

Mediterranean Archaeology and Archaeometry Vol. 20, No 3, (2020), pp. 1-12 Open Access. Online & Print.



DOI: 10.5281/zenodo.3871295

# ARCHAEOMETRICAL STUDY OF A RARE EMBROIDERED AND APPLIQUED LEATHER TAPESTRY FROM THE SAFAVID ARTWORKS. PART II: COLORED LEATHER

Nabil Mabrouk and Yosr Elsayed

Conservation Department Faculty of Archaeology, Damietta University 34517, New Damietta, Damietta, Egypt

Received: 14/05/2020 Accepted: 02/06/2020

*Corresponding author: Nabil Mabrouk (nsh00@du.edu.eg)* 

# ABSTRACT

The present study focuses on the investigation and analytical techniques used to study a rare Iranian leather tapestry dates to the 16<sup>th</sup>-17<sup>th</sup> century. This study is a complementary part of an earlier one on the fibers and dyes of the same object. Both parts concern a pioneered archaeomatrical study for such rare types of embroidered and appliqued leather tapestries. The present study reveals the type(s) of leather, tannins, pigments, and media used in the object, and the deterioration forms as well. The study used the SM, SEM-EDX, MA-XRF, ATR-FTIR, and MALDI-TOF MS. The obtained results revealed that the object is composed of; a textile substrate, a blank beige goatskin layer upon the textile substrate, a blackish goatskin layer colored with iron oxide and bone black in Arabic gum, white cattle leather patterns colored with calcium carbonates in Arabic gum and appliqued upon the blackish layer, the whole object is fixed and ornamented using dyed embroidery threads. Mimosa and alum were revealed as tanning materials for the leathers. The object suffers from many deterioration forms, namely dust and soiling matters, cracks, macro-cracks, drying, brittleness, shrinkage, lost parts, stains, and erosion of colored surfaces.

KEYWORDS: Leather tapestry, Embroidery, Investigation, Analysis, Pigments, Color, Spectroscopy

## 1. INTRODUCTION

Historical leathers, such as bookbinding, wall tapestry, upholstery, footwear, garments, armors, etc., are important objects of our cultural heritage, from ancient times to present (Forbes, 1965). The term 'leather' describes the animal skins, such as cow, deer, sheep, goat, etc., after mechanical and chemical manufacturing processes, which includes liming, unhairing, fleshing, drying, and tanning. vegetable tanning materials, such as oak wood, chestnut, mimosa, and sumac leaves, have been the sources of tannins used to produce ancient leather until the late 19th century and early 20th century when chromium mineral tanning came into use and gradually replaced vegetable tannins (Forbes, 1965; Thomson, 2006). Alum was commonly used as a tawing (tanning) material to produce white leather (Vest, 1999). Tanning process transforms animal skin into leather, with better properties, especially the stability and resistance to microbial attack. The residual organic and inorganic substances such as calcium carbonate, tannins, alum, silicates, etc., are commonly identified in leather, affecting its properties (Covington, 2006; Shukla et al., 1999; Thomson, 2006).

Leather materials were generally processed with different multi-artistic decorating techniques, such as coloring, dyeing, painting, printing, embroidering, gilding, etc., to be transferred into wonderful heritage objects, and help to protect the substrate leathers when covered with these decorative layers (Dross-Krüpe and Paetz, 2014; Göksel and Kutlu, 2016; Watt et al., 1997). The decorating techniques were ancient as making leather itself, applied to different types of crafts, such as gloves, boots, caskets, saddles, garments, pouches, hangings, tapestries, curtains, etc. (Dross-Krüpe and Paetz, 2014; Göksel and Kutlu, 2016; Ioele et al., 2011; Watt et al., 1997). Through the art history, many types of organic and inorganic pigments and dyes were mixed with water-based media, such as Arabic gum and animal glue, or with oil and turpentine since the middle ages (De Keijzer and Koldeweij). Investigation and analytical techniques of heritage artworks are im-

portant tools for identifying the components and deterioration forms all objects. It is well-known that a very thorough investigation and analysis of the object must be conducted before conservation works (Kabbani, 1997).

The case study object Fig. (1) is a Safavid leather tapestry dates to the 16<sup>th</sup>-17<sup>th</sup> century, the golden age of artworks in ancient Persia, where a growing interest in the arts and art collections was witnessed, not only in the Safavid empire (The dynasty ruled Persia from 1501 to 1736) but also in the Ottoman and Mongol empires (Lukonin and Ivanov, 2013). It is a unique piece of artwork, composed of several materials, crafted with different techniques. That's why it attracts much interest of the archaeologists and conservators as well. The novelty in the case study, and the high-tech used facilities, stands with the obtained significant results, which introduced an important type of artworks to the archaeological academia.



Figure 1. The case study object.

The object is preserved in The Cotton Museum, in Egypt. It is a rare artwork, an incredible combination of both leather and textile; composed of a textile substrate, topped with a blank beige leather layer, topped with a blackish-colored leather layer, upon which leather patterns are appliqued (pre-cut pieces of material, rather than threads, are stitched or adhered to another substrate). The case study is embroidered with textile threads dyed in different colors. The ornamentation style corresponds to the Sasanian art, affected by the ancient Chinese one. The items of ornamentation are; a Persian female face, flowers and leaves, four birds, arranged in a symmetric design, surrounded by three decorated frames. More details about the object, technical data, limits identifying the object, and the other limitations of the present work are available in part I of this study (Mabrouk, 2020).

### 2. MATERIALS AND METHODS

### 2.1. Sampling

Nine macro-samples (ca. 2x2 mm), Tab. (1), were collected from the case study object to identify the

different components of the colored leathers, namely the type(s) of leathers, pigments, media, and deterioration forms. To identify the type(s) of leathers, three macro-samples were collected from the flesh side of the leathers; blackish leather (BLf), beige leather (BiLf), and the white leather (WLf). To identify the tanning material(s), another three macro-samples were collected from the flesh side of the leathers also; blackish leather (BLt), beige leather (BiLt), and the white leather (WLt). The flesh sides are free from any added materials, such as pigments, media, etc., so, these sides are suitable to identify the type(s) of leathers and tanning material(s). To identify the pigments and media, three macro-samples were collected from the grain side of the leathers; blackish leather (BLg), beige leather (BiLg), and the white leather (WLg). Moreover, a small part of the object, which was found separated (SP), was non-invasively scanned by the Macro X-ray fluorescence (MA-XRF) scanner to identify the elemental distribution of the inorganic components in this part of the object. The MA-XRF scanner is not available in Egypt, and there is no legal way to transport the object abroad; so, this (SP) was only scanned.

	Sample	Abbr.	Analytical technique
1	Blackish leather (flesh side)	BLf	SEM, FTIR, MALDI-TOF MS
2	Beige leather (flesh side)	BiLf	SEM, FTIR
3	White leather (flesh side)	WLf	SEM, FTIR
4	Blackish leather (tannin)	BLt	FTIR
5	Beige leather (tannin)	BiLt	FTIR
6	White leather (tannin)	WLt	FTIR
7	Blackish leather (grain side)	BLg	SM, SEM-EDX, FTIR
8	Beige leather (grain side)	BiLg	SM, SEM-EDX, FTIR
9	White leather (grain side)	WLg	SM, SEM-EDX, FTIR
10	Separated part	SP	SM, MA-XRF

Table (1) Names and abbreviations of the investigated samples and the techniques used

#### 2.2. Stereo Microscope SM

To identify the anatomical structure of the case study layers, a Stereo Microscope SM (SMZ800, Nikon), integrated with the Canon EOS 700D camera was used. The SP was investigated using the SM from the cross-section side after trimming the higher parts. It was directly held to the stage then investigated without moulding in a resin. SM was also used to identify the deterioration forms in the leathers' layers and colored surfaces.

## 2.3. Scanning Electron Microscopy with EDX (SEM-EDX)

A Scanning Electron Microscope SEM (Quanta 3D FEG, FEI Company, USA) coupled with Energy Dispersive X-ray detector EDX was used to morpholog-

ically identify the type(s) of leathers used in both layers and appliques. It was also used to identify the deterioration forms in the leathers' macro-samples of the object. To identify the inorganic components in the leather layers and appliques, the EDX unit was used. The beam energy was 20 kV, acceleration voltage with ETD detector (secondary electron mode) at 10 mm working distance, and a spot size 5.5 (1kV/10pA) with a scale ranging from 10 $\mu$ m to 50 $\mu$ m. The spot size was 7 (20kV/4nA) with a scale of approximately 200 $\mu$ m. The EDX detector was calibrated, but not for standard quantification method.

## 2.4. Macro X-ray fluorescence (MA-XRF)

The MA-XRF scanning system (M6 JetStream, Bruker Nano GmbH, Berlin, Germany) was used in the mapping of the surface of the SP. It aimed to identify the distribution of inorganic elements in the object's surface. The scanning head consists of an X-ray tube with a rhodium target. The configuration used was: an X-ray tube at 50 kV, an anode current of 600  $\mu$ A, no filter, and a 30 mm2 SDD with a zirconium window. X-ray energy ranged from 0.35-40keV. The outstanding data were obtained from ~2-18keV. The pixel size was 650  $\mu$ m and the pixel time was 35 ms/pixel

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

FTIR spectroscopy (Thermo Nicolet 6700 FTIR spectroscopy, USA) was used to chemically identify the leather, tanning materials, pigments, and media,. The spectra were obtained in the reflection mode using ATR crystal in the spectral range from 400 to 4000 cm<sup>-1</sup> with a 4 cm<sup>-1</sup> resolution. The FTIR was basically used to help interpreting and confirming the other results obtained by the macroscopic and microscopic obtained results (Ebsen et al., 2019). BLf, BiLf, WLf, BLg, BiLg, and WLg were directly investigated without any preparation. BLt, BiLt, and WLt were extracted from different leathers to identify the tanning materials. They were prepared as follows; finely cut fibers were collected from the flesh side, then mixed with 1:1 aqueous-acetone (ratio: 1 ml of aqueous-acetone per 10 mg fibers), under stirring for 48 hours at room temperature. The three extracts were then filtered and analyzed by ATR-FTIR (Falcão and Araújo, 2013, 2014).

# 2.6. MALDI-TOF Mass spectrometry MALDI-TOF MS

While the microscopic techniques were capable of identifying the types of leathers in BiLg and WLg, but the paint layer upon the BLg limits to identify its type of leather. Due to this failure, MALDI-TOF MS was used to only identify the type of blackish leather, using a sample collected from the flesh side (BLf), it is free from the paint layer. Mass Spectrometer (Autoflex Speed MALDI-TOF-TOF, Bruker) was used. The instrument was equipped with a standard nitrogen laser (337nm) and calibrated using the six peptide markers designated A-G. A small sample (ca.  $1.5 \times 1.5$  mm) was washed in 0,1 M NaOH, then in 50 mM of NH<sub>4</sub>HCO<sub>3</sub>. It was then suspended in 75 µL 50 mM of NH<sub>4</sub>HCO<sub>3</sub> and digested with 1 µL of 1 mg/mL trypsin solution incubated at 37 °C for 18 h. the sample was spotted in triplicate, the three spectra were obtained, then averaged, and inspected with mMass 5.0.1 software. The spectra were acquired over the m/z range 1000–4000 in reflector mode (Buckley et al., 2009; Ebsen et al., 2019).

## 3. RESULTS AND DISCUSSION

#### 3.1. Microscopic and macroscopic results

The obtained macroscopic and SM results Fig. (2) showed that the object is composed of many layers; a substrate blank textile, topped with an intermediate beige leather, topped with an upper blackish leather, topped with small white leather patterns shaped and appliqued using dyed threads. The three layers and appliques are jointly embroidered with textile threads dyed in different colors. According to the literature (Ebsen et al., 2019; Elnaggar et al., 2017; Haines, 2006; Schmidt et al., 2011), the identified hair follicle patterns revealed that the BiLg is goatskin. After delicate cleaning its surface, WLg, was identified as cattle skin. On the contrary, the hair follicle patterns were not cleared enough to identify the BLg, which was suggested as goatskin, thanks to the visible hair remains, which had not been removed in the dehairing process (Ebsen et al., 2019).

The object is suffering from many deterioration phenomena, such as cracks, macro-cracks, crumbing, shrinkage, lost parts, stains, erosion of colored surfaces (in leathers), damaged fabric and threads, faded dyes, lost parts, stains (in fabric substrate and embroidery threads), dust, and soiling matters over the whole object. These are the most common deterioration phenomena identified in other textile and leather heritage objects (Amin, 2017; Amin, 2018; Dellaportas et al., 2014; Al-Gaoudi, 2020; Mansour et al., 2017). No notable microbial colonies were observed on either the obverse or the reverse of the object.



Figure 2. Macroscopic and SM microscopic results; (a) the cross-section of the layers, (b) hair follicle pattern of goatskin in BiLg, (c) hair follicle pattern of cattle skin in WLg, (d) surface of BLg with goat hair, (e) substrate fabric SF including embroideries, (f, g) lost parts, stains and soiling matters, (h)tears and damage, (i, j) shrinkage, crumbing, and eroded surface, (k, l) cracks, macro-cracks, and cleavage in the black paint layer.

The SEM results of the BLf, BiLf, WLf, BLg, BiLg, WLg Fig. (3) revealed that the blackish leather suffers from deformation, spilt, and separated surface in both the grain side and the flesh side as well. The cracks, macro-cracks, and cleavage of the paint layer are clearly observed. Most of the deterioration forms showed by SM and SEM are likely due to the illadapted museum environment in the Cotton Museum, where the conditions of preservation are not stable. Temperature is not controlled, and so the humidity. The air conditioner is daily turned on during the daytime, then turned off afternoon till the next day morning. This behavior, in addition to the ancient anthropic use of the object, usually leads to internal and external interaction in the object ingredients, hence, the occurrence of the mentioned above deterioration forms (Elsayed, 2019a). Moreover, the different materials used in leather manufacturing are almost accelerating the deterioration rate. The mechanism of leather deterioration is commonly assumed to include the following steps: thermal destabilization of collagen-tannin complex, de-tanning, thermal destabilization of chemically unmodified collagen, gelatinization, and denaturation (Carsote and Badea, 2019).



Figure 3. The SEM micrographs of the grain sides and the flesh sides of the collected samples revealing the damage of leather and cleavage of paint layer; (a, b, c) the grain sides of the BLg, BiLg, and WLg respectively, (d, e, f) the flesh sides of the BLg, BiLg, and WLg respectively

The results of the EDX unit for the BLg, BiLg, WLg revealed many chemical elements identified in all samples Table (2) Fig. (4). Major elements are C, N, O, and Fe. Minor elements are Na, Al, S, Cl, K, and Ca. Traces are F, Cu, Mg, Si, P, Sn, and I. The C, N, and O are almost corresponding to the major components of leather (Badea et al., 2008). In the BLg, the high proportion of C, P, Ca, Fe may refer to bone black  $(C,Ca_5(OH)(PO_4)_3)$ , mixed with dark brown iron oxide Fe<sub>2</sub>O<sub>3</sub>. That's why, the color is not completely black, but blackish. EDX was considered the most adapted technique to identify bone black, as it identifies Ca and P elements (Daveri et al., 2018; Elsayed, 2019c). Na and Cl may refer to halite NaCl. Other minor elements may refer to dust deposits and soiling matters, or to residues of some materials used in the leather's ancient manufacturing processes (Bicchieri et al., 2019; Forbes, 1965).

		Wt% detected elements															
	С	Ν	0	Fe	Na	Al	Si	S	Cl	Κ	Ca	F	Cu	Mg	Р	Sn	Ι
BLg	15.94	9.94	41.27	12.2	1.02	0.72	1.96	1.15	0.48	0.32	6.05	0.59	1.77	0.57	5.38	0.33	0.27
BiLg	9.93	13.38	40.96	0.23	4.35	6.63	1.86	6.93	4.5	7.8	1.73	0.49	0.39	0.31	0.55	0.05	0.14
WLg	10.85	10.39	42.74	0.5	3.54	4.87	2.54	5.82	5.12	4.19	6.54	0.67	0.63	0.67	0.61	0.13	0.19

Table (2) the analytical results of the EDX unit for the case study macro-samples



Figure 4. The EDX results; (a) BLg, (b) Bilg, (c) WLg.

with some soiling matters, while the WLg result is

The BiLg results point to an ancient blank leather distinct with the higher proportion of Ca. This suggests that the Ca may come from calcium carbonate,

which was applied to the surface of the appliqué leather as white paint (Franquelo et al., 2019). The Ca, in BiLg may refer to the use of lime or chalk, with other materials, during the leather preparation. The skin was likely rubbed while it was still wet and stretched on a frame, to smoothen and whiten the surface. The high proportion of Al, S, K, may refer to alum (KAl(SO<sub>4</sub>)<sub>2·12</sub>H<sub>2</sub>O), used in tanning the white leather. Na, Cl may refer to halite residues, used during leather manufacturing process. Other minor elements may refer to dust deposits and soiling materials (Forbes, 1965; Vest, 1999).

## 3.2. MA-XRF results

The MA-XRF maps of the SP of the object Fig. (5a) showed the elemental distribution of the highintensity detected elements. It indicated the availability of elements, their concentration, and the proposed underlying elements. The obtained spectra Fig. (5b) revealed many chemical elements, namely iron (Fe), copper (Cu), potassium (K,) calcium (Ca), strontium (Sr), and lead (Pb). Fe and Cu may refer to iron oxide/sulfate and small amounts of copper carbonates, jointly mixed with a medium to color the leather surface (Alfeld et al., 2013; Elnaggar et al., 2017). Ca is more concentrated in the threads than in the leather; it may be due to deposits of dust or soiling materials. The identified Ca in the leather area, with consideration to the likely undetected P, may refer to bone black. It was identified by EDX, not by MA-XRF. More elements were identified in the EDX-investigated samples (SF, BE, OE, GE, BiE, BLg, BiLg, WLg), in comparison with the SP investigated by MA-XRF.

Owing to the normal shortage in MA-XRF technical, some elements, such as C, O, S, P, Mg, Si, Al, are undetectable. However, the elemental distribution maps obtained by MA-XRF provides useful and unique informative data, which cannot be obtained by other techniques (Alfeld et al., 2013; Elsayed, 2019b). The small proportion of Pb may refer to lead white (Pb<sub>3</sub>CO<sub>3</sub>), which was commonly used in painted objects as a white ground layer. It was also sometimes used as a pigment, when mixed with the dark pigment, such as black or blue (Elsayed, 2019b; Ioele et al., 2011). The other elements, as mentioned above, are suggested to be accumulated dust, soiling materials, or impurities in the coloring pigment. due to identifying the same elements in the blank and dyed fibers, and normal more amount of soiling and dust deposits, compared to the mordants, no element is verified as a mordant (Amin, 2019; Trojanowicz et al., 2004).



Figure 5. The MA-XRF results of SP; (a) the elemental distribution maps of K, Ca, Fe, Cu, Sr, Pb, (b) the elemental spectra.

## 3.3. ATR-FTIR results

The ATR-FTIR obtained spectra of the investigated samples Fig. (6) BLg, BiLg and WLg revealed that BLg and BiLg are animal proteinous leathers. The spectra of collagenous materials are characterized by some identified bands: Amide I at ~1654 cm<sup>-1</sup> corresponding to  $_v$ C=O stretching of peptide (70-85%) with a small contribution from  $_{\delta ip}$ N-H; Amide II at ~1545 cm-1 associated with  $_{\delta}$ N-H (40-60%) and  $_v$ C-N stretching (18-40%); Amide III at ~1235 cm<sup>-1</sup> (very complex band according to the nature of side chains and hydrogen bonding) associated with  $_{\delta ip}$ N-H and  $_w$ CH2. Both Amide I and Amide II are the two major bands of the collagen infrared spectrum (Badea et al., 2008; Sendrea et al., 2016).

In the WLg, little bands related to collagenous materials were identified, due to the major peak of calcium carbonates (white pigment) used in painting the leather surface. Bands at ~715 cm<sup>-1</sup>, 880 cm<sup>-1</sup> and the  $\delta_{as}CO_3^{2-}$  (v3) at ~1500 cm<sup>-1</sup> correspond to calcite (Vetter and Schreiner, 2011). The presence of carbonate ion bands at ~1445 cm<sup>-1</sup> and 875 cm<sup>-1</sup> in BLg and BiLg is attributed to the manufacturing procedure of leather, including soaking in a lime (CaOH) bath, where lime residues, after washing, usually transform into CaCO<sub>3</sub> by reacting with the atmospheric CO<sub>2</sub> (Badea et al., 2008; Odlyha et al., 2009; Vetter and Schreiner, 2011). Bone black was identified in the BLg. Arabic gum was identified in the BLg and WLg as a medium for pigments. It is almost visible at ~3350 cm<sup>-1</sup> corresponding to vOH, ~2930 cm<sup>-1</sup> corresponding to vC-H, ~1650 cm<sup>-1</sup> corresponding to vasCOO-, ~1420 cm<sup>-1</sup> corresponding to vsCOO-, ~1090 cm<sup>-1</sup> corresponding to vC-O (Boyatzis et al., 2016; Daveri et al., 2018; Vetter and Schreiner, 2011).



Figure 6. The ATR-FTIR results of the investigated leather samples; BLg, BiLg, WLg, BLt, BiLt, WLt

Regarding the ATR-FTIR obtained spectra of BLt, BiLt, WLt samples, the bands at ~1646-1640 cm<sup>-1</sup>, ~1536-1555 cm<sup>-1</sup> and ~1300-1250 cm<sup>-1</sup> are attributed to the Amide I, Amide II, and Amide III respectively. This is due to the presence of some collagenous materials of the leather fibers mixed with the tanning materials (Falcão and Araújo, 2014). The results also revealed that BLt is basically a vegetable tanning material. Results agreed well with existing literature (Falcão and Araújo, 2013; Laghi et al., 2010; Nakagawa and Sugita, 1999) confirming that vegetable tannins present characteristic common bands, as follows; two bands at ~1615-1606 cm<sup>-1</sup> and ~1452-1446 cm<sup>-1</sup> assigned to <sub>v</sub>C=C, and two other bands at 1211-1196 cm<sup>-1</sup> and 1043-1030 cm<sup>-1</sup> assigned to vC-OH and <sub>ip</sub>C-H deformation. It is clear that BLt is a condensed tanning material. Its spectra in the informative region (1700-700 cm<sup>-1</sup>) shows the presence of strong bands at ~1285cm<sup>-1</sup>, ~1155 cm<sup>-1</sup> and ~1110 cm<sup>-1</sup> and weak bands at ~976 cm<sup>-1</sup> and ~848 cm<sup>-1</sup>

(Edelmann and Lendl, 2002; Falcão and Araújo, 2013, 2014).

According to existing literature (Falcão and Araújo, 2013, 2014; Laghi et al., 2010), alum is likely the tanning material used in BiLt and WLt, while mimosa was suggested to be the one used in BLt. It is to be noted that alum is the common tanning material to get white leather (Forbes, 1965; Vest, 1999). It was identified in some ancient Egyptian leather objects dating to the 17th and 18th dynasties (Elnaggar et al., 2017). Mimosa is one of the most common vegetable condensed tanning material used to convert skin to leather, and to retard decay of the archaeological leather since Neolithic times. It has progressively been replaced by chromium tanning in the 19th century (Covington, 2006; Thomson, 2006). The color of the tanned leather is dark brown, close to black. This is also due to tanning with mimosa, as it generally results in a reddish-brown color, which tends to darken with time. This type of leather is also likely to absorb pollutants, especially SO<sub>2</sub>, resulting in collagen acid hydrolysis. The brittleness of the object and the identified S element are likely related to this (Covington, 2006; Odlyha et al., 2009).

### 3.4. MALDI-TOF MS results

The obtained mass spectrum of the BLg Fig. (7a) MALDI-TOF MS revealed that it is a goatskin. The obtained m/z values, attributed to the peptide markers of known sequence, were accurately indicating the taxonomic discrimination of goat collagen. Among the peptide markers labeled A–G, 6 were identified as follows; A = COL1A2T80 was identified at m/z 1180.4 and 1196.4, B = COL1AT38 was identified at m/z 1427.5, C = COL1AT40 was identified at m/z 1580.4, D = COL1A2T40 was identified at m/z 2131.6, F= COL1A1T50/51 was identified at m/z

2883.1 and 2899.2, G = COL1A2T62 was identified at m/z 3077.6 and 3093.9 (Buckley et al., 2009; Ebsen et al., 2019).

It is worthy noticeable that G = COL1A2T62, which was identified at m/z 3077.6 and 3093.9, is the single peptide distinguishing goatskin than other similar species such as sheep and cattle. It is well-known that there are minor differences in the sequence of collagen type I in some species, for example, 5 peptide markers (A, B, C, D, F), Among the 6 peptide markers identified (A, B, C, D, F, G) are similar in both sheep and goat collagen mass spectra, only G = COL1A2T62 distinguishes the goat at m/z 3077.6 and 3093.9, on the contrary, distinguishes the sheep at ~m/z 3017 and 3033. E = COL1A2T37 is commonly unidentified in these leather species (Buckley et al., 2009; Kirby et al., 2013).



Figure 7. The MALDI-TOF MS results of the BLg

## 4. CONCLUSIONS

The present study, in addition to its part I, focused on the investigation and analysis of a rare case study object, classified as a wall hanging. It dates to the 16<sup>th</sup>-17<sup>th</sup> century in Iran and composed of textile substrate, topped with two layers of beige and blackish leather, topped with white leather patterns, embroidered with dyed-threads.

The conducted investigation and analyses revealed that both the blackish and beige leathers are goatskin, while the white leather is cattle skin. Mimosa was suggested as the tanning material of the blackish leather, while alum was suggested in the beige and white ones. A mixture of bone black and iron oxide in Arabic gum was identified to paint the surface of the blackish leather. The appliqued leather patterns were assumed pre-cut and painted using calcium carbonates mixed with Arabic gum as well. The anatomical structure of the object is weird. Embroidering colored leather using dyed threads from cotton fibers is also not common. The combination of all these art techniques and layers in one object is unknown. To the author's knowledge, no similar object could be found in other museums in Egypt, only a few pieces are available in the same museum. That's why it was suggested to classify this object as "embroidered and appliqued leather tapestry"

Due to the potentially deteriorative factors of the ill-adapted museum environment, namely the high difference in temperature and humidity in Egypt during the year, the huge amount of air pollutants, the oxygen-rich and strongly lit display halls, the absence of archaeologists and conservators, etc., all of these factors caused many deterioration to the object, which is now in dire need of treatment and preservation. If nothing is done, the ongoing deterioration will pursue, reducing the object until its full decay. The present study highlights this unique object in the small Cotton Museum to attract the interest it deserves, from the responsible authorities, and

## ACKNOWLEDGMENTS

The authors acknowledge the assistance provided by the Research Infrastructure NanoEnviCz, supported by the Ministry of Education, Youth and Sports of the Czech Republic under Project No. LM2015073. The authors thank Prof. Pavel Lejcek, Czech Academy of Science, Prof. Jerzy Łukaszewicz, and Prof. Peter Tarowski, Nicolaus Copernicus University in Torun, Poland for lab facilities. Thanks to the colleagues in the Cotton Museum for helping in the in-situ study of the case study object.

# REFERENCES

- Alfeld, M., W. De Nolf, S. Cagno, K. Appel, D. P. Siddons, A. Kuczewski, K. Janssens, J. Dik, K. Trentelman, and M. Walton, (2013) Revealing hidden paint layers in oil paintings by means of scanning macro-XRF: a mock-up study based on Rembrandt's "An old man in military costume", *Journal of Analytical Atomic Spectrometry*, 28(1), 40-51.
- Al-Gaoudi, H., (2020) Painted ancient Egyptian mummy cloth of Khonsuemrenep from Bab El-gasus excavation: scientific analysis and conservation strategy, *Scientific Culture*, 6 (2), 49-64.
- Amin, E., (2017) Study and treatment of selected decorated shawl in Applied Art Museum, Cairo, Egypt, *Scientific Culture*, **3**(**3**), 1-11.
- Amin, E., (2019) The documentation and treatment of a Coptic child's tunic in Egypt, *Egyptian Journal of Archaeological and Restoration Studies*, **9**(1), 1-11.
- Amin, E. A., (2018) Technical investigation and conservation of a tapestry textile from the Egyptian textile Museum, Cairo, *Scientific Culture*, **4**(**3**), 35-46.
- Badea, E., L. Miu, P. Budrugeac, M. Giurginca, A. Mašić, N. Badea, and G. Della Gatta, (2008) Study of deterioration of historical parchments by various thermal analysis techniques complemented by SEM, FTIR, UV-Vis-NIR and unilateral NMR investigations, *Journal of Thermal Analysis and Calorimetry*, 91(1), 17-27.
- Bicchieri, M., P. Biocca, P. Colaizzi, and F. Pinzari, (2019) Microscopic observations of paper and parchment: the archaeology of small objects, *Heritage Science*, 7(1), 47.
- Boyatzis, S. C., G. Velivasaki, and E. Malea, (2016) A study of the deterioration of aged parchment marked with laboratory iron gall inks using FTIR-ATR spectroscopy and micro hot table, *Heritage Science*, 4(1), 13.
- Buckley, M., M. Collins, J. Thomas-Oates, and J. C. Wilson, (2009) Species identification by analysis of bone collagen using matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry, *Rapid Communications in Mass Spectrometry: An International Journal Devoted to the Rapid Dissemination of Up-to-the-Minute Research in Mass Spectrometry*, 23(23), 3843-3854.
- Carsote, C., and E. Badea, (2019) Micro differential scanning calorimetry and micro hot table method for quantifying deterioration of historical leather, *Heritage Science*, 7(1), 48.
- Covington, A. D., (2006) The chemistry of tanning materials, in *Conservation of leather and related materials*, 44-57, Routledge.
- Daveri, A., M. Malagodi, and M. Vagnini, (2018) The bone black pigment identification by noninvasive, in situ infrared reflection spectroscopy, *Journal of analytical methods in chemistry*, 1-8. DOI: 10.1155/2018/6595643
- De Keijzer, M., and E. Koldeweij (2006) Analytical research on dated seventeenth and eighteenth century Dutch gilt and decorated leather. In: Theo Sturge (editor) Interim Meeting / Réunion intermédiaire Working Group "Leather and Related Materials" Groupe de Travail "Cuir et Matériaux Associés" The Conservation of Gilt Leather La conservation du cuir doré Post-prints Brussels, 25-27 March 1998, Royal Institute for Cultural Heritage, 12-15.
- Dellaportas, P., E. Papageorgiou, and G. Panagiaris, (2014) Museum factors affecting the ageing process of organic materials: review on experimental designs and the INVENVORG project as a pilot study, *Heritage science*, **2**(**1**), **2**.
- Dross-Krüpe, K., and A. Paetz, (2014) Unravelling the Tangled Threads of Ancient Emroidery: A Compilation of Written Sources and Archaeologically Preserved Textiles, *Greek and Roman Textiles and Dress, Oxford*, 207-235.
- Ebsen, J. A., K. Haase, R. Larsen, D. V. P. Sommer, and L. Ø. Brandt, (2019) Identifying archaeological leather-discussing the potential of grain pattern analysis and zooarchaeology by mass

spectrometry (ZooMS) through a case study involving medieval shoe parts from Denmark, *Journal* of Cultural Heritage, Vol.39, pp. 21-31.

- Edelmann, A., and B. Lendl, (2002) Toward the optical tongue: Flow-through sensing of tannin- protein interactions based on FTIR spectroscopy, *Journal of the American Chemical Society*, **124**(**49**), 14741-14747.
- Elnaggar, A., M. Leona, A. Nevin, and A. Heywood, (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), 133-147.
- Elsayed, Y., (2019a) Conservation of The Flowers Canvas Painting (1) at The Egyptian Agricultural Museum, *Egyptian Journal of Archaeological and Restoration Studies*, **9**(1), 39-51.
- Elsayed, Y., (2019b) Conservation of a Historic Panel Oil-painting Coated By An Ancient Varnish Layer, *Shedet*, **6**, 238-256.
- Elsayed, Y., 2019c, Identification of Painting Materials of An Unique Easel Painting for Mahmoud Sa'id, *Egyptian Journal of Archaeological and Restoration Studies*, **9**(2), 155-169.
- Falcão, L., and M. E. M. Araújo, (2013) Tannins characterization in historic leathers by complementary analytical techniques ATR-FTIR, UV-Vis and chemical tests, *Journal of cultural heritage*, **14(6)**, 499-508.
- Falcão, L., and M. E. M. Araújo, (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.
- Forbes, R. J., (1965) Studies in ancient technology. 5, v. 2, Brill Archive.
- Franquelo, M. L., A. Duran, and J. L. Perez-Rodriguez, (2019) Laboratory multi-technique study of Spanish decorated leather from the 12th to 14th centuries, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **218**, 331-341.
- Göksel, N., and N. Kutlu, (2016) Decorative elements in turkish garment culture from past to future: art of embroidery, *Journal of Textiles & Engineers/Tekstil ve Mühendis*, 23(103). URI: http://acikerisim.pau.edu.tr:8080/xmlui/handle/11499/9839.
- Haines, B. M., (2006) The fibre structure of leather, in *Conservation of leather and related materials*, 11-21, Routledge.
- Ioele, M., A. V. Jervis, M. Paris, L. Rissotto, A. Sodo, A. Giovagnoli, and T. Poli, (2011) Presence of Indigo in the Paint Layers of Gilt and Painted Leather Artefacts, *Proceedings of the ICOM Committee for Conservation, Lisbon, Portugal*, 19-23.
- Kabbani, R. M., (1997) Conservation a collaboration between art and science, *The Chemical Educator*, **2**(1), 1-18.
- Kirby, D. P., M. Buckley, E. Promise, S. A. Trauger, and T. R. Holdcraft, (2013) Identification of collagenbased materials in cultural heritage, *Analyst*, **138**(17), 4849-4858.
- Laghi, L., G. P. Parpinello, D. D. Rio, L. Calani, A. U. Mattioli, and A. Versari, (2010) Fingerprint of enological tannins by multiple techniques approach, *Food Chemistry*, **121**(**3**), 783-788.
- Lukonin, V. G., and A. A. Ivanov, (2013) Persian Art: The Lost Treasures, Parkstone Press.
- 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*, **20**(1), 163-171.
- Mansour, M., R. Hassan, and M. Salem, (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), 1-10.
- Nakagawa, K., and M. Sugita, (1999) Spectroscopic characterisation and molecular weight of vegetable tannins, *Journal of the Society of Leather Technologists and Chemists*, **83**(5), 261-264.
- Odlyha, M., C. Theodorakopoulos, J. de Groot, L. Bozec, and M. Horton, (2009) Fourier transform infra-red spectroscopy (ATR/FTIR) and scanning probe microscopy of parchment, *e-Preservation Science*, **6**, 138-144.
- Schmidt, A. L., T. Gilbert, E. Cappellini, and J. V. Olsen, (2011) Identification of animal species in skin clothing from museum collections. 16th Triennial Conference of the International Council of Museums, 1-8, ID:2265160182.
- Sendrea, C., C. Carsote, E. Badea, A. Adams, M. Niculescu, and H. Iovu, (2016) Non-invasive characterisation of collagen-based materials by NMR-mouse and ATR-FTIR, *University Politehnica* of Bucharest Scientific Bulletin Series B-Chemistry and Materials Science, **78**(3), 27-38.

- Shukla, Y. N., A. Srivastava, S. Kumar, and S. Kumar, (1999) Phytotoxic and antimicrobial constituents of Argyreia speciosa and Oenothera biennis, *Journal of ethnopharmacology*, **67**(**2**), 241-245.
- Thomson, R., (2006) Leather, in *Conservation Science: Heritage Materials*, 92-120, E. May, and M. Jones, eds., The Royal Society of Chemistry.
- Trojanowicz, M., J. Orska-Gawryś, I. Surowiec, B. Szostek, K. Urbaniak-Walczak, J. Kehl, and M. Wróbel, (2004) Chromatographic investigation of dyes extracted from Coptic textiles from the National Museum in Warsaw, *Studies in conservation*, **49**(2), 115-130.
- Vest, M., (1999) White tawed leather-aspects of conservation, The 9th International Congress of IADA, Copenhagen, Denmark, p. 67-72.
- Vetter, W., and M. Schreiner, (2011) Characterization of pigment binding media systems comparison of non invasive in situ reflection FTIR with transmission FTIR microscopy, *Sci*, **8**, 10-22.
- Watt, J. C. Y., Wardwell, A. E. and Rossabi, M., (1997) When silk was gold: Central Asian and Chinese textiles, Metropolitan Museum of Art.