Non-destructive NIR spectra measurement of dendrochronologically dated antique wood

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Introduction

Wood has played a major role in ancient civilizations throughout human history. It is, without any doubt, of importance to determine the absolute age and some properties of archaeological wood in order to understand the cultural or ethnological aspects of extinct civilizations. NIR spectroscopy has shown its significant potential to reveal the mechanical, physical and chemical information of wood retaining its cell wall structure.[1–7]

In the recent advances in the field of age determination, high-precision dating has been enthusiastically investigated, especially for the development of age calibration by combinations of some dating techniques.[8] Dendrochronology and radiocarbon dating are the most powerful tools in archaeological studies. The former, or tree ring dating, has the highest resolution since tree rings accumulate annual records of a periodic biological process along the calendar year;[9,10] while the latter can give accurate ages of any carbonaceous materials. Both of the two are destructive, since physical and/or chemical modification is usually required. Non-destructive feature of photometric measurements is fascinating for analysing cultural properties. FT-IR and Raman spectroscopy has been mainly applied to such materials. On the other hand, the potential of NIRS has not been investigated in the context of archaeological or chronological application.

In this study, we present the NIR spectra for modern and sub-fossil wood samples. The species of the samples is hinoki cypress (*Chamaecyparis obtusa*). Hinoki has been one of the most important, commonly used species as materials for construction (temples, shrines, and castles) and works of religious (Buddhism) art in Japan. All of the samples were dendrochronologically dated and some of them were later checked by radiocarbon dating with an accelerator mass spectrometer. Hence, the absolute ages of the samples are precisely determined. We investigated the temporal decay of antique wood by NIRS measurement. NIRS application to archaeological dating was also examined.

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Materials and methods

Samples

Sample trees were collected from a site at Kiso region, Nagano Prefecture, Japan. Disks were cut transversally out of stems of both living and buried dead trees with a chain saw. The tree species of the latter samples was identified by microscopic observation. Only Hinoki cypress was selected for the measurements of ring widths and NIR spectra. Buried dead trees were used instead of wood from cultural properties, since it is generally impossible to have permission of taking samples and naturally dead trees are abundantly available.

Age determination of the sample trees

Ring widths of the samples were measured for two or more radial directions in a single tree by a specially designed system (a single-axis stage with a linear encoder attached and a stereo-microscope). The accuracy of the measurement is *ca* 0.001 mm.

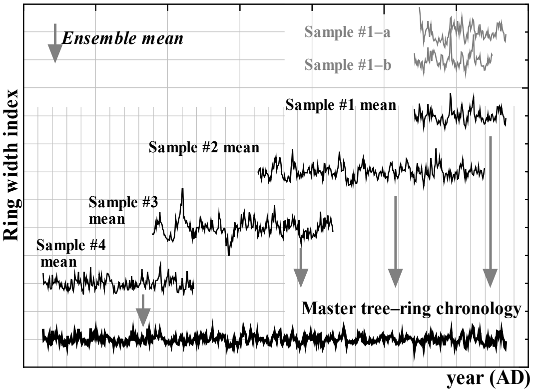

Figure 1. Building master tree ring chronology.

Figure 1 shows the schematic depiction of cross-dating and master tree ring chronology. The time-series data of ring widths displayed on the computer screen were visually compared within an each individual tree (intra-disk) and later among trees (inter-disk). This comparison to determine the dates of tree rings is called "cross-dating" or synchronization in the field of dendrochronology.[11] This is also useful for ad-hoc detection of missing, discontinuous, or false tree rings that could occasionally occur due to severe climate or air pollution. The time-series of raw ring widths was fitted to the growth curve [Equation (1)] and detrended to obtain ring width indices (in arbitrary unit) by dividing raw data by expected values [Equation (2)]:

$$\mathrm{E}[RW_t] = ae^{-kt} + b, \tag{1}$$

$$I_t = \frac{RW_t}{E[RW_t]} \tag{2}$$

where RW_t is a measured ring width at year t, E[] is an expected value, and a, k, and b are the coefficients. Intra- and inter-disk running correlation, i.e. cross correlation function (t_{lag}) was computed at the lag ranging from 0 until *ca* 25 years overlapping retained. The t-values (t_{lag}) were obtained from Equation (3) to sort out the dates when the values show more than 3.5 as the candidates of the date for the sample.

$$t_{lag} = r_{lag}\sqrt{\frac{n-2}{1-r_{lag}^2}} \tag{3}$$

where *n* is the number of tree rings overlapped between the two time-series. The candidates were visually checked visually again to verify the results of cross-dating.

The ensemble mean for thus dated and standardized time-series was computed to build the master tree ring chronology. The chronology obtained for *ca* 1300-year span covers the most important part of the Japan's history from Nara period to the modern time. The master tree ring chronology can be applied to various scientific fields, for example, absolute age determination of antique wood,[12] reconstructions of paleoclimate,[13] analysis of stand dynamics of forest eco-system[14] and so on.

Non-destructive measurement of NIR spectra

Table 1 shows the samples used for the NIR measurement. All of the samples were picked up from the members of the master tree ring chronology. The radial surface of the samples was finished with a belt sanding machine (grain sizes of 80, 400, and 600 mesh per inch, successively). The samples were stored in a uniform air condition for a week so that the moisture content was kept equivalently at air-dried state. NIR spectra were measured by a spectrophotometer (InfraAlyzer 500, Bran+Luebbe Co.) with an optical fibre cable. The wavelengths were ranging from 1100 to 2500 nm with an interval of 2 nm. In each measurement, the diffusedly reflected light was detected for the chronological centres from AD 1950 to 1750 (modern living tree) and from AD 1588 to 838 (antique wood) with an interval of 100 years. The diameter of the incident light was *ca* 1 cm, covering 10–12 tree rings for each of the date.

Table 1 Wood samples used for NIR spectra measurement.

Type	ID	Date (AD)
Modern living tree	10013a	1950
		1850
		1750
Antique wood	40135a	1588
	40083b	1438
	40071b	1333
	40151a	1238
	40126a	1138
	40136a	1038
	40017b	938
	40105c	838

Results and discussion

Change in wood properties as viewed from NIR spectra

Figure 2 shows the second derivative spectra for the wavelengths of 1650–1850 nm and 2280–2430 nm. The lines in the figure present the spectra of the modern wood dated AD 1950 (solid) and the doted and the antique wood dated AD 1438 and 1238 (dotted and dashed, respectively).
Several peaks of absorbance were found around the wavelengths of 1670, 1720, 1770, 1820, 2330, and 2380 nm. The absorption bands are characterized by the main chemical components of wood: for example, aromatic CH in lignin around 1670nm, CH in hemi-cellulose around 1720 and 2330 nm and OH in hemi-cellulose around 2380 nm.

In view of temporal change, the peak of absorption around 1670 nm (lignin) decreases and those of the rest increase in antique wood. The results suggest that decay process of antique wood progresses in relative amounts of main components of wood, since these never increase in absolute mass after trees are dead. Lignin has chemically stable property. Cellulose and hemi-cellulose are easily degraded. This agrees well with the results in the previous studies[15].

First NIR dating

Figure 3 shows the relationship between the tree-ring dates and the second derivatives of absorbance at *ca* 2380 nm. This absorption band appears due to OH in holo-cellulose that wood

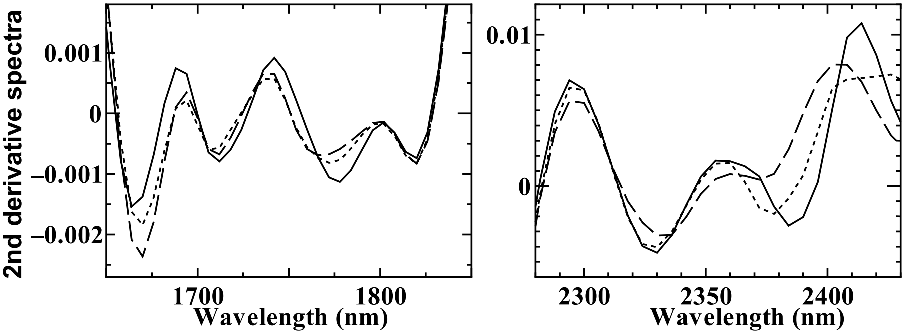

Figure 2. Temporal changes in the second derivative absorption of dendrochronologically dated wood for the wavelengths of 1650-1850 nm (left) and 2280-2430 m (right). Solid, dotted and dashed lines show the spectra at AD 1950, 1438 and 1238, respectively.

usually contains 40–50% of its mass. The correlation coefficient shows the value of –0.833 significant at 99% confidence level.

Date-absorbance calibration was made by a simple linear regression given in Equation (3):

$$T = a + bA'', \tag{3}$$

where T is an estimate of the date, A'' is the second derivative absorbance at ca. 2380 nm, and the coefficients $a(=1.240\times10^3)$ and $b(=-2.835\times10^5)$ are constant. The linear relationship thus obtained shows that the age measurement can be performed by NIR; herein, we call this method "NIR dating". This might be the first application of NIR to archaeological dating. The accuracy of NIR dating in this study is computed to be *ca* 15 years in one standard deviation, which is much less than that of *ca* 30 years or more in radiocarbon dating.

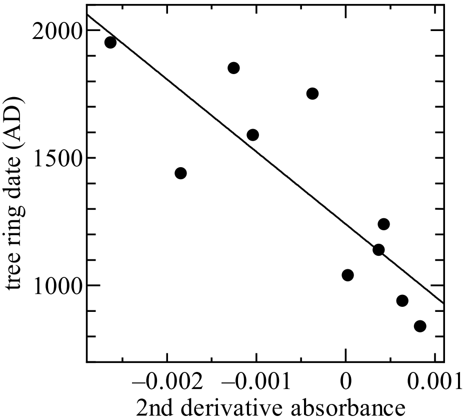

Figure 3. Relationship between tree-ring date and second derivative absorbance at ca. 2380 nm.

More data should be collected to clarify the potential of this new dating method, since the result in this study is obtained from the samples of only one tree species with limited age distribution of ca. 1300 years from the present. Multivariate statistical techniques with absorbance at some other wavelengths added would be more effective to improve the accuracy of estimation.

Conclusion

We measured NIR spectra for modern living trees and antique wood, i.e. sub-fossil trees, which were dendrochronologically dated. The NIR spectra showed typical absorption peaks as have ever revealed for the wood retaining its structure in the previous studies. Decrease of several peaks suggests the temporal changes in relative amount of chemical components of wood due to the decay process in antique wood. These results can be basic, but useful information for the conservation of cultural properties, since NIR spectroscopy has a fascinating feature, i.e. non-destructive measurement.

One interesting result we found is that the second derivative spectra around 2380 nm (CH in hemi-cellulose and OH in holo-cellulose) decrease in a linear manner against the tree ring dates. This evidence strongly implies the NIRS is applicable to the quite new technique of age determination, that is, NIR dating. It is often a time- and cost- consuming issue to determine ages by radiocarbon or some other dating methods that are usually destructive. On the other hand, non-destructive NIR dating is much less expensive, easier, and faster than other conventional methods.

At this moment, the potential of NIR dating is not fully unravelled. Some open questions are still left; for example, “can this technique determine the date relatively or absolutely”, “how long is the limitation of age measurement?” “how accurate is the measured age?” and so on. In addition, the calibration method in this study should be more sophisticated with some statistical techniques. However, even with the current result, it is obvious that NIR dating can be applied to the relative age determination of wood remnants excavated at a single site, since such materials are often excavated massively from stratified soil layers of a single ruin.

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