

Characterization of archeological oak (*Quercus* sp.) with mid and near infrared spectroscopy

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Abstract

Archeological wood, as most of natural materials, is slowly decomposing on the archeological site due to various biological factors. In a consequence of such degradation significant changes within physical, mechanical and chemical properties are occurring. Rapid and accurate estimation of the degradation level is extremely important as it influences the selection of optimal restoration and conservation procedures.

The goal of this research was to verify the usefulness of infrared (FT-ATR and FT-NIR) techniques for monitoring of the ageing process in archeological wood. The important advantage of the infrared spectroscopy is its accuracy, simplicity, and ability of performing very high number of tests without needs of any destruction to the workpiece. The methods explored in this research might be a novel tool assisting experts in evaluation of the degradation state of archeological and historical wooden materials. Examples of infrared application in to qualitative and quantitative evaluation have been presented. By linking both infrared techniques with novel signal processing methods it is possible to improve the knowledge and interpretation of spectra.

1. INTRODUCTION

Wood is considered as a very friendly and useful raw material used extensively for various purposes from ancient times. Archeological wood, as most of natural materials, is slowly decomposing on the archeological site due to various biological factors. In a consequence of such degradation significant changes within physical, mechanical and chemical properties are occurring. Rapid and accurate estimation of the degradation level is extremely important as it influences the selection of optimal restoration and conservation procedures.

Various analytical techniques might be applied for estimation of the archeological wood condition and degradation stage. Chemical methods are very accurate and allow detailed interpretation of the degradation process. An important limitation for use of chemical methods is however its destructive nature, as well as long time duration of the test and its relatively high costs.

Recent developments in the fields of optics and electronics opened new possibilities for nondestructive measurements of various physical and chemical properties of materials. Therefore, a tendency for application of various analytical techniques, such as infrared spectroscopy into measurement of the ancient wooden artifacts is observed nowadays [5]. The advantage, beside of the nondestructive character, is the simplicity of measurement and possibility of numerous repetitions what significantly increases the reliability and accuracy of data. Most of the state-of-the-art methods allow measurement directly on the object in the field, without the necessity of sampling or sample transportation. Instrumental methods, even possessing plenty of advantages, are rather rarely applied in the conservation laboratories due to lack of the dedicated (to archeological wood) calibrations or simply by limited trust to the novel equipment. In some cases the results provided by the equipment are not directly related to the degradation degree of wood and some further interpretation is necessary. It is important therefore to adopt the available instrumentation techniques for better serving a conservation tasks and correlate results provided by the instrument to the real state of the historical object.

Infrared spectroscopy, in both near and mid ranges, is well known technique with a great potential for chemical characterization of materials. It is very useful tool for identifying various inorganic and organic compounds, base on their selective absorption of radiation in the infrared region. However until recently, the sample preparation to be measured with infrared spectrometers has been rather complicated; for example solving the sample or preparation of potassium-bromide (KBr) pellets for sample analysis.

Fourier Transform Attenuated Total Reflectance (FT-MIR-ATR) is relatively new advancement of traditional mid infrared spectroscopy. It uses a phenomenon of absorbing infrared energy during reflection from the measured surface. This technique allows measurement of the wood powder or even wooden block surface without time consuming KBr sample preparation. It is expected that by applying FT-MIR-ATR in to area of archeometry, a new tool for estimation of the lignin, cellulose and hemicelluloses content might be developed. On the other hand Fourier Transform Near Infrared (FT-NIR) spectroscopy offers even simpler measurement. Unfortunately the signal-to-noise ratio is poorer than that of FT-MIR-ATR and interpretation of spectra more problematical.

The goal of this research was therefore to verify the usefulness of FT-MIR-ATR and FT-NIR techniques for monitoring of the ageing process in archeological wood. The performance of the both methods would be compared to each other and to well-established experimental reference methods.

2. MATERIALS AND METHODS

2.1. Experimental samples

Five oak (*Quercus* sp.) pieces of the archeological wood have been used as experimental samples. Each sample has been collected from the waterlogged site in the area of Poland. The details regarding geographical origin and waterlogging are summarized in table 1. A piece of contemporary wood of the same species has been also included in analyses for reference purposes. A small part of each wooden block has been milled with the laboratory mill (Pulverisette 15, Fritsch GmbH), to transform the structure into powder (fraction <0,5mm).

Table 1. Characteristics of the experimental materials

Sample code	Origin	Dating	Waterlogging period, years
Q1	Biskupin	VIII BC	2700
Q2	Bronisze (Warsaw)	III AD	1700
Q3	Lednica	X-XI AD	1000
Q4	Ostrow Tumski (Poznan)	IX-X AD	1000
Q5	Szczecin	XIII AD	700
Q6	Golabki	XX AD	0

2.2. Chemical analysis

Chemical analyses have been performed on the experimental samples in order to generate reference data for calibration and validation of the infrared methods. The analysis included determination of the main chemical components concentration in the wood samples. Quantity of cellulose has been determined according to the Seifert procedure (by using acetylacetone-dioxane-hydrochloric acid) and lignin was conducted according to the TAPPI standard T 222 om-06 [3].

2.3. FT-NIR measurement

All experimental samples were measured by using Fourier transform near infrared spectrometer VECTOR 22-N produced by Bruker Optics GmbH. The spectral range measured was between 4000 cm⁻¹ and 12000 cm⁻¹. The spectral resolution of the spectrophotometer was 8 cm⁻¹, each spectrum has been computed as an average of 32 successive measurements in order to minimize the measurement error. Five separate measurements have been performed on each sample.

2.4. FT-IR-ATR measurement

All experimental samples have been also measured by using Fourier transform attenuated total reflectance spectrometer Alpha produced by Bruker Optics GmbH. The spectral range measured was between 4000 cm⁻¹ and 600 cm⁻¹. The spectral resolution of the spectrophotometer was 4 cm⁻¹, each spectrum has been computed as an average of 32 successive measurements in order to minimize the measurement error. Five measurements have been performed on each sample. It has to be mentioned,

that all measurements for both techniques has been performed in climatic chamber (20°C and 65%RH) to minimize influence of temperature and humidity of environment.

2.5.Data processing

OPUS 6.5 and National Instruments LabView 8.6 software packages have been used for signal processing and data analyzes. Signal preprocessing included computation of derivatives, normalization and smoothing. Derivatives were calculated according to the Savitzky-Golay algorithm. For the mathematical management of the spectra and then for the evaluation of the results both Principal Component Analysis (PCA) and Partial Least Square (PLS) matching techniques were applied. For 2D correlation the algorithms based on the Noda [2] works has been implemented.

3. RESULTS AND DISCUSSION

Average spectra scanned from the archeological waterlogged oak samples by means of FT-NIR and FT-MIR-ATR are presented in figure 1 and figure 2 respectively. It is clear that the degradation of the waterlogged woods is evident on the spectra; however more detailed investigations are necessary to point the effects of waterlogging. Table 2 presents a collection of the knowledge related to interpretation of the spectra based on the literature data [4, 1].

Table 2 band assignments for interpretations of infrared spectra

	Wavenumber cm ⁻¹	band assignment	
FT-NIR	1	7000	OH stretching first overtone amorphous regions in cellulose
	2	6718	OH stretching first overtone semi-crystalline regions in cellulose
	3	6450	OH stretching first overtone crystalline regions in cellulose
	4	6287	OH stretching first overtone crystalline regions in cellulose
	5	5980	CH stretching first overtone aromatic skeletal due to lignin
	6	5883	CH stretching first overtone
	7	5800	CH stretching first overtone furanose/pyranose due to hemicellulose
	8	5587	CH stretching first overtone semi- or crystalline regions in cellulose
	9	5464	OH stretching + CO stretching semi- or crystalline regions in cellulose
	10	5219	OH stretching + OH deformation water
	11	4890–4620	OH stretching + CH deformation cellulose
	12	4404	CH ₂ stretching + CH ₂ deformation
	13	4280	CH stretching + CH deformation semi- or crystalline regions in cellulose
	14	4198	CH def. second overtone holocellulose
FT-MIR-ATR	15	1724	CO unconjugated groups in lignin and carboxylic acid ester hemicelluloses
	16	1587	Conjugated CO
	17	1500	Aromatic skeletal; Benzene ring vibration in lignin
	18	1450	CH deformation in lignin and carbohydrates;
	19	1450	CH ₃ , CH ₂ , benzene ring vibration in lignin
	20	1417	CH deformation in lignin and carbohydrates
	21	1417	Aromatic skeletal vibrations combined with CH in plane deformation
	22	1363	CH deformation in cellulose and hemicelluloses;
	23	1363	CH bending vibration in cellulose and hemicelluloses
	24	1319	CH vibration in cellulose; CO in syringyl derivatives
	25	1226	Syringyl ring; CO stretching lignin and xylan
	26	1151	COC vibration in cellulose and hemicelluloses
	27	1116	Aromatic skeletal; CC stretch;
	28	1116	OH association band in cellulose and hemicelluloses
	29	1024	CO stretch in cellulose and hemicelluloses;
	30	1024	CO of primary alcohol
	31	892	CH deformation in cellulose;
	32	892	C group frequency in cellulose and hemicellulose

The most significant differences in the spectra can be observed for lignin (5980 cm⁻¹, 1500 cm⁻¹, 1450 cm⁻¹, 1226 cm⁻¹), hemicelluloses (5800 cm⁻¹, 1724 cm⁻¹, 1363 cm⁻¹, 1151 cm⁻¹) and amorphous region in cellulose (7000 cm⁻¹). No much difference on the spectra has been however observed in the crystalline and semi-crystalline regions of cellulose (6718 cm⁻¹, 6450 cm⁻¹, 5587 cm⁻¹, 5464 cm⁻¹, 1024 cm⁻¹)

Interpretation of results obtained with FT-NIR and FT-MIR-ATR measurements of the waterlogged archeological oaks are similar to those reported by Tsuchikawa et al. [4]. They have concluded that the amorphous, and partially the semi-crystalline, regions of cellulose, hemicellulose and lignin changes during ageing. Conversely, the crystalline region in cellulose seems not to be affected by ageing.

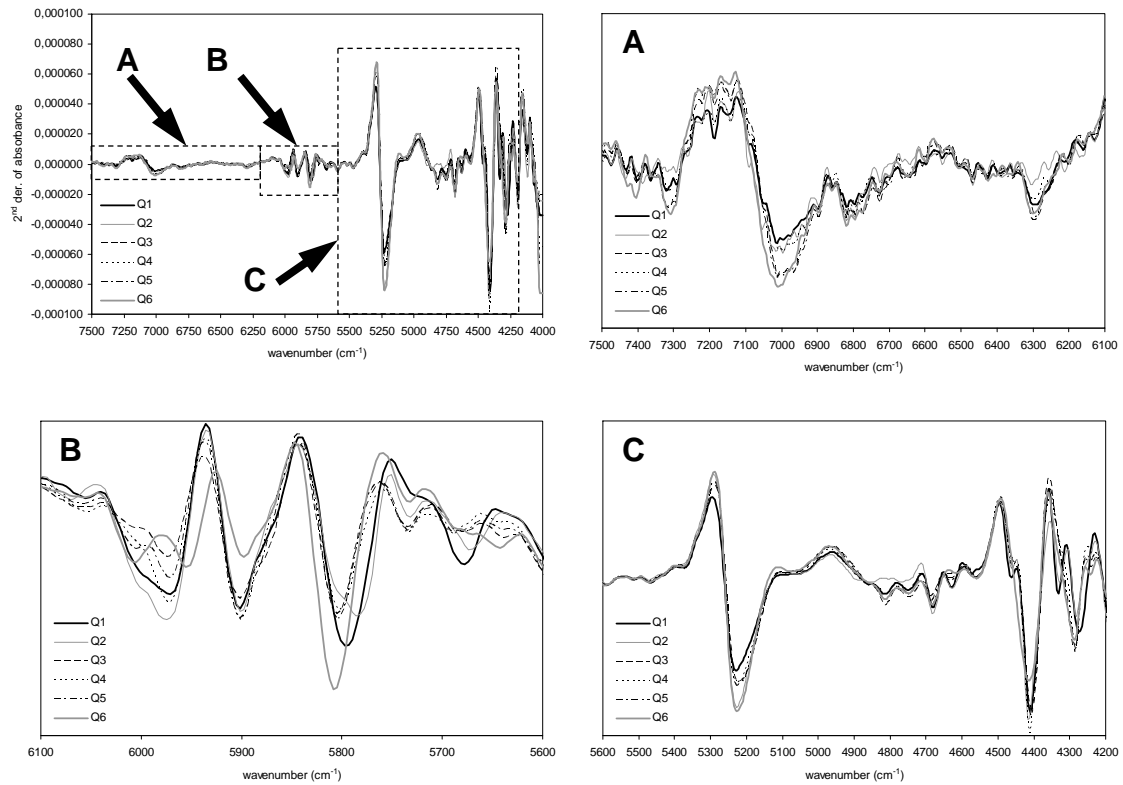


Figure 1 NIR spectra of waterlogged archeological oaks

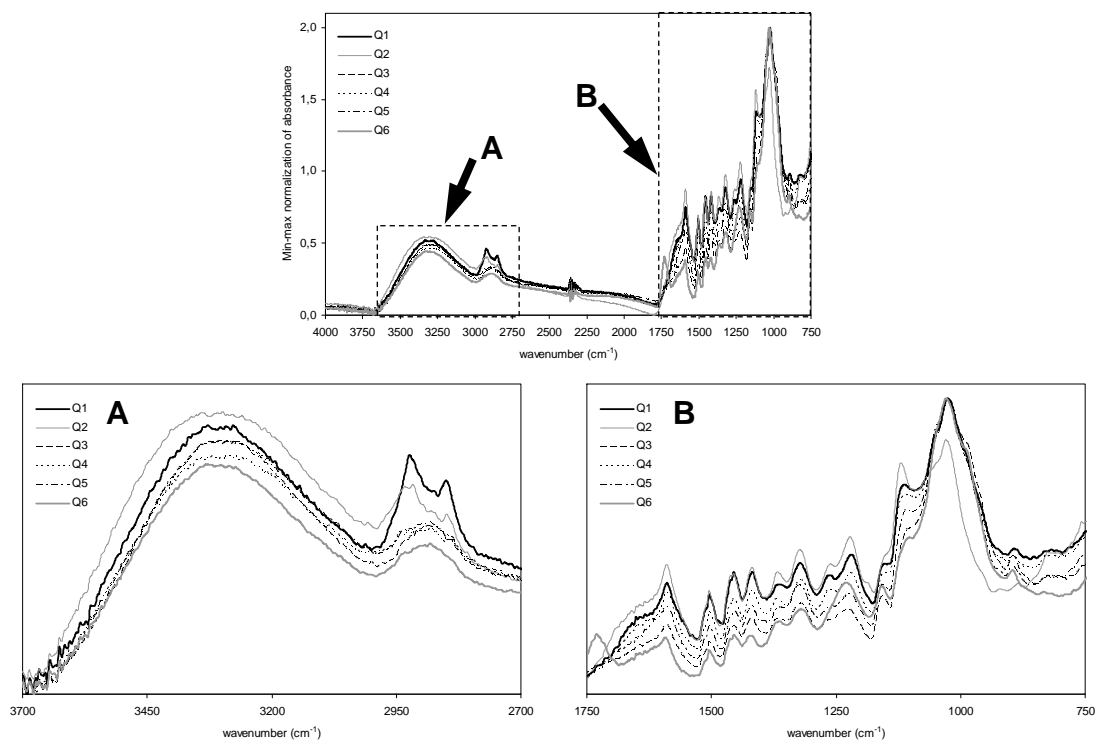


Figure 2 MIR-ATR spectra of waterlogged archeological oaks

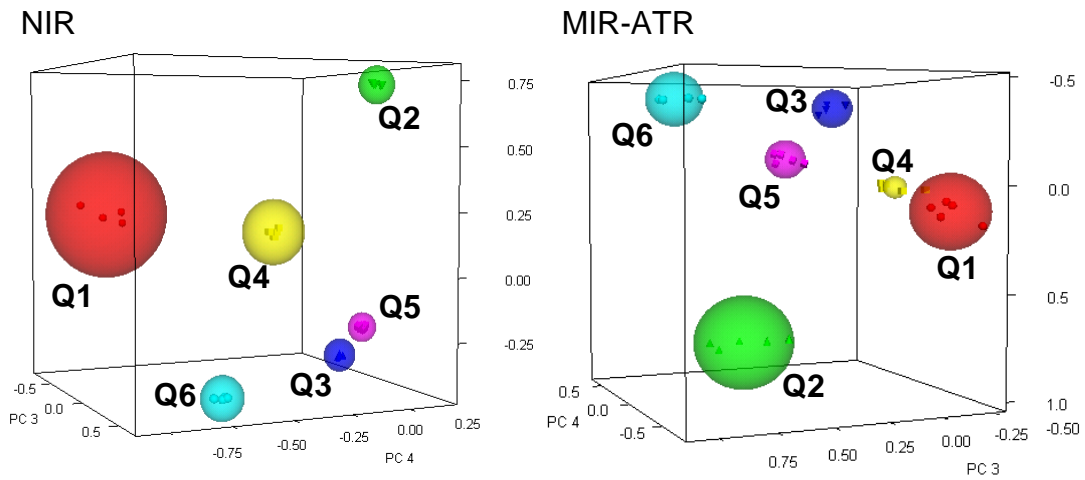


Figure 3 Discrimination of the archeological oak groups with Principal Components Analysis, Note: NIR; 1st derivative, vector normalization, 13 smoothing points, 3 factors, region 9000 to 4242 cm⁻¹ and MIR-ATR; vector normalization, 2 factors, region 1800 to 750 cm⁻¹

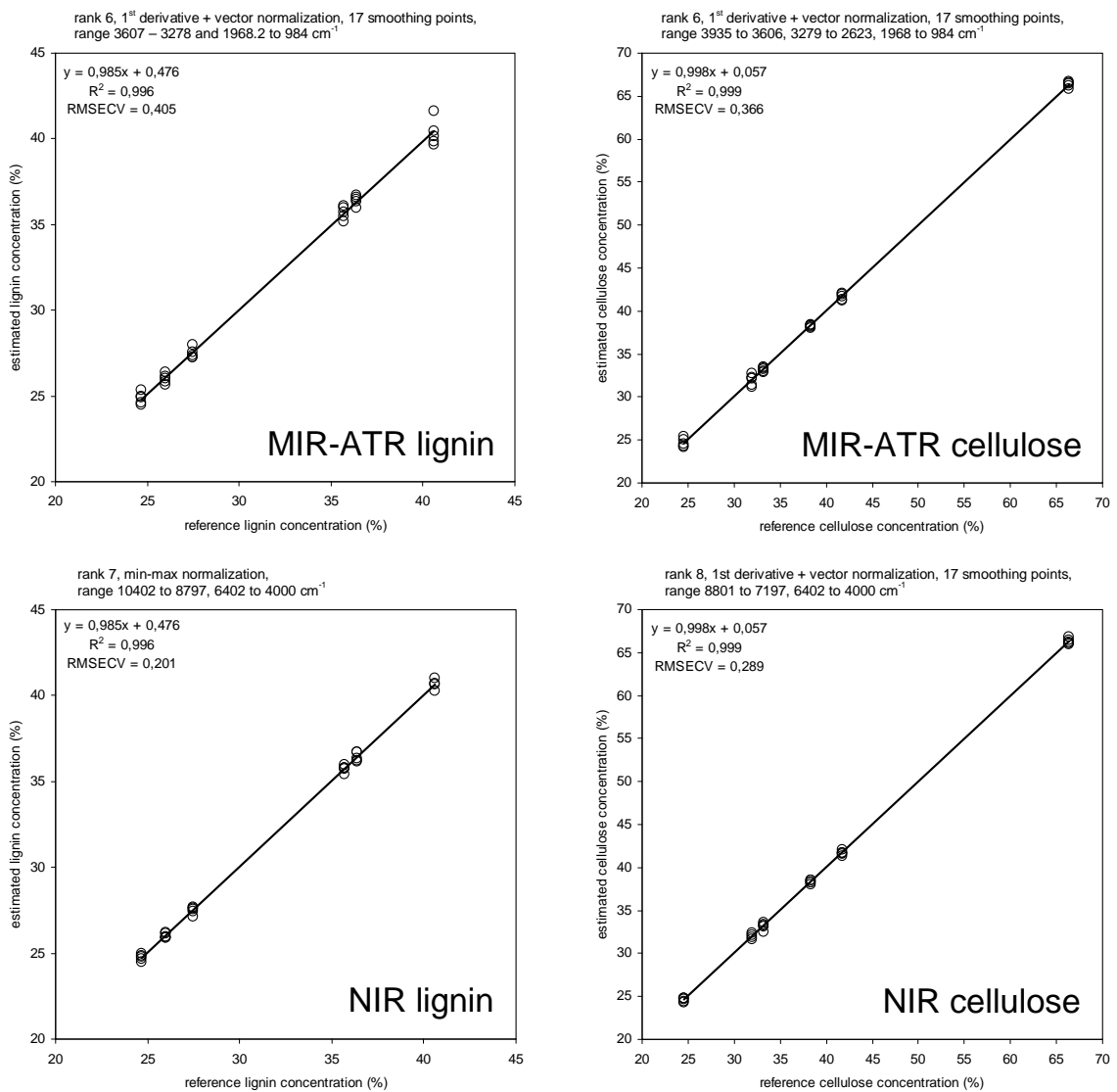


Figure 4 Partial Least Squares estimation of the lignin and cellulose content in archeological waterlogged oak woods by FT-NIR and FT-MIR-ATR spectroscopes

Other implementations of the FT-NIR and FT-MIR-ATR measurements, and its links to the reference analysis, might be related to qualitative and quantitative evaluation of the samples. Figure 3 presents an example of the discrimination of the samples of different degradation levels and/or provenances by means of Principal Components Analysis. Very clear separation has been obtained by both FT-NIR and FT-MIR-ATR techniques. Further improvement of this method (identification test) might be utilized for rapid recognition of both degradation and origin of samples.

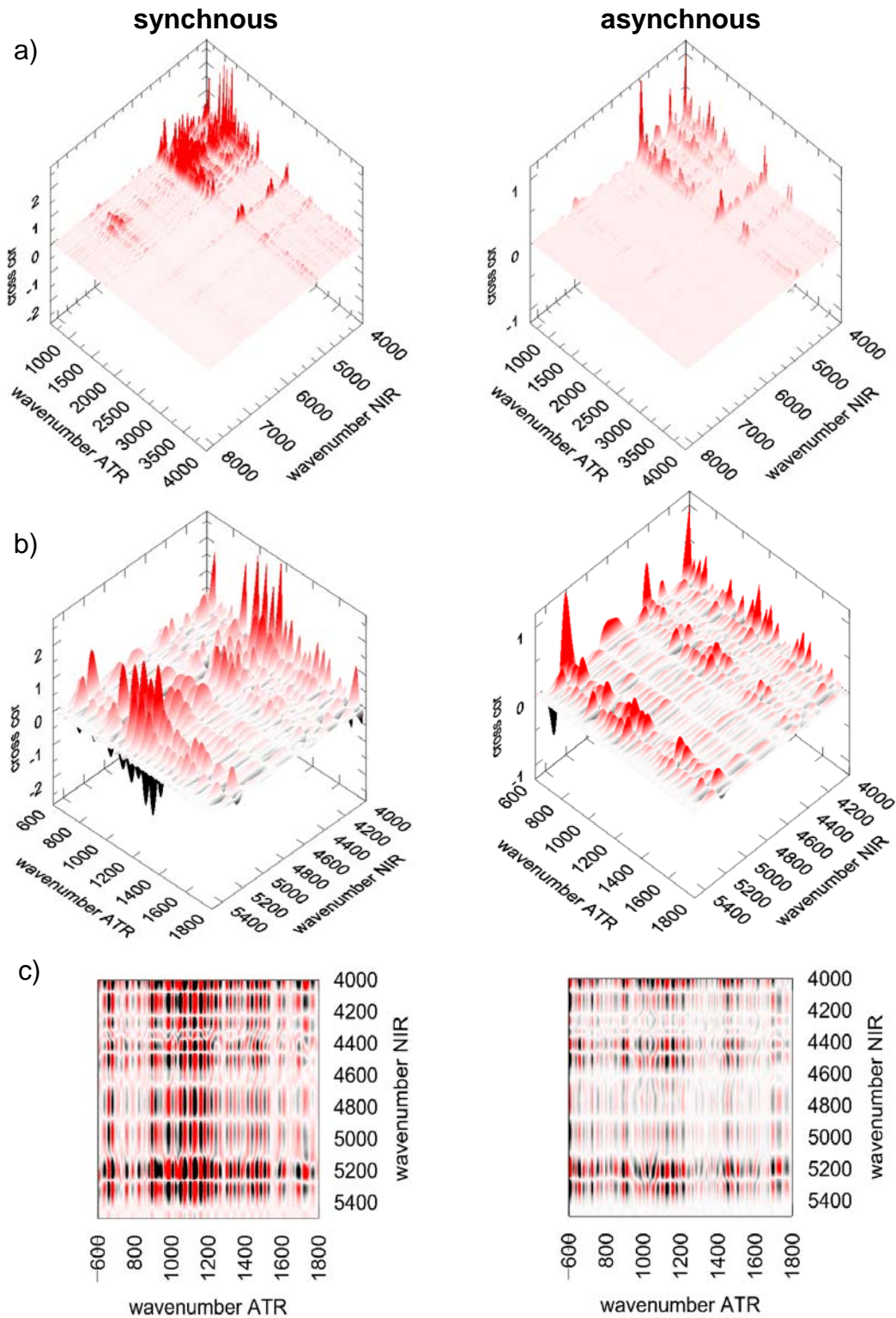


Figure 5 2D spectral correlation between NIR and MIR-ATR spectra of waterlogged archeological oaks; whole spectral range a), zoom to the significant ranges b), top view c)

Figure 4 shows an example of the infrared spectroscopy's potential for estimation of the chemical composition of the waterlogged samples. After processing spectra with Partial Least Squares algorithm it was possible to determine the calibration models to be used for further prediction in the unknown samples.

The last example of the spectra' processing is 2D spectral correlation. The method developed by Noda [2] bases on the computation of the auto-correlation or cross-correlation within/between several spectra. Typically it is applied for visualization of the changes in to spectra due to so called disturbances. These include temperature change, moisture change, concentration change, etc. In this research however the spectral band has been considered as a disturbing factor and such evaluation is called heterospectral. The specially designed software computed cross-correlation between FT-NIR and FT-MIR-ATR spectra scanned from the archeological woods. The resulting charts are presented in figure 5. Two diagrams are usually generated with 2D spectral correlation technique: synchronous and asynchronous relations. The synchronous spectrum represents simultaneous or coincidental changes to the spectrum. On the other hand asynchronous spectrum represents sequential or successive (but not co-incidental) changes to the spectrum. The vertical axis of each 3D chart is an indicator of the importance of the correlation between both spectral wavenumbers (NIR and MIR). It is clear the highest values have been computed for all the wavenumbers belonging to the fingerprint region. The magnified views are presented in figure 5 b and c.

The interpretation of the 2D spectral correlation is not straightforward, but if successful it can be very useful for improving the spectrum interpretation by linking of unknown band assignments of one technique to well established assignments of the second technique. Figure 6 is an example of the knowledge building with the support of 2D spectral correlation; the known NIR band related to hemicelluloses (#7, as in table 2) can be linked to the following bands discovered by MIR analysis (#29, #28, #26, #25, #20, #18, as in table 2).

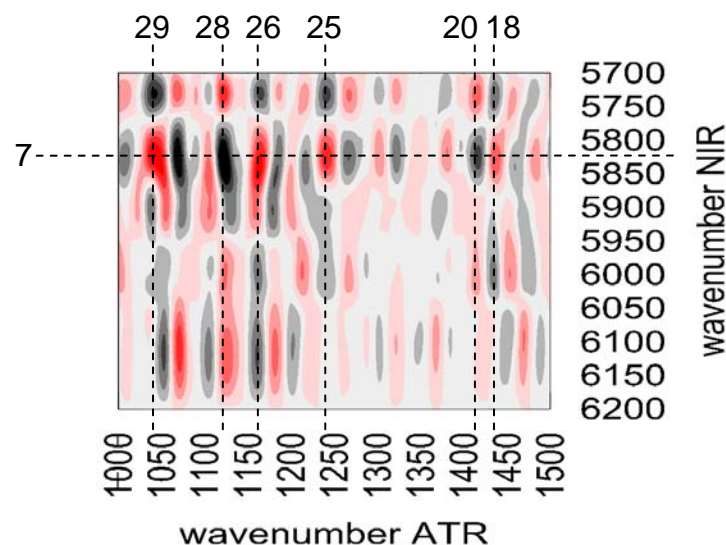


Figure 6 Example for interpretation of the 2D spectral correlation between NIR and MIR-ATR; hemicelluloses

4. CONCLUSIONS

The important advantage of the infrared spectroscopy is its accuracy, simplicity, and ability of performing very high number of tests without needs of any destruction to the workpiece. The methods explored in this research might be a novel tool assisting experts in evaluation of the degradation state of archeological and historical wooden materials. Examples of infrared application in to qualitative and quantitative evaluation have been presented. By linking both infrared techniques with novel signal processing methods it is possible to improve the knowledge and interpretation of spectra.

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