig. S6 (methanol sorption data in PBI).

4.6 Effect of samples' variability and best practices for accurate sorption/adsorption measurements. In this section we report some final recommendations to get accurate and reliable gas and vapor sorption/adsorption data. Vapor sorption/adsorption measurements require a very accurate estimate of the dry polymer mass and its density. A large amount of polymer sample should be used when its sorption capacity is expected to be small. If this is not possible, we recommend the following best practices: *i)* large activity jumps should be considered between subsequent sorption steps; *ii)* the integral method should be used instead of the differential one, by pulling full vacuum between subsequent sorption steps; *iii)* the dead (i.e., unoccupied) volume in the sorption cell should be reduced as much as possible by inserting stainless steel beads, which are available in the commerce and whose volume is reported by the factory with high accuracy. An accurate pressure transducer and chamber volume calibration is recommended as well.

A very accurate chamber volume calibration is the key factor to get reliable gas sorption/adsorption data. In any case, volume calibration should be run using the Burnett (i.e., expansions) method and helium as service gas[25]. Gravimetric calibration, to be run by weighing

the cell before and after filling it with a liquid whose density is known, is not recommended, as *i)* air bubbles may form inside the cell, which would introduce severe errors, *ii)* the liquid density may be sensitive to temperature, and *iii)* liquid droplets might inadvertently spill from the cell while pipetting.

It is well known that different samples of the same material may have vastly different sorption/adsorption properties. Since the scope of this study is to make sorption/adsorption data more comparable across laboratories and provide guidelines to propagate errors in lieu of repeating time-consuming experiments, it is important to show that the sample-to-sample variability is captured by the proposed error propagation method, and verify that uncertainty coming from sample-to-sample variability falls in the error bounds obtained from error propagation. As shown in the Supporting Information (cf. Fig. S7), two independent nitrogen sorption tests in TPBO-0.25 at 35°C and up to 35 atm were run on the same apparatus using two different virgin samples. The two datasets departed by about ±5% of each other, which falls within the bound predicted by the error propagation method. It is worth noting as well that sample-to-sample variability can arise largely from systematic and nonrandom components (e.g., different synthesis methods). Therefore, samples prepared in different ways may potentially reside outside of the errors calculated using the error propagation methods discussed in this work, which only account for random error and do not include systematic errors (with the exception of polymer density due to swelling, c.f., section 1, Supporting Information).

Another relevant point deserving some discussion is the correct determination of the final equilibrium pressure, which is essential to get reliable sorption/adsorption data. In the laboratory where this study was conducted, a given sorption step is considered to be at equilibrium when

the pressure does not change for at least 50% of the time needed to first reach that final equilibrium value. For example, if the final equilibrium pressure is reached for the first time 24h after the experiment started and it maintains that value for the next 12h, after that time (i.e., 36h) we consider the sorption step at equilibrium. In both gas and vapor sorption systems, when equilibrium is reached, the pressure uncertainty (i.e., the pressure noise) at equilibrium falls within the uncertainty of the reading provided by the factory specifications (cf., Tables 1 and 2 and Fig. S8, Supporting Information).

The way the apparatus is evacuated and degassed is also considered a critical step during sorption/adsorption measurements. In the laboratory where this study was conducted, vacuum is pulled throughout the system until the transducers (which are recalibrated at the beginning of the sorption experiment, when the vacuum is stable) indicate a pressure equal to zero and, starting from that moment (which is evaluated using the time-scale provided by automated data collection software), dynamic vacuum is maintained for the next 24h before starting the sorption test. At that moment, all valves are closed and at the system is left alone for 1h before starting the actual measurement, to identify any possible leaking.

5. Conclusions

A standard method to evaluate the experimental uncertainty of gas and vapor sorption/adsorption measurements in polymers is proposed and tested in a variety of operating conditions and using different experimental protocols. The individual influence of different experimental parameters, such as the mass and density of the polymer sample, the volume of the system, temperature, pressure, and equation of state parameters, on the total uncertainty

associate to sorption/adsorption data is evaluated and discussed. The hypothesis of neglecting polymer swelling in sorption calculations is also revisited and discussed quantitatively. The latter effort should help scientists design their experimental setup to generate data exhibiting the highest possible accuracy, and make experimental data coming from different laboratories in the world easier to compare. Of equal importance, the validity of the linear error propagation method, generally used to evaluate the uncertainty of sorption/adsorption data, is demonstrated by a *vis-à-vis* comparison with the Monte Carlo statistical method.

Acknowledgments

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Supporting Information Content

Analytical assessment of the effect of polymer swelling on sorption uncertainty. Comparison between LEP and Monte Carlo methods. Analytic expression for vapor sorption uncertainty. Coefficients of variation. Monte Carlo scatterplots. Effect of variability among samples. Evaluation of the final equilibrium pressure during barometric sorption measurements.

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