

Archaeological waterlogged oak wood characterization with near infrared spectroscopy

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Introduction

Archaeological wood, as is the case with most natural materials, slowly decomposes on the archaeological sites, due to various biological and environmental factors. Rapid and accurate estimation of the degradation level is extremely important for optimal restoration and conservation. The manual assessment of the degradation or “wet” chemical analyses of the wood chemical components are typical tools for archeologists for the moment. Some attempts to research the archaeological wood with near infrared (NIR) spectroscopy have been recently published.¹⁻³ The goal of the present research was to further explore the usability of the NIR in the field of archaeology. It focused especially on monitoring the degradation level of waterlogged wood, and supporting archaeological wood characterization.

Materials and methods

Ten oak (*Quercus robur* sp.) pieces of the archaeological wood were used as experimental samples. All samples were collected from the waterlogged sites in the area of Poland. 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 taken out and milled on a laboratory mill to reduce the material to powder. The samples were conditioned in a climatic chamber (20°C, 65%RH) to achieve equilibrium moisture content.

All the experimental samples were scanned using a VECTOR 22-N instrument produced by Bruker Optics GmbH. The instrument was equipped with a standard fiber-optic probe, germanium-diode detector and the thermoplastic resin Spectralon as a reference. 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 was computed as an average of 32 successive measurements. Five separate spectra were measured on each sample after mixing the powder between

Table 1. Waterlogged oak from the oldest settlements in Poland and its basic chemical composition.

Sample code	Origin	Dating	Waterlogged period, years	Waterlogged environment	cellulose (C)%	lignin (L) %	C/L ratio
①	Biskupin	VIII BC	2700	peat bog	32.0	40.6	0.79
②	Biskupin	VIII BC	2700	peat bog	30.4	42.3	0.72
③	Biskupin	VIII BC	2700	peat bog	42.5	43.7	0.97
④	Biskupin	VIII BC	2700	peat bog	32.5	37.3	0.87
⑤	Biskupin	VIII BC	2700	peat bog	38.7	32.5	1.19
⑥	Biskupin	VIII BC	2700	peat bog	11	64.1	0.17
⑦	Bronisze (Warsaw)	III AD	1700	peat bog	24.6	36.4	0.68
⑧	Lednica	X–XI AD	1000	bottom of the lake	41.7	27.5	1.52
⑨	Ostrow Tumski (Poznań)	IX–X AD	1000	river mud	33.2	35.7	0.93
⑩	Szczecin	XIII AD	700	soil	38.3	24.7	1.55
⑪	Golabki	XX AD	0	air dry	38.5	26.0	1.48

each scan. Supplementary tests on the waterlogged oak samples were performed on the mid infrared Bruker Optics GmbH Alpha MIR-ATR spectrophotometer.

Traditional “wet” chemical analysis was performed in parallel to the spectroscopic measurements. The quantity of cellulose was determined according to the Seifert procedure (by using acetylacetone-dioxane-hydrochloric acid).⁴ Lignin content was estimated according to TAPPI (T22om-06) standard.⁵ Details regarding the location, waterlogging condition and chemical composition for oak samples researched in this project are summarized in Table 1.

OPUS 6.5 and LabView software were used for spectra processing. Principal component analysis (PCA), partial least squares and 2D correlation techniques were applied for data evaluation.

Results and discussion

The content of cellulose and lignin varied very significantly in all samples analyzed. However, due to the relatively wide range of the contents of the main components content in wood, even of the same species, the analysis of percentage of lignin or cellulose content could be improved. The cellulose/lignin ratio (C/L) seemed to be a more reliable indication of the degradation process than individual determinations of cellulose or lignin. Such a ratio varied within the measured pieces in a range from 0.2 (for highly degraded wood) to ~1.5 (for contemporary and well preserved wood). It should be mentioned, however, that the C/L was not directly related to the waterlogging period. It can be seen that samples ① to ⑥, even if excavated in the same location, having been waterlogged for the same time, had degraded very differently.

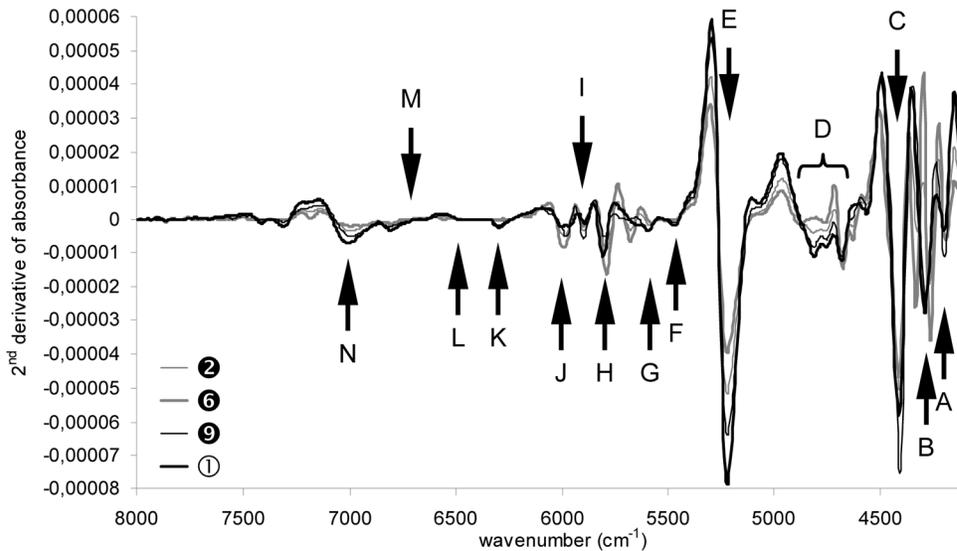


Figure 1. FT-NIR second derivative spectra of four oak samples with different degradation level.

Figure 1 shows a part of the spectral band (from 4000 cm^{-1} to 8000 cm^{-1}) measured with NIRS on three waterlogged and one contemporary oak samples.

All the samples selected differed significantly in term of the wood degradation; the C/L ratio varied in all cases. The black arrows indicate positions of peaks assigned to absorption bands of cellulose, hemicelluloses and lignin. The differences are related to dissimilar amounts of chemical substances removed or changed during waterlogging. Detailed explanation of the spectral changes can be obtained in the literature.^{1,6} It is most important to notice that:

- crystalline regions of cellulose (seen on Figure 1 as bands *F*, *G*, *K*, *L* and *M*) are relatively unaffected by the waterlogging, and only minute changes in the spectra are visible
- changes in the spectra related to the holocellulose (*A*) and lignin (*J*) are moderately significant
- chemicelluloses are the most easily destroyed components of wood, due to biological and environmental factors; and variations in the spectra in bands *I* and *J* are visible
- amorphous regions of cellulose (related to bands *N* and partially *D* and *B*) are evidence of considerable changes due to waterlogging
- significant variation in the band related to water (*E*) is an effect of the drastic changes in the hygroscopic properties of waterlogged wood

Partial least squares were applied for computation of regression models linking source spectra and reference values of cellulose and lignin. Such prediction models could be very useful for rapid assessment of the degradation level of archaeological wood, especially in the field, on the archaeological site. Resulting PLS models were validated and the accuracy of the estimation is presented in Figure 2.

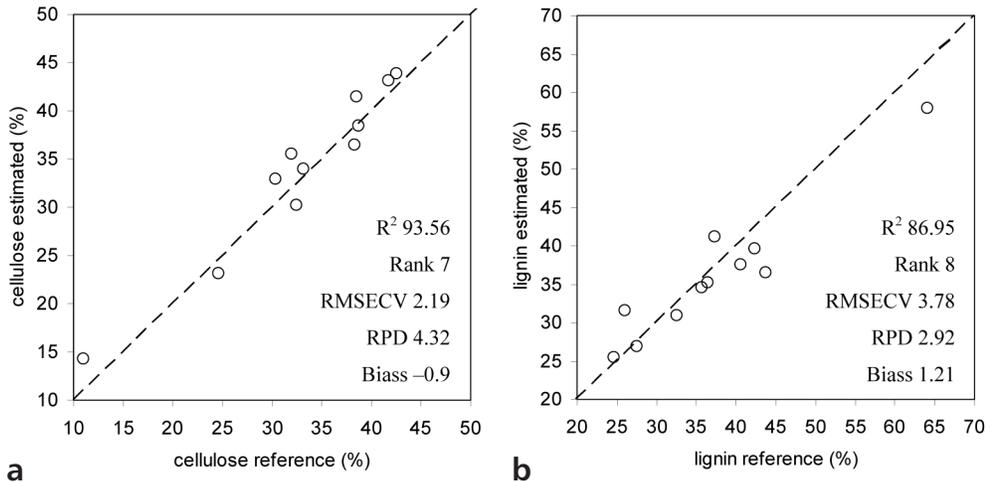


Figure 2. PLS analysis of the archaeological wood; (a) cellulose content and (b) lignin content.

Principal component analyses were conducted in order to investigate the NIR spectroscopy applicability for determination/differentiation of the archeological wood. As can be seen on the Figure 3, all samples were classified clearly. It can be assumed that the use of NIR spectroscopy in archaeometry is a very promising field for application.

The spectra obtained by both NIRS and MIR-ATR can be interlinked by means of hetero 2D spectral correlation.⁷ Such analyses were performed for the spectra of waterlogged oak wood. As

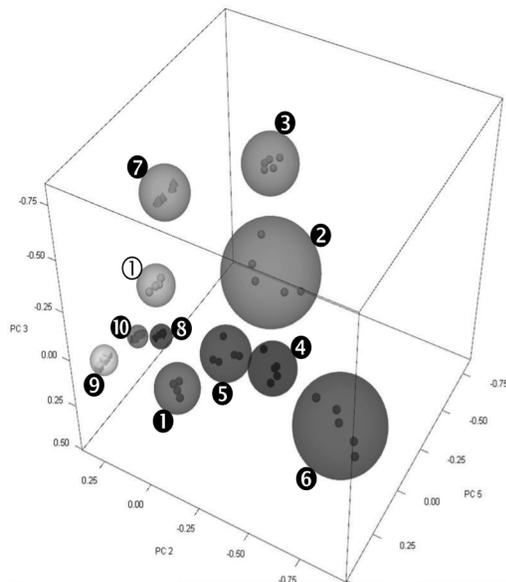


Figure 3. PCA of archaeological oak wood.

a result, changes to the spectra related to degradation (waterlogging) in both infrared techniques were clearly identified.

Conclusions

The ability of the NIR spectroscopy technique for rapid estimation of the cellulose and lignin contents, discrimination of the degraded woods, and estimation of the state of archaeological wood decomposition have been demonstrated. The method promises to be an innovative, flexible, and useful tool to assist experts in restoration and conservation of archaeological and historical wooden materials.

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