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THE USE OF FT-IR AND COMPUTED TOMOGRAPHY NON-DESTRUCTIVE TECHNIQUE FOR WATERLOGGED WOOD CHARACTERISATION

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ABSTRACT

The archaeological wooden oak piles of medieval "Poznan" bridge, situated at the bottom of Lednica Lake in Greater Poland, are a valuable relic of the beginnings of the Polish country. The assessment of the state of wood preservation will allow to propose the most appropriate conservation agents and methods in order to save this cultural heritage.

The aim of the study was to evaluate the degree of degradation of waterlogged piles by using traditional and non-destructive testing methods and to estimate the usefulness of non-destructive FT-IR and computed tomography techniques in such an assessment. The applied traditional, destructive methods, like chemical and physical, as well as non-destructive ones, like X-ray CT or FT-IR, showed that the archaeological oak wood elements are quite well preserved, especially their heartwood part. The obtained results clearly confirm that the modern X-ray CT measurement and FT-IR analysis can be very useful in archaeological wood research, giving a good insight into wood structure.

KEYWORDS: Waterlogged wood, archaeological oak, wood degradation, wood characterisation, FT-IR, X-ray CT.

INTRODUCTION

Wood, like other organic materials, deteriorates over time when exposed to degradation caused by microorganisms and non-biological processes. In most kinds of environment wood decomposes relatively rapidly, so very often there is no evidence of wooden objects from the past. But in some environments, deterioration processes are more or less restricted and archaeological wooden objects may remain there relatively unaltered.

Historic wooden objects obtained from water-logged archaeological sites are often found in a relatively good state. In underwater conditions the activity of aerobic bacteria, fungi and insects is significantly limited by low temperatures and low oxygen content. However, strong activity of anaerobic bacteria is often observed. Waterlogged wood usually looks relatively satisfactory, but erosion, cavitation, scavenger and tunnelling bacteria can considerably alter its composition mainly by causing loss of the polysaccharidic components cellulose and hemicellulose (Blanchette 2000, Bjordal et al. 1999). The loss of wood substance decreases its density and increases microporosity and permeability. The chemical, physical and mechanical properties of degraded wood deteriorate and it changes into a spongy substance full of water (Pizzo et al. 2010, Huisman et al. 2008). Wood in such a condition is highly susceptible to degradation during preservation – significant dimensional changes and cracking can occur during its drying because of the shrinkage and collapse of weakened cell walls (Bugani et al. 2009).

According to Manders et al. (2004), the degradation process cannot be stopped, it can only be slowed down through the appropriate conservation treatment. In order to preserve valuable archaeological objects and exhibit them in museums, accurate information of wood deterioration mechanisms is needed. This is important both for developing an appropriate conservation treatment and for developing successful methods of in situ preservation when it is necessary to rebury precious cultural resources or preserve them at the excavation site. Therefore, when doing a comprehensive research of any complex material, it is important to have a variety of complementary methods (for example, when dealing with waterlogged archaeological wood, it is good to have a set of methods, both non-destructive and destructive ones, for the most accurate determination of its state of preservation).

The estimation of the degree of archaeological wood degradation typically includes chemical analysis, determination of wood weight loss, a complete microscopic analysis and special instrumental methods enabling determination of the structure of wood tissue components (Gelbrich et al. 2008). Classical methods for assessing the degree of wood decay are associated with the need to collect and prepare a sample, which is connected with destruction of the integrity of the valuable object under inspection. Therefore in the field of cultural heritage the development of non-destructive measurement techniques is required, such as X-ray Computed Tomography and Fourier transform infrared spectroscopy, as used in the presented study.

X-ray Computed Tomography (CT) is considered as one of the best non-destructive testing techniques and it is increasingly being used for the full-volume inspection of archaeological objects. By using this technique, it is possible to look inside a wooden artefact, even under ambient conditions, and recognise its inner three-dimensional microstructure without any special need for specimen preparation, such as staining or slicing and without destruction of the integrity of the tested object. The CT technique is based on the collection of a set of two-dimensional radiographic projections (of cross sections) taken from different viewing angles. The collected 2D projections are then converted into 3D images by using a special reconstruction algorithm. The calculated images are maps of the X-ray photon attenuation caused by the tested sample which is related to many different factors like density or elemental composition of the object (Bugani et al.

2009; Morigi et al. 2010, Macedo et al. 2002). This technique is very useful for the study of the degraded waterlogged wood and for selecting the most appropriate strategy for the conservation of archaeological artefacts because it enables the wood morphology and composition to be visualized (Haneca et al. 2012).

Fourier transform infrared spectroscopy (FT-IR) is a versatile analytical technique for identifying a substance. The vibrational spectrum is characteristic and unique for a molecule, dependent on its chemical composition and structure. For this reason it seems to be useful for the qualitative analysis of an archaeological wood structure as well as for the estimation of cellulose and lignin content. The technique allows users to acquire fast spectral data and almost does not require sample preparation (Pizzo et al. 2013). Among others, FT-IR spectroscopy has been used for evaluation of the effects of the ammonia neutralising treatment on marine archaeological wood from the Vasa (Fors and Richards 2010), for studying the effect of early fungal decay on sycamore wooden masks dating back to the Greek-Roman period in Egypt (Darwish et al. 2013) or to characterise the distribution of the PEG in the wooden Vasa warship (Glastrup et al. 2006). The possibility of the fast assessment in the state of preservation of valuable wooden heritage objects must not be underestimated. Therefore, such methods like FT-IR should be developed.

The aim of the study was to evaluate the degree of degradation of wooden piles taken from Lednica Lake by using traditional and non-destructive testing methods and to evaluate the usefulness of non-destructive FT-IR and computed tomography techniques in such an assessment. The object of the research – the archaeological wooden elements of medieval "Poznan" bridge, situated at the bottom of Lednica Lake, are a valuable relic of the beginnings of the Polish country. Situated at the western side of the Ostrow Lednicki, where the borough of Mieszko I - the first ruler of Poland, was located, 280 meters from the south shore of the island, the bridge linked it with a road leading to Poznan. The wooden remains of the bridge are situated at the entire length of 436 m on the western side of the island, in a pass with a width of approximately 20 m. Precise wood characteristics combined with the evaluation of the degree of its degradation will allow a decision to be made on the most adequate conservation agents and methods in order to save this historical treasure.

MATERIAL AND METHODS

Material

The studied material was waterlogged archaeological oak wood (*Quercus robur* L.) excavated from Lednica Lake, taken from the 12 piles (the structural elements of the "Poznan" bridge, dating back to the 10-11th century, plot No. 4, pass No. 2, 11 meters beneath the water surface – Fig. 1) and samples of contemporary oak wood (*Quercus robur* L.) from Greater Poland region (CO) as a reference. Both sapwood and heartwood were found on beams marked with numbers 8, 9, 11 and 12. The outer zone - sapwood, the thickness of which varied in the studied samples from 20 to about 30 mm, was characterised by a light, honey colour, a high fragility and a spongy structure. This zone had remained on the pile surface only partially. The inner zone (heartwood) remained physically almost unchanged in all tested samples. It was characterised by a dark, nearly black colour and a greater hardness. A part of each wooden element sticking out from the mud at the bottom of the lake was taken out and milled on the laboratory cutting mill (Pulverisette 15, Fritsch GmbH) to obtain the powder. The powder was sieved and the finest fraction of it (particle size less than 0.5 mm) examined using wet chemical analysis and FT-IR measurement.

Tab. 1: The dimensions of 12 structural elements of the "Poznan" bridge.

Pile number	1	2	3	4	5	6	7	8	9	10	11	12
Length (cm)	30.5	44.5	42	55	32	21	38	92	54	63	79	51
Diameter (width/high) (cm)	16/12	14.5	15/11	15/10	15.5	16.5	12	16	15	17/13	19	14.5

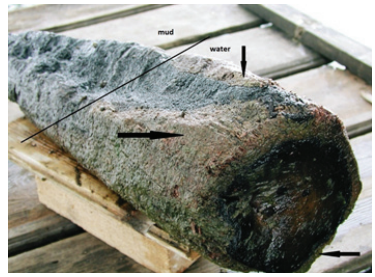

Fig. 1: One of the structural "Poznan" bridge elements - beam Nr. 10. The remains of the sapwood area can be seen as outer lighter parts (black arrows). The tapered end was located in the mud at the bottom of the lake, a sample was taken from the water-submerged part sticking out from the mud. By Królikowska-Pataraja.

Methods

In order to assess the state of preservation of archaeological waterlogged wood, the traditional research methods were used as the determination of the physical and chemical parameters, in combination with the non-destructive method of computed tomography and FT-IR spectroscopy. Such an interdisciplinary approach guarantees a much better evaluation of the state of wood degradation.

Chemical analysis

The chemical characterisation of archaeological wood was performed in order to recognise the changes in the percentage content of individual components of wood. This is important for assessing properly the nature and extent of degradation, and makes it easier to understand the processes associated with microbial decomposition of a wood tissue.

The analysis included determination of the content of main chemical components in the wood samples. Determination of cellulose was performed according to the Seifert procedure by using acetylacetone-dioxanehydrochloric acid (Browning 1967). Holocellulose was obtained from wood with an acid solution of sodium chlorite by using the procedure described by Browning (1967). The lignin was determined according to the Tappi standard (TAPPI 2006). Solvent extractive components and ash were measured according to Tappi standards respectively (TAPPI 2007a, b). The heartwood layers of archaeological wood samples were used as a whole.

Physical wood properties

Physical parameters such as density and moisture content are the most frequently determined parameters for the characterisation of the state of waterlogged archaeological wood preservation (Jensen and Gregory 2006).

The maximum moisture content and the basic density of waterlogged and contemporary wood were determined. Additionally, the loss of wood substance was calculated on the basis of obtained results (Grattan and Mathias 1986). The heartwood layers of archaeological wood

samples, as in the case of chemical analysis, were used as a whole.

The maximum moisture content of wood (MC_{max}) was determined on the basis of the measurement of wood mass (samples were repeatedly saturated with water in the pressure of 50 hPa and then dried for 24 h in the oven at temperature of 105°C) (m_{max}) and the mass of absolute dry wood (m_0) – Eq. 1.

$$MC_{\max} = \frac{m_{\max} - m_0}{m_0} \cdot 100 \quad (\%) \tag{1}$$

The basic wood density (ρ) was presented as a ratio of the weight of an absolute dry wood sample (m_0) to its volume in the state of maximum water saturation (V_{max}) according to Eq. 2.

$$\rho = \frac{m_0}{V_{\max}} \tag{2}$$

The loss of wood substance (LW), expressed as a relative decrease in the density of archaeological wood, was calculated according to the Eq. 3:

$$LW = \frac{\rho_c - \rho_a}{\rho_c} \cdot 100 \quad (\%) \tag{3}$$

where: LW - loss of wood substance (%)
ρ_c – the density of contemporary wood (kg. m^{-3})
ρ_a – the density of archaeological wood (kg. m^{-3}).

X-ray Computed Tomography (CT) technique

The study was conducted using a GE CT scannerwith 32 rows of detectors, the model Light Speed pro. Due to the necessity of saving the limited wood material, the density measurement had been performed for wet samples number 5, 7, 10 and 11 (5 and 7 – only heartwood zone, 10 and 11 – both sapwood and heartwood zones). The water contained in the wood tissue does not affect the measurement results – the water absorption coefficient is 0 Hounsfield units (HU). The Hounsfield unit scale is a linear transformation of the original linear attenuation coefficient measurement into one in which the radiodensity of distilled water at standard pressure and temperature is defined as zero HU, while the radiodensity of air at the same conditions is defined as -1000 HU. In order to obtain reliable results, 7 to 11 measurements for each sample were done to show the potential changes in an archaeological wood tissue structure in comparison with contemporary wood.

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) was used to obtain rapid information about the chemical changes taking place in the archaeological wood. The IR spectra of cellulose and lignin were performed. Powdered archaeological and contemporary wood samples were analysed for a comparative study.

The IR spectra were recorded at room temperature on solid samples in KBr pellets by means of a Thermo Fisher Scientific Nicoleti S 10 spectrometer, using the absorbance range from 4000 – 400 cm^{-1}. The concentration of the sample was of 2-3 mg/200 mg KBr. Processing of the spectra was done by means of Omnic programme. The detailed spectra analysis was examined in the range 1800 – 700 cm^{-1}.

RESULTS AND DISCUSSION

The chemical analysis

The study of the chemical composition is an important part of the process to assess the conservation status of archaeological material. The determination of loss or increase in the proportion of a given component is only possible when the chemical composition of the raw material is known before the start of degradation processes. Archaeological wood research requires a reference of the obtained results to the average characteristic values of the contemporary wood.

Tab. 2: The chemical composition of archaeological and contemporary oak wood (expressed as a percentage of degraded wood dry matter). 1 - 12 – archaeological oak heartwood samples, 11s – archaeological oak sapwood sample, CO – contemporary oak wood sample.

Sample number	Substances soluble in cold water (%)	Substances soluble in hot water (%)	Substances soluble in NaOH (%)	Substances soluble in organic solvents (%)	Cellulose content (%)	Lignin content (%)	Holo-cellulose content (%)	Mineral substances content (%)
1	1.59	2.71	15.13	2.26	40.24	29.22	59.42	1.97
5	0.33	3.58	16.53	2.81	42.52	28.45	62.60	1.97
6	1.14	3.54	18.71	1.84	39.63	28.31	63.57	2.90
7	0.72	1.01	13.91	2.26	44.49	28.99	66.59	2.08
8	0.80	3.36	15.30	2.45	40.40	29.59	66.94	2.29
10	1.16	3.62	16.57	2.87	41.55	26.75	61.58	3.13
11s	0.73	1.36	28.91	2.66	12.31	30.69	20.03	4.99
11	0.85	1.64	17.57	1.92	38.76	27.12	62.84	4.01
12	1.02	4.51	16.25	1.66	39.80	28.78	60.33	2.71
CO	5.03	7.74	9.41	2.97	37.72	27.92	69.48	1.05

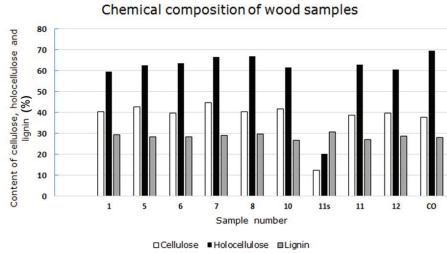

Fig. 2: The absolute content of cellulose, holocellulose and lignin in archaeological wood samples expressed as a percentage of degraded wood dry matter (DWDM) compared with contemporary oak wood (1, 5, 6, 7, 8, 10, 11, 12 – archaeological oak heartwood samples, 11s – archaeological oak sapwood sample, CO – contemporary oak wood sample).

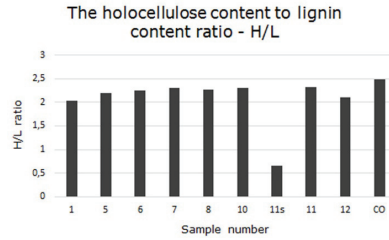

Fig. 3: The holocellulose content to lignin content ratio in archaeological wood samples compared with the contemporary oak wood (1, 5, 6, 7, 8, 10, 11, 12 – archaeological oak heartwood samples, 11s – archaeological oak sapwood sample, CO – contemporary oak wood sample).

All archaeological heartwood samples showed an average cellulose content of 41 % degraded wood dry matter (DWDM), being similar to the cellulose content in contemporary oak wood. In case of the sapwood sample the cellulose content was much lower – only 12.3 % DWDM, which indicates a high degree of wood degradation. Concerning the holocellulose content, the results were similar – for heartwood samples the values were comparable to the holocellulose content in CO (62.9 % DWDM) and the lowest holocellulose content was observed for the most degraded sapwood sample (only 20 % DWDM). In contrast, the lignin content in all archaeological wood samples was at a similar level as in contemporary wood (about 28.6 % DWDM). Sapwood sample 11s has a cellulose/holocellulose/lignin content "pattern" which differs from the pattern of CO and the archaeological heartwood samples. This pattern indicates a higher level of degradation - sapwood 11s is the most degraded sample. The content of cellulose and holocellulose in this case is the lowest and represents about 1/3 of the values for CO. The remaining heartwood samples exhibited a good state of preservation, cellulose, holocellulose and lignin content being comparable with values for sound contemporary wood.

The chemical composition of archaeological wood presented as a percentage of the dry weight of degraded wood does not take into account the fact that the wood is decomposed. The compiled data represents only the percentage of the determined components in the analysed material. Drawing the conclusions about the state of wood degradation is possible only based on the numerical relationships between the ratios of the individual components, for example: Holocellulose to lignin (H/L) or cellulose to lignin (C/L) (Sandak et al. 2010).

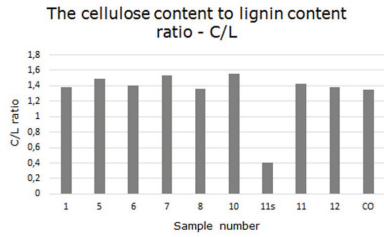

Fig. 4: The cellulose content to lignin content ratio in archaeological wood samples compared with the contemporary oak wood (1, 5, 6, 7, 8, 10, 11, 12 – archaeological oak heartwood samples, 11s – archaeological oak sapwood sample, CO – contemporary oak wood sample).

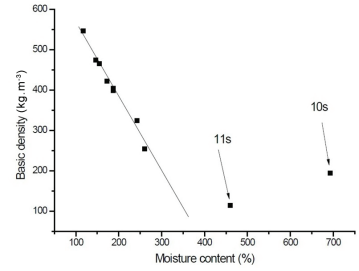

Fig. 5: Relationship between basic wood density and moisture content of archaeological oak wood. For all heartwood samples the results fall on the same line – the exceptions are sapwood samples: 10s and 11s.

Figs. 3 and 4 present the H/L coefficient (ratio of the percentage proportion of holocellulose to lignin) and the C/L coefficient (ratio of the percentage proportion of cellulose to lignin), respectively. The lower these values are, the more degraded the wood tissue is (Waliszewska et al. 2007). The value of the C/L ratio for sapwood 11s is 0.4 and it is almost 5 times lower than C/L of contemporary wood (1.35), which indicates the high degree of wood decomposition. For heartwood samples C/L is between 1.36 and 1.55 and resembles the C/L coefficient for sound contemporary wood. The value of the H/L coefficient for archaeological sapwood 11s is 0.68 and it is almost 4 times lower than H/L of CO. For heartwood samples H/L ranges from 2.2 to 2.32 and is equivalent to H/L of CO. Those results show the high degradation level of archaeological oak sapwood zone and indicate the good state of preservation of the heartwood zone despite the

long deposition at the bottom of the lake.

In the case of the sapwood sample 11s there is nearly a 3-fold increase in the content of substances soluble in 1 % NaOH observed with respect to the content of the substances in the CO - 9.41 %. This suggests a partial depolymerisation of structural polysaccharides in cell walls and evidence the decay of this material. For the heartwood samples, the values areat a comparable level from 13.9 to 18.71 % and are higher than the value for CO. The archaeological wood samples also contain much more mineral substances in comparison with contemporary wood (Tab. 2). The increase in the amount of minerals in archaeological wood from Lednica Lake is caused by increased solubility of carbohydrate components. The highest values of mineral substances content have been observed for the most degraded sapwood fraction of the sample number 11. This is a typical phenomenon for waterlogged wood connected with a mineralisation process, when insoluble minerals contained in water are deposited on the surface and inside the wooden tissue (Grattan, Mathias 1986; Hedges 1990; Hoffmann 1982).

Long wood exposure to water at the bottom of the lake resulted in almost complete elution of substances soluble in cold water (SSCW) and a significant reduction in the content of substances soluble in hot water (SSHW) in the archaeological wood tissues (Tab. 2). The lowest SSCW values were observed for sample No. 5 (0.33 %), a slightly greater amount of those compounds was determined for samples No. 7 (0.71), 11 (0.85), 11s (0.73), No. 8 (0.8 %), whereas for CO the SSCW value is 5.03 %. Only slightly more substances pass to solution after wood treatment with hot water. The least, as only 1.01 % of the SSHW has been determined in a sample 7, 1.36 % in sample 11s, a little more - 1.64 % - has been measured for sample 11. For CO the SSHW value was 7.74 %. The amount of substances extracted from archaeological wood with organic solvents was at a comparable level with the values obtained for contemporary oak wood and ranged from 2.26 to 2.87 %. Only in case of three haertwood samples, No 6, 11 and 12, the lower values were observed. No direct correlation between the state of wood degradation and the content of SSCW, SSHW, and substances extracted with organic solvent can be seen.

Physical properties of wood

Wood density is a commonly used and easily measurable parameter which allows the determination of the state of archaeological wood preservation. In combination with such parameters like maximum moisture content and wood mass loss it provides the information on the tendency of wooden artefacts to collapse during conservation and allows appropriate impregnation agents conservation methods to be applied (Jensen and Gregory 2006).

The obtained results of physical archaeological wood properties measurement (Tab. 3) has shown that, as was expected, the most degraded part of wood is the sapwood zone. The highest values of the maximum moisture content have been reported for sapwood samples (692.5 for sample 10s and 459.4 % for the sample 11s), which correlates with the lowest values of basic wood density (194.3 for 10s and 114.2 $kg.m^{-3}$ for 11s) as well as the highest level of wood mass loss (67.1 for 10s and 80.6 % for 11s). Such high moisture content and the mass loss values of sapwood samples indicate the extensive decay of that wood zone (Waliszewska et al. 2007).

In contrast, the results for heartwood samples indicate a quite good state of preservation of this wood zone. Opposite to the results for sapwood samples, with the decrease in maximum moisture content an increase of conventional density of tested wood samples is observed. The maximum moisture content ranges from 116.9 (sample No. 8) to 260.6 % (sample No. 10) and the wood mass loss ranges from 7.3 (sample No. 8) to 46.9 % (sample No. 10). Those values are about 3 to 5 times lower that in case of sapwood samples. The basic wood density of heartwood zone varies from 254.1 (sample No. 10) to 546.9 $kg.m^{-3}$ (sample No. 8), which is about 2 to 5

Tab. 3: Selected physical properties of archaeological oak wood excavated from Lednica Lake. 1 – 12 – heartwood samples; 10s, 11s – sapwood samples.

Sample number	Maximum moisture content (MC_{max}) (%)	Basic wood density (ρ) (kg m^{-3})	Loss of wood substance (LW) (%)
1	187.4	405.0	31.3
5	146.4	474.9	19.5
6	242.5	324.7	45.0
7	172.7	422.8	28.3
8	116.9	546.9	7.3
10s	692.5	194.3	67.1
10	260.6	254.1	46.9
11s	459.4	114.2	80.6
11	154.8	465.8	21.0
12	186.9	399.6	32.3

times higher than for sapwood samples. In comparison, according to Babiński and Sandak, the maximum moisture content value of contemporary oak wood is about 61 (or even about 90 %, concerning mathematical calculations), and the basic density value is 617 $kg.m^{-3}$ (Babiński et al. 2006; Sandak et al. 2010). Those parameters confirm a quite good state of preservation of waterlogged archaeological oak heartwood, especially for samples No. 5, 7, 8 and 11.

Density measurement – the X-ray Computed Tomography

CT scanning was used to determine archaeological wood density because it provides a means of evaluating the density of the whole cross section of the wood slice without its destruction. A set of measurements were performed for the sapwood and heartwood zones (Figs. 6 and 7).

Fig. 6: The cross-section of pile number 11. By Królikowska-Pataraja. Wood slice dimensions: Diameter - 21 cm, height – 3.4 cm, the thickness of sapwood - about 2.3 cm. The numbers in circles indicate the position of the CT measurements.

The biggest differences were observed between sapwood and heartwood, which is connected to natural, diverse density of those zones as well as to the state of wood degradation. Pursuant to the Hounsfield scale by De Vos (Tab. 5), the areas of the colour close to the white as well as the HU values above 0 indicate the compact tissue, like muscle, liver or bone. The higher the HU value, the more dense the measured object is. The heartwood on tomograms is visible as light parts, slightly differing in grey scale. The results of CT measurement of that zone range from 72.12 to 128.03 HU. It denotes the homogeinity of the archaeological oak heartwood zone and its high density which proves the good state of its preservation. In the CT pictures the archaeological

sapwood is visible as darker parts and the HU values for that zone range from -44.19 to -120.46. It indicates that this wood layer contains air or water, has lower density and consequently is much more degraded than heartwood zone.

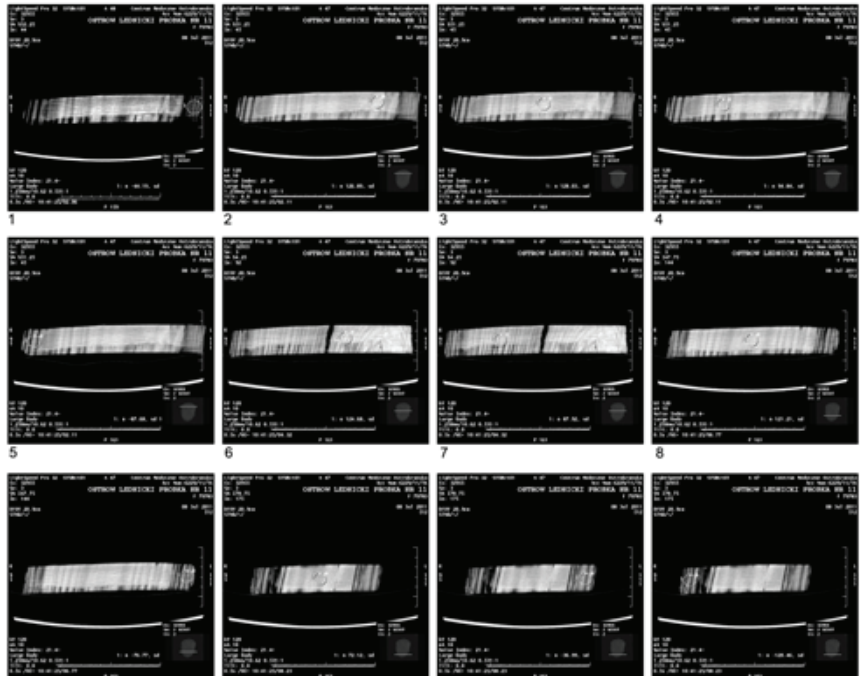

Fig. 7: The tomograms of archaeological oak wood sample No. 11. The circles show the exact location of the measurement. The numbers of pictures corresponds to the number in circles in Fig. 6 (which indicate the position of the CT measurements).

Tab. 4: The results of CT density measurement of archaeological wood from Ostrów Lednicki.

Sample number	Pile No. 11	
	Measurement zone	
	Heartwood (HU)	Sapwood (HU)
1		- 44.19
2	126.89	
3	128.03	
4	94.84	
5		- 87.68
6	124.68	
7	87.92	
8	121.21	
9		- 76.77
10	72.12	
11		- 36.99
12		- 120.46

Tab. 5: The Hounsfield scale applies to medical grade CT scans (De Vos et al. 2009).

Substance	HU
Air	–1000
Lung	–500
Fat	–100 to –50
Water	0
Kidney	30
Blood	+30 to +45
Muscle	+10 to +40
Grey matter	+37 to +45
White matter	+20 to +30
Liver	+40 to +60
Soft Tissue, Contrast	+100 to +300
Bone	+700 (cancellous bone) to +3000 (dense bone)

As samples cannot always be taken from waterlogged archaeological wooden artefacts, often of immeasurable value, the non-destructive methods as X-ray CT for determining the selected physical parameters are very useful and required. The results confirm the conclusions gained from the chemical and physical analysis about the state of preservation of archaeological wooden remains of the "Poznan" bridge. More precise tomographic study would allow us to determine the exact density of each point of the examined object. Even such estimated method of assessing the state of wood degradation allows us to draw conclusions without damaging valuable archaeological relics.

FT-IR analyses of archaeological wood

FT-IR spectra of wood

The explicit interpretation of the IR spectra made separately for sapwood and heartwood layers of contemporary oak wood and an averaged archaeological oak wood is difficult, due to the heterogeneous structure of wood, the vibrations of similar groups of atoms from different wood components overlapped. Therefore, a comparative analysis of the IR spectra of individual, isolated components of contemporary and archaeological wood has been done.

FT-IR spectra of cellulose

The infrared spectral analysis was performed in order to capture the significant structural changes between cellulose extracted from archaeological and contemporary oak wood. The analysed set of samples contained cellulose from archaeological heartwood (samples No. 1, 5, 6, 7, 8, 10, 11 and 12) and sapwood (11s) as well as from contemporary oak heartwood and sapwood, for comparison. No significant differences have been observed between spectra of archaeological heartwood cellulose of examined samples. The minor changes in the course of the spectra might arise from inhomogenity of the chemical composition of wood, the place of sampling and may also be related to the differences in cristallinity, degree of polymerization or "contaminations" in the extracted samples. There were also no essential differences between cellulose spectra of archaeological and contemporary heartwood, which can indicate the good state of preservation of that wood layer.

Figs. 8 and 9 present the IR spectra of cellulose extracted from heartwood and sapwood of contemporary and archaeological oak, respectively. Although collated images of IR spectra of

cellulose taken from archaeological oak samples 11s (sapwood) and 11 (heartwood) is slightly perturbed by bands derived from lignin and hemicellulose, a number of important differences can be observed between the mand the spectra of cellulose extracted from contemporary oak sapwood and heartwood.

IR spectra analysis of archaeological samples (Fig. 9) revealed that there are two weaker bands of C-H stretching vibration at wave numbers 2923 and 2851 cm^{-1} for sapwood cellulose, whereas for heartwood cellulose there was only a single strong band at 2900 cm^{-1}. At 1507 cm^{-1} there was outlined a strong band found only in the spectrum of sapwood cellulose. It is associated with skeletal C=C vibrations of aromatic rings and points to a contamination with lignin, which may indicate that the method used for wood components isolation is not appropriate for archaeological wood. That can also explain the fact, that the amounts of wood components, shown in Tab. 2, do not add up to 100 %.

There also appears a clear band at 1456 cm^{-1}, which is not so strongly marked in the spectrum of the cellulose extracted from the heartwood. The opposite effect can be seen in case of bands in the range between 1384 and 1318 cm^{-1}. They are associated with the deformation vibrations C-H and O-H of cellulose and hemicelluloses and O-H deformation of cellulose and hemicellulose, where the intensity in the spectrum of sapwood is significantly decreased. The highly reduced intensity of the bands at wave numbers 1159-1032 cm^{-1} is observed, which are assigned to C-O-C stretching vibration of cellulose and hemicelluloses, and to extending vibrations C-O and C-C of cellulose. In the spectrum of the cellulose extracted from sapwood there are two weak bands at 2900 cm^{-1}, and for heartwood cellulose there is clearly shown a shifted band specific for the a numeric carbonat 897 cm^{-1}. In the area 800-500 cm^{-1} the course of these two spectra are similar, but for cellulose isolated from the heartwood it is more pronounced. Such differences in IR spectra between archaeological sapwood and heartwood celluloses indicate that the sapwood zone is much more degraded than the heartwood zone.

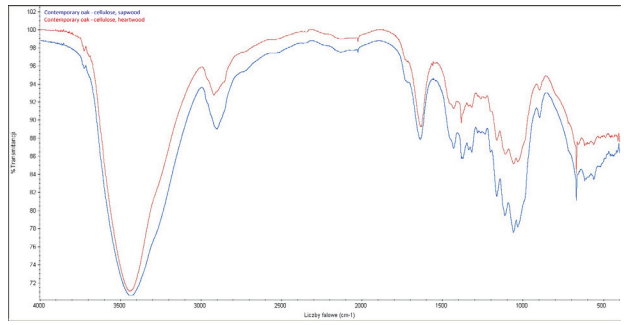

Fig. 8: FT-IR spectra of cellulose extracted from contemporary oak heartwood (upper line) and sapwood (bottom line).

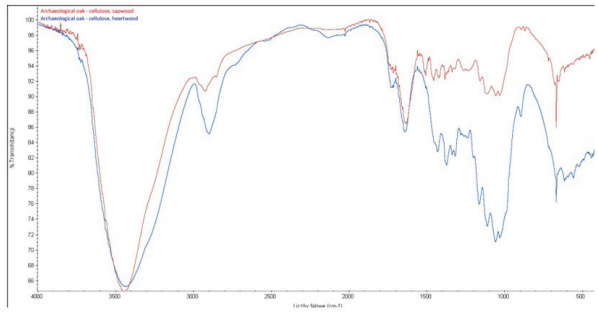

Fig. 9: FT-IR spectra of cellulose extracted from archaeological oak heartwood (bottom line) and sapwood (upper line).

FT-IR spectra of lignin

The infrared spectral analyses of lignin extracted from archaeological and contemporary oak wood has been performed in order to capture the significant structural changes between them. The analysed set of samples contained lignin from archaeological heartwood (samples No. 5, 7 and 11) and sapwood (10s, 11s) as well as from contemporary oak heartwood and sapwood, for comparison. The course of the IR spectra of lignin extracted from sapwood and heartwood of contemporary oak turned out to be identical.

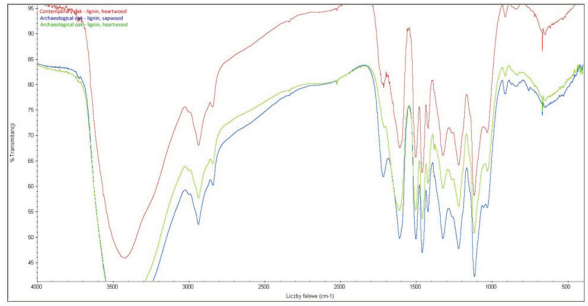

Fig. 10: IR spectra of lignin extracted from contemporary oak heartwood (red line), archaeological oak heartwood (green line) and archaeological sapwood (blue line).

A comparative analysis of IR spectra of lignin extracted from archaeological and contemporary oak also have not shown any substantial differences (Fig. 10). The shapes of the spectra are almost identical. On the spectrogram of the lignin from sapwood 11s the disappearance of the band at 1720 cm^{-1}, which is associated with the vibration of carbonyl groups C=O, can be observed. This band is also seen in all the other spectra with a comparable intensity. The only essential difference between the archaeological and contemporary lignin spectra is the appearance of the additional band at 1055 cm^{-1} and a decrease in the intensity of the band at approx. 1030 cm^{-1}, observed in the spectra of archaeological lignin.

Summarising, from the FT-IR analysis of oak samples and its main components it can be concluded that the chemical structure of archaeological wood in comparison with contemporary wood is almost identical. Minor differences may result from the heterogeneity of wood material. On the basis of this analytical method it can be confirmed that the condition of the wood residual in the lake waters is preserved well.

CONCLUSIONS

The applied traditional, destructive methods, like chemical and physical, as well as non-destructive ones, like computed tomography technique or FT-IR, which requires only little amount of wood, showed that the archaeological oak wood elements are quite well preserved, especially their inner heartwood part, which seems to be almost intact in comparison with contemporary wood.

By following the results for the archaeological wood sample No. 11: The data of the chemical analysis show, that the pattern of the chemical composition of the heartwood layer is almost the same like of contemporary oak wood, which indicates the good condition of this part of wood. On the contrary, the pattern of chemical composition of sapwood is completely different and indicates a high degree of degradation of this wood layer. Similar results can be observed for the C/L and H/L ratios – they are akin to archaeological heartwood and contemporary wood (1.42/1.35 and 2.31/2.49, respectively), but totally different for archaeological sapwood (0.4 and 0.65), which confirms the previous evaluation of the state of wood degradation. The FT-IR spectra of lignin and cellulose extracted from archaeological heartwood and sapwood as well as from contemporary oak wood certify the above hypothesis. Moreover, the FT-IR analysis could be helpful in estimation of cellulose and lignin content and structure, and as a method less destructive than typical chemical analysis, it seems to be more appropriate for archaeological wood study.

The archaeological wood density measured by traditional method was 465.8 $kg.m^{-3}$ for heartwood No. 11 and 114.2 $kg.m^{-3}$ for sapwood No. 11s, which indicates the good state of preservation of heartwood layer and quite high level of degradation of sapwood layer. It is reflected in the results obtained from the X-ray CT measurement.

The obtained results clearly confirm that the modern, non-destructive, rapid, simple and accurate methods like X-ray CT measurement and FT-IR analysis can be very useful in archaeological wood research, giving a good insight into wood structure.

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