ANALYSIS OF WATERLOGGED WOODS: EXAMPLE OF YENİKAPI SHIPWRECKS

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Abstract

In this study, the analyses carried out before and during the conservation were evaluated to manage the conservation works on the woods of Yenikapı Shipwrecks. The analyses comprise the maximum water content (U_{max})-density, SEM (Scanning Electron Microscopy), SEM-EDX (Scanning Electron Microscopy- Energy dispersive X-ray spectroscopy), FTIR (Fourier Transform Infrared Spectroscopy), XPS (X-ray Photoelectron Spectroscopy) and XRF (X-ray Fluorescence Spectroscopy) analyses. To carry out the conservation works on the woods of Yenikapı shipwrecks, the analyses start with the samples obtained from the woods before the conservation works and continue until the last phase in which chemical impregnation processes are completed.

Key Words: analyses, conservation, shipwreck, wood.

SUYA DOYMUŞ AHŞABIN ANALİZİ: YENİKAPI BATIKLARI ÖRNEĞİ

Öz

Bu çalışmada Yenikapı Batıklarına ait ahşaplar üzerinde konservasyon çalışmalarını yönetebilmek amacıyla konservasyon öncesinde ve konservasyon esnasında gerçekleştirilen analiz çalışmaları değerlendirilmiştir[1]. Bu analizler maksimum su miktarı (U_{max})-yoğunluk, SEM (Taramalı elektron mikroskobu), SEM-EDX (Taramalı elektron mikroskobu-enerji dağılım spektrometresi), FTIR (Fourier transform infrared spektroskopisi), XPS (X ışını fotoelektron spektroskopi) ve XRF (X Işını floresan spektroskopisi) analizlerinden oluşmaktadır. Söz konusu analizler batık ahşaplarının konservasyon işlemlerinin gerçekleştirilebilmesi amacıyla koruma işlemlerinin öncesinde ahşaplardan alınan örneklerle başlamakta kimyasal emdirme çalışmalarının tamamlandığı son aşamaya kadar devam etmektedir.

Anahtar Kelimeler: analiz, konservasyon, batık, ahşap.

[1] We would like to thank Prof. Dr. Ufuk Kocabaş and Yenikapı Shipwrecks Project Team for their help and support. The IU Yenikapı Shipwrecks Project has been realized with financial support of İstanbul University Scientific Research Projects Unit (Project no: 2294, 3907, 7381, 12765, SDK-2016-3777, SDK-2016-3776).

Introduction

The scientific works on 27 of the 37 shipwrecks found in the fillings of Theodosius Harbour that dates back to the Byzantine era have been carried out by a team founded under the chairmanship of Prof. Dr. Ufuk Kocabaş from the Department of Conservation of Marine Archaeological Objects, the Faculty of Letters within the scope of "İstanbul University's Yenikapı Shipwrecks Project". The conservation works of 31 of the 37 shipwrecks in total have been carried out by the Department. Documentation and removal of shipwrecks have been completed within the scope of the project reported in this study. The shipwrecks, which have been documented and disassembled, are conserved in the stainless steel tanks built in IU Yenikapı Shipwrecks Research Laboratory. The conservation works which were carried out within the scope of the project are also conducted in the IU Yenikapı Shipwrecks Research Laboratory (Kocabaş, 2015:5) (Fig.1).

Fig.1 IU Yenikapı Shipwrecks Research Laboratory.

The wooden elements that constitute Yenikapı shipwrecks comprise waterlogged woods. All of these elements undergo changes throughout the time they are under the water. As woods remain in moist or wet areas for a long time, they absorb water, and finally, undergo changes with the difference that occurs in chemical products and turn into wet and waterlogged woods. During this process, changes occur in the physical and chemical structures of woods (Jong, et al., 1982: 9). The conservation of such waterlogged woods is not only indispensable for them to be displayed in the museum but also a difficult and long process. Before starting the conservation of waterlogged woods, it is essential to know the aspects and problems of the material very well. Thus, to define the type, deterioration and problems of the wood in detail to determine conservation strategy is of great importance (Giachi, et al., 2010: 92). For example, tannic oak trees increase the acidity of impregnation solution, and this decreases the impregnation duration of Kauramin® (melamine formaldehyde) used in the solution. Some chemical impregnation products are not used in the oaks, the amounts of water of which are below 200%. In addition, the impregnation process may last longer for some types of trees. Such factors show that the wood should be defined very well in terms of every aspect before deciding upon impregnation process (Kılıç, 2013).

Defining the deterioration and conservation processes of the woods of Yenikapı shipwrecks that have gone through the deterioration process reported here briefly and become waterlogged using analyses helps determine which conservation methods will be used and clarify the changes to be caused on woods by the conservation work, and allows to compare the woods before deterioration process with the waterlogged woods after the conservation work.

Analyses

The analyses carried out on the conservation works of the woods of shipwrecks which constitute the subject of this article are the maximum amount of water (U_{max}) - density, SEM (Scanning Electron Microscopy), SEM-EDX (Scanning Electron Microscopy- Energy dispersive X-ray spectroscopy), FTIR (Fourier Transform Infrared Spectroscopy), XPS (X-ray Photoelectron Spectroscopy) and XRF (X-ray Fluorescence Spectroscopy) analyses.

Maximum water content:

The method of maximum water content used in determining the deterioration degree of woods based on the amount of water inside the woods is a very common practice (McConnachie, et al., 2008: 29). As the amount of water inside the object changes irregularly based on the deterioration degree of xylem, in this method to determine the amount and distribution of water using the samples obtained from different parts of the same wood are significant. It is therefore aimed to determine the water distribution properly carrying out the analyses of maximum water content and using the samples obtained from different parts of the woods of Yenikapı shipwrecks. Samples were taken from woods in a way to weigh no more than 1-1,5 grams to identify the maximum water content of the woods of Yenikapı shipwrecks (Fig. 2).

Fig. 2 The process of taking samples from the woods to identify the maximum water content.

The wet density of the samples taken was measured using a precision balance; then, the sample was measured on the tip of a needle when all of its pores are full of water to identify the densities of woods. Finally, the samples were dried inside a furnace until the water inside them were completely removed. The dried samples were re-measured when they reached the room temperature inside a desiccator, and their maximum water contents were calculated in percentages (Jordan, et al.., 2002). The densities of woods were also identified using the data obtained here (Babiński,et al., 2014) (Fig. 3). The densities of the wooden samples before deterioration were also identified according to their types within the scope of the density works. Thus, this allowed to determine the deterioration degrees of samples before and after deterioration and make comparisons.

Fig. 3 Analyses on the water saturation and density of the woods.

FTIR analysis:

After identifying the physical changes that woods went through, FTIR analyses were carried out to find out the changes that occurred chemically after deterioration. Although there are different analysis methods that have been used over the years, FTIR analysis is widely used in understanding the deterioration process of waterlogged woods (English Heritage, 2010: 27; Gelbrich, etc, 2012). FTIR spectroscopy analyzes the changes regarding the chemical deterioration in woods in a more sensitive way compared to wet chemical methods and/or gravimetric techniques (Fors, et al., 2011: 789-790). FTIR analysis is based on the principle of measuring the vibration of chemical bonds that occur through the absorption of infrared rays that are gone through sampling. The change in the vibrations of chemical bonds leads to the formation of spectral bands. Each functional group has its own vibration frequency, and each infrared spectrum is unique. Dust samples or small wooden parts can be directly analyzed using FTIR-ATR (Fig. 4). Since very small samples (until 100 μm^2) can be analyzed using this method, this technique is a useful method. A spectrum, which determines different chemical compounds and the amounts of lignin, cellulose and hemicellulose of woods, was obtained using FTIR method. Such spectrum can be used as an indicator of the chemical status of woods (English Heritage, 2010: 28; Pucetaite, 2012: 12). It is possible to obtain semi-quantitative spectra regarding the band heights of the compounds of some woods. Deterioration degrees could be estimated using the relative amounts of cellulose, hemicellulose and lignin according to the spectra obtained. The substances show characteristic infrared absorption bands on “finger print” wavelength region in waterlogged woods approximately between 1800 and 800 cm^{-1}. In many reports, quantitative differences in FTIR spectra that differ according to the exposure duration of woods to deterioration conditions could be identified (Fors, et al., 2011: 789-790).

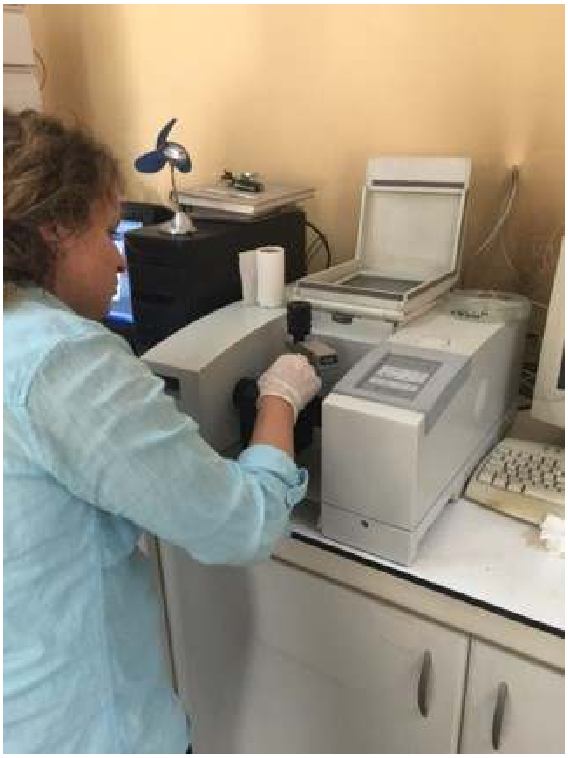

Fig. 4 The FITR analyses carried out on the woods.

The samples of waterlogged woods were compared with the durable reference samples to find out the chemical change that occurs after deterioration within the scope of FTIR analyses carried out on the woods of Yenikapı shipwrecks. The samples of waterlogged woods were taken, and reference samples were dried in drying oven at 75ºC and stored in closed containers inside a desiccator after being pulverized in the agate mortar. The analyses on the woods of shipwrecks were carried out using FTIR-KBr pellet technique. Spectra at resolution of 4 cm^{-1} were obtained on the medium infrared region of 4000-400 cm^{-1} for FTIR analyses through 16 scanning processes in Perkin Elmer Spectrum One. This analysis not only provides structural information about the chemical compound of woods but also allows to find out the changes in woods that have been processed chemically or are in the process of impregnation (Fors, Richards, 2010: 44).

The monitoring of the impregnation process of Yenikapı shipwrecks was carried out using FTIR analyses and SEM images. For both analyses, the woods were taken from different parts and depths to identify the distributions of impregnation in different parts of woods.

SEM

Following the PEG impregnation, for the success of this method to image the PEG distribution in woods is crucial. Such process can be carried out in waterlogged woods using the low vacuum SEM. It is also possible to find out the deterioration that occurs in waterlogged woods using SEM. In this context, SEM with a model of FEI Quanta 450 FEG-EDS was used to examine the woods of Yenikapı shipwrecks (Fig. 5). Such images were obtained using the samples taken from the woods of Yenikapı shipwrecks both during impregnation and drying processes, and the PEG distribution inside woods was identified using the images obtained.

Fig. 5 The examinations carried out on the woods using the SEM.

LV-SEM is different from SEM and allows for the pressure inside the sample chamber to be more than 10-6 Pa. The process makes it possible for the electrons to deviate through the sample surface with this pressure and makes it possible to conduct imaging and analyses at the pressure interval of 0-230 Pa for example, before spray coating. The fact that the device allows operating at such pressure intervals also makes it possible to operate with wet samples (Jensen, et al., 2005). In this context, the samples taken from the wooden parts of Yenikapı shipwrecks were placed transversely and longitudinally inside the chamber of the device without going through any process and examined (Fig. 6).

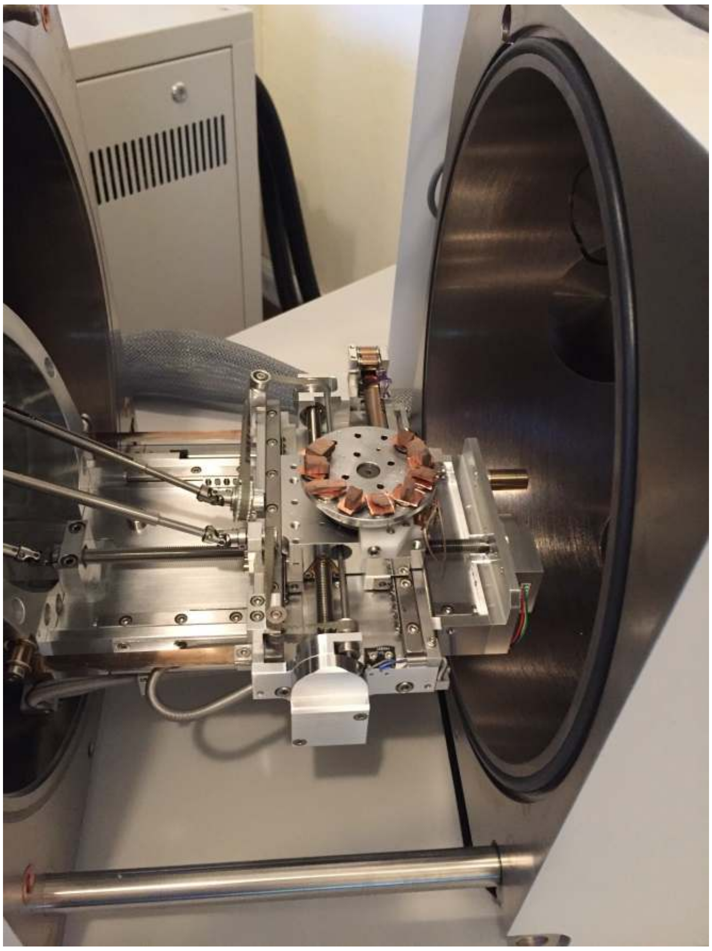

Fig. 6 The wet samples that are placed on the SEM chamber.

SEM-EDX analysis

In the examinations carried out before the conservation of many shipwrecks in Yenikapı, the existence of iron stains and corrosion originating from iron nails used in putting together the elements of ships was identified on the woods. Inorganic sulphide compounds, such as iron sulphide, may occur in case of the existence of corroded iron in woods. Iron sulphide is known to cause acidity under high moisture environment as a result of oxidation. Iron ions accelerate both the production of acid and oxidation processes that lead to corrosion in the structure of woods (Fors, 2008). It is possible to identify the distribution of elements in the micro-structure of woods using SEM-EDX. This analysis cannot directly identify the types of sulphide and iron compounds. However, it is possible to obtain information about the sulphide distribution in the parts of the cell wall of the micro-structure of woods, which are full of lignin, and the ratio of inorganic/organic sulphide compounds. Moreover, the ratio of S/Fe in the particles obtained on the woods of Yenikapı shipwrecks provided insights about their chemical compounds (Fors, et al., 2011: 786-787). The SEM-EDX analyses on the woods of Yenikapı shipwrecks were carried out using an SEM device with a model of FEI Quanta 450 FEG-EDS.

XPS analysis

XPS is a high-precision spectroscopic analysis technique, which is used in surface characterization researches and based on the electron-energy analysis. Both chemical composition and chemical statuses of surface compounds could be identified using XPS. In the woods obtained from Yenikapı shipwrecks, XPS analyses were carried out using the Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer. The samples taken from the woods of Yenikapı shipwrecks for XPS analysis were dried in drying oven at 75ºC, and then, were pulverized in the agate mortar. It is sufficient to take small amounts of samples from the woods of shipwrecks for such an analysis. In these samples taken from the woods, XPS was carried out to define the compounds of S and Fe. This analysis also identified the elemental contents of samples. The main elements that existed in the chemical structure of woods, such as C, O and N, which cannot be identified using XRF method, could be identified using this method (Sandström, et al., 2004: 193).

XRF analysis

The waterlogged wooden samples for XRF (Olympus INNOV-X DS2000) analyses to be carried out in the woods of Yenikapı shipwrecks were first dried in drying oven at 75ºC to prevent errors that may occur because of the existence of H_2O molecules, and then, measured after drying process. It is paid attention to prepare samples at the same sizes and weights to standardize the results obtained through these analyzes. The samples obtained from the woods for XRF analysis had different thickness, and measurements were done both on the bottoms and surfaces of the woods. The existence of elements, such as Fe and S, in the woods, could be identified through the measurements carried out in the woods of shipwrecks. The ratios of Fe% and S% obtained through these works were semi-quantitative values and used to compare the ratios of iron and sulphide in different samples (Fors, et al., 2014).

Conclusion

The PEG molecule weight suitable for the woods is decided after determining the maximum water content and densities of waterlogged woods. For example, high-molecular PEG impregnation is conducted in very corroded woods with low density (0,1 g/cm^3), and then, the woods are frozen, and an appropriate conservation technique can be applied through drying. On the other hand, low-molecular PEG impregnation is conducted on the very well-conserved woods (with a density of 0,4-0,5 g/cm^3), and then, controlled drying is done to prevent collapse (Jensen, Gregory, 2006: 551). The degradation of polysaccharides could be identified on the woods using the FTIR analyses carried out in the woods of Yenikapı shipwrecks. Likewise, FTIR analyses provide information as to whether PEG has been impregnated on the woods or not. In the FTIR analyses carried out on the samples taken from the woods on which impregnation has been conducted during the phase of chemical impregnation, it is possible to proceed to the next phase in the conservation after obtaining the spectra of PEG. The corroded structure of the woods is revealed using the SEM images. The changes in the elements, such as Fe and S, in the woods of shipwrecks before and after chemical cleaning are monitored using the SEM-EDX analysis. The existence and distribution of PEG in the wooden cell are very important to complete the conservation process successfully. Therefore, it is possible to observe the existence and distribution of PEG in the wooden cell using the SEM. XRF and XPS analyses were carried out to the existence of elements, such as Fe and S, in the woods. XPS analysis also identified multielement distributions of the total amount of an element of the samples (Fors, 2008: 83) The data obtained from all of these analyses are very important for the conservation of the woods of shipwrecks to be completed successfully.

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