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ORIGINAL

Quantifying and reducing errors in equilibrium moisture content measurements with dynamic vapor sorption (DVS) experiments

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Abstract Dynamic vapor sorption (DVS) measurements are widely used to collect water vapor sorption isotherms for wood and other cellulosic materials. Equilibrium moisture content (EMC) is typically assumed to have been reached when the rate of change in moisture content with time (dM/dt) drops below a certain value. However, the errors associated with determining EMC in this manner have never been characterized. Here, an operational definition of equilibrium for DVS measurements is provided, and twenty test cases over four cellulosic materials are presented where the relative humidity was stepped up or down and then held constant until equilibrium was reached. Then, both the time to reach various dM/dt "stop criteria" and the errors in EMC associated with those stop criteria are quantified. The errors in the EMC from the widely used 0.002% min^{-1} stop criterion are found to be as large as 1.2% MC, and the average error for 20 test cases is 0.5% MC, which are much larger than the 0.1% MC error claimed in the literature. Longer data collection times are recommended, and a more stringent dM/dt criterion (0.0003% min^{-1}, using a 2-h window) for cellulosic materials is proposed. The errors with this criterion are less than 0.75% MC, and the average error is 0.3% MC. Furthermore, it is shown that the errors for a given stop criterion are systematic and can be fairly well characterized with a simple linear regression. Finally, a correction for systematic error is proposed that results in more accurate EMC values with shorter hold times.

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Introduction

A water vapor sorption isotherm is the locus of points that relate the relative humidity (RH) of the environment to the "equilibrium moisture content" (EMC) of a material at a given temperature. The sorption isotherm is of particular importance for wood and other natural materials whose moisture content and material properties experience large changes with RH. EMC refers to the moisture content at which no net gain or loss of moisture occurs and is calculated as the ratio of the mass of water in the material to the dry mass of the material. Instead of a true thermodynamic equilibrium, the EMC is path dependent; it depends on whether the material reached EMC at a given RH from a lower or higher RH.

Measuring sorption isotherms has traditionally been a time consuming task. Although a range of measurement techniques have been used, the most common methods involved conditioning the wood above a saturated salt solution, sulfuric acid solution, or in an environmental chamber (Stamm and Loughborough 1935; Strømdahl 2000; Glass et al. 2014). The samples were then weighed at regular intervals spaced days to weeks apart. EMC was determined when successive weight readings were within a certain δ of the previous measurement, and the δ was either the resolution of the balance so successive readings were identical (Spalt 1957, 1958), or within the uncertainty of the calibration of the balance (Zelinka and Glass 2010). In addition to the labor required to take the measurements, the accuracy was limited by the ability to control RH and potential mass fluctuations.

With the advent of the dynamic vapor sorption (DVS) technique in the 1980s and 90s, it became possible to measure sorption isotherms with much less labor and potentially higher accuracy (Rasmussen and Akinc 1983; Astill et al. 1987; Benham and Ross 1989; Bergren 1994; Marshall et al. 1994; Williams 1995). In these experiments, a sample of less than 100 mg is suspended from a microbalance that continuously records mass as a function of time. The sample is located in a chamber maintained at constant temperature, and water vapor mixed with inert carrier gas (such as nitrogen) is flowed at a constant rate through the sample chamber. The RH is controlled by mixing dry and vapor-saturated streams of carrier gas using mass flow controllers. With computer control, DVS facilitates rapid step changes in RH and gravimetric measurement of moisture sorption kinetics. Because the resolution of the microbalance is so fine and the mass is continuously and automatically recorded, the EMC is not typically taken from identical successive readings, but instead a "stop criterion" is used to stop collecting data at an RH step and move to the next step. This stop criterion sets the hold time at the RH. Frequently, stop criteria are based upon the derivative of mass ($\mathrm{d}m/\mathrm{d}t$) or moisture content ($\mathrm{d}M/\mathrm{d}t$) with respect to time (where moisture content M is typically expressed as a percentage of sample dry mass).

The most widely used DVS stop criterion for wood and other cellulosic materials in the literature is a 0.002% change in mass per minute maintained over a 10 min window (Hill et al. 2009; Zaihan et al. 2009; Engelund et al. 2010; Hill et al. 2010a, b; Jalaludin et al. 2010a, b; Sharratt et al. 2010; Xie et al. 2010;

Zaihan et al. 2010; Engelund et al. 2011; Xie et al. 2011; Hill et al. 2012, 2013; Keating et al. 2013; Popescu et al. 2013). The mass change is typically calculated relative to the mass obtained after an initial drying step, and thus, the dm/dt criterion in fact becomes a dM/dt criterion. The 0.002%/min criterion has been claimed to yield a value within 0.1% MC of the equilibrium value at extended time (Hill et al. 2009). Recently, however, Glass et al. (2017) have highlighted that this and other stop criteria used for determining equilibrium in dynamic vapor sorption experiments in cellulosic materials actually mischaracterize the EMC. They observed changes in moisture content at long hold times that had an effect on EMC considerably larger than 0.1% MC. This work, however, did not go so far as to determine an appropriate criterion for stopping experiments.

Equilibrium is difficult to define in a DVS experiment, and a detailed operational definition has not been published up to this point. A reasonable approximation of equilibrium in a DVS experiment is to apply a dm/dt criterion that is similar in magnitude to the drift of the instrument, over a reasonably long period of time. Once equilibrium has been established in this way, it is then possible to quantify the errors associated with various (less stringent and more expedient) dM/dt stop criteria.

This article accomplishes three main objectives. First, an operational definition of equilibrium for DVS measurements is proposed by quantifying the mass drift in a DVS instrument. Second, DVS kinetic data are collected for four cellulosic materials under various RH conditions until the equilibrium criterion is fulfilled, and then the time to reach various practical stop criteria and the corresponding error in EMC are quantified. Third, new stop criteria for DVS measurements are proposed that yield more accurate EMC values than criteria currently in common use.

Materials and methods

Materials

Four different cellulosic materials were examined: loblolly pine (*Pinus taeda*), holocellulose extracted from loblolly pine, microcrystalline cellulose, and office paper. The microcrystalline cellulose (MCC) and office paper were obtained commercially. The holocellulose came from the same batch as previous work examining the kinetics of water vapor sorption at long hold times and water phase transitions in wood (Zelinka et al. 2012; Glass et al. 2017). Full details of the extraction of holocellulose can be found elsewhere (Yelle et al. 2008). The loblolly pine was cut from solid pieces 1.2 mm thick (longitudinal). In order to get a sample weight near 20 mg, two previously cut solid pieces approximately 4 mm (tangential) by 4.7 mm (radial) that included both earlywood and latewood were used together as a single sample.

Method for determining drift in DVS

Dynamic vapor sorption measurements were taken with an IGAsorp DVS analyzer manufactured by Hiden Isochema (Warrington, UK). The instrument has a

microbalance with a resolution of 0.1 μg, and the sample is placed in a stainless steel mesh basket suspended from the balance. The humidity around the sample is controlled by mixing dry and water vapor-saturated nitrogen streams at a total flow of 250 mL/min using electronic mass flow controllers, with feedback provided by an RH sensor placed in the chamber near the sample. Samples were dried prior to sorption measurements under flow of dry nitrogen at 60 °C for 6 h, and the dry mass was recorded after the temperature was brought to 25 °C under flow of dry nitrogen. In the authors' experience, this yields reproducible dry mass (Thybring et al. 2018) Sample dry mass ranged between 12 mg (office paper) and 28 mg (MCC). All sorption measurements were run at a constant temperature of 25 °C.

An operational definition of equilibrium was established by assessing the magnitude of mass drift of the DVS instrument. The mass of a 20-mg standard calibration weight was recorded continuously under constant humidity conditions for four test cases of varying duration. In some cases, small fluctuations were observed with magnitude of 2 μg or less; these fluctuations may be a result of vibration, as discussed previously by Glass et al. (2017). The rate of change in mass with respect to time (slope) from a linear fit to the data is reported below for the four test cases.

1. 28-h test at 0% RH: slope of − 0.9 μg/day
2. 40-h test at 50% RH: slope of − 2 μg/day
3. 92-h test at 10% RH: slope of + 0.6 μg/day
4. 193-h test at 50% RH: slope of + 0.2 μg/day

In all cases, the absolute value of the instrument drift was 2 μg/day or less. From prior experience with DVS measurements at long times, it was found that 24 h was a reasonable period over which to apply a drift criterion (Glass et al. 2017). This value was used as an equilibrium criterion in subsequent experiments on water vapor sorption or desorption in cellulosic materials following a step change in relative humidity. That is, the instrument collected data until the slope of a simple linear fit to the data over the prior 24-h period was less than this instrument drift value of 2 μg/day. For perspective, once a sample reaches this criterion, assuming this rate of change would continue indefinitely, a sample with 20-mg dry mass would take 10 days to change moisture content by 0.1%.

This equilibrium criterion is specific to the instrument and laboratory conditions. While in the absence of other data, it can be used to guide the determination of equilibrium and measurement errors in DVS, studies should be repeated on a range of DVS instruments to better understand inter-instrument variability in the accuracy of DVS measurements.

Measurements of sorption kinetics

The mass versus time behavior for a given material and RH step was recorded until the equilibrium criterion discussed above was met (2 μg over a 24-h period). An example is shown in Fig. 1, which includes moisture content data from loblolly pine in absorption from 90 to 95% RH along with its slope (dM/dt) as

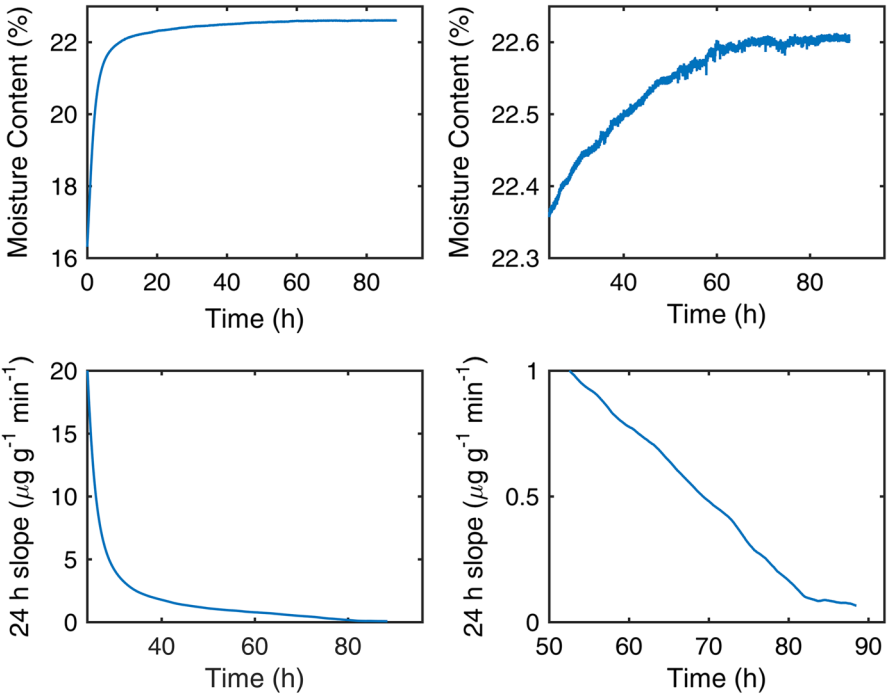

Fig. 1 Example of method for data collection until equilibrium defined by drift criterion. Top: moisture content as a function of time; bottom: slope (d*M*/d*t*) over 24 h as a function of time. In each case, the graph on the right is just an enlargement showing detail of the behavior at the end

a function of time. Although dM/dt values are typically expressed as a percentage change in moisture content per minute (e.g., 0.002% min^{-1}), it is found more convenient to express dM/dt with units of micrograms of water per gram of dry material per minute. This unit system is unambiguous and avoids an excessive number of zeros after the decimal. The commonly used value of 0.002% min^{-1} is equivalent to 20 μg g^{-1} min^{-1}. In the case of Fig. 1, the sample dry mass was 21.070 mg, so the equilibrium criterion of 2 μg over a 24-h period is equivalent to 0.066 μg g^{-1} min^{-1} (or 6.6×10^{-6} % min^{-1}).

Several absorption and desorption steps were examined for every material so that the slowest kinetics for each material could be observed. Table 1 contains a full list of the materials and RH steps that were tested along with the time needed to reach equilibrium as defined by the change in mass with time being less than the drift. Special attention was paid to both high RH conditions and desorption steps around 50% RH. The high RH conditions were examined because Spalt (1957) noted that it took a long time for wood to reach equilibrium at high RH levels. However, in a previous DVS study on these and similar materials, it appeared when modeled with a triple exponential kinetics model that the longest time constants were observed in the 55–50% RH step in desorption (Glass et al. 2017).

Table 1 Materials and RH steps examined along with time to reach equilibrium and errors in EMC with two different stop criteria: the commonly used 20 μg g^{-1} min^{-1} (with $\Delta t_{slope} = 10$ min and $\Delta t_{stab} = 10$ min) and 3 μg g^{-1} min^{-1} (with $\Delta t_{slope} = 2$ h)

	RH step	EMC (%)	Time to reach (h)			Error in EMC			
						20 μg g^{-1} min^{-1}		3 μg g^{-1} min^{-1}	
			Drift limit	20 μg g^{-1} min^{-1}	3 μg g^{-1} min^{-1}	Absolute (% EMC)	Relative (% error)	Absolute (% EMC)	Relative (% error)
Office paper									
Absorption	20–25	3.78	45.52	0.47	3.00	0.13	3.4	0.08	2.1
Absorption	70–75	9.17	88.01	0.58	2.87	0.30	3.3	0.25	2.7
Desorption	75–70	9.52	71.18	0.51	2.85	0.19	2.0	0.14	1.5
Desorption	55–50	6.94	143.96	0.45	2.92	0.32	4.6	0.27	3.9
Desorption	25–20	3.85	72.16	0.45	2.08	0.13	3.4	0.11	2.9
Holocellulose									
Absorption	20–30	6.74	69.33	1.37	5.20	0.26	3.9	0.13	1.9
Absorption	50–60	11.20	56.47	2.36	8.38	0.36	3.2	0.14	1.3
Absorption	70–80	16.28	16.28	2.58	6.58	0.34	2.1	0.20	1.2
Absorption	90–95	29.19	29.19	6.65	13.06	0.27	0.9	0.08	0.3
Desorption	55–50	10.86	184.25	0.52	2.83	0.52	4.8	0.45	4.1
Microcrystalline cellulose									
Absorption	20–30	4.19	47.97	0.95	3.51	0.12	2.9	0.05	1.2
Desorption	95–90	16.04	128.93	1.98	6.36	0.48	3.0	0.35	2.2
Desorption	60–50	7.02	109.61	1.36	6.11	0.38	5.4	0.23	3.3
Loblolly pine									
Absorption	20–30	5.67	62.75	1.68	5.88	0.26	4.6	0.12	2.1
Absorption	50–60	9.01	144.58	1.82	6.37	0.34	3.8	0.18	2.0
Absorption	70–80	13.39	135.00	5.00	17.13	0.87	6.5	0.40	3.0

Table 1 (continued)

	RH step	EMC (%)	Time to reach (h)			Error in EMC			
						20 μg g^{-1} min^{-1}		3 μg g^{-1} min^{-1}	
			Drift limit	20 μg g^{-1} min^{-1}	3 μg g^{-1} min^{-1}	Absolute (% EMC)	Relative (% error)	Absolute (% EMC)	Relative (% error)
Absorption	90–95	22.60	88.43	7.08	17.02	0.79	3.5	0.35	1.5
Desorption	95–90	20.41	325.78	1.67	13.42	1.13	5.5	0.75	3.7
Desorption	80–70	13.55	365.58	3.80	18.59	1.20	8.9	0.67	4.9
Desorption	60–50	9.92	224.26	2.33	14.57	1.00	10.1	0.54	5.4
Desorption	30–20	5.19	116.28	2.09	8.75	0.47	9.1	0.24	4.6
	Max		365.58	7.08	18.59	1.20	10.1	0.75	5.4
	Min		16.28	0.45	2.08	0.12	0.9	0.05	0.3
	Avg		120.26	2.18	7.98	0.47	4.5	0.27	2.7

After the full data sets were collected, various stop criteria were applied to the data retrospectively. The time required to reach each stop criterion and the "apparent EMC" values were determined, with the apparent EMC defined as the last recorded moisture content when the given criterion was met. These apparent EMC values were compared against the EMC values found by collecting data until the drift limit was reached. Typically, data have been reported in prior studies using a slope (dM/dt) that is determined over a 5 or 10 min window. It was found, however, that as the stop criterion became more stringent (or as the slope value was decreased), it was necessary to lengthen the time window used in calculating the slope (Δt_{slope}) to obtain meaningful results because the noise inherent in the measurements resulted in excessive oscillation in the slope when the window was too short. This is further discussed and illustrated in the next section.

For the commonly used stop criterion of 20 μg g^{-1} min^{-1} (0.002% min^{-1}) calculated over 10 min (Δt_{slope}), an additional stability criterion was applied such that $|dM/dt|$ had to remain below the threshold value over a 10 min stability period (Δt_{stab}). This is illustrated using data for loblolly pine desorption from 95 to 90% RH in Fig. 2. When this condition was met, then the apparent EMC was taken as the measured MC at the end of the 10 min stability period. If, during the 10-min stability period, the absolute value of the slope exceeded the threshold value (because of oscillation), then the 10-min stability clock was reset once the slope dropped below the threshold value. Other stop criteria used a much longer calculation period for the slope ($\Delta t_{slope} = 1$, 2, or 6 h). When these criteria were applied, the stability period was not an important consideration because the fluctuations in the slope were much smaller (Fig. 2).

Results and discussion

Figure 3a is an example moisture content vs time curve for loblolly pine in desorption from 95 to 90% RH. This is an example where the kinetics are slow and the errors are large. The "x" represents the apparent EMC with a stop criterion of 20 μg g^{-1} min^{-1} with $\Delta t_{slope} = 10$ min and $\Delta t_{stab} = 10$ min. This value is clearly far from the EMC at long time determined using the drift limit; the difference is about 1% MC. Figure 3b, c shows the slope (dM/dt in μg g^{-1} min^{-1}) as a function of time for different slope calculation periods. Figure 3b shows the three shortest time windows examined, 10 min, 1 h, and 2 h. Because of the oscillations in the slope when using the 10 min window, the dM/dt actually crosses 0 before 4 h. Therefore, without the additional stability criterion, any choice of $|dM/dt|$ with the 10 min window would have reached its stop criterion by this time. It is unclear whether a stability criterion would be useful for $|dM/dt|$ criteria less than 10 μg g^{-1} min^{-1} given the magnitude of the oscillations. The slopes from time windows of 1 and 2 h are much smoother and do not cross the zero line (until long after 10 h). Figure 3c shows a detail over a smaller range of dM/dt values for slopes calculated over time windows of 2 h and 6 h, out to longer times than Fig. 3b. Although there is less oscillation as the slope is averaged over a longer time period, the curves in Fig. 3c generally move in parallel and generally reach a given dM/dt within a small percentage of the same

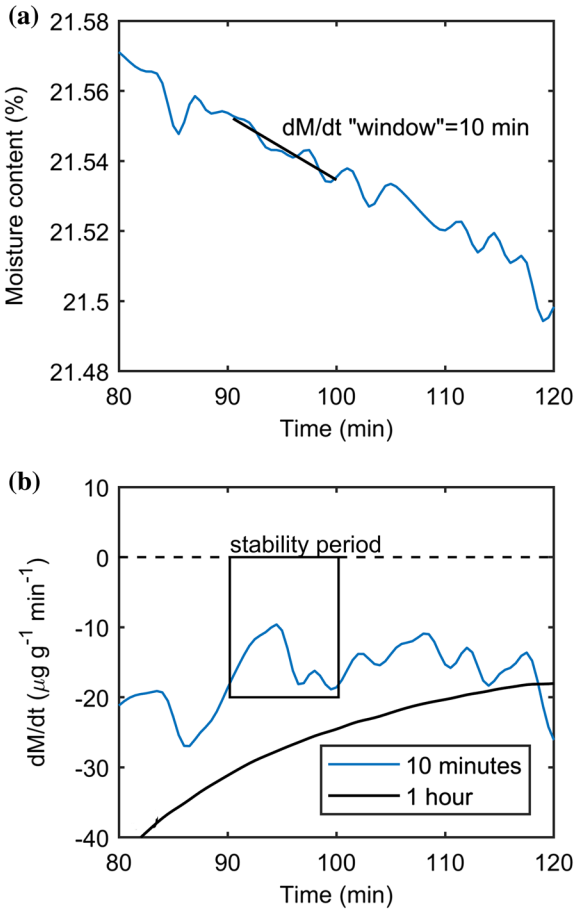

Fig. 2 **a** Raw moisture content of loblolly pine as a function of time in desorption from 95 to 90% RH showing the "d*M*/d*t*" calculated from a linear fit over 10 min. **b** Illustration of the implementation of the 10 min stability period on the 10 min slope. Note that when the slope is calculated over a 1-h window it is much smoother and the stability period is unnecessary

time. By using longer time windows, the d$M/$dt criterion can be specified without the need for a stability period, unlike in the case of the commonly used stop criterion of 20 μg g^{-1} min^{-1} (0.002% min^{-1}).

Figure 4 is a second example of a moisture content versus time curve for microcrystalline cellulose in absorption from 20 to 30% RH. This is an example where the kinetics are fast and the errors are small. The apparent EMC with a stop criterion of 20 μg g^{-1} min^{-1} ($\Delta t_{\text{slope}} = 10$ min; $\Delta t_{\text{stab}} = 10$ min) ("x" in Fig. 4a) is only slightly more than 0.1% MC from the EMC at long time determined using the drift limit. For this material, the drift limit was reached within 50 h. The slope has a steep decline and is less than 0.5 μg g^{-1} min^{-1} within 10 h of the start of the experiment. This can be contrasted against the data in Fig. 3c where it takes nearly 60 h to reach the same absolute value of the slope. The slopes for each calculation period in Fig. 4 also exhibit less oscillation than those in Fig. 3.

Graphs similar to Figs. 3 and 4 were analyzed for each RH step measured for each material (20 cases in total). The time required to reach the commonly used

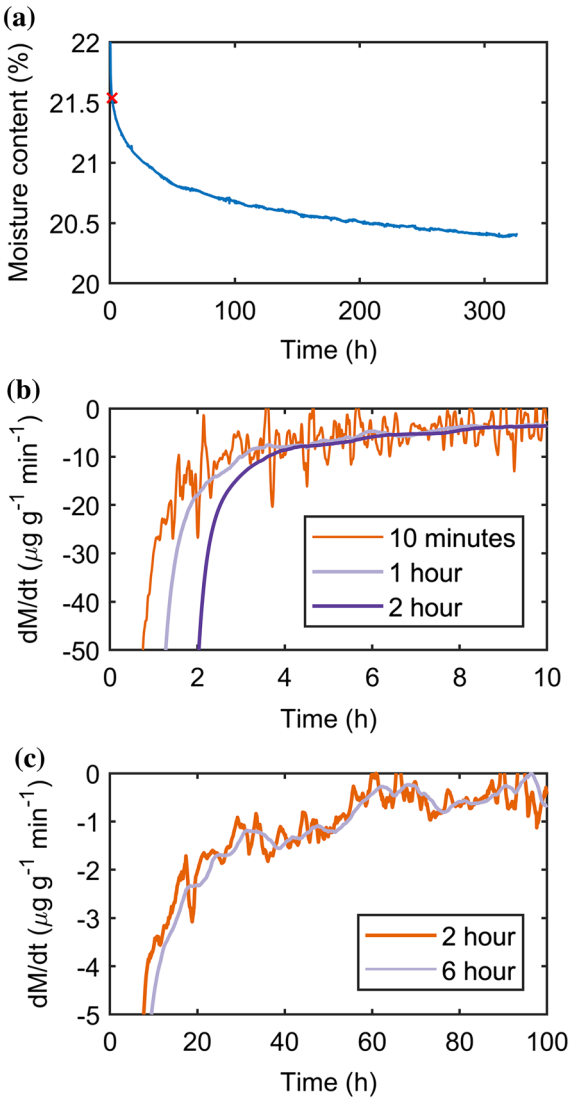

Fig. 3 **a** Moisture content as a function of time for loblolly pine desorption from 95 to 90% RH. **b**, **c** Graphs of d*M*/d*t* as a function of time over different slope calculation periods. The "*x*" in subfigure **a** represents the apparent EMC with a stop criterion of 20 μg g^{-1} min^{-1} calculated with $\Delta t_{slope} = 10$ min fulfilled over a 10-min stability period

stop criterion of $|dM/dt| < 20$ μg g^{-1} min^{-1} with $\Delta t_{slope} = 10$ min and $\Delta t_{stab} = 10$ min, and the error in EMC (the absolute value of the difference between EMC determined from the drift limit and apparent EMC determined at this stop criterion) are presented in Table 1. The time to reach the stop criterion is discussed later. From Table 1 it is clear that this criterion generates much larger errors than the previous claims of "within 0.1% (MC) of the equilibrium value" (Hill et al. 2009, 2010b). In fact, for none of the materials or RH steps examined was the error within 0.1% MC. In some cases for loblolly pine, the errors were larger than 1% MC. The average error using this criterion was 0.47% MC. The errors in determining EMC using a

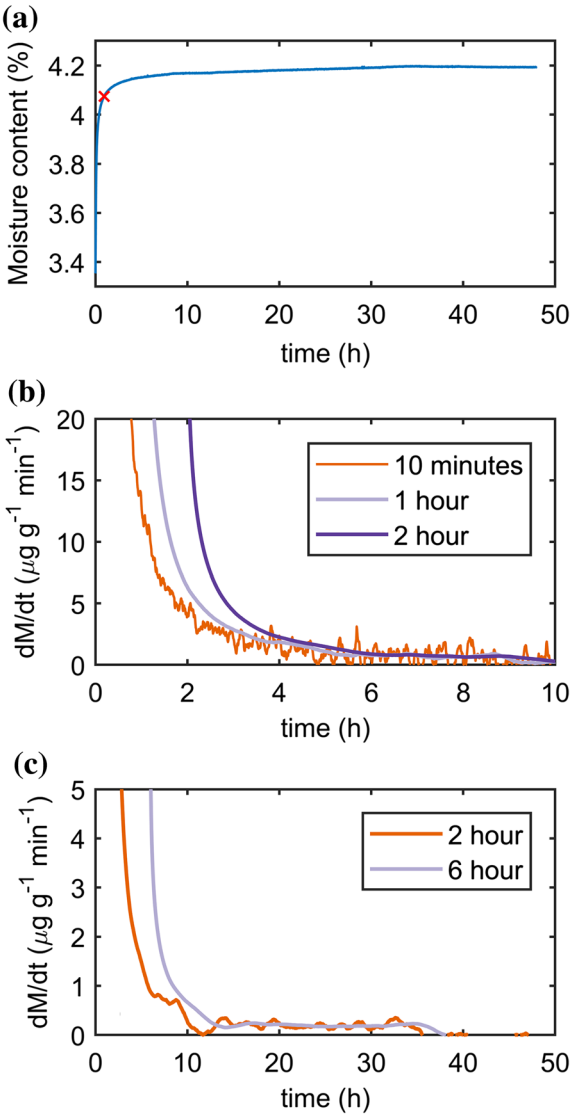

Fig. 4 **a** Moisture content as a function of time for microcrystalline cellulose absorption from 20 to 30% RH. **b**, **c** Graphs of d*M*/d*t* as a function of time over different slope calculation periods. The "*x*" in subfigure **a** represents the apparent EMC with a stop criterion of 20 μg g^{-1} min^{-1} calculated with $\Delta t_{slope} = 10$ min fulfilled in a 10-min stability period

stop criterion of 20 μg g^{-1} min^{-1} (0.002% min^{-1}) over a 10-min period are unacceptably high. In order to reduce the error in EMC, more stringent DVS stop criteria should be used for wood and other cellulosic materials.

Supposing the DVS user wants to achieve a 0.1% MC level of accuracy in EMC, it is apparent that much longer hold times are necessary. Figure 5 shows the trade-off between measurement time and error. In this figure, the measurement time is plotted on the abscissa (logarithmic scale) and the error is plotted on the ordinate; the stop criteria are plotted implicitly. Figure 5 is constructed similarly to Table 1 for many different d*M*/d*t* criteria, going to as small as 0.5 μg g^{-1} min^{-1}. As d*M*/d*t*

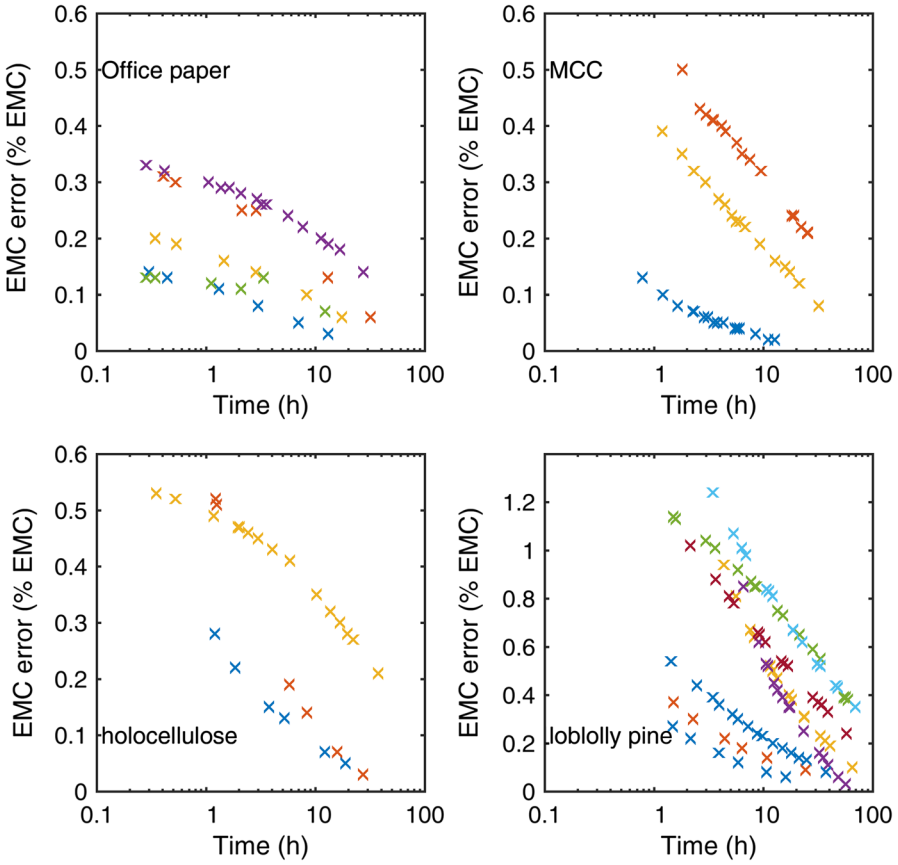

Fig. 5 Error in EMC as a function of the logarithm of measurement time for different materials and RH steps. Different shaded markers represent different RH steps

got smaller, it was calculated over a longer period of time, ranging from 10 min (20 μg g^{-1} min^{-1}) to 6 h (0.5 μg g^{-1} min^{-1}). For all materials, there is a roughly linear trade-off between the logarithm of time and the accuracy, that is, the errors decrease in a logarithmic fashion with time. However, both the slopes of the curves and the absolute level of error at any given time vary widely across both materials and RH steps. Holocellulose, for instance, has a 250% difference in the slope between the absorption 50–60% RH step and the desorption 55–50% RH step; in other words, each doubling of the measurement time only reduces the error of the desorption measurement 1/3 as much as the error of the absorption step. Therefore, it is difficult, perhaps impossible, to come up with a universal optimization scheme that could be applied across all materials and RH steps.

Figure 6 is another way to visualize the errors with various stop criteria. Data are presented for 6 stop criteria from 0.5 to 20 μg g^{-1} min^{-1} with the dM/dt calculated for time windows ranging from 10 min (0.17 h) to 6 h. The largest errors

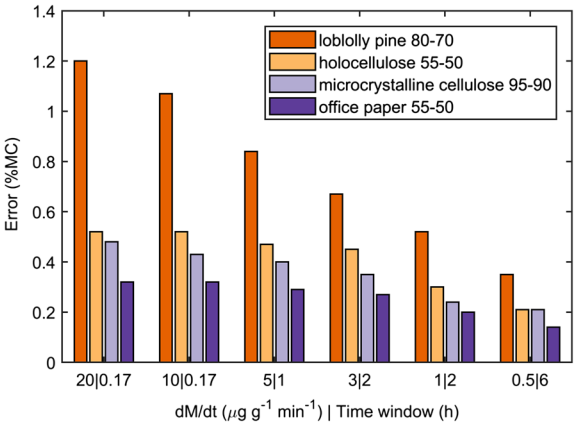

Fig. 6 Absolute error in EMC for various *dM/dt* criteria for the RH step with the largest error for each material

for each material were all found for desorption steps. From these data, it is clear that 20 μg g^{-1} min^{-1} (with $\Delta t_{slope} = 10$ min and $\Delta t_{stab} = 10$ min) gives unacceptably high errors, especially for wood. Slopes need to be calculated over a much longer window than 10 min when selecting stop criteria smaller than the commonly used 20 μg g^{-1} min^{-1}. Unfortunately, the most widely used commercial DVS instruments currently do not allow the automatic calculation of the slope longer than 10 min for stop criteria. A longer slope calculation period is recommended in future DVS software upgrades to improve the accuracy of EMC determination.

Although there is not a clear optimization of the trade-off between measurement time and accuracy, the authors propose the following stop criterion be implemented for routine measurements: a slope of 3 μg g^{-1} min^{-1} calculated over a 2-h window. With the small fluctuations in dM/dt by the 2-h slope window there is no need for a stability period. The errors for this stop criterion are included in Table 1 for reference. The maximum error for any material was 0.75% MC, observed for loblolly pine. The average error was less than 0.3% MC. The average time to reach the slope of 3 μg g^{-1} min^{-1} (with $\Delta t_{slope} = 2$ h) was 8 h per RH step. While this is longer than the 2 h average per RH step using the slope of 20 μg g^{-1} min^{-1} (with $\Delta t_{slope} = 10$ min and $\Delta t_{stab} = 10$ min), a 20 step isotherm could still be completed in less than 7 days.

EMC error can be further reduced by making a correction for measurement bias. The result of stopping data collection prior to equilibrium is that the MC values at the stop criterion are always less than EMC in absorption and always greater than EMC in desorption. This systematic error is inherent in stopping the measurements prior to equilibrium. Ideally, a correction for systematic error would be based on a model that considers the shape of the sorption isotherm and the kinetic response to step changes in RH. At this time, however, a general model is not within reach because the kinetic response appears to vary considerably depending on the material and the particular RH step, as shown above and in previous work (Glass et al. 2017). Instead of a theoretical model, a simple empirical approach is developed for characterizing systematic error and correcting for it.

Two trends can be observed in the absolute EMC errors listed in Table 1. First, the errors generally increase with increasing RH. Second, the errors are generally larger for desorption than for absorption. On the basis of these trends, the absolute EMC errors versus measured moisture content when the stop criterion is met are plotted in Fig. 7. The stop criterion selected for this analysis is $dM/dt = 5$ µg g^{-1} min^{-1} over 1 h, which is less stringent and results in higher raw absolute EMC errors than the criterion mentioned previously ($dM/dt = 3$ µg g^{-1} min^{-1} over 2 h) but reduces measurement time from an average of 8 h to 5 h per RH step. The plots are separated for absorption and desorption. In addition, the data for 5% RH steps and 10% RH steps are separated under the hypothesis that larger RH steps yield larger absolute EMC errors as was observed by Christensen and Hergt (1969). These graphs were

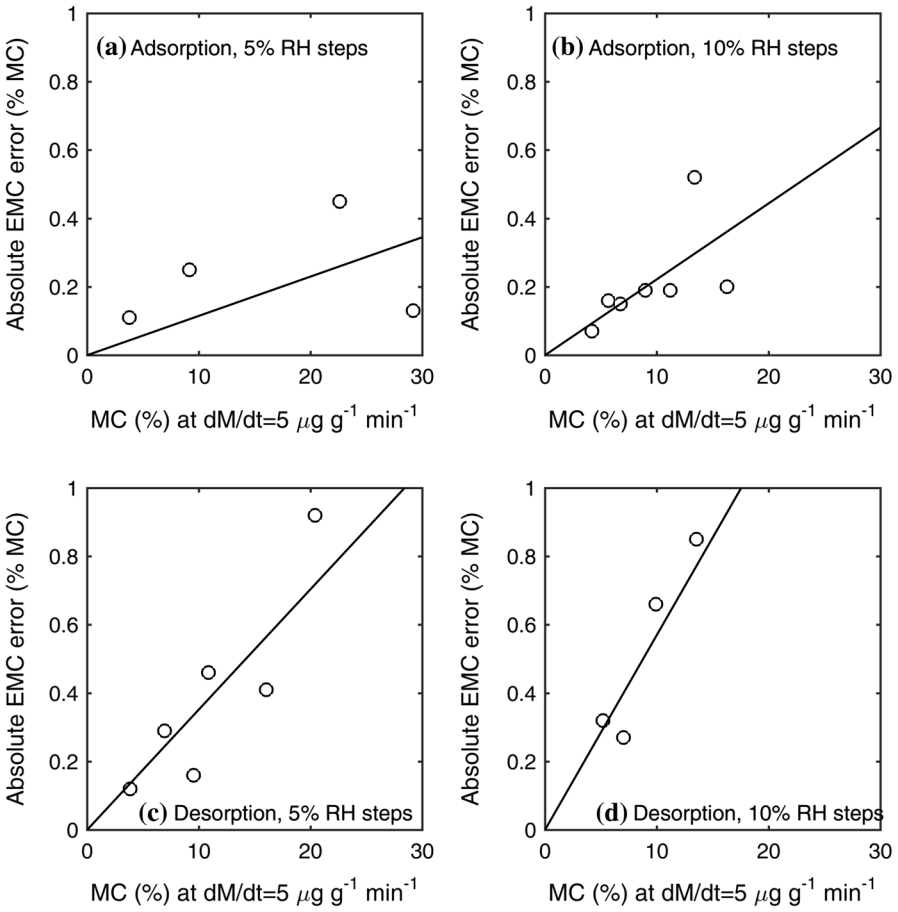

Fig. 7 Absolute EMC error versus moisture content in absorption for 5% RH steps (**a**) and 10% RH steps (**b**) and in desorption for 5% RH steps (**c**) and 10% RH steps (**d**), determined using a stop criterion of 5 µg g^{-1} min^{-1} (with $\Delta t_{slope} = 1$ h). The solid lines represent linear fits to the absolute errors forced through the origin and form the basis for the corrections given in Eqs. 1–4

based upon the data presented in this work and may not be an applicable correction across all materials or DVS instruments.

As shown in Fig. 7, the absolute EMC error can be reasonably approximated as a linear function of moisture content at the stop criterion. Applying a correction based on these linear fits results in an improved estimation of EMC. The correction equations are as follows:

For absorption:

$$5\%\,\text{RH steps: } \text{EMC}_{\text{cor}} = \text{MC}_{\text{stop}} \times 1.012 \tag{1}$$

$$10\%\,\text{RH steps: } \text{EMC}_{\text{cor}} = \text{MC}_{\text{stop}} \times 1.022 \tag{2}$$

For desorption:

$$5\%\,\text{RH steps: } \text{EMC}_{\text{cor}} = \text{MC}_{\text{stop}} \times 0.965 \tag{3}$$

$$10\%\,\text{RH steps: } \text{EMC}_{\text{cor}} = \text{MC}_{\text{stop}} \times 0.943 \tag{4}$$

EMC_{cor} is the equilibrium moisture content corrected for systematic error, and MC_{stop} is the measured moisture content when the stop criterion is met (5 μg g^{-1} min^{-1} with $\Delta t_{\text{slope}} = 1$ h in this case). This correction procedure reduces the mean absolute EMC error to 0.10% MC and the maximum absolute EMC error to 0.23% MC for the stop criterion of 5 μg g^{-1} min^{-1} (with $\Delta t_{\text{slope}} = 1$ h). Results are listed in Table 2. This procedure therefore yields more accurate EMC values and requires less data collection time compared to taking EMC as the measured (uncorrected) moisture content at a stop criterion of 3 μg g^{-1} min^{-1} (with $\Delta t_{\text{slope}} = 2$ h).

It is evident from Tables 1 and 2 that the EMC errors depend on the material being measured. Results for four different materials are combined in Fig. 7 and in Eqs. 1–4 to show that this correction approach can be applied across a variety of cellulosic materials. Tailoring this correction approach to each material separately would logically yield even smaller EMC errors.

The empirical corrections for systematic error given here are based on the materials, RH steps, and DVS instrument used in this study. It is recommended that corrections be developed for additional materials and DVS instruments according to the method outlined above.

An alternative approach to predicting EMC from DVS measurements is fitting a curve to the moisture content versus time data. Previously, the use of models in the literature in conjunction with the widely used 20 μg g^{-1} min^{-1} (0.002% min^{-1}) stop criterion was discussed and it was concluded that extrapolation using either a single exponential kinetics model or a parallel exponential kinetics model yields large errors compared with measured data at long hold times (Glass et al. 2017). Data at extended times could be fit with a triple exponential kinetics model, where the third time constant was on the order of 500–2000 min (approximately 8–34 h), which could not be identified when using shorter hold times. Curve fitting methods therefore require very long hold times for accurate modeling of the kinetics and prediction of EMC values. Hence, these methods were not considered further in this analysis. The empirical correction approach presented above yields accurate EMC values with an average measurement time of 5 h per RH step.

Table 2 Comparison of measured EMC using the drift criterion and EMC determined from Eqs. 1–4 using a stop criterion of 5 μg g^{-1} min^{-1} over 1 h

Material	RH step (%)	Equilibrium moisture content (%)		Difference
		Measured	Determined from Eqs. (1–4)	
Holocellulose	20–30	6.74	6.74	0.00
	50–60	11.20	11.25	0.05
	70–80	16.28	16.44	0.16
	90–95	29.19	29.39	0.20
	55–50	10.86	10.92	0.06
Loblolly pine	20–30	5.67	5.63	−0.04
	50–60	8.98	8.99	0.01
	70–80	13.39	13.16	−0.23
	90–95	22.60	22.40	−0.20
	95–90	20.41	20.58	0.17
	80–70	13.55	13.58	0.03
	60–50	9.92	9.98	0.06
	30–20	5.19	5.20	0.01
Microcrystalline cellulose	20–30	4.19	4.21	0.02
	95–90	16.04	15.87	−0.17
	60–50	7.02	6.87	−0.15
Office paper	20–25	3.78	3.71	−0.07
	70–75	9.17	9.02	−0.15
	75–70	9.52	9.34	−0.18
	55–50	6.94	6.98	0.04
	25–20	3.85	3.83	−0.02
			Average (absolute value)	0.10

Conclusion

An operational definition for obtaining equilibrium moisture content in DVS experiments was presented. Under constant RH following a step change, equilibrium was attained when the rate of change in mass with time was less than the drift limit of the instrument, which was found to be 2 μg over a 24-h period for the present instrument.

Using this definition of equilibrium, EMC was measured for four different cellulosic materials over a range of RH steps for a total of 20 cases. The time to reach various dM/dt stop criteria and the errors in EMC associated with those stop criteria were quantified.

The commonly used stop criterion of 20 μg g^{-1} min^{-1} (0.002% min^{-1}) over 10 min had much larger errors than claimed in the literature (< 0.1% MC). In fact, the errors with this criterion were as high as 1.2% MC and the average error across the materials examined was 0.47% MC. This criterion should not be used for measuring EMC of cellulosic materials.

To reduce the error in EMC, more stringent dM/dt stop criteria are needed, and the slopes need to be calculated over longer periods of time than 10 min. Slopes over time windows on the order of 1–6 h are appropriate for dM/dt values ranging from 0.5 to 10 μg g^{-1} min^{-1}. While current commercial DVS instruments currently do not allow calculation of the slope longer than 10 min for automatic stop criteria, it would be a relatively simple change to implement this into the software and would greatly improve the accuracy of the isotherm data.

The current measurements suggest a rough trade-off between error in EMC and the logarithm of measurement time. Although the magnitude of error and time needed to reach certain criteria varies across materials and conditions, the relationship is approximately logarithmic.

As an alternative to 20 μg g^{-1} min^{-1} (0.002% min^{-1}) calculated over 10 min with a stability period of 10 min, 3 μg g^{-1} min^{-1} calculated over 2 h with no stability period is instead suggested. With this criterion, the absolute EMC errors were always less than 0.75% MC with an average error of less than 0.3% MC. This criterion required an average of 8 h per RH step.

Furthermore, it was shown that stopping data collection before the drift limit results in systematic errors. The systematic EMC errors can be reduced by applying a linear correction to the data. The corrections were supplied for both absorption and desorption in 5% and 10% RH steps when stopping at 5 μg g^{-1} min^{-1} calculated over 1 h. This correction procedure reduced the mean absolute EMC error to 0.10% MC and the maximum absolute EMC error to 0.23% MC for four different cellulosic materials, with an average hold time of 5 h per RH step.

Although the measurements presented here may be specific to the instrument and laboratory conditions used in this study, in the absence of any other data, these results are useful for estimating the hold times and EMC errors that can be expected for various stop criteria. Further work by other laboratories using the methodology described here is recommended.

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References

Astill D, Hall P, McConnell J (1987) An automated vacuum microbalance for measurement of adsorption isotherms. J Phys E: Sci Instrum 20:19

Benham M, Ross D (1989) Experimental determination of absorption-desorption isotherms by computer-controlled gravimetric analysis. Z Phys Chem 163:25–32

Bergren MS (1994) An automated controlled atmosphere microbalance for the measurement of moisture sorption. Int J Pharm 103:103–114

Christensen GN, Hergt HFA (1969) Effect of previous history on kinetics of sorption by wood cell walls. J Polym Sci Part A-1 Polym Chem 7:2427–2430. https://doi.org/10.1002/pol.1969.150070839

Engelund ET, Klamer M, Venås M (2010) Acquisition of sorption isotherms for modified woods by the use of dynamic vapour sorption instrumentation: principles and practice. In: 41st Annual meeting of the International Research Group on Wood Protection, Biarritz, France, 9–13 May 2010. IRG Secretariat

Engelund ET, Klamer M, Venås TM (2011) Adsorption boundary curve influenced by step interval of relative humidity investigated by dynamic vapour sorption equipment. In: 42nd annual meeting

of the International Research Group on Wood Protection, Queenstown, New Zealand, 2011. IRG Secretariat, Paper IRG/WP 11-40547

Glass SV, Zelinka SL, Johnson JA (2014) Investigation of historic equilibrium moisture content data from the Forest Products Laboratory. Forest Service, Forest Products Laboratory, General Technical Report, FPL-GTR-229, Madison, WI

Glass SV, Boardman CR, Zelinka SL (2017) Short hold times in dynamic vapor sorption measurements mischaracterize the equilibrium moisture content of wood. Wood Sci Technol 51:243–260. https://doi.org/10.1007/s00226-016-0883-4

Hill CAS, Norton A, Newman G (2009) The water vapor sorption behavior of natural fibers. J Appl Polym Sci 112:1524–1537. https://doi.org/10.1002/app.29725

Hill C, Norton A, Newman G (2010a) The water vapour sorption properties of Sitka spruce determined using a dynamic vapour sorption apparatus. Wood Sci Technol 44:497–514

Hill CAS, Norton A, Newman G (2010b) The water vapor sorption behavior of flax fibers—analysis using the parallel exponential kinetics model and determination of the activation energies of sorption. J Appl Polym Sci 116:2166–2173. https://doi.org/10.1002/app.31819

Hill CA, Keating BA, Jalaludin Z, Mahrdt E (2012) A rheological description of the water vapour sorption kinetics behaviour of wood invoking a model using a canonical assembly of Kelvin–Voigt elements and a possible link with sorption hysteresis. Holzforschung 66:35–47

Hill CAS, Ramsay J, Laine K, Rautkari L, Hughes M (2013) Water vapour sorption behaviour of thermally modified wood. Int Wood Prod J 4:191–196. https://doi.org/10.1179/2042645313Y.0000000040

Jalaludin Z, Hill CA, Samsi HW, Husain H, Xie Y (2010a) Analysis of water vapour sorption of oleo-thermal modified wood of *Acacia mangium* and *Endospermum malaccense* by a parallel exponential kinetics model and according to the Hailwood–Horrobin model. Holzforschung 64:763–770

Jalaludin Z, Hill CAS, Xie Y, Samsi HW, Husain H, Awang K, Curling SF (2010b) Analysis of the water vapour sorption isotherms of thermally modified acacia and sesendok. Wood Mat Sci Eng 5:194–203

Keating BA, Hill CAS, Sun D, English R, Davies P, McCue C (2013) The water vapor sorption behavior of a galactomannan cellulose nanocomposite film analyzed using parallel exponential kinetics and the Kelvin-Voigt viscoelastic model. J Appl Polym Sci 129:2352–2359. https://doi.org/10.1002/app.39132

Marshall PV, Cook PA, Williams DR (1994) A new analytical technique for characterising the water vapour sorption properties of powders. Paper presented at the international symposium on solid oral dosage forms, Stockholm, Sweden

Popescu C-M, Hill CAS, Curling S, Ormondroyd G, Xie Y (2013) The water vapour sorption behaviour of acetylated birch wood: how acetylation affects the sorption isotherm and accessible hydroxyl content. J Mater Sci 49:2362–2371. https://doi.org/10.1007/s10853-013-7937-x

Rasmussen M, Akinc M (1983) Microcomputer-controlled gravimetric adsorption apparatus. Rev Sci Instrum 54:1558–1564

Sharratt V, Hill CAS, Zaihan J, Kint DPR (2010) Photodegradation and weathering effects on timber surface moisture profiles as studied using dynamic vapour sorption. Polym Degrad Stab 95:2659–2662. https://doi.org/10.1016/j.polymdegradstab.2010.07.011

Spalt H (1957) The sorption of water vapor by domestic and tropical woods. Forest Prod J 7:331

Spalt H (1958) The fundamentals of water vapor sorption by wood. Forest Prod J 8:288–295

Stamm AJ, Loughborough WK (1935) Thermodynamics of the swelling of wood. The Journal of Physical Chemistry 39:121–132. https://doi.org/10.1021/j150361a009

Strømdahl K (2000) Water sorption in wood and plant fibres. Technical University of Denmark. Danmarks Tekniske Universitet, Department of Structural Engineering and Materials Institut for Bærende Konstruktioner og Materialer

Thybring EE, Kymäläinen M, Rautkari L (2018) Experimental techniques for characterising water in wood covering the range from dry to fully water-saturated. Wood Sci Technol 52(2):297–329. https://doi.org/10.1007/s00226-017-0977-7

Williams D (1995) The characterisation of powders by gravimetric water vapour sorption. Int Labmate 20:40–42

Xie Y, Hill CA, Xiao Z, Jalaludin Z, Militz H, Mai C (2010) Water vapor sorption kinetics of wood modified with glutaraldehyde. J Appl Polym Sci 117:1674–1682

Xie Y, Hill CA, Jalaludin Z, Sun D (2011) The water vapour sorption behaviour of three celluloses: analysis using parallel exponential kinetics and interpretation using the Kelvin–Voigt viscoelastic model. Cellulose 18:517–530

Yelle DJ, Ralph J, Frihart CR (2008) Characterization of nonderivatized plant cell walls using high-resolution solution-state NMR spectroscopy. Magn Reson Chem 46:508–517. https://doi.org/10.1002/mrc.2201

Zaihan J, Hill CAS, Curling S, Hashim WS, Hamdan H (2009) Moisture adsorption isotherms of *Acacia mangium* and *Endospermum malaccense* using dynamic vapour sorption. J Trop Forest Sci 21:277–285

Zaihan J, Hill C, Curling S, Hashim W, Hamdan H (2010) The kinetics of water vapour sorption: analysis using parallel exponential kinetics model on six Malaysian hardwoods. J Trop Forest Sci 22:107–117

Zelinka SL, Glass SV (2010) Water vapor sorption isotherms for southern pine treated with several waterborne preservatives ASTM. J Test Eval 38:80–88

Zelinka SL, Lambrecht MJ, Glass SV, Wiedenhoeft AC, Yelle DJ (2012) Examination of water phase transitions in Loblolly pine and cell wall components by differential scanning calorimetry. Thermochim Acta 533:39–45. https://doi.org/10.1016/j.tca.2012.01.015