The Decay of Wooden Wreck at Two Sites in Dubrovnik Area

Propadanje drvene olupine na dvije lokacije na dubrovačkom području

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Summary

The preparation is presented of underwater wood, wood identification, wood properties and FT-IR analysis. Two samples of Oak (*Quercus petraea Liebl.; Quercus robur L.*) were analyzed from two sites in Dubrovnik area, island Koločep and Molunat. This paper presents the preparation of underwater wood, wood identification, wood roperties and FT-IR analysis. Three section of wood, cross section, radial section and tangential section made for microscopis hardwood and softwood identification. The best two samples are assumed to be Sessil oak (*Quercus petraea Liebl.*) and Pedunculate oak (*Quercus robur L.*).

KEY WORDS
wood anatomy
wood borers
wood identification
wood properties
FT-IR analysis

Sažetak

Opisana je priprema drva pod morem, identifikacija drva, karakteristike drva i FT-IR analiza. Analizirana su dva primjerka hrastovine (Quercus petraea Liebl.; Quercus robur L.) s dvije lokacije na području Dubrovnika, na otoku Koločepu i Moluntu. Napravljene su tri sekcije drva, poprečni presjek, radijalni i tangencijalni za mikroskopsku identifikaciju tvrdog i mekog drva. Najbolja dva primjerka su Quercus petraea Liebl i Quercus robur L.

KLJUČNE RIJEČI
anatomija drva
svrdla za drvo
identifikacija drva
karakteristike drva
FT-IR analiza

INTRODUCTION / *Uvod*

According to findings, pedunculate oak *(Quercus petracea* Liebl.) and sessile oak (*Quercus robur* L.) proved to be the best for structural elements of the ship due to its strength and durability. Holm-Česmina holm oak (*Quercus ilex* L.), is a very durable wood, hard, firm, and elastic, but is more difficult processes. It is used for making the keel, stem, ribs. Pine ordinary common pine (*Pinus sylvestris* L.) and spruce common spruce (*Picea excelsa* Dietr.) are lightweight, soft, good handle, are relatively resistant to moisture. They are used for making masts, wall paneling, and flooring. Mulberry- white mulberry (*Morus alba* L.) is permanent and waterproof timber.

European larch (*Larix europea* Mill.), grows in the mountains of Central Europe, resinous, durable, flexible, respected and sought shipbuilding timber, which is used areas of the ship permanently under water. It is used for making the deck, hull, keel, mast. Elm mountain elm (*Ulmus* L.) is a medium-hard, firm, easily treated and long lasting. In the shipbuilding industry it is used for making ribs, keel, gunwale, deck plating. Beech (*Fagus silvatica* L.) is widespread throughout Europe; it's hard, elastic, strong, and easy to process. It is used for parts of the ship that are either permanently under water, or outside, which means it cannot withstand the constant changes in humidity, the basics of the rudder, oars and the inner shell.

There are numerous chemical processes that affect materials in sea water, but the most damage is done by oxidation (Søreide, 2011). Oxygenation of the ocean depends on depth – shallow waters are more oxygenated due to phytoplankton photosynthetic activity that depends on light penetration. In deeper waters oxygen production decreases but oxygen consumption doesn't. This results with better chances of preservation of the wrecks in deep than in shallow waters, as well as low energy environment that provides material protection under the sediment. Wrecks in shallow waters are also exposed to currents and waves that may cause physical damage. This may be mitigated by marine organisms that settle and grow at the surface of the wreck and act as protective layer.

Any natural or artificial hard substratum that is immersed in the sea water is potentially settled by benthic organisms. Assemblage of fouling organisms depends not only on the natural species that are present in the area and their ability of settling and growing, but on environmental parameters, characteristics of the substratum and the period of immersion (Hellio et al, 2000). Fouling can prevent or accelerate decay of the substratum (Søreide, 2011).

Wooden substratum in the sea water is commonly attacked by borers from two groups: Mollusca and Crustacea.

Among hundreds of boring species around the world, the most common and the most destructive species is cosmopolitan

Fig. 1. Sample wood from the sea in the near of Molunat
Slika 1. Primjerak drva iz mora kod Moluнта

Fig. 1a. Sample wood, from the sea in the near of Molunat
Slika 2a. Primjerak drva iz mora kod Molunta

Fig. 2. Sample wood , Point Bezdan, the island of Koločep
Slika 2. Primjerak drva, točka Bezdan, otok Koločep

shipworm *Teredo navalis* Linnaeus, 1758 (Teredinae, Bivalvia, Mollusca). Besides, other Teredinae species such as *T. utriculus* Gmelin, 1791, *Lyrodus pedicellatus* Quatrefages, 1849, and *Bankia carinata* J.E. Gray, 1827 can be found in the submersed wood along the Mediterranean coasts, as well as piddoks *Barnea candida* Linnaeus, 1758 and *Pholas dactylus* Linnaeus, 1758 (Pholadidae, Bivalvia, Mollusca) (Riedl, 1991; Castagna, 1973). Shipworms bore deep into the wood making long tunnels parallel to the grain (Santhakumaran, 1994). They adapted to their habitats and peculiar way of life, so the body is elongated with a pair of reduced shells that enable boring of the wooden substratum. Some shipworm species contain enzymes capable of wood digestion, but in most of species wooden particles are throw out unchanged. Piddoks are boring clams with typical elongated bivalve shells that penetrates into wood by motion of a strong adductor mussel. They bore superficial tunnels that are almost right angled to the grain (Santhakumaran, 1994, Castagna, 1973).

Unlike shipworms and piddoks that penetrate deeply into the wood, boring Crustaceans (gribbles) excavate galleries under the surface that can be detached and flushed away. Their horny jaws are modified for boring. Mediterranean marine boring Crustaceans are *Limnoria quadripunctata* Holthuis, 1949, *L. tripunctata* Menzies, 1951 (Isopoda, Crustacea) and *Chelura terebrans* Philippi, 1839 (Amphipoda, Crustacea) (Riedl, 1991; Castagna, 1973).

MATHERIAL AND METHODS / *Materijal i metode*

Wood was sampled at two underwater locations: Molunt and the island of Koločep.

A piece of wood from the wreck of a type of boat called "Trabakula" was taken out of the sea by Point Bezdan, the island of Koločep, Dubrovnik (Fig. 1). It was found at a depth of 18m and was estimated to be in the sea for about 55 years.

Another piece of wood was taken out from the sea just in the near of Molunat (Konavle) was found at depth of 2,5 m (Fig. 2). This wooden wreck estimated to be in the sea for about 500 years. Some parts of it are well preserved owing to the hydrodynamism at the site, but there are the parts of the wreck that are settled by marine borers (Fig. 2a). Visual census technique out of the site was used for estimating the abundance of wood borers in the sample of 25 x 5 cm.

A destruction of the wood surface was observed, including the destruction of the grain as well as the wood cells located outside the wooden patterns.

Microscopic analysis identifying the type of wood physiologically transversal cross-section, radial and tangential section, and then the chemical analysis of wood FT-IR method (Fourier Transform Infrared Spectroscopy) were performed.

Samples of wood were extremely hard, so the sampling required a lot of effort and attention. Samples were taken with the aid of a scalpel and the needle brush and transferred to glass slides to which they had previously applied dropper 1-3 drops of glycerin, which is a needle for preparing glass syringes for preparing schedules on a little less area than the area Cover slips glass cover slips . Cover slip can be placed on slides, slowly, so that the first touch of glycerin, which displaces the excess air below the slide and cover the mixture. The process of making the preparation was repeated several times due to degradation of the wood structure. After labeling the samples approached the microscopic analysis of wood samples. Based on visual inspection of samples of wood and examination of microscopic slides, a comparison is made of the anatomical characteristics of the keys to identify species of wood (Torelli, 1991).

RESULTS / *Rezultati*

The analysis assumed microscopic histological structure of wood-sessile oak (*Quercus petraea* Liebl.) and pedunculate oak (*Quercus* robur L.).

Sessil oak (*Quercus robur* L.) of the lowland forests of central and southern Europe grows to 50 m in height with a yellowish white, tan core, rings clearly visible, pithy core bar close-rays, and vessels exclusively solitary. Wood is durable, medium-hard, firm pressure and strokes. It is easily treated, medium elasticity. First

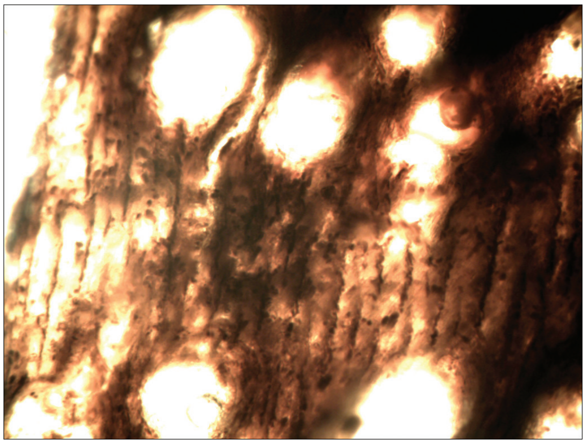


Fig. 3. Cross section of sessil oak *(Quercus robur L.) 100 ×*
Slika 3. Poprečni presjek oak
(Quercus robur L.) 100 ×

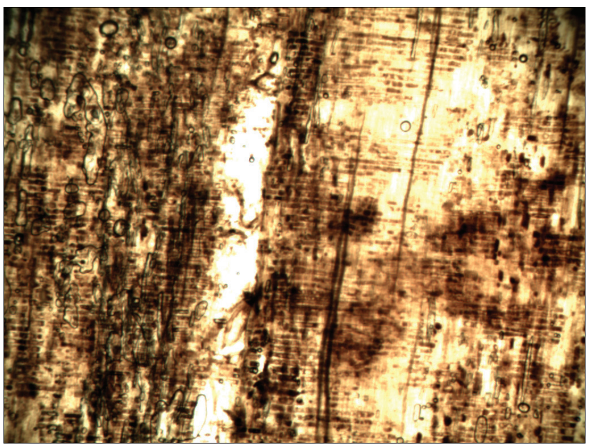


Fig. 4. Radial section of sessil oak *(Quercus Robur L.)* 100 ×
Slika 4. Radijalni presjek (Quercus Robur L.) 100 ×

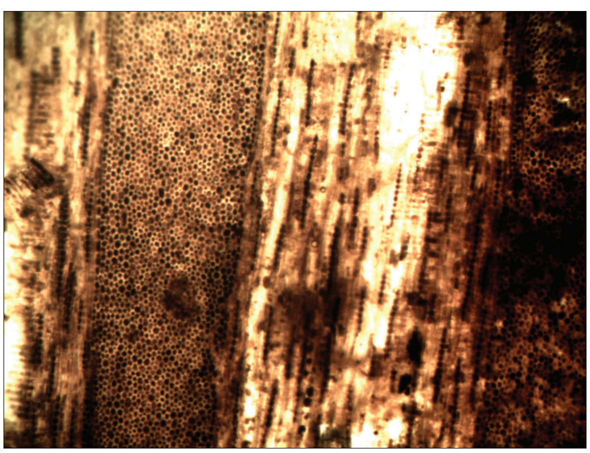


Fig. 5. Tangential section of sessil *(Quercus Robur L.)* 100×
Slika 5. Tangencijalni presjek
(Quercus Robur L.) 100×

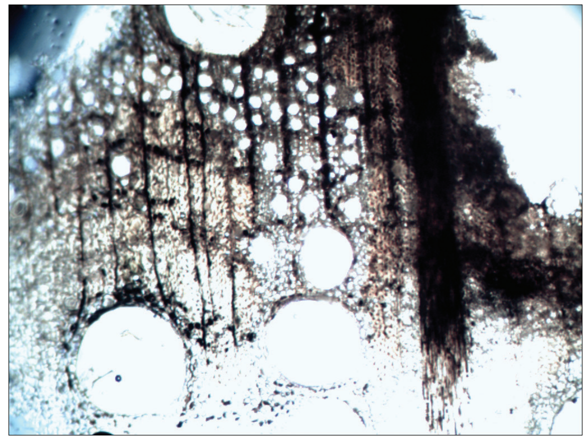


Fig. 6. Cross section of pedunculate Oak *(Quercus petraea Liebl.)*100×
Slika 6. Poprečni presjek (Quercus petraea Liebl.)100×

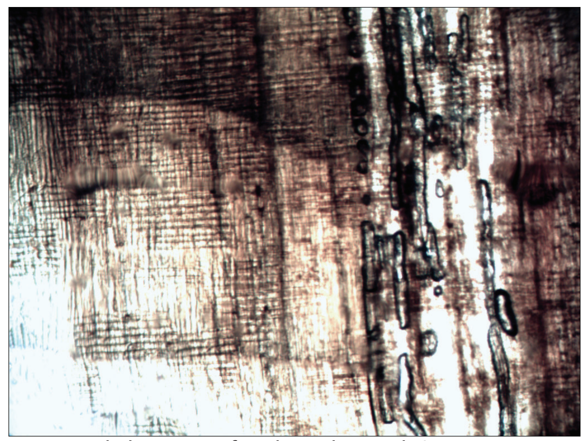


Fig. 7. Radial section of pedunculate Oak *(Quercus petraea Liebl.)* 100×
Slika 7. Radijalni presjek (Quercus petraea Liebl.) 100×

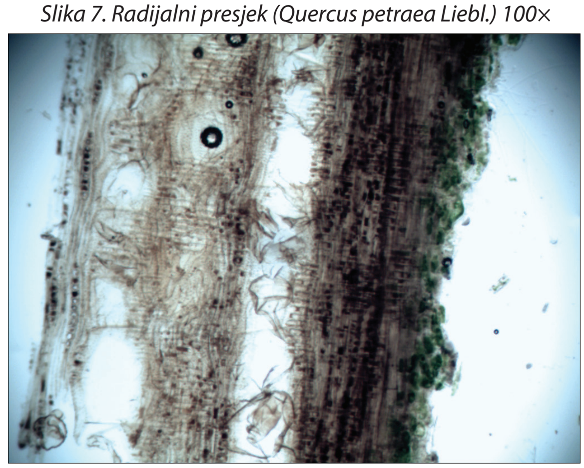


Fig. 8. Tangential section of pedunculate Oak *(Quercus petraea Liebl.)* 100×
Slika 8. Tangencijalni presjek (Quercus petraea Liebl.) 100×

class technical wood used in shipbuilding for making all major structural elements: ribs, outer and inner hull, keel, backbone, stem, stringers, crossroads, hatches, bollards,bitts and fenders.

Sessile oak (*Quercus petraea* Liebl.), the tree of central and southern Europe reaching up to 40 m in height, yellowish white, tan core, distinctive rings, ring porous. Libriformes fibers and fiber traheides, thick-walled, and pits to large vessels. Wood is durable, moderately hard, medium-hard, highly elastic and easily processed. In the shipbuilding industry, Sessile oak, as well as red oak are used for making many parts of the ship.

The infrared spectrometry, using the FT-IR instrument (Fourier transform infrared) Shimadzu FT-IR 8400 S, was used to analyse changes in the chemical composition of wood. The main reason for applying infrared spectrometry was to determine functional groups and to identify substances. Since each peak of the infrared spectrum is specific for a particular functional group, the molecular structure of substance was determined by the spectrum analysis. The KBr method was used for FT-IR analysis by mixing 10 mg of powder sample with 300 mg of KBr, by forming pellets and their scanning in the range of 400-4000 cm-1. Results of the analysis are presented in figure 9. and 10. and they represent the mean values of three measurements.

The change in chemical composition, regardless of the type of wood, was determined based on the FT-IR recordings obtained by observing the formation/disappearance of certain peaks, i.e. by observing changes in their intensity. The disappearance of peaks at 1735 cm-1 (sessile oak) and 1742 cm-1 (common oak), connected to the C=O bond stretching vibration of carbonyl groups of lignin, confirms its degradation. In case of sessile oak, lignin degradation is accompanied by an increase in the peak intensity at 1595 cm-1, which indicates aromatic skeletal C=C bond stretching vibrations, i.e. the rise of peak intensity at 1123 cm-1 related to the C-H bond vibration of the guaiacil and C-H bond of the siringil alcohol lignin. In case of common oak samples, with its features taken into account (a thin, porous structure protected with putty and stain on one side), the latter changes were not observed. Peak stretching at 1236 cm-1 (sessile) and at 1241 cm-1(common oak) points to the cellulose degradation, whereby the formation of new peaks at 1267 cm-1 and 1222 cm-1 (sessile) and 1259 cm-1 and 1226 cm-1 (common oak) confirms the stretching and degradation of C-O bonds in cellulose and hemicellulose (wood poliosis). The above mentioned additionally confirms the stretching and reduction of peak intensity at 1047 cm-1 (sessile) and 1044 cm-1 (common oak). The asymmetrical C-O-C bridge vibration in cellulose, occurring as a consequence of its degradation, also indicates the decline in peak intensity at 1158 cm-1 for both species. In case of common oak the decline in peak value at 898 cm-1 is connected to the degradation of cellulose C-H bonds. Based on the results of FT-IR analysis it is evident that the exposure to sea water inevitably led to the change in chemical composition of wood in terms of degradation of its specific components. Although wood was exposed to sea for a long time at elevated pressure, it is noteworthy that these changes were

Fig. 9. Results of FT-IR analysis of Penduculate oak *(Quercus petraea Libl.)*

Sl. 9. Rezultati FT-IR analize drva hrasta kitnjaka (Quercus petraea Libl.)

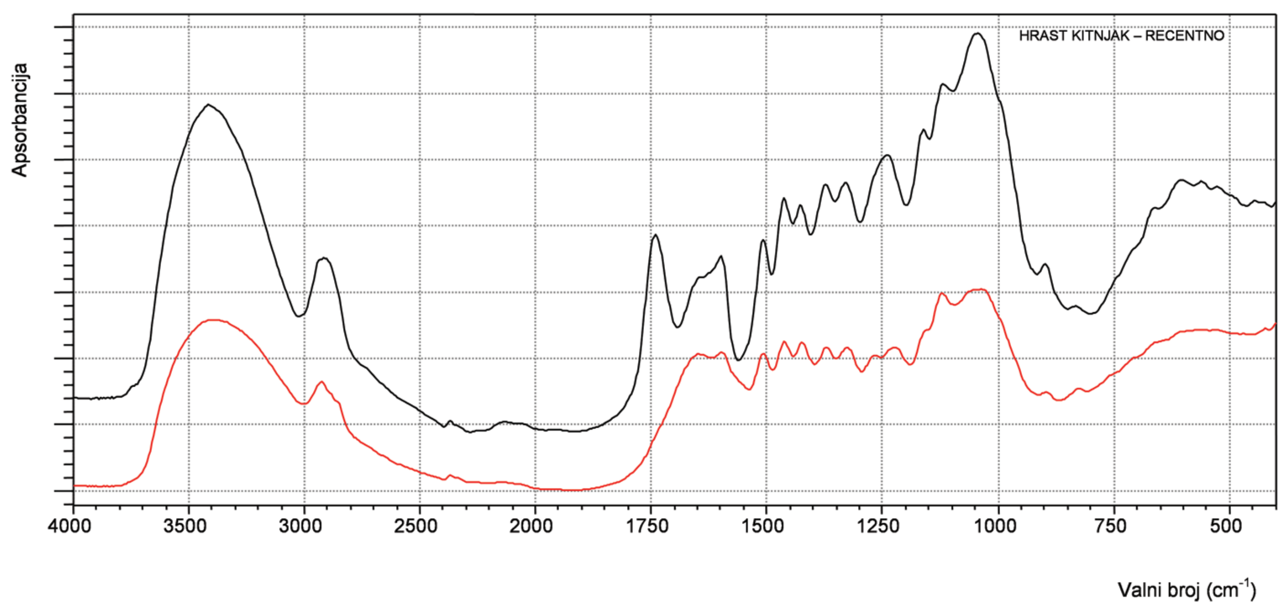
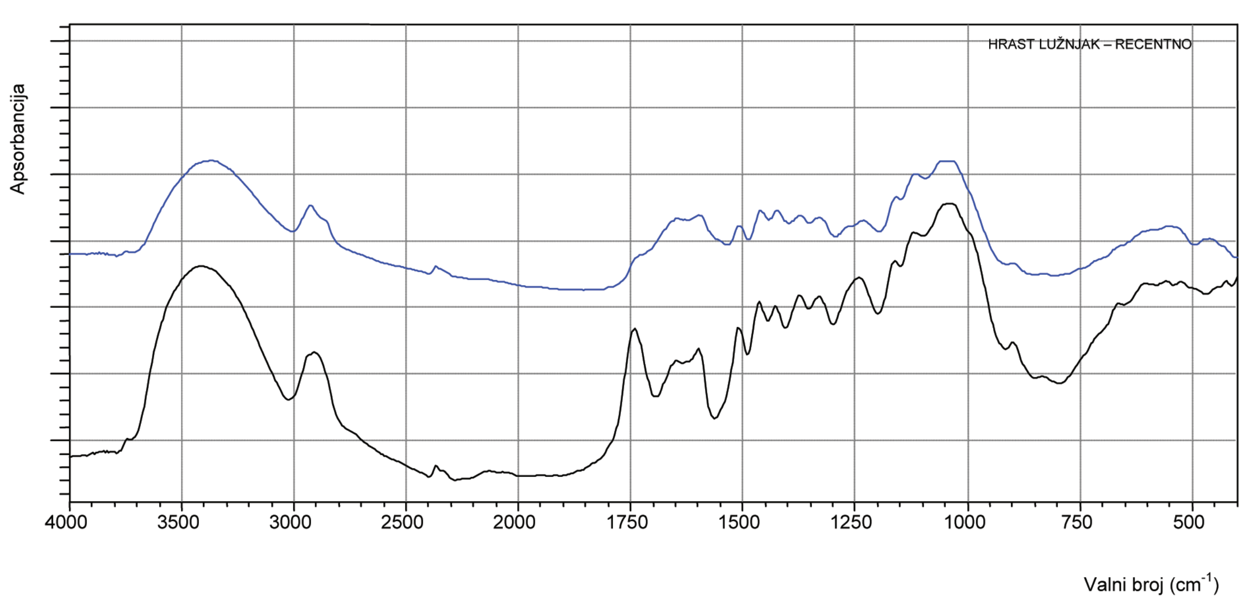


Fig. 10. Results of FT-IR analysis of Sessil oak *(Quercus robur L.)*

Sl. 10. Rezultati FT-IR analize drva hrasta lužnjaka (Quercus robur L.)



not significant compared to the recent wood of same species. The above mentioned particularly refers to the cellulose, which has lower degradation, while in case of lignins degradation is more pronounced due to the disappearance of some peaks.

The excavated tunnels lined with calcareous tubes, mostly parallel to the grain are most evident. Since the investigated piece of wood was not preserved at the site, according to the tubes it is supposed that they belong to the tubeworm *Terredo navalis*. The longest tube was 190 mm long, diameter of 9mm. There were 8 tubes at 5 square cm cross-cut.

11small holes (diameter 10-50 μm) per square centimetre were also observed, but upright to the grain. Since the investigated piece of wood was not preserved at the site, no species can be identified as the burrower of the holes.

CONCLUSION / *Zaključak*

Knowing the wood anatomy, we have successfully made preparations for microscopic wood analysis as it was in bad condition for a reliable macroscopic analysis. We identified wood with the key for macroscopic and microscopic identification of deciduous and coniferous wood (Torelli,1991) and with the interactive computer key for deciduous wood identification INTKEY (Richter i Dallwitz, 2002). By making histological preparations in the transverse, radial, and tangential sections, common oak (*Quercus petraea Liebl.*) and sessile oak (*Quercus robur L.*) were identified. Based on the results of FT-IR analysis it can be concluded that the long exposure of wood to sea salt led to the changes in its chemical composition in terms of degradation of its specific components. Although wood was exposed to sea for a long time at elevated pressure, it is noteworthy that these changes were not significant compared to the recent wood of same species. To identify the burrowers up to the species, next research should include preservation of the samples.

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