Reference isotherms for water vapor sorption on nanoporous carbon: results of an interlaboratory study

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Abstract

This paper reports the results of an international interlaboratory study sponsored by the Versailles Project on Advanced Materials and Standards (VAMAS) and led by the National Institute of Standards and Technology (NIST) on the measurement of water vapor sorption isotherms at 25 °C on a pelletized nanoporous carbon (BAM-P109, a certified reference material). Thirteen laboratories participated in the study and contributed nine pure water vapor isotherms and four relative humidity isotherms, using nitrogen as the carrier gas. From these data, reference isotherms, along with the 95% uncertainty interval ($U_{k=2}$), were determined and are reported in a tabular format.

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1 Introduction

Water covers most of the Earth's surfaces, largely as a liquid in lakes, seas, oceans, and as a solid in polar ice caps. Furthermore, water is found as vapor, droplets, and ice crystals in the atmosphere and is found in living organisms. The ubiquitous nature of water makes understanding its effects on the chemical structure and properties of materials important to the development, processing, and applications of materials associated with food production (Rückold et al. 2000; Schmidt and Lee 2012), pharmaceuticals (Levogeur and Williams 2006), construction (Benavente et al. 2021), separation processes (Mokhatab et al. 2019; Wang 2020), sorbent-based industries (Dawson et al. 2012; Lawrence and Katz 2022), and emerging water sorption applications such as water harvesting (Ejeian and Wang 2021) and thermal energy storage (Carrier et al. 2021). A primary way to characterize water and materials interactions is by measuring a water vapor sorption isotherm. A water vapor sorption isotherm is a measure of water content as a function of relative pressure (P/P_0) for pure water measurements or relative humidity (RH), when water is entrained in another gas. By providing the water content of a material, the effect of water uptake on the chemical structure and properties of materials can be investigated. In addition, a water vapor sorption isotherm can also be used to determine the stability, porosity, and hygroscopicity of a material. Given the ubiquity of water uptake processes, it is important to have reference data, reference materials and standardized protocols for water uptake measurements.

One way water vapor sorption isotherms are determined is by the tedious and time-consuming static desiccator method. In this method, a dry sample is placed in a desiccator at a fixed temperature with a salt slurry to create a given RH. The sample is repeatedly removed and weighed until the mass reading between successive weighing is nearly constant, thus determining the equilibrium water uptake at that temperature and RH. Repeating this at multiple RHs allows for an isotherm to be constructed. This method is prone to error due to disturbance of equilibrium by the opening and closing of the desiccator during weighing, and the uptake/release of water in the mass measurement environment (Lewicki and Pomaranska-Lazuka 2003). The use of salt slurry also limits which RH levels can be obtained. Using climate chambers, the RH can be generated at any desired levels by mixing wet and dry streams in different ratios to generate different RHs. In an alternative early method developed by McBain and Bakr, a helical quartz spring sorption balance is placed inside a vacuum tube, allowing a whole isotherm to be obtained without having to remove the sample between experiments and thus never exposing the sample to foreign gases or vapors (McBain and Bakr 1926; McBain et al. 1933). In this method, a bucket with sample is attached to a calibrated quartz fiber spring in the top part of a self-contained vacuum tube with the vapor generating liquid at the bottom, and two separate thermostats. The top thermostat controls the analysis temperature, and the bottom thermostat controls the vapor pressure. The system is sealed off after the sample is outgassed and the system is placed under vacuum, and then the liquid, which had been sealed off, is released into the system. The uptake mass is determined from the displacement of the spring.

Automated instruments for measuring vapor sorption isotherms were later developed and commercialized, (Benham and Ross 1989; Bergren 1994; Buckton et al. 2011; Czanderna and Vasofsky 1979; Dienstmaier 2014; Marshall et al. 1994; Rasmussen and Akinc 1983; Sandstede and Robens 1962; Williams et al. 2005) eliminating issues related to the desiccator method, and making it easier to measure vapor sorption isotherms. Common automated techniques include the following: dynamic vapor sorption (DVS), which combines continuous flow climate control with continuous mass measurements; automated vacuum sorption balances, which control water vapor pressure in an evacuated system and use an electronic microbalance; and automated manometric systems, which also control the water vapor pressure in an evacuated system and rely on pressure transducers to monitor changes in vapor pressure and determine uptake.

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With the large number of isotherms generated by automated instrumentation, there is an increasing need for standardized measurement protocols, reference materials, and reference data to ensure reliable and reproducible data. The National Institute of Standards and Technology (NIST), in partnership with the Department of Energy's Advanced Research Projects Agency (ARPA-E), initiated a program to develop reference materials, reference data, and measurement protocols to improve adsorption metrology. In consultation with the International Adsorption Society, NIST has identified the most important gases and parameters the community is interested in, which includes water vapor at ambient temperatures. The NIST Facility for Adsorbent Characterization and Testing (FACT Lab) has led two interlaboratory studies (ILSs) to develop reference isotherms. One study determined a reference high-pressure surface excess isotherm for adsorption of carbon dioxide on NIST Reference Material 8852 (ammonium ZSM-5 zeolite) at 20 °C up to 4.5 MPa (Nguyen et al. 2018). A second study, sponsored through Technical Working Area 39 of the Versailles Project on Advanced Materials and Standards (VAMAS), reported a reference surface excess isotherm for methane adsorption on NIST Reference Material 8850 (sodium zeolite Y) up to 7.5 MPa (Nguyen et al. 2020).

This paper reports a third ILS, also organized through VAMAS, investigating water vapor sorption on a pelletized nanoporous carbon at 25 °C as a function of relative pressure (P/P$_0$) for pure water measurements and relative humidity, when a carrier gas is used. Interest in the effect of atmospheric water on carbon has been dated to the early twentieth century in the rubber industry (Dewey et al. 1932). In addition to practical applications of water sorption on carbon materials, the surface functionality of carbons and their pore structures can lead to complex water adsorption, and this has been the subject of many fundamental studies (Liu et al. 2017). The sorbent used in this study is a certified reference material (CRM) with a BET specific surface area of 1396 ± 24 m^2/g, produced by the German Federal Institute for Materials Research and Testing (Bundesanstalt für Materialforschung und prüfung or BAM) and is known as BAM-P109 (Panne and Thünemann 2010). It was chosen because it is a widely available commercial nanoporous carbonaceous CRM. Although a water vapor sorption isotherm on this material has been reported, the measurement was made at 20 °C and only as a function of P/P$_0$ (Ross et al. 2016). Given that 25 °C is a more common temperature for water vapor sorption isotherms, 25 °C was chosen as the sorption temperature in this study. Whereas the two previous studies coordinated by the FACT Lab only looked at static measurements, the current study examines both static and dynamic measurements. While the previous studies focused on high-pressure measurements, the measurements in the current study are at subatmospheric and atmospheric pressures, because the saturation pressure of water at 25 °C is only 3.17 kPa (Wagner and Pruß 2002). Although

the effects of water sorption on the stability and proper use of biological reference materials and food CRMs have been studied and reported (Rückold et al. 2001; Rückold et al. 2003; Yazgan et al. 2006), this study is the first ILS to report reference data for a water vapor sorption isotherm using a CRM.

2 Experimental and data analysis methods

2.1 Methods

The ILS involved measurement of water vapor isotherms at 25 °C up to a relative pressure (P/P$_0$) of 0.95 or 95% relative humidity. BAM generously donated five bottles of BAM-P109, each containing ≈ 10 g of material, for the study. The five bottles were combined and divided through a spinning riffler into sixteen units of ≈ 3.1 g each. These units were distributed to the study participants. Thirteen laboratories participated in the ILS. The measurement capabilities of these laboratories included both manometric and gravimetric instruments and encompassed both static and dynamic measurements.

The measurement protocol instructions for the ILS were minimal. The protocol specified the use of liquid chromatography-mass spectrometry (LC-MS) grade water and that the carrier gas (N$_2$) for dynamic measurements have a minimum purity of 99.999%. Nitrogen was chosen as the carrier gas because standard humidity generators typically use carbon-dioxide free air, whose main component is nitrogen (Carroll et al. 2015; Hasegawa and Little 1977; Hyland and Wexler 1973; Scace et al. 1997). Enhancement effects were taken to be minimal (Hyland and Wexler 1973). Sample activation was to be heating over a period of 1 h to 200 °C and holding at that temperature for 3 h under vacuum with continuous pumping to a final pressure < 0.1 Pa. If the outgassing was performed in a separate manifold, exposure to air was to be minimized when transferring to the analysis port and the sample was to be re-outgassed in the instrument to 140 °C for at least 6 h to remove any adsorbed gases. The pressure range was from dry to 95% RH or P/P$_0 = 0.95$; twenty recommended equilibrium pressure points were provided. Measurements were to be conducted at 25 °C, which is nominally room temperature and is used in many practical applications. It was requested that a complete isotherm (with adsorption and desorption) be measured on two separate aliquots. It was recommended to perform a blank run (i.e., an isotherm in the absence of the adsorbent) to subtract from the isotherm measured with the adsorbent present (Nguyen et al. 2017). Participants were asked to submit an experimental report, which detailed their experimental procedures and data processing steps and to submit the isotherms in units of millimoles of adsorbed fluid per gram of activated carbon (mmol/g). Details of the experimental parameters and procedures employed by each of the study participants can be found in Table 1. Certain commercial items are identified in this paper. This identification does

Table 1 Experimental parameters of the participants

| Dataset	Measurement method	Gas purity (%)	Sample size (g)	Outgas condition[a]	Sample handling, weighing and transfer
1	Gravimetric, dynamic	N_2: 99.995 H_2O: distilled	0.010589, 0.008969	Heated ex-situ from room temperature to 200 °C at a rate of 3 °C/min, and held at 200 °C for 2 h in a N_2 stream	Activated ex-situ, transferred, and then reactivated in-situ at 80 °C for 10 h in N_2 stream. Mass after activation was then measured at 25 °C in the N_2 stream at 0% RH.
2	Gravimetric, dynamic	N_2: 99.998 H_2O: LC-MS grade	0.0438905, 0.0340408	Heated ex-situ from room temperature to 200 °C in 1 h, and held at 200 °C for 3 h (final pressure $< 10^{-5}$ Pa)	Activated ex-situ, then quickly transferred from the regeneration station to the instrument balance. The sample mass was measured in situ in N_2 flow after regeneration (ex-situ).
3	Gravimetric, dynamic	N_2: 99.999 H_2O: LC-MS grade	0.0251, 0.0275	Heated ex-situ from room temperature to 200 °C in 1 h, and held at 200 °C for 3 h (final pressure $< 1 \times 10^{-5}$ Pa)	Activated ex-situ, transferred, and then reactivated in-situ at 140 °C for 8 h in N_2 flow. Mass after activation was measured on microbalance at 0% RH in N_2 stream.
4	Gravimetric, dynamic	N_2: 99.999 H_2O: LC-MS grade	0.0508703, 0.0501845	Heated ex-situ from room temperature to 200 °C in 1 h, and held at 200 °C for 3 h (final pressure < 0.1 Pa)	Activated ex-situ, transferred, and then re-outgassed in-situ at 120 °C for 6 h in N_2 flow. Mass after activation was measured on microbalance at 0% RH in N_2 stream.
5	Gravimetric, dynamic	He: 99.999 H_2O: LC-MS grade	0.0241, 0.0269	Heated ex-situ from room temperature to 200 °C in 1 h, and held at 200 °C for 3 h (final pressure $< 1 \times 10^{-5}$ Pa)	Activated ex-situ, transferred, and then reactivated in-situ at 140 °C for 8 h with He flow. Mass after activation was measured on microbalance at 0% RH in He stream.
a, a*	Manometric, static	H_2O: distilled	0.2052, 0.2215	Heated ex-situ from room temperature to 200 °C in 1 h, and held at 200 °C for 3 h (better than 2.8 Pa/min)	Activated ex-situ, transferred, and then activated in-situ at 140 °C for 6 h. The sample was removed from the outgasser after activation for weighing.
b	Gravimetric, dynamic vacuum	H_2O: LC-MS grade	0.0408093, 0.0475303	Heated in-situ from room temperature to 200 °C in 1 h, and held at 200 °C for 3 h (final pressure $< 8.9 \times 10^{-4}$ Pa)	Sample activated in-situ. Sample mass was continuously measured during in-situ regeneration step under high vacuum and during in-situ cooling sample to 25 °C under high vacuum.
c	Gravimetric, static	H_2O: LC-MS grade	0.38400, 0.35542	Heated in-situ from room temperature to 200 °C in 1 h, and held at 200 °C for 3 h (final pressure < 0.2 Pa)	Sample activated in-situ. The dry mass of the samples was measured after the specified drying process.
d	Manometric, static	H_2O: LC-MS grade	0.1775, 0.1271	Heated in-situ from room temperature to 200 °C in 1 h, and held at 200 °C for 3 h (final pressure $< 1 \times 10^{-5}$ Pa)	Sample activated in-situ. After measurements, sample mass was determined after evacuation of the sample.
e	Manometric, static	H_2O: LC-MS grade He: 99.99995 (for V calc)	0.0934, 0.0986	Heated in-situ from room temperature to 200 °C in 1 h, and held at 200 °C for 1 h (final pressure < 0.1 Pa)	Sample activated in-situ. The sample was dosed with N_2 and the sample mass was determined statically after regeneration. The sample was reactivated in-situ at 140 °C for 3 h.
f	Gravimetric, static	H_2O: LC-MS grade	0.0206965, 0.0221180	Heated in-situ from room temperature to 200 °C in 1 h, and held at 200 °C for 3 h (final pressure: 1×10^{-4} Pa)	Sample activated in-situ. Sample mass was determined in-situ, under vacuum, using the instrument's microbalance, following the activation procedure.
g	Manometric, static	H_2O: LC-MS grade	0.1541, 0.1514	Heated ex-situ from room temperature to 200 °C in 1 h, and held at 200 °C for 3 h (final pressure: 0.5 Pa)	In-situ outgassing is unavailable in the instrument. Exposure to air was minimized during sample transfer to the measuring station. The sample mass was measured statically before and after the ex-situ activation with the sample cell backfilled with N_2.

Table 1 (continued)

Dataset	Measurement method	Gas purity (%)	Sample size (g)	Outgas condition[a]	Sample handling, weighing and transfer
h	Manometric, static	H_2O: 18 M-ohm	0.0488, 0.0529 Resubmission: 0.1473, 0.2009	Heated ex-situ at 200 °C for 3 h (final pressure: 13.3 Pa)	Activated ex-situ, transferred in air-free condition, and additionally activated in-situ at 140 °C for 6 h (to 6.7 Pa). Sample mass was determined after ex-situ activation.
i	Manometric, static	H_2O: LC-MS grade, degassed	0.1537, 0.1728	Heated in-situ from room temperature to 200 °C in 1 h, and held at 200 °C for 3 h (final pressure: 3.19×10^{-3} Pa)	Sample activated in-situ. Sample mass was measured statically before outgassing and an average mass loss of 2% was used to calculate the outgassed mass of the sample.

Dataset	Relative humidity or vapor pressure determination method and sorption equilibration criteria	Temperature and stability	Balance resolution and stability	Blank correction
1	Sensirion RH sensors SHT35RH. RH is generated by mixing dry and saturated N_2 streams using calibrated mass flow controllers (MFCs), with total flow of 200 mL/min. Humidity verification to within $\pm 1\%$ RH by measuring NaBr deliquescence point at 25 °C. Equilibration criteria = mass change (dm) < 0.02% in 60 min.	(25 ± 0.1) °C	0.01 µg, $< \pm 0.25$ µg	Yes
2	Rotronic HC2-SM Humidity probe with resolution: 0.1% RH and accuracy: $\pm 0.8\%$ RH at 20 °C. RH is generated by mixing dry and saturated N_2 streams using calibrated MFCs, with total flow = 100 mL/min. Equilibration criteria: at least 300 to 420 min followed by mass change/time [dm/dt] = 0.0001%/min.	(25 ± 0.2) °C	0.01 µg, n/a	Yes
3	Dew point analyzer calibrated with NaCl deliquescence point at 25 °C and Polyvinylpyrrolidone. RH accuracy $\pm 1\%$ RH. RH is generated by mixing dry and saturated nitrogen streams using calibrated MFCs, with total flow of 458 mL/min. Equilibration criteria: dm/dt < 0.001%/min for 99 min, or maximum of 480 min before going to the next RH point.	(25 ± 0.1) °C	0.01 µg, n/a	Yes
4	Rotronic HC2A-S humidity probe with resolution: 0.1% RH and accuracy: $\pm 0.8\%$ RH at 20 °C. RH is generated by mixing dry and saturated N_2 streams using calibrated MFCs, with total flow of 200 mL/min. Equilibrium criteria: dm/dt < 0.001%/min for a duration of 15 min, or maximum of 480 min before going to the next RH point with data points stored every 2 min.	(25.3 ± 0.1) °C	0.1 µg, n/a	Yes
5	Dew point analyzer calibrated with NaCl deliquescence point at 25 °C and Polyvinylpyrrolidone. RH accuracy $\pm 1\%$ RH. RH is generated by mixing dry and saturated N_2 streams using calibrated MFCs, with total flow of 458 mL/min. Equilibration criteria: dm/dt < 0.001%/min for 99 min, or maximum of 480 min before going to the next RH point.	(25 ± 0.1) °C	0.01 µg, n/a	Yes
a, a*	The absolute pressure was measured by pressure transducers accurate to $\pm 0.05\%$ of full scale (F.S.). P_0 at 25 °C was set to 3.17 kPa using NIST Chemistry Webbook, SRD 69, Thermophysical Properties of Fluid Systems (Lemmon et al. 2022). Equilibrium criteria: sorption rate change less than 1.33 Pa/min (calculated over 10 equilibrium points with sampling every 60 s).	(25 ± 0.01) °C	0.1 mg, ± 0.3 mg	Yes
b	The absolute pressure was measured by two pressure transducers (1.33 kPa and 133 kPa) with resolution of 0.01% F.S., and accuracy of 0.5% of reading. The relative pressure was determined by dividing measured absolute pressure by a fixed P_0 value of 3.17 kPa obtained from Dortmund Data Bank (DDBST). Mass equilibration criteria: dm/dt < 0.005%/min.	(25 ± 0.2) °C	0.1 µg, 0.1 µg	Yes
c	Absolute pressure measurement with piezoresistive transducer with a 16 bit A/D converter. The P_0 was set as the vapor pressure of the sample temperature at each point using NIST REFPROP (Lemmon et al. 2018) and the equation of state from Wagner and Pruß (Wagner and Pruß 2002). The average $P_0 = (3.17 \pm 0.003)$ kPa. Mass equilibration criteria: dm/dt < 50 µg/min.	(25 ± 0.1) °C	1 µg, 3 µg	Yes

Table 1 (continued)

Dataset	Relative humidity or vapor pressure determination method and sorption equilibration criteria	Temperature and stability	Balance resolution and stability	Blank correction
d	The absolute pressures were read with pressure transducers: 133 kPa (accuracy: ± 0.15% of F.S.), 1.33 kPa (accuracy: ± 0.5% of reading), and 13.3 Pa (accuracy: ± 0.25% of reading). The saturation vapor pressure of 25 °C was set to 3.17 kPa according to NIST REFPROP database. Equilibration criteria: dP < 0.1% in 300 s.	(25 ± 0.1) °C	0.1 mg, 0.1 mg	Yes
e	The absolute pressure was measured by pressure transducer: Range: 1.33 kPa F.S., accuracy: ± 0.5% of reading; Range: 133 kPa F.S., accuracy: ± 0.15% of F.S. The saturation vapor pressure of 25 °C is determined by the Wagner equation (Reid et al. 1987). Equilibration criteria: dP < 0.3% in 300 s.	(25 ± 0.1) °C	0.1 mg, 0.1 mg	Measured, but not subtracted
f	Absolute pressure measurement (capacitance manometer) with conversion to relative pressure using Antoine coefficients with the saturation vapor pressure set to 3.176 kPa. Equilibration criteria: using the instrument control software (kinetic curve to reach 99% of the predicted (asymptotic) uptake from fit), with equilibration times in the range from 3 to 10 h.	(25 ± 0.02) °C	0.1 µg, 1 µg	No
g	The absolute pressure was measured by three pressure transducers: < ± 0.11% F.S. (133 kPa range), < ± 0.15% of reading (1.33 kPa & 0.133 kPa ranges). The relative pressure was found by dividing absolute pressure by a fixed P_0 value of 3.2 kPa obtained from NIST REFPROP. Equilibration criteria: 3 min for each point.	(25 ± 0.1) °C	0.1 mg, ± 0.1 mg	Yes
h	The absolute pressure was measured by micropore capability pressure transducer (13.3 Pa) with saturation vapor pressure set to 3.17 kPa. Equilibration criteria: dP/dt < 0.01%/interval time (moving window calculation over 11 consecutive readings with interval time = 5 s).	(25 ± 0.1) °C	0.1 mg, ± 0.1 mg	Yes
i	The absolute pressure was measured by three types of pressure transducers: (1) 133 kPa, (2) 1.33 kPa, ± 0.12% of reading accuracy screen resolution 13.3 mPa and (3) 13.3 Pa, ± 0.15% of reading accuracy screen resolution 0.133 mPa. The relative pressure was found by dividing this pressure by a fixed P_0 value set to 3.1699 kPa. Equilibration criteria: equilibration interval = 60 s.	(25 ± 0.1) °C	0.1 mg, ± 0.1 mg	Yes

[a] The location of the thermocouple was not specified in the protocol nor reported by the participants
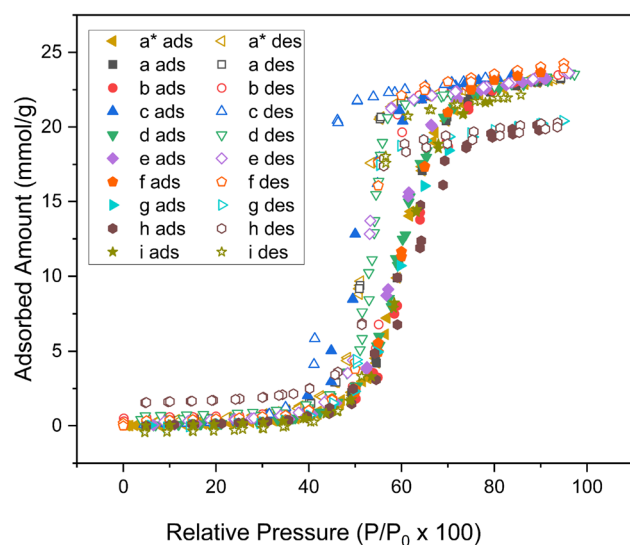
Fig. 1 As-submitted pure H_2O sorption isotherms at 25 °C for BAM-P109 up to $P/P_0 \times 100 = 95$. For individual datasets, see Figs. S1-S2. Dataset a* is a high-resolution version of dataset a. While both are displayed, only dataset a was treated in the statistical analyses. See Fig. S8 for isotherms in absolute pressure

not imply recommendation by NIST, nor does it imply that these items are the best available for the purposes described.

2.2 Data submission

Nine pure water datasets (a*, a to i) and four RH datasets (1 to 4) were submitted. A dataset is composed of two isotherms total from two aliquots of sorbent. Each isotherm measurement consists of the adsorption branch and then the desorption branch. Dataset a* is a high-resolution version of dataset a; while both are displayed, only dataset a was used in the statistical analyses.

2.3 Dataset display

To display clearly a plot including datasets from all participants, both isotherms for each dataset were plotted. These are shown in the figures in the text. The individual plots for each dataset can be found in the Supplementary Information.
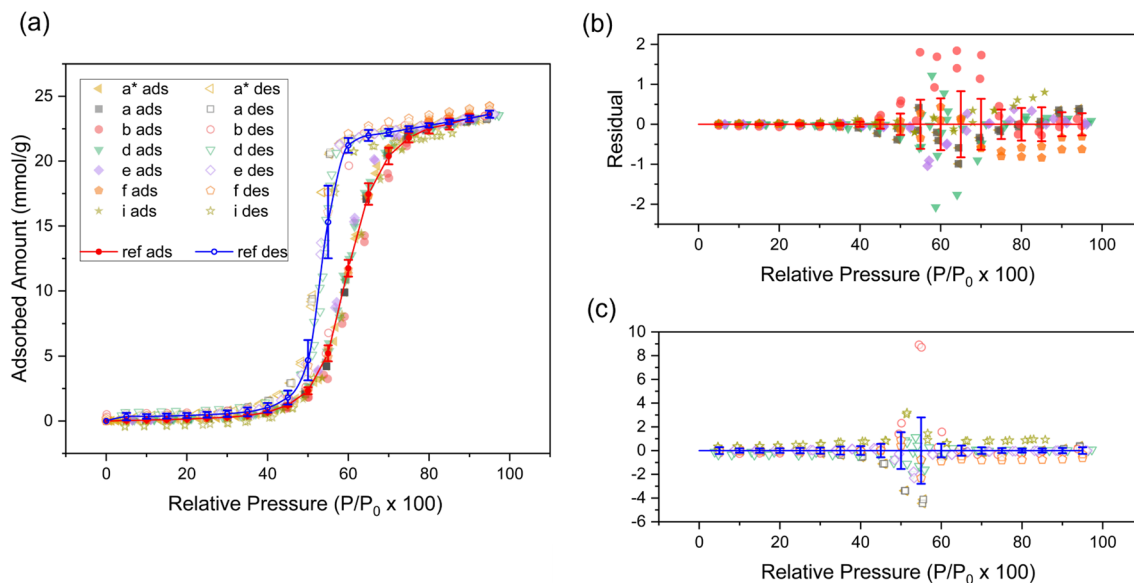
Fig. 2 **a** Pure water sorption isotherms at 25 °C for BAM-P109 used to determine the reference isotherm, along with the reference isotherm itself and the 95% uncertainty intervals. The lines through the reference data solely serve to guide the eye. **b** Residuals (reference – measured) for adsorption branch of isotherms. **c** Residuals for desorption branch of isotherms. The uncertainty associated with each data point is taken from uncertainty data in panel **a**. Note the difference in the scale in **b** and **c**. The legend is the same for **a**, **b**, and **c**. Dataset a* is a high-resolution version of dataset a. While both are displayed, only dataset a was used in the statistical analyses. See Fig. S9 for isotherms in absolute pressure
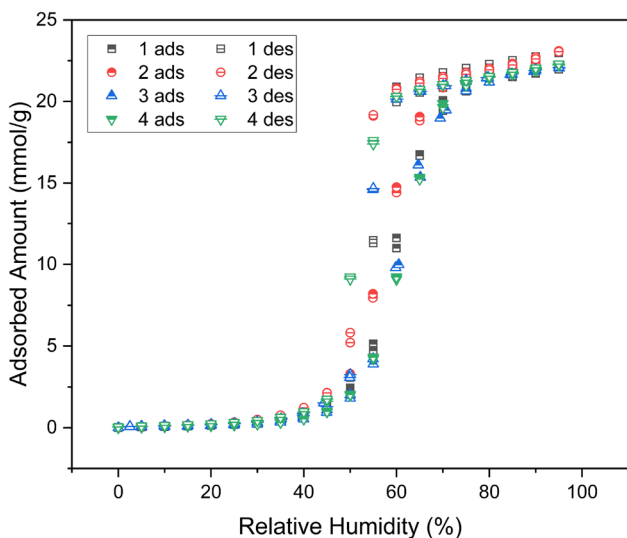
Fig. 3 As-submitted water sorption isotherms at 25 °C for BAM-P109 up to 95% RH using molecular nitrogen as the carrier gas. For individual datasets, see Fig. S3

The number of each dataset is random and does not correspond to the listing of authors.
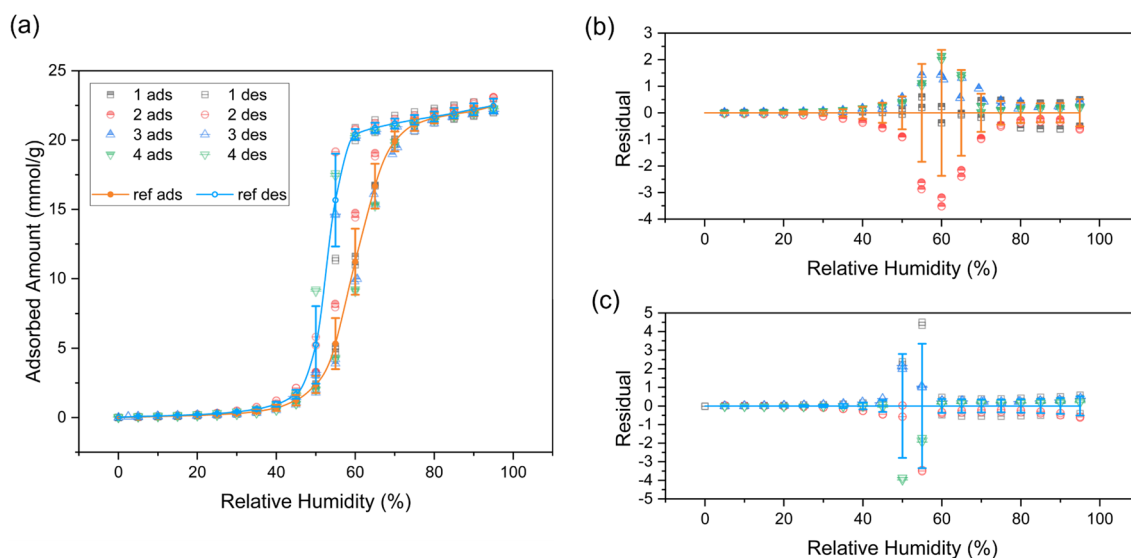
2.4 Reference isotherm determination

The individual datasets (P/P_0 adsorption, P/P_0 desorption, RH adsorption, and RH desorption) were subdivided into 20 groups according to the intended relative pressure ($P/P_0 \times 100$) or relative humidity, to wit: 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95. In each of these subsets the quantity of adsorbed water was determined using either a linear regression or a simple mean function, as deemed appropriate, for the collective set of the binned data. For the P/P_0 desorption data set, the subsets for 70, 75, 80, 85, and 90 were combined and a single linear regression was fitted. This produced a smoother function in this region. An uncertainty evaluation and 95% intervals were determined for each set of binned data. The calculations were done using the R function *lm*() (Chambers et al. 1992). See Section S6 in Supplementary Information for equations.

3 Results and discussions

In total, nine pure H_2O/BAM-P109 datasets were submitted. The as-submitted H_2O/BAM-P109 datasets for pure water isotherms are plotted together in Fig. 1. The isotherms exhibit Type V isotherm shape (Ross et al. 2016; Thommes et al. 2015), with little uptake until $P/P_0 \times 100 \approx 40$, suggesting the material to be hydrophobic in nature (Ross et al. 2016). The hysteresis loop in the water vapor isotherm is attributed to different mechanisms of adsorption/cluster formation and desorption/pore emptying (Ross et al. 2016; Thommes et al. 2012; Thommes et al. 2015). Preliminary analysis of the pure water datasets identified three datasets

Fig. 4 **a** Water sorption isotherms at 25 °C for BAM-P109 up to 95% RH using molecular nitrogen as carrier gas used to determine the reference isotherm, along with the reference isotherm itself and 95% uncertainty interval. The lines through the reference data solely serve to guide the eye. **b** Residuals (reference – measured) for adsorption branch of isotherms. **c** Residuals for desorption branch of isotherms. The uncertainty associated with each data point is taken from uncertainty data in panel **a** Note the difference in the scale in **b** and **c**. The legend is the same for **a**, **b**, and **c**

Table 2 The reference isotherm for pure water/BAM-P109 derived from experimental data presented in Fig. 2, with the associated 95% lower (ℓ95) and upper (u95) uncertainty bounds

| Adsorbed amount v. ($P/P_0 \times 100$): adsorption band				Adsorbed amount v. ($P/P_0 \times 100$): desorption band			
$P/P_0 \times 100$)	(mmol/g)	ℓ95	u95	$P/P_0 \times 100$)	(mmol/g)	ℓ95	u95
5	0.041	0.027	0.055	95	23.622	23.345	23.899
10	0.072	0.054	0.090	90	23.295	23.074	23.516
15	0.107	0.084	0.130	85	23.024	22.853	23.196
20	0.148	0.126	0.169	80	22.754	22.588	22.920
25	0.222	0.191	0.254	75	22.483	22.275	22.691
30	0.287	0.259	0.316	70	22.213	21.936	22.490
35	0.416	0.381	0.452	65	21.978	21.552	22.404
40	0.683	0.620	0.745	60	21.217	20.646	21.789
45	1.215	1.105	1.325	55	15.310	12.512	18.109
50	2.331	2.063	2.599	50	4.685	3.131	6.238
55	5.213	4.599	5.827	45	1.804	1.240	2.368
60	11.748	11.100	12.396	40	1.027	0.660	1.393
65	17.470	16.643	18.297	35	0.702	0.363	1.041
70	20.391	19.755	21.027	30	0.560	0.309	0.811
75	21.813	21.445	22.182	25	0.479	0.259	0.699
80	22.540	22.132	22.947	20	0.418	0.222	0.615
85	22.866	22.441	23.290	15	0.380	0.194	0.567
90	23.322	23.021	23.623	10	0.351	0.171	0.530
95	23.622	23.345	23.899	5	0.338	0.049	0.627

(c, g, and h) as statistical outliers (see Fig. S5). Participant c reported that condensation had occurred before the saturation pressure and, therefore, stopped measuring at 0.85 P/P_0. Condensation at 0.85 P/P_0 suggests the employed pressure sensor of participant c requires recalibration. Datasets g and h have lower adsorbed water amounts compared to the other datasets. Participant g reported transfer in air after ex-situ activation of the sample, which could not be re-outgassed after being attached to the instrument. Participant h reported activation at vacuum levels higher than that prescribed in

Table 3 The reference isotherm for water in nitrogen/BAM-P109 relative humidity measurements derived from the data presented in Fig. 4, with the associated 95% lower ($\ell95$) and upper ($u95$) uncertainty bounds

Adsorbed amount v. RH: adsorption band				Adsorbed amount v. RH: desorption band			
RH (%)	(mmol/g)	$\ell95$	$u95$	RH (%)	(mmol/g)	$\ell95$	$u95$
5	0.041	0.026	0.055	95	22.475	21.963	22.987
10	0.073	0.054	0.093	90	22.220	21.794	22.646
15	0.107	0.079	0.134	85	21.944	21.557	22.331
20	0.149	0.110	0.187	80	21.696	21.333	22.058
25	0.206	0.149	0.263	75	21.461	21.113	21.808
30	0.289	0.202	0.376	70	21.194	20.841	21.547
35	0.431	0.295	0.568	65	20.884	20.523	21.245
40	0.700	0.470	0.930	60	20.419	20.045	20.794
45	1.252	0.875	1.630	55	15.667	12.319	19.015
50	2.385	1.764	3.006	50	5.244	2.446	8.041
55	5.337	3.495	7.180	45	1.683	1.358	2.008
60	11.233	8.863	13.604	40	0.958	0.774	1.142
65	16.674	15.059	18.289	35	0.609	0.498	0.721
70	19.903	19.187	20.619	30	0.409	0.341	0.476
75	21.106	20.660	21.552	25	0.288	0.244	0.332
80	21.592	21.213	21.970	20	0.210	0.180	0.239
85	21.871	21.512	22.231	15	0.154	0.133	0.175
90	22.095	21.729	22.462	10	0.111	0.092	0.130
95	22.475	21.963	22.987	5	0.074	0.053	0.095
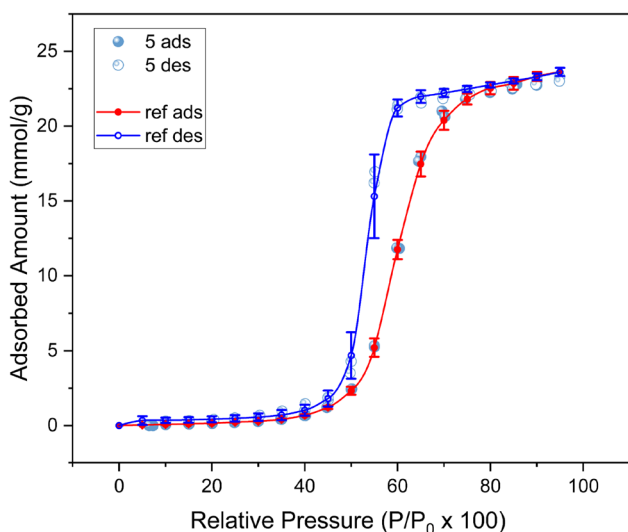
Fig. 5 Water sorption isotherms at 25 °C using He as carrier gas on BAM-P109, along with pure water reference isotherm data and 95% uncertainty bounds. The lines serve solely to guide the eye

the protocol. These participants were given the opportunity to remeasure or reprocess their results. Datasets c and g were not resubmitted. Dataset h was resubmitted, though analysis of the resubmitted data indicated this dataset to be an outlier too; notably, data resubmitted from participant h exhibited variability between the two aliquots (see Figs. S4 and S6). Ultimately six of the nine pure water datasets were used in determining the reference isotherm and are shown in

Figs. 2 and S7. Figure 3 shows the four RH datasets, which are relatively in good agreement, with only minor variability in the high RH region and some spread in the region of rapid uptake/release. All four RH datasets were used in the determination of the RH reference isotherm.

A series of reference values was determined for $P/P_0 \times 100$ up to 95 and RH up to 95% in intervals of 5/5%. These data are also shown in Figs. 2 and 4. Figures 2 and 4 also show the residuals of the datasets to the reference values. There is relatively good agreement at the low and high RH and P/P_0 regions, with more variability in the region of rapid uptake/release. This greater variability could potentially be attributed to uncertainties in RH, P, P_0, T, V, and equilibrium criteria having larger effects on the adsorbed amount due to the greater uptake or release per RH or P/P_0, i.e., larger derivative of the sorption isotherm in this area. For example, the "steeper" desorption compared to the adsorption in the region of rapid uptake/release leads to larger uncertainties in the desorption branch. The slightly larger uncertainties in the P/P_0 desorption branch throughout may be due to accumulated uncertainties, particularly in the manometric measurements. The reference isotherms for both the pure water (P/P_0) and the water in N_2 carrier gas (RH) measurements show closure of the hysteresis loop, as the desorption and adsorption branches are indistinguishable at the low P/P_0 and RH within the uncertainty bounds. The reference data values and the expanded uncertainties, $U_{k=2}$, are given in Tables 2 and 3, for P/P_0 and RH data, respectively. The datasets and the reference isotherm

data are also available through the NIST Database of Novel and Emerging Adsorbent Materials (Siderius et al. 2020).

Comparing the pure water and RH reference isotherms, it can be seen that uptake is slightly higher in the pure water isotherm compared to the RH isotherm (see Fig. S10). This observation suggests that some of the carrier gas is adsorbed in the RH measurements. A study by Fletcher et al. in which water vapor isotherms on an activated carbon material were measured under dynamic conditions using helium as the carrier gas found no significant difference in water uptake compared to that measured under static conditions (Fletcher et al. 2002). To determine if the lower uptake for RH measurements was due to the preadsorption and competing adsorption of the N_2 carrier gas, an experiment using helium as the carrier gas was performed (dataset 5, see Fig. S11). This yielded RH results with higher uptake compared to using molecular nitrogen as the carrier gas and matches well with P/P_0 data (see Figs. 5 and S11), indicating that some nitrogen may be adsorbed when used as the carrier gas with this material. The visible effect of adsorbed nitrogen on the water uptake could be attributed to the high surface area (1396 m^2/g) of the material, a nanoporous carbon, as well as its hydrophobic nature. The N_2 sorption isotherm on BAM-P109 at 25 °C (Fig. S12) confirmed that indeed BAM-P109 adsorbs N_2 (≈ 0.43 mmol/g) near ambient pressure (0.1 MPa). Given that the mass of the sample in the dynamic experiments is measured in N_2 flow throughout, the measured dry sample mass at RH = 0 (and throughout) includes preadsorbed N_2. From the N_2 sorption isotherm, the sample mass in N_2 is estimated to be slightly higher than in vacuum by around up to 0.012 g/g of sample, which equates to $\approx 1.2\%$ mass. Thus, from this study it is recommended to use helium as a carrier gas for dynamic measurements when a like-pure water vapor sorption isotherm is desired. This is a significant outcome of the study in light that the two measurements (RH and P/P_0) can be fundamentally different or converge depending on the choice of the carrier gas in the dynamic measurement. The choice of the carrier gas, therefore, should be reported and would depend on the application.

4 Conclusions and outlook

This work provides reference sorption isotherm data for H_2O on a pelletized nanoporous carbon (BAM-P109) at 25 °C as a function of pure water vapor (P/P_0) and as a function of relative humidity with molecular nitrogen as the carrier gas. This work has also shown that when helium is used as the carrier gas, dynamic RH measurements match well with pure water vapor measurements. These reference isotherms should prove useful for researchers interested in working with water as well as applications where the presence of water may play a significant role in the performance of materials.

Author contributions H.G.T.N., R.D.v.Z., M.T., and D.P.B. developed the study protocol. Other coauthors contributed data measured in their respective laboratories. H.G.T.N. led the analysis of submitted datasets. B.T. performed the statistical analyses. H.G.T.N. wrote the initial draft of the paper and finalized the manuscript with input from coauthors.

Declarations

Competing interest The authors declare no competing interest

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