Comparison of the Saturated Salt Solution and the Dynamic Vapor Sorption techniques based on the measured sorption isotherm of barley straw

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Abstract

For Heat, Air and Moisture modelling, one of the most crucial hygrothermal properties of porous construction materials is the sorption isotherm. Current techniques for measuring the sorption isotherm rely on the standardized Saturated Salt Solution (SSS) method which is known to be time consuming. Recently, a device called Dynamic Vapor Sorption was applied on building materials allowing faster measurements but limiting the mass and volume of the sample. As this technique is not yet standardized, an experimental procedure was developed and validated on barley straw. Results were also in good agreement with the measurements from the SSS technique.

Keywords: Sorption isotherm, Dynamic Vapor Sorption, Saturated Salt Solution, Measurement, Straw, Uncertainty

21 **Nomenclature**

22 Latin Symbols

23	A, B, C	fitting parameters	-
24	b	moisture effusivity	$\text{kg.s}^{-1}.\text{m}^{-1}.\text{Pa}^{-1}$
25	g	flux	$\text{kg.m}^{-2}.\text{s}^{-1}$
26	k	coverage factor	-
27	l	fitting parameter	-
28	M	molar mass	kg.mol^{-1}
29	m	mass of the sample	kg
30	n	number of points	-
31	N	number of samples	-
32	P	pressure	Pa
33	p	fitting parameter	-
34	q	number of parameters	-
35	R	ideal gas constant	$\text{J.K}^{-1}.\text{mol}^{-1}$
36	u	uncertainty	-
37	T	temperature	K
38	t	time	s
39	U	global uncertainty	-
40	x	variable	-
41	w	water content	%

42

43 Greek symbols

44	δ	water vapor permeability	$\text{kg}.\text{m}^2.\text{s}.\text{Pa})^{-1}$
45	μ	mean value	-
46	ρ	density	kg.m^{-3}

47	ξ	sorption capacity	(kg _v .kg ⁻¹)
48	σ	standard deviation	-
49	φ	relative humidity	[0:1]

50

51 Subscripts

52	_a	A-type (or random)
53	_b	B-type (or systematic)
54	_{Disp}	display
55	_h	holder
56	_{Lin}	linearity
57	₀	dry state
58	_s	saturation
59	_v	vapor
60	_w	water

61

62 1. Introduction

63 In buildings, moisture has an influence on comfort, energy consumption and durability [1]. Most
64 construction materials exchange water vapor with their surroundings, and this water vapor makes up
65 as much as one third of the total moisture released into the indoor air according to [2]. Hence,
66 assessing moisture transfer at room or building scale is crucial and relies on simulation through Heat,
67 Air and Moisture (HAM) models. Nowadays, as many as 50 different models can be found as noted in
68 [3]. Although every model has its own specificities, they all rely on the water mass balance [4], which
69 can be expressed as follows:

70 (1)
$$\frac{\partial w}{\partial t} = -\nabla \left(\vec{g} \right)$$

71 Most of the time, the models differ on the expression of the flux (right hand side of (1)). For the left
 72 hand term, however, there is a stronger consensus that it can be decomposed as presented in [5]
 73 when the moisture transfer is limited to the hygroscopic area :

74 (2)
$$\frac{\partial w}{\partial t} = \frac{\partial w}{\partial \varphi} \cdot \frac{\partial \varphi}{\partial t} = \xi \cdot \frac{\partial \varphi}{\partial t}$$

75 ξ , sometimes referred to as the sorption capacity, represents the variation of the moisture content of
 76 the material for a given variation of relative humidity (φ). It also corresponds to the slope of the
 77 sorption isotherm, which has to be determined experimentally. Consequently, knowing the sorption
 78 isotherm is a key step in the comprehension of moisture transfer and its modelling. To determine the
 79 sorption curves, samples are exposed to constant temperature and relative humidity until their mass
 80 stabilizes. By comparison with the mass obtained in the dry state (i.e. the mass obtained for $\varphi=0\%$), it
 81 is possible to determine the moisture content for the relative humidity in question. Then, samples
 82 are exposed to monotonically increasing values of relative humidity so that the absorption curve can
 83 be plotted. Repeating the procedure for monotonically decreasing values of relative humidity allows
 84 the desorption curve to be plotted. The complete method is described in standard NF EN ISO 12571
 85 [6].

86 The most common technique relies on the use of Saturated Salt Solution (SSS) to obtain a stable
 87 value of relative humidity. It should be underlined that SSS were used for calibrating relative
 88 humidity sensors [7] until recently. Consequently, SSS should be used if very good accuracy is
 89 desired. However, several researchers have acknowledged that this method is very time-consuming,
 90 as stated by [8] for example. It was also acknowledged that the increase of the experiment's duration
 91 leads to a greater chance of experimental errors. Improving the accuracy of such measurements is an
 92 on-going topic, as poor reproducibility of hygric properties has been reported in [9]–[11]. Even

though the discrepancies in the sorption values were reasonable compared to other hygric properties, they should be determined precisely so that the reliability of simulation works can be addressed. This can be handled by determining the experimental uncertainty using well-established calculations, as presented in [12], and allows the most influential sources to be identified. For example, Feng *et al.* [11] concluded that reliable results could be obtained with the SSS technique by one laboratory but that significantly higher differences were observed when the results obtained by different laboratories were compared. This conclusion also stresses the need for a precisely defined experimental protocol. Finally, knowledge of the uncertainty of the material properties is required if a sensitivity analysis is to be achieved, as in [13] for example. This technique determines how the uncertainty of the inputs influences the outputs. In the last mentioned study, it was concluded that the influence of the sorption isotherm on the modelling outcome (namely, the RH of indoor air) was not negligible.

For this reason, attempts have been made to reduce the duration of the tests. By assuming an excellent homogeneity of all the samples, one could divide the samples into small groups and subject each group to a different relative humidity. Feng *et al.* [14] used this method on autoclaved aerated concrete and compared the results to those obtained using the method proposed by NF EN ISO 12571. Alternatively, some authors have proposed relying on numerical techniques to predict the material properties, based on the analysis of dynamic behaviors. For example, inverse modelling of a MBV test (see [15] for a complete description) was proposed in [16] using Bayesian techniques. Similarly, Rouchier *et al.* [17] used the Covariance Matrix Adaptation evolution strategy to solve an inverse HAM problem in a multi-layer wall exposed to real climatic conditions. Reasonable agreement was obtained between computed and measured sorption curves but significant differences were observed above 70% RH. Even though these approaches sound promising, they first have to be tested with respect to reliable values.

117 In recent years, a technique initially used in the pharmaceutical field and known as Dynamic Vapor
118 Sorption (DVS) has been developed. This technique relies on the observation that the time for mass
119 stabilization to be obtained depends directly on the mass. In consequence, using lighter samples
120 leads to shorter tests. However, this is not straightforward as smaller samples may not be
121 representative, especially for construction materials such as concrete, which is very heterogeneous.
122 Having a representative material is of utmost importance for the DVS technique, this may explain
123 why it is currently not very popular in the field of civil engineering. Nevertheless, some examples can
124 be found in the literature as it can still be used for many construction materials. It was successfully
125 used in [18] for 5 materials (autoclaved aerated concrete, lightweight ceramic brick, a phase change
126 material, lime plaster and an old fashioned ceramic brick), in [19], [20] for unfired clay bricks and
127 earth blocks, and in [21] for natural fibers. Taking advantage of the shorter time needed to complete
128 the experiment, some authors used the DVS technique to get a more comprehensive understanding
129 of the physical phenomena. For example, Fort *et al.* [22] used this technique to investigate the
130 influence of temperature on the sorption isotherm. In [23], it was stated that the particle size/surface
131 area and pore diameter has a crucial role on the water sorption and desorption process for drug
132 substances.

133 The SSS and the DVS techniques were already compared in the literature, as in [24] for 5 different
134 materials (flax insulation, perlite insulation, cellulose insulation, glass wool insulation and cellular
135 concrete). No significant difference was observed between the two techniques but it was pointed out
136 that the determination of the dry mass had a significant effect. Good agreement was also obtained
137 in [8] based on 5 different types of food. Despite the extensive use of this technique, it was observed
138 that the literature is poor on detailed statistical analysis to compare the DVS and SSS techniques.
139 Therefore, these comparisons are rather qualitative. Moreover, some other examples can be found
140 where a lesser agreement was obtained, as in [25] for corn flakes samples for example. According to
141 the authors, this discrepancy may be related to the slow diffusion of the water vapor in the corn flake
142 matrix. A significant shift was observed in [26] measurements achieved on earth. Still, the shape of

the two isotherms was similar and this shift was explained by a difference in the dry state. In [20] and [26], it seems that the mass stabilization of the sample was not systematically obtained, especially for high relative humidity where the kinetic of adsorption was slower, which led to an underestimation of the water content of the material. On a more global point of view, it seems that the results obtained with the DVS technique are similar to those obtained with the SSS technique, yet this statement cannot be generalized to all materials. One of the possible reasons is that there is no standard which applies to the DVS technique, so that the default procedure proposed by the manufacturer may not always be relevant for all the materials, as the heterogeneity and so the vapor permeability are bound to serve as an influence.

Three points emerge from this short literature review:

1. It is necessary to quantify the sorption properties of construction materials for modelling purposes;
2. The reliability of the material properties is a current concern;
3. Two main experimental techniques are used nowadays. The SSS technique is well-established and documented but time-consuming. For the DVS technique, on the other hand, fewer measurements have been reviewed.

The main objective of this paper is to propose an experimental comparison between the two techniques, and to give elements of their advantages and drawbacks. Hence, results obtained with the DVS technique are compared to the ones obtained with the SSS technique. The latter will be achieved by using the standards NF EN ISO 12570 and NF EN ISO 12571. It was chosen to strictly follow the standards for this technique, yet it could be improved. However, this falls out from the topic of this study. For the DVS technique on the other hand, no such standard exists and the experimental procedures will be presented in detail. Results obtained with both techniques will then be discussed through the means of a statistical analysis: special care will be taken to estimate the experimental uncertainties, so that the reliability of both techniques will be compared.

To do this, the experimental method will be presented and discussed for the two techniques. The detailed procedure for the uncertainty calculation will be presented in section 3. As mentioned above, the DVS technique may not be suitable for heterogeneous materials and the SSS technique is very time-consuming. In this work it was decided to focus on a single material, namely barely straw, as explained in section 4. Finally, results obtained with both techniques will be exposed and discussed in section 5.

2. Presentation of the two techniques

2.1. Saturated salt solution technique

The SSS technique is covered by the standards NF EN ISO 12570 [27] and NF EN ISO 12571 [6], which describe the procedures for obtaining the dry mass and for measuring the sorption isotherm.

2.1.1. Procedure used to obtain the dry mass

According to [27], the samples should be “[dried] at the temperature specified in the relevant product standard to constant mass”, prior to testing. A ventilated oven able to maintain the relative humidity below 10% should be used. Finally, the balance has to be capable of weighing test specimens with an uncertainty not greater than 0.1% of their mass. Still according to the standard, the drying temperature depends upon the material. It should be:

- $40 \pm 2^{\circ}\text{C}$ for materials for which a higher temperature can drive out water of crystallization or affect blowing agents;
- $70 \pm 2^{\circ}\text{C}$ for materials in which changes in structure can occur between 70°C and 105°C ;
- $105 \pm 2^{\circ}\text{C}$ for materials having structures that do not change at 105°C .

According to [24], the use of a temperature of 105°C will remove all the physically bound water but not all materials can tolerate this temperature. This latest recommendation remains quite unclear,

which may explain why other drying temperatures have been used in the literature, as shown in Table 1.

Table 1 - Examples of drying temperature in the literature

Reference	Material	Drying temperature (°C)
[28]	Silt, kaolin, bentonite	105°C
[29]	Hemp concrete	23°C (use of silica gel)
[14]	Calcium Silicate	70°C
[26]	Earth bricks	50°C
[30]	Wood-based products	55°C
[31]	Concrete	44°C

Here, it was presumed that microstructural changes may occur in barely straw at 70°C. According to the standard, a drying temperature of 40°C should have been used. However, for practical reasons and to compare this work with previous studies in the same project, samples were dried at 50°C. The relative humidity in the oven was monitored hourly with a KIMO KH200 device and found to lie between 5.4 and 7.0%. Finally, the samples were weighed every day at the same time with a balance accurate to within $\pm 10^{-4}$ g until their mass stabilized.

2.1.2. Procedure used to obtain the sorption isotherm

The experimental procedure is presented in [6] and can be summarized as follows:

- A constant temperature ($\pm 0.5^\circ\text{C}$) has to be maintained during the whole experiment;
- At least 3 samples of the same material should be used;
- The sample holders should not be sensitive to humidity variations;
- A minimum of five different conditions should be selected in the humidity range considered, with relative humidity increasing in stages;

- The moisture content is obtained when the mass variation is less than 0.1% between three consecutive weighings;
- The balance has to be selected so that its accuracy is better than $\pm 0.01\%$ of the mass of the samples.

Here, all the samples were placed in a sealed box ($50 \times 35 \times 30 \text{ cm}^3$) equipped with two fans, in order to improve the RH uniformity and to avoid the water vapor to be absorbed locally from around the samples. Indeed, without the fans, the SSS method is relying on a very slow Fickian diffusion to redistribute the water vapor in the material, which could lead to a non-uniform absorption. Approximately 1.5 L of saturated salt solution was prepared in our laboratory, poured into a crystallizer (2.6 L) and placed inside the box (see Figure 1). Six different salts were used for this study. They were selected on the basis of their availability, cost and toxicity, and in order to cover the whole range of the sorption isotherm. The temperature was maintained at $(23 \pm 2^\circ\text{C})$. For five of the six salts, the associated theoretical values of the relative humidity with their uncertainties were mentioned in [6], and are presented in Table 2. For the remaining case, the value was found by [32], but no uncertainty was given.

Table 2 – Saturated salt solutions used for the SSS method

Salt	Chemical formula	Relative Humidity (%)	Cost for 1.5 L (€)
Sodium hydroxide	NaOH	7.6 ± 2.0 ¹	2
Potassium acetate	CH ₃ COOK	22.2 ± 0.4 ¹	332
Potassium carbonate	K ₂ CO ₃ , 2H ₂ O	43.2 ± 0.4 ¹	123
Ammonium nitrate	NH ₄ NO ₃	63.2 ²	4
Sodium chloride	NaCl	75.4 ± 0.2 ¹	1
Potassium nitrate	KNO ₃	94.0 ± 0.6 ¹	14

¹ According to [6]

² According to [32]

Figure 1 – Picture of the hermetically sealed box used for the SSS method

2.2. The DVS system

2.2.1. Apparatus

The device used in this study was developed by SMS (Surface Measurement Systems, London, United Kingdom). Its main component is a microbalance accurate to within ± 0.0110 mg that has an upper limit of 10 g. The sample was placed on one side of the microbalance in a holder (sample holder)

made of quartz or aluminium; a reference holder located on the other side of the balance was left empty. The holders were confined in two separate hermetically sealed cells and an air flow was applied at a controlled temperature and relative humidity. The desired relative humidity was obtained by mixing a dry gas (nitrogen), coming from a bottle located nearby, with the right proportion of water vapor. The mixing is done by means of a mass flow controller and a vapor humidifier. The properties of the moist air were measured in the hermetic cells by the means of temperature and humidity sensors: a Pt100 thermometer accurate to within $\pm 0.2^{\circ}\text{C}$ measured the dry bulb temperature and a dew point sensor accurate to within $\pm 0.5\%$ RH was used to determine the effective relative humidity. Finally, the whole device was placed in a small climatic chamber (50 x 50 x 75 cm³) to minimize the influence of the environment (see Figure 2). The device was placed in a room where the temperature was maintained at 21°C. Because of the very high sensitivity of the microbalance to vibrations, all other apparatus were removed from the room or turned off during the tests.

Figure 2 – Schematic representation of the Dynamic Vapor Sorption system

2.2.2. Procedures

Unlike for the SSS technique, there is no standard dedicated to the measurement of the sorption isotherm with the DVS technique. Because of the very small mass of the sample, mass stabilization was presumed to be obtained in less than 24 hours at each relative humidity step. Consequently, it would be pointless to apply the recommendation of the standards concerning the SSS technique and another criterion for mass stabilization had to be defined for the DVS technique.

Contrarily to the SSS technique for which no control was done on the air flow rate, a constant rate of 0.2 L/min with a pressure of 1.5 bars was applied here leading to a uniform absorption over the surface of the sample. These are the default values proposed by the manufacturer and their influence was not investigated in this study. The device is fully automated and two options were available: the first one consisted in setting a time for the sample to be exposed to constant conditions (for example, 6 hours). The second option was to define a mass variation criterion, referred to as “dm/dt” (for example 10^{-4} percent of mass change per minute, noted $\%.\text{min}^{-1}$). According to the manufacturer, the mass variation criterion is defined as follows:

$$(3) \quad \frac{dm}{dt} = 60 \cdot \frac{M \cdot \sum (t \cdot m) - \sum t \cdot \sum m}{M \cdot \sum t^2 \cdot (\sum t)^2}$$

Equation (3) is derived from the exact expression for the fit of a linear equation on M points and gives the slope, as shown in Figure 3. Here, the calculation is performed using a 5 min window with 15 points (i.e. one point every 20 seconds). The factor “60” intervenes to convert the result into minutes. Once this criterion is met over a 10 minute period, the mass is considered as stabilized.

Figure 3 – Illustration of the calculation of the dm/dt criterion

The second option seemed to be more relevant because the time needed for the mass to stabilize is not known a priori. Additionally, results will depend strongly on the value used for mass stabilization. Here, it should be observed that this technical specificity is not systematically mentioned in the papers reviewed but the following figures could be extracted: $2 \cdot 10^{-3} \text{ \%} \cdot \text{min}^{-1}$ in [21], $5 \cdot 10^{-4} \text{ \%} \cdot \text{min}^{-1}$ in [26], $4 \cdot 10^{-5} \text{ \%} \cdot \text{min}^{-1}$ in [22], and $10^{-4} \text{ \%} \cdot \text{min}^{-1}$ in [33]. The last value corresponds to the default value proposed by the manufacturer and is very close to the mass variation criterion proposed in the standard for the SSS technique (see section 2.1.2 - a simple conversion gives $8 \cdot 10^{-5} \text{ \%} \cdot \text{min}^{-1}$). Finally, a good compromise between duration and accuracy was obtained with this value as it was shown by a previous study on the dry mass (not presented in this paper) on the sensitivity of the results with the mass variation criterion. By extension, this criterion was also applied for the sorption isotherm measurement.

For the dry mass determination, all the samples were stored in a ventilated oven at 50°C as in the SSS technique. With the DVS technique, however, samples can be exposed to dry air (nitrogen), which should remove additional water from the material. Before the sorption isotherm was measured, samples were exposed to dry air flowing at a constant rate of 0.2 L/min with a pressure of 1.5 bars. The nitrogen was heated to 50°C and the exposure lasted 45 min. After this period, samples were

progressively cooled down to 23°C, before being exposed to moist air. This duration was based on the results of earlier experiments, where it was observed that a longer exposure did not lead to any significant mass decrease (approximately 0.05 mg loss for 1 hour). The time interval between the measurements is not explicitly given by the manufacturer as the value of dm/dt is calculated with numerous points (Figure 3) that are stored in a temporary buffer holding points but not saved in a file. This supposes a high number of points so that the estimated value of dm/dt is correct. The latter is given every minute.

3. Evaluation of the experimental uncertainties

Usually, two kinds of uncertainties are distinguished: random or A-type uncertainty (u_A) and systematic or B-type uncertainty (u_B). u_A represents the dispersion of the results from one experiment to another while u_B derives from the known accuracy of the different elements of the measuring process. The extended uncertainty U is defined as the combination of these two, given by (4):

$$(4) \quad U = k \cdot \sqrt{u_A^2 + u_B^2}$$

A careful reading of the theoretical background of uncertainty calculations ([12]) shows that they rely on the assumption of normally distributed measurements, which is the most common case. One interesting consequence is that the extended uncertainty can be interpreted as a confidence interval of 68.3% or 95.4% depending on whether k is equal to 1 or 2 respectively. Therefore, it is necessary to perform a statistical test to verify that the measurements are normally distributed and thus that the uncertainty calculations are valid. In the literature, several normality tests have already been presented and compared. Some of the most famous (Chi², Geary, Agostino, Kolmogorov-Lilliefors, and Shapiro-Wilk tests) are mentioned in [34]. The sensitivity of these tests to the number of samples is evaluated in [35] for normal laws. For a small number of samples, which is our case, the Shapiro-

Wilk test was found to be the most robust, a result confirmed by [36]. As this test can be easily achieved by using tables available in [37] , it was chosen for this paper.

3.1. Uncertainty on moisture content obtained with SSS

For the SSS technique, the water content of the materials is obtained as follows:

$$(5) \quad w_{SSS} = \frac{m - m_0}{m_0 - m_h}$$

This means that a single value of the water content requires at least 3 different mass measurements.

Assuming a normal distribution of the results, the random uncertainty on the mean value $u_A(\mu_w)$ is defined as follows [12]:

$$(6) \quad u_A(\mu_w) = \frac{\sigma}{\sqrt{N}}$$

u_B takes account of the influence of every parameter used to calculate w . As mentioned above, 3 measurements are needed to determine the mass content. u_B is obtained by summing the partial derivatives of each parameter:

$$(7) \quad u_B(w) = \sqrt{\sum_i \left(\frac{\partial w}{\partial x_i} \cdot u(x_i) \right)^2}$$

Applying this equation to our case leads to:

$$(8) \quad u_{B,SSS}(w) = \sqrt{\left[\frac{1}{m_0 - m_h} \cdot u_B(m) \right]^2 + \left[\frac{m_h - m}{(m_0 - m_h)^2} \cdot u_B(m_0) \right]^2 + \left[\frac{m - m_0}{(m_0 - m_h)^2} \cdot u_B(m_h) \right]^2}$$

As the mass varies from one sample to another, so does the systematic uncertainty. Therefore, the calculation has to be repeated for each sample and each relative humidity value.

323 The manufacturer of the balance does not indicate a systematic uncertainty. Instead, two
 324 uncertainties are mentioned:

- 325 • Display resolution (u_{Disp}): characterizes the smallest increment of weight that the numerical
 326 display can indicate;
- 327 • Linearity (u_{Lin}): characterizes the ability of the balance to follow a linear relationship between
 328 the weight on the balance and the value displayed on the screen. This uncertainty was
 329 applied twice: once for taring and once for the measurement.

330 With no information on the distribution associated with these uncertainties, a rectangular
 331 distribution (or equiprobable distribution) was assumed. The standard deviation corresponding to
 332 such a distribution is obtained by dividing the uncertainty by the square root of 3 (which is higher
 333 than with a normal distribution). Consequently, the u_B value was calculated as follows:

$$334 \quad (9) \quad u_{B,SSS}^2(m) = \left(\frac{u_{Disp}}{\sqrt{3}} \right)^2 + 2 \cdot \left(\frac{u_{Lin}}{\sqrt{3}} \right)^2$$

335 The same scale was used to measure m and m_0 but a different one was used for m_h for practical
 336 reasons. Finally, the extended uncertainty was obtained as follows (10):

$$337 \quad (10) \quad U = k \cdot \sqrt{\frac{\sigma^2}{N} + \left[\left(\frac{1}{m_0 - m_h} \right)^2 + \left(\frac{m_h - m}{(m_0 - m_h)^2} \right)^2 \right] \cdot u_B^2(m) + \left(\frac{m - m_0}{(m_0 - m_h)^2} \right)^2 \cdot u_B^2(m_h)}$$

338 3.2. Uncertainty on moisture content obtained with DVS

339 For the DVS technique, the sample holder was already positioned on the microbalance to set the
 340 tare. Consequently, the water content of the materials was obtained as follows:

$$(11) \quad w_{DVS} = \frac{m - m_0}{m_0}$$

Unlike the SSS technique, the DVS method allows tests to be run for one sample at a time. Moreover, this sample is relatively small, which raises questions about its representativeness. In this work, this problem was handled through repeatability and reproducibility tests. These tests are proposed in the NF ISO 5725 standard [38] and by other standardization organizations such as ASTM (ASTM C1699-09 standard [39]).

Repeatability is defined as the observed variation of the results provided by successive tests achieved under identical conditions (same device, operator, sample, method and environmental conditions). The tests were performed with a single sample having a mass of approximately 20 mg. The same protocol for measuring the sorption isotherm was repeated five times: the procedure for drying was included (see 2.2.2) in order to have the same initial conditions (dry mass) for all the 5 tests.

The value of u_A was obtained with equation (6) by considering $N=5$. The value of u_B was determined using equation (7). Here, $u_B(m)$ was explicitly stated by the manufacturer, so there was no need to distinguish the uncertainty of the display resolution from linearity. Consequently, u_B was calculated using equation (12):

$$(12) \quad u_{B,DVS}(w) = \sqrt{\left[\left(\frac{1}{m_0}\right)^2 + \left(-\frac{m}{m_0^2}\right)^2\right] \cdot u_{B,DVS}^2(m)}$$

Finally, the extended uncertainty was obtained by applying a quadratic sum as in (4).

Reproducibility is defined as the observed variation of the results when the conditions of the tests vary within an acceptable range (meaning that these conditions may be reasonably obtained during testing). In our case, the methodology, the device and the environment remained the same from one test to another. However, it seemed reasonable to assume that the sampling from a large bag of straw and the preparation of samples by the operator may have an influence on the result. Here, 10

straw samples weighing between 19 and 24 mg were prepared by four different operators and tested with the DVS technique. The uncertainty calculation was determined in the same way as for repeatability.

In this study, repeatability tests aimed to evaluate the accuracy of the device and the reliability of the experimental protocol, while reproducibility tests aimed to assess the representativeness of the samples and the influence of the operator. If the uncertainty calculated from the repeatability tests was of the same magnitude as the device accuracy, it gave confidence in the experimental procedure. If the results obtained from the reproducibility tests were similar, this meant that the sample was representative and the operator had no influence on the measurement.

4. Material and sample preparation

The work presented in this paper was carried out in the framework of a larger project focusing on earth and bio-based materials ([1], [40], [41], [42]). Preliminary tests were conducted on 4 different materials, which were selected because of their presumed high sorption capacity and high risk for mold growth, namely unfired clay, barley straw, hemp shiv and corncob. Early results (not presented in this paper) showed that the highest adsorption levels were obtained with barley straw. It was also observed that the mass stabilization was obtained faster for this material than for the others, which suggested high vapor permeability. In this work, only one material was chosen as it was decided to focus on the experimental procedure and the comparison between the DVS and SSS techniques rather than on the material.

Therefore, barley straw appeared to suit the purposes of this study. First, a high sorption level should lead to increased accuracy, as the ratio of mass content to systematic uncertainty would be higher. Second, a fast mass stabilization means that the time needed for a single experiment is reduced, which allows more ambitious experimental campaigns to be planned. In addition, straw samples can be easily prepared to fit into holders of different sizes and shapes and, unlike the situation for

powders, it is easier to notice material losses. Finally, there is renewed interest for this material as a building material, in Europe at least. Some examples of buildings made of straw were reported up to 1921 in France [43] as a solution for rebuilding after the war, but the development of straw buildings was interrupted because of World War II. The sorption property of straw was measured for the first time by Hedlin in 1967 [44]. The methodology used in Hedlin's study was equivalent to the SSS technique and five types of cereal straws were considered (thatcher wheat, cypress wheat, garry oats, jubilee barley and redwood flax). More than 40 years later, research on the sorption property of this material is still in progress ([45], [46]). In this study, barley straw samples were supplied by Calyclay, a small French company created in 2014 and specializing in straw constructions and coatings on straw support.

As building materials, bio-based materials like straw have gained popularity in the civil engineering field over the last decades. The fact that they are renewable, carbon neutral and low in environmental impact make them attractive [40]. Moreover, straw can be used to strengthen and/or lighten earthen construction materials [48]. Recent studies reported the use of barley straw to enhance the thermal insulation of plaster as presented in [49]. In [50], it was highlighted that straw is an excellent hydric regulator which may improve the hygrothermal comfort in buildings. These statements were confirmed and strengthened through a numerical modelling of the hygric response of a small room in [47]. According to [50], it can also slow carbonation of the binder matrix due to its property to make the environment more basic.

The straw was cut into 3 mm strands by means of triple-bladed scissors. This was done to ensure that the samples fit into the holders for both techniques. For the SSS technique, the straw strands were placed in a strainer of dimensions 2.5 x 6 cm² as illustrated in Figure 4. To avoid the loss of material through the mesh of the strainer, it was placed in suspension in a plastic box. Aluminium wedges were used to hold the strainer in place. For the DVS technique, all the samples were placed in a

411 hemispheric holder made of quartz (see Figure 4). The shape of this holder was selected because it
 412 prevented the strands from being removed by the gas flux.

413

414 **Figure 4 - Sample holder used with the SSS technique (left) and with the DVS technique (right)**

415 The number and dry masses of the samples used in this study are reported in Table 3. It should be
 416 noted that the weight of the samples used with the SSS technique was 50 times higher than with the
 417 DVS technique. This illustrates the main difference between the two techniques: faster mass
 418 stabilization is obtained with the DVS technique, but it might lead to representativeness issues.
 419 Second, although the DVS system can handle samples weighing up to 10 g, lighter samples were used
 420 here because of the size of the holder.

421

422 **Table 3 – Samples used for the different experiments**

Technique	Experiment	Number of samples	m_0 (mg)
SSS	Drying and sorption isotherm	13	[1048 : 1235]
DVS	Drying	15	[4.5 : 65.6]
	Repeatability	1	18.7
	Reproducibility	10	[19.3 : 24.3]

5. Results and discussion

5.1. Dry mass

For the SSS technique, the dry mass was obtained after 192 hours for all the samples; values are indicated in Table 3. An average mass loss of 6.1% was observed.

In the literature, the technique used to obtain the dry mass achieved with the DVS technique is not always specified, and may be improved. Indeed, a significant drop in the sample's mass when it was submitted to 0%RH was observed in [20] on clay masonry and in [26] on earth bricks. Similar behavior was found in [23] on drugs. This suggests that the sample was not completely dry. In fact, the procedure presented in the standard NF EN ISO 12570 allows decreasing the relative humidity of the samples to a very low level, but the theoretical dry mass cannot be obtained. Indeed, the use of an oven makes it impossible to reach 0% RH, unlike with nitrogen. An oven just heats up the ambient air but does not remove any water vapor from it, making it impossible for the relative humidity to decrease to 0%. In this paper, we have taken sides to compare the results obtained with a well-established method (the SSS technique) with the DVS technique. Therefore, we decided to scrupulously apply the standard with the SSS technique so that the samples were placed in an oven only. More precise results would have been expected if samples were exposed to nitrogen, but we assumed that this would not have been representative of the usual SSS technique. For the DVS technique, the samples were additionally exposed to dry air for 1 hour as already mentioned in section 2.2.2. Thus, an average mass loss of 7.6% was observed for the samples with DVS. As explained above, this result was expected.

As mentioned in section 2.1.1., the influence of the dry mass determination method has already been underlined by others ([11], [24], [26]), yet this influence is hard to analyze. For example, Peuhkuri et al. [24] showed that there was no significant difference between the results obtained with cellulose samples dried at 20°C and 70°C, but sizeable differences were obtained for cellular

concrete. On the other hand, a shift between the sorption isotherms measured with both techniques was observed in [26] for earth bricks. The debate on the determination of the dry mass is ongoing but it is not specific to the SSS or the DVS technique. Therefore, the study of the influence of the dry mass is slightly out of the scope of this paper. We will simply recall that the DVS system offers an interesting opportunity to get closer to the theoretical value of the dry mass by using nitrogen. Consequently, higher moisture content should be measured with the DVS technique.

5.2. Water content measured with the SSS technique

The results for the 13 barley straw samples are presented in Table 4. The whole experiment lasted 4 months and 9 days. According to the Shapiro-Wilk test, the values of the water content were found to be normally distributed except for the last relative humidity step (94% RH).

For this last value, mold growth was observed with the naked eye before the mass had stabilized. According to [51], there is a moderate risk of mold growth on wheat straw at 20°C and 75% RH, but mold growth is to be expected at higher relative humidity. In [52], it was stated that the development of mold is conditioned by the relative humidity of the environment rather than by the moisture content of the materials. In [8], visible mold growth was also observed at 93.6% RH on food materials. For this reason, it was presumed that repeating the experiment at 94% RH would systematically lead to mold growth, meaning that the SSS technique was not relevant at high humidity for materials like straw. The last measurement obtained before mold growth was achieved after one week of exposure. It was observed that the time needed for mass stabilization increased with relative humidity. As stabilization took almost one month at 75.4% RH, the value of the water content at 94% RH was probably not representative of the stabilized mass. However, it was also observed that 97% of the mass variation between 63.2% RH and 75.4% RH was achieved within the first week. So the magnitude of the last measurement, obtained at 94% RH, should be correct. It was therefore used in this study.

Table 4 – Mean value and uncertainties obtained with the SSS technique

Relative Humidity (%)	7.6	22.2	43.2	63.2	75.4	94.0
μ_w (kg _v .kg ⁻¹)	1.44	3.73	5.94	9.78	11.77	21.78
u_A (kg _v .kg ⁻¹)	0.03	0.05	0.09	0.12	0.18	0.63
u_B (kg _v .kg ⁻¹)	0.02	0.02	0.03	0.03	0.03	0.05
U (kg _v .kg ⁻¹) (k=2)	0.1	0.1	0.2	0.3	0.4	1

It was observed that the extended uncertainty U was generally dominated by the u_A value, which increased with the relative humidity. This led to a significant increase in the discrepancy of the results at high relative humidity. Such a result has already been observed by other researchers for a wide range of materials ([13], [18], [27], [41]). Several reasons were listed in [9], from the purity of the salts to the value chosen to define mass stabilization. Another interesting reason, mentioned in [11], is that the uncertainty on the RH of the salt solution has a much more significant effect for high values of RH because of the asymptotic behavior of the sorption isotherm. Still, the SSS technique is currently the only standardized method for obtaining a given value of relative humidity, in the field of civil engineering at least. Therefore, it can be concluded that the increase of the uncertainty at high relative humidity is not specific to straw and did not result from negligence in the experimental work. It is inherent in the SSS technique.

It should be mentioned that the normal distribution is a limiting distribution, meaning that it can be obtained for a very high number of samples only. When there are less than 20 samples, the estimated standard deviation may be underestimated. More reliable results could be obtained by considering a Student's distribution [54]. However, this technique relies on the assumption that u_B values are significantly lower than u_A values. As it was not clear whether the difference between the two values was significant here or not, the uncertainty calculation was repeated using this second

approach. The values obtained for the extended uncertainty U were the same, indicating that the first approach was valid.

5.3. Water content measured with the DVS technique

A first test was conducted using 20 steps in relative humidity (from 0 to 90% in steps of 5%, plus one point at 93%) and taking the default value of the mass variation criterion ($10^{-4} \text{ \%.min}^{-1}$). Results are presented in Figure 5.

Figure 5 - Mass variation of straw with time and relative humidity for a criterion value of $10^{-4} \text{ \%.min}^{-1}$

It took 180 hours to determine the whole sorption isotherm and the time required for the mass stabilization criteria to be satisfied was observed to increase significantly with relative humidity: the mass stabilized in less than 6h between 0 and 50% RH, in 6 to 12h between 50 and 75% RH and in up to 29 h at 93% RH. This trend is similar to the one observed in [20] on unfired clay. In that study, however, the device automatically stepped to the next value of relative humidity if mass stabilization was not obtained after 6 hours. This corresponds to the default setting proposed by the manufacturer. Results presented in Figure 5 clearly show that more accurate results can be obtained by considering the mass variation criterion only.

The mass variation criterion used here ($10^{-4} \text{ \%.min}^{-1}$) strongly depends on the kinetic of absorption of the material as its calculation on a 10 min window could be too short. Furthermore, the material could not absorb enough water to notice a significant mass change during the calculation window. Accurate results were obtained on barley straw, but this criterion might not be precise enough for other materials. However, this limitation also occurs for the SSS technique.

5.3.1. Repeatability tests

The repeatability tests were carried out for a reduced number of relative humidity steps (9, 33, 55, 76, and 93%). These values were selected to be in agreement with typical values obtained with saturated salt solutions. They do not correspond to the ones presented in Table 4 because some late amendments had to be made with the SSS technique.

For the first three tests, exactly the same dry mass was obtained (18.74 mg). However, for the last two tests, a slight increase was observed (+0.04 mg), which was higher than the balance uncertainty ($\pm 0.01 \text{ mg}$) but represented a mass variation of only 0.02%. This result raises some questions. If the procedure applied for drying was biased, different values for the dry mass should have been obtained because of the exposure to very high relative humidity (93% RH). However, this was not observed for the first three tests.

To compare the results from these five experiments, the same value for dry mass, e.g. the minimum of the mass for all of the experiments, was defined. The Shapiro-Wilk normality test was successfully applied to the measurements, indicating that the values were normally distributed. The mean water content μ_w and its uncertainty are presented in

527 Table 5 for all relative humidity steps.

528

Table 5 – Mean value and uncertainty obtained for the repeatability tests

Relative Humidity (%)	9	33	55	76	93
μ_w (kg _v .kg ⁻¹)	2.3	5.9	9.1	13.3	20.9
u_A (kg _v .kg ⁻¹)	0.03	0.03	0.04	0.04	0.08
u_B (kg _v .kg ⁻¹)	0.08	0.09	0.09	0.09	0.09
U (kg _v .kg ⁻¹) (k=2)	0.2	0.2	0.2	0.2	0.2

The extended uncertainties are quite small with respect to the water content: the ratio between these two values ranges from 1 to 9% (for 93% RH and 9% RH respectively). Moreover, the global uncertainty is dominated by u_B , except for the last relative humidity step, where u_A and u_B have the same magnitude. This result is in accordance with the one obtained with the SSS technique. Therefore, it can be concluded that an excellent repeatability was obtained for the measurement of the sorption isotherm of straw, meaning that the procedure is valid.

5.3.1. Reproducibility tests

The Shapiro-Wilk normality test was also successfully applied to the measurements. The results are shown in Table 6. Note that the values selected for relative humidity were slightly different from the ones used in Table 5.

Table 6 – Mean values and uncertainties obtained for the reproducibility test

Relative Humidity (%)	10	30	50	75	93
μ_w (kg _v .kg ⁻¹)	2.1	4.4	7.3	12.4	21.6
u_A (kg _v .kg ⁻¹)	0.06	0.12	0.09	0.11	0.22
u_B (kg _v .kg ⁻¹)	0.08	0.08	0.08	0.09	0.09
U (kg _v .kg ⁻¹) (k=2)	0.2	0.3	0.3	0.3	0.5

543 u_B values are very close to those obtained during the repeatability tests as they depend only slightly
544 on the mass of the sample. However, u_A has significantly increased compared to the values obtained
545 for the repeatability tests (see

Table 5), and is now of the same magnitude as u_B . It is logical for higher uncertainties to be observed with reproducibility tests than with repeatability tests because additional sources of uncertainty were introduced (the operator and the sampling of the material). However, the increase of u_A does not significantly influence the extended uncertainty, U , because of the quadratic sum (see (4)) and the observed excellent repeatability. This indicates that a straw sample of 20 mg is representative and that the influence of the operator and the samples has a limited impact on the results.

One notable exception concerns the highest relative humidity (93%) where u_A is more than twice as high as u_B , leading to an extended uncertainty of $\pm 0.5 \text{ kg.v.kg}^{-1}$. This trend is similar to the one observed with the SSS technique, which strengthens the idea that it is very hard to obtain reproducible high relative humidity values. However, it can be seen that the random uncertainties obtained here are higher than those obtained with the SSS technique for relative humidity below 50%. The inverse tendency is observed for relative humidity above 50%. Finally, it is important to note that all the experiments were performed in the same laboratory. Therefore, the same method and device were used in roughly the same environment. However, Feng et al. [14] mentioned that the biggest disparities were found when comparing results from different laboratories. This parameter was not investigated in the present work.

5.4. Comparison of the measurements obtained with the two techniques

The sorption isotherm obtained from the reproducibility tests with the DVS technique is compared with the one obtained from the SSS technique in Figure 6. It should be observed that all the isotherms were plotted by assuming that the water content was equal to 0% when the relative humidity was equal to 0%. However, the dry mass obtained with the SSS technique might be overestimated because of the ventilated oven, as mentioned in section 5.1. Also, Figure 6 compares the present results with the ones obtained in 1967 by [55] on five types of grain straws. Higher RH values were used in [55] (up to 99%), which resulted in a measured water content higher than

1 kg_v.kg⁻¹. For readability purposes, water contents have been plotted for relative humidity values up to 94% RH , as this corresponds to the highest value measured in our study.

Figure 6 - Comparison of the isotherm measured with the two techniques and from Hedlin [55]

First, it was observed that the sorption values measured here were lower than the ones obtained in [55], where jubilee barely straw was considered. However, no significant difference was observed over the five types of straw in [55] for the lowest values of relative humidity: the maximum difference of the water content was 0.3 kg_v.kg⁻¹ at 10% RH while the average difference was 1.1 kg_v.kg⁻¹ with the measurements made in our study. The influence of the type of straw was more significant at higher relative humidity, but the difference with the measurements achieved here is still noticeable. This raises questions on the reliability of the measured sorption values for general calculation purposes. Straw is generally obtained directly from crops: its composition is not well-known or controlled as may be the case for other construction materials. Therefore, it should be kept in mind that the low dispersion of the experimental results presented in this paper is not representative of the presumed variability of the real material.

Focusing on the measurements made in the present study, it can be observed that the results are very similar with both techniques, yet some differences can be observed. First, the moisture content

obtained with the DVS technique is slightly higher than the one obtained with SSS, although this difference is within the order of magnitude of the measurement uncertainty. This result was expected: because of the better drying of the samples with the DVS technique, the moisture content measurement was expected to be higher. Second, the uncertainty was significantly higher at high relative humidity for both techniques, as a result of a higher dispersion of the values (u_A). A similar phenomenon was identified in the literature for wood-based products [30], cob [53] and cereal straw ([21], [46], [55]). Here, the same mass variation criterion was used for each relative humidity step with both techniques. This criterion may not be robust enough for high values of relative humidity and may need to be reconsidered. This is also mentioned in [20] and [33]. Moreover, the slope of the sorption isotherm is steep at high relative humidity. As a result, a small difference in the relative humidity leads to a significant difference in the moisture content. Consequently, the uncertainty in relative humidity may be too great to allow a precise comparison as underlined in [21]. Other techniques can be used at high relative humidity, such as pressure plate, tension plate or pressure membrane but cannot be used as replacement for the DVS and SSS as they are typically desorption measurements.

Another issue is the development of mold at high relative humidity. As mentioned above, mold growth was observed on straw samples for the SSS technique at 94% RH after one week of exposure even though the boxes used to store the samples during the experiment were previously cleaned with a product containing bleach. This was not done with the DVS technique. The reason is probably that the time required for mass stabilization was shorter (approximately 30 hours) and there was a lack of oxygen (samples were exposed to a mixture of only nitrogen and water vapor). In consequence, it would be preferable to use the DVS technique at high values of relative humidity for materials sensitive to mold growth.

5.5. Comparison of the sorption curves

The standard NF EN ISO 12571 imposes at least 5 different relative humidity steps to measure a sorption isotherm. However, 5 points may be insufficient, especially as the sorption isotherm is non-linear. This is why sorption isotherm models are needed. In our case, this would also ease the comparison between the results obtained with the two techniques because different relative humidity steps were used.

However, many models can be found in the literature. Here, we aim to compare the results obtained with 13 models in order to choose the most appropriate for barley straw. All the equations are given in Table 8 (see Appendix). The comparison relies on the calculated value of the “adjusted R-squared” coefficient, the definition of which is very close to that of the widespread indicator R^2 , except that it includes the number of fitting parameters. This coefficient will allow the models to be compared and the most accurate to be selected. The adjusted R-squared is defined as:

$$\bar{R}^2 = 1 - (1 - R^2) \cdot \frac{n-1}{n-q-1}$$

The adjusted R-squared was calculated on sorption isotherms obtained by the DVS and the SSS methods. Hence, the number of points, n , was set to 5 for the first method and 6 for the second. The value of R remained between 0 and 1, where 1 corresponds to a perfect correlation and 0 to a total dispersion between the model and the experimental curve. The fitted coefficients were obtained by minimization of least squares applied to a point cloud [56]. In our case, best results were obtained with the GAB model (quoted in [57]) (Fig. 8, see Appendix) as the determination coefficient was equal to 0.9986 with measurements obtained with the DVS system and 0.9978 for those obtained with the SSS technique. It is defined as follows:

631 (14)
$$w = \frac{C_1 \cdot C_2 \cdot \varphi}{(1 - C_2 \cdot \varphi) \cdot (1 - C_2 \cdot \varphi + C_1 \cdot C_2 \cdot \varphi)} \cdot W_m$$

632 W_m is a physical parameter based on Langmuir's theory [58], which corresponds to the water content
 633 when water molecules have covered the solid surface with a unimolecular layer. It was considered
 634 here as a fitting parameter, the values of which remain between 0 and 0.1. The predominance of the
 635 GAB model has already been observed by other authors. It was used in [59] for bentonite, in [53]
 636 with cob and in [60] for clay. Moreover, a comparison made in [53] with the BET model and [59] with
 637 the Henderson model, ranked GAB as the best fitting model. The values of the fitting parameters for
 638 both techniques are given in Table 7.

639 **Table 7 - Fitted parameters for GAB model**

Fitting parameters	DVS	SSS
C_1	6.310	5.862
C_2	0.831	0.825
W_m (kg _v .kg ⁻¹)	0.051	0.053

640

641 As the fitted parameters are very close, so are the sorption curves. For ease of comparison, it was
 642 preferred to plot the difference between the calculated water content, as presented in Figure 7a. It
 643 can be observed that the difference between the two isotherms is lower than 0.1 kg_v.kg⁻¹ over the
 644 whole range of relative humidity used in this study. This means that the difference between the
 645 results is lower than the measurement uncertainty, leading to the conclusion that the results are
 646 independent of the method.

647 As mentioned in Section 1, the slope of the sorption isotherms are used in HAM models to compute
 648 mass balance (see equation (1)). For this reason, the two slopes are compared in Figure 7b. Note that

the difference is very small (less than $0.1 \text{ kg}_v.\text{kg}^{-1}$), so the influence on the simulation results should not be significant.

Figure 7 – 7a (left) Difference between water contents calculated by DVS and SSS, 7b (right) Slope of the sorption isotherm measured with both techniques

To sum up, the results obtained with the DVS technique are the same as the ones obtained with the SSS technique for barely straw: the differences between the two sorption curves were within the uncertainty range. At high relative humidity, however, mold growth was observed with the SSS technique, which led to the interruption of the experiment before its end. This did not happen with the DVS technique, probably because of the shorter time of exposure and the absence of oxygen. Nevertheless, it was acknowledged that the uncertainty increased with both techniques at such high values of relative humidity. Therefore, it can be concluded that the DVS technique constitutes a good alternative to the SSS technique for homogeneous materials such as straw. This statement applies within the hygroscopic range only and the measurements are less reliable for high values of relative humidity, as mentioned above.

Finally, it can be added that the operational costs were slightly lower for the DVS than for the SSS technique. Indeed, all the experiments with the DVS (meaning the 20 points isotherms, 5

repeatability tests and 9 reproducibility tests) have consumed 3 nitrogen bottles. Each bottle has a capacity of 9.4 m³ of gas and costs approximately 40 €, meaning 120 € for all the experiments. For the SSS technique, the preparation of the solutions costed a bit less than 500 €, as shown on Table 2, but the salts can be reused. While the operational cost of a DVS device is cheaper than preparing saturated salt solutions, it is a considerable investment since the whole device costs around 75k€.

6. Conclusion

An experimental comparison between two sorption isotherm measurement techniques (SSS and DVS techniques) was proposed in this paper. The SSS method was achieved as described by standards NF EN ISO 12570 and NF EN ISO 12571. As no standard exists for the DVS method, a specific protocol was proposed for obtaining the dry state and the sorption isotherm. All the experiments were carried out on a barley straw. The comparison was achieved thanks to the evaluation of the uncertainties.

Firstly, DVS gave excellent results for repeatability and reproducibility, validating the procedure and proving that the straw sample was representative. The sorption isotherm measured with the DVS technique was very close to the one measured with the SSS technique, the difference being lower than 0.1%. The SSS method led to greater disparities in the measurements at humidity above 50%, due to the impact of many factors inherent in the protocol, while the DVS method did not use them. In DVS, the sample was confined in a climatic chamber and the measurements were automated. Hence the environment had less influence and the impact of the operator was negligible. In contrast, the SSS method seemed to perform better for relative humidities below 50%. To continue, the DVS technique was much faster than the SSS technique because of the relatively small size of the sample tested and the dynamic nature of the experiment. Its speed could be advantageous for measurements on bio-based materials since a shorter exposure of the sample to high relative humidity prevented the development of mold.

Despite the advantages of the DVS system, it must be borne in mind that the mass and volume that can be tested with this device are limited: the microbalance can only deal with samples weighing less than 10 g and the holders have a limited volume, which may be problematic for most porous construction materials such as concrete.

Finally, the DVS technique can be advantageous to measure the kinetic of water uptake due to the automated weightings, contrarily to the SSS method for which they are done once a day. It could still be done with the latter method with the use of a data logging balance. However, one issue is a temporarily loss of stability in the relative humidity each time the sealed box is opened to change the saturated salt solution.

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861 Table 8 – Sorption isotherm models reviewed

Name of the model	Equation
Brunauer-Emmet-Teller (BET) [61]	$w = \frac{C \cdot \varphi}{(1 - \varphi) \cdot (1 - \varphi + C \cdot \varphi)} \cdot W_m$
Brunauer-Deming-Demming-Teller (BDDT) quoted in [18]	$w = \frac{C \cdot \varphi}{1 - \varphi} \cdot \frac{1 - (n+1) \cdot \varphi^n + n \cdot \varphi^{n+1}}{1 - (C-1) \cdot \varphi - C \cdot \varphi^{n+1}} \cdot W_m$
Frenkel-Halsey-Hill quoted in [18]	$w = \left[-\frac{A}{\ln(\varphi)} \right]^{\frac{1}{C}} \cdot W_m$
Van Genuchten (VG) quoted in [62]	$w = \left[1 + \left C_1 \cdot \frac{R \cdot T}{M \cdot g} \cdot \ln(\varphi) \right ^{C_2} \right]^{-\left(1 - \frac{1}{C_2}\right)} \cdot W_m$
Smith (Sm) [63]	$w = C_1 + C_2 \cdot \ln(1 - \varphi)$
Kumaran (Ku) ([64])	$w = \frac{\varphi}{A \cdot \varphi^2 + B \cdot \varphi + C}$
Harking-Jura (HJ) [65]	$w = \sqrt{\frac{n}{l - \ln(\varphi)}}$
Burch (Bu) quoted in [57]	$w = A \cdot \left(\frac{1}{1 - \varphi} - 1 \right)^B$
Henderson (He) [66]	$w = \left(-\frac{\ln(1 - \varphi)}{A \cdot (T + B)} \right)^{\frac{1}{C}}$

Oswin (Os) [67]

$$w = \frac{A + B \cdot T}{\left(\frac{1}{\varphi} - 1\right)^{\frac{1}{C}}}$$

Langmuir (La) [58]

$$w = \frac{C \cdot \varphi}{1 + C \cdot \varphi} \cdot W_m$$

Hailwood Horrobin (HH) [21]

$$w = \frac{1800}{C} \cdot \left(\frac{A \cdot B \cdot \varphi}{100 + A \cdot B \cdot \varphi} \right) + \frac{1800}{C} \cdot \left(\frac{B \cdot \varphi}{100 - B \cdot \varphi} \right)$$

862

863 **Figure 8 – Ranks of the adjusted R-squared values of the models of sorption isotherm based on the**

864 **measurements obtained with the DVS technique**