Application of near infrared spectroscopy to light-irradiated wood

S. Tsuchikawa,^a K. Inoue^a and K. Mitsui^b

^aGraduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601, Japan

^bGifu Preferectual Human Life Technology Research Institute, 1554, Yamada Takayama Gifu 506-0058, Japan

Introduction

A colour of material is generally defined by the tristimulus value in the visible range (i.e.; 380-780 nm), in which the irritability to light of human eyes is considered. On the other hand, the reflectance or transmittance spectra in the infrared range give us the useful information about the chemical structure of organic compounds. As a change in colour of the wood material arising from light-irradiation is closely related to the change in its physicochemical structure, some researchers reported the relationship between the tristimulus values and the infrared spectra.^{1,2} Such basic researches may be available to materialize a new colouring method of wood without something paints³. However, the infrared measurement requires some limitation for a sample preparation, so that another spectroscopic method is desirable to monitor successfully the change in its colour with the light irradiation. In this study, the applicability of NIR spectroscopy to the light-irradiated wood was examined to accomplish the purpose described above.

Materials and method

Materials

Wood species used were Japanese cypress (*Chamaecyparis obutusa*), Japanese cedar (*Cryptomeria japonica*), Spruce (*Picea sitchensis*), Japanese beech (*Fagus crenata*), and Hackberry (*Celtis occidentalis*). The samples were stored before and between the light-irradiation treatments in a desiccator over H_2SO_4 at room temperature. The dimension of each sample was 50 mm in width, 50 mm in length, and 10 mm in thickness. The light-irradiations were applied to the widelong surface (i.e.; flat grain). The three samples for each wood species were prepared. During experiment periods, no significant changes in measurement values were observed. The following results are therefore presented as the average values of three measurements.

Method

Samples were irradiated with ultra-violet lamp (wavelength: 254 nm, irradiance: 1013 μ Wcm⁻²) for up to 300 minuets. Light-irradiation time was defined as t_{ir} .

The colour of sample was measured with a colorimeter (NR3000: Nippon Denshoku Industries Co., Ltd). The sensor head was 10 mm in diameter. Measurements were made using a D₆₅ illuminant and a 2-degree standard observer. The CIELAB colour parameter (L^* , a^* and b^*) were computed, and the difference in the L^* (i.e. ΔL^*) and chroma coordinates (i.e. Δa^* and Δb^*) were calculated using the following formulae.

$$\Delta L^* = L^*_{\ t} - L_s^* \tag{1}$$

$$\Delta a^* = a^*_{\ t} - a_s^* \tag{2}$$

$$\Delta b^* = b^*_{\ t} - b_s^* \tag{3}$$

where the subscripts *t* and *s* indicate the measured value at t_{ir} and control reference, respectively. In this study, the measured colours before light-irradiation ($t_{ir}=0$) for each sample were employed as the control reference.

NIR spectra were measured with a spectrophotometer (InfraAlyzer 500: Bran+Luebbe Co.). The wavelength of incident light varied from 1100 nm to 2500 nm at a step of 2 nm.

Results and discussion

Figure 1 shows the variation of ΔL^* , Δa^* and Δb^* of spruce and Japanese beech with lightirradiation time t_{ir} , respectively. Δb^* increased as t_{ir} increased independent of wood species, whereas ΔL^* decreased with the increment of t_{ir} . Such phenomena mean that the sample have yellowed by the light-irradiation. The variation of Δa^* differed with wood species.

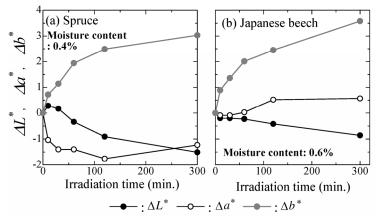


Figure 1. Variation of ΔL^* , Δa^* and Δb^* of spruce and Japanese beech with light-irradiation time t_{μ} .

Figure 2 shows the second derivative spectra of absorbances $d^2 A/d\lambda^2$ for spruce and Japanese beech, respectively. The absorption band at λ =1672 nm and 1712 nm are assigned to the second overtone of CH stretching vibration in aromatic skeletal and them in furanose (or pyranose), respectively. The lignin and the holocellulose (mainly composed of cellulose and hemicellulose) in wood contain aromatic skeletal and furanose (or pyranose), respectively, whereas the ratio of them depends on wood species. Absolute values of both absorption bands decreased as t_{ir} increased. Therefore, they may be useful index for the light-irradiation condition of wood sample.

Figure 3 shows the ratios of $d^2 A/d\lambda^2$ after irradiation of t_{ir} to them before irradiation of $t_{ir}=0$, R_{λ} . That is,

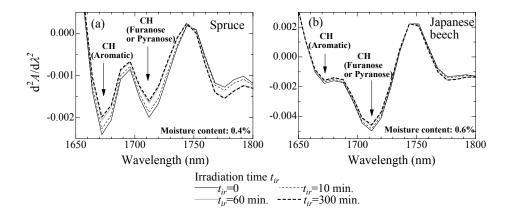


Figure 2. Second derivative spectra of absorbances for spruce and Japanese beech.

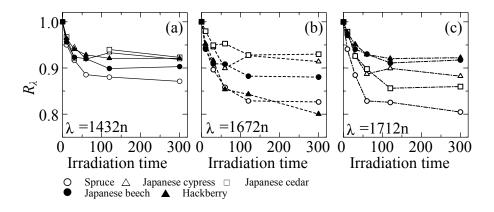


Figure 3. Variation of the ratios of $d^2 A/d\lambda^2$ after irradiation to those before irradiation, R_{λ} , with light-irradiation time

$$R_{\lambda} = \left[\left(\frac{d^2 A}{d \lambda^2} \right)_{t_{ir}} / \left(\frac{d^2 A}{d \lambda^2} \right)_{t_{ir}=0} \right]$$
(4)

 R_{λ} decreased rapidly with increment of t_{ir} , and approached the constant value. In either absorption band, the change of R_{λ} up to $t_{ir} = 50$ min was remarkable. In the case of $\lambda = 1432$ nm, which is the absorption band of OH groups in amorphous region mainly concerning to cellulose, we could not find the obvious difference in the trend of R_{1432nm} between wood species. On the other

hand, the trend of R_{1672nm} varied with wood species. This means that the decrease of lignin by lightirradiation varies with wood species. R_{1712nm} also shows same tendency, however, we could find the difference in characteristics between softwood (white mark) and hardwood (black mark). Such results may be associated with the difference in the constituents of hemicellulose between softwood and hardwood.

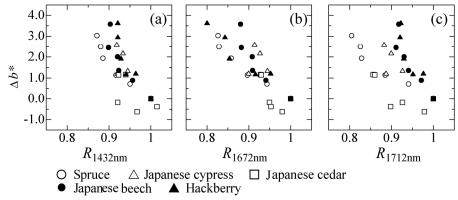


Figure 4. Relationships between R_{λ} at 1432nm, 1672nm, and 1784 nm and colour parameter (Δb^*) on each wood species.

Figure 4 shows the relationships between R_{λ} at 1432 nm, 1672 nm, and 1712 nm and colour parameter (Δb^*) on each wood species, respectively. Especially in the case of λ =1672 nm, we can find the significant correlation between R_{1672nm} and Δb^* independent of wood species. In the case of R_{1712nm} , we could find two groups of softwoods and hardwoods. The trend of CH in aromatic skeletal with the irradiation time, which is closely related to a change in colour of wood, is not inconsistent with the previous report^{1,4)}. However, these results directly mean that the light absorption of CH in aromatic skeletal due to the lignin and CH in furanose (or pyranose) due to mainly hemicellulose decrease as the increment of yellowing of the wood sample.

In this way, NIR spectroscopy becomes a useful method for the detection of a change in chemical structure of wood with light-irradiation. It is practical and useful for materialisation of a new colouring method of wood.

Acknowledgements

This research was supported by a grant from the New Energy and Industrial Technology Development Organization, of Japan.

References

- 1. L. Tolvaj and O. Faix, Holzforschung 49, 397 (1995).
- 2. B.S. Park, T. Furuno and T. Uehara, Mokuzai Gakkaishi 42, 1 (1996).
- 3. K. Mitsui, H. Takada, M. Sugiyama and R. Hasegawa, *Holzforschung* 55, 601 (2001).
- 4. E. Barta, L. Tolvaj, T. Nagy, S. Szatmari, O. Berkesi and G. Papp, Drev Vysk 44, 13 (1999).