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NEAR INFRARED SPECTROSCOPY AS A TOOL FOR CHARACTERIZATION OF WOOD SURFACE

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SYNOPSIS. The goal of this research was to exploit the potential of near infrared spectroscopy to measure and characterise various types of surfaces common in the wood/related products and to present their capabilities for application into wood research and industry. Wooden blocks originated from different countries, of various wood species and different finishes have been evaluated. Characterisation of the archaeological wood was also performed by measuring fragments of wood excavated at the site. It has been found that near infrared spectroscopy can be successfully utilized for: recognition of wood species, quantify chemical composition of wood, detection of surface finish type and monitoring of the wood/coated wood weathering. The near infrared technique could be used for analyses of archeological wood and determination of its geographical origin. Dedicated tests performed on spruce (*Picea abies* sp.) originated from Finland, northern Poland, southern Poland and various valleys of Italian Dolomites confirmed that it is possible to determine the wood proveniences by measuring its near infrared spectra.

KEY WORDS: FT-NIR, wood chemical composition, wood ageing, wood origin

INTRODUCTION

Recent developments in the fields of optics and electronics opened new possibilities for measurements of various physical and chemical properties of materials. One of such techniques is Fourier Transform Near Infrared Spectroscopy (FT-NIR). Energy of infrared light is exciting particular parts of molecules on the surface of matter and part of the light energy is absorbed (Pasquini 2003). Different molecule combinations (such as C-H, O-H or N-H) are stimulated to vibrations, depending on the molecular structure, chemical composition or physical properties of the surface measured (Antti 1999, Coates 2000). As an effect of this phenomenon the infrared radiation reflected from the surface can be used for estimation of the physic-chemical structures of materials. The spectral signal generated by the system is composed of overlapping peaks, overtones or diverse combinations depending on the surface properties. It should be mentioned therefore that for the complete exploit of the FT-NIR capabilities it is necessary to employ various mathematical/chemometric techniques, such as principal components, partial least squares, two-dimensional correlation spectroscopy and so on.

FT-NIR technique is relatively young, but even that it is more and more utilized in various application fields (Tsuchikawa 2007). The most important applications include chemical industry, food and beverages, pharmaceutical analysis, microanalysis, polymers, surface science, petrochemistry, textile industry, art conservation, forensics, process control quality and also wood and paper industry. FT-NIR technique has been successfully applied for prediction of lignin (Schwanninger and Hinterstoisser 2001, Kelley et al. 2004) and cellulose contents (Raymond and Schimleck 2002, Yeh et al. 2005, Jones et al. 2006). Some investigations have been related to determination phenolic substances and extractives quantity (Gierlinger et al. 2002, So et al. 2004, Taylor et al. 2008). Schimleck et al. (2004) and Via et al. (2007) used the FT-NIR technique to characterise anatomical parameters of wood (such as microfibryl angle, tracheid length and wall thickness). Schwanninger et al. (2004) investigated an effect of modification temperature on the thermally treated beech wood spectra.

FT-NIR procedure has been also used for estimation of the mechanical properties of wood: prediction of stiffness and modulus of elasticity (MOE) (Via et al. 2003, Kelley et al. 2004), assessment of tensile strength of wood within elastic and plastic deformation (Baillères et al. 2002, Via et al. 2003) or estimation of specific gravity and modulus of rupture (Kelley et al. 2004). The near infrared spectroscopy has been also successfully applied for monitoring the wood degradation (Via 2004, Fackler et al. 2006, Stirling et al. 2007), prediction of natural durability and wood resistance (Gindl et al. 2001), distinguishing preservative types and retention time (Feldhoff et al. 1998, So et al. 2004) and for monitoring wood modifications caused by light irradiation and heat treatment (Mitsui and Tsuchikawa 2003). The technique has been also utilized for on-line process control of laminated veneer lumber, particleboards and medium-density fiberboards (So et al. 2004).

Other investigations were focused on the wood species recognition (Brunner et al. 1996, Schimleck et al. 1996, Tsuchikawa et al. 2003) or identification of mature/juvenile wood (Via 2004). FT-NIR spectroscopy was successfully applied in paper industry for characterization of the moisture content in paper, on-line process control, estimation of kappa number (Alves et al. 2007) and for rapid characterization of row materials used in paper production (So et al. 2004).

Near infrared spectroscopy could be an interesting alternative to expensive and time consuming genetic fingerprinting technology, especially in applications such as timber tracking or illegal logging detection. Rana et al. (2008) used mid infrared technique for separation of beech coming from four different sites. Separation of the wooden samples was accurate, but according to the experimental requirements the sample preparation was much more complicated in comparison to near infrared technique. Gierlinger et al. (2004) applied NIR spectroscopy for sub-species classification of three different larch woods.

The goal of this research was to evaluate the potential of the near infrared spectroscopy into measurements and characterization of diverse types of surfaces typical in the wood/wood-related products.

MATERIAL AND METHODS

All the spectra presented in this study were measured by using FT-NIR spectrometer VECTOR 22-N produced by Bruker Optics GmbH and installed in the Wood Quality Laboratory of IVALSA/CNR. The measured spectral range was between 4000 cm^{-1} and 12000 cm^{-1} with a resolution of 8 cm^{-1}, which are standard conditions for such measurements. Each spectrum has been computed as an average of 25 internal scans in order to increase the signal-to-noise ratio. OPUS 6.5 and National Instruments LabView 8.5 software packages have been used for signal processing and data analyses.

The FT-NIR technique has been tested in several experiments dedicated for evaluation of specific wood properties. Representative wooden samples have been measured with the spectrometer, varying in terms of wood species, age, provenance, consistence or finishing. Number of measurements and samples evaluated varied in every experiment. Further details related to the methodology are presented in the following chapters describing singular experiments.

RESULTS AND DISCUSSIONS

FT-NIR application for wood species recognition

Twenty different wood species have been scanned in order to validate the system ability to discriminate the species according to FT-NIR spectra; eight softwoods: *Picea abies* (1), *Tsuga* sp. (2), *Abies alba* (3), *Pinus ponderosa* (4), *Pinus cembra* (5), *Larix* sp. (6), *Pinus sylvestris* (7), *Thuja plicata* (8), three domestic hardwoods: *Quercus* sp. (9), *Robinia pseudoaccacia* (10), *Castanea sativa* (11), and nine exotic wood species: *Chlorophora exelsa* (12), *Tectona* sp. (13), *Pericopsis elata* (14), *Milletia laurentii* (15), *Entandrophragma utile* (16), *Aucoumea klaineana* (17), *Lophira alata* (18), *Arariba* sp. (19), *Shorea laevifolia* (20). All the samples were conditioned to the same moisture content of 12%. Each sample has been measured four times.

Cluster analyses have been applied for the data processing. All samples were separated into two clusters representing softwoods and hardwoods, as it is presented in Figure 1. The hardwood cluster was subdivided according to the provenance of samples; European species were placed in one minor sub-cluster and exotic woods formed the second group. It should be mentioned, that all samples were correctly discriminated into proper classes and none misclassification of the species occurred.

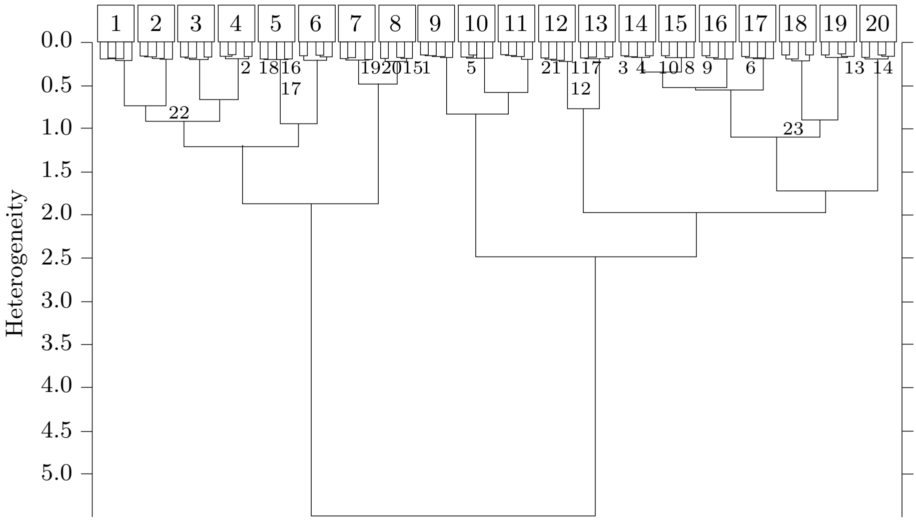

Fig. 1. Cluster analysis of different wood species. Note: bands: 4247-9500 cm^{-1}, second derivative and vector normalization

Monitoring of thermal modification of wood

Other research has been dedicated to verification of the FT-NIR capabilities for evaluation of the thermally treated wood. Thermally modified pine (*Pinus* spp.) and beech (*Fagus* spp.) wooden blocks have been compared to twin samples of non-modified wood. An evidence of the chemical changes due to the thermal treatment is shown on the spectra presented in Figure 2. Ten measurements have been performed on both thermally treated and not-treated wood, but for the spectra interpretation single average spectrum has been computed for each sample.

Degradation of lignin and hemicelluloses were observed in the second derivative spectra (peak 1 and 2 respectively). The primary peak (5950 cm^{-1}) is assigned to first overtone of aromatic skeletal in lignin. The second (5800 cm^{-1}) represents characteristic band of the first overtone C-H stretching, and is related to the degradation of hemicellulose (Schwanninger et al. 2004).

Estimation of the chemical composition of wood

As it was mentioned in the literature review, FT-NIR technique has been already applied for prediction of cellulose and lignin contents, among others. For this project evaluation of the 8 clones of willow (*Salix* spp.) had been performed in order to build statistical models linking FT-NIR spectra with reference results obtained by reference wet-chemical analysis. Regression curves for lignin, cellulose, pentozanes, holocellulose, solubility in NaOH and organic substances as well as solubility in cold and hot water were computed for each clone variation. Measurements were performed on two different fractions: wooden chips (fraction 0.5-1.0 mm) and fine powder (< 0.5 mm). Partial Least Squares technique has

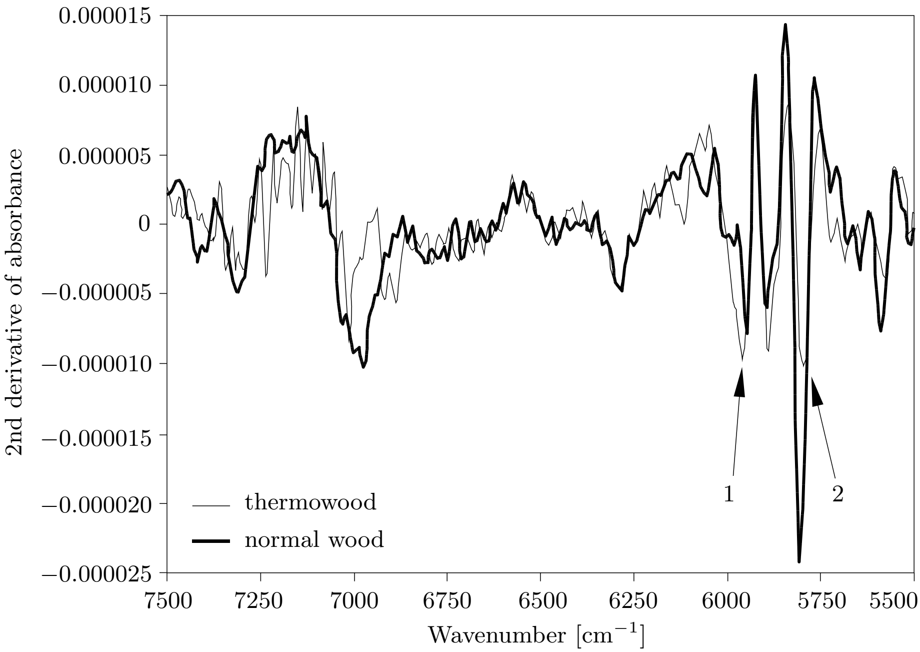

Fig. 2. FT-NIR second derivative spectra of the untreated and thermally treated beech wood

been employed to build statistical models. The value of determination coefficient (R^2) in case of wooden chips was between 60.78 and 91.53 depending on the estimated component (Table 1). Measurement of powders increased the accuracy of statistical models even more as R^2 reached in some cases to the level of 97.84% (RMSECV = 0.292).

Table 1. Determination coefficient (R^2) and root mean square error of cross validation (RMSECV) value for wood components

Specification	Fraction 0.5-1.0 mm region 7502-4597.6 cm^{-1}		Fraction < 0.5 mm region 7502-5446.2 and 4601.5-4424.1 cm^{-1}	
	R^2 [%]	RMSECV	R^2 [%]	RMSECV
Cellulose	84.31	0.97	96.65	0.525
Lignin	76.91	0.689	95.51	0.287
Pentozanes	65.64	0.397	95.19	0.13
Holocelluloses	60.78	1.17	95.27	0.405
Solubility in hot water	86.31	0.634	97.45	0.239
Solubility cold water	80.91	0.418	97.57	0.0136
Solubility in 1% NaOH	75.1	0.942	97.84	0.292
Solubility in organic	91.53	0.276	96.88	0.151

Monitoring of the coated wood surface

FT-NIR technique has been applied for evaluation of the surfaces changes during weathering. Twenty three different wooden species were coated with various commercially available products and exposed to the climatic factors (natural weathering) for 21 months. Each sample has been measured five times in the same position on the surface with regular intervals of time. Figure 3 presents Principal Component Analysis of 6 different types of coatings applied. Spectra are evidently grouped according to the type of varnish even that the coatings were provided by different producers. The evidences of the chemical change to the surface were clearly noticed on the spectra depending on the finish type. The spectra changed significantly in case of water/acrylic-coated surfaces. On the other hand nearly no differences were noticed in case of organic/alkyd.

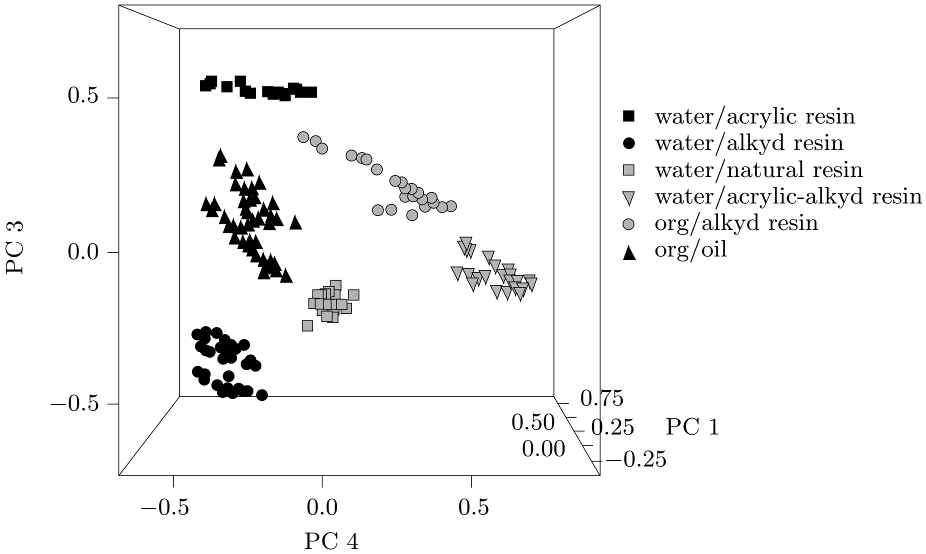

Fig. 3. Identification of different types of treatment applied on the wooden surface. Note: band: 4200-10000 cm^{-1}, second derivative, 5 smoothing points, vector normalization, 2 factors

Determination of wood origin

A dedicated research has been conducted in order to validate a possibility of recognizing Norway spruce origin growing in various locations. 439 samples collected from Italy, southern and northern Poland as well as Finland were measured on the radial section in the zone of the mature wood. Principal component analysis has been performed on all spectra measured (2195 spectra). It has been found that spectra were clearly separated creating four main point-clouds covering Finland, southern and northern Poland as well as Italy (Fig. 4). None of the spectra has been miss-classified.

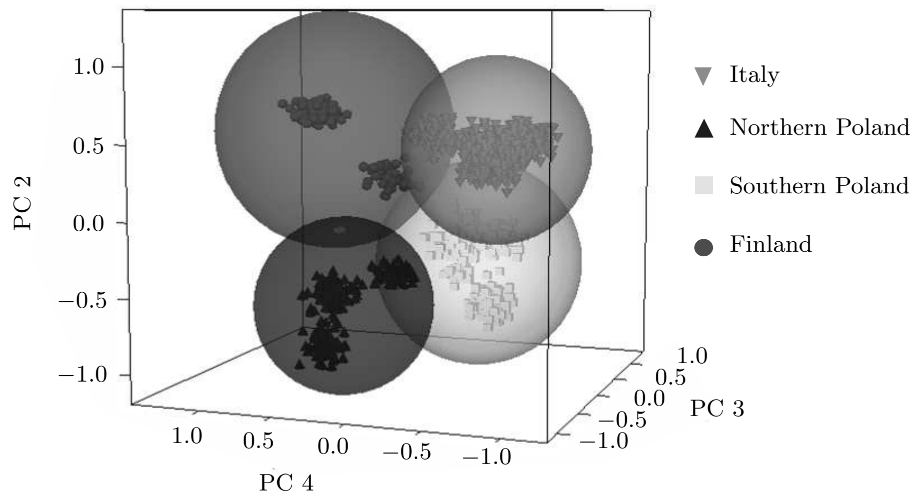

Fig. 4. PCA of wooden samples from four locations in Europe. Note: band 10005-4227 cm^{-1}, second derivative, 5 smoothing points, 4 factors

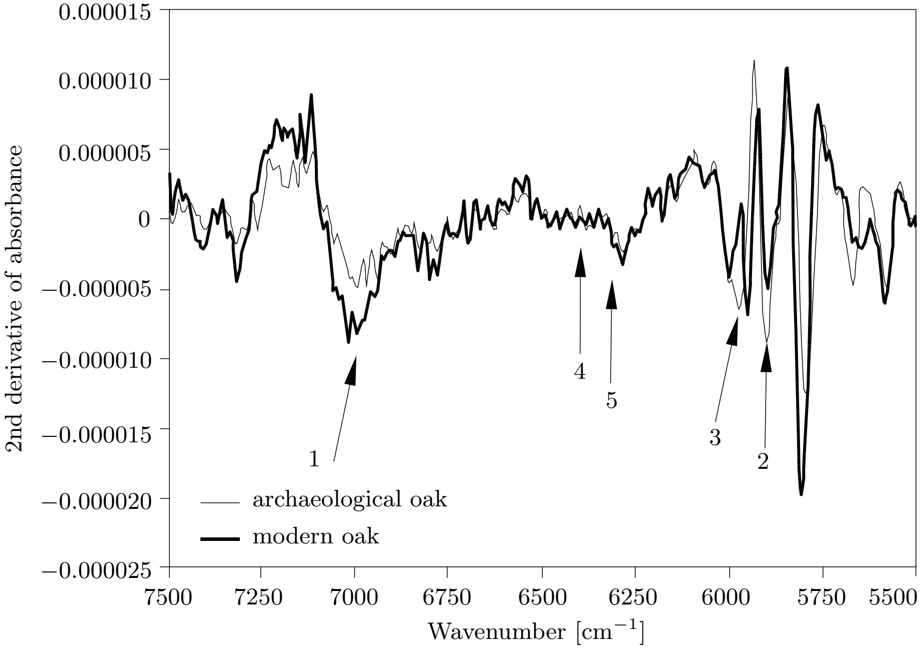

Fig. 5. FT-NIR second derivative spectra of modern and archeological wood samples. Note: second derivative, 9 smoothing points

Archeological wood analysis

Subsequent trials have been performed in order to verify the FT-NIR applicability into archeometry. Six powder samples of oak (*Quercus* sp.) excavated from archeological sites and with different degradation level were measured five times. As a reference the contemporary wood has been milled and analysed parallelly to the archeological one. The average spectra obtained were then analysed in order to validate the changes into chemical structure.

Clear difference between spectra taken from modern and archeological woods can be observed in Figure 5. Such differences are related to decreasing amount of chemical substances due to degradation. Peak 1 linked to the OH stretching first overtone is correlated with the amorphous region in cellulose. Similar phenomenon is observed in absorption band in peak 2, which is associated to the CH stretching of first overtone in hemicellulose and 3 assigning the vibration in aromatic skeletal due to lignin. Nearly no differences are noticed in crystalline regions in cellulose (peak 4 and 5), what can demonstrate that such regions are not/little damaged by the waterlogging.

CONCLUSIONS

Summarising all the results presented it is possible to assume that FT-NIR is:

- fast and easy tool for detection and monitoring of thermally treated wood, with a potential of in-process quality control
- very useful tool for recognition of varnish type and monitoring of the coated surfaces ageing
- sensitive enough to detect differences in the chemical composition of trees coming from different origins
- non-destructive and rapid technique with a big potential and prospective in characterization of archeological and historical materials

FT-NIR technique with support of advanced statistical methods and proper sample preparation is a very useful tool for wood research. Several experiments performed in the Wood Quality Laboratory at IVALSA/CNR, in cooperation with industry, demonstrate high potential of this method and encourage authors to consider near infrared technology as very promising supplement for the recent measurement chain.

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