植生史研究

Ken Watanabe¹, Hisashi Abe^{1,*}, Yutaka Kataoka¹ and Shuichi Noshiro¹: Species separation of aging and degraded solid wood using near infrared spectroscopy

Abstract Applicability of near infrared (NIR) spectroscopy to identify species of degraded and aging solid wood was examined among species important to Japanese art history and archaeology. NIR spectra were obtained from wood blocks of five softwood species collected over the last 80 years from various sites and stored in the wood library of the Forestry and Forest Products Research Institute, Tsukuba in Japan. Partial least square (PLS) discriminant analysis was employed for the separation of three pairs of species, i.e., *Chamaecyparis obtusa* and *Torreya nucifera*, *Chamaecyparis obtusa* and *Chamaecyparis pisifera*, *Thuja standishii* and *Cryptomeria japonica*. The effects of spectral pre-processing and wavelength range were also evaluated. Under the limitation of sample volume, PLS discriminant analysis calibrated using second derivatives and wavelengths spanning 830 to 1150 nm could separate the samples into each pair of species in the 100 % accuracy. These results suggest that NIR spectroscopy combined with PLS discriminant analysis is a powerful technique for distinguishing species for degraded and aging wood nondestructively without any sample preparations.

Introduction

The identification of wood species is important not only for timber industry, but also for such purposes as ecology, art history, archeology, forensics, and customs procedures (e.g., Kaneko et al., 1998, 2003, 2010; Noshiro et al., 2002, 2007; Abe et al., 2005). A piece of wood is usually identified based on anatomical characteristics observed under a microscope. However, occasionally it is difficult to separate tree species or genera that have similar anatomical characteristics, especially for conifer species belonging to Cupressaceae and Taxodiaceae that have few distinct differences in anatomical characteristics (IAWA Committee, 2004).

In Japan, wood of Cupressaceae, Taxodiaceae, and Taxaceae were frequently used for Buddhist statues made during the 7–9th centuries AD (Kaneko et al., 1998, 2003, 2010). For the identification of the wood used for the construction of these statues, we collected small pieces of wood that were naturally removed from the statues. The samples were then identified by means of observation with a light microscope and/or a scanning electron microscope. In Japan it is prohibited to obtain samples directly from cultural property, and it was sometimes difficult to obtain wood samples of sufficient quality and quantity for identification. Thus, it is important to develop new alternative methods to investigate these wooden statues using nondestructive techniques. The chemical composition, especially second metabolites of wood, have been used for taxonomic purposes (Erdtman, 1963), and the identification and classification of wood species were tried on some species of conifers of Pinaceae and Cupressaceae (Erdtman, 1963; Zavarin et al., 1967). Recently, spectroscopic methods, such as infrared, ultraviolet, and nuclear magnetic resonance, were employed for the identification of wood species based on their chemical composition (Nuoppenen et al., 2006; Huang et al., 2008). Among the aforementioned spectroscopic methods, near infrared (NIR) spectroscopy is not affected by atmospheric conditions compared to the other methods, and this technology has become popular because of its utility and availability.

The application of NIR spectroscopy for the identification and classification of wood species has been improving since the publication of seminal papers by Schimleck et al. (1996) and Brunner et al. (1996). Both used principal components analysis (PCA) and the subsequent score plots to show the potential of NIR spectroscopy to differentiate between wood samples of various species. Since then, the successful identification of wood species or wood-based materials has been carried out using NIR spectroscopy combined with several chemometric analyses, such as the Mahalanobis' generalized distance (Tsuchikawa et al., 2003a, 2003b; Tsuchikawa & Yamato, 2003), K nearest neighbors

¹ Forestry and Forest Products Research Institute, 1 Matsunosato, Tsukuba, Ibaraki 305-8687, Japan

^{*} Corresponding author (e-mail: abeq@affrc.go.jp)

(Tsuchikawa et al., 2003b; Tsuchikawa & Yamato, 2003), soft independent modeling of class analogy (SIMCA) (Tsuchikawa et al., 2003b; Tsuchikawa & Yamato, 2003; Gierlinger et al., 2004; Adedipe et al., 2008), and partial least square (PLS) discriminant analysis (Furumoto et al., 1999; Flæte et al., 2006).

These studies were, however, restricted to small clean samples with ideal highly controlled conditions because the NIR spectra are influenced by surface roughness (Hein et al., 2010) as well as the physical and chemical properties of the wood. In these papers, the NIR spectra were obtained from samples collected from a single site, or the irradiation surfaces were carefully cut in the same manner. Because wood has inherent anatomical and morphological variability within species, it is still unknown whether NIR spectroscopy is applicable for the species identification of aging and/or degraded wood that has been collected from various sites. Such conditions are common in the study of ancient wooden statues. To evaluate the applicability of NIR spectroscopy to identify the species of degraded and aging wood, three pairs of five historically important conifer species used in the construction of wooden statues in Japan was studied using NIR spectroscopy.

Materials and Methods

1. Sample preparation

Wood specimens of five species that were collected from various sites in Japan and stored over the past 80 years in the wood library of the Forestry and Forest Products Research Institute, Tsukuba (TWTw) in Japan were used in our analysis (Table 1). They include 18 specimens of *Chamaecyparis obtusa*, 19 of *Torreya nucifera*, 11 of *Thuja standishii*, 19 of *Chamaecyparis pisifera*, and 24 of *Cryptomeria japonica*. The specimens were stored in the collection room, which is

Table 1 Samples used in this study showing the years and sites of collection

Sample	Species	TWTw	Calibration/	Collection	Collection	Sample	Sample Species	TWTw	Calibration/	Collection	Collection
no.		no.	Validation set	years	sites	no.		no	Validation set	years	sites
1	Chamaecyparis obtusa	1168	calibration	1928	Saitama	47	Thuja standishii	22003	validation	2005	Gifu
2	Chamaecyparis obtusa	11951	calibration		Saitama	48	Thuja standishii	649	validation	1951	Nagano
3	Chamaecyparis obtusa	12166	calibration	1931	Yaku Isl.	49	Chamaecyparis pisifera	11952	calibration		Saitama
4	Chamaecyparis obtusa	13263	calibration	1970	Chiba	50	Chamaecyparis pisifera	13264	calibration	1970	Chiba
5	Chamaecyparis obtusa	1345	calibration		Saitama	51	Chamaecyparis pisifera	1347	calibration		Saitama
6	Chamaecyparis obtusa	14666	calibration		Tokyo	52	Chamaecyparis pisifera	14390	calibration	1979	Tokyo
7	Chamaecyparis obtusa	15	calibration		Tokyo	53	Chamaecyparis pisifera	14563	calibration		Chiba
8	Chamaecyparis obtusa	1770	calibration		Tochigi	54	Chamaecyparis pisifera	22065	calibration	2005	Ibaraki
9	Chamaecyparis obtusa	2264	calibration		unknown	55	Chamaecyparis pisifera	24266	calibration	2008	Nagano
10	Chamaecyparis obtusa	4791	calibration		unknown	56	Chamaecyparis pisifera	24588	calibration	2008	Miyagi
11	Chamaecyparis obtusa	7991	calibration		Nagano	57	Chamaecyparis pisifera	3330	calibration	1929	Chiba
12	Chamaecyparis obtusa	873	calibration		Nagano	58	Chamaecyparis pisifera	4792	calibration		unknown
13	Chamaecyparis obtusa	14665	validation		Chiba	59	Chamaecvparis pisifera	874	calibration		Nagano
14	Chamaecyparis obtusa	14668	validation		unknown	60	Chamaecyparis pisifera	8881	calibration		The Netherlands
1.5	Chamaecyparis obtusa	18791	validation	2000	Miyazaki	61	Chamaecyparis pisifera	21822	calibration	2004	Hokkaido
16	Chamaecyparis obtusa	3329	validation	1929	Chiba	62	Chamaecyparis pisifera	12169	validation		unknown
17	Chamaecyparis obtusa	6371	validation	1981	Tokyo	63	Chamaecyparis pisifera	14391	validation	1979	Tokyo
18	Chamaecyparis obtusa	9293	validation	1961	Nagano	64	Chamaecyparis pisifera	24196	validation	2008	Nagano
19	Torreva nucifera	12158	calibration	1931	Kumamoto	65	Chamaecyparis pisifera	242.93	validation	2008	Nagano
20	Torreva nucifera	14506	calibration	1964	Tokyo	66	Chamaecyparis pisifera	651	validation	1951	Nagano
21	Torreva nucifera	14507	calibration	1701	Tokyo	67	Chamaecyparis pisifera	9294	validation	1961	Nagano
22	Torreya nucifera	14755	calibration		Chiba	68	Cryptomeria iaponica	1173	calibration	1928	Saitama
23	Torreva sp *	15979	calibration		China	69	Cryptomeria japonica	1346	calibration	1720	Saitama
24	Torreva nucifera	18403	calibration	2000	Okayama	70	Cryptomeria japonica	14590	calibration		Chiba
25	Torreva nucifera	19683	calibration	2000	Tsushima Isl	70	Cryptomeria japonica	14593	calibration		Yaku Isl
26	Torreva sp **	20112	calibration	2002	unknown	72	Cryptomeria japonica	14594	calibration		Yaku Isl
27	Torreva nucifera	3321	calibration	1929	Chiba	73	Cryptomeria japonica	14914	calibration	1991	Ishikawa
28	Torreva nucifera	4332	calibration	1981	Saitama	74	Cryptomeria japonica	1769	calibration	1771	Tochigi
20	Torreva nucifera	471	calibration	1950	Chiba	75	Cryptomeria japonica	19512	calibration	2002	Amami Iel
30	Torraya mucifara	4772	calibration	1750	unknown	76	Cryptomeria japonica	4785	calibration	2002	unknown
31	Torrana nucifara	1191	validation	1928	Saitama	70	Cryptomeria japonica	6427	calibration	1983	Saitama
32	Torreya nucifera	11938	validation	1720	Saitama	78	Cryptomeria japonica	6428	calibration	1983	Saitama
32	Torrana mucifara	13247	validation	1970	Chiba	79	Cryptomeria japonica	6429	calibration	1983	Saitama
34	Torreva nucifera	13662	validation	1987	Tokyo	80	Cryptomeria japonica	817	calibration	1705	Akita
35	Torrana mucifara	14504	validation	1707	Tokyo	81	Cryptomeria japonica	9290	calibration	1967	Alcita
36	Torraya sp *	15978	validation		Chipa	82	Cryptomeria japonica	9291	calibration	1967	Shizuoka
27	Torreya sp.	052	validation		Miwaralii	02	Cryptomeria japonica	96	calibration	1996	Talwo
20	Thuiz et an dishii	12441	validation		wilyazaki	0.3	Cryptomeria japonica	10275	validation	1996	TOKYO
20	Thuja standishii	14527	calibration		Chiba	04	Cryptomeria japonica	14591	validation		Chiba
39	Thuis standishi	24227	calibration	2008	Nama	83	Cryptomeria japonica	14502	vandation		Ciliba
40	Thuja standishii	4700	calibration	2008	INagano	80	Cryptomeria japonica	14372	validation	1000	unknown Al-ite
41	Thuja standishti	4/90	calibration	1050	C site and s	8/	Cryptomeria japonica	18528	validation	1200	Akita
42	1 nuja stanaisnii Thui a standishii	373	calibration	1930	Saitama	88	Cryptomeria japonica	3322	validation	1929	Cniba Ta abiai
43	1 nuja stanaisnii Thui a standishii	8/3	calibration	10/1	Nagano	89	Cryptomeria japonica	4/8/	validation	10/2	1 ocnigi
44	1 nuja stanaisnu	9293	calibration	1961	Nagano	90	Cryptomeria japonica	9289	validation	1962	Miyazaki
45	1 nuja standishii	12186	validation	1924	unknown	91	Cryptomeria japonica	9292	validation		Aomori
46	i nuja stanaisnii	14639	validation		IOKYO						

*Species other than Japanese Torreya nucifera, **Species not identified.

conditioned with a temperature range of $20-30^{\circ}$ C and a relative humidity of about 50–80%. The dimensions of the samples were $10 \times 2 \text{ cm}^2$ in cross section and 15 cm long. Prior to making the NIR measurement, one of the end-grain surfaces was cut using a circular saw to expose a fresh surface, while the other end-grain surface was left untouched. Among samples of each species, two thirds were used as the calibration set, and the remaining one third were used as the validation set.

2. NIR measurement

The diffuse reflectance spectra on a spot diameter of ca. 3 mm were collected at 4 cm⁻¹ intervals over the range 12,000–4000 cm⁻¹ (830–2500 nm) using a MA-TRIX-F spectrometer (Bruker Optics) equipped with an NIR fiber optic probe in August 2010. A piece of commercial resin spectralon was used as the reference material. Five spectra were randomly collected from the heartwood zone of both end-grain surfaces (fresh and degraded surfaces), respectively. A total of 10 (5 x 2) spectra were obtained from each sample.

3. Pre-processing of NIR spectra

NIR spectra were pre-processed with multiplicative scatter correction (MSC) and Savitzky-Golay second derivations with 29 convolution points, respectively. The effect of the reduced spectral range was also evaluated. Two reduced wavelength ranges, 830–1150 and 1300–2500 nm, were selected for discriminant analysis. Previously, the visible range plus only a narrow NIR range was shown to be useful for the prediction of the chemical components in the wood (Kelley et al., 2004a) and the discrimination of wood-based materials (Tsuchikawa et al., 2003b). In contrast, wavelengths above 1300 nm were known to be associated with many absorption bands of hydroxyl groups derived from water (Bokobza, 2002) and cellulose (Mitsui et al., 2008).

4. Discriminant analysis

Partial least squares (PLS) discriminant analysis was performed using the Unscrambler software version 9.1 (CAMO, OR, USA). PLS discriminant analysis involves developing a partial least square (PLS) regression model. The PLS regression models for each pair of species, namely *Chamaecyparis obtusa* vs *Torreya nucifera*, *Chamaecyparis obtusa* vs *Chamaecyparis pisifera*, and *Thuja standishii* vs *Cryptomeria japonica*, were constructed individually using the calibration set with full cross-validation. The response variable was a binary class indicator variable instead of a continuous variable. The γ variables for one class ("species A") and the other class ("species B") were labeled with +1 and 0,



Fig. 1 Five raw spectra measured from the fresh surface of *Chamaecyparis pisifera* (TWTw-24588) and the coefficient of variation for each wavelength.

respectively. The model was then used to separate two species in the validation set by means of PLS discriminant analysis. The correct identification of "species A" was arbitrarily assigned to samples with a predicted γ > 0.5, and the correct identification of "species B"was assigned when γ < 0.5. The maximum principal components (PCs) used to compute the PLS regression models were set at four to prevent over-fitting. The optimal PCs used in the models were determined by observing the response of the residual variance with added PCs. When additional PCs did not substantially decrease the residual variance, iterations were terminated.

The fresh and degraded surfaces of each sample were individually judged as being correctly identified, when more than three out of five spectra fell into the right species. The percentage of correct identification was defined as the proportion of the number of each species identified correctly compared to the total number of each species.

Results

1. Spectroscopic characterization

The variability of the NIR spectra by the location of the NIR scan was observed in five raw spectra measured from the fresh surface of *Chamaecyparis pisifera* (TWTw-24588)(Fig. 1). The spectra shifted vertically in the overall NIR region, and it is difficult to characterize differences among the five spectra. So the coefficient of variation (CV) for each wavelength was calculated to evaluate the relationship between the wavelength



Fig. 2 The typical second derivatives of NIR spectra for each species. Absorption peaks and bands assigned to cellulose (C), lignin (L), and water (W) are shown by arrows.

and the differences among the five spectra. The CV was inversely proportional to absorbance and had a tendency to decrease with increasing wavelength. The wavelength below 1300 nm showed a large CV, and a sharp decline in the CV was found at a wavelength of about 1300 nm.

Spectral difference in typical second derivative spectra from the fresh surfaces among the five species was evident at the absorption bands of 1366, 1592, 1672, 1910, and 2270 nm (Fig. 2). These absorption bands are assigned to wood components of water, cellulose, and lignin (Ali et al., 2001; Tsuchikawa & Siesler, 2003; Bokobza, 2002, Schenk et al., 2008). The absorption bands at 1366, 1592, and 2270 nm were assigned to cellulose, 1672 nm to lignin, and 1910 nm to water, respectively.

2. PLS discriminant analysis

The regression coefficients of the PLS regression models calibrated using second derivative spectra were useful to determine important spectral regions that correlate to species separation (Fig. 3). Overall, the wavelengths with an impact on the model were above 1300 nm in all pairs of species. The wavelengths with high impact were labeled in response to the absorption bands assigned to water, cellulose, and lignin (Fig. 3) (Ali et al., 2001; Tsuchikawa & Siesler, 2003; Bokobza, 2002; Schenk et al., 2008). The regression coefficients provided a strong relationship with the chemical composition of the wood. To our knowledge, no assignment to specific wood components corresponding to



Fig. 3 Regression coefficients from the PLS regression of second derivative spectra for the separation *Chamaecyparis obtusa* vs *Torreya nucifera*, *Chamaecyparis obtusa* vs *Chamaecyparis pisifera*, and *Thuja standishii* vs *Cryptomeria japonica*, respectively. Bands assigned to cellulose (C), lignin (L), and water (W) are shown by arrows.

the absorption bands at 1870, 2245, and 2300 nm has been reported in the past studies.

The score plots of the first and second PCs for the PLS regression models showed clear separation between Chamaecyparis obtusa vs Torreya nucifera, Chamaecyparis obtusa vs Chamaecyparis pisifera, and Thuja standishii vs Cryptomeria japonica (Fig. 4). The models were developed using second derivative spectra with the wavelengths spanning 830-1150 nm. The PLS regression models showed distinct clusters in all the pairs of species, although the score plots of the degraded surfaces were widely spread compared with those of the fresh surfaces. The difference between Thuja standishii and Cryptomeria japonica was less pronounced compared to Chamaecyparis obtusa and Torreya nucifera or Chamaecyparis obtusa and Chamaecyparis pisifera. Some plots of Cryptomeria *japonica* samples overlapped with the cluster of *Thuja* standishii. Thus, another PLS regression model of Thuja standishii vs Cryptomeria japonica was constructed excluding the 21 overlapped spectra of Cryptomeria japonica samples that we regarded as outliers. Contrary to our expectation, the cluster difference between each species was not observed in the score plots of the PLS regression models calibrated by MSC and other wavelengths spanning 1300-2500 and 830-2500 nm (not presented here).

PLS discriminant analysis was employed to identify the validation set of six specimens of *Chamaecyp*-



Fig. 4 PLS discriminant analysis score plots of the first and second principal components calibrated by the wavelengths spanning 830–1150 nm for (a) *Chamaecyparis obtusa* (black) vs *Torreya nucifera* (white), (b) *Chamaecyparis obtusa* (black) vs *Chamaecyparis pisifera* (white), and (c) *Thuja standishii* (black) vs *Cryptomeria japonica* (white).

aris obtusa, seven of *Torreya nucifera*, four of *Thuja standishii*, six of *Chamaecyparis pisifera* and eight of *Cryptomeria japonica*. The identification results show that the PLS regression models can provide highly separated pairs that led to their correct taxonomic identification (Table 2).

Root mean square error of prediction (RMSEP) provides an objective means of evaluating the effect of the data pre-treatment of the identification process. The ability for identification is largely reflected by the RM-SEP values, with the best overall identification, being achieved in 100% accuracy using the second derivative spectra with the wavelengths spanning 830–1150 nm for each pair of species (Table 2).

Discussion

1. Spectroscopic characterization

Because of the variability of the NIR spectra within a sample (Fig. 1), we identified species for each spectrum individually without averaging the five spectra. The variability of the spectra may be explained by the size of the spot area of NIR probe and the density variation induced by annual rings. The distance between adjacent annual rings was larger than the spot diameter of 3 mm in some samples, especially those of *Chamaecyparis pisifera* and *Cryptomeria japonica*. Thus, the mean density of the spot area was different between each location of the NIR scan, resulting in the variability of the NIR spectra. The larger the spot area of the NIR spectra. In reality, however, the spot area is restricted by the sample size and the condition of the sample.

The CV provides the difference among the five spectra, that correspond to wavelength. The decrease of CV inversely to absorbance (Fig. 1) may be due to an increase in water absorption as wavelength increases. This inverse relationship shows that the larger the water absorption, the less variable the NIR spectra. The wavelength spanning 830–1300 nm showed a large CV, indicating that this wavelength range is more sensitive to the location of the NIR scan compared to wavelengths above 1300 nm.

Spectral differences among the five species were observed at absorption bands of 1366, 1592, 1672, 1910, and 2270 nm. The wavelengths correspond to the water, cellulose, and lignin components of the wood. This result shows that the amount of the wood components, characteristics of each species, is different among the five species.

2. PLS discriminant analysis

In the regression coefficients of the PLS regression

Separation species	D	W /1		DMCED	correct identification (%)		
A vs B	Pre-processing	wavelength (nm)	Optimal PCs	KW3EP	True species A	True species B	
	MSC	830-2500	5	0.24	100	100	
	MSC	830-1150	5	0.18	100	100	
Chamaecyparis obtusa	MSC	1300-2500	4	0.26	92	100	
vs Torreva nucifera	2nd	830-2500	5	0.23	100	100	
	2nd	830-1150	4	0.13	100	100	
	2nd	1300-2500	5	0.25	100	100	
	MSC	830-2500	5	0.41	83	100	
	MSC	830-1150	5	0.24	83	100	
Chamaecyparis obtusa	MSC	1300-2500	5	0.39	75	100	
Vs Chamaecvparis pisifera	2nd	830-2500	5	0.23	100	100	
	2nd	830-1150	3	0.14	100	100	
	2nd	1300-2500	5	0.26	100	100	
	MSC	830-2500	5	0.33	88	100	
	MSC	830-1150	5	0.24	88	100	
Thuia standishii	MSC	1300-2500	4	0.35	100	100	
VS	2nd	830-2500	5	0.30	88	100	
Cryptomeria japonica	2nd	830-1150	3	0.27	88	100	
	2nd	1300-2500	5	0.31	88	100	
	2nd*	830-1150	3	0.19	100	100	

Table 2 Summary of validation of PLS regression models and percentages of correct identification

Identification for each true species. 2nd, second derivative; *, without outliers.

models, the wavelengths above 1300 nm showed a high impact on the models in all pairs of species. Thus, the wavelengths above 1300 nm, which contains the most distinct spectral information on the first overtone and combination bands (Bokobza, 2002), was expected to contribute to the separation of the species. This agrees with the suggestion by Gierlinger et al. (2004) that the NIR spectral region below 1300 nm is characterized by low intensity and a low signal-to noise ratio, and that this region was consequently not suitable for species identification. The regression coefficients provided a strong relationship with the absorption bands assigned to chemical composition, namely, water, cellulose and aromatic groups of lignin (Fig. 3), demonstrating important differences in wood chemistry between the three pairs of species. On the other hand, no assignment to specific wood components that correspond to the band peaks (1870, 2245, and 2300 nm) has been reported in the past studies. It may be possible to ascribe these unknown band peaks to anatomical wood structure, as well as other chemical components in the wood. Further studies on the assignment of the NIR absorption bands for wood components and structure are thus required.

The distinct clusters in the score plots calibrated by the wavelengths spanning 830–1150 nm (Fig. 4) demonstrate that the NIR spectra obtained from both fresh and degraded surfaces contain information that is relevant for differentiating species. On the other hand, the lack of differentiation between each species in the score plots with wavelengths spanning 1300–2500 and 830–2500 nm indicates that these wavelengths have poor identification capability compared to those spanning the 830–1150 nm range.

It is not surprising that the model using the wavelengths of 830-1150 nm showed a higher percentage of correct species identification compared to that of 1300-2500 nm (Table 2). Contrary to our expectations, however, the score plots demonstrate that the effective wavelengths for wood identification does not necessarily match the wavelength corresponding to strong regression coefficients in the PLS regression models (Fig. 3). The wavelengths spanning the 830-1150 nm range are difficult to assign to specific wood components, but can be attributed to second overtones of hydroxyls and third overtones of C-H stretching vibrations (Kelley et al., 2004b). The successful prediction of wood chemical composition using the reduced NIR spectral region was reported by Kelley et al. (2004b) and Axrup et al. (2000). Our results support the usefulness of the reduced spectral region for wood species identification, in addition to chemical composition. This reduced spectral region enables the use of a light-weight, inexpensive handheld spectrometer with rapid acquisition times. It has a huge advantage to identify wood species under field conditions.

In all pairs of species, the PLS regression models calibrated using the second derivative spectra and wavelengths spanning 830–1150 nm separated two species with 100% accuracy. The percentage of correct identification in this study were comparable to the separation of three larch species (*Larix decidua*, *L kaempferi*, and *L. eurolepis*) (Gierlinger et al., 2004) and three spruce species (*Picea abies*, *P. lutzii*, and *P. sitchensis*) (Flæte et al., 2006). Meanwhile, the percentage of correct identification in the SIMCA analysis for the separation of two oak species (*Quercus rubra* and *Q. alba*) (Adedipe et al., 2008) showed slightly lower percentages ranging from 80–98%.

In addition to reveal the separation of historically important softwood species, this study showed for the first time that NIR spectroscopy has a potential to identify the species of degraded and aging wood. Ali et al. (2001) showed that NIR could be used to monitor the aging of paper treated by high temperature, and that the development of carbonyl/carboxyl peak, which can be seen in the wavelength range spanning 1700-1900 nm, a characteristic of aging. It is likely that the wavelength range impacted by aging should be excluded from the identification of variably-aged wood species. Under the limitation of sample volume, it can be concluded that the PLS discriminant analysis using second derivative spectra and wavelengths spanning 830–1150 nm has the potential to separate degraded and aging wood between Chamaecyparis obtusa and Torreya nucifera, Chamaecyparis obtusa and Chamaecyparis pisifera, and Thuja standishii and Cryptomeria japonica.

Conclusions

The applicability of NIR spectroscopy to separate species of degraded and aging wood, an important application for the study of Japanese art history, was examined. NIR spectra were obtained from wood blocks of several softwood species that were collected over the past 80 years from various sites in Japan and stored in the wood library of the Forestry and Forest Products Research Institute in Japan. Partial least square (PLS) discriminant analysis was employed to discriminate between Chamaecyparis obtusa and Torreya nucifera, Chamaecyparis obtusa and Chamaecyparis pisifera, and Thuja standishii and Cryptomeria japonica. PLS discriminant analysis using second derivative and wavelengths spanning 830 to 1150 nm separated the samples into each pair of species with 100% accuracy. The results suggest that NIR spectroscopy combined with PLS discriminant analysis is a powerful tool for the identification and classification of species for degraded and aging wood using nondestructive techniques.

Acknowledgements

This research was supported by a Grant-in-Aid for Scientific Research (No21300332) from the Japan Society for the Promotion of Science (JSPS). We are grateful to Dr. Ben A. LePage for the linguistic check of the final manuscript.

References

- Abe, H., Itoh, S., Shibata, M., Ogata, K., Kitin, P. & Fujii, T. 2005. Tree species of timber imported to Japan from Southeast Asia. JIRCAS Working Report No. 39: 251– 253.
- Adedipe, O. E., Dawson-Andoh, B., Slahor, J. & Osborn, L. 2008. Classification of red oak (*Quercus rubra*) and white oak (*Quercus alba*) wood using a near infrared spectrometer and soft independent modeling of class analogies. *Journal of Near Infrared Spectroscopy* 16: 49–57.
- Ali, M., Emsley, A. M., Herman, H. & Heywood, R. J. 2001. Spectroscopic studies of the ageing of cellulosic paper. *Polymer* 42: 2893–2900.
- Axrup, L., Markides, K. & Nilsson, T. 2000. Using miniature diode array NIR spectrometers for analyzing wood chips and bark samples in motion. *Journal of Chemometrics* 14: 561–572.
- Bokobza, L. 2002. Origin of near-infrared absorption bands. In: Siesler, H. W., Ozaki, Y., Kawata, S. & Heise, H. M., eds., Near-Infrared Spectroscopy—Principles, Instruments, Applications, 34–35. Wiley-VCH, Weinheim, Germany.
- Brunner, M., Eugster, R., Trenka, E. & Bergamin-Strotz, L. 1996. FT-NIR spectroscopy and wood identification. *Holzforschung* 50: 130–134.
- Erdtman, H. 1963. Some aspects of chemotaxonomy. *In*: Swain, T. ed., *Chemical Plant Taxonomy*, 89–125. Academic Press, London, New York.
- Flæte, P. O., Haartveit, E. Y. & Vadla, K. 2006. Near infrared spectroscopy with multivariate statistical modeling as a tool for differentiation of wood from tree species with similar appearance. *New Zealand Journal of Forestry Science* 36: 382–392.
- Furumoto, H., Lampe, U., Meixner, H. & Roth, C. 1999. Infrarotanalyse zur messing der holzqualität. *Holz als Rohund Werkstoff* 57: 23–28 (in German).
- Gierlinger, N., Schwanninger, M. & Wimmer, R. 2004. Characteristics and classification of fourier-transform near infrared spectra of the heartwood of different larch species (*Larix* sp.). Journal of Near Infrared Spectroscopy 12: 113–119.
- Hein, P. R. G., Lima, J. T. & Chaix, G. 2010. Effects of sample preparation on NIR spectroscopic estimation of chemical properties of *Eucalyptus urophylla* S. T. Blake wood. *Holzforschung* 64: 45–54.
- Huang, A., Zhou, Q., Liu, J., Fei, B. & Sun, S. 2008. Distinc-

tion of three wood species by Fourier transform infrared spectroscopy and two-dimensional correlation IR spectroscopy. *Journal of Molecular Structure* 883–884: 160–166.

- IAWA Committee. 2004. IAWA list of microscopic features for softwood identification. *IAWA Journal* 25: 1–70.
- Kaneko, H., Iwasa, M., Noshiro, S. & Fujii, T. 1998. Wood types and material selection for Japanese wood statues of ancient period: Particularly the 7th–8th centuries. *Museum* No. 555: 3–54 (in Japanese).
- Kaneko, H., Iwasa, M., Noshiro, S. & Fujii, T. 2003. Wood types and material selection for Japanese wood statues of ancient period 2: Particularly of the 8th–9th centuries. *Museum* No. 583: 5–44 (in Japanese).
- Kaneko, H., Iwasa, M., Noshiro, S. & Fujii, T. 2010. Wood types and material selection for Japanese wood statues of ancient period 3: Further thoughts on 8th and 9th century sculptures. *Museum* No. 625: 61–78 (in Japanese).
- Kelley, S. S., Rials, T. G., Groom, L. H. & So, C.-L. 2004a. Use of near infrared spectroscopy to predict the mechanical properties of six softwoods. *Holzforschung* 58: 252–260.
- Kelley, S. S., Rials, T. G., Snell, R., Groom, L. H. & Sluiter, A. 2004b. Use of near infrared spectroscopy to measure the chemical and mechanical properties of solid wood. *Wood Science and Technology* 38: 257–276.
- Mitsui, K., Inagaki, T. & Tsuchikawa, S. 2008. Monitoring of hydroxyl groups in wood during heat treatment using NIR spectroscopy. *Biomacromolecules* 9: 286–288.
- Noshiro, S., Suzuki, M. & Tsuji, S. 2002. Three buried forests of the Last Glacial Stage and middle Holocene at Ooyazawa on northern Honshu Island of Japan. Review of Palaeobotany and Palynology **122**: 155–169.
- Noshiro, S., Suzuki, M. & Sasaki, Y. 2007. Importance of *Rhus verniciflua* Stokes (lacquer tree) in prehistoric periods in Japan, deduced from identification of its fossil woods. *Vegetation History and Archaeobotany* 16: 405–411.
- Nuoppenen, M. H., Wikberg, H. I., Birch, M. G., Jääskeläinen, A.-S., Marunu, S., Vuorinen, T. & Stewart, D. 2006. Characterization of 25 tropical hardwoods with Fourier transform infrared, ultraviolet resonance Raman, and ¹³C-NMR cross-polarization/magic-angle spinning spectroscopy. *Journal of Applied Polymer Science* 102: 810–819.
- Schimleck, L., Michell, A. J. & Vinden, P. 1996. Eucalypt wood classification by NIR spectroscopy and principal components analysis. *Appita Journal* 49: 319–324.
- Shenk, J. S., Workman, J. J. & Westhaus, M. O. 2008. Application of NIR spectroscopy to agricultural products. *In:* Burns, D. A. & Ciurczak, E. W., eds., *Handbook of Near-Infrared Analysis*, 3rd ed., 356–357. Taylor & Francis Group, New York.
- Tsuchikawa, S. & Siesler, H. W. 2003. Near-infrared spectroscopic monitoring of the diffusion process of deuteriumlabeled molecules in wood. Part I: Softwood. *Applied Spectroscopy* 57: 667–674.
- Tsuchikawa, S. & Yamato, K. 2003. Discriminant analysis of wood-based materials with weathering damage by near

infrared spectroscopy. Journal of Near Infrared Spectroscopy 11: 391–399.

- Tsuchikawa, S., Inoue, K., Noma, J. & Hayashi, K. 2003a. Application of near-infrared spectroscopy to wood discrimination. *Journal of Wood Science* 49: 29–35.
- Tsuchikawa, S., Yamato, K. & Inoue, K. 2003b. Discriminant analysis of wood-based materials using near-infrared spectroscopy. *Journal of Wood Science* 49: 275–280.
- Zavarin, E., Smith, L. & Bicho, J.G. 1967. Tropolone of Cupressaceae 3. *Phytochemistry* 6: 1387–1394.

(Accepted: 4 Feb. 2011)