

Available online at www.sciencedirect.com



Journal of Magnetic Resonance 171 (2004) 364-372

JDUR JOURNAL OF Magnetic Resonance

www.elsevier.com/locate/jmr

Determination of moisture fraction in wood by mobile NMR device

C. Casieri^a, L. Senni^b, M. Romagnoli^c, U. Santamaria^d, F. De Luca^{b,*}

^a INFM-CRS SOFT and Dipartimento di Fisica, Università di L'Aquila, V. Vetoio 10, I-67010 Coppito, L'Aquila, Italy

^b INFM-CRS SOFT and Dipartimento di Fisica, Università "La Sapienza," P.le A. Moro 2, I-00185 Rome, Italy

^c Dipartimento di Tecnologie, Ingegneria Scienze dell'Ambiente e delle Foreste (DAF), Università della Tuscia,

V. San Camillo de Lellis, I-01100 Viterbo, Italy

^d Laboratori Scientifici dei Musei Vaticani, Città del Vaticano, Italy

Received 22 July 2004; revised 17 September 2004 Available online 14 October 2004

Abstract

A mobile NMR probe has been used as a non-destructive and non-invasive tool for water content analysis on wood samples. The porosity index, express as the fraction of the sensitivity volume of the probe occupied by water, is here proposed as an alternative to the moisture content index, namely the amount of water mass with respect to the mass of dried sample. In principle the method can be applied to any kind of porous media that has not detectable proton signal from the rigid matrix as, for instance, in building materials. In wood, where proton signal can be detected also from cellulose and others macromolecular components, some considerations and artifices are here proposed for eliminating this contribution. The method has allowed performing moisture volume fraction analysis on wood samples characterized by different wood species, cutting and moisture contents. The NMR data of moisture detection as volume fraction have successfully been compared with those obtained by the gravimetric method. © 2004 Elsevier Inc. All rights reserved.

Keywords: NMR in wood; Wood moisture contents; Single-sided NMR; NMR porosity

1. Introduction

It is well known that many mechanical properties of wood are greatly affected by its moisture content. The moisture content is normally below the so-called fiber saturation point (FSP), that is the point above which water starts to fill up the cell cavities (lumens) of wood. The FSP for all wood species corresponds to water content of roughly 30% in mass [1,2]. Below FSP, wood is in its hygroscopic interval and it can absorb or release water in response to thermo-hygrometric environmental modifications. The reference method to establish the moisture content of a wood sample is that gravimetric [1,2], which defines the moisture content M_C as

* Corresponding author.

E-mail address: francesco.deluca@roma1.infn.it (F. De Luca).

$$M_{\rm C} = \frac{m_{\rm WA}}{m_{\rm D}} = \frac{m_{\rm T} - m_{\rm D}}{m_{\rm D}},$$
 (1)

where $m_{\rm D}$ is the dry weight of the sample, $m_{\rm T}$ is its whole mass, and m_{WA} the mass of water. This method, however, has some important limitations that concern the sensitivity with which $m_{\rm T}$ or $m_{\rm D}$ may be evaluated on large sample and the intrinsic invasiveness of the ovendry way to get $m_{\rm D}$. Also an electric approach is used for this purpose. It is based on measurements of the conductivity between two nails inserted into the wood and on the use of some models, which relate the amount of water to conductivity [1,2]. The conductivity testing is size-independent and is probably the most worldwide practiced. It, to some extent, is invasive and cannot be applied to delicate samples; it is imprecise because its result may depend on many chemical and physical factors such as impurities, wood grain direction and defects, and others that may change the electrical current

^{1090-7807/\$ -} see front matter @ 2004 Elsevier Inc. All rights reserved. doi:10.1016/j.jmr.2004.09.014

patterns between nails. Usually the results of conductivity measurements must be corrected according to the woody species and temperature.

To account non-invasively of water fraction in wood, either since Cultural Heritage interest or because manufacturing purposes, with limited restrictions about both the sample size and its place of residence, it is here proposed a single-sided NMR approach [3–5].

Low-resolution 1H-NMR can investigate wood on both macroscopic and microscopic levels and it can provide quantitative information about water and other components of wood [6–9]. A number of NMR studies have been performed to characterize the behavior of water in wood [10–18] and it has been proved that NMR is quite effective in providing information about the distribution and concentration of water in wood during drying and absorption [12,15]. The great part of the NMR works on wood has been approached with methodologies that are normally applied to porous media. Wood, in fact, is a particular porous material whose matrix includes macromolecules (mainly cellulose) that link water by hydrogen bonds [1,2]. Water can play two main roles in the microscopic structure of wood, that is hydration water (cell wall water) and free water (lumen water). Therefore, wood has three different 1H-NMR signal sources: the cell wall water, the lumen water, and some hydrogen pertaining to wood macromolecules.

It has been demonstrated that NMR signal coming from macromolecules has a spin-spin relaxation time (T_2) of tens of microseconds, making it readily separable from that of the cell wall water, which has a T_2 of hundreds of microseconds. At FSP the cell walls are water saturated and cell cavities empty; above FSP the water that fills lumens has T_2 ranging from tens to hundreds of milliseconds [10,11,14].

Up to now the gravimetric-like determination of water content via traditional NMR has been based on the formula [11,15]

$$M_{\rm C} = \frac{M_0^{\rm (WA)}}{M_0^{\rm (T)} - M_0^{\rm (WA)}} \frac{\rho_{\rm WO}}{\rho_{\rm WA}},\tag{2}$$

where $M_0^{(T)}$ is the value of the total equilibrium magnetization while $M_0^{(WA)}$ refers to that of water fraction. The spin densities of water (ρ_{WA}) and of wood (ρ_{WO}) have the dimensions of a magnetization over mass and their ratio must be known to proceed with the NMR valuation. This requirement is not trivial because the nuclear spin density is not within the parameters that are normally used to characterize wood.

In this paper, the use of single-sided NMR to apply NMR for non-invasive and accurate measurement of moisture content in wood is proposed. This approach, which is based on the definition of the porosity index, utilizes a semi-empirical model and it may be used for on field analysis of Cultural Heritage [4,5] as well as for manufacture testing because it can be employed on objects of almost whatever dimensions and/or unmovable.

It is known that unilateral NMR devices are characterized by some natural spatial selectivity, which is delimited by the sensitivity volume of the probe [3,19]. Such a characteristic allows one to measure the NMR parameters in a precise and fixed volume of the sample. That makes possible, by utilizing proper calibration procedures, to relate the NMR magnetization to the water content of this volume and therefore to the volume fraction occupied by it. After the estimate, by a semi-empirical approach, of the contribution of wood macromolecular hydrogen to NMR signal, it has been possible to obtain a NMR response that has successfully been related to gravimetric results.

The method has been tested and elaborated through various measurements on numerous wood samples distinguished by water content, wood species, and wood anatomical direction. The results indicate that the porosity index evaluated by single-sided NMR can constitute an alternative and operatively simple way for the evaluation of the water content in wood.

2. Materials and methods

2.1. Calibration

The Bruker Eureka-Mouse10 utilized in this work is characterized by a magnetic field gradient of about 10 T/m, by a resonance frequency of about 18 MHz and by a pulse dead time of about 18 μ s.

The sensitivity volume of the instrument is roughly a parallelepiped of dimension $20 \times 2 \times 8$ mm [19]. Moreover, since the strong gradient along the axis perpendicular to the probe surface, different sensitive volumes may be tailored by using different RF coils. If no signal comes from the rigid matrix, whatever kind of porous media is analyzed, the porosity index $I_{\rm P}$, which represents the amount of volume occupied by water $V_{\rm WA}$ with respect to the sensitivity volume of the probe $V_{\rm T}$, is simply

$$I_{\rm P} = \frac{V_{\rm WA}}{V_{\rm T}} = \frac{M_0^{\rm (WA)}}{\Theta},\tag{3}$$

where Θ is the angular coefficient of the calibration line (see below).

The calibration procedure has been based on the measurements of the NMR signal versus the fraction of water V_{WA} . The fraction of water was constituted by the fraction of normal water contained in different water-deuterium oxide samples with volumes larger than V_{T} . The sample volumes have therefore been fixed to

30 ml; the solutions were contained in very thin plastic film. Some trials were made to be sure that the protons of the plastic film did not contribute to NMR signal and that the sample volumes were larger than $V_{\rm T}$.

The NMR magnetization measured versus the water fraction is reported in Fig. 1. The data of Fig. 1 confirm the linear relationship (the correlation factor is 0.9998) between the number of protons, and therefore the fraction of the sensitive volume occupied by water, and the NMR signal detected by the Eureka-Mouse10. Besides, Fig. 1 establishes also a quantitative relationship between the volume fraction occupied by water and the NMR signal acquired by the device. Because of the high stability of the tuning conditions of the apparatus, which are independent by shape, volume and nature of the sample, the calibration reported in Fig. 1 should be unique. Nevertheless, in presence of detuning effect or because some change in the electronic gain, the apparatus may be re-tuned or the gain modified to set the water/signal slope to that of Fig. 1 by utilizing a large 100% water sample. Alternatively, a new calibration line can be traced by utilizing the experimental point produced by a 100% water sample and the origin of the signal/water fraction reference frame. For all the measurements reported in this paper, a control of calibration has always been made before any measurements, utilizing a large sample containing 100% water: the controls have always confirmed the calibration line reported in Fig. 1.

The equilibrium magnetization M_0 and the transverse relaxation time T_2 have been calculated by the decay signal of Carr–Purcell–Meiboom–Gill (CPMG) sequences, each with 1024 scans, 2000 echoes, 300 µs of echo time, and 10 s of recycling time. The CPMG sequence has been chosen with respect to the spin-echo (SE) one because it is the main sequence used for the measurements on wood (see below).



Fig. 1. Calibration line that relates the volume fraction occupied by water to the signal acquired by the single-sided NMR device with CPMG sequences. For the Eureka-Mouse10 device the calibration line is described by the function $I_{\rm P} = M_0^{\rm (WA)}/\Theta$, with $\Theta = 0.65$.

To take in account for the residual self-diffusion effects on the transverse decaying, the experimental data of water solutions have been fitted with stretched exponential function with a stretch parameter α

$$M(t) = M_0 e^{-(t/T_2)^{\alpha}} + C,$$
(4)

where C is a fitting constant which takes in account the signal baseline.

2.2. Wood samples preparation

Three species of wood have been selected (Chestnut or Castanea sativa Mill, Walnut or Juglans regia L. and Sessile Oak or Quercus petraea Liebl) and, for each species, three different samples were cut, according to the orthogonal direction, in slices of approximately $50 \times 4 \times 50$ mm. In the three samples, the largest area is respectively in cross-section (X), radial section (Y), and tangential section (Z). When wood is cut in transverse or cross-sections (X), the annual rings appear like concentric bands, with rays extending outward like the spokes of a wheel. Moreover, wood may be cut longitudinally in two different planes: radial and tangential. Radial sections (Y) are made along the rays or radius of the log, at right angles to the annual rings. The rings appear like closely spaced, parallel bands. The rays appear like scattered blotches. Finally, tangential sections (Z) are made perpendicular to the rays and tangential to the annual rings and face of the log. The annual rings appear in irregular, wavy patterns. In figures and tables the samples were indicated by capital letters which refer to the trees species: C, Castanea sativa, N, Juglans regia, and R, Quercus petraea; the second letter indicates the cut section (X, Y, Z) and the number distinguishes samples with same characteristics.

Samples have been placed in a shrine with saturated saline solutions to regulate the relative humidity (RH) of environment; the values of RH and temperature were recorded by a data-logger opportunely interfaced with a personal computer. The salts used for shrine conditioning were Silica Gel to reach a RH of about 20%, potassium carbonate (1150 g/L) for RH of about 45%, magnesium nitrate hexahydrate (1300 g/L) for a RH of about 60%, and sodium chloride (400 g/L of distilled water) for a nominal RH of 75%. These nominal RH values refer to a temperature of 293 K.

According to the environmental thermo-hygrometric conditions wood reaches its equilibrium moisture content: with the temperature and RH indicated above, wood samples reach typical moisture contents of about 5, 8, 10, and 12%.

Equilibrium moisture content has been measured through an adsorbing cycle, by using the method of double weighting, which requests that their weights were stable over a temporal interval of 12 h. After the cycle was completed, samples have been placed in an oven

Table 1 The moisture content $M_{\rm C}$ (%), determined by gravimetric method, is reported

| RH (%) | СХ | CY1 | CY2 | CZ1 | CZ2 | NX | NY | NZ4 | RX | RY1 | RZ4 |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 20 | 3.47 | 4.29 | 4.33 | 4.12 | 3.60 | 3.16 | 3.41 | 3.85 | 3.55 | 5.66 | 5.04 |
| 45 | 8.33 | 8.59 | 8.30 | 8.46 | 8.05 | 8.25 | 8.15 | 8.57 | 8.12 | 8.74 | 10.24 |
| 60 | 10.94 | 11.09 | 10.83 | 11.06 | 10.59 | 10.70 | 10.81 | 11.36 | 10.83 | 11.33 | 11.22 |
| 75 | 12.33 | 12.88 | 12.64 | 13.02 | 12.29 | 12.63 | 12.74 | 13.29 | 12.69 | 13.11 | 13.01 |

The wood samples are localized by the nominal relative humidity, RH (%), and the specie of wood: C, *Castanea sativa*, N, *Juglans regia*, and R, *Quercus petraea*. The second letter indicates the section in which the sample has been cut: X, transverse section; Y, longitudinal radial section; Z, longitudinal tangential section; finally, the last number distinguishes samples with same characteristics.

at 103–105 °C for 24 h and then weighted to determinate their dried weights $m_{\rm D}$.

The moisture contents, evaluated by gravimetric method, have been calculated according to Eq. (1): the results are reported in Table. 1 for all samples and different RH values.

2.3. NMR measurements on wood

Transverse relaxation decays on wood have been measured by SE and CPMG pulse sequences, this latter being that mostly used for the higher signal-to-noise it furnishes in shorter time with respect to SE and because its ability in reducing eventual self-diffusion effect on decay. However the SE sequence allows having denser experimental points with respect to CPMG and, at early time, this means more details on the solid-like relaxation. Therefore we utilize the SE sequence uniquely for the characterization of the solid-like relaxation component of wood. Measurements have been performed for each thermo-hygrometric condition and were repeated 1024 times for signal averaging with a recycling time of 0.5 s (the maximum longitudinal relaxation time T_1 measured on wood samples was few tens ms). The SE data have been obtained with echo times ranging from 44 µs, which is the shorter echo time available on Eureka-Mouse10, to 10 ms. The SE signal fit has been made by a double exponential characterizing two relaxation components

$$M(t) = M_{0S} e^{-t/T_{2S}} + M_{0L} e^{-t/T_{2L}} + C.$$
 (5)

CPMG was used with 2000 echoes with 44 μ s of echo time. The fit function used for CPMG signal was a simple exponential characterizing a single relaxation component

$$M(t) = M_0 e^{-t/T_2} + C.$$
 (6)

3. Results and discussion

Normally a generic wood sample, below FSP, shows two magnetization component: a component with shorter transverse relaxation time, T_{2S} , which is assigned to some protons of macromolecules, while the other component, with longer relaxation time, T_{2L} , is assigned to protons of water. When the measurement is made by CPMG sequence, even at the shorter available interpulse delay, the two signal components are not well separable because it is usually possible to sample only few experimental points of the faster decay. Because in our case only the contribution of water is of interest, some initial points of the experimental CPMG relaxation may be neglected in order to reduce more the signal contribution from macromolecules. With this artifice, the CPMG data fit function can be the single exponential of Eq. (6) with $T_2 \approx T_{2L}$ and $M_0 \approx M_{0L} \equiv M_0^{(WA)}$, that is the equilibrium magnetization of water.

The results of the best fits of CPMG data by Eq. (6), after the removal of the first two echoes, are reported in the first two rows of Table. 2 for cuts, species of woods, and RH of the different samples. The criterion utilized for the removal of the first two echoes has been established through the condition $3 \times 44 \,\mu s \approx 5 \overline{T}_{28}$, where $\overline{T}_{2S} = 28 \ \mu s$ is the average value of the faster relaxation component measured on all wood samples by SE. The porosity index, valuated according to Eq. (3), has been obtained for each wood sample by extrapolating the equilibrium magnetization from the CPMG simple exponential data fit and relating it to the volume fraction of water by the calibration line of Fig. 1. The porosity indices Eq. (3) versus the total weight of sample, for all wood samples and different RH's, are reported in the third row of Table. 2 and in Fig. 2.

How it can be seen in Fig. 2, the data of each sample do not align along the line

$$I_{\rm P} = \frac{(m_{\rm T} - m_{\rm D})}{\delta_{\rm WA} V_{\rm T}} = \frac{m_{\rm T}}{\delta_{\rm WA} V_{\rm T}} - \frac{\delta_{\rm WO}}{\delta_{\rm WA}}$$
(7)

connecting the dried weight to the weights at different RH's; here δ_{WA} is the density of water, δ_{WO} the density of dried wood and their ratio, $P = \delta_{WO}/\delta_{WA}$, is the specific gravity of dried wood. This mismatch occurs because the elimination based on \overline{T}_{2S} of a fixed number of points from the CPMG data is evidently able to take in account only the more rigid part of macromolecular hydrogen. Because some hydrogen of macromolecules, as those of the hydroxyl groups of cellulose, change their

| M_{0L} (a.u.), | T_{2L} (ms), at | nd $I_{\rm P}$ (%) is i | reported in the | he first three | rows of each | n RH value | | | | |
|------------------|-------------------|-------------------------|-----------------|----------------|--------------|------------|-------|-------|-------|-------|
| RH (%) | CX | CY1 | CY2 | CZ1 | CZ2 | NX | NY | NZ4 | RX | RY1 |
| 20 | 5.19 | 5.69 | 5.36 | 4.30 | 4.96 | 5.69 | 6.02 | 4.52 | 6.22 | 6.37 |
| | 0.275 | 0.264 | 0.286 | 0.297 | 0.269 | 0.250 | 0.253 | 0.285 | 0.236 | 0.338 |
| | 7.98 | 8.75 | 8.25 | 6.62 | 7.63 | 8.75 | 9.26 | 6.95 | 9.57 | 9.80 |
| | 3.41 | 4.43 | 4.80 | 3.49 | 3.09 | 3.49 | 4.94 | 3.37 | 3.08 | 6.49 |
| 45 | 7.09 | 7.08 | 7.08 | 6.12 | 6.12 | 6.77 | 7.27 | 5.94 | 7.15 | 7.72 |
| | 0.418 | 0.400 | 0.426 | 0.400 | 0.401 | 0.508 | 0.535 | 0.355 | 0.449 | 0.407 |
| | 10.91 | 10.89 | 10.89 | 9.42 | 9.42 | 10.42 | 11.18 | 9.14 | 11.00 | 11.88 |
| | 8.35 | 8.20 | 8.60 | 6.72 | 6.72 | 8.14 | 8.88 | 6.78 | 8.29 | 8.97 |
| 60 | 8.00 | 7.78 | 7.72 | 6.30 | 6.60 | 6.97 | 7.45 | 6.00 | 7.68 | 8.36 |
| | 0.635 | 0.629 | 0.617 | 0.621 | 0.586 | 1.03 | 1.06 | 1.08 | 0.701 | 0.612 |
| | 12.31 | 11.97 | 11.88 | 9.69 | 10.15 | 10.72 | 11.46 | 9.23 | 11.82 | 12.86 |
| | 11.61 | 11.38 | 10.80 | 9.15 | 9.03 | 10.72 | 11.46 | 9.23 | 11.24 | 11.51 |
| 75 | 8.53 | 8.52 | 8.64 | 7.10 | 7.15 | 7.69 | 8.32 | 6.71 | 8.66 | 9.30 |
| | 0.716 | 0.690 | 0.686 | 0.700 | 0.678 | 1.33 | 1.40 | 1.37 | 0.771 | 0.686 |
| | 13.12 | 13.11 | 13.29 | 10.92 | 11.00 | 11.83 | 12.80 | 10.32 | 13.32 | 14.31 |

Table 2 M_{01} (a.u.), T_{21} (ms), and $I_{\rm P}$ (%) is reported in the first three rows of each RH value

12.68

In the fourth row, the value of $I_{\rm P}$ (%) is reported after the correction of the macromolecular contribution to water signal.

10.50

11.83

10.41



12.60

12.65

Fig. 2. I_P versus m_T determined by the calibration curve of Fig. 1, for all the wood samples and for the different RHs. The capital letter indicates the specie of wood: C, *Castanea sativa*, N, *Juglans regia*, and R, *Quercus petraea*. The second letter indicates the section in which the sample has been cut: X, transverse section, Y, longitudinal radial section, and Z, longitudinal tangential section. Finally, the last number distinguishes the samples with same characteristics. The line indicates the way that the experimental points of the NY sample should follow.

mobility with the hydration degree, a more accurate cancellation of CPMG experimental points should be related in some way to T_{2L} , which changes with the RH, wood species and cut.

By the behaviors of all groups of data in Fig. 2, a simple function has empirically been derived in order to eliminate more effectively the proton signal coming from macromolecules. The curve, which describes the initial time interval τ to be cut-off from the CPMG data versus T_{2L} , which applies to all wood species, cuts and RH utilized in this work, it is reported in Fig. 3 (the data refer



12.71

10.32

12.80

RZ4 6.20 0.285 9.54 5.40 7.09 0.400 10.91 8.20 8.36 0.612 12.86 11.10 9.22 0.662 14.18

13.54

13.63

Fig. 3. The curve describes the empirical function Eq. (8) which gives time that must be cut-off from the initial CPMG single exponential decay in order to remove effectively the signal coming from macro-molecules. The ordinate of figure indicates the time to be cut-off as the number of echoes $N_{\rm E}$ to be detached from the initial part of the CPMG decay. The data of figure refer to a *Juglans regia* sample, specifically the NY sample.

to Juglans regia, NY sample, because it was the sample with longer T_{2L} value). Its analytical expression is given by

$$\tau = \tau_0 \exp\left(-\frac{T_{2L}}{0.3}\right),\tag{8}$$

where $\tau_0 = 0.73$ ms and T_{2L} is expressed in milliseconds.

The empiric function Eq. (8) implicitly assumes that the signal contribution from the mobile hydrogen of macromolecules becomes exponentially relevant in the whole NMR signal as $T_{2L} \sim 0.3$ ms. The fact that the time constant of Eq. (8) is greater than \overline{T}_{2S} confirms that some hydrogen of macromolecules increase their mobility with hydration. The empirical function of Fig. 3 has been set up simply by looking for the number of initial echoes to be excluded from the CPMG relaxation data to allow that the points of Fig. 2 shift and align along a line connecting, for the same sample, the point with maximum water contents to the dried one. The line



Fig. 4. The values of $I_{\rm P}$ versus $m_{\rm T}$, after the solid-like contribution correction based on the curve reported in Fig. 3, are reported. On the legend the indication of samples is given as in Fig. 2. The lines report the best-fit results for each wood sample.

has been traced between these two points because the sample with the greater water contents allows minimizing, as said above, the role of signal from the solid matrix. The alignment of points of Fig. 2 depends only by water content and therefore it excludes that water is confused with macromolecular mobile hydrogen. The curve of Fig. 3 works well for all samples because the more rigid solid-like contribution is characterized in average by \overline{T}_{2S} and only a minor amount of macromolecular hydrogen increase its T_2 in reason of hydration and not much in reason of the wood species and cuts. The value of \overline{T}_{2S} , moreover, seems to be general in the sense that the shorter relaxation component of wood is in the order of \overline{T}_{2S} independently by water contents, cuts, and wood species [10,11,14].

The NMR results, opportunely filtered according to the above criterion, are summarized in the last row of Table. 2 and Fig. 4. The best-fit results, obtained with a line function, are also reported in Fig. 4 for every sample: it is evident that all lines have very similar angular coefficients, as expected from Eq. (7).

As remarked above, while the moisture content valued by the gravimetric method is expressed by a mass ratio (Eq. (1)), that valued by the surface NMR probe



Fig. 5. The moisture content M_CP (small dots), I_P data and best fits results (—) versus m_T are reported for *Castanea sativa* (A), *Juglans regia* (B), and *Quercus petraea* (C) with their *Ps*.

refers to a volume ratio (Eq. (3)). It appears obvious that the single-sided NMR results do not coincide with those found by gravimetric method; it is noteworthy that the differences have origin in the specific gravity factor of dried wood.

To compare the gravimetric results with those obtained with the single-sided probe, I_P must be written in term of mass instead of volume, therefore

$$M_{\rm C} = \frac{V_{\rm WA}}{V_{\rm T}} \frac{\delta_{\rm WA}}{\delta_{\rm WO}} \equiv I_{\rm P} P^{-1}.$$
(9)

The comparing factor P between $M_{\rm C}$ and $I_{\rm P}$ should be measured or valuated by means of the density of cellular walls of wood; alternatively it may be deduced by the intercept of the Eq. (7) best-fit lines with the $m_{\rm T} = 0$ axis of the $(I_{\rm P}, m_{\rm T})$ plane (Fig. 4). The $M_{\rm C}P$ and $I_{\rm P}$ data for all samples are reported in Fig. 5 versus $m_{\rm T}$ with their best-fit lines. The accord is very high.

The results confirm that both experimental approaches are really consistent each other and that their difference is only given by the *P* term, which is close to one. Therefore, besides to consider $I_{\rm P}$ as an alternative and effective method by means of which to re-define the moisture contents in wood, this approach can made fully coincident with the gravimetric one by the knowledge of the specific gravity factor of dried wood, which may determined directly through Eq. (7).



Fig. 6. A wood table of Juglans regia $(130 \times 5 \times 130 \text{ cm})$ has been marked in 21 different points individuated by a number followed by the letter A, which indicates the sapwood or the letter D for heartwood.



Fig. 7. (A) The electric-hygrometer moisture content data, $M_{\rm E}$ (+), and $I_{\rm P}$ (×) are compared for all the points indicated in Fig. 6. (B) The $M_{\rm E}$ (+) points are compared to T_2 relaxation times (×).

To demonstrate the great potentiality of the singlesided NMR device for spatial selected water content evaluation, we performed measurements on a large wood table of *Juglans regia* $(130 \times 5 \times 130 \text{ cm})$ on different sampling points, as enumerated in Fig. 6 (A indicates the sapwood and D the heartwood). For this kind of measurement it is impossible to apply the gravimetric method and our data are only comparable with the electric-hygrometer ones.

In Fig. 7A the $I_{\rm P}$ data acquired on all the points are reported with the electric-hygrometer ones $(M_{\rm E})$ for comparison. While for the moisture content acquired with the NMR method the behavior is quite constant (the points from 10 to 15 refer to the pith of tree part of wood which has effectively a higher moisture content) that determined with electric-hygrometer measurements shows an oscillating behavior that appears to be correlated to sapwood and heartwood. This kind of oscillations is confirmed also by the T_2 data, reported in Fig. 7B together with $M_{\rm E}$. The physical origins of such a different behavior may therefore be attributed to different amounts of molecules and extractives or ions contained in sapwood and heartwood, which may differentiate the conductivity and the relaxitivity of wood also independently by its water content.

4. Conclusion

A NMR approach that redefines the moisture content in wood and which is highly consistent with the gravimetric one has been proposed. The method may be applied on field in a non-destructive and non-invasive manner, being based on the utilization of a mobile NMR probe, and it is applicable also on other porous materials. The method is based on a proper calibration procedure, which makes possible to determine the water content of wood in very short measuring time and with good precision and reproducibility.

Although the method needs that a new definition of moisture content would be adopted by wood technologists, being I_P slight different from M_C , it can however made coincident to the gravimetric definition by means of tables with the specific gravity of dried woods, which is less specific than the dried weight or, when disposable, utilizing dried small samples to get this particular information or, as showed above, by extracting this parameter through Eq. (7). The gravimetric and the NMR volume fraction method give however very similar results: their difference depends by a parameters which is related to the density of macromolecules in wood. The study of this aspect will be performed in future.

The single-sided NMR approach to moisture content measurements could constitute an attractive alternative for wood technologists or Cultural Heritage conservator and restorer, which need simple logistic and accurate quantitative information. The price which should be paid for such alternative is the adoption of a definition for moisture content which is little different from that gravimetric but with the same practical utility. In fact, while I_P expresses the moisture content through the volume occupied by water, the definition of M_C utilizes the mass of water: the two definitions differ just for an adimensional constant, close to one, which is the specific gravity of dried sample.

We presented also measurements on a large wood table by which electric-hygrometric data are compared with those obtained with the unilateral NMR device. On wood object of such a size, but also for Cultural Heritage objects or for sample that, for whatever reasons, one would not damage, the $M_{\rm C}$ evaluation cannot be made because the $m_{\rm D}$ assessment is impossible or because it is invasive.

Acknowledgments

The Eureka-Mouse10 has been made available to the Department of Physics group by Bruker Biospin s.r.l. Italy, in the framework of the Eureka Σ ! 2214-Mouse Project. We thank the Bruker Biospin s.r.l., in particular Dr. Giovanni Bizzaro, Dr. Fabio Tedoldi, and Dr. Roberto Melzi, for their kind collaboration. We wish to thank also A. Menna for her contribution to samples preparation and their gravimetric analysis.

References

- J.G. Haygreen, J.L. Bowyer, Forest Products and Wood Science, Iowa State University Press, Ames, Iowa, 1996.
- [2] G. Giordano, Tecnologia del Legno, vol. 1, UTET, Torino, Italy, 1984.
- [3] F. Balibanu, K. Hailu, R. Eymael, D.E. Demco, B. Blumich, Nuclear magnetic resonance in inhomogeneous magnetic fields, J. Magn. Reson. 145 (2002) 246–258.
- [4] C. Casieri, S. Bubici, I. Viola, F. De Luca, A low resolution noninvasive NMR characterization of ancient paper, Solid State Nucl. Magn. Reson. 26 (2004) 77–85.
- [5] I. Viola, S. Bubici, C. Casieri, F. De Luca, The codex major of the Collectio Altaempsiana: a non-invasive NMR study of paper, J. Cultural Heritage 5 (2004) in press.
- [6] A.J. Nanassy, Use of wide line NMR for measurement of moisture content in wood, J. Wood Sci. 5 (1973) 187–193.
- [7] A.J. Nanassy, Water sorption in green and remoistened wood studied by the broad line component of the wide line NMR spectrum, J. Wood Sci. 7 (1974) 61–68.
- [8] A.R. Sharp, M.T. Riggin, R. Kaiser, M. Schneider, Determination of moisture content of wood by pulsed magnetic resonance, Wood Fiber Sci. 10 (1978) 74–81.
- [9] S.L. Maunu, NMR studies of wood and wood products, Prog. Nucl. Magn. Reson. Spectrosc. 40 (2002) 151–174.
- [10] N. Labbé, B. De Jèso, J.C. Lartigue, G. Daudé, M. Pétraud, M. Ratier, Moisture content and extractive materials in Maritime Pine wood by low field ¹H NMR, Holzforschung 56 (2002) 25–31.

- [11] X. Yu, C.D. Araujo, A.L. MacKay, K.P. Whittall, Proton spinlattice relaxation in wood— T_1 related to local specific gravity using a fast exchange model, J. Magn. Reson. B 110 (1996) 55–64.
- [12] I.D. Hartley, F.A. Kamke, H. Peemoeller, Absolute moisture content determination of Aspen wood below the fiber saturation point using pulsed NMR, Holzforschung 48 (1994) 474–479.
- [13] E. Hsi, R. Hossfeld, R.G. Bryant, Nuclear magnetic resonance relaxation study of water absorbed on Mill Northern White-cedar, J. Colloid Interf. Sci. 62 (1977) 389–395.
- [14] M.T. Riggin, A.R. Sharp, R. Kaiser, M. Schneider, Transverse NMR relaxation of water in wood, J. Appl. Polym. Sci. 23 (1979) 3147–3155.
- [15] R.S. Menon, A.L. MacKay, J.R.T. Hailey, M. Bloom, A.E. Burgess, J.S. Sawnson, An NMR determination of the physio-

logical water distribution in wood during drying, J. Appl. Polym. Sci. 33 (1987) 1141–1155.

- [16] C.D. Araujo, A.L. MacKay, J.R.T. Hailey, K.P. Whittall, H. Le, Proton magnetic resonance techniques for characterization of water in wood, Wood Sci. Technol. 26 (1992) 101–113.
- [17] C.D. Araujo, A.L. MacKay, K.P. Whittall, J.R.T. Hailey, A diffusion model for spin-spin relaxation of compartmentalized water in wood, J. Magn. Res. B 101 (1993) 248–261.
- [18] H. Haranczyk, W.P. Węglarz, Z. Sojka, The investigation of hydration process in Horse Chestnut (*Aesculus Hippocastanum* L.) and Pine (*Pinus Silvestris* L.) bark and bast using proton magnetic relaxation, Holzforschung 53 (1999) 299–310.
- [19] C. Casieri, S. Bubici, F. De Luca, Self-diffusion coefficient by single-sided NMR, J. Magn. Reson. 162 (2003) 348–355.