

A single point NMR method for an instantaneous determination of the moisture content of wood

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Abstract

Nuclear magnetic resonance (NMR) enables an instantaneous determination of the proton density in liquids and is thus convenient for determining the moisture content (MC) of wood. We demonstrated that the MC of a wood sample can be determined instantaneously on the basis of its mass (m) and the amplitude of its NMR free-induction-decay (FID) signal. The measurement is based on the assumption that the only liquid in the wood is water and that the relationship between the amplitude of the FID signal (S) and the mass of the water (m_w) in the sample is linear, i.e., $S = k m_w + k' (m - m_w)$, and can be precisely calibrated for a given NMR probe and NMR spectrometer setup (in our case $k = 10^5$ AU g⁻¹ and $k/k' = 34$). With the FID signal converted into the mass of water, the MC is calculated as: $MC = (S - m k') / (m k - S)$. After the initial calibration of the FID signal with respect to the content of water, the correctness of the method was verified on samples of different wood species with various MCs. The results confirmed that the proposed method is comparable in terms of accuracy and reliability to the gravimetric method, regardless of the species of wood. As the method is instantaneous, it might become the method of choice in applications where a short measurement time combined with a high accuracy is demanded.

Keywords: free-induction-decay signal; gravimetric method; moisture content determination; nuclear magnetic resonance; wood.

Introduction

From among the many methods used to measure the moisture content (MC) of wood (Kollmann 1951; Skaar 1988), nuclear magnetic resonance (NMR) was successfully employed for studying the spatial distribution of water and wood-water relationships (Sharp et al. 1978; Wang and Chang 1986; Flibotte et al. 1990; Araujo et al. 1992; Hartley et al. 1994; Labbe et al. 2002; MacMillan

et al. 2002; van Houts et al. 2004; Almeida et al. 2007). Soon after the first encouraging attempts to evaluate the moisture in wood by continuous wave NMR, the precision and efficiency of the measurements were improved significantly with the introduction of the pulsed NMR method (Gil and Neto Pascoal 1999). Sharp et al. (1978) measured the free-induction-decay (FID) signal from a pulsed NMR of a sample to determine the MC of wood relative to a known standard. From measurements on maple and spruce it was demonstrated that the FID increases linearly with the MC of wood. It was later stated more precisely (Menon et al. 1987; Hartley et al. 1994) that this method performs even better if it is supplemented with additional information about the chemical composition of the wood. The MC was calculated based on the relationship:

$$MC = \frac{M_0}{S_0 - M_0} \cdot \frac{\rho_{Hwood}}{\rho_{Hwater}} \cdot 100 [\%]. \quad (1)$$

Here, M_0 and S_0 are the zero-time intercepts of the mobile and total signal components of the FID, ρ_{Hwood} denotes the proton density in terms of the number of protons per gram, i.e., of the cellulose and the lignin, while ρ_{Hwater} denotes the proton density of the water. Accuracy of the NMR MC determination of wood can also be improved by using partial least squares (PLS) calibration of the FID (Thygesen 1996).

In this paper, we will demonstrate that the MC of a wood sample can be determined instantaneously from the amplitude of its NMR FID signal and from its weight. The determination is based on the assumption that the amplitude of the NMR FID signal is linearly proportional to the water content of the sample and that this relationship is identical for all wood species and can be calibrated for a given radio frequency (RF) probe and NMR spectrometer setup. The proposed method is insensitive to the chemical composition of wood and it does not require absolutely dry samples. Instead, the immediate mass of the wood sample from which the mass of water (which is determined from the NMR FID signal) is subtracted and the dry mass of the sample can be calculated. This procedure makes the method instantaneous and, furthermore, the accuracy of the method is not adversely affected and remains comparable to that of the standard gravimetric method.

Theory

The MC is defined as the ratio between the mass of water (m_w) in the moist wood sample and the mass of the absolutely dry sample of wood (m_0):

$$MC = \frac{m_w}{m_0} \cdot 100 = \frac{m_w}{m - m_w} \cdot 100 [\%], \quad (2)$$

where $m = m_w + m_0$ is the mass of the moist sample of wood.

The amplitude of the NMR FID signal, S , linearly depends on the mass of water in the sample. However, it is also, to some extent, dependent on the mass of the absolutely dry sample as the solid protons in the cellulose and the lignin of the sample can give rise to a very short NMR signal that might still not disappear entirely at the starting point of the FID, i.e., in the amplitude of the FID. Therefore, the amplitude of the FID can be written as:

$$S = k \cdot m_w + k' \cdot m_0 = k \cdot m_w + k' \cdot (m - m_w), \quad (3)$$

where k and k' are proportionality constants between the water (k), the absolutely dry wood (k') and the amplitude of the FID signal. Water, as any other liquid, has a Lorentzian spectral line shape and exponentially decaying FID signal (Abragam 1961; Fukushima and Roeder 1981), from which it follows that the proportionality constant k in Eq. (3) can be written in the form $k = f(N_w/m_{1w})\exp(-t/T_{2w})$. Here, the constant f depends on the characteristics of the RF coil and the NMR spectrometer used to measure the FID signal – i.e., the magnetic field strength, the Q factor of the RF coil, the temperature of the RF coil, the frequency bandwidth in the signal detection and the amplification of the pre-amplifier (Hoult and Richards 1976) – N_w is the number of protons in a water molecule, m_{1w} is the mass of a single water molecule, T_{2w} is the water spin-spin relaxation time and t is the time between the NMR signal excitation and the starting FID acquisition point, in which the FID amplitude is measured. Solid protons have a Gaussian spectral line shape so that their decay profile is also of a Gaussian shape (Abragam 1961; Fukushima and Roeder 1981), and therefore $k' = f(N_0/m_{10})\exp(-(t/T_{20})^2)$, where f and t are the same as for the water part, T_{20} is the spin-spin relaxation time of solid wood, while N_0 and m_{10} are the number of protons and the mass of an average solid wood molecule, respectively. As different water components, of which proportions as well as their spin-spin relaxation times in wood are MC-dependent (Almeida et al. 2007), the parameter k is also MC-dependent unless t is much shorter than the shortest T_{2w} .

With knowledge of the coefficients k and k' , determined in the calibration of Eq. (3), the mass of water in the wood can be calculated from the amplitude of the FID, S , and the mass of the moist sample of wood m :

$$m_w = \frac{S - k' \cdot m}{k - k'}. \quad (4)$$

Eq. (4) was obtained from Eq. (3) from the relation $m_0 = m - m_w$. Finally, by inserting Eq. (4) into Eq. (2), the MC can be expressed based on the following relation:

$$MC = \frac{S - mk'}{mk - S} \cdot 100 [\%]. \quad (5)$$

Materials and methods

Five 15-mm-long samples of beech and five samples of oak were cut from fresh branches which were approximately 8 mm in diameter. Next, a 3-mm hole was drilled in the longitudinal direction through the center of each sample to eliminate the pith from the xylem tissue and enlarge the surface area of the sample for faster equilibration at different relative humidity (RH) quantities. To obtain clear samples of wood, the bark was also removed. Afterwards, the samples were gradually dried in closed boxes over five different saturated salt solutions with RH = 88%, 76%, 65%, 34%, and 20% until the equilibrium MC was reached. Thereafter, the samples were dried to absolute dryness at $103 \pm 2^\circ\text{C}$. In the green state and in each of the successive equilibrium states, the amplitude of the NMR FID and the weight of the samples were measured to determine the MC gravimetrically.

For NMR spectrometry, a TecMag (Houston, TX, USA) instrument equipped with a 2.35 T Oxford (Oxon, UK) superconducting magnet was utilized. Detection of the FID amplitude was carried out with a 10-mm saddle-shaped Bruker (Ettlingen, Germany) RF coil. The specimens were put in a small glass tube, which was sealed to prevent drying during the measurement. The amplitude of the FID signal was measured 30 μs after the initial excitation 90° RF pulse for each sample at every successive equilibrium moisture state. In the experiments, no signal averaging was used as the signal-to-noise ratio (SNR) of the measured data was sufficiently high (SNR = 76 at MC = 7%). However, in cases where water signal is low signal averaging could help in improving SNR and in combination with phase cycling it could also help in reducing some hardware errors, such as the receiver offset. The experimental data of the amplitudes of the FID vs. their mass of water and their mass of absolutely dry wood were analyzed by the OriginPro computer program (Origin Lab Corporation, Northampton, MA, USA), i.e., the best fit between the data and the model in Eq. (3) was sought for, i.e., the parameters k and k' were calculated.

To verify the NMR-based MC measuring, the amplitudes of the FID and the sample weights of other green wood samples (*Fraxinus excelsior*, *Tilia* spp.), beech dowels, and small samples of Norway spruce were recorded. The measurements were performed under identical experimental setup conditions as applied to calibration of the system (identical RF probe, spectrometer parameters, pre-amplifier amplification, etc.), while the volume of the samples varied between 700 mm^3 and 250 mm^3 . Based on the known calibration parameters k and k' the MC values were calculated from the NMR data with Eq. (5). For comparison, the MC values were also determined gravimetrically.

Results and discussion

The graph in Figure 1 depicts a linear relationship between the amplitude of the NMR FID signal, S , and the mass of water (m_w) in the moist samples of beech and oak. The experimental data from the graph were the basis for calculating the proportionality constants k and k' of Eq. (3). Values of $k = 100,000 \pm 2000 \text{ AU g}^{-1}$ and $k' m_0 = 660 \pm 10 \text{ AU}$ were determined from the best fit between the data and the model. The value $k' m_0$ represents a slight zero offset of the model line in the graph due to the solid proton signal of the samples. The model, depicted by the solid straight line in the graph, fits to the data very well ($R^2 = 0.998$). The arbitrary units (AUs) here correspond to the NMR signal after digitalization in the 14-bit ADC of the spectrometer. As all the samples had

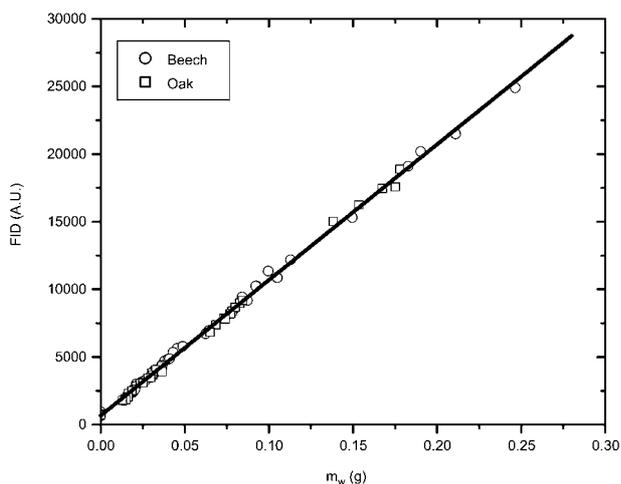


Figure 1 Linear relationship between the amplitude of the NMR FID signal and the mass of water in beech (circles) and oak (squares). The solid, straight line represents the best fit between the data and the model.

a similar size, they also had a similar sample mass in an absolutely dry state ($m_o = 0.23 \pm 0.03$ g), yielding an average value $k' = 2900 \pm 400$ AU g^{-1} .

A comparison between the MC values determined from the NMR data based on the proposed method with those obtained by the conventional gravimetric method is presented in Figure 2. The graph with experimental data from very different samples (different wood species of different sizes) which were used for the calibration reveal an excellent agreement between the results of the two methods ($R^2 = 0.996$).

The accuracy of the proposed method depends on the degree of suppression of the solid proton signal of the samples. The different tree species have slightly different proportions of solid wood components and have, therefore, in principle, a different proportionality constant k' . According to the literature (Fengel and Wegener 1984), the ratio between the number of protons in the molecule and its mass is in favor of the water, where this ratio is from 1.7 to 2 times higher than in solid wood, i.e., $(N_w/m_{1w})/(N_o/m_{1o}) = \rho_{Hwater}/\rho_{Hwood} = 1.7-2$. The variability of

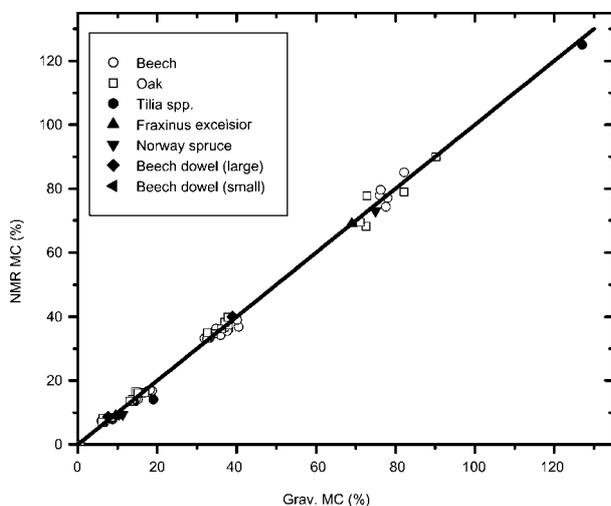


Figure 2 Moisture content of wood: results of the NMR method vs. the gravimetric method.

the parameter k' for the different wood species is also within these limits. Therefore, to maximize the accuracy of the method it is important to choose an acquisition delay t (the time between the excitation RF pulse and the first acquisition point) such that the FID amplitude consists of a practically unrelaxed water signal and, ideally, a fully relaxed solid proton signal, i.e., to maximize the parameter k and to suppress the parameter k' .

The spin-spin relaxation time for solid wood is approximately $T_{20} = 15$ μ s (Hartley et al. 1994), whereas the shortest spin-spin relaxation time for bound water is $T_{2w} = 300$ μ s (Almeida et al. 2007). Therefore, in our experiments, where $t = 30$ μ s, the signal of the solid wood decreased to less than 2% of the initial value, while the bound water with the shortest possible T_{2w} decreased to not less than 90%. The value of $t = 30$ μ s corresponds to a maximum difference between signals of equal populations of solid wood protons with $T_{20} = 15$ μ s and water protons with $T_{2w} = 300$ μ s. In practice, for most water components in wood, the decrease due to spin-spin relaxation is negligible and the signal remains identical to the initial water signal. In our opinion, the chosen acquisition delay parameter t of 30 μ s represents an optimum in terms of the maximized accuracy of the proposed NMR-based method for determining the MC.

The presented new method has few technical limitations which are mainly related to stability of calibration parameters and associated repeatability of measurements. Before each set of measurements, the spectrometer has to be calibrated on reference samples with known MC to obtain the calibration parameter k . Once this is known k' is calculated from the known k/k' ratio, which should depend only on the delay t (in our case $k/k' = 34$). During the measurement, calibration parameters can still change if the RF coil is detuned, the RF power is changed, background humidity is changed, etc. It is also desirable to use samples of identical sizes and geometry to reduce possible coil detuning problems due to different RF coil filling factors. In addition, the method is not directly applicable to in situ or NMR mouse type measurements as the sample volume and mass are not known. However, solutions for such cases already exist (Casieri et al. 2004).

The advantage of the presented new method over the method proposed by Menon et al. (1987) is the significantly lower susceptibility of the method to errors originating from a lack of prior information on the chemical composition of the wood sample. In other words, in the Menon method the MC depends linearly on the number of protons in the solid wood [Eq. (1)], while in our method just the correction coefficient k' depends on this relation. However, the price for the reduced susceptibility to errors in our method is the need for sample weighing, which is not required with the Menon method.

Conclusion

In this paper, a new NMR-based method is presented for an accurate, instantaneous determination of the MC of wood. The method is based on the linear relationship between the amplitude of the FID and the mass of water

in moist wood samples. For a given RF probe and spectrometer setup, the relationship can be precisely calibrated with test samples of comparable sizes and with various MC values. Once the system is calibrated, the MC of any sample, providing that it is of an appropriate size, can be determined from the amplitude of its FID and its weight. The method is robust, fast and non-invasive and could therefore be applied for industrial purposes to obtain MC values rapidly and instantly.

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