ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

CHARACTERISATION OF METAL THREADS FROM ARCHAELOGICAL TEXTILES RELIGIOUS BY METHODS OF ARCHAEOMETRY.

VORNICU Nicoleta[1], BIBIRE Cristina [1], ZALTARIOV Mirela Fernanda[2]

[1]Metropolitan Research Center T.A.B.O.R, 9 Closca Str.,700066, Iasi, Romania, E-mail: cmctaboriasi@yahoo.com

[2]Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley 700487 Iasi, Romania, E-mail: zaltariov.mirela@icmpp.ro

Corresponding author: Nicoleta Vornicu, E-mail:cmctaboriasi@yahoo.com

***Abstract**: The paper presents the experimental results regarding the study of the chemical nature and the state of conservation of the metal filters used in the decoration of two textile garments (stihar and chess) of archaeological origin, recovered from the tomb of Metropolitan Gavriil Banulescu Bodoni, located in Căpriana monastery, monastic settlement from the medieval period in the Republic of Moldova.*
Textile and metallic yarns in the structure of liturgical garments were analyzed following a multi-technical, non-invasive approach, using optical microscopy, pXRF and FTIR to identify the type of yarn and their morphological characteristics, manufacturing techniques used for yarn production and metal composition / alloys. The major elements detected during the XRF analysis are gold, silver alone or combined, lead and copper. Gold is usually found as a surface coating film for silver wires and silver bands. All the wire threads studied are drawn, the surface of these threads either bears the characteristic striations from the draw plate or the signs of the rolling process. Silver-copper alloys were detected in the strips that were cut from a metal sheet, whether gilt at one side or not. All of the fabrics now appear more or less brownish or blackish due to the decomposition of the human remains, and maybe also the degradation of the natural dyestuffs used for the silks.

***Key words:** metal thread, silver layer, corrosion, OM, pXRF, FTIR.*

1. INTRODUCTION

Textiles play an important role in the rituals of the Orthodox Church, they can be consecrated objects that officially serve the liturgical act or the funeral ritual according to the hierarchy. The clothes also carry messages that are reflected in specific colors and symbols. The use of metals to decorate textiles began in the Middle Ages and the analytical research of metal threads began almost 35 years ago. [1,2] Metals were used in the manufacture of liturgical textiles for structural (buttons, buckle buttons, fasteners) or decorative purposes. Precious metals, gold and silver were used to brighten textiles. The manufacture of gilded silver and gold threads involves several stages of work such as gilding, hammering, spinning, rolling and wrapping around a textile core of silk or cotton. [3,4]

The research of archaeological textiles can bring information about the materials from which they were made but can also contribute to the description of the social environment in which they were created. Historical textiles are made of materials accessible to authors at that time. Knowledge of

complex mechanisms of degradation of archaeological textiles is essential for the correct application of conservation-restoration techniques.
The typology of alterations / degradations (physico-chemical) and the state of conservation of archaeological textiles depends on the following factors: the burial environment, the nature of the fibers and the microclimate existing at the opening of the site. For many centuries, Orthodox bishops and bishops were buried dressed in liturgical vestments to emphasize the identity of the deceased. Tombs identified during archaeological excavations can have a variety of preservation conditions, clothing usually survive for a long time only when processed with metal wires.

The analysis of such textiles from archaeological contexts is performed using optical microscopy and electron microscopy, X-ray fluorescence spectrometry, FTIR spectroscopy, microstratigraphic description and the like. [5,6]

The paper presents the results of physical-chemical investigations of textile and metallic yarns in two archaeological textiles (sack and stihar), extracted on August 25, 2016 from the tomb of Metropolitan Gavriil Bănulescu-Bodoni from Căpriana Monastery, Republic of Moldova.

Fig.1. *Stihar*

Fig.2. *Sacos*

2. MATERIALS AND METHODS

The purpose of these scientific investigations is to know the composition, structure and establishment of a diagnosis of the observed alterations that determined the state of conservation. The methods used for the scientific investigation of the textile materials studied are:

Macroscopic investigations

Macroscopic investigations refer to the types of physico-chemical and biological degradations of the textile material visible to the naked eye or with a magnifying glass due to microclimate and biological factors.

Photographic analysis (macrophotography, microphotography)

Traditional white light shooting techniques were used, with the light beam placed perpendicularly, using an Olympus digital camera and shooting software corresponding to the Olympus SZX 160 and U500XST2 microscopes. The photographic documentation obtained is used as a support in the interpretation of analytical data.

Optical Microscopy an UV

The microscopical researches have been carried out on an Olympus SZY 160 microscope correlated with program Quick Capture Pro 2.0 software and fluorescence illuminator RFA-16 and a Novex stereomicroscope Ap-8 Euromex at various magnifying powers up to the maximum 500 X.

XRF Spectrometry

We has use of XRF technique to know the elemental composition of the metals from which the objects are made. The experimental measurements were realized using an XRF spectrometer, type Innov X Systems Alpha Series (SUA). The analyzes carried out the presence of filters during the analysis, the absence of vacuum during the analysis, the absence of an inert gas flow.

Spectoscropie FT-IR

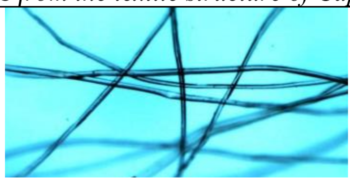
Fourier transform IR spectroscopy was performed with the Vertex 70 Bruker spectrometer, analyzing the composition of corrosion products and colored fibers in the structure of the analyzed archaeological textiles.

3. RESULTS AND DISCUSSIONS

The macroscopic analysis (visual, magnifying glass) found that the two pieces of clothing show the following types of destruction: tears, chamois, bends, stains (green, white, reddish), the fragility of the material, traces of earth and corrosion on metal accessories.

During the research by optical microscopy in incident white light, the presence of 4 types of threads was found: textile threads from fabric, textile threads from embroidery, metallic threads from fabric and metallic threads from embroidery. The textile yarns are made of natural fibers and are of a protein (silk) nature according to the results provided by OM-UV. Simple metal wires are tape or wire type and metal wires helically wound on textile core, tape type and wire type.

***Table 1**. Morphological characterization of textile yarns from the textile structure of Căpriana*

 Textile yarn taken from Sacos	 Silk fiber, UV x160
 Textile thread taken from sack embroidery	 Yellow silk fiber, UV x500
 Textile thread taken from Sacos embroidery	 White silk fiber, UV x500

 Textile yarn taken from velvet Sacos	 Silk fiber, x500
 Textile thread taken from Stihar embroidery	 White silk fiber, UV, x500
 Textile thread taken from Stihar fabric	 Silk fiber, x500

The identification of textile yarns from embroidery and fabric was made based on the longitudinal microscopic appearance of the fibers obtained by defibrating the yarns in ultraviolet light. I noticed that in the case of the metal wire bag, they are in two colors, gold and silver, and in the case of silver, only silver. For the production of textiles, fabrics made of degummed natural silk yarns were used, which under a microscopic appearance have pigmentary inclusions suspected of being caused by active biological attack or traces of it. The presence of metal wires generates mechanical and chemical damage through corrosion products.

The technique of X-ray fluorescence spectrometry is widely used for a first determination of the nature of composite elements in the structure of ecclesiastical textiles.

Table 2. Composition of metal wires and accessories (XRF)

Part name	Sample	**Cu**	**Au**	**Pb**	**Ag**	**Base metal**	**Coating film**
Sacos	Embroidery thread 1	-	-		100	Ag	-
	Embroidery thread 2	-	-	0.10	99.90	Ag	-
	Embroidery thread 3	0.75	-	-	99.25	Ag	-
	Wire gallon 1	1.53	-	-	98.47	Ag	-
	Wire gallon n 2	-	-	0.08	99.92	Ag	-
	Fabric thread 1	1.59	-	-	98.41	Ag	-
	Fabric thread 2	-	-	-	100.00	Ag	-
Stihar	Wire little gallon	-	1.52	13.36	85.12	Ag	Au
	Embroidery thread 1	2.28	2.94		94.78	Ag	Au
	Embroidery thread 2	4.32	-	0.41	95.27	Ag	-

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

According to the results obtained, we identified the following types of metal wires: pure silver wires; silver wires with secondary elements (Pb); silver wires with secondary elements (Cu); silver wires with secondary elements (Cu, Pb); gilded silver threads. The determined elemental compositions indicate that all wires are silver-based and some of the investigated wires are contaminated with oxide and cupric chloride corrosion products.

The spectral analysis in the IR domain of the two textile samples taken in red and green was performed in order to know their nature.

Fig.3. *Silk thread fabric, Sacos.*

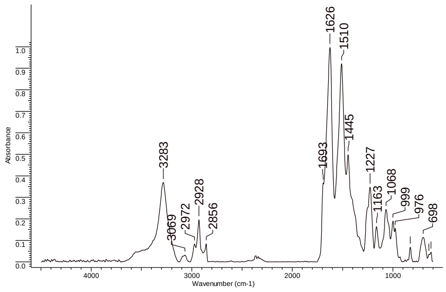


Fig. 4. *FTIR spectrum of green threads*

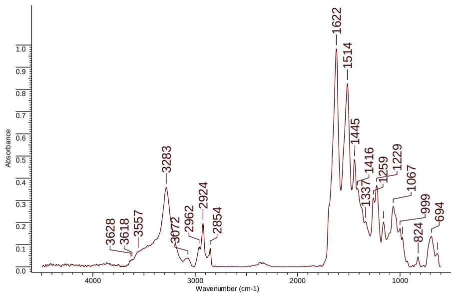


Fig.5. *FTIR spectrum of red threads*

As a result of the results obtained by interpreting the vibration spectra, he observes small variations in the vibration domains of the two samples, green wire and red wire.

Table 3. Results of the FTIR analysis (characteristic bands and their allocation

Green thread	Red thread
3283cm^{-1}; ν NH asymmetric (valence vibration)	3283 cm^{-1}; ν NH asymmetric (valence vibration)
3069 cm^{-1};ν NH symmetric (valence vibration)	3072 cm^{-1}; ν NH symmetric (valence vibration)
2972 cm^{-1}; ν CH (valence vibration)	2962 cm^{-1}; ν CH (valence vibration)
2928 cm^{-1}; ν CH_2 asymmetric (valence vibration)	2924 cm^{-1}; ν CH_2 asymmetric (valence vibration)
2856 cm^{-1};ν CH_2 symmetric (valence vibration)	2854 cm^{-1}; ν CH_2 symmetric (valence vibration)
1626 cm^{-1};δ C=O (deformation vibration) (amide I)	1622 cm^{-1}; δ C=O (deformation vibration) (amide I)
1510 δ NH (deformation vibration) (amide II)	1514 cm^{-1}; δ NH (deformation vibration) (amide II)
1227 cm^{-1}; ν C-O + ν C-N+ ν C-C	1229 cm^{-1}; ν C-O + ν C-N+ ν C-C
1068 cm^{-1}; δ NH	1068 cm^{-1}; δ NH

The presence of the groups -NH and - C = O clearly indicates the protein nature of these fibers, namely natural silk, a result confirmed by the morphological structure determined by OM.

The small differences between the experimental results are probably due to the degree of destruction and the degree of hydration of the protein chain.

4. CONCLUSIONS

The textile threads in the structure of the hierarch's sack and of the styrofoam are made of natural fiber, white silk and slightly yellowish. The metal accessories, the large buttons on the bags are based on Ag-Cu alloy covered with a thin gold envelope, and the small buttons are based on Cu-Ag alloy. The metal threads used in the sack and stitch fabric are based on Ag. At the level of the band-type threads in the braid and the embroidery of the styrum, the presence of a thin film of gold was identified. The determinations were performed in areas where the metal surface was with insignificant destruction in order to avoid errors due to possible corrosion products.

Two main types of metal threads were used in weaving and embroidery, namely threads and strips. Both have also been used in combination with organic yarns to produce more elaborate blended yarns. The wires and strips are wrapped around a fibrous core of plant origin, silk.

Based on their morphological characteristics we found that metal strips belong to two categories and were produced using two different techniques. The first type comprises strips with sharp edges, which have irregular width and variable thickness. These strips were cut from sheets of metal (Ag). The second type of tape was produced by flattening a silver wire. These strips have more rounded edges and a very uniform width along their length. The wrapped metal strips are based on the twisting of the tape around the fibrous core in S or Z formations. Most of the wrapped strips are twisted in an S shape. thread thickness and diameter, as well as the type and color of the organic core.

The presence of a small amount of copper or lead in the wires with a high silver content was probably made to strengthen the metal and to make it cheaper.

REFERENCES

[1] M., Járó, *Metal threads in Historical Textiles* in Molecular and Structural Archaeology: Cosmetic and Therapeutic Chemicals. NATO Science Series, Series II: Mathematics, Physics and Chemistry, G Tsoucaris & J Lipkowski (eds), 117, 2003, p. 163-178.

[2] E., Photos-Jones, A., Hendry, P., Kavasila, *SEM and TEM examination of Byzantine and Post-Byzantine metal threads in Greek Orthodox ecclesiastical textiles*, Archaeometry Issues in Greek Prehistory and Antiquity, Hellenic Society of Archaeometry, Y Bassiakos, E Aloupi & Y Facorellis (eds), Society of Messenian Archaeological Studies, (Athens), 2001, p. 429-434.

[3] N., Vornicu, C., Bibire, *Non-destructive XRF analysis of metals the ecclesiastical garments a 19-20 th century,* Art d'aujourd'hui, patrimoine de demain. Conservation-restauration de l'art contemporain", Colloque SFIIC (13es journées d'études), INP, Paris, 2009, pg 343.

[4] A., Karatzani, *Study and analytical investigation of metal threads from Byzantine/Greek ecclesiastical textiles***,** X-Ray Spectrometry, 4, 37, 2008, p. 410–417.

[5] A.M., Hacke, C.M., Carr, A., Brown, *Characterisation of metal threads in Renaissance tapestries*, Proceedings of Metal , National Museum of Australia Canberra ACT, 2004, p.415-426.

[6] N. A., Sharairi, I. C. A., Sandu, Characterization of Dyeing Techniques of Late 19th Century Ottoman-Style Costumes from the Jordanian Museum of Cultural Heritage, Revista de chimie,vol. 69, 4, 2018, p.901.