



## Original article

# Evaluation of some wood-water relations and chemometric characteristics of recent oak and archaeological oak wood (*Quercus robur*) with archaeometric value

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## ABSTRACT

The present paper studied wood-water relations and their effects on color changes. Additionally, FTIR analysis of recent and archaeological oak wood was completed. Comprehensive knowledge of wood-water relations in recent and archaeological oak wood will facilitate the use of treatment material in the restoration and conservation process of the investigated artefacts. Wood samples were impregnated with tetraethyl orthosilicate. Sorption time until equilibrium moisture was reached increased significantly as a result of the treatment. Thus, the saturation time for treated recent oak wood was 43% longer than it was for untreated recent oak. Additionally, the treatment increased sorption time to equilibrium moisture in archaeological oak by 63%. The treatment resulted in significant color changes for both recent and archaeological oak wood. Samples displayed less color difference when they were dry compared to when they were wet. According to the FTIR analysis, tetraethyl orthosilicate causes the increase of the amount of O-H groups in archaeological oak wood and also caused an increase in the amount of C=O groups. This change is due to the hiding effect of xerogel formation on the functional group of wood.

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## 1. Introduction

Wood is considered one of the oldest construction materials, used traditionally for buildings and other types of construction the world over [1]. Throughout recorded history, people have utilized this strong and versatile base material in everything from art to construction [2]. During utilization or storage, wood is exposed to a wide variety of abiotic and biotic factors, including weathering, moisture fluctuation, fungi, insects, or termites [3]. Among these, moisture change is a key factor as this phenomenon influences all other factors. Moisture in wood occurs in two distinct forms: as free water stored as a liquid in wood pores or vessels, and as bound water trapped within cell walls. Wood reaches what is referred to as the fiber saturation point (FSP) only after all the free water within it has been lost. All cell wall polymers are hydroscopic (cellulose, hemicellulose, and lignin). Each cell wall poly-

mer's sorption of moisture depends not only on its hydrophilic nature, but also on the water accessibility of the hydroxyl groups of the polymer [4]. If the wood stays at stable RH for long periods of time, an equilibrium moisture content (EMC) will be achieved [5,6].

As a biodegradable material, wood can degrade in many different ways. Wood submerged in water or buried in soil under waterlogged conditions leads to a severe form of moisture-induced degradation. As the conditions might vary from site to site, chemical changes in the material tend to vary as well, leading to the diverse chemical compositions of archaeological wood. Findings indicate archaeological wood contains a lower cellulose content and a higher lignin content than recent wood does. The presence of excessive water is always a key factor in chemically-induced and, especially, biologically-induced wood degradation. [7,8,9,10,11,12] In addition to cell wall macromolecule degradation, the deposition of inorganic substances during fossilization also occurs. This process is highly dependent on the sub-surface environment [6,13,14]. The variations in chemical composition, which includes wood-water relations, cause inconsistencies in wood behavior [12].

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Wooden objects are usually treated to protect against the risk of degradation and damage. This is particularly true for wooden objects extracted from waterlogged, wet, or underground conditions. Commonly used traditional treatments include linseed oil, waxes, sugars, alum, resins (e.g. melamine formaldehyde) Paraloid B72 (a low molar mass methyl acrylate/ethyl methacrylate copolymer) and poly(ethylene glycol) (PEG). Among these, PEG is by far the most frequently used for different wooden artefacts [15]. Over the past decades, many wooden objects of great historical importance have been discovered. Most of these have been conserved with one of the materials mentioned above. Several new methods were developed in the meantime; among them a promising solution of silicone alkoxides. These are among the most widely investigated silicon compounds to improve the wood properties; wood treated with these compounds demonstrate favorable properties (decay resistance, hydrophobization, non-toxic nature) [16,17,18,19,20,21]. Several other advantages can be attributed to these compounds as well including polymer network formation on and within the cell wall, a cell-wall bulking effect, leaching reduction, UV and dimensional stability, fire retardancy, outdoor application suitability, a simple treatment process, and possible retreatment due to the usually porous network [15,18,22,23,24].

Among alkoxysilanes, tetraethoxysilane (TEOS) is a commonly used compound for wood modification processes, with the aim to improve the dimensional stability of wood [25,26]. This work explores a simple method of in situ sol-gel synthesis of porous silica xerogel inside the cellular structure of wood using TEOS as a precursor. Silica gels are high surface area, porous materials with low density and a typical morphology consisting of silica particles in an open porous 3D particle network [27].

Many reference works in the literature for the authentication of old wood artifacts have studied either a certain artifact or a structural component in this respect, using chemical and physico-structural analysis data from wood samples through the utilization of a set of archaeometric or chemometric values. For example, elemental composition, hygroscopic moisture, ash and extractable components, together with the morphology and distribution of anatomical components, porosity, specific weight, etc., are archaeometric characteristics which enable the dating of the old wood by corroboration [28,29,30,31].

## 2. Research aim

The aim of this study was to improve water-related properties of archaeological 14<sup>th</sup>-century oak wood found in Iasi (Romania) through the application of a simple silicone alkoxide-based conservation method. A comparison with recent wood, using various analytical approaches, was also completed. The studied archaeological oak wood served as fencing material along a pavement for over 100 years. After the pavements were demolished, the fence poles remained buried under damp soil conditions for over 200 years. The wood has endured underground for approximately 400–500 years (from the period of use to the extraction period). After long-term soil contact, wood material can become very sensitive to cracking during drying; however, the cell wall structure of the investigated archaeological oak wood was only slightly affected by the soil contact. Therefore, it was possible to completely dry the test material before treatment using controlled exsiccation/drying without using a consolidant [32]. Thus, using complicated drying methods like freeze-drying or solvent-aided drying before treatment was unnecessary [33,34,35]. This led to a more successful impregnation process with the silicon compound. However, conservation processes using different silica-based compounds and the effect these have on the dimensional stability or mechanical properties of archaeological wooden objects were investigated [18,36,37]. Information on the sorption properties and color changes of both

the treatment and alternating moisture is lacking. In addition to the effect on wood-water relations, color change is also an important factor during the conservation process as it is usually necessary to maintain the material's original color. FT-IR spectroscopy characterizations of the materials and sorption/desorption tests were conducted. Interactions between archaeological wood material and the silica xerogel indicate the mode of treatment action investigated by FTIR analysis.

## 3. Materials and methods

### 3.1. Raw materials and preparation

Samples of fresh cut oak wood (*Quercus robur* L.) from the Iasi Region, Romania were prepared. The archaeological oak wood samples dated from the 14<sup>th</sup> century. This wood was originally used as fencing material along a pavement in the old urban center of Iasi, Romania. When a large amount of archaeological wood was used for dendrochronological research and other scientific investigations, their conservation status was precarious, but it was possible to separate fragments that possessed good conservation status within the anatomical elements, which were cut crosswise. The wood resided in the soil for centuries, causing the wood color to blacken. Despite this, the structure of the wood remained intact. However, most porosities within the archaeological wood were full of foreign matter in the soil. In Fig. 1, this difference is clearly seen in the archaeological and recent oak wood. The oven dry densities of the recent wood and archaeological wood samples were 0.73 g/cm<sup>3</sup> and 0.66 g/cm<sup>3</sup>, respectively. However, the difference is significant, the oven dry density of the archaeological wood is still in the normal range, according to literature data [38]. The oven dry density within the archaeological wood cannot be explained solely by long-term soil contact degradation, at least not with any certainty. It is within the normal range of wood density variation. Five wooden samples with 10 × 10 × 30 (±0.5) mm dimensions were cut from both the recent wood and archaeological oak wood. Wooden samples of the same dimensions and weights were selected in each group of recent and archaeological oak wood.

### 3.2. Sorption and desorption processes

In this study, two desiccators were used to evaluate moisture content in archaeological and recent oak. Five archaeological and five recent wood samples with 10 × 10 × 30 (±0.5) mm dimensions were used (Fig. 2). A desiccator containing water for sorption and a desiccator containing silica gel for desorption process were employed. The relative humidity (RH) in the desiccator containing water was 100%, while the relative humidity in the desiccator containing silica gel RH was 0%. A Testo 174H sensor monitored RH inside the desiccators. The interiors of the desiccators were kept at room temperature. As a first step, the samples were placed in an oven at 105 ± 3 °C for 24 h. After weighing, the samples were placed in a desiccator containing water to reach the equilibrium moisture content (EMC) that, in this case, is theoretically equal to the fiber saturation point (FSP). Weight was measured by the gravimetric method using an analytical balance (Sartorius 2007 MP) with the accuracy of ± 0.0001 g. Samples were weighed every hour for one day, then every 12 h for three days, and then once every day until they achieved constant mass. The samples were then placed in a desiccator containing silica gel to achieve dry weight. The schedule described above was used for this process as well. Samples were stored in the desiccator until they reached the initially measured oven dry weight again. The same procedure was repeated for the samples treated with TEOS. The moisture content in the sorption and desorption process of

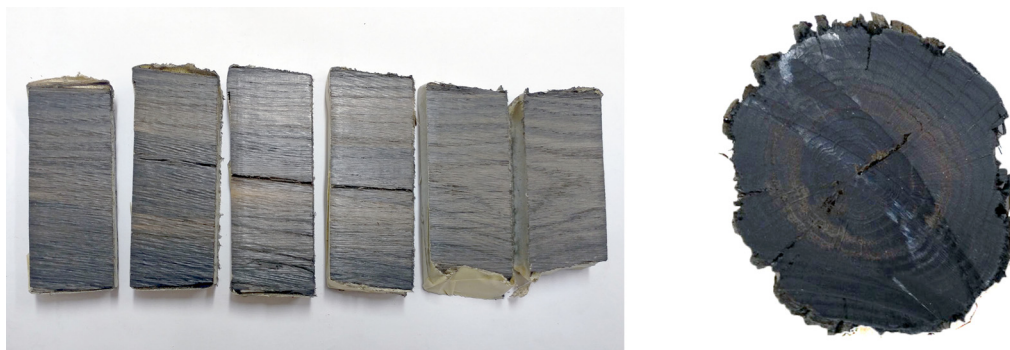


Fig. 1. Pieces of an archaeological oak column from the 14<sup>th</sup> century, found underground in Iasi.

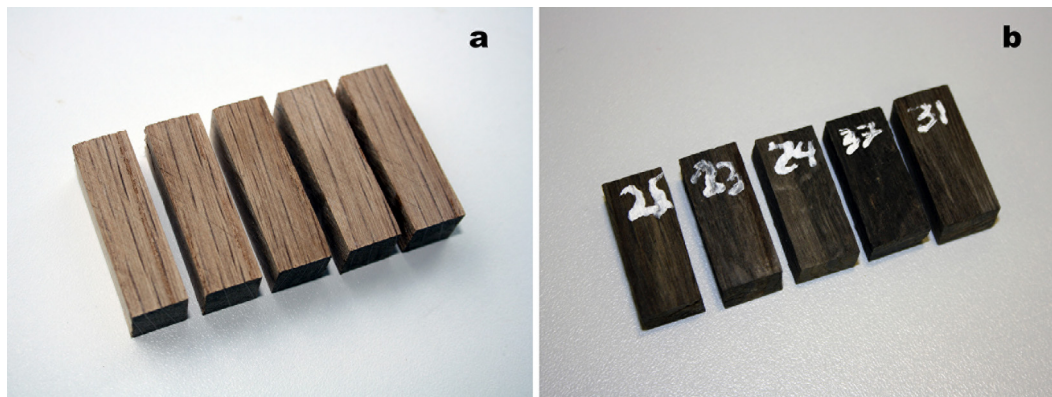


Fig. 2. Recent oak (a) and archaeological oak (b) wood samples used for the sorption/desorption tests, the TEOS treatment and color measurements.

wood samples was calculated according to Eqn 1:

$$EMC(\%) = \frac{W_w - W_d}{W_d} \times 100, \quad (1)$$

Where EMC is the equilibrium moisture content of the samples as a result of the sorption process,  $W_w$  is the wet weight of the samples, and  $W_d$  is the oven dry weight of the samples.

### 3.3. Impregnating formulation

In this study, a hydrolyzed solution of TEOS was prepared by mixing 10 g of TEOS with 4.9 g of a 40 vol% solution of ethanol in water. The molar ratio of  $H_2O:TEOS$  was 4:1. As a catalyst to promote hydrolysis, 0.12 g of 1 M hydrochloric acid (HCl) was added to the TEOS solution. The solution was stirred for ca. 1 h at room temperature. It was assumed that the complete hydrolysis of TEOS was achieved after 1 h, which resulted in a transparent gel of silicic acid  $Si(OH)_4$ .

### 3.4. Impregnation method

Five recent wood samples and five archaeological wood samples with  $10 \times 10 \times 30 (\pm 0.5)$  mm dimensions were used. Before impregnation, the samples were dried and weighed in an oven at  $105 \pm 3$  °C for 24 h. The weight of dried samples was measured. A conventional vacuum method was used to impregnate the wood samples; 15 min under vacuum conditions (0.8 kPa), followed by 2 h under atmospheric pressure. The wood samples were reweighed after impregnation.

### 3.5. Color measurements

The surface darkening phenomenon for any porous material, such as wood, that comes into contact with water occurs from

a change in the refractive index as water enters air-filled pores. At high RH, the complete darkening of wood is related to capillary condensation. Liquid water present in the cell lumen often caused the hue to darken and intensify. After vacuum impregnation with water, the darkening was even more pronounced [39]. To investigate color changes, color coordinates were determined according to the CIELab system (Fig. 2). Measurements were conducted using a colorimeter (Konica-Minolta 2600d). The  $L^*$ ,  $a^*$ ,  $b^*$  color co-ordinates were calculated based on the D65 illuminant and 10° standard observer with a test-window diameter of 4 mm. Five samples of untreated and five samples of treated oak wood were analyzed. The color changes of untreated and treated recent and archaeological wood for each sorption and desorption process were measured. Total color change resulting from both the TEOS treatment and the moisture content change was calculated. The difference between two colors (total color change) can be calculated according to Eq. 2:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}, \quad (2)$$

where  $\Delta E$  is the total color change and  $\Delta L^*$ ,  $\Delta a^*$  and  $\Delta b^*$  are the differences in  $L^*$ ,  $a^*$  and  $b^*$  coordinates, respectively, of the two colors.

### 3.6. FTIR analyses

Square samples with an edge length of 5 mm and 1 mm thickness were cut out of from the middle of each initial wood sample used in other tests. On the Bruker Invenio R spectrometer equipped with a diamond ATR unit (Bruker Optik GmbH, Ettlingen, Germany), the ATR FTIR spectra were recorded in the range of 4000–400  $cm^{-1}$  using 64 scans at a resolution of 4  $cm^{-1}$ . To ensure reproducibility and constant power, the samples were pushed onto

**Table 1**

Summary of the equilibrium moisture contents and the time necessary for the sorption and desorption processes of recent and archaeological oak before and after treatment with TEOS.

Sample	Untreated			Treated		
	EMC (%)	Sorption time (h)	Desorption time(h)	EMC (%)	Sorption time (h)	Desorption time(h)
Recent oak	21.95 ( $\pm 0.49$ ) <sup>a</sup>	585 <sup>a</sup>	249 <sup>a</sup>	20.80 ( $\pm 0.34$ ) <sup>a</sup>	839 <sup>a</sup>	431 <sup>a</sup>
Archaeological oak	24.80 ( $\pm 0.39$ ) <sup>b</sup>	513 <sup>b</sup>	393 <sup>b</sup>	24.90 ( $\pm 0.3$ ) <sup>b</sup>	839 <sup>a</sup>	359 <sup>b</sup>

EMC: equilibrium moisture content as a result of the sorption process; the values are the mean  $\pm$  the SD. Mean values that are followed by the same letters (a or b) were not significantly different at  $P < 0.05$ .

**Table 2**

Color changes of recent and archaeological oak before and after treatment with TEOS in wet and dry state.

Color coordinates	After sorption (wet state)				After desorption (dry state)			
	Untreated recent oak	Treated recent oak	Untreated archaeol. oak	Treated archaeol. oak	Untreated recent oak	Treated recent oak	Untreated archaeol. oak	Treated archaeol. oak
L*	62.28 ( $\pm 4.14$ ) <sup>a</sup>	44.62 ( $\pm 1.52$ ) <sup>b</sup>	27.92 ( $\pm 5.84$ ) <sup>a</sup>	65.14 ( $\pm 1.23$ ) <sup>b</sup>	62.64 ( $\pm 2.95$ ) <sup>a</sup>	51.78 ( $\pm 2.38$ ) <sup>b</sup>	29.63 ( $\pm 2.8$ ) <sup>a</sup>	40.87 ( $\pm 3.62$ ) <sup>b</sup>
a*	8.68 ( $\pm 1.45$ ) <sup>a</sup>	6.89 ( $\pm 0.47$ ) <sup>b</sup>	0.75 ( $\pm 0.33$ ) <sup>a</sup>	1.51 ( $\pm 0.31$ ) <sup>b</sup>	8.33 ( $\pm 0.95$ ) <sup>a</sup>	15.90 ( $\pm 0.41$ ) <sup>b</sup>	1.20 ( $\pm 0.3$ ) <sup>a</sup>	7.95 ( $\pm 1.25$ ) <sup>b</sup>
b*	40.09 ( $\pm 4.74$ ) <sup>a</sup>	13.69 ( $\pm 0.9$ ) <sup>b</sup>	12.71 ( $\pm 0.84$ ) <sup>a</sup>	0.89 ( $\pm 0.98$ ) <sup>b</sup>	25.05 ( $\pm 1.47$ ) <sup>a</sup>	31.43 ( $\pm 1.16$ ) <sup>b</sup>	10.27 ( $\pm 0.91$ ) <sup>a</sup>	26.07 ( $\pm 1.7$ ) <sup>b</sup>
$\Delta E$	31.81		39.06		14.7		20.53	

$\Delta E^*$ : color difference; L\*: lightness; a\*: green-red chromatic coordinate; b\*: blue-yellow chromatic coordinate; the values are the mean  $\pm$  the SD. Mean values that are followed by the same letters (a or b) were not significantly different at  $P < 0.05$ .

the ATR-crystal with an integrated applicator. A background spectrum with an empty specimen compartment was registered prior to measurements and automatically subtracted from the spectra in the measurements below. Two samples from each kind of wood were analyzed, and their spectra were averaged. Based on the software OPUS version 8.2 (Bruker Optik GmbH, Ettlingen, Germany), the spectra were corrected and vector-normalized.

### 3.7. Statistical analysis of the results

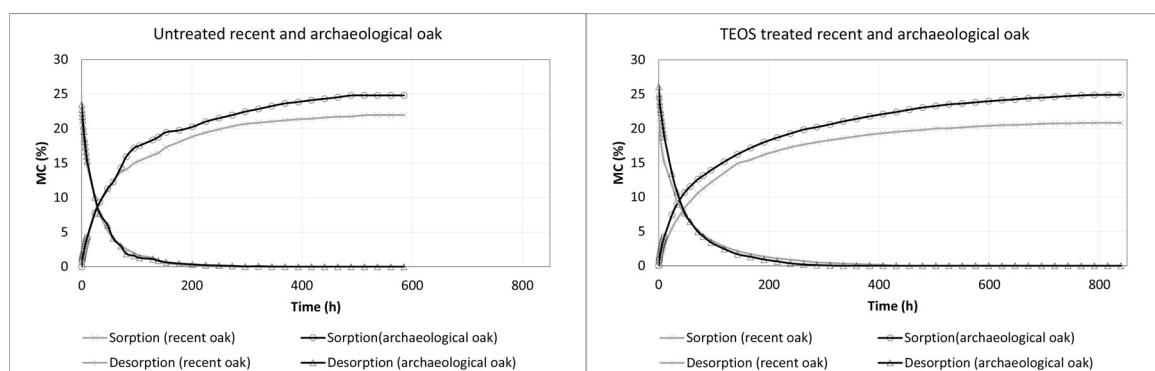
Distribution normality of the data was verified and statistical significance tests (ANOVA, Fischer LSD-test,  $p < 0.05$ ) were conducted on the investigated material properties with the software Statistica 13.0 (Statsoft).

## 4. Results and discussion

### 4.1. Sorption and desorption process

Table 1 summarizes the moisture contents as a result of the sorption process and the time necessary for the sorption and desorption processes until equilibrium (EMC). Results are indicated as mean ( $\pm$ standard deviation). Different superscript letters in one column indicate significant difference between archaeological and recent samples at  $p < 0.05$  level.

According to the results in Table 1, EMC of untreated recent and archaeological oak wood were significantly different. The higher EMC of the archaeological wood can be attributed to the higher number of pores, or looser structure in the archaeological wood compared to the recent wood [40]. Microfibril states change with ageing; consequently, compared to the fibril arrangement of recent wood, the elementary fibrils of archaeological wood were loosely arranged. This leads to the higher accessibility of hydroxyl groups of the cell-wall polymers to water molecules [41]. The sorption time, which here means the time necessary for the saturation of the cell-wall by moisture (reaching EMC), was significantly higher for untreated recent oak than it was for untreated archaeological wood. Despite this, desorption time (time necessary for drying) was significantly higher for archaeological wood. These results indicate that the long-term soil contact of oak wood increased the EMC of the material, and the sorption process became significantly faster as well. Another interesting result was discovered in addition to this; though long-term soil contact quickened sorption, it made desorption (drying) slower. This result, taking the presumable higher porosity of the archaeological material into consideration [40,42,43], indicates a stronger water bonding ability of the cell wall components of archaeological wood compared to recent oak wood. This finding contrasts with the results of other researchers who examined dry-exposed archaeological wood [44], indicating the importance of the conditions under which the archaeological wood was stored until excavation and conservation.



**Fig. 3.** Sorption and desorption curves of untreated and treated recent and archaeological oak wood ( $T = 23^\circ\text{C}$ ;  $RH_{\text{sorption}} = 100\%$ ;  $RH_{\text{desorption}} = 0\%$ )



**Table 3**

Color differences as a result of moisture change of untreated and treated oak wood.

Color coordinates	Untreated recent oak		Treated recent oak		Untreated archaeological oak		Treated archaeological oak	
	After desorption (dry state)	After sorption (wet state)	After desorption (dry state)	After sorption (wet state)	After desorption (dry state)	After sorption (wet state)	After desorption (dry state)	After sorption (wet state)
L*	62.64 ( $\pm 2.95$ ) <sup>a</sup>	62.28 ( $\pm 4.14$ ) <sup>a</sup>	51.78 ( $\pm 2.38$ ) <sup>a</sup>	44.62 ( $\pm 1.52$ ) <sup>b</sup>	29.63 ( $\pm 2.8$ ) <sup>a</sup>	27.92 ( $\pm 5.84$ ) <sup>a</sup>	40.87 ( $\pm 3.62$ ) <sup>a</sup>	65.14 ( $\pm 1.23$ ) <sup>b</sup>
a*	8.33 ( $\pm 0.95$ ) <sup>a</sup>	8.68 ( $\pm 1.45$ ) <sup>a</sup>	15.90 ( $\pm 0.41$ ) <sup>a</sup>	6.89 ( $\pm 0.47$ ) <sup>b</sup>	1.20 ( $\pm 0.3$ ) <sup>a</sup>	0.75 ( $\pm 0.33$ ) <sup>a</sup>	7.95 ( $\pm 1.25$ ) <sup>a</sup>	1.51 ( $\pm 0.31$ ) <sup>b</sup>
b*	25.05 ( $\pm 1.47$ ) <sup>a</sup>	40.09 ( $\pm 4.74$ ) <sup>b</sup>	31.43 ( $\pm 1.16$ ) <sup>a</sup>	13.69 ( $\pm 0.9$ ) <sup>b</sup>	10.27 ( $\pm 0.91$ ) <sup>a</sup>	12.71 ( $\pm 0.84$ ) <sup>b</sup>	26.07 ( $\pm 1.7$ ) <sup>a</sup>	0.89 ( $\pm 0.98$ ) <sup>b</sup>
$\Delta E$	15.05		21.15		3.01		35.56	

$\Delta E^*$ : color difference; L\*: lightness; a\*: green-red chromatic coordinate; b\*: blue-yellow chromatic coordinate; the values are the mean  $\pm$  the SD. Mean values that are followed by the same letters (a or b) were not significantly different at  $P < 0.05$ .

After treatment, the sorption time for treated recent and archaeological wood was the same, but EMC was significantly different. These differences in untreated wood can be due to the increased porosity of the archaeological oak wood. A similar result has been reported by other authors as well [45,46]. These results are attributable to the liquid tension and drying stress during the desorption processes in the cell walls, as accompanying phenomena of the drying process [47]. A remarkable point of this process were the saturation and desorption times before and after treatment. As shown in Table 1, the saturation for recent oak compared to archaeological oak increased by a significant 43% as a result of TEOS treatment. In addition, the saturation time for archaeological oak compared to untreated archaeological oak increased by a notable 63% as a result of TEOS treatment. These differences can be attributed to the deposition of TEOS gel in the wood structure [47,48]. These results show that TEOS gel treatment did not significantly influence the EMC of the investigated materials under saturated humidity conditions (RH = 100%), but instead greatly slowed the moisture uptake process. The desorption time in recent oak samples increased by 73%. Despite this, desorption time of archaeological samples decreased by 9%. This is a favorable property regarding the conservation of the archaeological wood materials as they take the moisture in slower, but release it at the same rate, or even a little faster than before the treatment. This phenomenon might be explained by the markedly different porosity of the recent and archaeological materials. Furthermore, the silica xerogel treated materials can easily dry after a sorption process because its pores remain open for diffusion [49]. Fig. 3 shows the sorption/desorption curves of the tested materials.

#### 4.2. Color measurements

The color of recent and archaeological oak wood specimens was measured before and after TEOS treatments as well as in dry and wet states (before and after the sorption process) (Table 2).

After the sorption process,  $\Delta E$  was 31.81 between treated and untreated recent oak. In archaeological oak it was 39.06, which is a significant difference. This result indicates that TEOS reduces the brightness of recent oak [50,51,52,53,54,55]; however, the degree of brightness in the archaeological oak increased after treatment. The reason for this increase may be that the extracts in the archaeological oak were dissolved in the treatment solution and reduced the degree of brightness [50,51,52,53,54,55]. In addition to brightness, TEOS treatment remarkably decreased the yellow hue of wet materials. The change of red hue was only slight, but statistically significant. However, differences between treated and untreated materials in wet state were not that large.  $\Delta E$  between untreated recent oak and treated recent oak was 14.70, and between untreated archaeological oak and treated archaeological oak it was 20.53. The reason for these low variations could be the following: moisture alone changes wood color, and when the mois-

**Table 4**

Assignment of absorption IR spectra peaks in wood.

Wave number (cm <sup>-1</sup> )	Assignments and remarks
3180/3590	O–H stretching
2938	C–H stretching
1743	Non-conjugated C=O in hemicellulose
1650	(xylans)
1602	Conjugated C=O in lignin
1507	Aromatic skeletal vibration in lignin
1464	Aromatic skeletal vibration in lignin
1375–1427	C–H deformation in lignin and carbohydrates
1333	C–H deformation in lignin and carbohydrates
1262	C–H vibration in cellulose; C–O vibration in
1135/1172	syringyl derivatives
1000	Syringyl ring and C–O stretch in lignin and
997	xylan
897	C–O–C vibration in cellulose and hemicellulose
	Si–OH stretching
	C–O stretch in cellulose and hemicellulose
	C–H deformation in cellulose

ture is reduced, the color changes in the wood decrease as well [51,52,53,54,55].

The color of specimens between wet and dry states of untreated and treated recent and archaeological wood were also measured (Table 3). Between the wet and dry states of untreated recent oak,  $\Delta E$  was 15.05 and in the case of treated recent oak,  $\Delta E$  was 21.15. On the other hand, with archaeological oak,  $\Delta E$  between wet and dry states of untreated samples was 3.01. The color change in treated archaeological oak was 35.56. In treated materials, both red and yellow hue decreased as a result of wetting, while red hue in untreated materials did not change and yellow hue increased. The reason for these color changes as a result of moisture changes in wood could be due to wood moisture content changing wood color [50,51,52,53,54].

#### 4.3. FTIR analyses

FTIR-ATR analysis was carried out to detect the penetration of treatment products (TEOS). In order to detect the penetration of TEOS, two FTIR-ATR spectra (untreated recent and archaeological oak wood, treated recent and archaeological oak wood with TEOS solution) were obtained. In the fingerprint region between 800 and 1800 cm<sup>-1</sup>, there were many well-defined peaks providing abundant information on various functional groups present in wood constituents [56] (Table 4). Fig. 4 shows the information of untreated recent and archaeological oak and Fig. 5 presents the information of treated recent and archaeological oak wood.

The attributions of the peaks in the finger-print region between 1800 and 600 cm<sup>-1</sup> were assigned to the wood components [56]. According to the spectra in the Fig. 4, the O–H peaks between 3180/3590 in the archaeological oak wood decreased because of

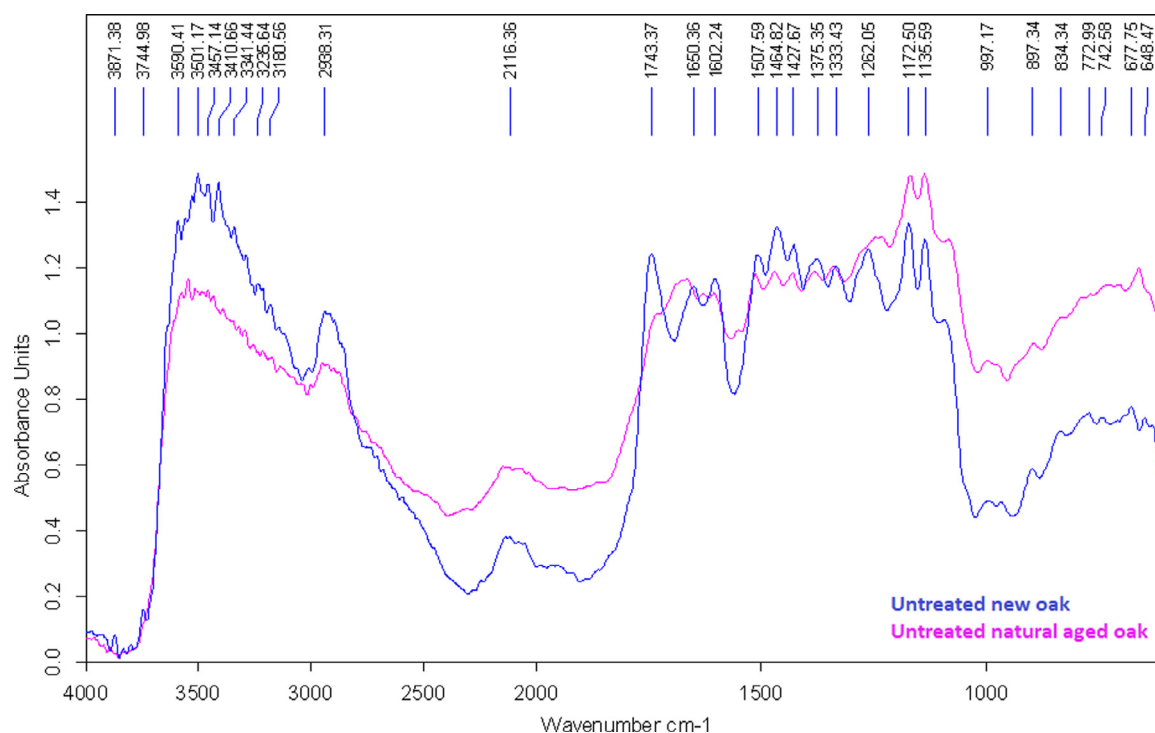


Fig. 4. ATR-FTIR spectra of the untreated recent and archaeological oak wood.

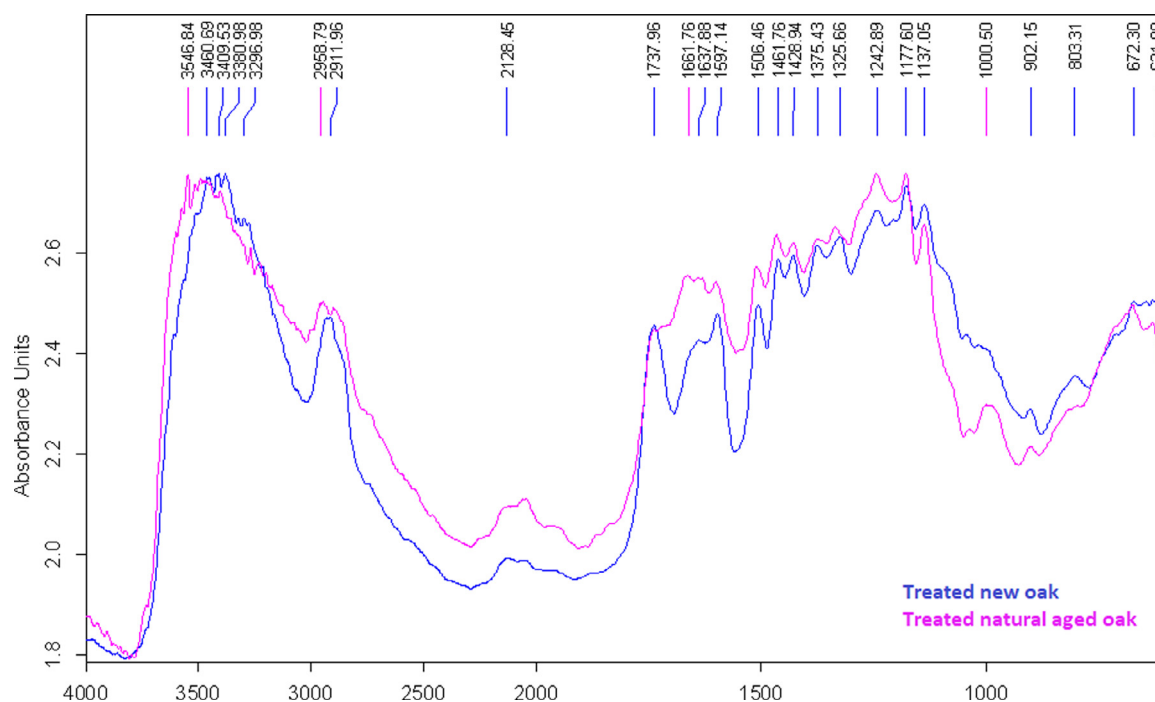


Fig. 5. ATR-FTIR spectra of the treated recent and archaeological oak wood with TEOS.

aging. An absorption band was observed in the carbonyl group region of wood samples at  $1743\text{ cm}^{-1}$ , indicating a reduction in peak intensity due to aging caused by hemicellulose degradation. The reduction might also be caused by the leaching of remaining acetic acid in the archaeological wood. The reduced intensity due to aging confirms the removal of fats and waxes through the aging procedure, as observed for oak. The intensity of peak at  $1506\text{ cm}^{-1}$  was also slightly reduced, which suggests the removal of aromatic extractives such as dehydroabietic acid, lignans, and

stilbenes [57] due to aging. But according to the spectra in the Fig. 5, O-H bands increased and shifted to the left in recent and archaeological oak wood after TEOS treatment. This increase may be due to the treatment with TEOS substance. In addition, belonging to wood components and C=O groups increased between  $1661$  and  $1600\text{ cm}^{-1}$ . This fact may be due to the formation of xerogel, which hid the functional wood group. The peak around  $1000\text{ cm}^{-1}$  appears increased due to the absorption of Si-O-Si linkage [50].

## 5. Conclusions

According to the results on untreated and tetraethyl orthosilicate-treated recent and archaeological oak wood materials, the archaeological wood showed higher potential for sorption, as significantly higher equilibrium moisture content and shorter sorption time was observed for it. Treatment with tetraethyl orthosilicate gel remarkably increased the time necessary for reaching the equilibrium moisture content of the materials under saturated relative humidity conditions. However, the treatment did not change the equilibrium moisture content of the tested recent or archaeological wood, but it did considerably slow the moisture uptake process. Desorption time increased significantly in recent oak, while desorption time in archaeological oak decreased slightly. Nevertheless, though slight, this decrease in archaeological wood is still significant because it indicates the favorable effect of the treatment regarding the further storage of archaeological wooden objects conserved by this method. The differences are the result of the different effects of the tetraethyl orthosilicate treatment on the sorption/desorption behavior on the recent and archaeological oak materials due to the different porosity and chemical composition originating from the natural aging process. Also, treatment of recent and archaeological wood with tetraethyl orthosilicate caused significant color changes in recent and archaeological oak wood. In recent wood, tetraethyl orthosilicate treatment decreased brightness. Conversely, the brightness of archaeological oak wood increased significantly as a result of the treatment. The color difference was lower in when the samples, were in a dry state than they were in a wet state. According to the FTIR analysis, after recent and archaeological oak wood was treated with tetraethyl orthosilicate, O–H bands increased and shifted to the left. This increase is due to the tetraethyl orthosilicate treatment. Moreover, peaks belonging to wood components and C=O groups increased. This fact is due to the hiding effect of xerogel formation on the functional group of wood.

## Declaration of Competing Interest

None.

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