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Dynamic vapour sorption protocols for the quantification of accessible hydroxyl groups in wood

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Abstract: This study investigated several key parameters of deuterium exchange measurements in a dynamic vapour sorption apparatus to optimise the measurement protocol for hydroxyl (OH) group accessibility determination. The impact of changing the sample mass, the deuterium oxide (D_2O) vapour exposure time and the rate of change in moisture content ($dm\ dt^{-1}$) during the drying steps on the measured OH group accessibility were analysed. A sample mass of more than 10 mg, an exposure to D_2O vapour of at least 10 h and a $dm\ dt^{-1}$ of 0.0005% min^{-1} over a 10-min period during the drying steps gave the most reliable results. We also investigated the necessity of adding a method stage that eliminates the effect of inclusion compounds (ICs). The addition of an initial drying and wetting stage enabled the release of entrapped solvents.

Keywords: accessibility, DVS, OH group, wood

Introduction

Wood is a hygroscopic material and, therefore, many of its properties, such as dimensional stability, stiffness, strength and ductility, are associated with the moisture content (MC) (Stamm 1964; Glass and Zelinka 2010). Wood adsorbs or desorbs water (H_2O) molecules depending on the relative humidity (RH) and the temperature (T) of the surroundings as well as on the moisture history of the material. When T and RH remain constant, adsorption and desorption of H_2O molecules reach an equilibrium state, eventually, at which no further change in wood mass takes place. This state is

denoted the equilibrium moisture content (EMC), which can be quantified gravimetrically by relating the mass of adsorbed H_2O to the dry mass of wood. By measuring the EMC at varying RH and constant T, characteristic H_2O vapour sorption isotherms are determined. The shape of the isotherm is dictated by the chemical composition and structure of the material. Usually, the sorption isotherm of wood has a sigmoidal shape with a convex course at low RH and a concave course at high RH (Skaar 1988). Although the sorption of H_2O to wood is presumably related to the accessibility of the hydroxyl (OH) groups, the concentration of the accessible OH groups cannot be derived from sorption isotherm measurements. The accessible OH group concentration in wood has traditionally been difficult to measure and therefore it is not commonly included in the basic wood research protocols. Nonetheless, the quantification of accessible OH groups may contribute to our existing knowledge about the sorption behaviour of wood, or its reactivity in modification treatments that rely on the formation of covalent bonds to the cell wall polymers (Popescu et al. 2014; Kymäläinen et al. 2015).

OH groups are present in all of the cell wall components, with the majority being present in cellulose and hemicellulose. Some of these groups are accessible to molecules, such as H_2O and deuterated H_2O (deuterium oxide, D_2O), which interact with them through hydrogen bonding. However, some OH groups in wood are inaccessible to H_2O , because wood derived cellulose may contain as much as 65% of crystalline cellulose that is accessible only on the microfibril surfaces (Rowell et al. 2005). It has long been known for cellulose that the OH group accessibility can be determined by the use of hydrogen-deuterium exchange (Sepall and Mason 1961). This approach is based on the exposure of wood to D_2O . Thereby, accessible OH groups that form hydrogen bonds to the D_2O have their protium exchanged to deuterium. This hydrogen-deuterium exchange can be measured by infrared (IR) spectroscopy using the increase in the band at around $2500\ cm^{-1}$. This approach provides an estimation of the OH accessibility and can be used only for assessing differences in the hydroxyl accessibility between sample groups (Tsuchikawa and Siesler 2003; Hofstetter et al. 2006; Suchy et al. 2010). However, an

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actual concentration of accessible OH groups in wood is achieved by recording the increase in the sample dry mass by deuterium exchange, because deuterium has $1.00616 \text{ g mol}^{-1}$ higher atomic mass than protium due to the additional neutron (Pönni et al. 2014), as illustrated in Figure 1. For reliable results, this dry mass increase needs to be determined with a precise balance while preventing the re-exchange of the deuterated OH groups in the presence of H_2O vapour. Both requirements are met when using a dynamic vapour sorption (DVS) apparatus for deuterium exchange experiments, which was first applied to bacterial cellulose (Lee et al. 2011) and later also to wood materials (Rautkari et al. 2013; Pönni et al. 2014; Popescu et al. 2014, 2015; Kymäläinen et al. 2015; Thybring et al. 2017).

Although there is limited number of published research that quantify accessible OH groups in wood in a DVS apparatus, the applied methodology differs, for example, with regard to the sample mass, the deuteration time, the drying protocol and the number of cycles. In earlier studies, multiple deuteration steps were applied to reach the complete deuterium exchange (Rautkari et al. 2013; Popescu et al. 2014). However, Pönni et al. (2014) found that the time of the exposure to D_2O

vapour is the most important factor and recommended the use of a single, sufficiently long deuteration step. This is why more recent studies conducted the deuterium exchange in a single step (Kymäläinen et al. 2015; Thybring et al. 2017). However, to the best of our knowledge, the parameters for measuring the accessibility of OH groups in a DVS apparatus have never been studied systematically.

In addition to methodical uncertainties, Hergt and Christensen (1965) noticed that there was residual H_2O trapped inside the wood structure in samples even after prolonged drying. This trapped H_2O disappeared after re-wetting and re-drying. Besides H_2O , compounds that become volatile during sorption isotherm analyses are also present after wood extraction (Vahtikari et al. 2017) or thermal modification (Wentzel et al. 2018). In this study, we denote the molecules that are trapped within the wood sample during the first drying step and are released during subsequent steps of vapour sorption measurements as ‘inclusion compounds’ (ICs). During the quantification of accessible OH groups, the release of ICs would result in a decrease in dry sample mass that counterbalances the mass increase induced by hydrogen-deuterium exchange. Therefore, an additional test was performed with the

Figure 1: The scope of dynamic vapour sorption apparatus.

(a) Apparatus in open position. (b) Applying H_2O vapour allows for measurement of sorption curves. (c) Values for accessibility of OH groups are gained with D_2O vapour. (d) The atomic structure of hydrogen vs. deuterium (P, proton; N, neutron; E, electron).

hypothesis that there could be residual compounds in the samples after the first drying step.

According to earlier studies, it is not clear how OH accessibility of solid wood should be measured with DVS apparatus to gain reliable and comparable results. The aim of this study is to find suitable measuring parameters considering the sample mass, the exposure time to D₂O vapour and the rate of moisture change (dm dt⁻¹) during the drying step, as well as the occurrence of ICs within the sample.

Materials and methods

Material

Never-dried green wood boards of Scots pine (*Pinus sylvestris* L.) were used and only the sapwood region of the wood material was selected for testing. The material was free of knots and visible defects. Prior to testing, samples were dried at 20°C and RH 50% for 1 month, excluding the samples used in IC analysis.

Method

The experiments were carried out in a DVS apparatus (DVS Elevated Temperature ET, Surface Measurement Systems Ltd., London, UK), coupled with liquid deionised H₂O and liquid D₂O (Sigma Aldrich 99.9%) (Helsinki, Finland). All measurements were carried out at a temperature of 25°C and a gas flow of 200 cm³ min⁻¹.

Sample mass optimisation: Six different types of samples were cut with a razor blade, the mass varying from 1 mg up to 80 mg. The size of the samples was 3 × 3 mm (radial × tangential) dimensions, and longitudinal dimension was changed to meet the required mass. Samples were cut in duplicates. Care was taken that the samples contained both, early- and latewood at a constant ratio. Therefore, this factor was not considered during data analysis. In the initial drying step, the samples were first dried at 0% RH until the mass change rate (dm dt⁻¹) remained at 0.0005% for 10 min. This was followed by a rewetting step, where the samples were conditioned at 95% RH (H₂O vapour) for 24 h and finally dried for 24 h in 0% RH.

IC analysis: Samples of 15 mg were soaked in four different liquids [H₂O, methanol and ethanol and 2-propanol (Sigma-Aldrich, Helsinki, Finland)] to evaluate the amount of IC. Triplicate of samples were cut with a razor blade and then soaked in the liquids for 48 h prior to testing. The initial drying step, as well as the other stages in the process, were carried out until the sample mass change rate remained at less than 0.0005% min⁻¹ (dm dt⁻¹) for 10 min. After drying, the samples were conditioned in 95% H₂O vapour RH and then dried again. The IC was calculated with Equations 1 and 2.

$$\text{IC (\%)} = \frac{(m - m_i)}{m_i} \times 100\% \quad (1)$$

$$\text{IC (mmol g}^{-1}\text{)} = \frac{(10 \cdot \text{IC (\%)})}{M_{\text{Solvent}}} \quad (2)$$

where IC is the inclusion compound, m_i is the initial dry mass of the sample (mg), m is the dry mass of the sample after second drying (mg) and M_{Solvent} is the molar mass of the used solvent.

D₂O vapour expose time optimisation: A sample of 15 mg was dried at 0% RH and then exposed to a set point RH of 95% using D₂O vapour for different time intervals, followed by another drying step. Drying was carried out until the dm dt⁻¹ remained below 0.0005% for 10 min. The conditioning time in D₂O vapour was varied between 30 min to 36 h. The accessibility of OH groups was calculated according to Equation 3 (Thybring et al. 2018).

$$A \text{ (mol kg}^{-1}\text{)} = \frac{(m_s - m_3) \cdot 10^3}{m_3 \cdot 1.00616} \quad (3)$$

where A (mol kg⁻¹) is the accessibility of OH groups, m_3 is the initial dry weight of the sample (mg) and m_s stands for the dry weight of the sample after deuterium exchange (mg). The calculations were based on the measured average mass during the last 10-min time interval. The average was used to minimise the effect of mass oscillation on the calculated results. Adsorbed D₂O was calculated with Equations 4 and 5.

$$D \text{ (\%)} = \frac{(m_4 - m_5) \times 100}{m_3} \quad (4)$$

$$D \text{ (mol kg}^{-1}\text{)} = \frac{D \text{ (\%)} \times 10}{20.0276} \quad (5)$$

where D is the adsorbed D₂O, m_3 is the initial dry weight of the sample (mg), m_4 is the weight of the sample after deuterium exchange (mg) and m_5 stands for the dry weight of the sample after deuterium exchange (mg). The molar mass of D₂O (mol g⁻¹) is 20.0276.

Equilibrium demand optimisation: The data from the D₂O exposure time optimisation test was evaluated to find the optimum dm dt⁻¹ setting for the drying step. Accessibility was calculated using different dm dt⁻¹ values from the data. Selected values were: 0.01, 0.005, 0.002, 0.001, 0.0007 and 0.0005% min⁻¹, and the mass average was calculated from these points onward for the next 10 min.

Results and discussion

Sample mass optimisation

Our results verify a considerable impact of the sample mass on the DVS measurement. In particular, the sample mass affected the mass oscillation and the time to reach a set dm dt⁻¹ criterion. The sample mass oscillation occurring during the drying and wetting stages of the process is presented in Figure 2. The data is taken from the last 60 min of a 24 h measuring step. During drying, there was a clear tendency of a reduced mass oscillation with

Figure 2: Change in mass (%) when (a) drying (b) wetting samples with different mass. Time zero-point is the beginning of the last hour in step duration of 24 h.

increasing sample mass. With 1 mg sample mass, it proved impossible to get accurate data. It should be noted, that as the variation in T and RH were the same for all sample masses, the increase in mass oscillation must be a weighing error caused by an inadequate sample mass. The same applied to the wetting stage of the process, but when the sample mass was increased to 60 mg, mass oscillation could be observed again. A correlation to changes in T or RH was not detected, and the cause for the mass oscillation has yet to be identified. A pattern remaining in the residuals have been reported in an earlier study where sorption kinetics were studied with curve fitting algorithms (Hill et al. 2012). This pattern observed by Hill et al. (2012) could be related to the mass oscillation that was observed in our study. To eliminate errors in DVS operation, the wood sample mass should be chosen to minimise mass oscillation.

Figure 3 shows the change in dm/dt as a function of time for the different sample masses. In theory, a larger

Figure 3: Time for different sample masses to reach a set value of dm/dt .

sample mass increases the total amount of H_2O molecules that ad- or desorb, which should increase the time to reach a set dm/dt . However, the time to reach a dm/dt of $0.001\% \text{ min}^{-1}$ was not a simple function of the sample mass. When using a sample mass of 1 and 5 mg, the time to reach the dm/dt criterion was comparably long, which was caused by the severe mass oscillation that delayed the achievement of a stable dm/dt over a 10-min period. Thereby, samples of different mass may be in a different state, even if the same dm/dt criteria are reached. The same effect might also explain why there was no difference in time to reach a dm/dt of $0.001\% \text{ min}^{-1}$ between 10 and 20 mg sample mass. Therefore, we recommend a sample mass larger than 10 mg to achieve reliable results with our setup.

IC analysis

Never-dried samples were solvent exchanged to methanol, ethanol and 2-propanol. The aim was to evaluate the amount of trapped molecules, denoted as an IC, in the wood samples. The results for the four liquids are presented in Figure 4. There was hardly any IC detected with H_2O , thus the effect on the accessibility results is negligible. An IC for H_2O near zero mmol g^{-1} also indicates that there were no significant differences in the residual MC between subsequent drying steps and that the dry mass determination was not affected by a potential mass balance drift. Methanol had slightly more IC, still less than 1% with 0.2 mmol g^{-1} . However, ethanol already presented a significant amount of IC, over 3% with 0.7 mmol g^{-1} , and 2-propanol twice as much with approximately 6% (1 mmol g^{-1}). These results support the study of Hergt and Christensen (1965), even though the IC values for H_2O were

Figure 4: Results of IC measurement drawn with molecule structure of used liquid.

even lower than reported previously. Hergt and Christensen (1965) found retained H₂O up to 1%. The results are also similar to Vahtikari et al. (2017) who found clear evidence of residual acetone as an IC. Of the used chemicals, 2-propanol has the most complex molecular structure, with the greatest number of atoms, chemical bonds and highest molar mass of all the four. H₂O has the lowest values in all these three properties. Ethanol and methanol fall in between the two, with methanol being simpler in structure than ethanol.

The results show clearly that the bigger the molecules of the liquid, the greater the number of moles that remain trapped inside the structure of the wood sample during the initial drying step. With ethanol and 2-propanol, the IC may affect the accessibility results significantly. Nevertheless, the IC hardly prevents the change of the OH groups to the deuterium groups, the dry mass changes that are caused by the release of ICs will cause problems with the calculation of the accessible OH groups in wood. Therefore, an initial drying and wetting stage should be added to the accessibility measurement procedure with DVS to eliminate this effect, if ICs are present, for example, after extraction (Vahtikari et al. 2017) or after thermal modification (Wentzel et al. 2018). Further research is needed to investigate if the ICs can also be removed by a drying step at elevated temperatures, already suggested by Thybring et al. (2017). However, the use of elevated temperatures is beyond the scope of this study, as this may be accompanied by additional changes in the physical state of wood (Čermák et al. 2016). An additional benefit of initial drying and wetting steps would be that EMC of the samples could be determined alongside the accessibility measurement.

D₂O vapour exposure time optimisation

The optimal exposure time to D₂O vapour was studied in this experiment. Exposure time results at 95% RH (D₂O) are presented in Figure 5a, where the concentration of accessible OH groups is plotted against the exposure time. The concentration of accessible OH groups increased rapidly for short exposure times and reached a maximum of 10.2 mol kg⁻¹ at an exposure time of 14 h. However, the OH group concentrations determined between an exposure time of 10 and 36 h varied around the same average value (10.04 mol kg⁻¹) with the lowest value of 9.9 mol kg⁻¹ measured after an exposure time of 36 h. We conclude that the hydrogen-deuterium exchange is nearly completed within 10 h, which is also supported by the research done for fully amorphous cellulosic films (Hishikawa et al. 1999). Also, Figure 5b supports the conclusion as mass gain is rather stabilised after 10 h. While the narrow range of measured OH group concentrations (9.9–10.2 mol kg⁻¹) for exposure times of 10–36 h indicates a high repeatability of the measurements, it does not rule out a systematic

Figure 5: Data from the exposure time experiment. (a) Accessibility results using varying exposure times to D₂O vapour are plotted with squares. Horizontal black line is the average value of the results from 10 to 36 h, and grey lines are the standard deviation. (b) Mass gain of the sample in the 36 h measurement.

error that could be caused by residual MC after drying. The measured accessible OH group concentration of about 10 mol kg^{-1} slightly exceeds the concentration that was theoretically calculated ($7.8\text{--}8.5 \text{ mol kg}^{-1}$) and measured (8.4 and 9.3 mol kg^{-1} for early- and latewood, respectively) by Thybring et al. (2017) for Norway spruce. However, our results are well in line with the accessible OH group concentrations that were measured in previous studies (Altgen et al. 2018; Kymäläinen et al. 2018). Furthermore, nearly identical OH group concentrations were determined when comparing a deuterium exchange protocol as applied in this study with a deuterium exchange protocol that involves drying of the sample at 60°C for 6 h using a pre-heater (Altgen et al. 2018).

Figure 5a also shows the amount of adsorbed D_2O molecules at the end of the D_2O vapour exposure for the different time intervals. The concentration of adsorbed D_2O increases in a similar way as the accessible OH group concentration, but reaches $11.3\text{--}11.7 \text{ mol kg}^{-1}$ after an exposure time of at least 10 h, which refers to $1.13\text{--}1.17$ adsorbed D_2O molecules per the accessible OH-group. However, the full occupancy of accessible OH groups by D_2O may not be required. This is indicated by the results after 0.5 h D_2O vapour exposure, where the accessible OH group concentration exceeds the concentration of adsorbed D_2O . The sorption of H_2O is a dynamic process that involves ad- and desorption so that the individual (deuterated) H_2O molecules can switch between the accessible OH groups, even if their total number remains constant. In contrast, deuterated OH groups are not re-exchanged as long as the surrounding atmosphere consists of D_2O vapour and/or nitrogen. Taniguchi et al. (1978), who showed that the measured accessible OH group concentration remains the same when applying a vapour pressure of D_2O in the range between 0.6 and 0.95, even though the MC decreases strongly, also evidenced this.

Equilibrium criteria optimisation

This experiment was aimed at finding the optimum dm dt^{-1} setting for the drying steps of the accessibility measurements. As seen from Figure 6, the accessibility decreases, while the measurement time increases with decreasing dm dt^{-1} values. As explained by Thybring et al. (2018), residual H_2O molecules after incomplete drying result in an overestimation of the actual concentration of accessible OH groups. This is caused by the mass increase due to the change from residual H_2O molecules after the initial drying step to residual D_2O molecules after the final drying step. In line with this explanation, we observed a drastic decrease in the measured concentration of accessible OH groups until

Figure 6: Data from the equilibrium optimisation experiment. (a) Accessibility value changing depending on the dm dt^{-1} criteria used in the measurement. (b) Time results to reach the set dm dt^{-1} criteria.

the dm dt^{-1} decreases to $0.001\% \text{ min}^{-1}$. By tendency, a small decrease in the measured accessibility is still evident when further decreasing the dm dt^{-1} setting to $0.0005\% \text{ min}^{-1}$. However, the measured accessibility varies in a narrow range between 10.2 and 10.5 mol kg^{-1} for dm dt^{-1} settings between 0.001 and $0.0005\% \text{ min}^{-1}$. Nonetheless, we recommend using dm dt^{-1} of $0.0005\% \text{ min}^{-1}$ to avoid an overestimation of the actual concentration of accessible OH groups. It should be noted, though, that the decrease in dm dt^{-1} from 0.001 to $0.0005\% \text{ min}^{-1}$ prolongs the drying step by 2.7 h, which refers to an increase in the total measurement time of the DVS protocol shown in Table 1 of about 8 h.

Suggested method for accessibility measurement

According to the presented results, a sample mass of more than 10 mg should be used. The steps of the recommended DVS protocol are shown in Figure 7 and Table 1.

Table 1: Different stages of accessibility measurement.

Steps	T (°C)	RH (%)	Vapour	Equilibrium
1. Drying	25	0	–	<0.0005% dm dt ⁻¹ for 10 min
2. H ₂ O vapour	25	95	H ₂ O	>10 h
3. Drying	25	0	–	<0.0005% dm dt ⁻¹ for 10 min
4. D ₂ O vapour	25	95	D ₂ O	>10 h
5. Drying	25	0	–	<0.0005% dm dt ⁻¹ for 10 min

Figure 7: Example of the suggested method to measure accessibility of OH-groups in wood sample.

Step 1 (initial drying) and step 2 (H₂O vapour exposure) prevent ICs to interfere with the measurements. They may be omitted in case no IC is present. The hydrogen-deuterium exchange occurs in step 4 and the concentration of accessible OH groups is calculated based on the mass difference of step 3 and 5 by using Equation 1 by taking the average mass from the last 10 min of the measurement step. The dm dt⁻¹ in these drying steps should be below 0.0005% for 10 min. The exposure to D₂O vapor should be at least 10 h. It is well known that also the shape of the specimen has influence on the needed exposure time, the thinner the sample, the faster the sorption. Therefore, all the specimens that will be compared should have similar shape.

Conclusions

The aim of this article was to find optimal parameters for measuring accessibility of OH groups in wood sample with DVS apparatus. Experiments covered the sample mass and measuring step optimisation, deuteration time and equilibrium criteria optimisation. These were recognised as the most important parameters, when considering the

reliability of accessibility results in general. Naturally, several other variables may affect the results and further work in both quantitative and qualitative analysis is needed to improve the accuracy of the DVS method. However, justified guidelines for OH-group accessibility measurements were successfully created in this study and the development of a standardised and widely accepted DVS method for bulk wood samples is all the more closer.

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