Protocol for Obtaining Reference Isotherms Using BAM-P109 and Water.[*]

Materials: The adsorbent is a certified reference material, BAM-P109 (nanoporous carbon).[‡] The sample mass to be used should be optimized to achieve the best signal-to-noise ratio, according to the experimental parameters of the instrument being used. The adsorptive, water, should be LC/MS grade, and carrier gas, molecular nitrogen, should have purity ≥ 99.999 %.

Sample pretreatment: The nanoporous carbon should be outgassed in vacuum at room temperature, then heated over a period of 1 h to 200 °C and held at that temperature for 3 h under vacuum with continuous pumping (final pressure < 0.1 Pa). If the outgassing is performed in a separate manifold, minimize exposure to air when transferring to the analysis port and re-outgas in the instrument to 140 °C for at least 6 h to remove any adsorbed gases.

Measurement of adsorption isotherms: Water (H_2O) adsorption and desorption isotherms are to be measured on BAM-P109 at 25 °C as a function of P/P_0 or percent RH. It is recommended that data be recorded at the following interval: 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.85, 0.9, 0.95 P/P_0, or 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, and 95 % RH. The same measurement is also to be done without the adsorbent to perform a “blank correction.” This blank should be subtracted from the adsorption isotherm.[†]

Comparison to the empirical reference isotherm data: Measured isotherms should fall within the 95% uncertainty interval of the reference isotherms for pure water and water entrained in nitrogen shown in the Tables 1 and 2, respectively.

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[*] H. G. T. Nguyen et al., Reference isotherms for water vapor sorption on nanoporous carbon: results of an interlaboratory study, *Adsorption* **29** (2023) 113−124. Available On-line.

[‡] D. Panne & A. Thünemann (2010). Certified Reference Material BAM-P109. Available On-line.

[†] H. G. T. Nguyen, J. C. Horn, M. Thommes, R. D. van Zee, L. Espinal, Experimental Aspects of Buoyancy Correction in Measuring Reliable High-pressure Excess Adsorption Isotherms Using the Gravimetric Method, *Meas. Sci. Technol.* **28** (2017) 125802. Available On-line.

Table 1. The reference isotherm for pure water/BAM-P109 along with the associated 95 % lower (ℓ95) and upper (u95) uncertainty bounds.

Adsorbed amount v. (P/P_0 × 100): adsorption band				**Adsorbed amount v. (P/P_0 × 100): desorption band**			
P/P_0 × 100	**(mmol/g)**	**ℓ95**	**u95**	**P/P_0 × 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

Table 2. The reference isotherm for water in nitrogen/BAM-P109 relative humidity measurements along with the associated 95 % lower (ℓ95) and upper (u95) uncertainty bounds.

Adsorbed amount v. RH: adsorption band				**Adsorbed amount v. RH: desorption band**			
RH (%)	(mmol/g)	ℓ95	u95	RH (%)	(mmol/g)	ℓ95	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

To reiterate, the following recommendations for measurements of static pure BAM-P109/H_2O sorption isotherm are offered:

- Sample Activation: Sufficiently complete sample activation is crucial. As noted above, the nanoporous carbon must be activated at 200 °C for 3 h under high vacuum (≤0.1 Pa) to realize the reported reference isotherm. If the sample is activated ex-situ, minimize exposure to air and moisture to obtain the correct sample mass and re-outgas in the instrument at 140 °C for at least 6 h to remove any physiosorbed gases.

- Sample Volume Determination: Proper determination of sample volume is needed both for buoyancy correction in a gravimetric system, as well as the void volume determination in a volumetric system. When required in data analysis, a skeletal density of 2.18 g/cm^3 should be used for BAM-P109.[1]

- Buoyancy Correction/Void Volume Correction: A buoyancy correction must be applied when using a gravimetric system. Although less important at low-pressures, buoyancy effects are significant for high-pressure measurements and cannot be overlooked. This is analogous to the use of void volume in a volumetric instrument to determine surface excess uptake, and the effect of using the wrong volume also becomes more significant with increasing pressure.

- Equation-of-State: In general, identify the equation-of-state used to calculate fluid density, and use critically evaluated equations, such as those contained in the NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP). The Wagner and Pruss equation of state[2] should be used for H_2O at 25 °C to replicate the reference data.

- *T*, *P*, and *m*: Ensure good control and measurement of temperature, pressure, and sample mass, as these are important in accurate determination of the uptake.

- Blank Correction: A blank run subtraction should be performed whenever possible, as it corrects for small uncompensated transducer nonlinearities, effects of temperature heterogeneities coupled with the compressibility of the adsorptive, and other experimental effects.

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[1] BAM (2020). Safety Data Sheet for CRM BAM-P109.

[2] W. Wagner and A. Pruss, The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use," J. Phys. Chem. Ref. Data, **31**(2002) 387. Available On-line.

To reiterate, the following recommendations for measurements of dynamic BAM-P109/H_2O in N_2 sorption isotherm are offered:

- Sample Activation: Sufficiently complete sample activation is crucial. As noted above, the nanoporous carbon must be activated at 200 °C for 3 h under high vacuum (≤0.1 Pa) to realize the reported reference isotherm. If the sample is activated ex-situ, minimize exposure to air and moisture to obtain the correct sample mass and re-outgas in the instrument at 140 °C for at least 6 h to remove any physiosorbed gases.

- Carrier gas: The carrier gas used is extremely important and will affect the data obtained. Nitrogen gas should be used to obtain reference data associated with RH experiments using nitrogen as carrier gas. Helium should be used if like-pure water vapor sorption data is desired.

- *T*, *RH*, and *m*: Ensure good control and measurement of temperature, relative humidity, and sample mass, as these are important in accurate determination of the uptake. In general, calibration of relative humidity sensors is highly recommended. Common calibration materials include salts with known deliquescent point. Mass flow controllers should also be calibrated, if possible.

- Blank Correction: A blank run subtraction should be performed whenever possible, as it corrects for small uncompensated effects.