Diffuse optical techniques applied to wood characterisation

Ilaria Bargigia, Austin Nevin, Andrea Farina, Antonio Pifferi, Cosimo D’Andrea, Marcus Karlsson, Patrik Lundin, Gabriel Somesfalean and Sune Svanberg

We propose an optical method for non-invasive characterisation of wood samples based on two optical techniques: time-resolved diffuse optical spectroscopy and gas in scattering media absorption spectroscopy. While the latter is sensitive to gases present inside wood pores, the former extracts information on the bulk material regarding light scattering and absorption. Measurements on spruce samples, cut along different wood fibre directions, are presented to show an example of the advantages of this combined approach: by applying these two non-destructive techniques together, in fact, relevant information on wood such as porosity, permeability and moisture content can be assessed. Furthermore, the chemical composition, internal structure and the anisotropy due to the wood fibres can be investigated.

Keywords: wood spectroscopy, wood, near infrared, gas in scattering media absorption spectroscopy, time-resolved spectroscopy, diffusive media

Introduction

Wood is a complex system made of an intricate and extremely organised network of tracheids (or vessels) which is responsible for its highly anisotropic structure. It is a porous material with cavities embedded in a solid matrix and is mainly composed of cellulose, hemicellulose, lignin, extractives and water. The pore and fibre structure, together with the density, have an impact on impregnability, adsorption capability and heat conductivity. An understanding of the material and pore structure is useful for monitoring wood degradation and impregnation processes (for example, for the preservation of archaeological artefacts). Moreover, the pores of the solid wood matrix are filled with gases which impact on the chemical and physical stability of the material; wood exchanges water vapour within the environment and the equilibrium moisture content of wood is dependent on the relative humidity of the surroundings. Changes in environmental conditions induce changes in dimension and water content in wooden materials. Hence, it is important to be able to characterise the water content in wood.

The most commonly used techniques for the study of the internal structure of wood are based on X-rays, ultrasound (US), solid and liquid nuclear magnetic resonance (NMR), chemical analysis and microwaves. For the assessment of porosity, pycnometric procedures are usually based on gas adsorption (for example, water vapour, He, N₂), electron microscopy or on mercury intrusion porosimetry (MIP). The moisture content (MC) can be determined using commercial instruments based either on the electric resistance of wood or on its dielectric constant.

Recently, alternative non-invasive portable optical techniques, mostly operating in the near infrared range,
have been proposed for the analysis of wood and archaeological wooden artifacts. Moreover, during the last 20 years, advances have been achieved in the biomedical field in the analysis of highly diffusive biological samples by means of diffuse spectroscopy. Specifically, time-resolved spectroscopy (TRS) is able to separately recover the absorption and the scattering properties of light. Absorption and scattering are linked to the chemical composition of the probed medium. TRS has found many applications which include analysis of biological tissues, optical characterisation of agricultural or pharmaceutical products, small animal molecular imaging and clinical studies. TRS has also been proposed for the analysis of wood at wavelengths up to 1100 nm. However, TRS cannot be used for the assessment of gases present in scattering media.

A unique optical technique for probing molecular gases in pores of highly diffusive media is gas in scattering media absorption spectroscopy (GASMAS). GASMAS combines narrow-band, tuneable laser spectroscopy, developed for atmospheric gas monitoring, with the principles of light propagation in diffusive media. The method has been applied in the biomedical field where it has found applications for the study of water vapour and oxygen in human sinuses, for the investigation of gases in food packaging and for the analysis of gases in nanoporous materials. Furthermore, this technique has been applied to study gases present in wood and to the monitoring of wood drying processes.

In this work, we proposed, for the first time, the combined use of GASMAS and TRS to the same wood samples to gain extensive information on wood condition by means of non-destructive techniques. Simulations of the oxygen and water vapour diffusion in samples of wood were measured by GASMAS by changing the environmental conditions; in parallel, TRS was used for the assessment of dynamic changes in water content in the same wood samples.

**Basic principles of the optical techniques**

**GASMAS**

GASMAS is a technique employing tuneable diode lasers to probe molecular gases situated in the pores of highly diffusive media. The wavelength or frequency of the light, which has a narrow bandwidth, is swept across the specific wavelengths associated with the absorption of gases of interest (for example, oxygen or water vapour), while the detector records the intensity of the light propagated through the sample as a function of time. When the laser wavelength during the scan is equal to the wavelength of the absorption line, the intensity of the detected laser radiation is slightly lower. Since the spectral absorption features of the bulk material, i.e. the wood itself, are in the order of 10,000 times broader, the gaseous absorption is easy to distinguish and the decrease in the detected signal can be directly related to the product of gas concentration and the path-length of light through gas, as long as the gas and its extinction coefficient are well known.

Since the amount of absorbed light is often very small, sensitivity enhancing methods are employed. In this work, wavelength modulation spectroscopy (WMS) was used where the drive currents to the diode lasers and, therefore, the lasers output wavelengths, are not only scanned but are also modulated with a high frequency sine function. By doing this, it is possible to use digital lock-in techniques in gas detection and in this work the second overtone of the modulation frequency was used (with \( f \) being the frequency of the fast sinusoidal modulation). To retrieve the absorption strength, a fitting procedure was performed between the \( 2f \) signals collected from the samples and reference measurements through 1 m of air in known ambient conditions. Since the relative humidity and the temperature of the environment were known and the oxygen concentration in air is 21%, the fit expresses the relative strength of the absorption inside the sample with respect to the absorption of ambient air. This relative ratio multiplied by the length travelled through ambient air is called the equivalent path-length, \( L_{eq} \), and is given in mm units. \( L_{eq} \) represents an indirect measurement of the amount of gas within the pores of the medium. \( L_{eq} \) is not only influenced by the amount of gas trapped inside the sample cavities but also by the optical properties of the solid matrix which dictate how photons propagate inside the medium and, therefore, how much gas is probed during analysis.

**TRS**

In the range 700–1200 nm wood behaves as a highly light scattering medium, as described elsewhere. Briefly, TRS techniques are based on the injection of a short laser pulse into the diffusive sample. After the pulse has travelled inside the material, its temporal distribution is changed by the optical characteristics (absorption and scattering) of the material. Roughly speaking, the absorption mainly acts on the asymptotic slope of the detected photon time distribution whereas the scattering results in a broadening and a temporal shift in the peak of the time distribution. Thus, detecting the light pulse exiting the sample surface and applying adequate models for describing photon propagation in diffusive media, TRS techniques are able to separately recover the absorption coefficient \( \mu_a \) and the scattering coefficient \( \mu_s \). Since the absorption and scattering are linked to the chemical composition and to the internal microstructure, respectively, their coefficients can effectively be used for extracting valuable information on wood.

**Materials and methods**

**Set-up**

**GASMAS**

A scheme of the GASMAS set-up is shown in Figure 1. The light sources are two diode lasers (Nanoplus, Gerbrunn, Germany)
DFB 213/6-24 and Nanoplus, DFB 111/1-2), introduced for simultaneous acquisition of the oxygen and water vapour signals, respectively. The lasers are controlled in temperature and current. A Thorlabs (Newton, New Jersey, USA) LDC 201C and a Thorlabs TED 200C are, respectively, controlling the current and temperature of the laser for water vapour detection, while a Melles Griot (Carlsbad, California, USA) 06PLD103 is used for controlling both temperature and current of the laser for oxygen detection, as described in detail by Lewander et al. The wavelength of the oxygen probing laser is tuned to emit in conjunction with a molecular oxygen line in the A-band, situated around 760 nm; the water vapour probing laser has a wavelength of around 935 nm to match an absorption line of water vapour. The optical power at the tip of the sample fibre is around 5 mW for each of the two wavelengths. A data acquisition (DAQ) Card [NI-6120 National Instrument (Austin, Texas, USA)], PC-controlled via a LabVIEW (National Instruments, USA) program, in turn controls the temperature- and current drivers to deliver an injection current which is a superposition of a triangular ramp at 5 Hz for both lasers and a sinusoidal signal at 9015 Hz and 10,295 Hz for the lasers used for water vapour and oxygen detection, respectively. The two modulation frequencies enable detection of both gases simultaneously through lock-in band-pass filtering of the detected signal. Both lasers are fibre-coupled and the two wavelengths are first combined together into a single fibre, after which the light is split up to send about 10% of the light (both wavelengths) directly to a large area photodiode (PD, Hamamatsu (Hamamatsu City, Japan) S3590-01, active area $10 \times 10 \text{mm}^2$) used as a reference arm (to monitor the exact intensity behaviour of the light when entering the sample) and the remaining 90% (both wavelengths) to the sample. A mechanical dithering is added to the injecting fibre and sample in order to reduce possible etalon fringes which can severely affect the measurements. The light transmitted through the sample is collected either by another PD (active area $10 \times 10 \text{mm}^2$ (Hamamatsu S3590-01) or $18 \times 18 \text{mm}^2$ (Hamamatsu S3204-08)) or by a photomultiplier tube (PMT, Hamamatsu R5070A, active diameter 21 mm), depending on the power of the received signal: for wood samples with a low transmission, the PMT is used due to its suitability for light with very low intensity. The detector is placed directly in contact with the sample surface to maximise light throughput. Due to the scattering and absorption properties of the sample,
the amount of light reaching the active area of the detector is small and the photo-current needs to be amplified by a trans-impedance amplifier [TIA (Femto, Berlin, Germany), Femto DLPCA-208]; the voltage signal from the TIA is fed to the same DAQ board used for controlling the laser drivers; the sampling rate is set to 400 kHz and data are stored in the computer memory after an adjustable averaging time. The lock-in procedure needed to extract the gas signature from the recorded signal is performed via software with a routine written in Matlab (MathWorks, Natick, Massachusetts, USA).

TRS
The set-up for TRS is shown together with GASMAS in Figure 1 and is constituted by a broadband system described in detail elsewhere. Briefly, the source is a supercontinuum fibre laser [NKT Photonics, (Birkerød, Denmark) SuperK Extreme] emitting pulsed white light radiation over the spectral range 450–1750 nm with an overall power of 5 W. Typical pulse duration is in the order of tens of picoseconds, the repetition rate is adjustable between 2 MHz and 80 MHz and, for these measurements, it was kept at 80 MHz. A beam expander [Thorlabs, (Newtown, New Jersey, USA) BE04R] is used to reduce the beam divergence, then the white light is dispersed by an F2-glass Pellin–Broca prism (Bernhard Halle Nachf., Berlin, Germany) and the wavelength selected is focused onto an adjustable slit to achieve better spectral selection. Light is then coupled into a 100 µm core graded-index optical fibre and is subsequently injected into the sample. Power levels at the sample can be controlled by means of a motorised, circularly variable, neutral-density filter placed in front of the fibre. Diffused light is collected in transmittance geometry on the opposite side with respect to the injection point using a 1 mm core multimodal step-index fibre and it is separated into two beams by a dichroic mirror [Thorlabs, DMLP900] with a cut-off wavelength around 930 nm. Wavelengths shorter than 930 nm are sent to a Hybrid detector [Becker and Hickl, (Berlin, Germany) HPM-100-50], whereas wavelengths in the range 930–1200 nm are coupled to a photomultiplier tube [Hamamatsu, H10330A-25]. The electronic signals arising from the detectors are connected to two different time-correlated single-photon counting (TCSPC) boards (Becker and Hickl, SPC-130) together with the synchronisation signal from the laser. The system is completely automated for data acquisition, wavelength selection and power attenuation by means of custom software written in C language using the LabWindows-CVI environment (National Instrument, USA).

Sample preparation
The wood samples we analysed are made of spruce (Picea abies), from the softwoods family. In total, 24 rectangular samples of 15 mm and 7 mm thickness were cut in three different orientations of the wood fibres, as reported in Figure 2: the alignment of the wood vessels with respect to the optical fibres were parallel (P), tangential (T) or radial (R).

For the assessment of the moisture content of wood, 7 mm pieces of spruce in different orientations were analysed. The wood pieces were conditioned at different RH (relative humidity) values achieved by placing the samples in plastic boxes containing supersaturated solutions of water and different soluble salts. Magnesium chloride was used to achieve an RH of 33%, calcium nitrate for an RH of 50%, sodium chloride for an RH of 75%, potassium chloride for an RH of 84%, potassium nitrate for an RH of 95% RH and beads of silica gel for an RH of 12%. The samples were measured when they reached approximately the equilibrium with the artificial atmospheres thus created.

Measurement procedures
Transmission geometry was used both for TRS and GASMAS measurements.

For the measurement of gas permeability, the samples were conditioned in an oxygen atmosphere inside a plastic enclosure prior to the measurements performed in ambient air. During analysis in air, wood samples exchanged oxygen with the environment [21% oxygen] and this exchange was monitored continuously for hours.

For the static assessment of moisture content with GASMAS, we measured the samples at three different points and for each point three measurements were taken.

To dynamically follow the changes in gas content and in the optical properties of wood following a change in RH, we
followed absorption (12%–84% RH) or desorption (84%–12%) of moisture in the samples.

**Data analysis**

**GASMAS**

For monitoring the oxygen release in wood samples using the GASMAS technique, a sliding average of the signal was applied with a temporal window related to the rate of the gas exchange. In particular, at the beginning of the experiment, when the gas diffusion is more rapid, the temporal window was set initially to 10 s for approximately the first 20 min. Following this, a window of 20 s was applied for approximately 15 min and then it was set to 100 s.

For the assessment of the moisture content of wood, both statically and dynamically, the results obtained were normalised to the measured thickness of the samples, thus they are not expressed in mm as is usual for $L_{eq}$ values but in arbitrary units.

**TRS**

To retrieve the absorption and reduced scattering coefficients, $\mu_a$ and $\mu'_s$, for each wavelength, the time-resolved curves were fitted to an analytical solution of the diffusion approximation to the radiative transfer equation, applying extrapolated boundary conditions for a laterally-infinite homogeneous slab. The theoretical curve was first convolved with the instrumental response function of the system, which takes into account the temporal width of the light pulse, fibre dispersion and the finite full-width at half maximum (FWHM) of the detector response; then, a Levenberg–Marquardt optimisation algorithm was applied to retrieve the optical properties.

For wood, the reduced scattering coefficient $\mu'_s$ is constant over the spectral range: thus, to strengthen the fit, we performed an initial fit to recover $\mu'_s$ and $\mu_a$; the average value of the scattering spectrum was then fixed during a second analysis in which only the absorption coefficient was set as a free fitting parameter.

To determine the moisture content of wood, we averaged the optical properties recovered from samples stored at the same RH with the same fibre orientation with respect to the optical probes.

**Results**

**Bulk optical properties**

Previous work has demonstrated the dependence of scattering on the orientation of the wood fibres and of absorption on the species of wood analysed but, in the past, the analysis was limited to the wavelength range up to 1100 nm. In this work, we have explored, for the first time, an extended wavelength region, reaching up to 1200 nm.

Figure 3 shows the absorption spectra of two samples of spruce. As can be seen, the spectral extension in the infrared allows us to better investigate the wavelength region around 1100 nm; this area is particularly interesting, since the absorption of wood has a minimum and the absorption of lignin and extractives is close to 0.25,45 hence, radiation can penetrate more deeply into the material and the sensitivity to the presence of water and cellulose increases. In contrast, around 850 nm, where there is another minimum in the wood absorption spectrum, the absorption of lignin and extractives is higher.

Since we are using a time-resolved technique, the absorption is independent of the orientation of the wood fibres with respect to the optical probe,25 as shown by Figure 3. This is important, since it implies that we do not need to control how the wood is cut to extract spectral information.

Also reported in the figure are the scattering spectra which are flat. It is worth noting that measurements at only a few selected wavelengths allow the extraction of scattering information. However, unlike the absorption spectrum, the scattering coefficient is strongly influenced by the configuration of the wood fibres: the $R$ configuration yields higher scattering values, while the scattering retrieved for the $P$ sample is lower. The spectra of the reduced scattering coefficient reported in Figure 3 are those obtained just after the first initial fit, i.e. before fixing the scattering to its average value for fitting only the absorption.

**Porosity and gas permeability**

The equivalent pathlength depends on both the gas concentration and on the distance travelled by photons inside the gaseous part. This information could be used for monitoring changes in wood and for determining the porosity of samples.

Figure 4 shows the values of the oxygen $L_{eq}$ plotted as a function of time during measurements of the loss of oxygen from a sample of spruce. For comparison, we also report the results obtained for a sample of pine ($Pinus sylvestris$). The density of the two samples is 0.50 g cm$^{-3}$ for the spruce and...
0.47 g cm\(^{-3}\) for the pine, respectively. To better display the decrease in the concentration of oxygen inside the samples after they have been re-exposed to ambient air, only the first 7.5 h over an overall measurement time of about 17 h are shown.

As seen in this logarithmic plot, there are great differences in the temporal behaviour of the release of the excess oxygen situated in the pores of the wood. The oxygen in the pine is lost very rapidly compared to what happens in spruce. The spruce has a quite linear slope (in this logarithmic scale), suggesting a fairly uniform diffusion constant. Both curves have been normalised to their maximum value since the amount of gas the light can probe is influenced by wood scattering properties: the higher the scattering, the more the light is diffused inside the material and the more it can probe the gas entrapped in the pores, because of the increased light path length.

The dynamic changes in oxygen \(L_{eq}\) could be related to the permeability of the samples and to the extent to which the capillaries are interconnected among themselves and with the external environment. The first time constant is faster for the pine and slower for the spruce, both of which have similar densities (of about 0.5 g cm\(^{-3}\)). This difference might arise because gas diffuses more rapidly through the coarser structures in the pine sample.\(^{35}\)

As the time passes and the number of averaged scans increases, the oxygen signal decreases and the curves become noisier. On the other hand, the dynamic changes are rapid at the beginning and few data points are recorded immediately after the environmental change: for this reason, the curves have been fitted with a bi-exponential function excluding the first minute.

**Moisture content**

Figure 5 reports the absorption coefficients of wood samples at 975 nm, 990 nm, 1100 nm, 1170 nm and 1185 nm, kept in controlled relative humidity environments. Results are displayed as a function of wood RH and a linear trend-line is also added to the graphs. The absorption increases for increasing RH values, while the scattering coefficient is always uncorrelated with the RH of the samples.

As shown in the graphs, we obtained a linear trend; the better results were retrieved in the new wavelength range explored, beyond 1100 nm.

While with time-resolved techniques we are sensitive only to liquid water, with GASMAS we are able to detect a change in the water vapour content.\(^{36}\) stemming, for instance, from a different humidity in the environment: exactly the same samples as those considered above have been tested and the results are reported in Figure 6. We plotted the average values for the \(L_{eq}\) for oxygen and water vapour; the error bars represent the data standard deviation. The water vapour \(L_{eq}\) increases with the RH both for parallel and perpendicular fibre configurations. A tendency towards saturation for the
highest RH values can be noted for all the cases examined. The oxygen $L_{eq}$ values are almost independent of the RH.

The wood fibre configuration does not influence the general trend of the $L_{eq}$ with respect to increasing RH but, in the case of a perpendicular cut, the values retrieved are higher. This could be attributed to the fact that, in this configuration, light is able to better probe the gases trapped inside since it experiences a higher scattering and, thus, travels longer distances.

We dynamically followed the change in moisture content in wood samples. In Figure 7, the absorption coefficients for 970 nm, 990 nm, 1150 nm, 1170 nm and 1180 nm are reported as a function of time. We can see that, when the sample is placed in a higher RH, the absorption gradually increases for all the selected wavelengths whereas, when the samples go from a high RH environment to a low level RH, the absorption decreases.

With GASMAS we obtained the same results, as shown in Figure 8: the oxygen level in the wood is practically unchanged when wood passes from an RH environment to the other.

**Discussion**

From the measurements of the optical properties of wood, it is possible to obtain both the absorption and the scattering spectra of the samples separately. In the absorption spectra, we can recognise the presence of extractives in the steep rising edge towards shorter wavelengths, the combined effect of water and cellulose identifiable with the broad peak around 1000 nm and a major peak around 1200 nm. These characteristics could allow us to gather valuable information, for example, on the state of preservation of the wood, strictly connected to cellulose, and its moisture content, as demonstrated by the experiments presented in this paper.

The advantages in using an extended IR range are clear, as it is possible to assess materials which have a stronger absorption in the visible range and to investigate a region of the spectrum where the main contribution comes mostly from cellulose and water.

GASMAS static measurements on natural samples, or on samples conditioned at different RH values, are particularly interesting, since the results can be related both to different
porosity and to gas content. It is not trivial to disentangle these two contributions, since the $L_{eq}$ depends both on the gas concentration and on the path travelled by photons inside the gas-filled pores.

It is also possible to retrieve information on wood porosity by looking at oxygen behaviour in a dynamic situation. In fact, gas diffusion is different according to the dimensions of pores and their inter-connections. The first dynamic is actually faster for pine, probably because gas spreads faster through its coarser structures.

Changes in relative humidity can be assessed with both GASMAS and TRS. By increasing the MC, the water in the pores exceeds the fibre saturation point, thus condensing, and this fact results in an increase in the bound water content and in the consequent increase in the absorption coefficient extracted from TRS.

Similarly, GASMAS reveals a trend towards saturation for the highest RH values; in fact, when the RH starts to increase, the water vapour content increases as well but, at 75% RH, the signal from the water vapour appears to diminish because it condenses or transforms itself into bound water. This type of water is detectable with time-resolved techniques, as has already been proved.

Conclusions

By combining measurements and results obtained using these two optical techniques, it is possible to extract a wealth of information on wood in a non-destructive way. GASMAS assesses the gases enclosed in the hollow spaces of the solid wood matrix, whereas TRS is sensitive to the composition of the solid matrix itself. By combining the techniques, we can gather a more detailed knowledge of wood and its properties.

In particular, the parameters we recover are sensitive to:

i. the chemical composition of the sample, for example, wood moisture content ($\mu_a$);

ii. wood internal structure and anisotropy ($\mu'_s$);

iii. gas porosity and gas permeability, RH ($L_{eq}$).

Thus, these parameters of the wood could be used to monitor the physical response of wood to treatments. Moreover, these techniques could be particularly helpful for the dynamic assessment of the physical properties of wood (for example, in cultural heritage studies, the analysis of wood degradation).

Indeed, the use of a system for combined analysis of TRS and GASMAS could also prove valuable for the study of waterlogged wood, providing information on wood composition and structural information which are crucial to study the state of wood conservation.

For the first time, using the time-resolved technique, we systematically explored the wavelength range beyond 1100 nm: the spectral extension may prove particularly useful for the development of a portable system operating at few discrete wavelengths of interest, which could be selected in this new range.

Future work will focus on quantifying the wood constituents, such as cellulose, lignin and extractives, exploiting the absorption spectra of wood and of the pure constituents. While in this work we have worked in transmission, previous studies have demonstrated that TRS can investigate the material down to a few centimetres beneath the surface. Moreover, the adoption of a single-fibre approach, exploiting a time-gated acquisition, could permit investigation even further inside the medium with a minimally invasive probe.

In this framework, TRS may prove useful for recovering that part of the pathlength spent by photons in gas; for this purpose, we are working on the development of a theoretical model.

Further work will be aimed at the analysis of wood components and to correlate the data obtained from TRS and GASMAS with results obtained from destructive techniques.

Another future aim is to make the system entirely portable for applications in the field and to employ more powerful lasers to increase the signal-to-noise ratio.
Acknowledgements

The research leading to these results has received funding from the Ministero dell’Istruzione, dell’Università e della Ricerca of the Italian Republic and by the Swedish Research Council under the “Executive Programme for Scientific and Technological Cooperation between Italy and Sweden” and from LASERLAB-EUROPE (grant number 284464, EC, FP7).

References

24. E. Molteni, D. Contini, M. Caffini, G. Baselli, L. Spinelli, R. Cubeddu, S. Cerutti, A.M. Bianchi and A. Torricelli,
Diffuse Optical Techniques Applied to Wood Characterisation


