# DETERMINATION OF MOISTURE CONTENT OF WOOD BY PULSED NUCLEAR MAGNETIC RESONANCE[1,2]

*Allan R. Sharp, M. Thomas Riggin,*[3] *Reinhold Kaiser*

Department of Physics
University of New Brunswick, Fredericton, N.B. CANADA E3B 5A3

and

*Marc H. Schneider*

Department of Forest Resources
University of New Brunswick, Fredericton, N.B. CANADA E3B 5A3

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ABSTRACT

Pulsed nuclear magnetic resonance techniques have been used to measure the moisture content of sugar maple and white spruce sapwood in the range from 0 to 176%. The technique is found to be complementary to other methods of measuring moisture content in wood-cellulose systems.

*Keywords*: *Picea glauca*, *Acer saccharum*, nuclear magnetic resonance, moisture content, moisture meters.

## INTRODUCTION

It is well known that wood is a hygroscopic substance whose ability to absorb or desorb water is dependent on the temperature and relative humidity of its environment (Panshin and de Zeeuw 1970; Skaar 1972; U.S. Forest Products Laboratory 1974). Furthermore, the physical properties of wood are greatly influenced by the quantity of moisture present so that in using wood as a raw material it is often essential to determine its water content. The technique used for this determination should be fast, easily performed, unambiguous, precise, and nondestructive. The method should be applicable over a broad range of moisture contents from green wood to oven-dry and should be independent of ambient temperature, species of wood, grain direction, and the previous history of the sample. Present techniques do not meet many of these criteria (Kollmann and Hockele 1962; Skaar 1972). In particular, there is a great need in forest products research for a nondestructive moisture meter which can give accurate readings in bulk wood above the fibre saturation point.

In this paper we report the use of Pulsed Nuclear Magnetic Resonance to determine the moisture contents (MC) of white spruce and sugar maple over a range from 0% to 176% MC. A critical evaluation shows that the technique meets most of the above criteria, making it a viable method for determination of moisture content in water-cellulose systems.

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[3] Present address: Herzberg Institute for Astrophysics, National Research Council, Ottawa, Ontario, Canada.

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## NMR METHOD

Many nuclei possess a nuclear magnetic moment associated with a nonzero intrinsic angular momentum or "spin." When these nuclei are placed in a static magnetic field $H_0$ the magnetic moment precesses about the direction of $H_0$ with frequency (Schumacher 1970)

$$\nu_0 = \frac{\gamma}{2\pi} H_0 \tag{1}$$

where $\gamma$ is called the gyromagnetic ratio and is characteristic of the species of nucleus. For $^1$H-nuclei, the proportionality constant $\gamma/(2\pi)$ has a value 4.257 kHz per gauss (Chemical Rubber Co. 1972).

Consider a system of spins in a homogeneous magnetic field after a net magnetization of the spin system has been established parallel to $H_0$. If an alternating magnetic field of frequency $\nu_1$ is applied at right angles to $H_0$, the spin system will absorb power from the oscillating magnetic field when the resonance condition $\nu_1 = \nu_0$ is satisfied. One way of observing nuclear magnetic resonance is to maintain $\nu_1$ constant and to sweep the precession frequency $\nu_0$ through resonance by varying $H_0$. In practice, spin-spin interactions and inhomogeneity in $H_0$ result in the resonance condition being met over a range of fields $\Delta H$. The power absorption by the spin system near $H_0$ thus yields information about the average magnetic environment of the resonant spins. This steady-state method of detecting nuclear magnetic resonance has been used to investigate the properties of water-cellulose systems (Swanson et al. 1962; Forslind 1971; Carles and Scallan 1973; Nanassy 1973, 1974) but has proven to be somewhat slow for convenient moisture content determinations.

A second way to observe nuclear magnetic resonance is the pulse method used in this experiment. As in the steady-state method, time is allowed for a net equilibrium magnetization to be established parallel to $H_0$. For the samples studied in this experiment, times of about one second are sufficient. Next, a short, intense burst of a magnetic field oscillating in resonance with the spin precession frequency is applied at right angles to $H_0$. By proper choice of the intensity and duration of this pulse (Abragam 1961; Slichter 1963; Farrar and Becker 1971; Poole and Farach 1971), the net magnetization may be rotated into a plane perpendicular to $H_0$. Immediately following the pulse, the individual magnetic moments comprising the total magnetization precess in that plane, thereby inducing a voltage in a coil surrounding the sample. However, the individual magnetic moments have different magnetic environments arising either from spin-spin interactions or from inhomogeneities in $H_0$. They therefore precess at different frequencies, causing them to lose their phase coherence. This results in a decay of the induced voltage to zero with a characteristic time $T_2^*$ which may be related to $\Delta H$ (Slichter 1963). For obvious reasons, the induced voltage is known as the free induction decay (FID). Generally, the more restricted the motion of the molecule containing the nuclei, the shorter the value of $T_2^*$ and the greater the line width $\Delta H$ measured in the steady-state experiment.

The magnitude of the induced voltage immediately following a pulse of duration negligible with respect to $T_2^*$ is proportional to the number of nuclei of the resonant species in the sample (Slichter 1963). In principle, measurements of the induced voltage immediately after a pulse applied at the $^1$H resonance frequency

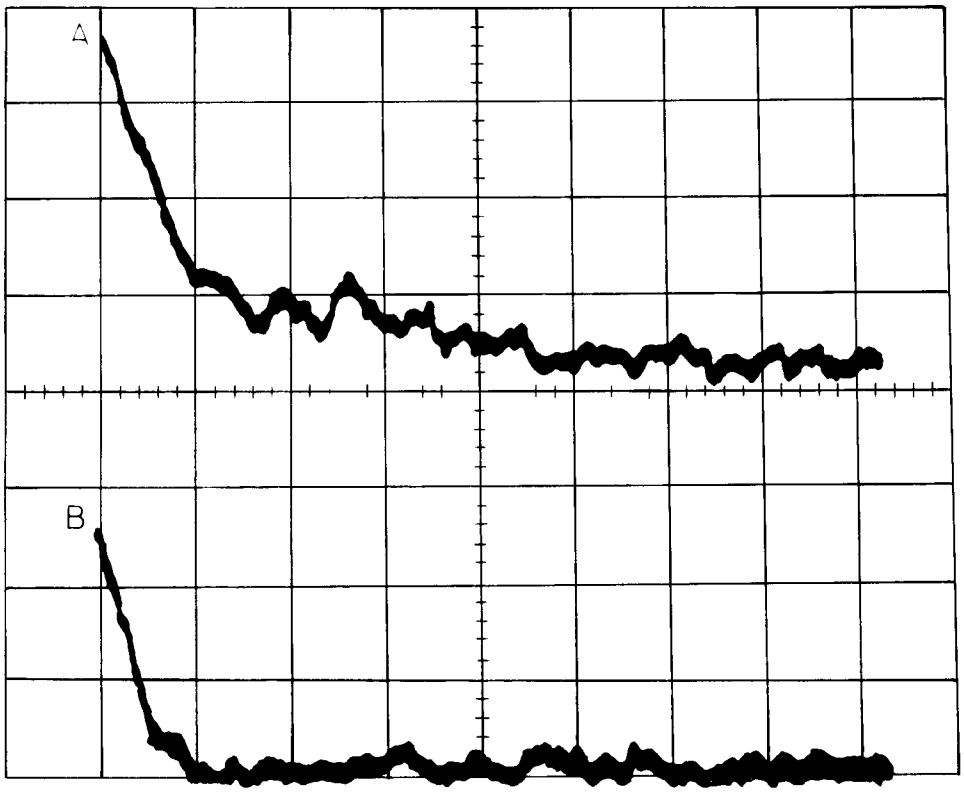


FIG. 1. The free induction decay of $^1H$ nuclei in moist [(A) MC = 30%] and oven-dried [(B) MC = 0%] maple is shown as a function of time following a $\pi/_2$-pulse. One large division along the time axis (abscissa) is 10 $\mu$s, while the displacement along the ordinate is proportional to the number of $^1H$ nuclei in the sample.

give a measure of the relative numbers of $^1H$ nuclei in different samples. Absolute numbers may be obtained by measuring relative to a sample containing a known number of $^1H$ nuclei. The pulsed nuclear magnetic resonance method of moisture content determination reported in this paper is based on this principle.

For moisture content determinations in wood-cellulose systems, two difficulties arise in practice which slightly complicate the interpretation of pulsed nuclear magnetic resonance signals. The first problem is that $^1H$ nuclei in other constituents of the wood as well as those in water molecules contribute to the signal. The second problem is that the oscillating magnetic field overloads the receiver for a few microseconds following the pulse, preventing observation of the voltage induced in the coil at precisely zero time after the pulse. However, careful analysis of the free induction decay allows both of these problems to be overcome, as shown below (see Eq. (2) and Fig. 1).

## EXPERIMENTAL METHOD

Cylindrical samples of diameter 0.35 cm and length 1.0 cm were cut with the cylinder axis parallel to the grain from a block of green white spruce sapwood [*Picea glauca* (Moench) Voss] and of green sugar maple sapwood (*Acer saccha-*

*rum* Marsh). These samples were dried for various lengths of time to generate different moisture contents and were then sealed with picine vacuum wax in glass tubes where they were allowed to equilibrate at ambient temperature (20 C) for several days before being examined. The pulsed nuclear magnetic signal amplitude of individual samples was independent of time for as long as three weeks indicating that the water content of the samples was independent of time.

After the magnetic resonance experiments were completed, the wax seal was removed and the tube and sample were quickly weighed to an accuracy of 0.1 mg on a microbalance. Then the sample and tube were oven-dried at 105 ± 2 C for 12 hours. Previous experience with the oven indicated that samples attained a constant weight in this time. Finally, the tube and sample were reweighed to obtain their dry weights. This allowed the sample water content in milligrams to be calculated. Typical dry sample weights were 40 mg.

The measurements were made using a 17.130 MHz Spin-Lock Electronics Model CPS-2 Pulsed NMR Spectrometer. The magnetic field of 4024 G was provided by a Magnion 9-inch electromagnet with a two inch pole gap. For a fixed intensity, the pulse duration was adjusted for maximum signal, which corresponds (Slichter 1963) to the magnetization due to the $^1H$ nuclei being rotated by the pulse into the plane perpendicular to $H_0$ ($^{\pi}/_2$-pulse). The FID following the pulse was observed directly from the spectrometer using a Tektronix model 475 oscilloscope. The experiment was repeated every second for at least 20 seconds by reapplying the pulse.

## RESULTS

Figure 1 shows a photograph of the FID of $^1H$ nuclei for maple with water contents of A) 30% and B) 0%. The FID of the moist sample, (curve A in Figure 1) exhibits two different time constants $T_2^*$, one very short, the other quite long, while the FID of the dry sample (curve B) decays to zero with a time constant nearly equal to the short $T_2^*$ of curve A. In Figure 2 the FID of five different maple samples with varying moisture contents are shown on a lengthened time base to exhibit only the decay corresponding to the long $T_2^*$. Similar results were obtained on spruce samples.

The rapidly decaying portion of the signal is contributed by $^1H$ nuclei in the solid matter (cellulose, lignin, etc.) and possibly from some water which may be strongly hydrogen bonded in the cell walls and may not be removed by oven-drying. The more slowly decaying components of the signal are contributed by the water in these samples which may be removed by oven-drying.

For those samples with the largest water content, $T_2^*$ of the water component is determined by magnetic field inhomogeneities. At water contents less than about 30%, $T_2^*$ of the water component begins to decrease (indicating that it is determined by spin-spin interactions) and continues to decrease as the water content is diminished. Detailed analysis of our results suggests that the motions of the water molecules in wood become progressively more restricted as MC decreases (Riggin et al. 1979).

The portion of the signal attributed to the solid component of the sample decays to zero about 35 $\mu$s after the pulse. Therefore, signal components observed at times greater than 35 $\mu$s are attributable to removable water protons and their

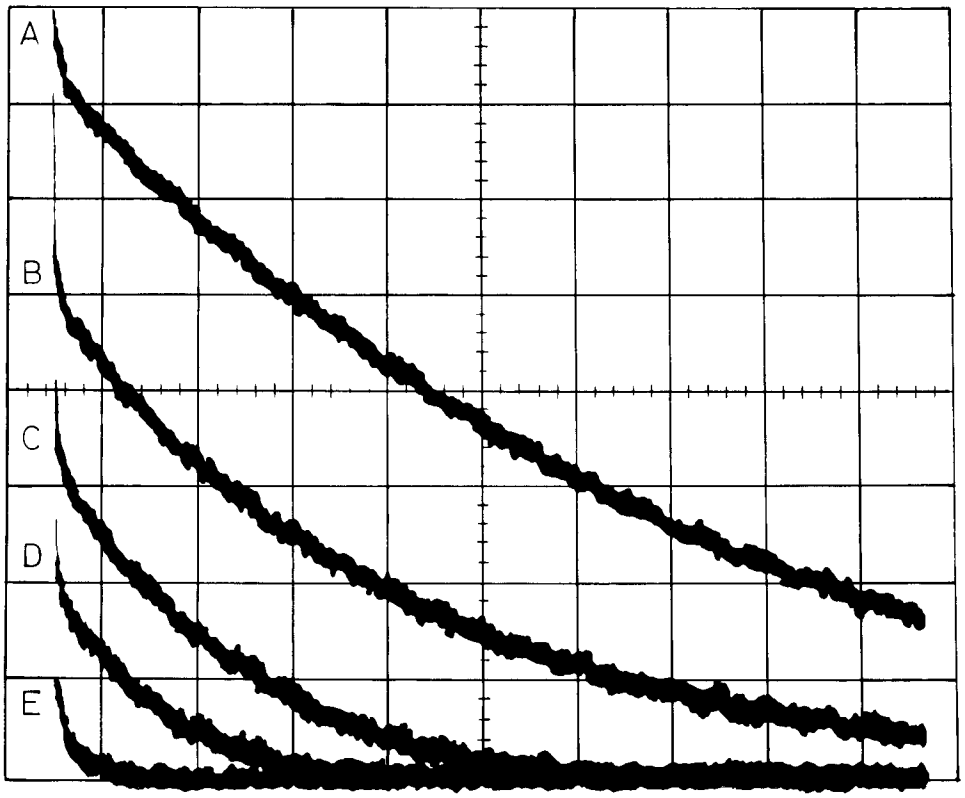


FIG. 2. The free induction decays of $^1H$ nuclei in maple with varying moisture contents are shown as a function of time following a $\pi/2$-pulse. The moisture contents are: A) 73.9%, B) 55.9%, C) 30%, D) 21% and E) 6%. In this figure the time base is lengthened (one large division along the abscissa is 500 $\mu$s) as explained in the text.

amplitude is related to the removable water content. In order to obtain a measurement that is directly proportional to the water content, it is necessary to account for the decay in the signal amplitude between the end of the pulse and the point at which the amplitude is measured.

The amplitude of the signal from the water protons decays exponentially after the pulse with time constant $T_2^*$. Therefore, the water proton signal amplitude $S_0$ immediately after the pulse is related to the amplitude S(t) measured a time t after the pulse by

$$S_0 = S(t)e^{t/T_2^*} \tag{2}$$

Measurements of S(t) at t = 50 $\mu$s for each sample may be used to obtain $S_0$ for that sample from Equation 2. The ratio of $S_0$ in different samples gives the relative water content of those samples.

For precise determinations of water content, particularly at low values, the ratios of $S_0$ should be used. However, estimates of MC within 2% can be achieved by taking the ratios of S(t) at t = 50 $\mu$s. The reason is that the factor $e^{t/T_2^*}$ differs significantly from unity only when $t \gtrsim T_2^*$. Throughout most of the

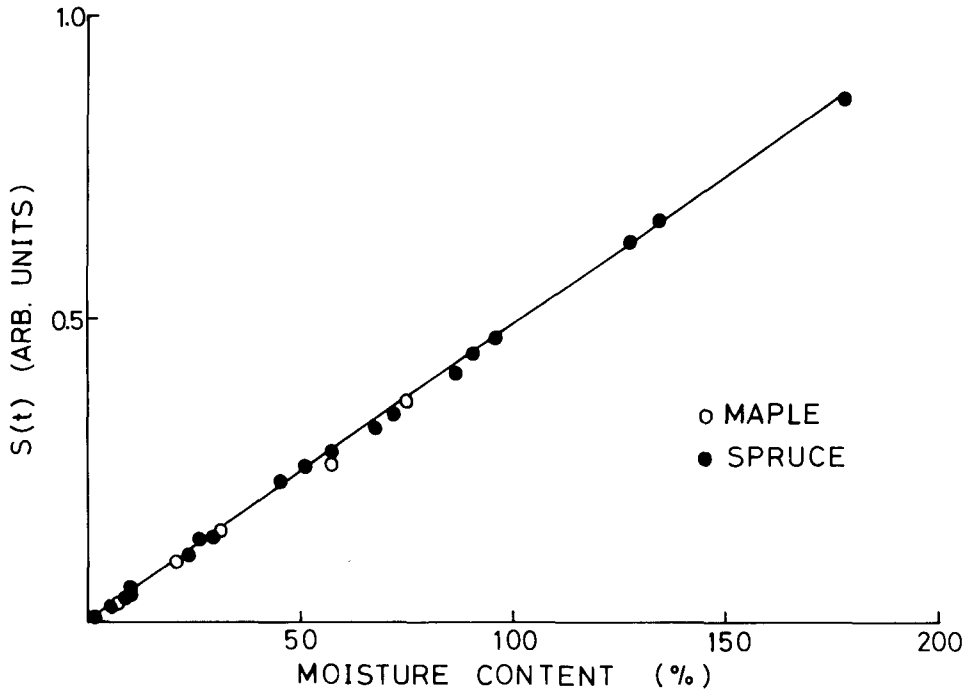


FIG. 3. The free induction decay S(t), as measured at t = 50 $\mu$s, is shown as a function of moisture content for both spruce and maple samples. Results given for the maple samples correspond to those recorded in Figure 2.

range of moisture contents, $T_2^*$ is several milliseconds in which case the $e^{t/T_2^*}$ factor is nearly one. The smallest $T_2^*$ observed in these measurements was 130 $\mu$s for a sample with 7% moisture content. In this case the factor $e^{t/T_2^*}$ has a value of 1.35, and use of S(t) rather than $S_0$ would yield 5% MC.

In Figure 3, the free induction decay amplitude of spruce and maple wood measured at t = 50 $\mu$s, is plotted versus the moisture content of the sample. The graph extrapolates through the origin indicating that all sample water which can be removed by oven-drying has contributed to the signal. The slope of the graph is determined by the gain of the spectrometer. The water signal was experimentally found to be independent of the wood grain direction.

## ASSESSMENT

The pulsed nuclear magnetic resonance signal is directly related to the number of water molecules which can be removed from the wood by oven-drying. This is the reason for the signal being independent of grain direction. For this same reason the signal should be independent of the previous history of the wood. The technique is applicable over a wide range of moisture contents. The authors know of no practical or theoretical upper limit to the range of applicability so that it also may be used for MC determinations of cellulosic gels at high moisture contents. No calibration is required to obtain the relative moisture contents of different samples while absolute values can be determined by measuring relative to a known standard.

The results using this technique are unambiguous because the signal amplitude is a single-valued function of the moisture content. It is also theoretically independent of the distribution of water inside the sample although only equilibrated samples were used in this study. The accuracy of measurements using our spectrometer was determined by the resolution of the oscilloscope which amounted to better than 1% MC for a sample with 30% MC. A typical measurement using a scope to monitor the free induction decay may be made in about 30 seconds. If greater precision is required, particularly at low moisture contents, a signal averaging device such as a box-car integrator may be used to improve the signal to noise ratio and the resolution, and account should be taken of the dependence of S(t) on $T_2^*$.

The pulsed magnetic resonance technique is not truly nondestructive. Although the sample is unaffected by the measurement, it is necessary to extract the sample from the bulk wood resulting in a small amount of waste. There is also a risk that the sample is not representative of the bulk wood, because moisture content gradients do exist in timber and are known to affect electrical methods of moisture content determination (Skaar 1972). This problem can be minimized by boring a core radially and cutting it into several samples for direct evaluation of the moisture gradient.

Theoretically there is also a slight temperature dependence of the signal amplitudes. To a good approximation, $S_0$ is inversely proportional to the absolute temperature (Abragam 1961) and therefore, samples to be compared must all be at the same temperature or their temperatures must be known. For example, if allowance is not made for the temperature dependence of $S_0$, the moisture content as determined by nuclear magnetic resonance would give 30% and 29% MC for two samples having 30% MC at 20 and 30 C, respectively.

For moisture content measurements the pulsed nuclear magnetic resonance technique is more reliable than steady-state methods. The area under the steady-state resonance curve is proportional to the number of spins contributing to the signal (Slichter 1963), but the removable water line is superimposed on the line arising from $^1H$ nuclei in the other constituents so determination of the area under the water line is slow and difficult to perform accurately. In the pulsed nuclear magnetic resonance experiment, only an amplitude needs to be measured instead of an area.

The amplitude $S_0'$ of the signal at $t = 0$ arising from the solid part is proportional to the number of $^1H$ nuclei in the solid and therefore is related to the mass of the solid. In principle, a comparison of $S_0$ for the water signal to that of the solid signal $S_0'$ would give a direct measure of the water content. However, for the solid component, $T_2^*$ is typically a few microseconds and extrapolation of $S'(t)$ to $t = 0$ is inaccurate, particularly in samples of high moisture content where the solid component is a small fraction of the total observed signal. Furthermore, the exact relationship between $S_0'$ and the sample mass is not well known and is probably species dependent. Further experiments are planned to attempt to overcome these difficulties and obtain a direct measure of the water content in this way.

Presently, the major disadvantages of the NMR technique of moisture content measurement are cost and the time required for boring the wood samples, both of which may restrict the applicability to the research laboratory for the time

being. The quality research spectrometer and electromagnet used in this study have a commercial value of about two orders of magnitude greater than commonly used electrical moisture meters. However, suitable inexpensive permanent magnets are available, and combined with modern solid-state technology it seems possible that a small, dedicated pulse spectrometer could be developed which would be cost competitive. A small spectrometer using a permanent magnet would still be restricted to studying small samples of similar size to those used in this experiment.

## CONCLUSION

The techniques of Pulsed Nuclear Magnetic Resonance have been used successfully to determine the moisture contents of samples of white spruce and sugar maple over the range from green to oven-dry. Most criteria desirable for moisture content measurements are met, making pulsed nuclear magnetic resonance a viable method for such determination in water-cellulose systems. Future development is likely to eliminate cost objections to the technique, but there are no immediate prospects for eliminating the need for sampling the wood. The method may therefore be more adaptable to the laboratory than to industry.

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