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Mediterranean Archaeology and Archaeometry
Vol. 20, No 3, (2020), pp. 107-119
Open Access. Online & Print.

DOI: 10.5281/zenodo.3930404

PHYSICOCHEMICAL CHARACTERIZATION OF LEATHER OBJECTS OF THE BYZANTINE PERIOD

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Received: 11/06/2020
Accepted: 12/07/2020

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ABSTRACT

Excavations carried out at the Yenikapı quarter of Istanbul under the Directorate of the Istanbul Archeological Museum between 2004-2013 and have brought the historical importance of the port to light. During the salvage excavations in Yenikapı, hundreds of leather sandals and leather objects from the Byzantine period have been uncovered. The aim of this study is to determine both tanning and coloring materials of eight leather objects belonging to the Byzantine period and physicochemical characterize the leather structure. A complementary analytical approach has been used to characterize leather objects. The ATR-FTIR analysis revealed that the leather objects were tanned with vegetable tannins (gallotanins, condensed tannins and hydrolyzable tannins). By HPLC-DAD analysis, it is known that tannin dye plants were used to color the leather (*Quercus infectoria* or *Quercus ithaburensis*). The EDS analysis result showed the possible use of cupric sulfate ($CuSO_4$) for preliminary preparation before tanning leathers during the Byzantine period. In addition, SEM was used for visual assessment of the degree of deterioration of leathers. Based on the EDX analysis, biological deterioration factors and changes in the element ratio have shown that the leather objects deteriorate. In addition, pH, moisture content and CIE* Lab values show that there is a deterioration in the structure of leathers under the sea. The study will sheds light to leather conservation studies.

KEYWORDS: Yenikapı, Byzantine leatherworks, ATR-FTR, HPLC-DAD, SEM-EDX, Leather conservation

1. INTRODUCTION

In 2004 Istanbul Archaeological Museums initiated salvage excavations at the Uskudar, Sirkeci and Yenikapı station sites of the Marmaray Project, which unites Asian and European continents in Istanbul by rail for the first time in history via a crossing under the Bosphorus. The excavations lasted for nine years without interruption and were completed in 2013 (Kocabas, 2019; Akkemik and Kocabaş, 2014; Kocabaş, 2015). The excavation area in Yenikapı lies within the region that is known as Langa Gardens in the Ottoman Period and located in Istanbul's Aksaray district (Öncü and Sırrı, 2015). The Yenikapı (MRY) excavation area is presented in (Figure 1).

Figure 1. Aerial view showing the Yenikapı (MRY), area and borders of the excavation site (Kocabaş, 2015).

In the project, a total area of 58,000 sqm of approximately +3(plus three) to -9(minus nine) meters sea-level was excavated (Öncü and Sırrı, 2015). This excavation consists of the Early Turkish Republican Period to Ottoman, Byzantine, Roman and Hellenistic Periods (Düzgün and Emre, 2018). In addition to thousands of archaeological artefacts, 37 excavated shipwrecks from the Byzantine period, also provide new information about the commercial life of the city during these periods (Akkemik and Kocabaş, 2014; Akkemik et al., 2019; Kiliç, 2016; Kocabas, 2019; Namik and Kiliç, 2018; Polat, 2019; Turkmenoglu, 2018; Kocabaş, 2015). The findings demonstrate that the port was a vibrant commercial center for the Roman and Byzantine Empires. In the Byzantine Period 4th-5th century, it is known that many goods came to Constantinople (Constantinople is an ancient city in modern-day Turkey), especially from India and Iran, China, Egypt, and Russia (Asal, 2010). One of the most important pieces of evidence of trade in the Byzantine Period were leather goods and objects.

Hundreds of leather sandals and unidentified leather objects found from Yenikapı (MRY) excavations are under the inventory of the Istanbul Archeology Museum. In this study, only eight leather objects were analyzed among hundreds of archeological leather objects. The studied leather objects were found at about -3.85 and -4.50 meters below sea-level (Table 1). While selecting leather objects for the study; attention was paid to the fact that they were from the same period but in different regions of Yenikapı excavation and in different years.

Table 1. Location of the leather objects.

Samples №	Excavation area	Year of excavation	Plan square	Code (sea-level)	Dates of the objects
1(a)	*MRY'11*	2011	J1	-4.30/ -4.40	5th century
2(b)	*MRY'06*	2006	3.Unknown	-	-
3(c)	*MRY'11*	2011	J2	-4.03/ -4.08	5th century
4(d)	*MRY'10*	2010	J147	-4.06/-4.16	5th century
5(e)	*MRY'08*	2008	A28	-4.50	5th century
6(f)	*MRY'08*	2008	M25	-4.15/ -4.30	5th century
7(g)	*MRY'11*	2011	J144	-4.31/ -4.39	5th century
8(h)	*MRY'06*	2006	G15	-3,85	4th century

MRY - Marmaray Yenikapı archaeological site and year of excavation, Plan square- Yenikapı area, Code- Sea level.

Analytical techniques used in the study of archaeological leathers are important tools to identify the components and distortions that make up all objects. It is known that the object should be researched and analyzed very extensively before conservation studies. In recent years, analytical studies have been carried out on archaeological leathers. Regarding analytical studies, Ganitis and others determined with FTIR and SEM analyzes that lead white, caput mortuum (cardinal or royal purple), bonnet tenon, red and yellow ocher, cinnabar, carbon black and smalt were used for coloring the leather used in the Byzantine period St Nicholas Icon [located in the city of Kastoria in Northern Greek (Macedonian)] (Ganitis et al., 2004).

Malea and others exposed problems of deterioration on fifteen archaeological wet leathers from Great Britain and Greece using pH, Ts, HPLC, SEM analytical methods (Malea et al., 2010).

Mansour and others detected the fungi Cladosporium cladosporioides, Aspergillus tamarii, Eurotium chevalieri, Aspergillus fumigatus, Wallemia sebi and Fusarium poae fungi by FTIR and SEM-EDX analytical methods that cause deterioration of archaeological leathers (Mansour et al., 2017). Using the ATR-FTIR, Falcao and Araujo produced herbal tanning materials in historical leathers (Falcão and Araújo, 2013).

Carşote and others performed FTIR analytical analysis in the Slavo-Byzantine Research Center (Ivan Dujčev) to evaluate the damages affecting parchment manuscript and leather binding of the Byzantine period (Carşote et al., 2014).

By FTIR, HPLC and SEM-EDX analysis Elnagger and others determined using of vegetable tannins, alum salts and natural dyes in tanning and coloring materials of Ancient Egyptian leathers (Elnaggar et al., 2017).

In the study of Al-Gaoudi, the mummy gland (excavated in one of the major excavations in Deir El-Bahari in Luxor 1891, the Bab El-Gasus tomb) of Khonsuemrenep (a priest from the 21st Dynasty and the author of Amun) was examined by using many analytical approaches. She explained the properties, methods and materials used in the production of a textile object with analytical techniques and the strategies of the protection processes (Al-Gaoudi, 2020).

Characterization and provenancing, dating methods, cyber-archaeology, location of ancient works with geophysical methods, archeoastronomy, bioarchaeology, geoarchaeology, conservation sciences and main applications are discussed for archeometry or archaeological sciences (Liritzis et al., 2020).

This study revealed the characterization of eight leather objects belonging to the Byzantine period currently preserved in the Istanbul Archaeological Museum. pH, moisture content and L* a* b* values of leather objects were measured, and tanning tannins were analyzed with ATR-FTIR, dye pigment was analyzed with HPLC-DAD, surface image was analyzed with SEM-EDX. With this study, which was carried out with complementary analytical approaches, new information about Byzantine leather workmanship was obtained and some deterioration factors in underwater leather finds were identified.

Determination of materials used in archaeological leathers from Yenikapı excavation and evaluation of the causes of deterioration also attract the attention of archaeologists and conservator. Innovation and high technology analysis in this work have important results for archaeological academy, conservator and restorators.

2. MATERIALS AND METHODS

2.1. Sampling

In this study, eight leather object samples (Byzantine period, 4th-5th century, which was named as Constantinople) obtained from the (Istanbul, *Turkey*), Istanbul Archaeological Museum. Analysis of leather objects were shown in (Fig. 2) and (Tab. 1).

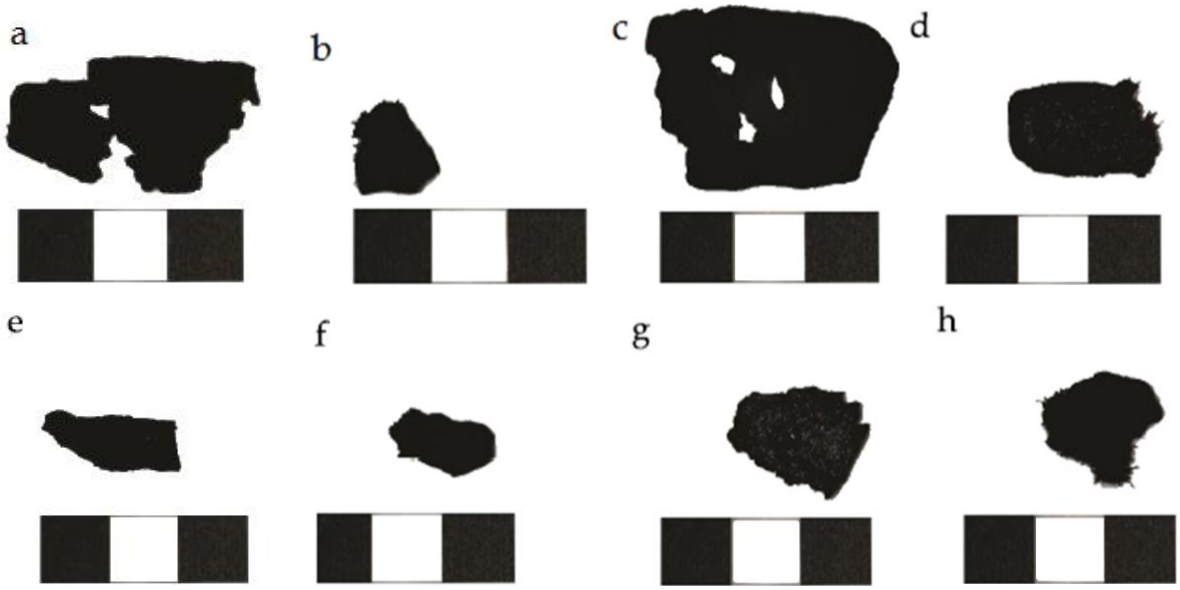


Figure 2. Scale photos of leather objects; a (MRY'11), b (MRY'06), c (MRY'11), d (MRY'10), e (MRY'08), f (MRY'08), g (MRY'11), h (MRY'06).

2.2. *Measurement of pH*

Leather objects are kept in pure water in proper storage. pH measurements were analyzed in two types. First the pH of pure water (Hanna HI 99171 Ph meter) was measured, then the pH of the leather surface was measured. Analysis results are given in (Table 2).

2.3. *Moisture content*

The leather objects were removed from the pure water and 1 cm^2 samples were prepared. Samples were placed in incubator in the laboratory for thirty minutes at 110°C. Samples were then left under appropriate atmospheric conditions. The moisture level of leather objects was measured using the Hygrometer (4000 TC Thermohygrometer. Bresciani Srl Via Breda 142 - 20126 Milan - Italy) The results are shown in (Table 2).

2.4. *Colour coordinates*

Color measurement on the leather objects were carried out by using Konica Minolta (CM-700d. Sensing, Inc., Japan) (D65 illuminant, 10° standard observer) and the results are shown in (Table 2). The system is a three-dimensional space, with coordinate axes L*, a* and b*. The L* axis denotes the lightness of the color (an L* of 0 corresponds to black, while an L* of 100 denotes white), a* represents the green–red axis (a* negative: green, a* positive: red), and b* represents the blue–yellow axis (b* negative: blue, b* positive: yellow) (Güzel and Karadag, 2019; Karadag and Yurdun, 2010; Pizzi et al., 2004).

2.5. *ATR Fourier-transform Infrared Spectroscopy (ATR-FTIR)*

FTIR (Fourier transform infrared spectroscopy) analyses were carried out using a (Perkin Elmer Spectrum UATR Two FT-IR) spectrometer in reflectance mode using an attenuated total reflectance (ATR) slide-on accessory with diamond crystal, spectral range 4000–400 cm^{-1} and resolution 4 cm^{-1}, to attempt. FTIR has been described as useful analytical tool for the molecular characterisation of leather samples.

2.6. *High - performance liquid chromatography (HPLC-DAD)*

Chromatographic measurements of leather objects were carried out using an Agilent 1200 series system (Agilent Technologies, Hewlett-Packard, Germany) including G1322A Degasser, G1311A Quat pump, G1329A auto-sample, G13166 TCC, and G1315D Diode-Array Detector. DAD detection was performed by scanning from 191 to 799 nm with a resolution of 2 nm, and the chromatographic peaks were monitored at 255, 268, 276, 350, 491, 520, 580, and 620 nm. A Nova Pak C18 analytical column (39 × 150 mm, 4µm, Part No. WAT086344, Waters) was used. Analytical and guard columns were maintained at 30°C and data station was the Agilent Chemstation. Two solvents were utilized for chromatographic separations of the samples; solvent A: H_2O- 0.1% TFA and solvent B: CH_3CN - 0.1% TFA.

The dye compositions were based on the literature, the chromatograms and the absorption spectra acquired with the standard reference compounds (Deveoglu et al., 2012). 8.0 mg of each sample was weighed before the dyestuff analysis. The samples

were hydrolyzed in 400 µL of 37% HCl/MeOH/H_2O (2:1:1, v/v/v) kept at 100°C for 8 min to extract the organic dyes. Then, the samples were evaporated under gentle nitrogen flow. The dry residue was dissolved in 400 µL MeOH/H_2O (2:1, v/v) and the samples were centrifuged. If necessary, further dilution was carried out (and then centrifugation 4000 rpm/25°C/10 min.) and HPLC analysis was performed. All the samples were injected in 100 µL to HPLC system. Identified colouring compounds based on the dyestuff analysis are shown in (Tab. 5). Scanning Electron Microscopy with EDX (SEM-EDX)

The leather objects were analyzed by Scanning Electron Microscope equipped with Energy Dispersive X-ray Spectrometer (SEM-EDX) for surface imaging and elemental analysis. In this study, TESCAN VEGA3 SEM (Brno, Czech Republic) and Bruker EDX detector (Massachusetts, ABD) were used. EDX has 600 Mini silicon drift detector (SDD), a small electronics unit and the intuitive software ESPRIT Compact (Esprit 1.9). The system performs qualitative and quantitative analyses of all materials within the element range from boron (5) to californium (98). Qualitative microanalysis was carried out using the ZAF method, which is based on the correction of the matrix effect in multi-elemental analysis that takes place in the simultaneous determination of the concentration of each element present in a multi-element material.

The leathers were coated using Au/Pd (60/40) target in a sputter coater for surface imaging. The SEM images of the leathers are shown in (Figure 6), the results of elemental analysis are also shown in (Table 5). The samples for elemental analysis were coated with a carbon target. Therefore, the carbon element was ignored in the analysis results.

3. RESULTS

3.1. pH

The pH values of the leather objects were measured between 4.69 and 7.20, (Table 2). pH values of number MRY'11 (c) and MRY'10 (d) samples have shown similarity with studies on vegetable tanned leather. Historic leather that has not deteriorated normally has a pH between 2 and 6, depending on the conditions under which they are stored (Larsen, 2000). pH value of the all samples were shown similarity with studies on historical leathers showed that a safe pH range lies between pH 4 and 8 (Strzelczyk et al., 1997). For historical leather it is reported that when pH values are above 8 then the leather becomes darker in colour, tends to be stiff and cracks (Bowes and Raistrick, 1961; Malea et al., 2010). In general in the archaeological leather has been found in old cities or villages, in cesspits and in dumped levels with wet bog or clay soils whose pH is <7 (Van Dienst, 1985).

3.2. Moisture

Measurements of moisture content are given in (Table 2). Leather objects showed a moisture content of 0.7 to 3.8% by weight. Only one example showed a 6.8% higher value. The display of different values (%) of the samples maybe depends on the type of leather, the production stage and the historical process.

3.3. Color

CIE* Lab color values of leather objects are given in (Table 2). When color measurements of leather samples are evaluated; showed that the surface image (L*) was severely darkened and that a small amount of redness and yellowness was noted in a * and b * values.

Table 2. pH, moisture and color measurements of the leather objects.

		pH value		Moisture content	Colorimetric measurement		
Number	***Samples***	pure water	wet leather	(% w/w)	L*	a*	b*
1(a)	*MRY'11*	7,80	6,82	3,4	19,11	3,57	3,57
2(b)	*MRY'06*	7,45	6,61	1,5	16,15	0,72	0,69
3(c)	*MRY'11*	4,93	5,37	2,1	15,20	0,99	1,07
4(d)	*MRY'10*	4,97	4,69	6,8	13,94	1,02	0,65
5(e)	*MRY'08*	7,44	6,76	3,8	18,93	1,08	1,49
6(f)	*MRY'08*	7,78	6,97	3,1	19,03	1,28	1,80
7(g)	*MRY'11*	8,23	7,20	0,7	19,70	3,11	3,94
8(h)	*MRY'06*	7,94	7,03	1,9	14,94	1,02	0,65

3.4. ATR-FTIR

ATR–FTIR spectroscopic study of leather samples was performed and the major bands of the eight historic samples are presented in (Fig. 3). In this study, the spectral data confirmed that leathers have been vegetable tanned. As expected, the five common bands of tannins are present: 1615–1606 and 1452–1446 cm^{-1} (aromatic ring stretching vibration), 1211–1196 and 1043 1030 cm^{-1} (C-O bond stretching vibration) (Koochakzaei and Achachluei, 2015) and 1518–1507 cm^{-1} (Amide II band of leather protein) (Puică et al., Florescu, 2006; Mansour et al., 2017; Falcão and Araújo, 2018; Rushdya, 2016; Papliaka et al., 2017). The presence of the four strong bands at 1615–1030 cm^{-1}, as referred above, is a strong indication that the

material had been tanned with vegetable tannins, (Falcão and Araújo, 2013, 2014; Falcão and Araújo, 2018; Giurginca et al., 2007).

The protein materials were detected by broad band at 3281- 3307 cm^{-1} (due to O–H). The broad band at 2325 cm^{-1} in the MRY'06 (b) sample can be sulfur (S). The band can be drive from pollution in the environment (Rushdya, 2016). Amide bands (amid I: 1646-1640 cm^{-1}; amid II: 1536-1554 cm^{-1} and amid III: 1300-1250 cm^{-1}) of the collagen structure of the leather are shown in (Tab. 3).

Hydrolysable tannin compounds were determined in the 1317-1388 cm^{-1}. Gallotannins were determined in the 1088-1082 cm^{-1} and condensed tannin compounds were determined in the 1116-1110 cm^{-1} and 844-842 cm^{-1}. Condensed tannins were determined in the MRY'11 (c) and MRY'08 (e) samples and gallotannin was determined in the MRY'08 (f) sample.

Table 3. Characteristic bands of leather objects.

Samples	*MRY'11*	*MRY'06*	*MRY'11*	*MRY'10*	*MRY'08*	*MRY'08*	*MRY'11*	*MRY'06*	**Functional group**
No	**1(a)**	**2(b)**	**3(c)**	**4(d)**	**5(e)**	**6(f)**	**7(g)**	**8(h)**	
Characteristic bands (cm^{-1})	3293*s*	3288*s*	3284*s*	3307*s*	3281*s*	3280*s*	3283*s*	3306*m*	*v* O-H carboxylic acid
	-	2325	-	-	-	-	-	-	*v* C=S sulfur ion
	1632*s*	1633*s*	1633*s*	1633*s*	1630*s*	1631*s*	1631*s*	1633*s*	*v* C=O aromatic ring
	1554*s*	1549*s*	1549*s*	-	1549*s*	1549*s*	1554*s*	1557*s*	Amide II band of leather protein
	1453*s*	1452*s*	1403*s*	1453*s*	1451*s*	1449*s*	1453*s*	1451*s*	C=O aromatic ring
	1241*m*	1241*m*	1241*m*	-	1389*m*	1241*m*	1241*s*	-	Amide III band of leather protein
	1032*s*	1032*s*	1031*s*	1033*s*	1031*s*	1033*s*	1032*s*	1033*s*	*v* C-O aromatic ester

Characteristic band of leathers: *v*, stretching; *s*, strong; *m*, medium.

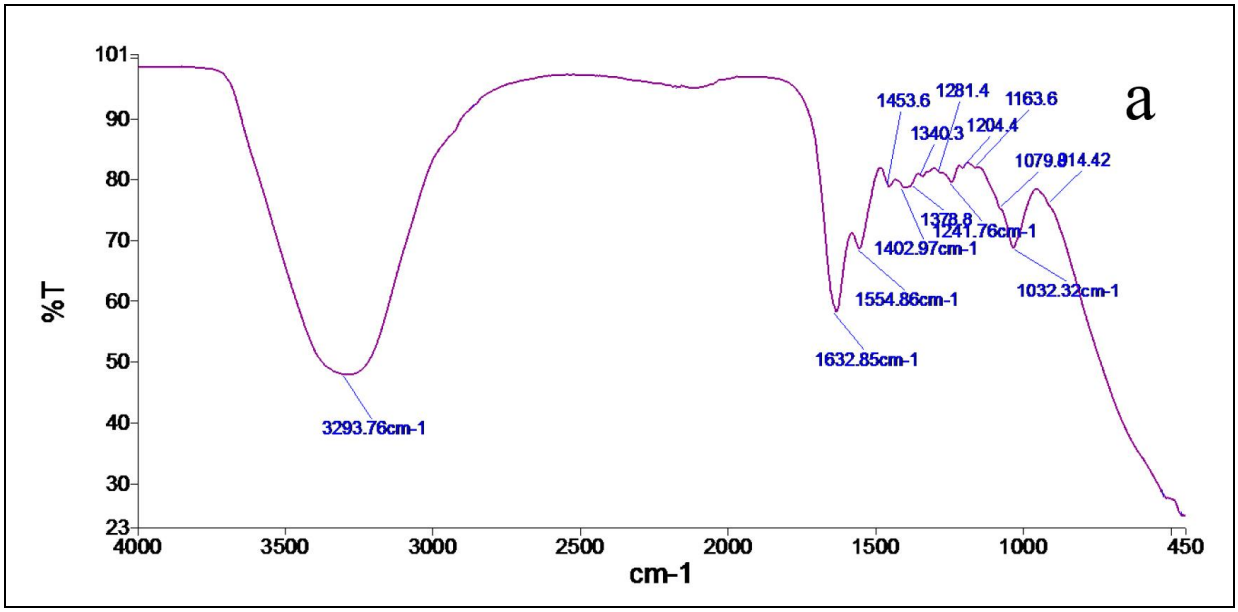


Figure 3. FTIR spectra of leather samples; a (MRY'11).

3.5. HPLC-DAD

Eight archaeological leather objects were analyzed in this study. Dye identification of archaeological objects is generally based on comparison with standard reference materials (paint materials) (Kahraman and Karadag, 2017; Karadag and Dolen, 2007). Leather objects; HPLC-DAD chromatograms and spectras (Figure 4). (Figure 5), identified coloring compounds and probability biological sources are given in (Tab. 4). The colored compounds were identified by HPLC-DAD, and dye source of the archaeological leathers are given in (Tab. 4). The leathers were determined to contain gallic acid, ellagic acid and their derivatives. It is known that tanning plants are used in leather coloring (*Quercus infectoria* or *Quercus ithaburensis*) (Karapanagiotis and Karadag, 2015). (*Quercus infectoria* or *Quercus ithaburensis*) was used for both tanning and coloring of leathers. Peak area percentages of the

colored compounds were determined semi-quantitatively by High Performance Liquid Chromatography (HPLC) using Diodes. HPLC-DAD is ideal for identifying natural dyes found in such materials.

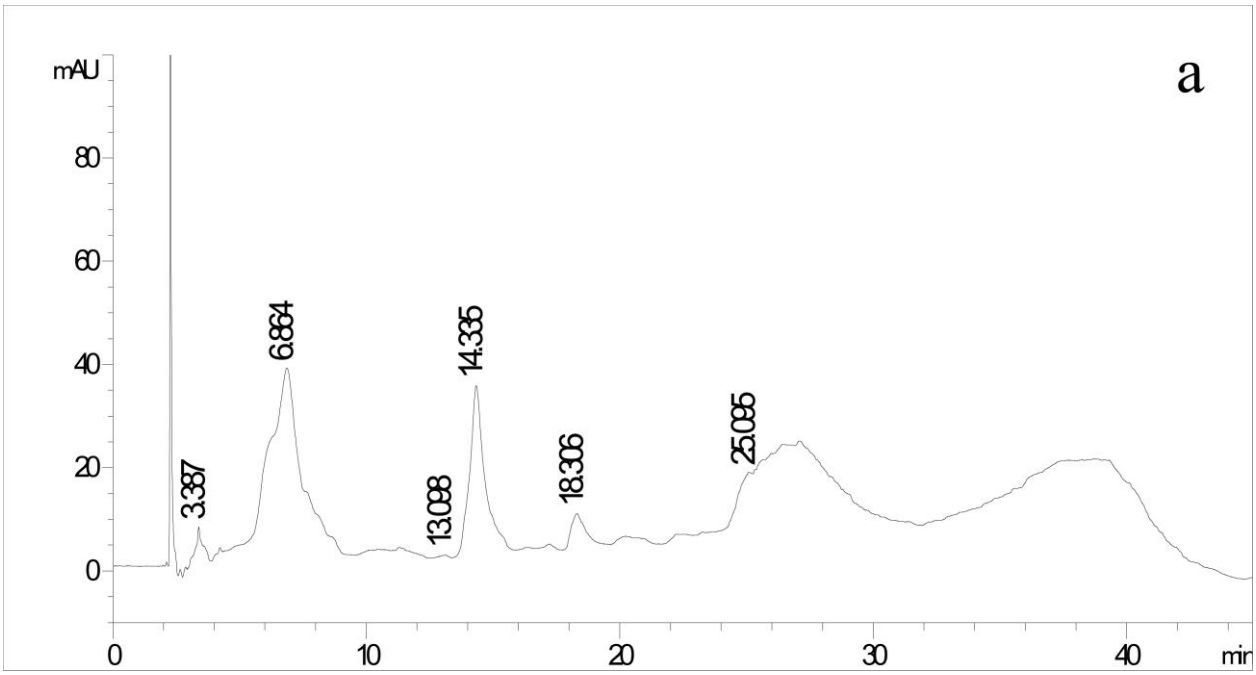
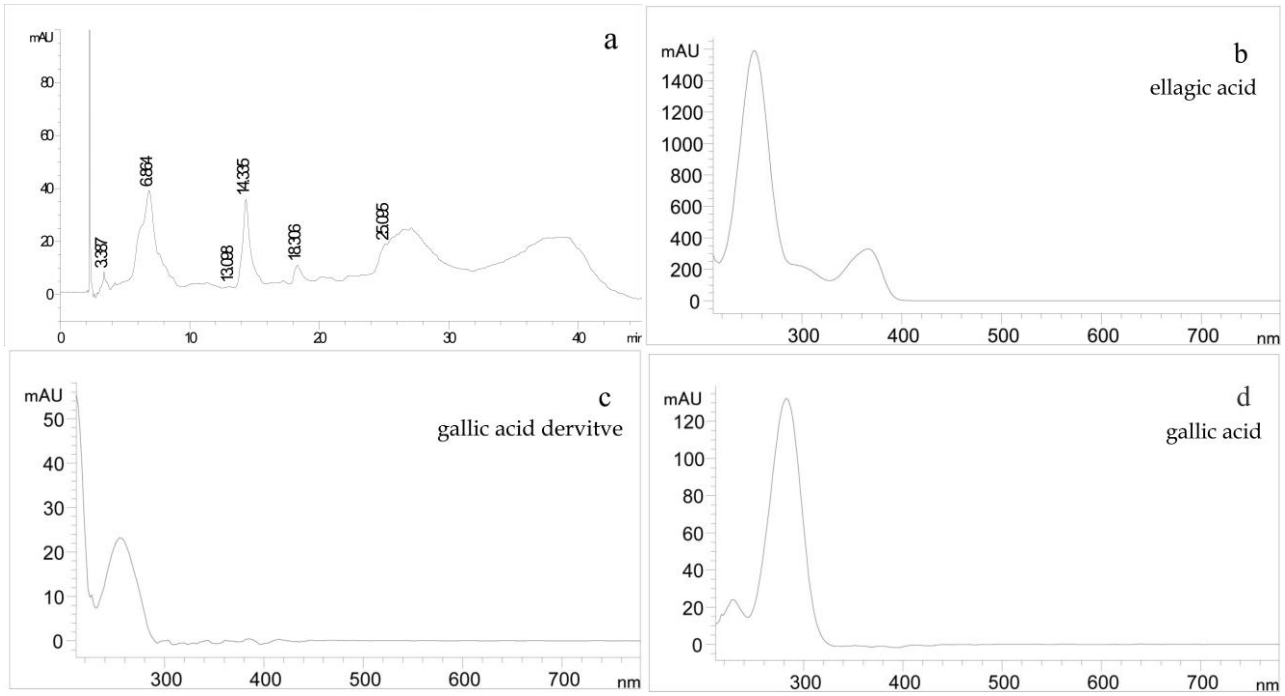


Figure 4. Chromatograms of the leather objects; a (MRY'11).



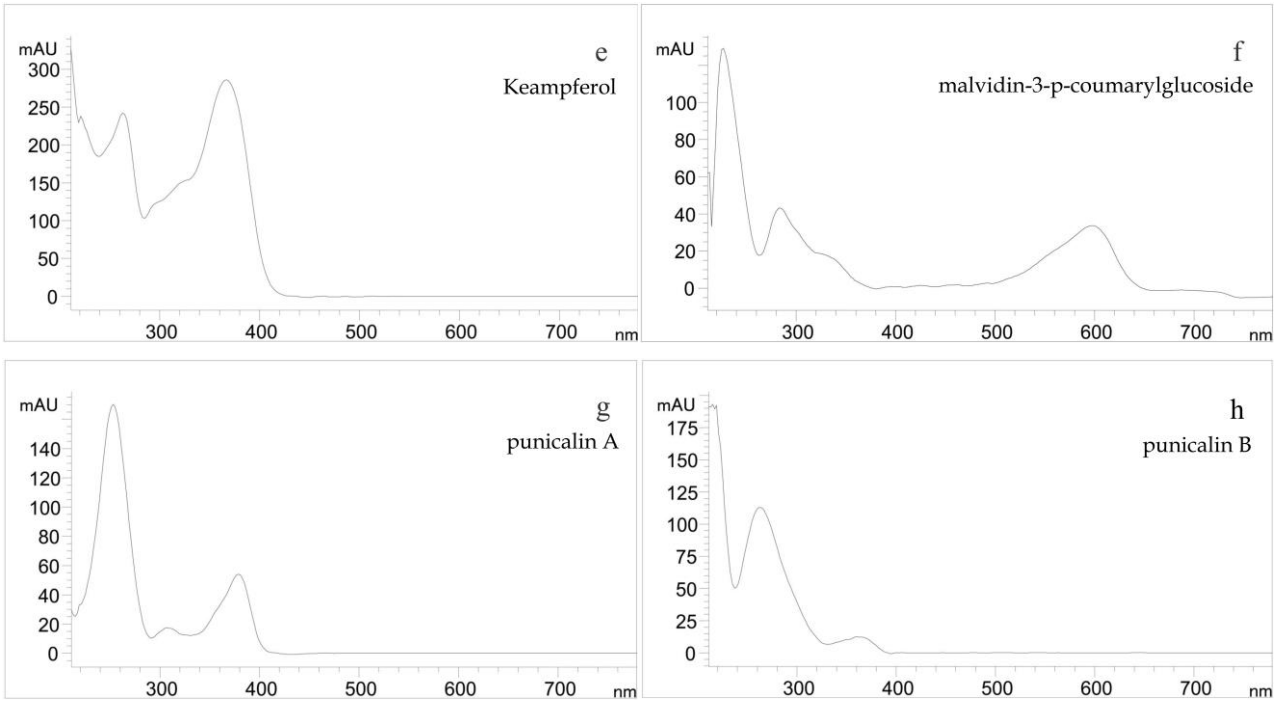


Figure 5. Spectra of identified coloring compounds; a (MRY'11), b (MRY'06), c (MRY'11), d (MRY'10), e (MRY'08), f (MRY'08), g (MRY'11), h (MRY'06).

Table 4. Identified colouring compounds and possibility biological sources.

Number	*Samples*	Identified dyestuff	Possibility Sources
1(a)	*MRY'11*	gallic acid ellagic acid gallic acid derivative ellagic acid derivative malvidin-3-p-coumarylglucoside	*Quercus infectoria* or *Quercus ithaburansis* or Tannin dye plants
2(b)	*MRY'06*	ellagic acid ellagic acid derivative	*Quercus infectoria* or *Quercus ithaburansis* or Tannin dye plants
3(c)	*MRY'11*	gallic acid gallic acid derivative	*Quercus infectoria* or *Quercus ithaburansis* or Tannin dye plants
4(d)	*MRY'10*	gallic acid gallic acid derivative punicalin A punicalin B	*Quercus infectoria* or *Quercus ithaburansis* or Tannin dye plants
5(e)	*MRY'08*	gallic acid gallic acid derivative punicalin A punicalin B	*Quercus infectoria* or *Quercus ithaburansis* or Tannin dye plants
6(f)	*MRY'08*	gallic acid ellagic acid	
7(g)	*MRY'11*	gallic acid ellagic acid punicalin A punicalin B kaemferol Keampferol darivative	*Quercus infectoria* or *Quercus ithaburansis* or Tannin dye plants

8(h)	*MRY'06*	gallic acid ellagic acid punicalin A punicalin B	*Quercus infectoria* or *Quercus ithaburansis* or Tannin dye plants

3.6. SEM-EDX

SEM presented the surface morphology of the leathers. EDX analysis gave the results of all elements such as C, O, Na, S, Al, Si and Cl (Table 5). The results of SEM obtained (Fig. 6), showed that the structure of the leather is disrupted. When the SEM surface image is examined, cracks and splitting of the leather objects in the fibers are clearly visible. In addition, there are large and small crystal (salt) particles among the leather fibers. Crystal particles also affected the collagen structure of the leather. Most forms of the disruption shown by SEM are caused by submarine chemicals and the marine environment (Hadîmbu et al., 2018; Della Gatta et al., 2005). The EDX results of the leather objects revealed many chemical elements identified in all examples (Tab. 5), (Fig. 6). The elements C, N and O found in the leather objects almost correspond to the main components of the leather. However, none of the leather objects contains nitrogen (Mansour et al., 2017). Small elements that do not constitute the main component of the leather may have originated from different chemicals in sea water or some materials used in the production of leather.

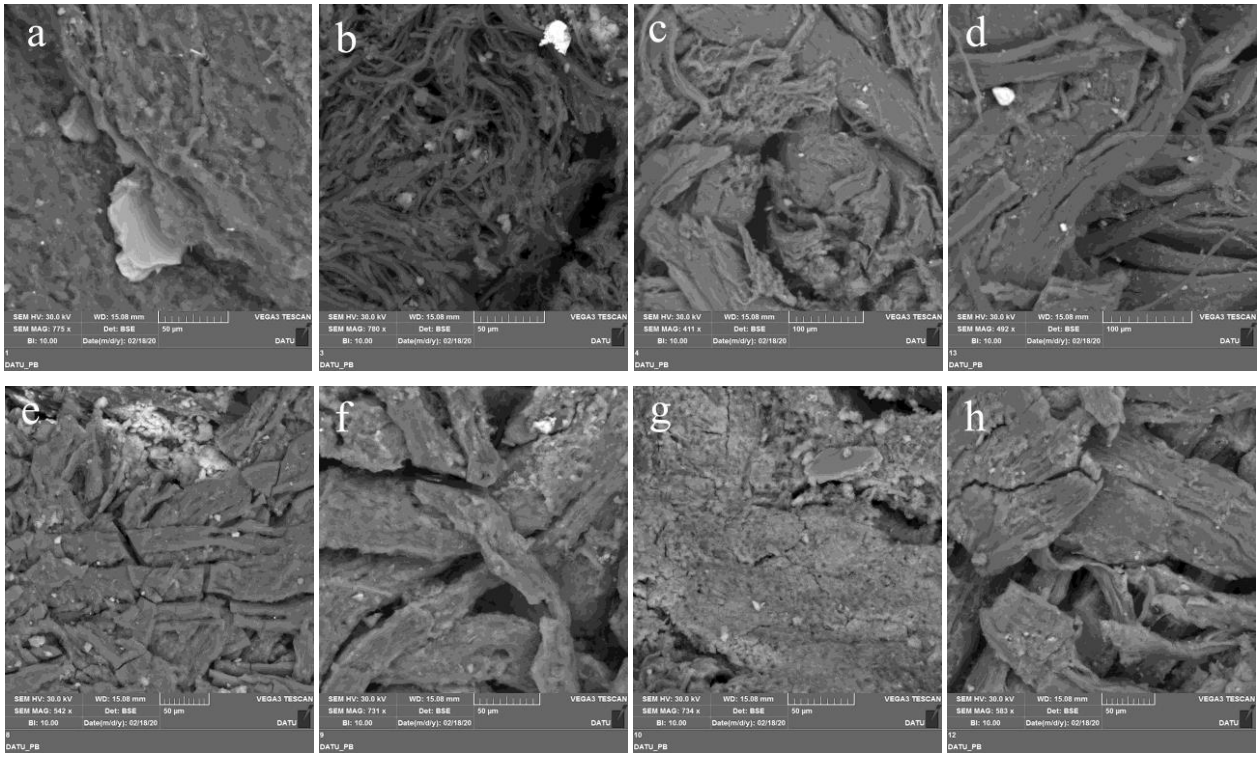


Figure 6. SEM micrographs of the investigated leather objects; a (MRY'011; 775x), b (MRY'06; 780x), c (MRY'11;441x), d (MRY'10; 492x), e (MRY'08; 542x), f (MRY'08; 731x), g (MRY'11; 734x), h (MRY'06; 583x).

Table 5. Elemental analysis of the leather objects.

	Chemical composition (wt% detected elements)															
Samples	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**	**Ti**	**Fe**	**Ba**	**Cu**	**Zu**
1(a)	58.68	33.44	-	0.23	0.79	1.74	0,03	0,43	0,02	0,27	2,54	0,07	1,75	-	-	-
2(b)	56.60	33.32	0.15	0.33	0.99	2.39	0,01	0,23	-	0,23	2,13	0,10	2,60	-	0,4	0,8
3(c)	62.91	33.25	-	0.02	0.23	0.39	0,02	0,69	-	0,05	0,97	-	0,49	-	-	-
4(d)	56.07	36.43	-	0.21	0.81	1.18	-	1,12	0,04	0,12	1,28	0,20	2,55	-	-	-
5(e)	54.21	32.52	-	0.25	0.15	0.40	0,03	1,42	-	0,04	3,57	-	7,41	-	-	-
6(f)	51.60	39.45	-	0.31	0.55	1.21	0,02	0,93	-	0,10	1,65	-	4,20	-	-	-
7(g)	50.54	20.86	-	0.03	0.30	0.43	0,02	0,04	-	0,05	0,19	-	27,53	-	-	-
8(h)	49.07	42.42	-	0.35	0.89	1.46	-	1,08	-	0,14	1,91	-	2,55	0,13	-	-

4. DISCUSSION

When the characterization of the leather objects was examined, it showed a similar chemical composition and biological degradation. The pH value and moisture content of wet leather is important before canning (Van Dienst, 1985). Therefore, the values of these properties were obtained for wet archaeological leather, pH values were found between (4.69 and 7.20) and moisture content (0.7 and 6.8). If the archaeological leather is covered with water, it can be assumed that hydrolysis occurs to some degree without the catalytic effect of acids (Larsen, 2008). pH values showed that samples showed signs of oxidative deterioration. Moisture varies according to the thick and thin leather. In addition, excess moisture inflated the fibers of the leather, thereby became a cause of its deterioration. L* a* b* values have been shown to be low as a result of the reactions between salt and ferrous ions and tannins coming from leathers' sunken area (Jenssen, 1987). Therefore, the color of the leather was found very dark brown. Archaeological leather materials can carry proof of vegetable tanning even after thousands of years. Two-thirds of the leather samples showed the presence of vegetable tanning between BC 2500- BC 1750 (Kite et al., 2006). In FTIR analysis, protein materials were detected with wide band at 3281- 3307 cm^{-1} (depending on O-H), since the leathers were found in aqueous media. It also showed the breakdown of the collagen complex in the leather structure. In the MRY'06 (b) sample, wide band (sulfur ion tension band) at 2325 cm^{-1} was detected (Rushdya, 2016). Sulfur ion is generally regarded as the primary substance of acidic hydrolysis in historical leathers, caused by environmental pollution. These sulfur ions break the connections between the amino acids in the collagen polymer chain (Florian, 2006). FTIR analysis revealed the presence of characteristic tanning tannins of leather, gallotanins, condensed tannins and hydrolyzable tannins. Therefore, it can be assumed that tannin mixture is present in tanning of leathers (Falcão and Araújo, 2013). The spectrum of the identified coloring compounds of the leather objects (Figure 5), and the determined coloring compounds and probability biological resources are given in (Tab. 4). Using HPLC analysis, the leathers were determined to contain gallic acid, ellagic acid and their derivatives (Karapanagiotis et al., 2011). It was difficult to determine the type of leathers in the SEM surface image. Due to the biological degradation under the sea, the bristle points on the leather are closed and worn. EDX results revealed many chemical elements (Table 5). Elements C, N and O almost correspond to the main components of the leather. None of the leather objects contain nitrogen (Mansour et al., 2017). The low calcium content may have been caused by underwater fungi. High Fe ratio dark brown iron oxide Fe_2O_3 can be shown in MRY11(g) sample (Mabrouk, 2020). A small amount of sulfur, aluminum and potassium were also found in leathers. This indicates that the leather was probably prepared with screed and vegetable tannins. While sodium and chlorine may be associated with wet salting of the leather, the presence of sulfur and copper revealed the presence of $CuSO_4$ in leather making MRY'06 (b) Cu (0.4%). Cupric sulfate has been used as a leather protector before tanning in traditional leather making recipes (Koochakzaei and Achachluei, 2015). Na (0.15%) was found in the MRY'06 (b) sample, Cl (0.02%) was found in MRY'11 (a) sample and Cl (0.04%) was found in MRY'11(c) sample. Their formation may indicate halite (rock salt) NaCl (Mabrouk, 2020). In general, the analytical results of archaeological leather objects primarily reveal the deterioration agents and the leather production stage.

5. CONCLUSIONS

Morphological examinations of archaeological leather objects provide new information about Byzantine leatherwork. Physicochemical characterization of leather objects by using ATR-FTIR, HPLC-DAD and SEM-EDX chromatographic research, the following are defined related to Byzantine leatherwork;

- By ATR-FTIR analysis, it is seen that vegetable tannins (gallotanins, condensed tannins and hydrolyzable tannins) are used in tanning of leathers. The reason why archaeological leathers can survive until the present day is the use of vegetable tannins as tanning material.
- HPLC-DAD analysis revealed that vegetable tannins are used for dyeing leather. As tannin dyes; (*Quercus infectoria* or *Quercus ithaburansis*) are known to be used (Karadag and Dolen, 2007; Falcão and Araújo, 2013; Alpaut, 1957).
- SEM combined with EDS allows the qualitative determination of the chemical elements of the sample under investigation. In addition, organic components in the leather structure were determined by SEM examination. Analysis with EDS showed the possible use of cupric sulfate for leather preparation prior to tanning in the processing of leathers in Byzantine.

All results show that there is a deterioration in the structure of leathers found under the sea. It was determined that vegetable tanning and natural dyes were used in the processing of leathers (usually pieces of sandals were used in the study) during the Byzantine period.

ACKNOWLEDGEMENTS

The authors would like to thank the Istanbul Archaeological Museums Directorate for permission to excavate Yenikapı. Thanks to Marmara University Scientific Research Projects Unit for their financial support in carrying out the study.
In addition, we would like to thank the "Marmara University, Textile and Manuscripts Conservation and Restoration R&D Laboratory" and "DATU- Cultural Heritage Preservation and Natural Dye Laboratory", which provide support for the analysis of leathers.
This study has been supported by Marmara University Scientific Research Projects Coordination Unit. Project Number: FEN-C-DRP- 120619-0.

REFERENCES

Akkemik, Ü. and Kocabaş, U. (2014) Woods of Byzantine trade ships of Yenikapi (Istanbul) and changes in wood use from 6 th to 11 th century, *Mediterranean Archaeology & Archaeometry*, *14*(2).

Akkemik, Ü., Köse, N., Wazny, T., Kızıltan, Z., Emre, Ö. Öncü. and Martin, J. P. (2019) Dating and dendroprovenancing of the timbers used in Yenikapı historical jetty (Istanbul, Turkey), *Dendrochronologia*, 57, 125628.

Al-Gaoudi, H. A. (2020) Painted ancient Egyptian mummy cloth of Khonsuemrenep from Bab El-Gasus excavation: Scientific analysis and conservation strategy, *Scientific Culture*, *6*(2), 49-64.

Alpaut, A. (1957) *Applied Leatherworking* (İstiklal Matbaası).

Asal, R. (2010) Istanbul is Roman and Byzantine sea trade in the light of finds from Yenikapı Marmaray and Metro Rescue Excavations, Master Thesis, Trakya University.

Bowes, J. H. and Raistrick, A. S. (1961) The action of heat and moisture on leather: Part III. The effect of pH on the deterioration of vegetable, chrome, semichrome, and chrome retan leathers, *Journal of the Leather Chemists Association*, *56*, 632-44.

Carşote, C., Budrugeac, P., Decheva, R., Haralampiev, N. S., Miu, L. and Badea, E. (2014) Characterization of a Byzantine manuscript by Infrared Spectroscopy and thermal analysis, *Rev Roum Chim*, *59*(6), 429-36.

Della Gatta, G., Badea, E., Ceccarelli, R., Usacheva, T., Maši, A. and Coluccia, S. (2005) Assessment of damage in old parchments by DSC and SEM, *Journal of Thermal Analysis and Calorimetry*, *82*, 637-49.

Deveoglu, O., Cakmakcı, E., Taskopru, T., Torgan, E. and Karadag, R. (2012) Identification by RP-HPLC-DAD, FTIR, TGA and FESEM-EDAX of natural pigments prepared from datisca Cannabina L, *Dyes and Pigments*, *94*(3), 437-42.

Düzgün, K. G. and Emre, E. (2018) Marmaray Project Sirkeci Rescue Excavations in the case of stratification as an urban archaeology example and its effects on city planning, In *The IAFOR Conference on Heritage & the City – New York 2018*. New York: The International Academic Forum.

Elnaggar, A., Leona, M., Nevin, A. and Heywood, A. (2017) The characterization of vegetable tannins and colouring agents in ancient Egyptian leather from the collection of the Metropolitan Museum of Art, *Archaeometry*, *59*(1), 133-47.

Falcão, L. and Eduarda, M., Araújo, M. (2013) Tannins characterization in historic leathers by complementary analytical techniques ATIR-FTIR, UV-VIS and chemical tests, *Journal of Cultural Heritage*, *14*(6), 499-508.

Falcao, L. (2018) Vegetable Tannins Used in the Manufacture of Historic Leathers, *Molecules*, *23*(5), 1081.

Falcão, L. and Eduarda, M., Araújo, M. (2014) Application of ATR–FTIR Spectroscopy to the analysis of tannins in historic leathers: The case study of the upholstery from the 19th century portuguese Royal Train, *Vibrational Spectroscopy*, *74*, 98-103.

Florian, M. L. E. (2006) The mechanisms of deterioration in leather. In Kite, K. and Thomson, R (eds.), *Conservation of leather and related materials* (Routledge: Oxford, UK).

Ganitis, V., Pavlidou, E., Zorba, F., Paraskevopoulos, K. M. and Bikiaris, D. (2004) A post-Byzantine icon of St Nicholas painted on a leather support. Microanalysis and characterisation of technique, *Journal of Cultural Heritage*, *5*(4), 349-60.

Giurginca, M., Badea, N., Miu, L. and Meghea, A. (2007) Spectral technics for identifying tanning agents in the heritage leather items, *Revista De Chimie-Bucharest-Original Edition*, *58*(9), 923.

Güzel, E. T. and Karadag, R. (2019) Sustainability of organic cotton fabric dyeing with a natural dye (Gallnut) and analysis by Multi-Technique approach, *Journal of Natural Fibers*, 1-12.

Hadîmbu, E., Badea, E., Carşote, C., Şendrea, C. and Miu, L. (2018) Halloysite nanotubes as innovative consolidants for historical leather, In *Proceedings Book of the 7th International Conference on Advanced Materials and Systems (Icams 2018). Bucharest: Certex*, 189-94.

Jenssen, V. (1987) Conservation of wet organic artefacts excluding wood, In, *Conservation of Marine Archaeological Objects* (Elsevier), 122-163.

Kahraman, N. and Karadag, R. (2017) Characterization of sixteenth to nineteenth century Ottoman silk brocades by Scanning Electron Microscopy–Energy Dispersive X-Ray Spectroscopy and High-Performance Liquid Chromatography, *Analytical Letters*, *50*(10), 1553-67.

Karadag, R. and Dolen, E. (2007) Re-Examination of Turkey Red, *Annali di Chimica: Journal of Analytical, Environmental and Cultural Heritage Chemistry*, *97*, 583-89.

Karadag, R. and Yurdun, T. (2010) Dyestuff and colour analyses of the Seljuk carpets in Konya Ethnography Museum, *Studies in Conservation*, *55*, 178-83.

Karapanagiotis, I. and Karadag, R. (2015) Dyes in post-Byzantine and Ottoman textiles: A comparative Hplc Study, *Mediterranean Archaeology and Archaeometry*, *15*, 177-89.

Karapanagiotis, I., Mantzouris, D., Kamaterou, P., Lampakis, D. and Panayiotou, C. (2011) Identification of materials in post-Byzantine textiles from Mount Athos, *Journal of archaeological science*, *38*(12), 3217-23.

Kiliç, N. (2016) Conservation of a group of frames from YK 16 shipwreck, *Art-Sanat* (6), 85-97.

Kite, M., Thomson, R. and Angus, A. (2006) Materials and techniques: Past and Present. In, *Conservation of Leather and Related Materials* (Routledge).

Kocabas, I. O. (2019) The anatomy of a Byzantine vessel: Yenikapi 8 Shipwreck, *Art-Sanat*, (11), 325-38.

Kocabaş, U. (2015) The Yenikapı Byzantine-era shipwrecks, Istanbul, Turkey: A Preliminary report and inventory of the 27 wrecks studied by Istanbul University, *International Journal of Nautical Archaeology*, *44*(1), 5-38.

Koochakzaei, A. and Achachluei, M. M. (2015) Red stains on archaeological leather: Degradation characteristics of a shoe from the 11th–13th centuries (Seljuk Period, Iran), *Journal of the American Institute for Conservation*, *54*(1), 45-56.

Larsen, R. (2000) Experiments and observations in the study of environmental impact on historical vegetable tanned leathers, *Elsevier Science*, (365), 85-99.

Larsen, R. (2008) The chemical degradation of Leather, *Chimia International Journal For Chemistry*, *62*(11), 899-902.

Liritzis, I., Laskaris, N., Vafiadou, A., Karapanagiotis, I., Volonakis, P., Papageorgopoulou, C. and Bratitsi, M. (2020) Archaeometry: An Overview, *Scientific Culture*, *6*(1), 49-99.

Mabrouk, N. (2020) Archaeometrical study of a rare embroidered and appliqued leather tapestry from the safavid artworks. Part I: Weaving fibers and dyes, *Mediterranean Archaeology & Archaeometry*, *13*(1).

Malea, E., Vogiatzi, T. and Watkinson, D. E. (2010) Assessing the physical condition of waterlogged archaeological leather, In *11th ICOM-CC WOAM WG Conference in Greenville*, 24-28.

Mansour, M., Hassan, R. and Salem, M. (2017) Characterization of historical bookbinding leather by FTIR, SEM-EDX and investigation of fungal species isolated from the leather, *Egyptian Journal of Archaeological and Restoration Studies*, *7*(1), 1.

Namik, K. and Kiliç, A. G. (2018) Analysis of waterlogged woods: Example of Yenikapı shipwreck, *Art-Sanat*, (9), 1-11.

Öncü, E. and Sırrı, Ç. (2015) Yenikapı excavations and amphora finds from the Byzantine period, In *XI-th Congress AIECM3 on Medieval and Modern Period Mediterranean Ceramics Proceedings*, edited by Defne Karakaya and Glenn Little Timothy, 15-29. Antalta, Turkey: VEKAM.

Papliaka, Z. E., Konstanta, A., Karapanagiotis, I., Karadag, R., Akyol, A. A., Mantzouris, D. and Tsiamyrtzis, P. (2017) FTIR imaging and HPLC reveal ancient painting and dyeing techniques of Molluskan Purple, *Archaeological and Anthropological Sciences*, *9*(2), 197-208.

Pizzi, A., Simon, C., George, B., Perrin, D. and Triboulot, M. C. (2004) Tannin antioxidant characteristics in leather versus leather light stability: Models, *Journal of applied polymer science*, *91*(2), 1030-40.

Polat, T. (2019) Ottoman period unglazed ceramics in Marmaray Project Excavations (Yenikapi, Üsküdar, Sirkeci), *Journal of Art History*, *28*(1), 93-117.

Puică, N. M., Pui, A. and Florescu, M. (2006) FTIR Spectroscopy for the analysis of vegetable tanned ancient leather, *European Journal of Science and Theology*, *2*(2), 49-53.

Rushdya, R. A. H. (2016) A preliminary study on using linseed oil emulsion in dressing archaeological leather, *Journal of Cultural Heritage*, 21, 786–95.

Strzelczyk, A. B., Bannach, L. and Kurowska, A. (1997) Biodeterioration of archeological leather, *International biodeterioration & biodegradation*, *39*(4), 301-09.

Turkmenoglu, E. (2018) The Yenikapi 17 shipwreck found in the harbour of Theodosius and preliminary results on its construction technology, *Art-Sanat*, (9), 23-33.

Van Dienst, E. (1985) Some remarks on the conservation of wet archaeological leather, *Studies in Conservation*, *30*(2), 86-92.