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ANALYTICAL CHARACTERIZATION OF BIBLE AND TEXTILES ARTIFACTS FROM SINOPE BALATLAR CHURCH EXCAVATIONS FOR CONSERVATION PURPOSES

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ABSTRACT

Archaeological textile and paper materials shed light on cultural studies in different fields. In this study, a composite textile material and 2 printed Biblical artifacts of the 19th c., found during the excavation of the Balatlar Building Complex were investigated. The building complex, also known as the Balatlar Church or Mithridates Palace, is an imperial hamam complex belonging to the Roman Period, located in the Ada Street of Sinope province in the north of Turkey. It was found that different materials such as metal yarn, paper used under embroidery, and decorative beads used on textile material were used in the textile fragment recovered from tomb VIII of the Balatlar Building Complex. The investigation concerned the fiber types and dyestuffs for textile material, paper types and dyestuffs used for biblical artifacts by using non-destructive and microanalysis methods for these unique heritage objects. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), Optical microscope (OM), Digital Microscope (DM), Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX) and High-Performance Liquid Chromatography -Diode Array Detector (HPLC-DAD) was used. It was determined that the textile find consists of two different fabrics, the main fabric, and the lining, and the dye that gives the main fabric its red color is the root dye (*Rubia tinctorum* L.). Also, Alizarin and madder (*Rubia tinctorum* L.) was determined as a plant source. It has been established that only the pattern threads are silk threads.

HPLC-DAD chromatograms has been analyzed of paper pieces of the, written and unwritten sides, paperboard and leather sides archaeological L.(Large) Bible and S. (Small) Bible books. It was concluded that natural dyestuffs were not used in the production of the paper and leather parts of the L.Bible and S.Bible books.

For the written text Iron (III)-gallic acid binary complex vibration bands were detected. Documentation and research studies conducted on 2 discovered Biblical artifacts have shown that biological degradation has occurred on the surface of the artifact. As a result of microscopic examination, it was found that the cover part of the L.Bible was made of cardboard and there were remnants of gray side paper. Remnants of leather-prepared binding were found on the surface of S.Biblical artifact.

KEYWORDS: composite artifacts, archaeological textile, archaeological books, Bible, ATR-FTIR, HPLC-DAD, SEM-EDX, gallic acid, ink

1. INTRODUCTION

It is known that archaeological sites within the cultural heritage have unique importance. Unearthing, interpreting, protecting, and evaluating archaeological sites is a matter that requires the joint work of experts from different disciplines (Özomay et al., 2021). Archaeological Sinope Island center (Sinope is a province in the Black Sea Region of Turkey) (Fig. 1) which stood out since the Hellenistic and Roman periods in the 7th century B.C until today is one of the most important ruins in the city. Sinope province is a tombolo (sandy or shingle isthmus) formed as a result of the merging of an island and the mainland. The provincial area was generally formed in the 2nd geological time [1] (Alcan, 2017; Ceylan, 2012). Known as the "Mithridates Palace" or "Balatlar Church", the building complex in Sinope's "Ada District" is an imperial bath complex belonging to the Roman Period (2nd/3rd century) (Fig. 2) (İnanan, 2016; Gülgün Köroğlu & Emine, 2018). Data obtained from excavations that started in 2010 reveal that the findings belong to a long period from the sixth century BC to the twentieth century BC (Gülgün Köroğlu & Emine, 2018). Being at a key point from the Roman Empire to Anatolia with its political, economic, and cultural aspects; and located in the north of Turkey, in the Black Sea region; Sinope is the home to (Bakiler et al., 2016). The Balatlar Church is significant as it is the only structure remaining from the Roman Period and whose function can be determined. The reason why an imperial bath complex is called the Balatlar Church is that the building was used as a church from the 5th century to the first quarter of the 20th century. After the 13th century, the north-western corner of the building in the city, which was dominated by the Seljuks and then the Ottoman Empire, served as the church of the Greek Orthodox monastery until the first quarter of the 20th century. Especially after the 18th century, the whole monastery area and its surroundings were used as the Greek Orthodox cemetery of the city (Gülgün Köroğlu & Emine, 2018).

The phases of different usages of the building complex, which has gained different functions over the years and has a history of about 1700 years starting from the Late Hellenistic-Early Roman period are as follows: Roman Imperial Period bath, Late Roman-Early Byzantine Church, Early Byzantine Period ceramic-glass and mosaic workshops, 7th century chapel and burial chamber, 13th century church and cemetery, 14-16th century Greek Orthodox Monastery Church and Greek Orthodox Cemetery.

During the excavation in Room VIII; The archaeological textile and two Bible obtained from the tomb (G Köroğlu, 2010; Gülgün Köroğlu & Emine, 2018) of the senior clergy (who served in the Late Ottoman period monastery) which was built with large stone plates, was examined within the scope of this study.

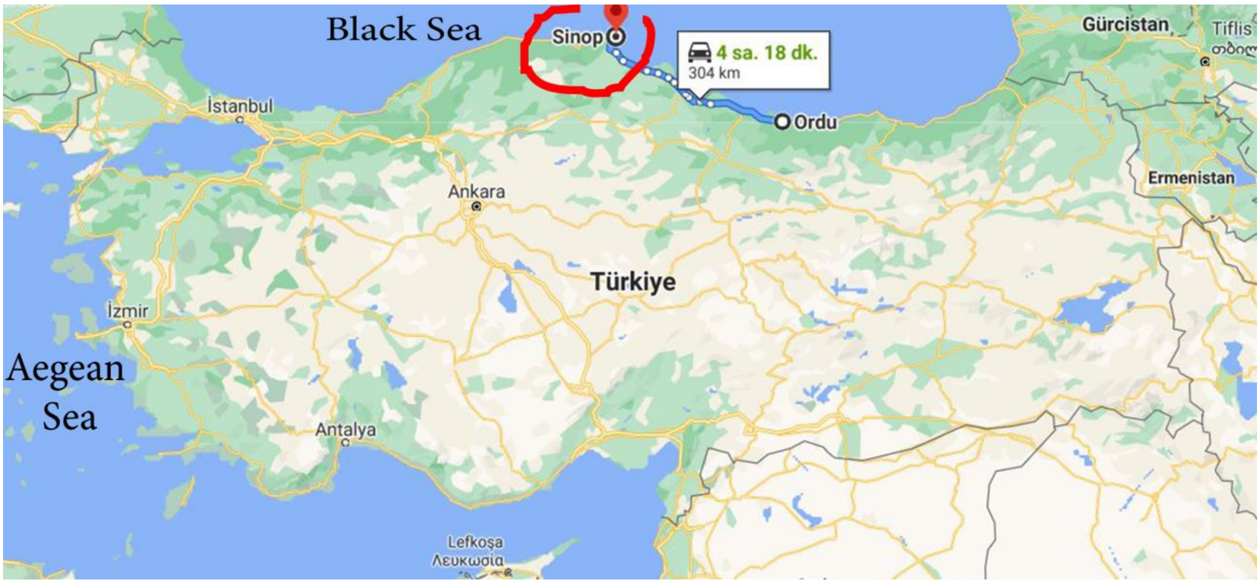


Figure 1. Sinope region, Aegean and Black Sea.

[1] The 2nd geologic time is the Mesozoic Era. The Mesozoic Era spanned 165 million years from 230 million years ago until 65 million years ago.

Figure 2. a. Excavation Site Map, b. Excavation Area General View.

Two (2) pieces of 15x22 cm, and 7x12 cm, Biblical artifacts, printed on the Greek alphabet and belonging to the 19th century were found in 2010, at the grave in the location No. 1, from the archaeological excavations of 'Balatlar Church' which located in the city of Sinope, and one of the most important historical monuments, covering the phases of late Roman, early Byzantine, Seljuk, and Ottoman periods (Fig. 3).

After the documentation and research studies carried out on the 2 Biblical artifacts were removed (Fig. 3), to stop the activation of the destructions caused by biological degradation on the surface of the artifact, in 2019, the decontamination of textiles and manuscripts was carried out for 21 days in the Nitrogen cabin within the T.R. Marmara University, Faculty of Technology, Department of Textile Engineering, Conservation and Restoration R & D Center for Textiles and Manuscripts.

After disinfection was applied to 2 archaeological Biblical artifacts (L, S), for active restoration and conservation applications on the artifact, they were delivered to the Restoration and Conservation Laboratory of Portable Cultural Assets, attached to the Istanbul Beylerbeyi Sabancı Maturation Institute, T.R. Ministry of National Education, on 09.01.2020. Before starting the restoration and conservation applications, the appearance of the artifacts was analyzed (Liritzis et al., 2020), and the restoration and conservation inventory began to be completed (Abdel-Kareem, 2022). Before making any intervention in the work, general and detailed photographs of the Biblical works were taken and documented (Fig. 3).

Figure 3. Two Printed Biblical Artifacts Recovered during Excavations in 2010: a. Large Bible, b. Small Bible.

Since the area where the findings unearthed in the Sinope Balatlar Church excavation belong to the graves of the clergy of the church, the areas opened were defined according to the numbered graves and surface codes (Yao, Liu, Yang, & Liu, 2008). Our study also includes cotton-silk archaeological textile in the SBK-2012-04 inventory number and found in the box coded 29, and it was excavated from the tomb numbered VIII on the walkway at a depth of 1,30 meters during the excavations carried out in the Balatlar Church on 04.07.2012 (Fig. 4). The surface cleaning process was applied to the sample with a brush.

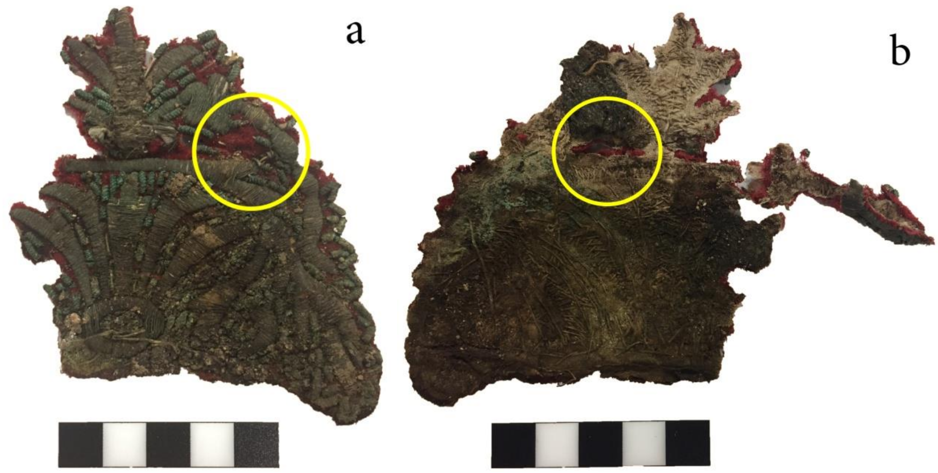


Figure 4. Archaeological textile: a. front side, b. backside (Examples are taken from the yellow round area).

This study aims to determine the chemical structure of different materials on archaeological textiles and Books 'Bible' and the source of dyestuff used in coloring by microanalysis and non-destructive analysis methods. These analyzes and measurements constitute important data for conservation and restoration. Every organic artifact that can be carried to the present gives information about its production methods and uses. It is important to determine all the physical and chemical properties of the artifact and to apply appropriate protection and repair methods according to these features before intervening on the artifact. All organic artifacts are living documents of human history and are affected by many environmental conditions day by day. If the right interventions are made by protecting it from factors such as heat, light, humidity, air pollution, microorganisms and insects, its endurance can be extended.

Questions regarding the material's composition and decoration help determining the steps of the process during the implementation phase, and the answers contribute in the direction of the path that the conservator or restorer should follow. Moreover to ensure that the information obtained from these analyzes is recorded in the inventory records of the works and provide information to the current and future researcher (Özomay et al., 2021).

2. EXPERIMENTAL

2.1 Materials

The source of this study is 2 pieces of 7x12 CM, and 15x22 CM printed Biblical works, belonging to the 19th century, and recovered from 2 different graves in the location No. 1 in 2010 from the archaeological excavations of 'Balatlar Church', located in the city of Sinope, and covering the late Roman, early Byzantine, Seljuk, and Ottoman periods (Fig. 4), and textiles in a box with the code 29, which were removed from grave No. 8 on the walking path in 2012 (Fig. 4).

2.2 Methods

2.2.1. Microscope

The fibers of all the yarns detected in the archaeological textile were determined at 40x magnification using a Motic BA210 optical microscope. Thread samples were first separated into fibers and then prepared by dropping glycerin between slide and cover glass. Optical microscope images are given in (Fig. 5). 2 printed Biblical works were examined microscopically. Microscopic examination using polarized Dino-Lite Digital Microscope AM7013MZT Premier HR with 5-megapixel, surface distortion details were seen (Fig. 7).

2.2.2. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR)

FTIR (Fourier Transform Infrared Spectroscopy) analysis is performed using a spectrometer (Perkin Elmer Spectrum UATR Two FTIR) in reflection mode using a diamond crystal attenuated total reflectance (ATR) sliding fixture. The spectral range is 4000-400 cm^{-1}, and the resolution is 4 cm^{-1}. FTIR has been reported as a useful analytical tool for the molecular characterization of archaeological samples of textile fabrics and Bibles. The analysis result is shown in (Fig. 10 and Table 2).

2.2.3. High-Performance Liquid Chromatography-Diode Array Detector (HPLC-DAD)

Chromatographic measurements of archaeological samples were conducted using a SHIMADZU Prominence-i LC-2030C 3D Plus series system (Shimadzu

Corporation, Tokyo, Japan). DAD detection was completed by scanning from 190 to 800 nm with a resolution of 4 nm, and the chromatographic peaks were monitored at 255, 270, 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 the data station was Lab Solutions. Two solvents were utilized for chromatographic separations of the samples; solvent A: H_2O-0.1% (v/v) TFA and solvent B: CH_3CN-0.1% (v/v) TFA. The flow rate was 0.5 mL/min. and the following elution program was applied: 0– 1 min: 5% B isocratic; 1–20 min: linear-gradient to 30% B; 20–25 min: linear-gradient to 60% B; 25–28 min: 60% B isocratic; 28–33 min: linear-gradient to 95% B; 33–35 min: 95% B isocratic; 35–40 min: linear-gradient to 5% B isocratic.

Each sample (1-4 mg) of the colored lengthways, diagonally yarns and fabric pile are dependent on analysis. The sample was hydrolyzed in 400 µL 37% HCl/MeOH/H_2O (2:1:1, v/v/v), kept at 100°C for 8 min, and the organic dye was extracted. The sample is then evaporated under a gentle stream of nitrogen. The dried residue was dissolved in 400 µL of MeOH/H_2O (2:1; v/v), and the sample was centrifuged. If necessary, further dilutions were made (then centrifuged at 4000 rpm/25°C/10 minutes) and analyzed by HPLC. Then, 25 µL and/or 50 µL of the supernatant were injected into the HPLC instrument. The dye compounds determined based on dye analysis are shown in (Figs 11, 12, 13 and Table 3).

2.2.4. Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX)

Scanning electron microscopy (SEM) was performed using a JEOL JSM-6301F operated at an acceleration voltage of 5 kV for surface imaging and elemental analysis of the round bead and metal pattern thread used on the pattern. Samples were coated with a thin layer of gold for 60 seconds using Quorum Q1500R ES (Quorum Technologies Ltd., UK). Surface images and elemental analyzes of the metal pattern thread and the embroidery bead found on the textile findings are presented. The surface images and elemental analyzes of the Bibles are presented in (Fig. 17 and Table 5).

3. EXPERIMENTAL

3.1. Microscope and examination of the fabric and paper structure

Morphological examination of fibers taken from archaeological textiles was carried out using OM. Examination of the longitudinal section of the fibers by optical microscopy provides sufficient information to confirm the type of fibers (Osman, Michael, & Gohar, 2010). The archaeological textile piece (Fig. 5) is divided into 9 examples. Each received part is coded separately: fabric of the archaeological textile (29.a), (29.b), (29.c), the samples of lining fabric (29.d), (29.e), pattern thread (29.g), sewing thread (29.h), pattern stitch thread (29.i) were observed in the optic microscopy. When the longitudinal section images of the fibers were examined, (29.a, 29.b, 29.c, 29.d, 29.h) archaeological textile were cotton. Only the sample (29.i) was detected as a silk fiber. The cross-section test was not applied to the fibers, whose longitudinal section images gave a certain result (100%).

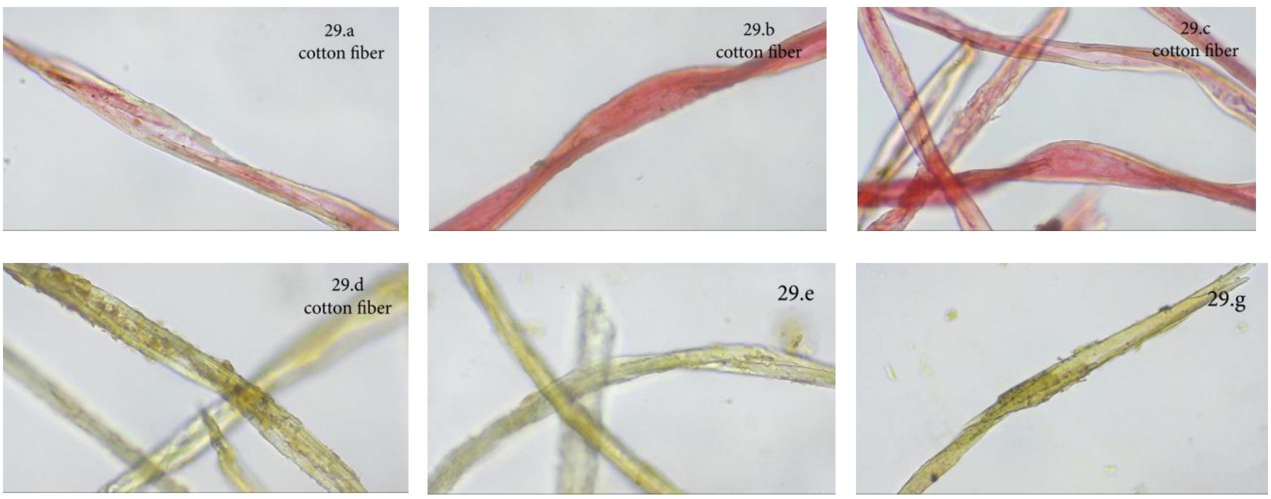


Figure 5. Optical microscope images of piece of archaeological textile; (29.a) Main fabric warp thread , (29.b) Main fabric weft thread, (29.c) Main fabric pile surface, (29.d) Lining fabric warp thread, (29.e) Lining fabric weft thread, (29.g) Pattern thread, (29.h) Sewing thread used in the main, (29.i) pattern stitch thread.

On the surface of 2 archaeological books, which are thought to belong to the 19th century BC, we observe that the damages detected because of physical, chemical, and biological distortions. Before restoration and conservation, layers of foreign accumulation and remains of microorganisms are observed on the surface of the artifacts, which were preliminarily examined under a microscope (Fig. 7).

As a result of microscopic examination, it was found that the cover part of the L.Bible was made of cardboard and there were remnants of gray side paper. It is observed that the pages of the Biblical work harden due to being under the soil for a long time, the pages are stuck together, and the structure of the page is pulped due to moisture. It is seen as a result of microscopic examinations that there is a dense foreign accumulation layer consisting of straw and soil residues in the Biblical artifacts. As a result of biological degradation, the remains of microorganisms – mold fungi are found intensively. Remnants of leather-prepared skin were found on the surface of S.Biblical artifact. Due to the conditions under the soil, it was determined that the pages of the Bible were hardened by pressing. The bond between the cellulose chains that make up the paper pages and the pages, loses its strength due to constant heat and moisture change, causing the pages to crumble and decay. Microorganisms have penetrated the page structure at a high rate and caused the structural disorder. The detected distortions were documented in detail in the technical drawings of the archaeological Biblical artifacts (Fig. 8).

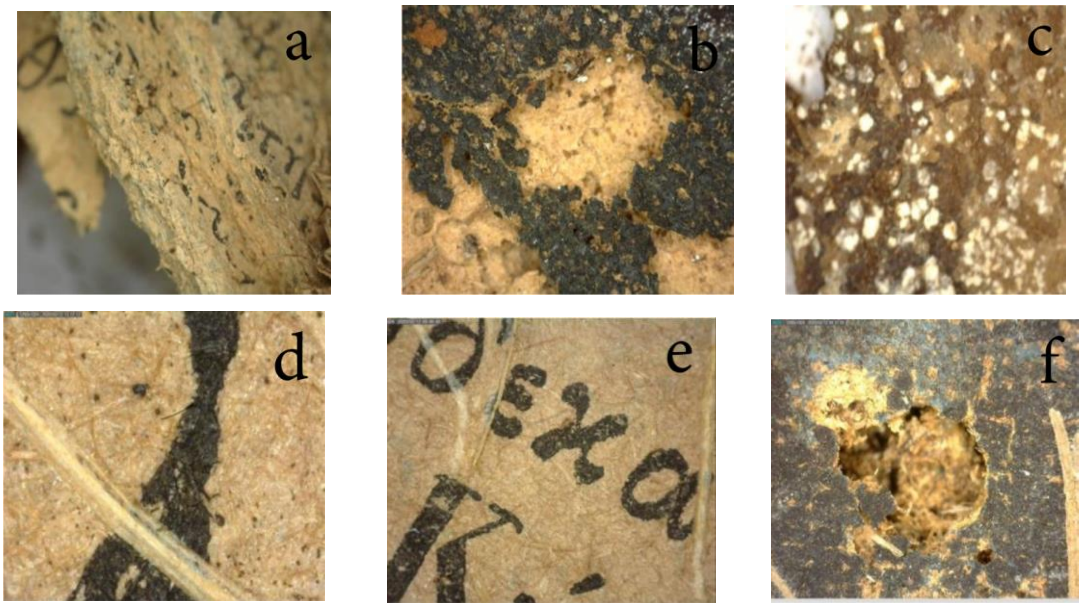


Figure 6. Detail Microscope Images of L.Biblical Work. X20: a. written side., b. the unwritten side., c. the unwritten side., d. the unwritten side., e. written side., f. leather side

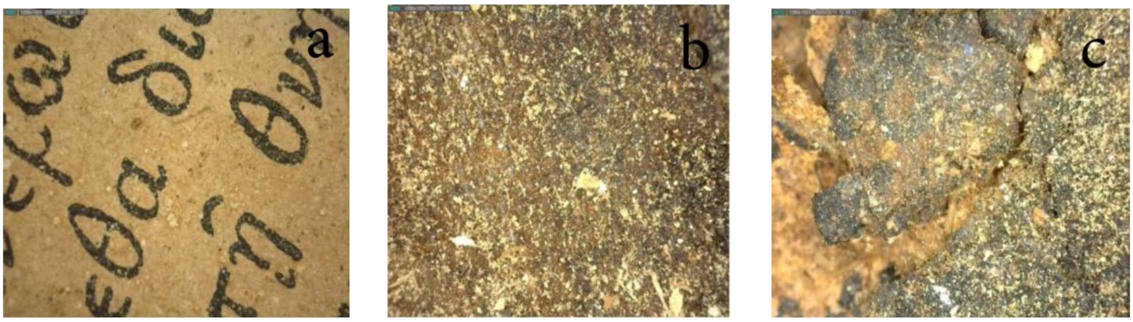


Figure 7. Detail Microscope Images of S.Biblical Work. X20: a. writtin side., b. unwritten side., c. Leather side.

Figure 8. Mechanical cleaning stage on the Bibles surface.

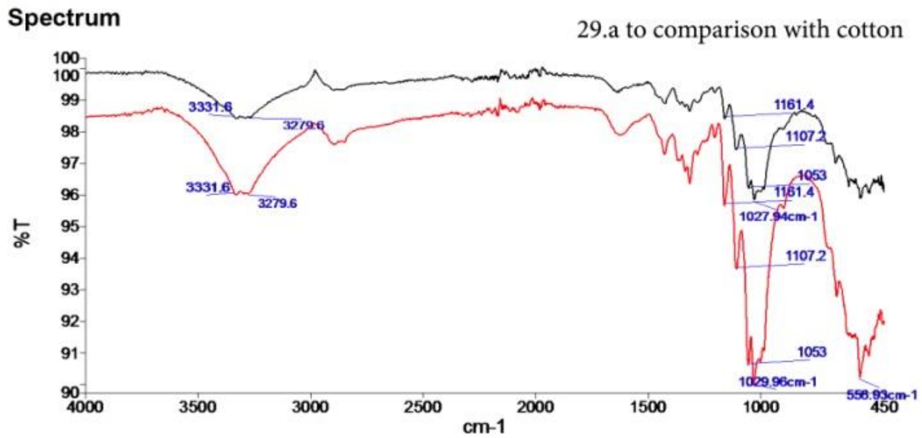
3.2. *ATR-FTIR analysis*

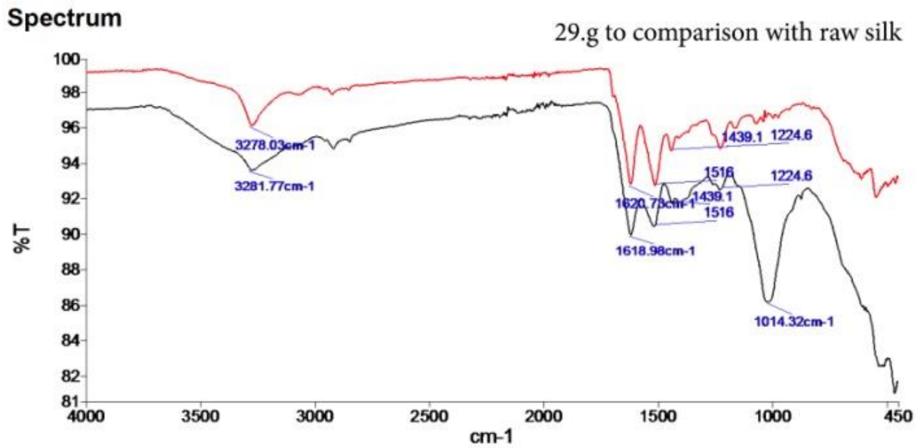
IR spectral band analysis of the warp (29.a), weft (29.b), pile (29.c) surface of the main fabric of the archaeological textiles were made. In addition, the IR spectrum bands of the warp (29.d) and the weft (29.e) of the lining fabric were determined. Finally, the IR bands of the pattern (29.g), stitch (29.h), and pick stitch (29.i) threads on the main fabric were analyzed. FTIR spectrum of all threads is given in (Fig. 9) and analysis results are given in (Table 1). All samples analyzed demonstrated similar IR spectrum bands. In the samples: 3273-3355 cm^{-1} tension band N-H amine was seen. The absorption band at 3273-3355 cm^{-1} assigned to the N-H stretch is common among indigo dye (E. M. Osman et al., 2010; Parmar & Giri, 2001). 1618-1639 cm^{-1} tension band C=C alkene was detected. The 1421-1437 cm^{-1} band C-H alkene was determined. A physically absorbed water molecule shows a characteristic peak at 1630 cm^{-1} (Y. Liu, 2013; Schwanninger, Rodrigues, Pereira, & Hinterstoisser, 2004). While 1313-1317 cm^{-1} stretch band C=H was found in all samples, it was not detected in only (29.g) samples. The 1372 cm^{-1} vibration is assigned to the C=H twist and maybe most suitable for demonstrating cellulose crystallinity in cotton production (Fleming & Williams, 1966; Lipp-Symonowicz, Sztajnowski, & Kutak, 2012). Similarly, while all samples have 1156-1161 cm^{-1} tension band CO aliphatic ether, 1102-1109 cm^{-1} tension band C-O alcohol, and 1027-1031 cm^{-1} tension band S=O sulfoxide, only (29.g) is not detected in the sample. These regions represent the C-O stretch of indigo and cystine oxides (mono and dioxides) for cotton fabric and are known to be the fingerprint region of indigo dye (E. M. Osman et al., 2010; Xiaoning Zhang, Gong, & Gong, 2019; XiaoMei Zhang & Wyeth, 2010).

On the contrary, in the example (29.g), it was determined that silk thread was used as the pattern thread of the 1519 cm^{-1} tension band N-O nitro compound and 1224 cm^{-1} tension band C-O alkyl aryl ether. In the IR spectrum of the archaeological silk thread (29.g), characteristic broad bands were seen at 3281, 1618, 1519, 1437, and 1224 and 1014 cm^{-1} (Akada, Sato, Okuyama, & Imadzu, 2009; Wang, Guan, Hawkins, & Vollrath, 2018). Raw silk is used to evaluate the archaeological silk thread (Fig. 9). However, the band at 1014 cm^{-1} in the (29.g) sample is abnormal. The more detailed spectral analysis confirmed that the sericin did not exist, but that other component contributed to the absorption. Characteristic fibroin bands at 1000 and 975 cm^{-1} are usually seen as confirmation of the absence of a prominent sericin coating (Akada et al., 2009; Łojewska, Lubańska, Miśkowiec, Łojewski, & Proniewicz, 2006; Zięba-Palus, Trzcińska, Wesełucha-Birczyńska, Moskal, & Sacharz, 2020). In addition, the IR spectrum bands of the paper (29.f) sample used to support the pattern on the main fabric of the archaeological textiles were detected at 3280, 1426, 1161, 1107, 1027, and 817 cm^{-1}.

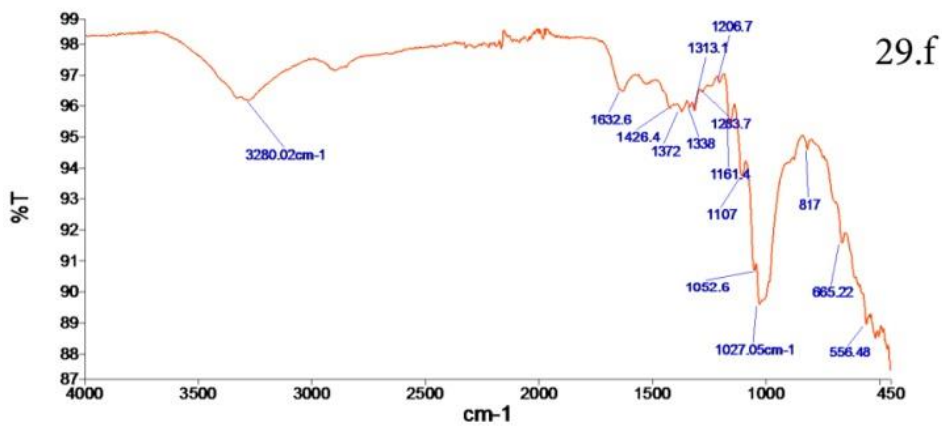
FTIR spectrum of the analyzed paper sample (29.f) is given in (Fig. 9) and analysis results are given in (Table 1). ATR-FTIR provides information on the type of filler used (talc, kaolin, calcium carbonate) on the paper surface using X-ray absorption spectroscopy. The band seen at 1420 cm^{-1} indicates the crystallinity of cellulose in the paper structure. Other bands at 1161 and 1107 cm^{-1} result from cellulose can also be observed. Apart from these, characteristic bands have been found in the paper structure. The bands have been identified with extenders such as kaolinite at 1027 cm^{-1} and carbonates at 870 cm^{-1} (Karadag, Torgan, & Yurdun, 2010; J. Liu et al., 2013).

ATR-FTIR analysis results of the textile piece revealed the structural sources of the fabric fibers. Images seen on the optical microscope supported the ATR-FTIR results. According to this, the structural properties of samples were determined to be as follows: textile samples (29.a, 29.b, 29.c, 29.d, 29.e) were cellulose-based; (29g) was protein-based; the paper sample (29.f) was cellulose, kaolinite, and carbonate based.





29.a- cotton **29.g- silk**



29.f-paper

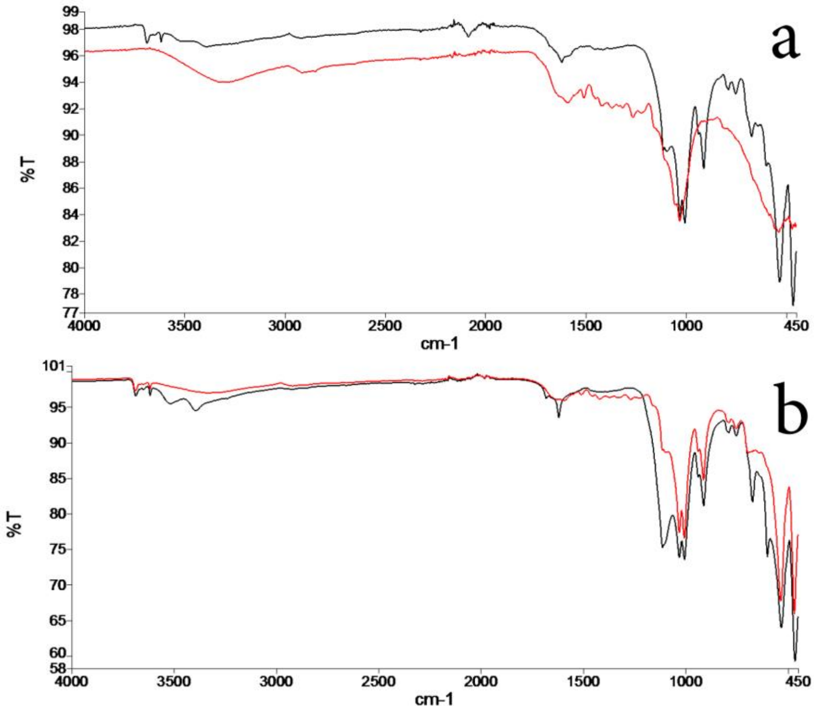
Figure 9. ATR-FTIR spectra of the samples; (29.a) Main fabric warp thread-raw cotton comparison; (29.g) Pattern thread-raw silk comparison; (29.f) Pattern support paper sample.

Table 1. ATR-FTIR analysis results of textile material.

	Functional Group										
Samples	N-H stretching amine	OH stretching kaolinite	C=C stretching alkene	N-O stretching nitro compound	C-H bending	C=H bending	C-O stretching alkyl aryl ether	C-O stretching aliphatic ether	C-O stretching alcohol	S=O stretching sulfoxide	n2(CO3)2 out-of-plane-bending
29.**a**	3329*m*	-	1639*s*	-	1421*m*	1315*s*	-	1159*s*	1107*s*	1027*s*	-
29.**b**	3338*m*	-	1634*s*	-	1426*m*	1315*s*	-	1161*s*	1104*s*	1030*s*	-
29.**c**	3355*m*	-	1637*s*	-	1426*m*	1314*s*	-	1159*s*	1109*s*	1028*s*	-
29.**d**	3273*m*	-	1625*s*	-	1426*m*	1313*s*	-	1156*s*	1107*s*	1028*s*	-
29.**e**	3277*m*	-	1628*s*	-	1426*m*	1317*s*	-	1156*s*	1107*s*	1027*s*	-
29.**f**	-	3280*s*	-	-	1426*m*	-	-	1161*s*	1107*s*	1027*s*	817*s*
29.**g**	3281*m*	-	1618*s*	1519*s*	1437*m*	-	1224*s*	-	-	-	-
29.**h**	3282*m*	-	1633*s*	-	1426*m*	1314*s*	-	1156*s*	1104*s*	1031*s*	-
29.**i**	3275*m*	-	1634*s*	-	1424*m*	1314*s*	-	1161*s*	1102*s*	1029*s*	-

Characteristic band (cm^{-1})

ATR-FTIR analysis, at the range of 4000-400 cm^{-1}, was carried out on eight samples of Biblical book fragments of the L. Bible and S. Bible. The FTIR spectra obtained for the analyzed samples (Fig. 10) present information about both the cellulose part of the samples and the fillers and other parts used in the production process. It has also helped to determine the characterization of the writing ink material on the written paper. Looking at (Table 2), the written and unwritten side of the L. and S. Bible book fragments are divided into 3 columns as cardboard and leather skin samples. When the IR spectra of the written and unwritten sides of the piece of paper are evaluated, 3689-3691 cm^{-1}, and 3614-3621 cm^{-1} specific bands were detected in four samples. 3524 cm^{-1} and 3395 cm^{-1} were observed only in the d) sample. These bands correspond to the tensile vibrations of OH groups bound to hydrogen. (Fierascu et al., 2020; Lee et al., 2015). The bands b) 3331cm^{-1} and d) 3395 cm^{-1} are usually the intramolecular hydrogen bond in cellulose. a) 2849 cm^{-1}, it has been found that it is proportional to the amount of monoclinic cellulose Iβ, the predominant form of cellulose found in vegetable plants (Poletto, Ornaghi, & Zattera, 2014). The spectrum in sample a) 2917 cm^{-1}, the band corresponds to the C-H symmetric stretching of cellulose and hemicellulose (Dai & Fan, 2010; Lee et al., 2015). The vibration bands in the samples c) 1619 cm^{-1} and d) 1620 cm^{-1} contain a lot of information about both the cellulosic material and the fillers (Lee et al., 2015). These bands correspond to the δ(OH) bending of adsorbed water, while the vibration bands a) 1592 cm^{-1} and b) 1596 cm^{-1} constitute the N-H of the Amide-II group (Poletto et al., 2014; Vyskočilová, Ebersbach, Kopecká, Prokeš, & Příhoda, 2019). These vibration bands are an additive of waxes such as gelatin or calcium stearate used in the production process. The vibration bands a) 1453 cm^{-1} and b) 1449 cm^{-1} correspond to the OH in-plane bending. a) 1412 cm^{-1} and b) 1417 cm^{-1} OH corresponds to in-plane bending (Campanella, Costanza, & Tomassetti, 2006). a) 1265 cm^{-1} and b) 1270 cm^{-1} C-O offers the band corresponding to the aryl group. The region from 1200 to 900 cm^{-1} is known as the fingerprint region of cellulose (Fierascu et al., 2020). The characteristic features of the ink structure found on the written side of the Large and Small Bible were also evaluated. These bands correspond to the δ(OH) bending of adsorbed water, while the vibration bands a) 1592 cm^{-1} and b) 1596 cm^{-1} constitute the N-H of the Amide-II group (Poletto et al., 2014; Vyskočilová et al., 2019). These vibration bands are an additive of waxes such as gelatin or calcium stearate used in the production process. The vibration bands a) 1453 cm^{-1} and b) 1449 cm^{-1} correspond to the OH in-plane bending. a) 1412 cm^{-1} and b) 1417 cm^{-1} OH corresponds to in-plane bending (Campanella et al., 2006). a) 1265 cm^{-1} and b) 1270 cm^{-1} C-O offers the band corresponding to the aryl group. The region from 1200 to 900 cm^{-1} is known as the fingerprint region of cellulose (Fierascu et al., 2020). The characteristic features of the ink structure found on the written side of the Large and Small Bible were also evaluated. In a) L.Bible and c) S.Bible samples, Iron (III)-gallic acid binary complex vibration band is found in 1093-1095, 749-751, 640-633 cm^{-1} absorption bands (Doncea & Ion, 2014a). a) L.Bible and c) S.Bible samples (3619-3614 cm^{-1}) are the iron (III)-gallic acid binary complex. Also the a) L.Bible sample absorptions (1453-1396 cm^{-1}) may signify the presence of Gallic acid (Ferrer, et al., 2012). In areas where there is low absorption of cellulose and is of interest for inks, according to literature reports, 1265 cm^{-1}, 911 cm^{-1}, and 532 cm^{-1}, form ink compounds and degraded celluloses (Doncea & Ion, 2014b). From 1417 cm^{-1}, the band is the ink binding agent in good harmony with the literature (Ferrer et al., 2012). Moreover, the band in 1417 cm^{-1} can be due to the H-C-H and O-C-H in the plane bending vibrations, while the 1315 cm^{-1} shows the C-O-H and H-C-C bending vibrations. The bands around 937 cm^{-1} of IR spectra of paper pieces correspond to the C=C alkene. The bands around 898 cm^{-1} are assigned to the amorphous region in cellulose (Sistach, Ferrer, & Romero, 1998). This amorphous region shows around the bands 787 cm^{-1}, which is probably due to the O-C-O bending (in-plane deformation) of calcite in the samples. The bands after that usually present the bands assigned to the filler content. The most likely used fillers (given the historical data) are calcium carbonate with bands around 1449 cm^{-1}, calcium sulfate 3395, 1682, 1663, 1112 and 659 cm^{-1}, kaolin 3691, 3621, 911 and 467 cm^{-1}, talc 1032 and 671cm^{-1}, chlorite 939 cm^{-1}, SO_{4-2} also in the regions 1091, 680 and 532 cm^{-1}, there is asymmetric stretching (Nelson & O'Connor, 1964). Bands around b) 1162 cm^{-1} correspond to C-O symmetrical stretching in cellulose and hemicellulose. b) 1111 cm^{-1}, and d) 1112 cm^{-1} bands in the vibrational can be assigned to the stretching of C-O. The bands a) 1093 cm^{-1}, b) 1091cm^{-1}, and c) 1095 cm^{-1} show secondary alcohol C-O tensing, while the bands around 1026 cm^{-1} the samples of (a,b,c) and d) show the tensing of primary alcohol C-O vibrations (Fierascu et al., 2020). The paperboard samples examined in (Table 2) and paper fragments of Large and Small Bibles exhibit IR spectra of similarity. It has been determined that the samples of cardboard pieces of Bible e) Large and f) Small are cellulose-based. When the IR spectra of the other skin fragment samples of (Table 2) were evaluated, g) 3282 cm^{-1} and h) 3286 cm^{-1} skin samples OH vibration bands were detected. In both skin samples, protein materials were determined with a 2919 cm^{-1} vibration band. The amide bands of the collagen structure of the skin (I: 1627-1605 cm^{-1}; middle: h) 1514 cm^{-1} and middle III: 1372-1267 cm^{-1}). Hydrolysable tannin compounds were determined at h) 1372 cm^{-1}. Gallo tannins were determined at 1029-1030 cm^{-1}, and condensed tannin compounds at g) 1134 cm^{-1} and 871 cm^{-1} (Ioelovich, 2008; Rushdya, 2016). This information reveals that vegetable tannins and dyestuffs are used in leather tanning and leather dyeing. As a result, the microanalysis of the L. and S. Bible has determined the IR spectrum values, and characteristic features of the paper surface, ink, cardboard, and leather parts. Such microanalysis methods should be used in the examination of archaeological finds.



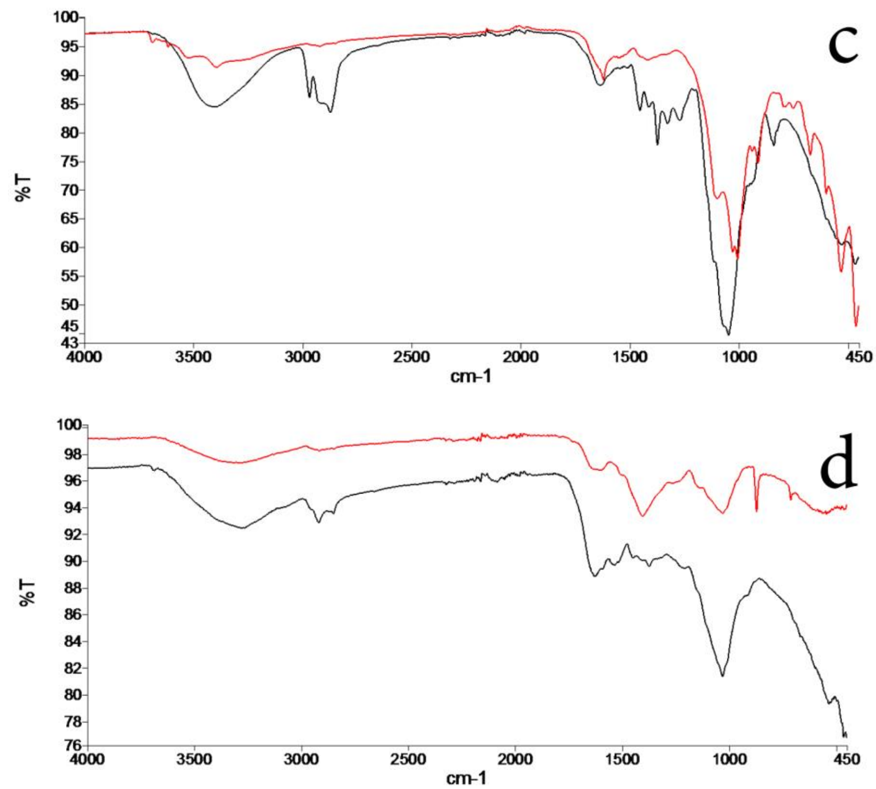


Figure 10. ATR-FTIR analysis results of L. Bible and Small Bible book fragments: a. Comparison L.Bible and S. Bible of the written sides., b. Comparison L.Bible and S.Bible of the unwritten sides., c. Comparison L.Bible and S.Bible of the cardboards., d. Comparison L.Bible and S.Bible of the leather sides.

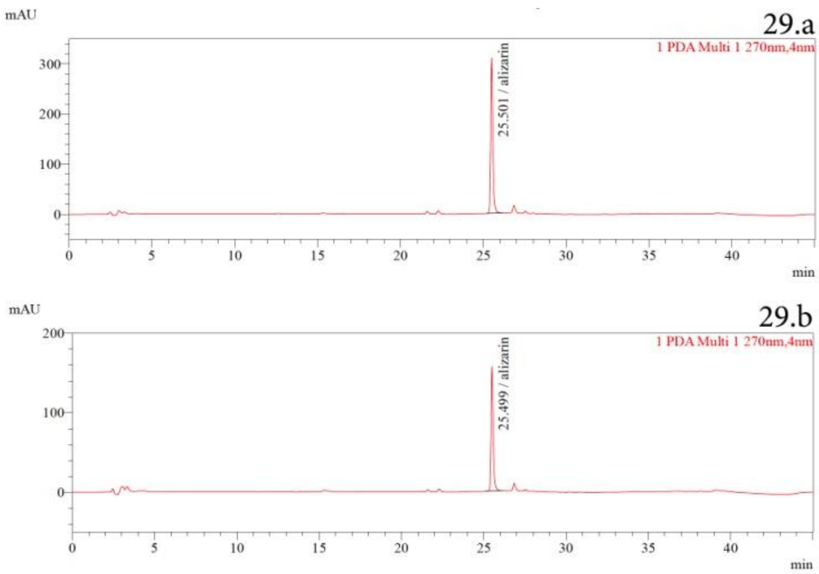
Table 2. ATR-FTIR analysis results of Large Bible and Small Bible book fragments.

	Examples of pieces of paper				Cardboard		Leather		
Samples	**a.** L. Bible written side	**b.** L. Bible unwritten side	**c.** S. Bible written side	**d.** S. Bible unwritten side	**e.** L. Bible paperboard	**f.** S. Bible paperboard	**g.** L. Bible leather material	**h.** S. Small piece of leather	**Functional Group**
Wave number (cm^{-1})	3691*m*	3689*m*	3689*m*	3689*m*	3691*m*	-	-	-	O-H stretching alcohol
	3619*w*	3621*w*	3614*w*	3619*w*	3619*w*	-	-	-	O-H stretching
	-	-	-	3524*m*		-	-	-	O-H stretching alcohol
	-	3331	-	3395*m*	3400*m*	3402*m*	-	-	O-H stretching amine
	-	-	3279*w*	-	-	-	3286*s*	3282*s*	C-H stretching alkyne
	2917	-	-	-	-	2970*m*	2919*m*	2919*m*	C-H stretching alkane
	2849	-	-	-	-	-	-	-	-
	-	-	2088*w*	-	-	-	-	-	C=H stretching alkyne
	-	-	-	1682*s*	-	-	-	-	C=O stretching ketone
	-	-	1619*s*	1620*s*	1621*s*	1634*s*	1605*s*	1627*s*	C=C stretching ketone
	1592*m*	1596*m*	-	-	-	-	-	-	N-H bending amine
	1508*s*	1508*s*	-	-	-	-	-	1514*s*	N-O stretching nitro compound
	1453*m*	1449*m*	-	-	-	1455*m*	-	1446*m*	C-H bending alkane
	1417*m*	1412*m*	-	-	1424*m*	1415*m*	1406*m*	-	O-H bending alcohol

1396*s*	-	-	-	-	1373*s*	-	1372*s*	S=O stretching sulfonate
1315*s*	-	-	-	-	1327*s*	-	-	S=O stretching sulfonamide
1265*s*	1270*s*	-	-	-	1270*s*	1267*s*	-	C-O stretching alkyl aryl ether
-	1163*s*	-	-	-	-	1134*s*	-	C-O stretching aliphatic ether
-	1111*s*	-	1112*s*	1104*s*	-	-	-	C-O stretching secondary alcohol
1093*s*	1091*s*	1095*s*	-	-	-	-	-	C-O stretching primary alcohol
1029*s*	1030*s*	1032*s*	1029*s*	1029*s*	1049*s*	1029*s*	1030*s*	C-O stretching
1005	1005	1005	1011	1005	-	-	-	-
937*s*	934*s*	937*s*	939*s*	934*s*	-	-	-	C=C bending alkene
911	911	911	910	911	-	-	909	-
-	-	-	-	-	839*m*	871*m*	-	C=C bending alkene
787*s*	789*s*	785*s*	794*s*	792*s*	-	-	-	C=C bending
749	749	751	749	751	-	710	-	-
692*s*	692*s*	672*s*	671*s*	672*s*	-	-	-	C-Br stretching halo compound
640	636	633	659	-	-	-	-	-
532*s*	533*s*	531*s*	530*s*	530*s*	531*s*	533*s*	-	C-I stretching halo compound
466	467	464	463	463	466	-	-	-

3.3. HPLC-DAD analysis

High-Performance Liquid Chromatography (HPLC) analysis was applied to samples (29.a), (29.b), and (29.c) of the main fabric samples of archaeological textiles. The dye compositions were based on the literature, the chromatograms, and the absorption spectra acquired with the standard reference compound (Yurdun, Karadag, Dolen, & Mubarak, 2011). The dyestuff and plant materials (identified by HPLC-DAD) were determined. Analysis chromatograms and spectra are presented in (Fig. 12). Identified dyestuff and plant resources are given in (Table 3). Alizarin was found in samples (29.a, 29.b and 29.c) madder (*Rubia tinctorum* L.) was determined as a plant source (Karadag et al., 2010; Yurdun et al., 2011). Anthraquinones, found in madder roots (roots and rootstocks of *Rubia tinctorum* L.), have been used in dyeing textile fibers specifically to give red color and have also been used as pigments since ancient times (Al-Gaoudi, 2020; Karadag et al., 2010; Recep et al., 2014).



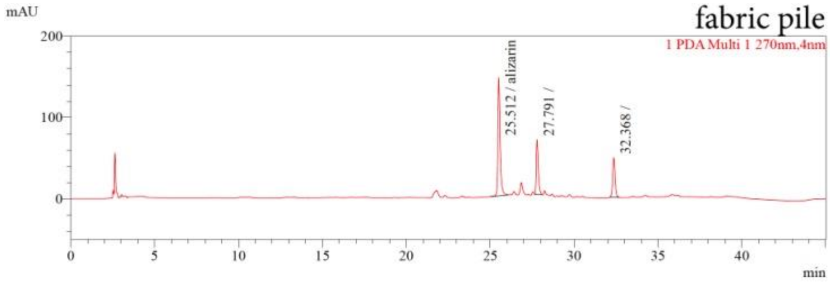


Figure 11. Chromatograms of main fabric samples; 29.a Main fabric warp thread, 29.b Main fabric weft thread, 29.c Main fabric pile surface. (29.a, 29.b, 29.c): Chromatograms obtained at 270 nm.

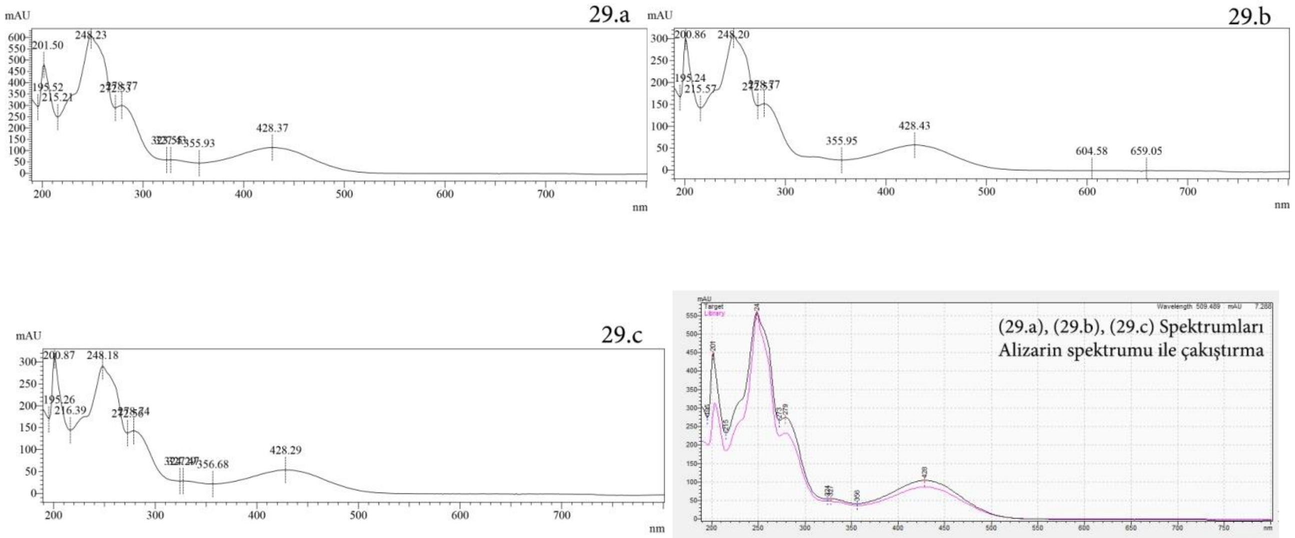


Figure 12. Spectra of main fabric samples; 29.a Main fabric warp thread, 29.b Main fabric weft thread, 29.c Main fabric pile surface. 29.a, 29.b, 29.c: Overlapping spectra with alizarin standard compound spectrum.

Table 3. The detected compounds and the identified dye source for samples.

Samples	Detected compounds (absorption maxima 248, 272, and 428 nm)	Identified dye source
29.**a**	alizarin (Rt min: 25.501)	(*Rubia tinctorum* L.)
29.**b**	alizarin (Rt min: 25.499)	(*Rubia tinctorum* L.)
29.**c**	alizarin (Rt min: 25.512)	(R*ubia tinctorum* L.)

It was revealed that the examined textile piece was dyed with natural dyes. As a natural dye, madder is often found in archaeological textile materials. Root dye (*Rubia tinctorum* L.) is the most important dye plant for red color (Salman et al., 2022). The dyeing process of the plant is done with the dried and ground laterals (roots) with the mordant dyeing method. Root dye, which has gained importance in history for centuries, has contributed to the preservation of archaeological textiles. Although archaeological textiles found under the ground have been exposed to the soil for a long time, they can protect the antimicrobial properties of root dye (Hekim, 2019; E. Osman, Zidan, & Kamal, 2014).

Archaeological evidence from the Sinope Balatlar excavation site, chromatograms of HPLC-DAD analysis of paper, cardboard, and leather fragments of the L. and S. Bible books are shown in (Fig. 13). The obtained chromatograms have established that natural dyes are not used in book fragments of the Large and Small Bibles (Al-Gaoudi, 2020).

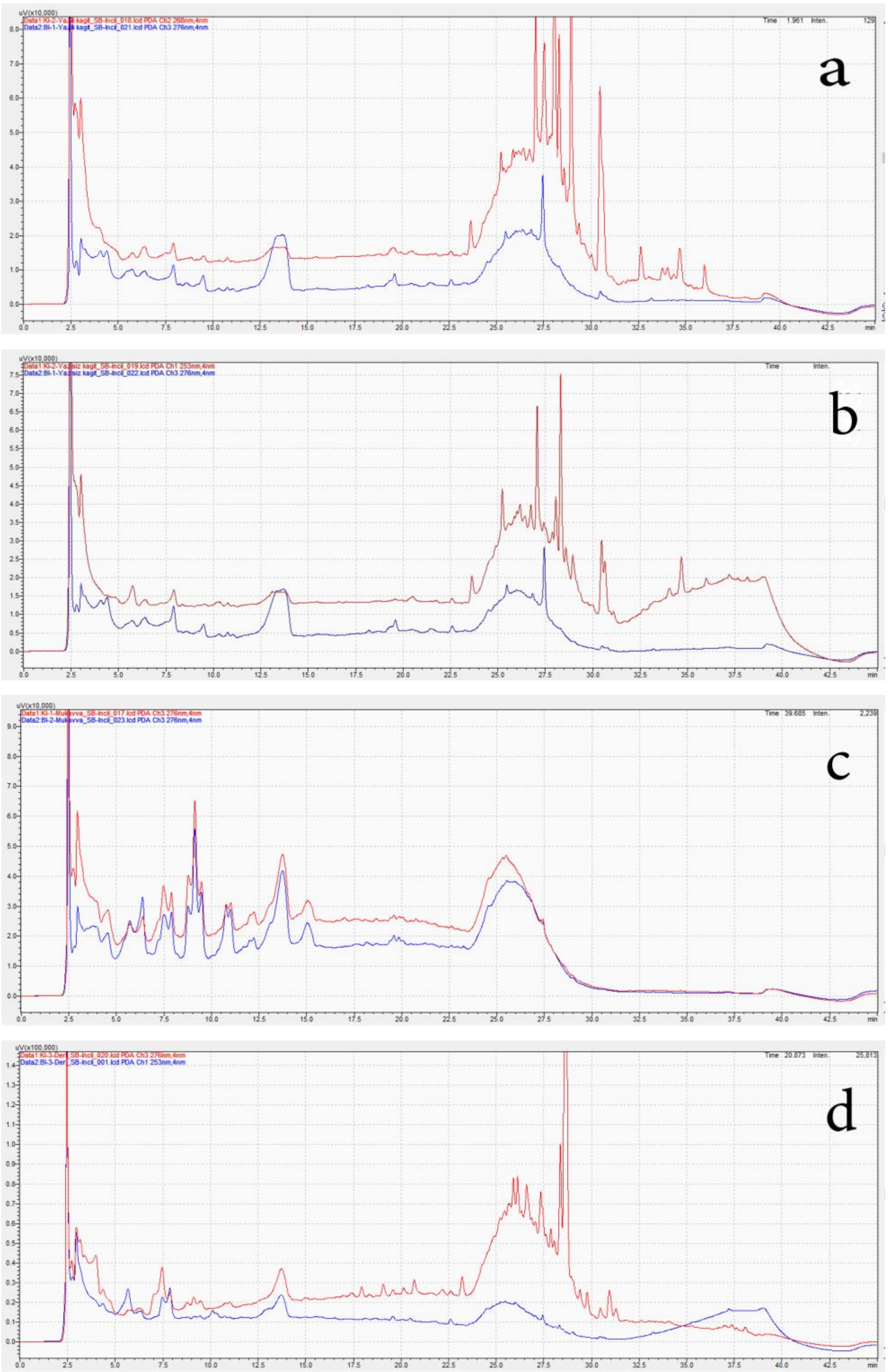


Figure 13. HPLC-DAD analysis of paper pieces of the Sinope Balatlar archaeological Large Bible and Small Bible books: a. Comparison L.Bible and S.Bible of the written sides., b. Comparison L.Bible and S.Bible of the unwritten sides., c. Comparison L.Bible and S.Bible of the paperboard sides., d. Comparison L.Bible and S.Bible of the leather sides.

3.4. SEM-EDX analysis

The images of the metal pattern thread (29.j) and round beads (29.k) used for decoration in the pattern on the main fabric of the archaeological text were taken using a Scanning Electron Microscope (SEM). First, the surface image of the samples was taken, and then closer images were taken for element analysis. Pattern yarn and round bead SEM images are shown in (Fig. 15). Since the archaeological textile comes out of the archaeological excavation area, dirt, cracks, fiber breaks and missing parts have been detected on its surface. The degradation of the fibers may have occurred at different times after the fabrics were buried or dug (E. Osman et al., 2014). The elements found in the metal pattern thread (29.j) and round bead (29.k) samples in EDX analysis are given in (Table 4). In the (29.j) sample, 74.35% silver (Ag) was detected. The presence of silver element by weight indicates that the pattern thread is silver plated. In addition, EDX analysis showed the presence of elements carbon (C), oxygen (O), and sulfur (Cl). Aluminum (Al) and silicon (Si) elements have been found in inorganic particles (Kramell et al., 2014). Carbon (C), oxygen (O), silicon (Si), copper (Cu), phosphorus (P) were detected in sample (29.k). It was understood that the (29.j) 1.71% and (29.k) 10.45% silicium (Si) in the samples originated from clayey soil. In addition, copper (Cu) is the main material of the metal thread by weight with a ratio of 43.75%. Additionally, phosphorus contamination is thought to result from metal thread production (Abdel-Kareem, 2022; Abdel-Kareem & Harith, 2008; Amin, 2018; Massadikova et al., 2020; Osman et al., 2014).

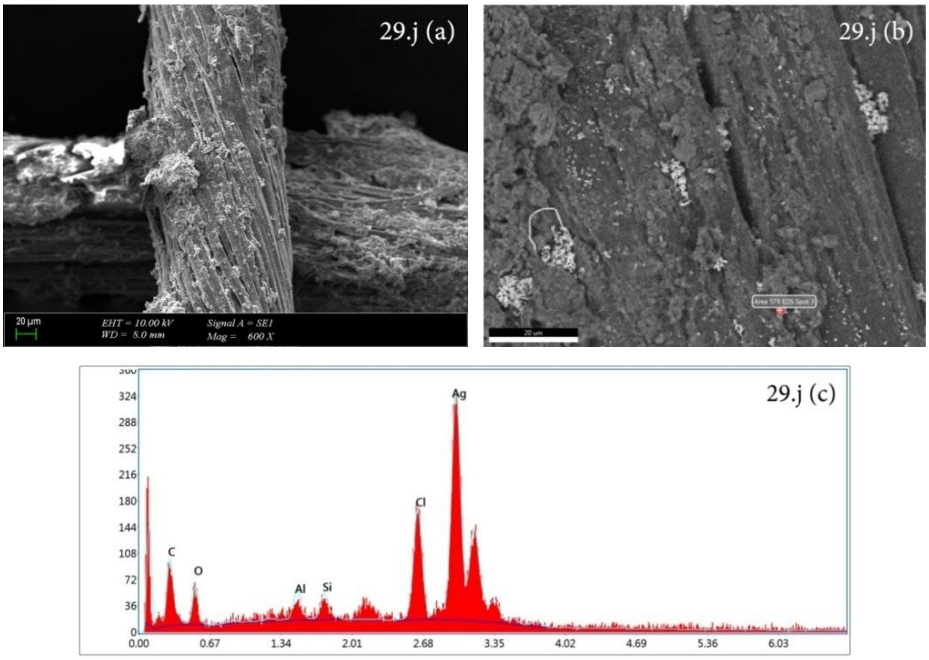


Figure 14. Metal pattern thread; 29.j (a) Metal pattern thread image, 29.j (b) Large view of the metal thread up close, 29.j (c) Metal pattern thread element analysis.

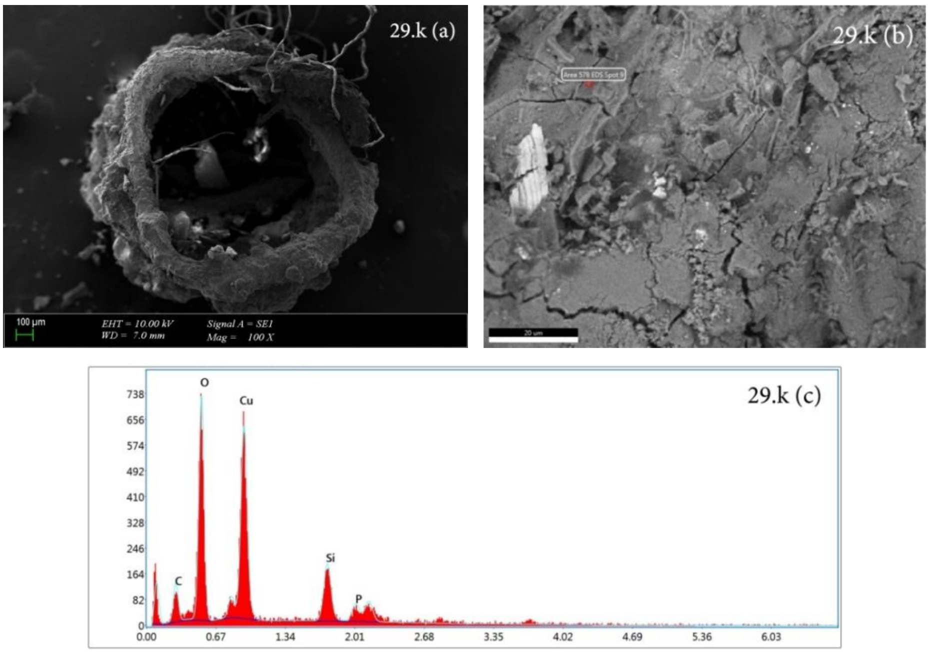


Figure 15. 29.k (a) SEM image of round bead, 29.k (b) Large close-up view of round bead, 29.k (c) Round bead elemental analysis.

Table 4. Metal pattern thread and round bead are used in red fabric.

Samples	Element (wt%)							
	C	**O**	**Al**	**Si**	**Cl**	**Ag**	**Cu**	**P**
29.**j**	4.38	4.96	2.08	1.71	12.52	74.35	-	-
29.**k**	11.17	30.04	-	10.45	-	-	43.75	4.59

Observations performed with scanning electron microscopy show the morphology and the structure of the fibers of the paper samples taken from the L. and S. Bible book fragment (Fig. 17). SEM analysis of the L. and S. Bible paper fragments shows the state of deterioration and fragility. It is important to pay attention to the random distribution of fibers with a typical structure consisting of bundles (Franzoni, Volpi, Bonoli, Spinelli, & Gabrielli, 2018; Hajji et al., 2015; Kousouni, 2018). There are a lot of dust and white dots that spread over the entire surface of the paper. At (Fig. 16), SEM images of cardboard fragments of the L. and S. Bible reveal a blistered and corroded structure. Morphological images of the leather parts of the L. and S. Bible book reveal that dust and dirt particles are formed in the fiber bundles (Fig. 16). Energy dispersive spectrometer (EDX) and analyzed samples of the L. ad S. Biblical book fragments primarily show the following: what kind of organic structure the Sinope Balatlar archaeological excavation site has and how these different chemicals or organic compounds interact with the book. According to the observed information, this excavation shows that the area has a more metal and copper-weighted structure, however, in previous studies found from the same excavation site, the (Ti) element was predominantly found (Table 5). It is thought that these high values may also be partly due to the soil where the beads are buried, and which are found on their surface (Dardeniz & Öztan, 2020). However, titanium is associated with the soil formation of archaeological findings (Kalkan, 2017; Wahba, 2020). This is because titanium is not water soluble, so it differs from one area to another only by physical transport.

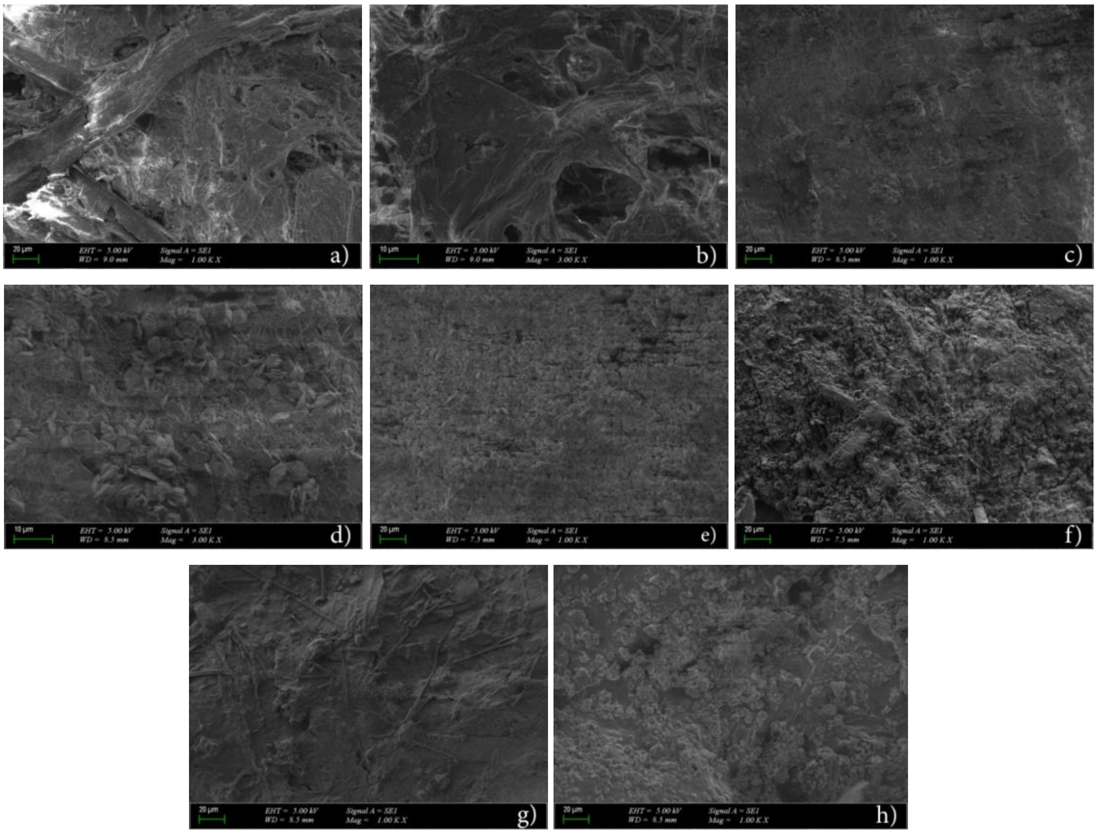


Figure 16. SEM images of Sinope Balatlar archaeological L.Bible and S.Bible: a. L. Bible written side, b. Unwritten side of the L.Bible, c. S. Bible written side, d. unwritten side of the S. Bible., e. L. Bible paperboard, f. S. Bible paperboard. g. L. Bible leather side, h. S. Bible leather side.

Table 5. Elemental analysis of the Sinope Balatlar archaeological Bibles.

Samples	**Element (wt%)**		
Examples of pieces of paper	**C**	**O**	**Ti**
a. L. Bible piece of paper	56,32	43,68	-
c. S. Bible piece of paper	43,76	56,24	-
Cardboard			
e. L. Bible paperboard	-	42.74	57.26
f. S. Bible paperboard	52.89 47.11		-
Skin part			
g. L. Bible leather piece	-	53.69	46.31
h. S. Bible leather piece	25.49	34.95	39.56

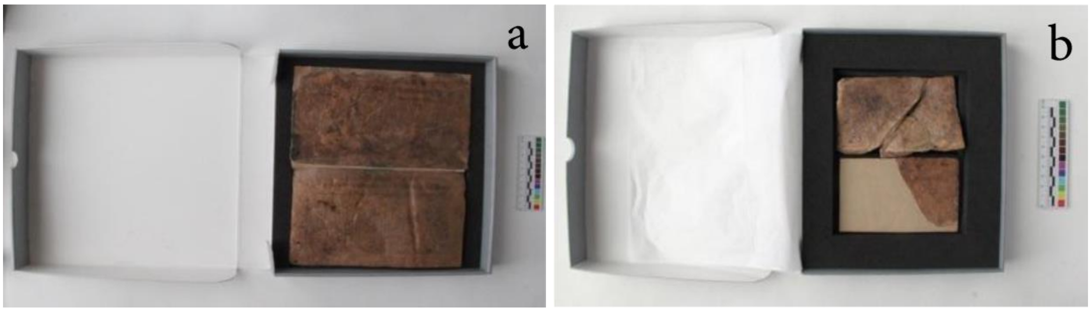


Figure 17. Packing stage of 2 bibles: a. L. Bible., b. S. Bible.

4. CONCLUSION

The metal, paper, and beads used in the patterned embroidery of the archaeological textile, which was unearthed from the tomb numbered VIII during the Sinope Balatlar Church excavation, were analyzed by non-destructive and microanalysis methods. The combination of non-destructive and microanalysis methods is very informative in shedding light on the characterization of historical textile materials and coloring agents. Results show that the main fabric and lining fabric of the analyzed archaeological textiles are produced from cotton (OM, ATR-FTIR). However, it has been determined that the pattern thread is produced from silk fibers (Table 1, Figs 5 and 9). It was determined that the alizarin dye, which gives the main fabric its red color, originates from madder (*Rubia tinctorum* L.) and the same dye is used in the warp, weft, and pile threads of the fabric. The characterization of the metal pattern thread and the round embroidery bead of the finding, which is a composite artifact, was examined. It has been determined that the metal pattern thread is produced with a silver coating and the round embroidery bead with a copper mixture. Since the archaeological textile is found from the archaeological site, elements of soil or different chemicals have been found. The written and unwritten parts of the Bible works examined within the scope of the study and the covers made of cardboard and leather were examined, and within the framework of the analysis results obtained, it was concluded that both bibles were produced in a similar way and the inner pages were straw paper. Gallic acid was found in the analyzes made from the written parts of the Bibles. This indicates the presence of black iron gallic acid in the inks. In addition, tannin compounds were detected in the analyzes made from leather pieces. This result reveals that vegetable grains were used in the tanning or dyeing of the leather. The data obtained from the analyzes constituted a resource for the practitioner in the conservation and restoration phase to recognize the work and to determine the appropriate methods for the work. In addition, the obtained analysis results were recorded in the inventory records of the artifacts when they were delivered to the museum, and it was provided to be a guide for future researchers.

The biblical artifacts, whose conservation and restoration processes were completed at Mimar Sinan University, were first placed in Ethafoam 220 and then in acid-free boxes (Fig. 17) and delivered to the Sinope Archeology Museum within the scope of preventive protection. Conservation and restoration work of textile materials continue. At the end of the process, it will be delivered to the same museum.

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AUTHOR CONTRIBUTIONS

Guzal Massadikova: Textile material analysis and FTIR analysis, writing—original draft preparation, resources, analysis, methodology, software. Meral Ozomay: Textile material analysis and dyestuff analysis, HPLC, investigation, formal analysis, validation, methodology. Zafer Ozomay: Analysis of paper material and SEM, visualization, formal analysis. Ragsana Hasanova: Conservator and Restorer of the textile and books, detailed information about the excavation site, OM.

All authors have read and agreed to the published version of the manuscript.

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