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COMPARISON OF THE CHEMICAL COMPOSITION OF THE FOSSIL AND RECENT OAK WOOD

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ABSTRACT

This study was perform to compare the chemical composition of fossil oak wood and recent oak wood. About 2500 years old fossil oak wood and 100 years old recent oak wood were examined. Samples were gained from the outer wood, middle wood and heartwood on the cross section of three stems (both fossil and recent). Contents of extractives, cellulose, 1 % NaOH soluble substances, lignin and ash were analysed. Additionally, concentrations of elements such as Ca, K, Mg, Fe, Mn, Na, Zn and Cu were examined. The results show that there is lower content of cellulose and higher content of lignin in fossil oak wood in relation to recent wood. There is also much higher amount of calcium and iron, and lower amount of potassium in fossil wood.

KEY WORDS: archaeological wood, oak, chemical composition

INTRODUCTION

Wood undergoes progressive destruction by the action of abiotic and biotic external factors. Wood durability is the time in which wood keeps usable properties. It depends on the wood kind (species) and the environment.

Time in the destruction process plays secondary role (Krutul and Kocoń 1982, Dzbeński 1969, 1970, Reinprecht 1992, Dzbeński et al. 1996). High-density wood, which most often corresponds to heartwood, shows higher extractives concentration and is much more durable than sapwood. The living cells are the most susceptible to decomposition. Pectins and hemicelluloses are the components of cell walls, which undergo degradation the most readily (Fengel 1971, 1991). Lignin is much more resistant for destruction as it contains phenolic groups which hinder expansion of majority of microorganisms (Prądzyński and Cichocka 2002). The oak heartwood possesses the highest natural durability among deciduous species of temperate zone. It is confirmed by examples of excavation wood samples of perfect constitution, (2500 years old) from gravel mine in Latoszyn.

The aim of this work is the comparison of chemical composition of wood on the cross-section of oak stem received from Latoszyn and recent oak wood (100 years old).

MATERIAL AND METHODS

The oak wood from "Kruszywa" mine, situated in Latoszyn near Dębica, was studied. Wood from Latoszyn was dated with the ^{14}C method at the AGH University of Science and Technology in Cracow, about 30 years before. It was 2500 years old. Samples were collected from outer wood, middle wood and heartwood, on the cross-section of three trunks with diameter about 700 mm. Similar studies were performed on the recent oak wood (100 years old) obtained from Mazovia-Podlasie region. The fraction passing 1.2-mm and remaining on 0.49 mm mesh sieve was taken for analysis. The extractives content was analysed in the Soxhlet apparatus using ethanol-benzene (1:1) mixture. Cellulose content was examined using Kürschner-Hoffer method, lignin content according to PN-74/P 50092 standard, content of 1% NaOH soluble substances according to Krutul (2002). The analysis of ash content was performed according to PN-92/P-50092 standard.

Contents of calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), natrium (Na), manganese (Mn), zinc (Zn) and copper (Cu) were examined using Perkin-Elmer 300 Atomic Absorption Spectrometer (AAS). Microscopic wood structure analysis was performed on the JSM-35 scanning microscope. Samples were placed on the microscope table, which was covered with silver paste layer. Samples were then vacuum sputtered with carbon-silver powder (pressure 10^{-5} Tr). Photos were made with current intensity of 10^{-12} A and voltage of 25 kV.

RESULTS AND DISCUSSION

The content of extractives in fossil oak wood is 25 % higher than in recent oak wood in outer zone and respectively 14 % and 9 % in middle and heartwood zone. It is shown in the Tab. 1. According to Fengel (1971), Prądzyński and Cichocka (2002) the extractives content in fossil oak wood is about twice lower than in the recent oak wood. It can be stated that the extractives content in fossil oak wood is dependent on the environment, where the fossil wood lays.

Tab. 1: Major components of fossil and recent oak wood

Components	Zone of wood	Content (%)	
		fossil wood	recent wood
ethanol-benzene (1:1) extract	outer	4.1	3.1
	middle	4.4	3.8
	heart	4.6	4.2
cellulose (Kürschner-Hoffer method)	outer	34.4	49.2
	middle	35.2	48.1
	heart	32.1	46.3
substances soluble in 1% NaOH	outer	22.3	21.8
	middle	21.5	22.6
	heart	22.8	23.1
lignin	outer	39.5	26.5
	middle	39.3	27.1
	heart	40.8	28.0
ash	outer	2.4	0.6
	middle	1.4	0.3
	heart	1.1	0.3

Cellulose content in the fossil oak wood is 30 % lower in outer wood and heartwood and 27 % lower in middle wood in relation to corresponding zones in recent oak wood (Tab. 1). According to Kudela and Reinprecht (1990) cellulose content in the fossil oak wood (*Quercus robur* L.) is 5 % higher than in the recent oak wood. The alpha-cellulose content in fossil spruce wood is 78 % lower than in the recent wood, as it arises from the data presented by Fengel (1971).

The 1% NaOH soluble substances content is comparable in the fossil and recent oak wood (Tab. 1). There is 70 % lower amount of polysaccharides in the fossil oak wood than in the recent wood, according to Fengel (1971). Prądzyński and Cichocka (2002) stated that there is 47 % fewer 1 % NaOH soluble substances in fossil degraded oak wood and 55 % fewer in non-degraded fossil oak wood than in the recent oak wood. The 1 % NaOH soluble substances content is 32 % higher in the fossil outer wood of pine (*Pinus massaniana*) in relation to recent wood of the same species (Kim, Y. S., 1990). This content is similar in heartwood (fossil and recent pine wood). The cellulose content in studied oak wood is much lower than in the recent wood. It may be caused by the degradation of cellulose molecules – shorter chains of cellulose are soluble in 1 % NaOH.

Lignin content in the fossil oak wood is much higher than in the recent wood. It is 33 % higher in fossil outer wood and 31 % higher in fossil middle wood and heartwood (in relation to corresponding parts of recent wood – Tab. 1). As it arises from the data presented by Fengel (1971), lignin content in the fossil spruce wood is about 2.5 times higher in relation to recent wood. According to Kudela and Reinprecht (1990), lignin content in the fossil oak wood (*Quercus robur* L.) is about 35 % higher than in the recent wood. This phenomenon can be explained by the decrease of polysaccharides content.

The highest differences between fossil and recent wood go for the ash content (Tab. 1). This content in the outer wood and heartwood of the fossil oak is four times higher in relation to corresponding parts of recent wood. This ratio for middle wood is equal to 4.5. Kudela and Reinprecht (1990) state that the ash content in the fossil oak wood is 5 times higher than in the recent oak wood. According to Prądzyński and Cichocka (2002), the ash content in degraded fossil oak wood is 18 times higher in relation to recent wood, and in non- degraded wood this ratio is equal to 15. The ash content in outer wood is twice higher than in heartwood, both for fossil and recent wood (Tab. 1).

The biggest differences in metals content between fossil and recent oak wood are observed for calcium, iron and potassium (Tab. 2). The calcium concentration in fossil outer, middle and heartwood is about 6-7 times higher in relation to corresponding zones of recent wood. The iron content is even about 250 times higher in all zones of fossil oak wood. It oscillates between 800 mg. kg^{-1} in the fossil heartwood and 1700 mg. kg^{-1} in the outer wood. Its value in middle wood is intermediate and equal to 1000 mg. kg^{-1}. The iron content in recent oak wood varies from 3.0 up to 7.5 mg. kg^{-1} (Tab. 2).

The intensity of dark pigmentation of fossil oak wood depends on the iron concentration. The examined oak wood was black in the outer wood and dark brownish in the heartwood. The middle wood has intermediate colour.

Tab. 2: Content of elements in fossil and recent oak wood.

Wood	Zone of wood	Content of elements mg.kg^{-1}							
		Ca	K	Fe	Mg	Na	Mn	Zn	Cu
fossil	outer	5125.0	47.5	1700.0	239.0	75.0	135.0	7.5	3.2
	middle	4300.0	45.0	1000.0	243.0	121.0	51.0	7.5	2.7
	heart	4950.0	66.2	800.0	282.0	108.0	110.0	9.2	3.2
recent	outer	700.0	1170.0	7.5	170.0	51.0	35.0	0.2	2.0
	middle	740.0	980.0	4.3	120.0	42.0	28.0	0.8	2.0
	heart	770.0	420.0	3.0	70.0	20.0	21.0	1.2	2.0

Dark pigmentation of fossil oak wood is caused by the reaction between water-soluble iron compounds and tannins, which are components of wood. Additionally, the mineral iron compounds are dark brown, which also changes the wood pigmentation.

The potassium concentration in the fossil oak wood is much lower in relation to the recent wood. It is about 95 % lower in outer and middle wood, and about 85 % lower in heartwood (Tab. 2). The magnesium content in fossil outer wood is 40 %, in middle wood twice and in heartwood four times higher than in corresponding zones of the recent wood. Manganese, natrium, zinc and copper concentrations are also higher in the fossil wood (Tab. 2). Kim (1990) stated that recent pinewood (*Pinus manssoniana*) contains higher amount of potassium, calcium, magnesium and lower amount of sulphur and iron in relation to fossil wood.

According to Krutul and Kozakiewicz (2003), the fossil oak wood from Biskupin contains higher amount of iron, calcium, copper, zinc and manganese than the recent oak wood. For example iron and calcium content in the fossil oak wood equal to 7350 mg.kg^{-1} and 7800 mg.kg^{-1} respectively, and for the recent oak wood corresponding values are 120 mg.kg^{-1} and 480 mg.kg^{-1}. Potassium concentration is much lower in the fossil wood (25 mg.kg^{-1}) than in the recent wood (1250 mg.kg^{-1}). Content of iron in the recent oak wood obtained by Krutul and Kozakiewicz (2003) differs significantly from the content in presented paper (120 and 3.0-7.5 mg.kg^{-1} respectively). It can be explained by the fact that iron content in wood depends on the forest site and its age. Krutul and Kozakiewicz (2003) used 80 years old oak from Masuria- Podlasie region as the recent wood. 100 years old oak from Mazovia-Podlasie region was used in presented paper. Iron content in this recent wood is exceptionally low.

The recent oak wood micro-structure on the cross-, radial and tangential section is presented in the Figs. 1, 2 and 3 respectively. No evidence of crystallized mineral substances can be stated both in vessels and fibres.

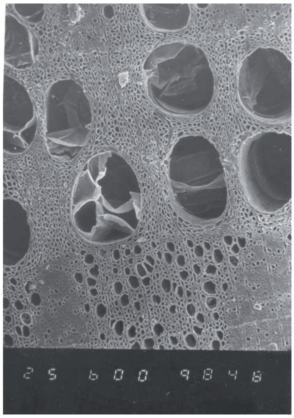

Fig. 1: Cross section of the recent oak wood (600x)

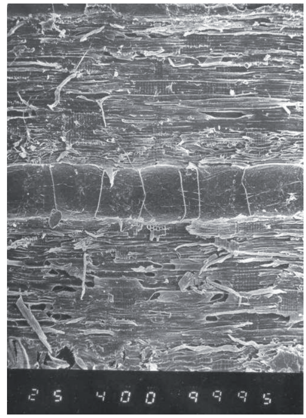

Fig. 2: Radial section of the recent oak wood (400x)

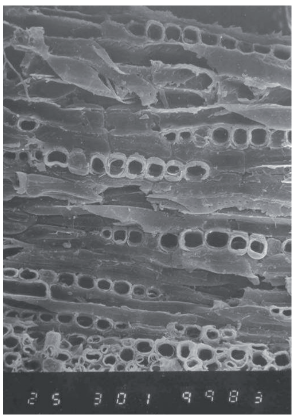

Fig. 3: Tangential section of the recent oak wood (300x)

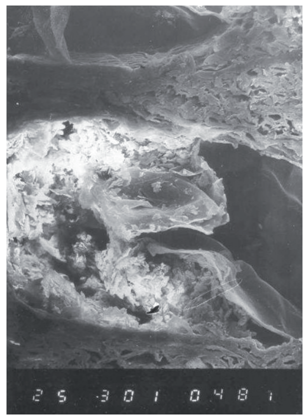

Fig. 4: Cross section of the fossil oak wood (300x)

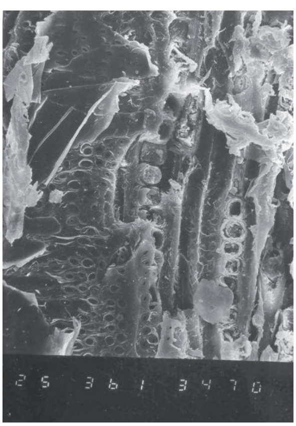

Fig. 5: Radial section of the fossil oak wood (360x)

Fig. 6: Tangential section of the fossil oak wood (600x)

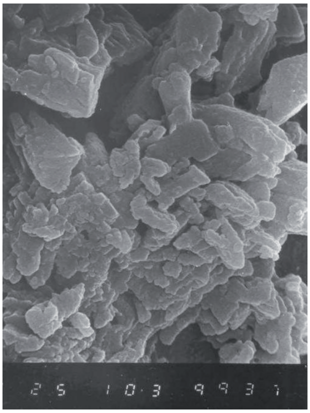

Fig. 7: Silica in the vessel of the fossil oak wood (10000x)

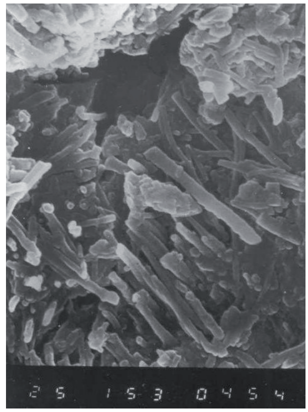

Fig. 8: Mineral cluster in the fossil oak wood vessel (15000x)

Figs. 4, 5 and 6 present the fossil wood micro-structure on the cross-, radial and tangential section respectively. There are visible incrustations of crystallized mineral substances in vessels and fibres as well. Silica is the element that is present in the fossil oak wood micro-structure at the highest concentration (Fig. 7). The structure of silica is also presented in the Fig. 8.

CONCLUSION

1. Cellulose content is lower in the fossil oak wood than in the recent wood in all wood zones. The lignin content is much higher in the fossil wood (all zones).
2. There is about 6-7 times higher amount of calcium, about 250 times higher amount of iron and about 10 times lower amount of potassium in the fossil oak wood in relation to the recent wood.
3. The presence of crystallized mineral substances was identified in fibres and vessels on the cross and tangential section of the fossil oak wood (using scanning microscope).

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