Time-resolved near infrared spectroscopy for wood as a discontinuous body with anisotropic cellular structure

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Introduction

The chemical composition of biological material like wood can be determined in a straightforward way if a sample is pulverised uniformly to reduce the profound influence of particle size on the near infrared (NIR) analysis. However, wood is required to maintain specified shapes in its applications. Therefore, a complete analysis of wood calls for the development of a non-traditional NIR technique for the solid sample, capable of analysing the physical state of a biological material having a cellular structure as well as the chemical composition. Such a truly non-destructive measurement system is very desirable to make an article with high quality and reliability, without waste of the raw material, time and energy.

The behaviour of NIR diffusely reflected or transmitted light, radiated from a cellular structural material, is affected directly by the arrangement and orientation of cells.[1–3] We constructed the optical characteristics models to provide a background and framework for developing a non-destructive measurement system applicable to the biological materials.[1,2,4,5] As a result, such a non-traditional application of NIR made it possible to analyse both physical conditions and chemical components of biological material retaining its cellular structure.[6,7] In a series of experiments, a commercial spectrophotometer with low output power[1,2,4–7] and a semiconductor NIR laser system with specified wavelengths have been employed to find the fundamental nature of the light-absorbing or -scattering process in a sample. By using such systems, we could successfully acquire the useful information about the wood samples, but their thickness was restricted to less than a few millimeters.

To make an advanced step forward in this investigation, the construction of a new measurement system, by which some inner information for a wood sample of large size could be detected exactly, was essential. Thus, an optical measurement system, which was composed of a parametric tunable laser and a near infrared photoelectric multiplier, was introduced to accomplish this purpose at the viewpoint of time-resolved spectroscopy. This system combines the best features of the spectrophotometer and the laser beam, and more advantageously, the time-resolved profile of transmitted output power can be measured sensitively in nanoseconds. In this study, the effects of the dimension of the sample, wavelength of the laser beam and detecting position of light on the time-resolved profile were investigated in detail as follows.

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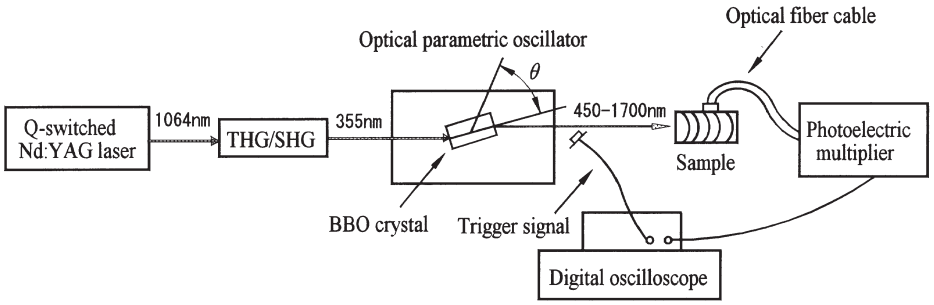


Figure 1. Outline of measuring system.

Experimental

Measuring apparatus

The outline of the measuring system used is illustrated in Figure 1. This system consists of the exciter laser (Surelite I-10, Continuum Electro-Optics Inc.), the parametric tunable laser (X2852, HAMAMATSU Photonics Co.), the near-infrared photoelectric multiplier (R5509-71, HAMAMATSU Photonics Co.) and the digital oscilloscope (Model 9362, LeCroy Co.). A Q-switched Nd: YAG laser, having an output energy of 60 mJ pulse^{-1} at 335 nm, a pulse width of 5 ns, a pulse repetition frequency of 10 Hz and a beam diameter of 6 mm, was employed as the exciter laser. The wavelength of the pulsed laser was tuned from 450 nm to 1700 nm by the optical parametric oscillation of a BBO (β-BaB_2O_4) crystal[8,9]. The output power of the tuned laser beam ranged from 1 mJ pulse^{-1} (at 420 nm) to 10 mJ pulse^{-1} (at 1800 nm). The transmitted output power from the sample was measured by an NIR photoelectric multiplier, which was cooled to –80°C, through an optical fibre cable having a diameter of 7 mm.

Samples

The wood sample used was from a species called Western Hemlock that had an oven-dried density of 0.47 g cm^{-3}, annual ring width of 0.95 mm, late wood percentage of 20% and moisture content of 8.7%.

Experiment

Specimens having various dimensions were used to examine the combined effects of the dimension of the sample, the wavelength of the laser beam and the detecting position of light on the time resolved profile. The optical fibre cable was directly in contact with the wood sample. The sample was concealed with aluminum foil to shut off the stray light. Furthermore, the sample, the cooling box containing the near-infrared photoelectric multiplier and the optical fibre cable were also covered with black cloth. The sampling time and the average number of the transmitted output power were 100 ns and 300 times, respectively.

Results

Effect of sample thickness on transmitted output power

First, we confirmed the measurable sample thickness using this system. The sample of 35 mm in thickness, 130 mm in width and 35 mm in length was prepared. The edge grain, which is found at the

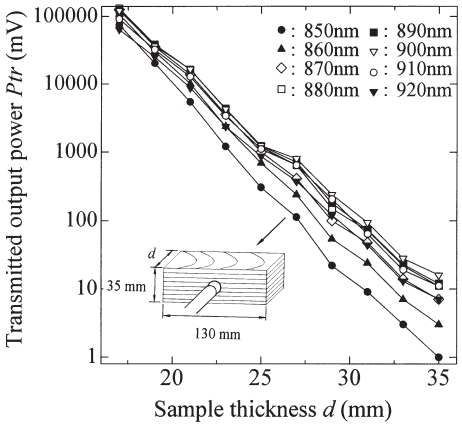
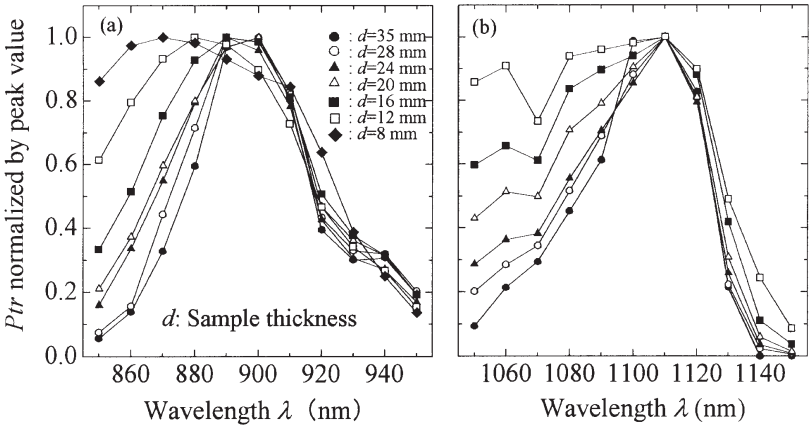


Figure 2. Relationship between sample thickness and transmitted output power for various wavelengths.

vertical section for radial direction of annual rings, was irradiated with the laser beam and the transmitted output power, *Ptr*, was detected at the opposite side of them. Then, time-resolved profiles were measured ten times for every 2 mm decrease in thickness. The wavelength of laser beam, λ, was tuned from 850 nm to 920 nm and from 1050 nm to 1150 nm.

Figure 2 shows the relationship between the sample thickness, *d* and *Ptr*. When $d < 23$ mm, the intensity of the input pulse was reduced by some neutral density filters to keep away from carrying a large voltage to an NIR photoelectric multiplier. As shown from this figure, *Ptr* could be detected even at $d = 35$ mm. The optical penetrating length has a striking improvement as compared to the previous measuring system.[1–7] This figure shows that *Ptr* increases rapidly as *d* decreases. However, the variations of *Ptr* with *d* differ slightly according to . Figure 3 shows the spectral curves of *Ptr* normalised by the peak value of each spectrum at a specified sample thickness. When 850 nm $\leq\lambda\leq$950 nm [Figure 3(a)], the wavelength indicating the peak value of transmitted output power, λ_P, is shifted to a shorter wavelength as *d* decreases. It is known from this figure that the spectrum itself also changes with *d*. The similar spectral curves in the range of 1050 nm $\leq\lambda\leq$50 nm are shown in Figure 3(b). In this case, λ_P (= 1110 nm) did not vary with *d* and another peak of λ_P = 1060 nm appeared as *d* decreased. Such phenomena are directly related to the wavelength dependency of the scattering and absorption coefficients, whereas the output power of the tuned laser beam varies with the wavelength. In this way, it revealed that the light propagation in a cellular structural material varied characteristically with sample thickness and the wavelength of the laser beam. To clarify such results further, it will be important



3. Spectral curves of transmitted output power.

to distinguish the light scattering at the inner cell wall from that caused by the multiple specular reflection between cells.

Variation of transmitted output power with detecting position of light

Wood (as well as other biological material) is commonly used in applications where both the cellular structure and the original physical shape are retained.[10] Thereby, we must focus on the circumstance of transmitted output power at various detecting positions of light in consideration of the arrangement and orientation of cells. *Ptr* at some specified detecting positions of light were measured by varying the width of sample. The sample of 35 mm in thickness, 145 mm in width and 45 mm in length was prepared and its width was decreased at a step of 20 mm by sawing. The flat grain, which was found at the vertical section for tangential direction of annual rings, was irradiated with the laser beam.

The effect of the sample width, *W*, on *Ptr* is shown in Figure 4.When *Ptr* is measured at flat grain (indicated as squares) or edge grain (indicated as triangles), *W* has little effect on them. On the other hand, *Ptr* at the cross-section (indicated as circles) increases rapidly as *W* decreases. Such results prove that the laser beam propagates preferentially along the longitudinal direction of the lumen of tracheids.

Time-resolved profile of wood sample

As mentioned above, we have analysed the variation of the transmitted output power with the dimension of the sample and detection position of light. Next, the time resolved profile of wood sample itself was examined in detail. At this stage, each profile was normalised by the peak value of transmitted output power to compare the variation of profile with the sample thickness, *d*, or the wavelength of the incident laser beam, λ.

The normalised time profiles of wood sample at various sample thickness are shown in Figure 5. The sample (30 mm in thickness, 130 mm in width, 35 mm in length) was prepared and the planing-machine decreased its thickness. The edge grain was irradiated with the laser beam at 880 nm and the transmitted output power was detected at the opposite side of it. This figure shows that the time-resolved profile varies characteristically with *d*. The time delay of the laser beam, caused by passing through the sample, *Ttr* (the difference between the peak time without the sample and with a sample) decreases as *d* decreases. Furthermore, we can also find that the profile broadens as *d* increases.

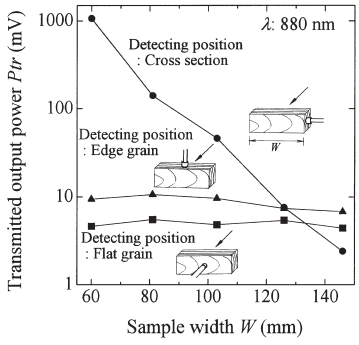


Figure 4. Effect of sample width on transmitted output power.

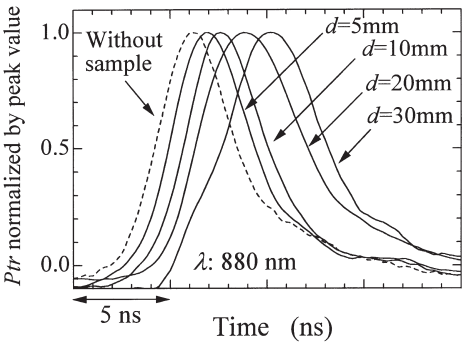


Figure 5. Normalised time resolved profiles of wood sample.

The variation of *Ttr* with the combination of d, λ and the detecting position of light is shown in Figure 6. The dimension of a sample was 35 mm in thickness, 130 mm in width and 35 mm in length. The edge grain was irradiated with the laser beam at various wavelengths. In this figure, black marks and white marks indicate *Ttr* detected at the edge grain and the cross section, respectively. In the range of 800 nm to 1370 nm, where the scattering coefficient *S* holds some value and the absorption coefficient *K* amounts to about 0,[1,4,5] *Ttr* detected at the edge grain is so long that an increase of 10 mm in the thickness of a sample will increase *Ttr* by 1.2 ns. This means that the optical path length through a sample may account for 25 times as large as that through the air, in consideration of the refractive index of wood (about 1.5). In the range of 1370 nm to 1700 nm, where *S* decreases gradually with increasing wavelength and *K* may vary with the characteristics for each wavelength,[1,4,5] *Ttr* detected at the edge grain is shorter compared with that in the range of 800 nm to 1370 nm. On the other hand, *Ttr* detected at the cross section is hardly affected by the sample thickness.

These results suggest that the laser beam in the cellular structural material is multiply scattered.

Dependence of time-resolved profile on wavelength

The time delay of the laser beam, caused by passing through the sample, varied characteristically with the combination of the dimension of the sample, the wavelength of the laser beam and the detecting position of light.

To investigate such circumstances of time-resolved spectroscopy more fully, we must examine the variation of the time-resolved profile with λ. A sample of 18 mm in thickness, 40 mm in width and 35 mm in length was prepared. The edge grain of the sample was irradiated with the laser beam at various wavelengths and *Ptr* was detected at the opposite side of the sample (edge grain) or the cross-section, perpendicular to the irradiated surface. λ was tuned from 500 nm to 1650 nm at a step width of 50 nm.

Figure 7 shows the wavelength dependence of the time delay of the laser beam caused by passing through the sample, *Ttr*. As mentioned above, it corresponds to the difference between the peak time without the sample and with a sample. In this figure, black circles and white circles indicate *Ttr* detected at the edge grain and the cross section, respectively. *Ttr* decreases as λ increases regardless of the detecting position of light, while the fluctuation of *Ttr* with λ may reflect the absorbing or scattering condition of a wood sample.

It has been found previously that the behaviour of diffusely-reflected light in cellular structural material fell into three categories according to the characteristics of *S* and *K* (Band I: 800–1400 nm,

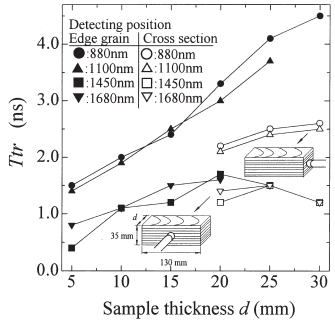


Figure 6. Variation of time delay of laser beam passing through the sample, *Ttr*.

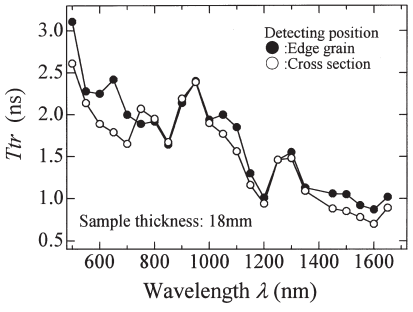


Figure 7. Wavelength dependence of time delay of laser beam passing through the sample, *Ttr*.

Band II: 1400–1860 nm, Band III: 1860–2500 nm).[1,4] These classifications may also be applicable to the time resolved profile because it will be governed by *Ttr* or half width of time-resolved profile.

Conclusion

In this study, the newly constructed optical measurement system, which was composed of a parametric tunable laser and a near-infrared photoelectric multiplier, was introduced and the optical characteristics of cellular structural material keeping a large size were clarified by means of time-resolved spectroscopy. The transmitted output power from the wood (Western Hemlock) was investigated in detail.

The time-resolved profile varied characteristically with the combination of the dimension of sample, the wavelength of the laser beam and the detecting position of light. Such results are directly related to the cellular structure of the wood samples. It became clear that the laser beam propagated preferentially along the longitudinal direction of the lumen of the tracheids.

In the range of 800 nm to 1370 nm, where the scattering coefficient *S* holds a some value and the absorption coefficient *K* amounts to about 0, the time required for the laser beam to pass through the sample, *Ttr*, is so long that an increase of 10 mm in the thickness of a sample will increase *Ttr* by 1.2 ns. In the range of 1370 nm to 1700 nm, where *S* decreases gradually with increasing wavelength and *K* may vary with the characteristics of absorption for each wavelength, *Ttr* is shorter compared to that in the range of 800 nm to 1370 nm. These results suggest that the laser beam in the cellular structural material is multiply scattered.

Ttr varied characteristically with the wavelength of the laser beam. Such results involving an alternate action meant that the time resolved profile is governed directly by the trend of *S* and *K*. Thus, our optical characteristics models, which express the behaviour of light propagation in the cellular structural material, taking into consideration *S* and *K*, are supported experimentally by time-resolved spectroscopy.

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