Advanced Micro-chemical Investigation of Golden Threads from Romanian Byzantine Embroideries by Micro-Particle Induced X-ray Emission (micro-PIXE)

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In the present study, golden threads from two, apparently identical, medieval epitrachelions considered masterpieces of the Romanian Byzantine embroidery art, were investigated by using Micro-Particle Induced X-ray Emission (micro-PIXE) and optical microscopy. PIXE measurements allowed to accurate identify the elemental composition, distribution of the trace elements, the layered structures (depth profiling) and thicknesses of the gold layer. Useful information for the characterization of the gilded silver threads due to elemental maps concerning the constituent elements spatial distribution in the sample was also obtained.

Keywords: Romanian Byzantine embroideries, metal threads, Micro-Particle Induced X-ray Emission, optical microscopy

Romanian medieval liturgical embroidery worked in the Byzantine traditional technique represents one of the most remarkable artistic fields due to the refinement and expressivity of the drawn figures, execution and the luxurious materials used. The combination of the golden and silver threads, pearls and precious stones with silk in ample religious compositions using a rich variegated palette of colors and characterized by a monumental approach similar to that of icons and wall paintings, gives splendor and harmony to these sumptuous textiles often regarded as needle painted. Worn by priests as church vestments or used during the religious services (epitrachelion, nabedernita, altar door curtain, aer, epimankia, etc.), most of them were produced locally in the embroidery schools of the monasteries. These embroideries were worked in the traditional Byzantine technique of pattern couching, using the cartoon models painted on religious themes similar to those in the mural paintings dating from the 15th to 17th centuries. Epitrachelion, an attribute of priesthood which symbolizes the grace of God that descends onto the priest, is the Orthodox vestment equivalent of the Catholic stole in Western churches, and it hangs straight instead of being crossed over the chest, as in the case of the stole. It ends with tassels that represent the souls of the believers for whom the priest is responsible.

The process of restoring and preserving cultural heritage artifacts needs knowledge of cultural, social and religious life in different old periods of time, requiring multiple and advanced analysis techniques to answer the questions raised by these types of objects [1]. Technical and characterization studies on metal threads from Romanian historical textiles by using modern analytical techniques have been done in our country for more than 15 years [2-5]. In our study, golden threads from two twin liturgical embroideries: Epitrachelion/ Inv. no. 50 (E50), considered Byzantine [6], and Epitrachelion/ Inv. no. 70 (E70) with the Stephan the Great's donor inscription [6], were investigated by using an advanced nuclear analysis method (µ-PIXE) in order to determine their dating. In figure 1 are shown the two epitrachelions as they were presented by Gabriel Millet in his book [7].

Fig.1. Byzantine epitrachelion (left) and Moldavian epitrachelion (right) images as shown in Gabriel Millet's book Broderies religieuses de style byzantin

Until the beginning of this study, both epitrachelions were studied only from the artistic and stylistic point of view and never in regards to their constituent materials and the original technique of production. Furthermore, to our knowledge, no scientific investigation has been done in order to determine the real nature and micro-chemical structure of the precious metal threads used to adorn these very valuable and old embroideries.

Experimental part

Materials and methods

According to the Monastery of Putna historical inventory documents, Epitrachelion E50 was produced in a Byzantine workshop and donated by Stephan the Great to the monastery. Some historians date it back to the 14th century [6-8], and others to the 15th century [9, 10]. Moldavian epitrachelion E70, made between 1472 and 1477, is assumed being produced in the Putna’s Monastery embroidery school and considered to be a copy of the Byzantine epitrachelion E50 [6]. It was worked in the same Byzantine technique and has an inscription of donation.
Embroidery is better kept in the Moldavian epitrachelion, the latter is more colorful, Byzantine epitrachelion has, at the bottom, two extra decorative resemblances striking, also their original manufacturing. The two embroideries iconographic and compositional resemblance is striking, also their original manufacturing. Restoration process their technical differences became clearer, the following being observed: saints faces are well preserved in the Byzantine epitrachelion only, metal thread embroidery is better kept in the Moldavian epitrachelion, the latter is more colorful, Byzantine epitrachelion embroidery design is more complex and Moldavian epitrachelion has, at the bottom, two extra decorative embroidery bands worked in the Byzantine style which frame the donor inscription written with Slavonic characters.

Three different types of samples were analyzed: wires twisted on a dyed silk yarn, strips wrapped around a dyed or undyed silk yarn and wires with no core yarns. The length of the metal thread was of approximately 3-7 mm. From epitrachelion E70 were prelevated the samples: A1 from St. John the Baptist band, A2 - St. Basil halo, A5 - St. Athanasios frame, A6 - St. Athanasios cloak, A7 - St. Athanasios halo and A12-St. Dimitrios cloak, while samples studied from epitrachelion E50 were: P1 from epitrachelion’s frame, P2 - St. George vestment, P3 - blue tassel, original and P4 from the red original tassel.

Optical microscopy examinations in reflected and polarized light, at different magnifications, was performed in order to determine the metal threads technological and morphological characteristics, also the wires diameters (in cross-sections), with a Nikon Eclipse LV100D microscope equipped with a D90 digital camera, a Camera Control Pro 2.0 imaging software and a NIS Elements - BR 3.0 image analysis software. Samples were further analyzed in vacuum by micro-PIXE using a proton beam of 3 MeV energy and a 100-500 pA intensity, directly on the metal thread samples and on cross-sections prepared by embedding the samples in the resin, for obtaining more accurate in-depth information on their micro-chemical structure. PIXE measurements were carried out at the Institute of Nuclear Research of the Hungarian Academy of Science ATOMKI-HAS scanning nuclear microprobe (Debrecen, Hungary) within the European CHARISMA programme and at the Ion Beam Analysis Laboratory 2MV Tandetron accelerator (University of Surrey Ion Beam Centre, UK) within the European SPIRIT programme. PIXE analysis was performed in three different modes: full scan of the sample, selected areas of 500 µm² scan size and point analysis [11, 12]. The raw data was analyzed by deconvolution of the PIXE spectra with the GUPIX code.

Results and discussions

Preliminary optical microscopy measurements showed that the metal strips had a total width of 0.2 - 0.6 mm and a thickness of 0.01 - 0.05 mm, while the wires diameters were of approximately 0.1 - 0.3 mm.

Microscopic examinations of the metal threads from Moldavian epitrachelion showed that, considering their morphological characteristics, they are very different from each other, with the exception of samples A5 and A12 which look similar. Both types of the samples – wires and strips wrapped around a dyed or undyed silk yarn, from Byzantine epitrachelion, was observed to be very used and older than those from the Moldavian epitrachelion. Microscopic images of the samples from both embroideries are shown in figure 2.

Samples P1 and P2 from Byzantine epitrachelion was observed to be twisted wires similar with samples A5 and A12 from the Moldavian epitrachelion. Samples P3 and P4 are cut strips, uneven in width all along their length, and of variable thickness, therefore is supposed to have been produced between 13th and 14th century, according to the historical literature [13]. Sample A5 is a metal wire twisted on a blue silk yarn, similar with samples A12, P1 and P2 which is supposed that lost their colored silk core yarn, the wire being not so tightly wound on silk (fig.2). Metal wires twisted on blue, red, green or purple silk yarns are rare and considered of Byzantine origin (Oxford Dictionary of Byzantium), and from our knowledge, no studies on their characteristics and composition have been carried out so far.

PIXE results on bulk composition and PIXE elemental maps indicated that samples from both epitrachelions were produced from silver of high purity (Ag concentration > 95%), refined by cupellation, and gilded most probably with pure gold. In table 1 are presented the elemental compositions of the samples analyzed with micro-PIXE. PIXE maps have clearly shown the differences and similarities between the metal threads from both epitrachelions, with regards to their morphological and technological characteristics: uneven sizes, different diameters for wires and different widths along the strips, parallel striations from the drawing process, different distribution of the constituent elements indicating different production and gilding technologies. PIXE maps of samples A1, A2, P1 and P3 are presented in figure 3.

Gilding by amalgamation with mercury was an ancient technique employed long ago before the 14th century only in Orient and Byzantium and later on, towards the end of the 15th century also in the Western Europe. Biringuccio refers to a mercury amalgamation technique used in silver extraction from lead ores, but that appears to start expanding in Europe only at the beginning of 16th century [14]. Differences and similarities on composition between samples resulted not only from the presence or absence.
of the trace elements of historical interest like mercury, lead or bismuth, but mainly from the gold content in the silver bulk, considered to be a good indicator for silver dating. Gold concentration in samples P1 and P2 was about 0.5 to 0.6%, and in A5 and A12 of 0.7%, which is in accordance with the values mentioned in literature [15] for the gold content in the ancient early medieval silver (table 1).

Concerning the lead content, no lead was detected in A1, A6, A7, P1 and P2 wires, while in samples A2, A5 and A12, lead concentration was determined to be between 0.1 and 0.2% which is in accordance with the lead content mentioned in the literature for medieval silver obtained by cupellation [15, 16]. In the strips P3 and P4, high amounts of lead of 1.08 and 0.84% was measured, which indicated that different technologies of production may have been used. It could be assumed that these samples may belong to a different older period of time [4, 17] and have a different provenance.

Metal threads from Moldavian epitrachelion are varied and very different from each other, and seem to be recovered and reused from older textiles, possibly of Byzantine origin (samples A1, A2, A5, and A12). Metal threads from Byzantine epitrachelion appear to be older (possible from the 14th century) than those from Moldavian epitrachelion, and older than the period of time that artifact was dated by historians - 15th century, which is in accordance with some historical sources that date it 14th century [6, 8].

The results obtained support the hypothesis according to which the Moldavian epitrachelion would be a copy of the Byzantine epitrachelion [6 - 8]. Furthermore, identification of dye sources such as Kermes vermilio (kermes) and Porphyrophora polonica (Polish carmine scale insect) in Byzantine epitrachelion and the absence of the combination between Kerria lacca (lac dye) and Rubia tinctorum L. (madder) identified in the embroidery thread from the Moldavian epitrachelion, support the hypothesis according to which the Byzantine epitrachelion has a Byzantine origin and does not belong to the epoch of Stephen the Great [17].

For most of the samples, PIXE results estimated with the GUPIX software indicated a non-uniform and variable thickness of the gilding layers for the wires, of about 0.2 to 0.5 µm, that was assumed to be due to the non-homogeneity in the manufacturing process, extensive wear or defects into the gold layer.

In figure 3, PIXE elemental maps for samples P1 and P2 show a relatively high lead and a small copper content in the silver core, high copper and a small lead content in samples A1, A2 and A5, traces of mercury in the gold coating (A1, A2, P3) and a lot of calcium in the silk core yarn (P3). It could be observed that sample A1 have a thin gold layer and a smooth surface compared to A2 and P1. Sample A2 have a smooth thick gold coating on the lower

![Fig. 3. PIXE elemental distribution maps as resulted for samples A1, A2, P1 and P3](http://www.revistadechimie.ro)
half, while the upper half shows evidence of drawing lines on silver suggesting that the Byzantine cold mercury amalgamation technique was used for gilding.

In figure 4 shown the PIXE maps resulting for the cross-sections of the samples, could be clearly seen the distribution of the constituent elements in the silver bulk, gilding layer and the silk core yarn.

Conclusions

The obtained results add useful information for the characterization of the two important, apparently identical, Romanian medieval embroideries, which have never been studied through scientific analytical techniques in the past.

Our results revealed that Byzantine epitrachelion could be a model for the Moldavian epitrachelion, which was made later. In accordance with the written sources, metal threads from Byzantine epitrachelion appear to be older and do not correspond neither to the dating of the object nor to the period of time when the Moldavian epitrachelion was made. Metal threads from the Moldavian epitrachelion are very varied and different from each other, and seem to be reused and retrieved from other, probably more damaged and older, embroideries. Some of the metal threads analyzed have Byzantine provenience and could have been done in the 13th or 14th century.

Micro-beam PIXE combined with microscopy proved to be a powerful tool, capable to reveal new insights into the micro-chemical nature and structure of the very small and extremely thin gold threads for an accurate and complete characterization.

Present paper highlights the complexity of the proposed problem and the large amount of information that expects to be decoded, hidden in the materials in objects of artistic and historical interest.

The aesthetic, stylistic and chemical evolution of the metal threads in time provides reference scales that could be used to interpret technological and artisical changes throughout the centuries and to recognize the physico-chemical characteristics that either are or are not inconsistent with the supposed age of the textile artifact, highlighting the potential anachronisms towards the composition, structure or the metalworking technological methods used in the middle ages in accordance with the medieval written sources or the results previously reported [18, 19].

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