Published in final edited form as:

Meas Sci Technol. 2017 December ; 28(12): . doi:10.1088/1361-6501/aa8f83.

Experimental aspects of buoyancy correction in measuring reliable highpressure excess adsorption isotherms using the gravimetric method

Huong Giang T Nguyen¹, Jarod C Horn¹, Matthias Thommes^{1,2}, Roger D van Zee¹, and Laura Espinal¹

¹Facility for Adsorbent Characterization and Testing, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States of America

²Quantachrome Instruments, Boynton Beach, FL, United States of America

Abstract

Addressing reproducibility issues in adsorption measurements is critical to accelerating the path to discovery of new industrial adsorbents and to understanding adsorption processes. A National Institute of Standards and Technology Reference Material, RM 8852 (ammonium ZSM-5 zeolite), and two gravimetric instruments with asymmetric two-beam balances were used to measure high-pressure adsorption isotherms. This work demonstrates how common approaches to buoyancy correction, a key factor in obtaining the mass change due to surface excess gas uptake from the apparent mass change, can impact the adsorption isotherm data. Three different approaches to buoyancy correction were investigated and applied to the subcritical CO₂ and supercritical N₂ adsorption isotherms at 293 K. It was observed that measuring a collective volume for all balance components for the buoyancy correction (helium method) introduces an inherent bias in temperature partition when there is a temperature gradient (i.e. analysis temperature is not equal to instrument air bath temperature). We demonstrate that a blank subtraction is effective in mitigating the biases associated with temperature partitioning, instrument calibration, and the determined volumes of the balance components. In general, the manual and subtraction methods allow for better treatment of the temperature gradient during buoyancy correction. From the study, best practices specific to asymmetric two-beam balances and more general recommendations for measuring isotherms far from critical temperatures using gravimetric instruments are offered.

Keywords

high-pressure adsorption isotherm; excess adsorption isotherm; gravimetric method; buoyancy correction; blank correction; RM 8852; ZSM-5

ORCID iDs

Laura Espinal <https://orcid.org/0000-0002-1894-366X>

Supporting information: N₂ isotherms at 77 K for Si shot, PXRD patterns for RM 8852, excess N₂ isotherms at 293 K for RM 8852 and Si shot, excess CO₂ isotherms for empty sample holder and Si shot, blank-corrected excess CO₂ isotherms (using empty sample holder as blank), blank-corrected excess CO₂ isotherms using manual method with correct and wrong balance component volumes, collective and sample volumes determined from helium isotherm, excess N₂ and CO₂ isotherms at 293 K corrected using expected collective volume values.

Introduction

Adsorbents are promising candidates for carbon dioxide capture [1, 2], methane and hydrogen storage [3–7], gas separation [8], and catalysis [9] via the adsorption, or enrichment, of the gas (i.e. the adsorptive) to the adsorbent's surface [10, 11]. Thus, there has been great interest in designing and developing new porous adsorbents [12]. The gas capture/storage performance of an adsorbent can be determined by measuring its gas sorption isotherm, a plot of gas uptake at various equilibrium pressure points, over the relevant pressure range at a constant temperature [10, 13]. The amount of gas adsorbed by the adsorbent can be determined based on gravimetry, which directly measures the mass of the adsorbent as it changes due to the adsorption/desorption of the adsorptive [10, 13]. After taking into account the effect of the buoyancy force on the mass measurement, which requires that the volume of the adsorbent be known, the quantity typically obtained experimentally is the surface excess adsorption (n_a^{ex}), also known as the Gibbs excess adsorption [10, 14]. It is equal to the absolute adsorption (n_a) minus the amount of gas (equal to volume of adsorbate phase, V_a , times the density of gas, ρ_g , over the molecular weight of the gas, M_g) that would have been where the adsorbed phase is had there been no adsorption (equation (1)) (for details, see IUPAC recommendations [14]).

$$n_a^{\text{ex}} = n_a - \frac{\rho_g V_a}{M_g} \quad (1)$$

Although guidelines and protocols exist for low-pressure (< 1 atm) gas sorption measurements, which are typically used to characterize surface and structural properties of materials [14], standard protocols on how to accurately measure high-pressure gas adsorption isotherms currently do not exist, making the comparison of high-pressure results obtained among different laboratories difficult [2, 15]. Herein, we demonstrate that the buoyancy correction for the gravimetric technique can play a significant role. The suitable approach to buoyancy correction is more sensitive in high pressure measurements as compared to low pressure measurements, given that the density of a non-ideal adsorptive can change drastically with increasing pressure and temperature. Moreover, a bias in the buoyancy correction that may be insignificant at low pressures can be magnified at high pressures and become significant.

This article is aimed at providing measurement guidelines. The high-pressure subcritical CO₂ and supercritical N₂ isotherm data at 293 K on a National Institute of Standards and Technology (NIST) Reference Material RM 8852¹⁶ (ammonium ZSM-5 zeolite) obtained from two gravimetric systems equipped with asymmetric, two-beam microbalances was used as a case study. We will demonstrate the effect of temperature gradient on the data and illustrate how to best apply three buoyancy correction methods (helium, manual, and subtraction). We will also demonstrate that for the experiments described in this work, the inclusion of a blank correction is important to further improve the reliability of the adsorption data. Lastly, we propose best practices for buoyancy correction, blank correction (if required), and data reporting to generate reliable high-pressure surface excess adsorption

data from the gravimetric technique at temperatures far from the critical point. These recommended best practices are based on the steps we used to arrive at the matching adsorption isotherms using two different instruments and the three buoyancy correction methods.

Theory for gravimetric technique and buoyancy correction

The gravimetric instrument relies on a highly sensitive microbalance to measure the small changes in the mass of the adsorbent due to the adsorbate. There are two types of balances: (1) *single-beam* and (2) *two-beam* microbalances [13]. Figure 1 shows a two-beam, asymmetric balance, a common commercially available set-up that was employed in this work. Hanging from the two-beam balance are sample holders attached via hangdown wires on each side, holding some form of counterweight on the counterweight side and the sample on the sample side.

Common procedures for using an asymmetric balance in the gravimetric technique to measure the gas adsorption isotherm include (1) taring the balance with an empty sample holder, (2) loading the adsorbent, and (3) tracking its mass as it is exposed to different gas equilibrium pressures to calculate the mass change from the initial mass (figure 1). The change in the measured weight ($m_m g$, where m_m is the measured mass and g is the acceleration due to gravity) can be linked to the weight of adsorbate ($m_a g$), but it must be corrected for the buoyancy force (equation (2)). In equation (2), $m_s g$ is the sample weight and the buoyancy force is an upward force acting on the all the components hanging from the balance equal in magnitude but opposite in direction to the acceleration due to gravity times the mass of the volume of gas displaced by the adsorbate, the adsorbent, and the balance components. The mass of the displaced gas can be determined from the density of the adsorptive gas (ρ_g) and the volume of gas displaced (V_g) by all the components of the balance.

$$m_m g = m_s g + m_a g - \rho_g V_g g \quad (2)$$

The density of the gas is dependent upon the pressure and temperature during the measurement. When measurements are carried out at low pressures, i.e. gas density is low, the buoyancy force is very small. However, at higher pressures, especially with a non-ideal gas such as CO₂, the density of the gas is increasing and thus, the effect of the buoyancy force becomes more significant. The volume of gas displaced, V_g , is equal to the sum of the volumes of the sample (V_s), the adsorbate (V_a), and all of the components hanging from the balance ($V_B = V_{hdw} + V_{sh}$, where V_{hdw} is the volume of the hangdown wire, V_{sh} is the volume of the sample holder basket, etc). For a two-beam balance, the volumes of all the components in the counterweight side (V_B^{CWS}) must also be considered. However, the buoyancy force acting on the counterweight side acts in opposition to the buoyancy force on the sample side. Thus, for a two-beam balance, the actual mass, m_{act} (mass of adsorbent + adsorbate), can be determined using equation (3). The mass change due to the absolute

amount of adsorbate, m_a , is given then by equation (4). The initial masses, m_m^i , m_{act}^i , and m_s , are typically identical given that no adsorbate is initially present.

$$m_{act}=m_m+\rho_g V_s+\rho_g V_a+\rho_g V_B-\rho_g V_B^{CWS}$$

(two- beam balance, actual mass) (3)

$$m_a=\Delta m_{act}=\Delta m_m+\rho_g V_B+\Delta \rho_g V_a+\Delta \rho_g V_s-\Delta \rho_g V_B^{CWS}$$

(two- beam balance, absolute uptake mass of adsorbate) (4)

The effect of the buoyancy force attributable to the adsorbed phase is hard to account for, as the volume of the adsorbed phase (V_a) can change as a function of pressure and is conceptually and physically hard to measure. Thus, V_a is typically left as an unknown. When the buoyancy effect is accounted for on all displaced volumes except for that by the adsorbed phase, we get the mass change due to the excess amount of adsorbate, m_a^{ex} , which is given by equation (5); notice the first part of equation (5) reflects equation (1).

$$m_a^{ex}=m_a-\rho_g V_a=\Delta m_m+\Delta \rho_g V_s+\Delta \rho_g V_B-\Delta \rho_g V_B^{CWS}$$

(two- beam balance, excess uptake mass of adsorbate) (5)

In equation (5), m_m is measured, and ρ_g is determined from an equation of state; however, additional measurements or calculations are required for the volumes of the various components of the balance. Those volumes can be determined directly *in situ* with a helium isotherm, where the collective volume ($V_c=V_s+V_B-V_B^{CWS}$) is determined after the sample is loaded. Assuming helium to be a non-adsorbing gas, the observed change in the sample mass as a function of pressure, P , can be attributed solely to the buoyancy factor. The collective volume, absent V_a , can then be calculated from the slope, m_m/P , through equation (6), where R is the universal gas constant, T is the temperature in Kelvin, M is the atomic weight of helium, and Z is the compressibility factor. Alternatively, the collective volume can be calculated through the slope of a plot of m_m versus ρ_g . When the volume is determined collectively, the excess uptake mass of the adsorbate from the buoyancy correction is given by equation (7), and we will refer to this direct approach to buoyancy correction as the **helium method** [10, 13]. This method is especially attractive when the mass and density of the sample and all the balance components are unknown.

$$V_c=-\left(\frac{\Delta m_m}{\Delta P}\right)\left(\frac{RT}{MZ}\right)=-\frac{\Delta m_m}{\Delta \rho_g}$$

(6)

$$m_a^{\text{ex}} = \Delta m_m + \Delta \rho_g V_c \quad (7)$$

Alternatively, the individual volumes of the different components on the balance can be determined *ex situ* from measured density and mass. It is important to note that for porous materials, the skeletal density is used to determine surface excess uptake. The skeletal volume of a sample is the volume occupied by the sample minus all accessible pore volumes, and the skeletal density is calculated from the mass and skeletal volume of the sample. The volume of each part can then be determined by multiplying its density with its respective mass. We will refer to buoyancy correction by this indirect approach as the **manual method** [10].

In a third method, the buoyancy correction can be accounted for by running a ‘blank’ isotherm with the adsorptive gas for a non-porous sample, such as silicon shot (Si shot), that has a negligible specific surface area (see figure S1 (stacks.iop.org/MST/28/125802/mmedia)) and shows no appreciable gas adsorption. Here all the mass change is attributed to the effect of the buoyancy force, and the sample is assumed to adsorb none or only a negligible amount of the adsorptive. In this **subtraction method**, the excess uptake is obtained by simply subtracting the raw blank isotherm from the raw sample isotherm (see equation (8)). However, the collective volume of the blank run must be the same as (or as close as possible to) the sample run. If none of the components of the balance are changed out, this method only requires that the skeletal density of the adsorbent and non-porous blank be known to ensure that the same volume of each sample is used. Sircar described a similar method, where the isotherm of a reference non-porous blank ran with helium was used as the baseline in the context of determining the amount of helium adsorbed by a porous sample [17].

$$m_a^{\text{ex}} = \Delta m_m^{\text{adsorbent}} - \Delta m_m^{\text{blank}} \quad (8)$$

Experimental and methods

Materials

RM 8852 (ammonium ZSM-5 zeolite) [16, 18] was acquired from the National Institute of Standards and Technology. Silicon shot was received from National Renewable Energy Laboratory³. Carbon dioxide (99.999%), helium (99.999%) and nitrogen (99.999%) were purchased from commercial sources.

³Certain commercial equipment, instruments, or materials are identified in this article. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

Ex situ sample activation

For measurements made in the helium pycnometer, RM 8852 was activated in a tube furnace attached to turbomolecular pumping station that is equipped with a dry scroll pump (10^{-4} mbar)⁴ backing a turbomolecular high-vacuum pump (10^{-7} mbar). Under high vacuum the temperature was ramped from room temperature to 623 K at a rate of 1 K min⁻¹, held at 673 K for 12 h, and then cooled down to room temperature. After activation, the sample was transferred under vacuum from the activator tube to an argon glovebox for storage until the skeletal density measurement.

Helium pycnometer

Skeletal densities were measured using a helium pycnometer. Before each measurement, activated RM 8852 was loaded into a sample holder, capped with the fritted cap inside the glovebox, and then quickly transferred to the He pycnometer sample chamber to avoid uptake of moisture. Si shot, not requiring outgassing, was loaded to the sample holder in air. Each measurement was made by dosing the sample chamber with helium (1.34 bar), which was then allowed to expand into the reference chamber. The skeletal density of each sample was determined from the average of at least six aliquots. The skeletal density of each aliquot is an average of 50 measurement cycles. The expanded uncertainty (U) in the skeletal density is 0.005 g cm⁻³. The skeletal densities of RM 8852 and Si shot were found to be (2.355 ± 0.005) g cm⁻³ and (2.315 ± 0.005) g cm⁻³, respectively.

Sample loading and outgassing with 20 bar gravimetric instrument

RM 8852 was loaded into a 20 bar unit in a stainless-steel mesh pan. RM 8852 was degassed at room temperature under vacuum at an evacuation rate of 200 mbar min⁻¹ until a pressure of approximately 5 mbar and then heated up to 623 K at a heating rate of 1 K min⁻¹ and held at this temperature for 18 h 40 min under high vacuum (10^{-7} mbar). The sample was then cooled down to 293 K before the CO₂ isotherm measurement. Si shot could be run with or without activation following the procedure for RM 8852 without affecting the CO₂ isotherms.

Measurement of adsorption isotherms with 20 bar gravimetric instrument

Each CO₂ adsorption isotherm is an average of measurements made in at least two separate aliquots of activated RM 8852 (~0.1 g) or Si shot (~0.1 g) at 293 K (20 °C) up to 20 bar on the 20 bar system, which is equipped with a balance with a weighing resolution of 0.1 µg. The system is configured with automated switching between two pressure measurement/control ranges: Range 1: 0 bar to 20 bar is measured with a silicon sensor pressure transducer with an accuracy of ±8 mbar (0.04% of Full Scale (F.S.), combined non-linearity, repeatability, hysteresis) and a resolution of 12 mbar (0.006% F.S.). Range 2: 0–100 mbar is measured with a capacitance manometer with an accuracy of ±0.150 mbar (0.15% reading, combined non-linearity, repeatability, hysteresis) and a resolution of 1×10^{-3} mbar (0.001% F.S.). The temperature of the stainless-steel sample chamber was kept constant by a circulator bath with a temperature stability of ±0.02 K. The temperature of the

⁴10 bar = 1 MPa.

counterweight and upper hangdown wires was controlled using an anti-condensation system (ACS) air bath that was set to either 298 K or 313 K. As a function of temperature and pressure, the instrument determines the apparent measured mass change of the sample, which is due to a combination of gas adsorption and buoyancy effect. The excess amount of gas adsorbed (m_a^{ex}) was determined by correcting the measured apparent mass change for buoyancy effect using either subtraction (equation (8)) or manual method (equation (5)); ρ_g was determined from version 9.1 of the NIST REFPROP database [19]. Each V_B or V_B^{CWS} (i.e. *volume of each separate component*) was determined externally from known mass and density. The density of the stainless-steel sample holder and stainless steel counterweight were set to 7.9 g cm^{-3} , lower hangdown wire set to 21 g cm^{-3} , upper hangdown wire set to 19.3 g cm^{-3} as provided by the instrument manufacturer.

Sample loading and outgassing in 50 bar gravimetric instrument

The NIST RM 8852 was loaded into a 50 bar gravimetric system in a 12 mm diameter quartz sample holder. The sample was degassed at room temperature until the pressure was $<2 \text{ mbar}$ and then heated up to 623 K at a heating rate of 1 K min^{-1} and held at this temperature for 14 h under high vacuum (10^{-5} mbar). The sample was then cooled down to 298 K or 323 K before the helium measurement was collected. Before each CO_2 or N_2 measurement, the sample was reheated to 383 K at a heating rate of 1 K min^{-1} and held at this temperature for 1 h under high vacuum (10^{-5} mbar) to remove all residual adsorbed gas molecules from the previous He run before being cooled down to 293 K for the isotherm measurement. Si shot could be run with or without activation following the procedure for RM 8852 without affecting the CO_2 or N_2 isotherms.

Measurement of adsorption isotherms with 50 bar gravimetric instrument

Each CO_2 or N_2 adsorption isotherm is an average of measurements collected for at least two separate aliquots of activated RM 8852 ($\sim 0.2 \text{ g}$) or Si shot ($\sim 0.2 \text{ g}$) at 293 K up to 45 bar on the 50 bar gravimetric unit equipped with a 2-beam null balance with a weighing accuracy of 0.1% . The instrument has two pressure transducers in two pressure ranges. Below 1.27 bar , the instrument uses a temperature-regulated capacitance manometer (pressure range of $2.67 \times 10^{-5} \text{ bar}$ to 33.3 bar) with an accuracy of 0.12% of reading (including non-linearity, hysteresis, and non-repeatability) and a resolution of 13.3 mbar (0.002% of F.S.). Above 1.27 bar , the instrument uses a silicon-sensor pressure transducer with an accuracy of $\pm 20 \text{ mbar}$ (0.04% F.S., combined non-linearity, repeatability, hysteresis). The temperature of the stainlesssteel sample chamber is kept constant by a circulator bath with temperature stability of $\pm 0.1 \text{ K}$. The instrument is housed in a heating cabinet air bath, allowing the temperature in the rest of the instrument to be kept at $T_2 = 298 \text{ K}$ or 323 K . The subtraction and manual methods were performed as described above for the 20 bar instrument. The density of the fused quartz sample holders was set to 2.2 g cm^{-3} and that of the stainless steel hangdown wires was set to 7.8 g cm^{-3} . The volume was also determined collectively from a helium isotherm measurement, in which case the excess uptake was determined from equation (7). Each He adsorption isotherm was collected with T1 at either 298 K or 323 K up to 40 bar before the CO_2 or N_2 isotherm measurement.

Subtraction method and blank subtraction

For the subtraction method, the raw data (apparent uptake, m_m) for the sample and non-porous blank were used. For the helium and manual method, the raw data for the sample and blank were both corrected for buoyancy using the corresponding method to obtain the surface excess uptake (m_a^{ex}) before subtracting the blank data. For all methods, subtraction of the blank was performed using units of mass of adsorbate (g or mmol) instead of mass of adsorbate per mass of adsorbent (wt%, mmol g⁻¹).

Other experimental considerations

While sample preparation and activation can affect the resulting isotherm, *these differences can be accounted for when the sample activation conditions are properly followed and reported*. For isotherm measurement using gravimetric instruments, instrument calibration and isotherm equilibrium conditions should be ensured. These can be checked with standard masses and reproducibility of runs. A material that is stable to high pressure is desirable. In this work, duplicate runs of the same aliquot consistently yielded the same result after reactivation, indicating that the structural integrity of the pores of RM 8852 is maintained (also supported by PXRD patterns, see figure S2). In addition, the adsorption isotherm is fully reversible (the desorption branch follows the same path of the adsorption branch), which is associated with a gas/solid system that does not undergo phase transition of the gas or the solid. During the data collection (measurement), an area of concern is the temperature of all the components of the instrument/microbalance. In the asymmetric two-beam balance, typically only the sample side, where the adsorbent is loaded, is enclosed by either a circulator bath or other means of temperature control set to the desired analysis temperature (figure 1, yellow box). The shorter counterweight side and the upper part of the hangdown wire on the sample side are either at room temperature or possibly another temperature. Some instrument designs come with an air bath (heat cabinet or heating enclosure) that controls the temperature (T2) of all other components of the instrument beside the sample section of the balance. Such an air bath can be set at various temperatures (usually from room temperature to 313 K or 323 K) to prevent the condensation of gases or to keep the microbalance at an optimal temperature.

Results and discussion

The temperature gradient of the balance components is expected to affect the raw data collected (as measured mass is affected by gas density). However, *given that the sample is controlled at the analysis temperature, T1, regardless of the temperature setting of the air bath (that controls the temperature (T2) of the counterweight and other instrument components), we hypothesized that the appropriate buoyancy correction and blank correction will result in the same isotherm (i.e. the gas uptake of the same sample must be consistent at the same analysis temperature)*. As we will demonstrate, the method used to apply buoyancy correction is critical here.

Given our aforementioned hypothesis, we tested the effect of setting the air bath (counterweight and upper balance components) to different temperatures (298 K, 313 K and 323 K, T2 in figure 1) on the resulting high-pressure CO₂ and N₂ isotherms of RM 8852 at

293 K. The experiments were conducted using gravimetric systems capable of going up to 20 bar or 50 bar. For simplicity, only the raw data isotherms for CO₂ collected from the 50 bar instrument are shown in figure 2.

As illustrated in figure 2, there are two features in the raw datasets that demonstrate the effect of the two temperature gradients (293 K to 298 K and 293 K to 323 K): (1) the apparent gas uptake in the raw isotherm when T₂ is at 323 K is lower than when it is at 298 K, and (2) the raw isotherms diverge with increasing pressure. These observations can be explained by the pressure-volume-temperature property of CO₂ as shown in figure 3. Figure 3(A) is a plot of the density of CO₂ as a function of pressure at three different temperatures (293 K, 298 K, and 323 K). The density of CO₂ at the higher temperature is lower than its density at the lower temperature. The illustrations in figures 3(B) and (C) show that the buoyancy force on the sample portion is the same in both measurements since it is always set to 293 K (T₁). However, the magnitude of the opposing buoyancy force on the counterweight and upper hangdown wires when T₂ is set to 323 K is smaller than when it is set to 298 K. This is expected because CO₂ is less dense (and the buoyancy force is smaller) at 323 K compared to 298 K. The smaller opposing buoyancy force from the counterweight side means a larger overall buoyancy force on the sample side, causing the measured mass, m_m , to be smaller. The second observation, that there is increasing difference in the raw data isotherms as a function of pressure, is a reflection of the increasing difference in CO₂ density as a function of pressure at any two different temperatures in figure 3(A).

The resulting excess adsorption isotherms for the two datasets after correcting for the buoyancy effect using the three different buoyancy correction methods (helium, manual, and subtraction) are shown in figure 4. The corrected datasets with T₂ at 298 K and 323 K using the subtraction method match with each other closely ($\text{uptake}_{44\text{bar}} = (3.56 \pm 0.02) \text{ mmol g}^{-1}$ and $(3.55 \pm 0.02) \text{ mmol g}^{-1}$), in contrast to their noticeable difference before any correction ($\text{uptake}_{44\text{bar}} = (2.09 \pm 0.01) \text{ mmol g}^{-1}$ and $(1.95 \pm 0.02) \text{ mmol g}^{-1}$) (see figure 2). There is a slight deviation between the two datasets after the manual correction ($\text{uptake} = (3.50 \pm 0.01) \text{ mmol g}^{-1}$ and $(3.60 \pm 0.01) \text{ mmol g}^{-1}$), and the helium-method-corrected datasets show the biggest discrepancy in the amount of CO₂ adsorbed ($\text{uptake}_{44\text{bar}} = (3.47 \pm 0.02) \text{ mmol g}^{-1}$ and $(3.36 \pm 0.01) \text{ mmol g}^{-1}$) among the three methods.

The helium-corrected isotherm with T₂ at 323 K is notably different than the others. Further examination revealed that the helium method is inappropriate when the temperature of the other components of the microbalance (upper hangdown, counterweight, etc) is not the same as the sample analysis temperature (i.e. T₂ ≠ T₁). A major reason for this is that when the volume is measured collectively, the entire volume can only be assigned to one gas density, usually that at the analysis temperature. However, because the density of CO₂ changes so drastically with temperature, and it is impossible to know the volumes of each individual component based on the helium isotherm, the helium method begins to fail when there is a temperature gradient and the correction deviates more with increasing temperature gradient and pressure. For gases with more ideal behavior and smaller changes in density as a function of temperature, the effect on the calculated uptake resulting from assigning a single gas density to all the displaced volumes is smaller, although still present (See figures S3–S6, particularly figure S6, in supporting information on excess N₂ isotherms for comparison). In

contrast to the helium method, the manual method is more rigorous when there is a temperature gradient because it can account for the various volumes at the various temperature zones. The same is true of the subtraction method. Given that the density of CO₂ at the analysis temperature of 293 K is much closer to its density at 298 K than that at 323 K, the helium correction of the data with T2 at 298 K is indeed closer to the values found using the other correction methods, as expected.

Although the manual-corrected datasets display a much better agreement between the two different temperatures and with the subtraction-corrected datasets, there is still a difference in the data (figure 4(B)). This problem can be fixed by measuring the CO₂ isotherm of a blank, such as an empty sample holder or a non-adsorbing, non-porous sample, under the same experimental conditions. The blank isotherm is adjusted with the same buoyancy correction method, and then subtracted from the excess CO₂ isotherm of the RM 8852 adsorbent. Si shot was chosen as the blank because it shows no appreciable adsorption compared to an empty pan (figure S7), its skeletal density is similar to that of the sample (2.315 g cm⁻³ and 2.355 g cm⁻³, respectively) allowing a similar mass and volume to be used, and its data had already been collected for the subtraction method.

The subtraction method essentially already does the background correction (blank correction), along with the buoyancy correction, which is why it has the best agreement between the two datasets among the three buoyancy correction methods. See figure 5 for raw data isotherm for Si shot used in the subtraction method. The excess CO₂ isotherms of Si shot corrected using the helium and manual methods are shown in figure 6, and the excess CO₂ isotherms of RM 8852 after the blank correction are shown in figure 7. For comparison, figure 7 also shows subtraction-corrected datasets and data from the 20 bar instrument. A major benefit of having multiple sorption instruments in our laboratory is the ability to cross check results. As can be seen in figure 7, the subtraction method and blank-corrected manual method are in better agreement (within the expanded uncertainty in uptake) than the blank-corrected helium method. Furthermore, the agreement of the resulting CO₂ isotherms from the two instruments using the manual and subtraction methods and the blank correction suggests the correction has achieved accuracy independent of instrument used.

For comparison with blank-corrected excess N₂ adsorption data, see figure S8, which also demonstrates that the manual and subtraction methods are in better agreement with each other than with the helium method. Figure S9 shows that when using the helium and manual methods, data blank-corrected using the CO₂ isotherm of an empty sample holder is essentially the same as data blank-corrected with the CO₂ isotherm of Si shot (figure 7). However, an empty sample holder does not work with the subtraction method, which requires that a blank with the same volume as the sample be used.

As a non-porous sample, we expected Si shot not to adsorb CO₂. For the manual correction, any apparent adsorption by Si shot can be attributed to balance calibration, transducer nonlinearity, small uncertainties in mass and density measurements of the various balance components, any difference in apparent volumes of balance components used versus that probed by the adsorptive gas [20], as well as effects in temperature partitioning across the different volumes. As we can see in figure 7, after the blank correction the data with T2 =

298 K matches the data with $T_2 = 323$ K well using the manual method ($\text{uptake}_{44\text{bar}} = (3.53 \pm 0.01) \text{ mmol g}^{-1}$ for both). The same observation was made for the excess N_2 adsorption data (figure S8). We note that this blank correction will cancel out the small errors in the temperature partition and the mass and density measurements of the hangdown wires, sample holder, and counterweight if these components are not changed out between the sample and blank runs. However, it is less applicable to error in the density/volume measurement of the sample or the non-porous blank sample because the subtraction of the non-porous material cannot cancel out these components. We would like to stress the importance of running a blank as a good way to identify and correct for errors in the *ex situ* determined density and mass of the different components of the balance. When we purposefully used the wrong mass for a balance component, we could still arrive at the same final isotherms by subtracting the Si shot CO_2 isotherms (also treated with the same wrong value) (see figure S10, right for illustration).

The deviation in the helium-corrected CO_2 isotherm for the blank (Si shot or empty pan) from zero uptake can be attributed to the inherently confounding factor that one cannot account for different gas densities at different temperatures. Other notable factors include uncertainties in collective volume measurements, balance calibration, transducer nonlinearity, as well as any difference in apparent collective volume of balance components probed by He and the adsorptive gas [20]. As expected, there is a greater blank correction to the T_2 at 323 K dataset because the error in the helium correction due to temperature gradient with the T_2 at 323 K is expected to be greater than at 298 K. In addition, the helium-corrected datasets with the T_2 at 298 K and 323 K after the blank correction are in much better agreement with each other ($\text{uptake}_{44\text{bar}} = (3.45 \pm 0.02) \text{ mmol g}^{-1}$ and $(3.44 \pm 0.02) \text{ mmol g}^{-1}$) and to the other two methods; however, they do not match up exactly with the blank-corrected manual-corrected and subtraction-corrected datasets. Below, we offer an explanation for this.

It was observed that the helium isotherm for RM 8852 consistently yielded a lower collective volume than that of Si shot. After accounting for the collective volume without any sample (empty pan), the helium isotherms on average were consistent with the expected volume of the Si shot, but underestimated the volume for RM 8852 at both temperatures (sample-specific underestimation) (see table S1). This factor led to a systematically lower uptake after the blank correction. As previously mentioned, the blank subtraction is less forgiving to error in the sample volume. However, by using the expected collective volume in the helium method, we could obtain highly agreeable excess uptake using all three methods for both CO_2 and N_2 adsorption isotherms (see figures S13 and S16) after applying the blank correction.

We believe the sample-specific error in volume measurement is the result of helium adsorption, which has been discussed in several adsorption studies [21–25]. The adsorption of helium can be expected in RM 8852, a microporous sample with high surface area. This would cause the calculated sample volume for RM 8852 to be lower than for Si shot, as the mass change due to buoyancy force will appear smaller with He adsorption, which adds mass to the sample, and counters the buoyancy force.

Previously, Maggs *et al* and Suzuki *et al* have measured the adsorption of helium in carbons and zeolites, respectively, using differential analysis temperature in volumetric gas sorption systems [23, 24]. Sircar *et al* looked at correction to helium data from the Henry constant calculated over a large temperature range, assuming no adsorption at the highest temperature [17]. Gumma and Talu illustrated the adsorption of helium on a silicalite and proposed a method to correct for helium adsorption without the assumption that He is non-adsorbing at the highest analysis temperature [26]. Given the complexity of some of the corrections developed for helium adsorption, the researchers have suggested a need for a standard set of conditions in which to perform the helium measurement, which would make comparison of data easier even if helium adsorption is not fully corrected [26].

As suggested in the literature, increasing the temperature of the helium isotherm has been shown to reduce the adsorption of helium [23, 24]. We note that both the helium isotherm and measurements using the helium pycnometer (from which expected values were determined) were carried out at 298 K. However, the helium isotherm was measured to much higher pressure range (40 bar versus 1.34 bar; 40 bar was chosen to ensure reproducibility of the measured collective volume). In addition, the collective volume is determined from a relatively small change in sample mass (typically less than 1 mg for our experiments), where a small change in mass due to even a very small amount of helium adsorption would be expected to have a large effect. Thus, the amount or effect of helium adsorption or entrapment on the determined sample volume/density would not be expected to be the same for the two methods. Given that the air bath for our 50 bar system can only go up to 323 K, the analysis temperature (T1) of the helium isotherm was increased from 298 K to 323 K, while keeping T2 at 323 K. Indeed, the resulting collective and sample volumes from the helium isotherms are very close to anticipated values for both Si shot and RM 8852 (see table S2). While this set of experiments worked for the RM 8852 sample, different porous samples may require different temperatures or methods to minimize or correct for helium adsorption. With the hightemperature helium isotherm data, the experimental results for CO₂ data at 293 K collected with T2 at 323 K corrected using the subtraction method, and blank-corrected (with an empty pan or Si shot) helium and manual methods are shown in figure 8. All datasets are in good agreement (all have uptake_{44bar} = 3.53 ± 0.02 mmol g⁻¹). Along with the tremendous improvement in the helium-corrected data, the slight improvement in the subtraction-corrected data is due to more rigorous use of a close as possible sample and Si shot volumes.

Conclusions

In this paper, we demonstrated that if a sample is activated using consistent methods, variation in measurement conditions (temperature gradient, instrument calibration, etc) can still be corrected using the appropriate protocol for three buoyancy correction methods to arrive at the same resultant excess CO₂ and N₂ adsorption isotherms. A blank correction with a non-porous blank or empty sample pan with the analysis gas is required for the helium and manual methods to account for error in temperature partition, balance component volume, or instrument calibration. In the subtraction method, the effect of buoyancy force and error in instrument calibration are already accounted for so long as the same volume of the adsorbent and non-porous blank is used. Although the manual correction

requires that the volume of all individual components be known, it can better account for the difference in the temperature at the sample site and the rest of the microbalance sites and does not require additional helium isotherms to be run for the sample and blank. While the accuracy of the *in situ* helium measurement required above ambient temperature in our system, the helium method can determine the collective volume with just one isotherm. Even though the helium correction is really only applicable when the temperature at all the microbalance sites are consistent, if care is taken to accurately determine the collective volume, this method could still arrive at the true uptake after the blank correction even if the analysis and air bath temperatures are not the same.

In the larger picture, this best practice and standardization of high-pressure gas sorption measurement can improve the accuracy with which different materials are being compared and enhance the pace of material design principles. The recommended best practices below for collecting and reporting high-pressure data for gravimetric adsorption instrument are based on the techniques we used to arrive at the matching adsorption isotherms using two different gravimetric instruments and the three buoyancy correction methods.

- Ensure all instrumental sensors (temperature controllers, pressure transducers, balance) are calibrated. Calibrate the balance with standard masses.
- Activate the sample based on recommended activation conditions. Ensure that the integrity of the sample is maintained and that activation is complete. Report the activation conditions.
- Make sure the equilibrium condition is met for the isotherm. This can be checked with reproducibility of data as well as looking at kinetic data to ensure mass change is stabilized for each pressure step.
- Select and report the appropriate buoyancy correction based on instrument design. Whenever possible, cross check results with different instruments or buoyancy correction methods.
 - Determine gas density using a critically evaluated equation of state. Report which equation of state was used. We recommend using NIST REFPROP database to obtain PVT properties.
 - Subtraction method: ensure that the same volume of sample as nonporous blank is used. The skeletal density of both the sample and blank must be known and comparable.
 - Manual method: determine the mass and skeletal density of all balance components. Determine the volume of each component and the temperature zone (e.g. T1 or T2) where each volume is located. A blank correction should be performed to minimize small uncertainties and error in volumes and the temperature partition.
 - Helium method: determine the collective volume with a helium isotherm. Ensure that helium adsorption is minimized by measuring the helium isotherm at a higher temperature, if needed. The method inherently fails when there is a temperature gradient. However, a blank

correction can fix the error in temperature partition, volume errors that are not sample-specific, and a small error in instrument calibration.

- Measure the blank run with the same analysis gas and identify the correct unit (typically mass, for gravimetric system) to be used for the blank subtraction.
- Report the experimental conditions (skeletal density used/determined, instrument setup, gas purity, temperature, and pressure).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

H G T N is supported by the NIST-NRC postdoctoral research associateship program. J H acknowledges support from the NIST-SURF program. The Facility for Adsorbent Characterization and Testing was funded by the Department of Energy, Advanced Research Projects Agency in Energy (ARPA-E) through Interagency Agreement No. 1208-0000. We thank Dr Augie Venero from L&C Science for helpful discussion about the subtraction method and Dr Virgil Debique from Hiden Isochema for helpful discussion using the manual method. We thank Dr Phil Parilla from the National Renewable Energy Laboratory for helpful technical discussion and for providing the Si shot sample.

References

1. Rochelle GT. Amine scrubbing for CO₂ capture. *Science*. 2009; 325:1652–4. [PubMed: 19779188]
2. Espinal L, Poster DL, Wong-Ng W, Allen AJ, Green ML. Measurement, standards, and data needs for CO₂ capture materials: a critical review. *Environ Sci Technol*. 2013; 47:11960–75. [PubMed: 24060087]
3. Yu C-H, Huang C-H, Tan C-S. A review of CO₂ capture by absorption and adsorption. *Aerosol Air Qual Res*. 2012; 12:745–69.
4. D'Alessandro DM, Smit B, Long JR. Carbon dioxide capture: prospects for new materials. *Angew Chem, Int Ed*. 2010; 49:6058–82.
5. Olajire AA. CO₂ capture and separation technologies for end-of-pipe applications—a review. *Energy*. 2010; 35:2610–28.
6. Feng K, Davis SJ, Sun L, Hubacek K. Drivers of the US CO₂ emissions 1997–2013. *Nat Commun*. 2015; 6:7714. [PubMed: 26197104]
7. Peng Y, Krungleviciute V, Eryazici I, Hupp JT, Farha OK, Yildirim T. Methane storage in metal-organic frameworks: current records, surprise findings, and challenges. *J Am Chem Soc*. 2013; 135:11887–94. [PubMed: 23841800]
8. Li J-R, Kuppler RJ, Zhou H-C. Selective gas adsorption and separation in metal-organic frameworks. *Chem Soc Rev*. 2009; 38:1477–504. [PubMed: 19384449]
9. Liu Q, Wu L, Jackstell R, Beller M. Using carbon dioxide as a building block in organic synthesis. *Nat Commun*. 2015; 6:5933. [PubMed: 25600683]
10. Rouquerol, F., Rouquerol, J., Sing, K. Adsorption by Powers & Porous Solids: Principles, Methodology and Applications. New York: Academic; 1999.
11. ISO 15901-2:2006(E). Pore Size Distribution and Porosity of Solid Materials by Mercury Porosimetry and Gas Adsorption—Part 2: Analysis of Mesopores and Macropores by Gas Adsorption. Geneva: ISO; 2006.
12. Wang J, Huang L, Yang R, Zhang Z, Wu J, Gao Y, Wang Q, O'Hare D, Zhong Z. Recent advances in solid sorbents for CO₂ capture and new development trends. *Energy Environ Sci*. 2014; 7:3478–518.

13. Keller, J., Staudt, R. Gas Adsorption Equilibria: Experimental Methods and Adsorption Isotherms. Berlin: Springer; 2010.
14. Thommes M, Kaneko K, Neimark Alexander V, Olivier James P, Rodriguez-Reinoso F, Rouquerol J, Sing Kenneth SW. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC technical report). Pure Appl Chem. 2015; 87:1051–69.
15. Broom DP, Thomas KM. Gas adsorption by nanoporous materials: future applications and experimental challenges. MRS Bull. 2013; 38:412–21.
16. Turner S, et al. Characterization of chemical properties, unit cell parameters and particle size distribution of three zeolite reference materials: RM 8850—Zeolite Y, RM 8851—Zeolite A and RM 8852—Ammonium ZSM-5 Zeolite. Microporous Mesoporous Mater. 2008; 107:252–67.
17. Sircar S. Measurement of Gibbsian surface excess. AIChE J. 2001; 47:1169–76.
18. NIST. Reference Materials. 2017. www.nist.gov/srm
19. Lemmon, EW., Huber, ML., McLinden, MO. NIST standard reference database 23: reference fluid thermodynamic and transport properties-REFPROP, Version 9.1. www.nist.gov/srd/refprop
20. Staudt R, Sailer G, Tomalla M, Keller JU. A note on gravimetric measurements of gas-adsorption equilibria. Ber Bunsenges Phys Chem. 1993; 97:98–104.
21. Robens E, Keller JU, Massen CH, Staudt R. Sources of error in sorption and density measurements. J Therm Anal Calorim. 1999; 55:383–7.
22. Lorenz K, Wessling M. How to determine the correct sample volume by gravimetric sorption measurements. Adsorption. 2013; 19:1117–25.
23. Maggs FAP, Schwabe PH, Williams JH. Adsorption of helium on carbons: influence on measurement of density. Nature. 1960; 186:956–8.
24. Suzuki I, Kakimoto K, Oki S. Volumetric determination of adsorption of helium over some zeolites with a temperature-compensated, differential tensimeter having symmetrical design. Rev Sci Instrum. 1987; 58:1226–30.
25. Springer C, Major CJ, Kammermeyer K. Lowpressure adsorption of helium on microporous solids. J Chem Eng Data. 1969; 14:78–82.
26. Gumma S, Talu OG. Dividing surface and helium adsorption. Adsorption. 2003; 9:17–28.

Figure 1. Schematic of the instrumental set-up of a gravimetric gas sorption instrument with an asymmetric two-beam microbalance: initially, the balance is tared so that $m_m \cong m_{act} = 0$; (A) sample is loaded; $m_m \cong m_s$ assuming buoyancy force is insignificant; (B) sample is exposed to the adsorptive gas and adsorption takes place; $m_m = m_s + m_a - \rho_g V_{SS} + \rho_g V_{CWS}$; $m_{act} = m_s + m_a$; T1 = isotherm temperature; T2 = air bath temperature, which is the temperature of any component not inside the analysis temperature controller; pink circles = adsorptive. See text for symbol definition.

Figure 2.

Raw CO₂ adsorption isotherms of RM 8852 at 293 K (T1) with T2 at 298 K (blue symbols) and 323 K (red symbols) collected on the 50 bar instrument. R = raw data (squares). (T1/T2) is indicated in parentheses. The expanded uncertainty in the uptake is $U = 0.02 \text{ mmol g}^{-1}$.

Figure 3.

(A) Pressure-volume-temperature properties of CO₂ and He plotted as gas density as a function of pressure. The density of CO₂ and He was generated using the NIST REFPROP database. Diagrams showing the different forces acting on the balance and the effect of the air bath temperature, T₂ = 298 K (B) and 323 K (C), on the magnitude of the buoyancy force on the counterweight side and upper hangdown wire. Only forces affecting the mass reading after the balance is tarred are shown.

Figure 4. (A) Excess CO₂ adsorption isotherms of RM 8852 at 293 K (T₁) with T₂ at 298 K (blue symbols) and 323 K (red symbols) corrected using the three buoyancy correction methods. (B) Figure (A) enhanced in the y-axis. M = manual-corrected data (triangles); H = helium-corrected data (diamonds); S = subtraction-corrected data (circles). (T₁/T₂) is indicated in parentheses. The expanded uncertainty in the uptake is $U = 0.02 \text{ mmol g}^{-1}$.

Figure 5.

Raw CO₂ adsorption isotherms for RM 8852 (filled-in symbols) and Si shot (open symbols) at 293 K (T₁) with T₂ at 298 K (blue symbols) and 323 K (red symbols). The effect of the buoyancy force on the measured mass is revealed in the deviation in CO₂ adsorption isotherms for Si shot from zero uptake. R = raw data (square). (T₁/T₂) is indicated in parentheses. The expanded uncertainty in the uptake is $U = 0.02 \text{ mmol g}^{-1}$.

Figure 6.

(A) Manual-corrected and (B) helium-corrected excess CO₂ adsorption isotherms of RM 8852 (filled-in symbols) and Si shot (open symbols) at 293 K (T1) with T2 at 298 K (blue symbols) and 323 K (red symbols) showing some small deviation in Si shot CO₂ adsorption isotherms from zero uptake. M = manual-corrected data (triangles); H = helium-corrected data (diamonds). (T1/T2) is indicated in parentheses. The expanded uncertainty in the uptake is $U = 0.02 \text{ mmol g}^{-1}$.

Figure 7.

Blank-corrected excess CO₂ isotherms from (A) 50 bar and (B) 20 bar instruments. Comparison of the CO₂ adsorption isotherms of RM 8852 at 293 K (T1) with T2 at 298 K, 313 K and 323 K corrected with the subtraction method and after blank correction using the helium and manual methods. S = data processed with subtraction method (circles). M-MB = manual-corrected data minus manuallycorrected blank (triangles). H-HB = helium-corrected isotherm minus helium-corrected blank (diamonds). (T1/T2) is indicated in parentheses. The expanded uncertainty in the uptake is $U = 0.02 \text{ mmol g}^{-1}$.

Figure 8.

Comparison of the excess CO₂ adsorption isotherms of RM 8852 at 293 K (T1) with T2 at 323 K corrected with the subtraction method and after blank correction using the helium and manual methods. The helium method was performed at 323 K to minimize helium adsorption by RM 8852. After blank subtraction, the three methods resulted in the same surface excess CO₂ adsorption isotherm. S = data corrected with subtraction method. M-MB = manual-corrected data minus manual-corrected blank (triangles). H-MB = helium-corrected data minus helium-corrected blank (diamonds). Superscripts 1 and 2 indicate the use of Si shot (blue symbols) and empty pan (red symbols) as blank, respectively. (T1/T2) is indicated in parentheses. The expanded uncertainty in the uptake is $U = 0.02 \text{ mmol g}^{-1}$.