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

3 Bui Rudy<sup>1\*</sup>, Labat Matthieu<sup>1</sup>, Aubert Jean-Emmanuel<sup>1</sup>

4  
5 <sup>1</sup> LMDC, Université de Toulouse, INSA, UPS, France

6 \* Corresponding author: rbui@insa-toulouse.fr

7 LMDC, INSA/UPS Génie Civil, 135 Avenue de Rangueil, 31077 Toulouse cedex 04 France.  
8

9 **Abstract**

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

17  
18 **Keywords:** Sorption isotherm, Dynamic Vapor Sorption, Saturated Salt Solution, Measurement,  
19 Straw, Uncertainty

## 21 **Nomenclature**

### 22 Latin Symbols

23	A, B, C	fitting parameters	-
24	b	moisture effusivity	$\text{kg}\cdot\text{s}^{-1}\cdot\text{m}^{-1}\cdot\text{Pa}^{-1}$
25	g	flux	$\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
26	k	coverage factor	-
27	l	fitting parameter	-
28	M	molar mass	$\text{kg}\cdot\text{mol}^{-1}$
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	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
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	$\delta$	water vapor permeability	$\text{kg}\cdot(\text{m}^2\cdot\text{s}\cdot\text{Pa})^{-1}$
45	$\mu$	mean value	-
46	$\rho$	density	$\text{kg}\cdot\text{m}^{-3}$

47	$\xi$	sorption capacity	$(\text{kg}_v \cdot \text{kg}^{-1})$
48	$\sigma$	standard deviation	-
49	$\varphi$	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	o	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) 
$$\frac{\partial w}{\partial t} = -\nabla \cdot \vec{g}$$

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  $\xi$ , 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 ( $\varphi$ ). 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

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

105 For this reason, attempts have been made to reduce the duration of the tests. By assuming an  
106 excellent homogeneity of all the samples, one could divide the samples into small groups and subject  
107 each group to a different relative humidity. Feng *et al.* [14] used this method on autoclaved aerated  
108 concrete and compared the results to those obtained using the method proposed by NF EN ISO  
109 12571. Alternatively, some authors have proposed relying on numerical techniques to predict the  
110 material properties, based on the analysis of dynamic behaviors. For example, inverse modelling of a  
111 MBV test (see [15] for a complete description) was proposed in [16] using Bayesian techniques.  
112 Similarly, Rouchier *et al.* [17] used the Covariance Matrix Adaptation evolution strategy to solve an  
113 inverse HAM problem in a multi-layer wall exposed to real climatic conditions. Reasonable  
114 agreement was obtained between computed and measured sorption curves but significant  
115 differences were observed above 70% RH. Even though these approaches sound promising, they first  
116 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

143 the two isotherms was similar and this shift was explained by a difference in the dry state. In [20] and  
144 [26], it seems that the mass stabilization of the sample was not systematically obtained, especially  
145 for high relative humidity where the kinetic of adsorption was slower, which led to an  
146 underestimation of the water content of the material. On a more global point of view, it seems that  
147 the results obtained with the DVS technique are similar to those obtained with the SSS technique, yet  
148 this statement cannot be generalized to all materials. One of the possible reasons is that there is no  
149 standard which applies to the DVS technique, so that the default procedure proposed by the  
150 manufacturer may not always be relevant for all the materials, as the heterogeneity and so the vapor  
151 permeability are bound to serve as an influence.

152 Three points emerge from this short literature review:

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

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

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

## 174 2. Presentation of the two techniques

### 175 2.1. Saturated salt solution technique

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

#### 178 2.1.1. Procedure used to obtain the dry mass

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

- 184 •  $40 \pm 2^{\circ}\text{C}$  for materials for which a higher temperature can drive out water of crystallization or  
185 affect blowing agents;
- 186 •  $70 \pm 2^{\circ}\text{C}$  for materials in which changes in structure can occur between  $70^{\circ}\text{C}$  and  $105^{\circ}\text{C}$ ;
- 187 •  $105 \pm 2^{\circ}\text{C}$  for materials having structures that do not change at  $105^{\circ}\text{C}$ .

188 According to [24], the use of a temperature of  $105^{\circ}\text{C}$  will remove all the physically bound water but  
189 not all materials can tolerate this temperature. This latest recommendation remains quite unclear,

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

192 **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

193

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

### 200 2.1.2. Procedure used to obtain the sorption isotherm

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

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

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

211 Here, all the samples were placed in a sealed box ( $50 \times 35 \times 30 \text{ cm}^3$ ) equipped with two fans, in order  
212 to improve the RH uniformity and to avoid the water vapor to be absorbed locally from around the  
213 samples. Indeed, without the fans, the SSS method is relying on a very slow Fickian diffusion to  
214 redistribute the water vapor in the material, which could lead to a non-uniform absorption.  
215 Approximately 1.5 L of saturated salt solution was prepared in our laboratory, poured into a  
216 crystallizer (2.6 L) and placed inside the box (see Figure 1). Six different salts were used for this study.  
217 They were selected on the basis of their availability, cost and toxicity, and in order to cover the whole  
218 range of the sorption isotherm. The temperature was maintained at  $(23 \pm 2^\circ\text{C})$ . For five of the six salts,  
219 the associated theoretical values of the relative humidity with their uncertainties were mentioned in  
220 [6], and are presented in Table 2. For the remaining case, the value was found by [32], but no  
221 uncertainty was given.

222 **Table 2 – Saturated salt solutions used for the SSS method**

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

<sup>1</sup> According to [6]

<sup>2</sup> According to [32]

223



224

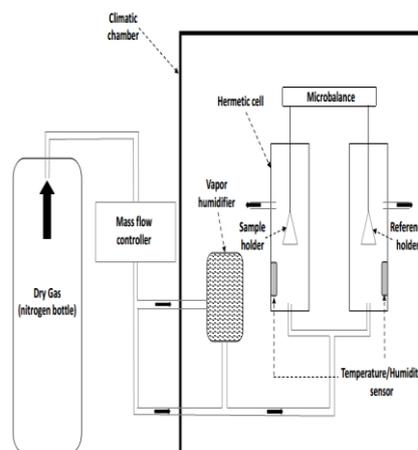
225 **Figure 1 – Picture of the hermetically sealed box used for the SSS method**

226 **2.2. The DVS system**

227 **2.2.1. Apparatus**

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

231 made of quartz or aluminium; a reference holder located on the other side of the balance was left  
232 empty. The holders were confined in two separate hermetically sealed cells and an air flow was  
233 applied at a controlled temperature and relative humidity. The desired relative humidity was  
234 obtained by mixing a dry gas (nitrogen), coming from a bottle located nearby, with the right  
235 proportion of water vapor. The mixing is done by means of a mass flow controller and a vapor  
236 humidifier. The properties of the moist air were measured in the hermetic cells by the means of  
237 temperature and humidity sensors: a Pt100 thermometer accurate to within  $\pm 0.2^{\circ}\text{C}$  measured the  
238 dry bulb temperature and a dew point sensor accurate to within  $\pm 0.5\%$  RH was used to determine  
239 the effective relative humidity. Finally, the whole device was placed in a small climatic chamber (50 x  
240 50 x 75  $\text{cm}^3$ ) to minimize the influence of the environment (see Figure 2). The device was placed in a  
241 room where the temperature was maintained at  $21^{\circ}\text{C}$ . Because of the very high sensitivity of the  
242 microbalance to vibrations, all other apparatus were removed from the room or turned off during  
243 the tests.



244

245 **Figure 2 – Schematic representation of the Dynamic Vapor Sorption system**

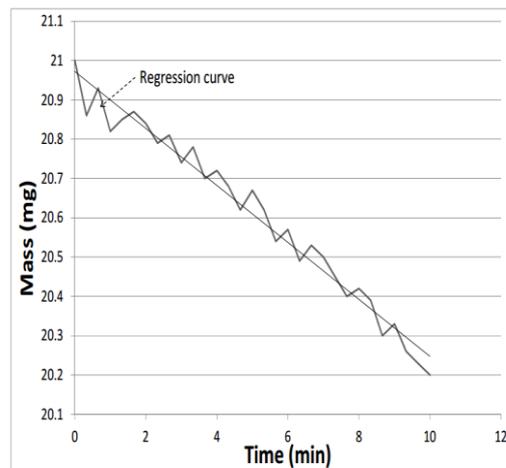
246 2.2.2. Procedures

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

252 Contrarily to the SSS technique for which no control was done on the air flow rate, a constant rate of  
253 0.2 L/min with a pressure of 1.5 bars was applied here leading to a uniform absorption over the  
254 surface of the sample. These are the default values proposed by the manufacturer and their  
255 influence was not investigated in this study. The device is fully automated and two options were  
256 available: the first one consisted in setting a time for the sample to be exposed to constant  
257 conditions (for example, 6 hours). The second option was to define a mass variation criterion,  
258 referred to as “dm/dt” (for example 10<sup>-4</sup> percent of mass change per minute, noted %.min<sup>-1</sup>).  
259 According to the manufacturer, the mass variation criterion is defined as follows:

260 (3) 
$$\frac{dm}{dt} = 60 \cdot \frac{M \cdot \sum(t \cdot m) - \sum t \cdot \sum m}{M \cdot \sum t^2 \cdot (\sum t)^2}$$

261 Equation (3) is derived from the exact expression for the fit of a linear equation on  $M$  points and  
262 gives the slope, as shown in Figure 3. Here, the calculation is performed using a 5 min window with  
263 15 points (i.e. one point every 20 seconds). The factor “60” intervenes to convert the result into  
264 minutes. Once this criterion is met over a 10 minute period, the mass is considered as stabilized.



265

266 **Figure 3 – Illustration of the calculation of the  $dm/dt$  criterion**

267 The second option seemed to be more relevant because the time needed for the mass to stabilize is  
 268 not known a priori. Additionally, results will depend strongly on the value used for mass stabilization.  
 269 Here, it should be observed that this technical specificity is not systematically mentioned in the  
 270 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  
 271 [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  
 272 proposed by the manufacturer and is very close to the mass variation criterion proposed in the  
 273 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  
 274 good compromise between duration and accuracy was obtained with this value as it was shown by a  
 275 previous study on the dry mass (not presented in this paper) on the sensitivity of the results with the  
 276 mass variation criterion. By extension, this criterion was also applied for the sorption isotherm  
 277 measurement.

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

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

### 290 3. Evaluation of the experimental uncertainties

291 Usually, two kinds of uncertainties are distinguished: random or A-type uncertainty ( $u_A$ ) and  
292 systematic or B-type uncertainty ( $u_B$ ).  $u_A$  represents the dispersion of the results from one  
293 experiment to another while  $u_B$  derives from the known accuracy of the different elements of the  
294 measuring process. The extended uncertainty  $U$  is defined as the combination of these two, given by  
295 (4):

$$296 \quad (4) \quad U = k \cdot \sqrt{u_A^2 + u_B^2}$$

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

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

### 308 3.1. Uncertainty on moisture content obtained with SSS

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

$$310 \quad (5) \quad w_{SSS} = \frac{m - m_0}{m_0 - m_h}$$

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

312 Assuming a normal distribution of the results, the random uncertainty on the mean value  $u_A(\mu_w)$  is

313 defined as follows [12]:

$$314 \quad (6) \quad u_A(\mu_w) = \frac{\sigma}{\sqrt{N}}$$

315  $u_B$  takes account of the influence of every parameter used to calculate  $w$ . As mentioned above, 3

316 measurements are needed to determine the mass content.  $u_B$  is obtained by summing the partial

317 derivatives of each parameter:

$$318 \quad (7) \quad u_B(w) = \sqrt{\sum_i \left( \frac{\partial w}{\partial x_i} \cdot u(x_i) \right)^2}$$

319 Applying this equation to our case leads to:

$$320 \quad (8) \quad u_{B,SSS}(w) = \sqrt{\left[ \frac{1}{m_0 - m_h} \cdot u_B(m) \right]^2 + \left[ \frac{m_h - m}{(m_0 - m_h)^2} \cdot u_B(m_0) \right]^2 + \left[ \frac{m - m_0}{(m_0 - m_h)^2} \cdot u_B(m_h) \right]^2}$$

321 As the mass varies from one sample to another, so does the systematic uncertainty. Therefore, the

322 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:

341 (11) 
$$w_{DVS} = \frac{m - m_0}{m_0}$$

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

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

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

356 (12) 
$$u_{B,DVS}(w) = \sqrt{\left[ \left( \frac{1}{m_0} \right)^2 + \left( -\frac{m}{m_0^2} \right)^2 \right]} \cdot u_{B,DVS}^2(m)$$

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

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

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

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

#### 372 4. Material and sample preparation

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

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

387 powders, it is easier to notice material losses. Finally, there is renewed interest for this material as a  
388 building material, in Europe at least. Some examples of buildings made of straw were reported up to  
389 1921 in France [43] as a solution for rebuilding after the war, but the development of straw buildings  
390 was interrupted because of World War II. The sorption property of straw was measured for the first  
391 time by Hedlin in 1967 [44]. The methodology used in Hedlin's study was equivalent to the SSS  
392 technique and five types of cereal straws were considered (thatcher wheat, cypress wheat, garry  
393 oats, jubilee barley and redwood flax). More than 40 years later, research on the sorption property of  
394 this material is still in progress ([45], [46]). In this study, barley straw samples were supplied by  
395 Calyclay, a small French company created in 2014 and specializing in straw constructions and  
396 coatings on straw support.

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

406 The straw was cut into 3 mm strands by means of triple-bladed scissors. This was done to ensure that  
407 the samples fit into the holders for both techniques. For the SSS technique, the straw strands were  
408 placed in a strainer of dimensions 2.5 x 6 cm<sup>2</sup> as illustrated in Figure 4. To avoid the loss of material  
409 through the mesh of the strainer, it was placed in suspension in a plastic box. Aluminium wedges  
410 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]

## 423 5. Results and discussion

### 424 5.1. Dry mass

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

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

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

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

## 453 5.2. Water content measured with the SSS technique

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

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

471 **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
$\mu_w$ (kg <sub>v</sub> .kg <sup>-1</sup> )	1.44	3.73	5.94	9.78	11.77	21.78
$u_A$ ( kg <sub>v</sub> .kg <sup>-1</sup> )	0.03	0.05	0.09	0.12	0.18	0.63
$u_B$ ( kg <sub>v</sub> .kg <sup>-1</sup> )	0.02	0.02	0.03	0.03	0.03	0.05
$U$ ( kg <sub>v</sub> .kg <sup>-1</sup> ) (k=2)	0.1	0.1	0.2	0.3	0.4	1

472

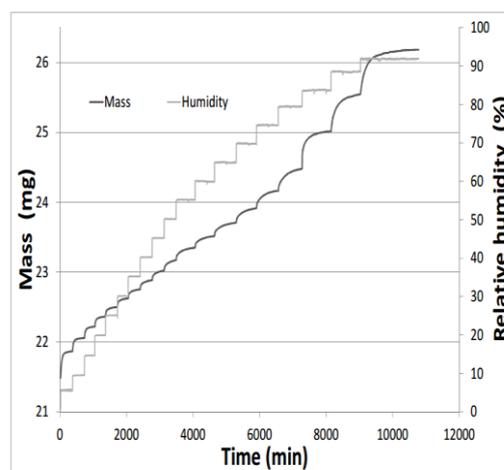
473 It was observed that the extended uncertainty  $U$  was generally dominated by the  $u_A$  value, which  
 474 increased with the relative humidity. This led to a significant increase in the discrepancy of the  
 475 results at high relative humidity. Such a result has already been observed by other researchers for a  
 476 wide range of materials ([13], [18], [27], [41]). Several reasons were listed in [9], from the purity of  
 477 the salts to the value chosen to define mass stabilization. Another interesting reason, mentioned in  
 478 [11], is that the uncertainty on the RH of the salt solution has a much more significant effect for high  
 479 values of RH because of the asymptotic behavior of the sorption isotherm. Still, the SSS technique is  
 480 currently the only standardized method for obtaining a given value of relative humidity, in the field of  
 481 civil engineering at least. Therefore, it can be concluded that the increase of the uncertainty at high  
 482 relative humidity is not specific to straw and did not result from negligence in the experimental work.  
 483 It is inherent in the SSS technique.

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

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

### 492 5.3. Water content measured with the DVS technique

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



496

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

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

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

### 512 5.3.1. Repeatability tests

513 The repeatability tests were carried out for a reduced number of relative humidity steps (9, 33, 55,  
514 76, and 93%). These values were selected to be in agreement with typical values obtained with  
515 saturated salt solutions. They do not correspond to the ones presented in Table 4 because some late  
516 amendments had to be made with the SSS technique.

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

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

527 Table 5 for all relative humidity steps.

528

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

Relative Humidity (%)	9	33	55	76	93
$\mu_w$ (kg <sub>v</sub> .kg <sup>-1</sup> )	2.3	5.9	9.1	13.3	20.9
$u_A$ (kg <sub>v</sub> .kg <sup>-1</sup> )	0.03	0.03	0.04	0.04	0.08
$u_B$ (kg <sub>v</sub> .kg <sup>-1</sup> )	0.08	0.09	0.09	0.09	0.09
U (kg <sub>v</sub> .kg <sup>-1</sup> ) (k=2)	0.2	0.2	0.2	0.2	0.2

530

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

537 **5.3.1. Reproducibility tests**

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

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

Relative Humidity (%)	10	30	50	75	93
$\mu_w$ (kg <sub>v</sub> .kg <sup>-1</sup> )	2.1	4.4	7.3	12.4	21.6
$u_A$ (kg <sub>v</sub> .kg <sup>-1</sup> )	0.06	0.12	0.09	0.11	0.22
$u_B$ (kg <sub>v</sub> .kg <sup>-1</sup> )	0.08	0.08	0.08	0.09	0.09
U (kg <sub>v</sub> .kg <sup>-1</sup> ) (k=2)	0.2	0.3	0.3	0.3	0.5

542

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

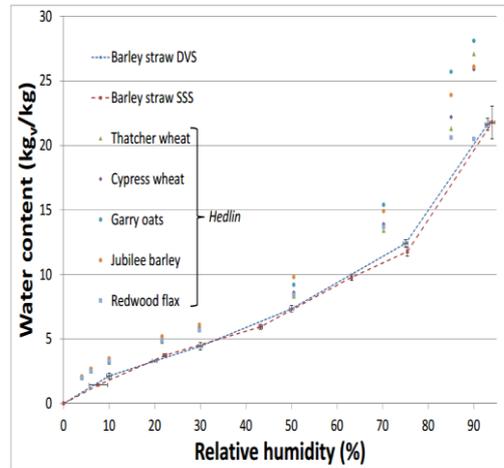
546 Table 5), and is now of the same magnitude as  $u_B$ . It is logical for higher uncertainties to be observed  
547 with reproducibility tests than with repeatability tests because additional sources of uncertainty  
548 were introduced (the operator and the sampling of the material). However, the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

552 One notable exception concerns the highest relative humidity (93%) where  $u_A$  is more than twice as  
553 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  
554 observed with the SSS technique, which strengthens the idea that it is very hard to obtain  
555 reproducible high relative humidity values. However, it can be seen that the random uncertainties  
556 obtained here are higher than those obtained with the SSS technique for relative humidity below  
557 50%. The inverse tendency is observed for relative humidity above 50%. Finally, it is important to  
558 note that all the experiments were performed in the same laboratory. Therefore, the same method  
559 and device were used in roughly the same environment. However, Feng et al. [14] mentioned that  
560 the biggest disparities were found when comparing results from different laboratories. This  
561 parameter was not investigated in the present work.

#### 562 5.4. Comparison of the measurements obtained with the two techniques

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

570 1 kg<sub>v</sub>.kg<sup>-1</sup>. For readability purposes, water contents have been plotted for relative humidity values up  
571 to 94% RH , as this corresponds to the highest value measured in our study.



572

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

574 First, it was observed that the sorption values measured here were lower than the ones obtained in  
575 [55], where jubilee barely straw was considered. However, no significant difference was observed  
576 over the five types of straw in [55] for the lowest values of relative humidity: the maximum  
577 difference of the water content was 0.3 kg<sub>v</sub>.kg<sup>-1</sup> at 10% RH while the average difference was  
578 1.1 kg<sub>v</sub>.kg<sup>-1</sup> with the measurements made in our study. The influence of the type of straw was more  
579 significant at higher relative humidity, but the difference with the measurements achieved here is  
580 still noticeable. This raises questions on the reliability of the measured sorption values for general  
581 calculation purposes. Straw is generally obtained directly from crops: its composition is not well-  
582 known or controlled as may be the case for other construction materials. Therefore, it should be kept  
583 in mind that the low dispersion of the experimental results presented in this paper is not  
584 representative of the presumed variability of the real material.

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

587 obtained with the DVS technique is slightly higher than the one obtained with SSS, although this  
588 difference is within the order of magnitude of the measurement uncertainty. This result was  
589 expected: because of the better drying of the samples with the DVS technique, the moisture content  
590 measurement was expected to be higher. Second, the uncertainty was significantly higher at high  
591 relative humidity for both techniques, as a result of a higher dispersion of the values ( $u_A$ ). A similar  
592 phenomenon was identified in the literature for wood-based products [30], cob [53] and cereal straw  
593 ([21], [46], [55]). Here, the same mass variation criterion was used for each relative humidity step  
594 with both techniques. This criterion may not be robust enough for high values of relative humidity  
595 and may need to be reconsidered. This is also mentioned in [20] and [33]. Moreover, the slope of the  
596 sorption isotherm is steep at high relative humidity. As a result, a small difference in the relative  
597 humidity leads to a significant difference in the moisture content. Consequently, the uncertainty in  
598 relative humidity may be too great to allow a precise comparison as underlined in [21]. Other  
599 techniques can be used at high relative humidity, such as pressure plate, tension plate or pressure  
600 membrane but cannot be used as replacement for the DVS and SSS as they are typically desorption  
601 measurements.

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

## 610 5.5. Comparison of the sorption curves

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

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

$$622 \quad (13) \quad \bar{R}^2 = 1 - (1 - R^2) \cdot \frac{n-1}{n-q-1}$$

623 The adjusted R-squared was calculated on sorption isotherms obtained by the DVS and the SSS  
624 methods. Hence, the number of points,  $n$ , was set to 5 for the first method and 6 for the second. The  
625 value of  $R$  remained between 0 and 1, where 1 corresponds to a perfect correlation and 0 to a total  
626 dispersion between the model and the experimental curve. The fitted coefficients were obtained by  
627 minimization of least squares applied to a point cloud [56]. In our case, best results were obtained  
628 with the GAB model (quoted in [57]) (Fig. 8, see Appendix) as the determination coefficient was  
629 equal to 0.9986 with measurements obtained with the DVS system and 0.9978 for those obtained  
630 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**

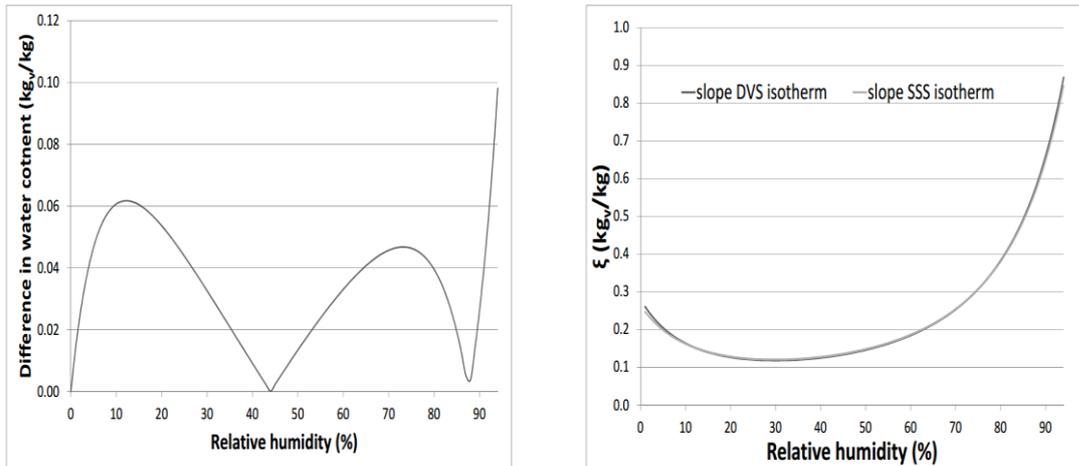
Fitting parameters	DVS	SSS
$C_1$	6.310	5.862
$C_2$	0.831	0.825
$W_m$ ( $\text{kg}_v \cdot \text{kg}^{-1}$ )	0.051	0.053

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  $0.1 \text{ kg}_v \cdot \text{kg}^{-1}$  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

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



651

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

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

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

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

## 671 6. Conclusion

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

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

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

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

## 698 7. Acknowledgements

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- 859

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]

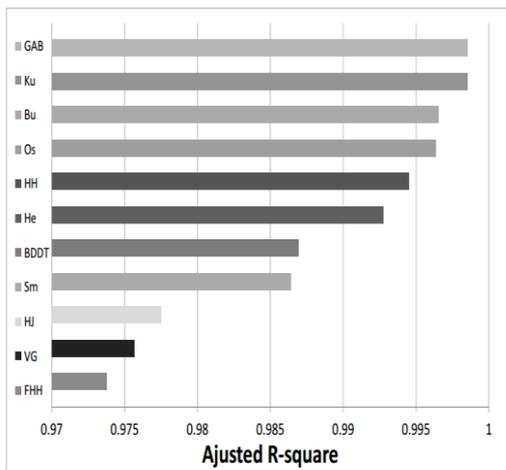
$$w = \frac{A + B \cdot T}{\left(\frac{1}{\varphi} - 1\right)^{\frac{1}{C}}}$$

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**