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Comparative analysis of textile metal threads from liturgical vestments and folk costumes in Croatia

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ABSTRACT

Textile is essential for everyday life in all societies. It is used in clothes for protection and warmth but also to indicate class and position, show wealth and social status. Threads from precious metals have also been used in combination with fibres for decoration in order to create luxury fabrics for secular and religious elites.

We performed elemental analysis of 17th to 20th century metal threads from various textile articles of liturgical vestments and festive folk costumes collected in the museums of northern, southern and central Croatian regions.

In order to determine elemental concentrations in threads we performed comparative X-ray Spectroscopy measurements using: (i) Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX) at the Faculty of Textile Technology, (ii) X-ray Fluorescence Spectroscopy (XRF) at the Croatian Conservation Institute and (iii) Particle Induced X-ray Spectroscopy (PIXE) at the Ruđer Bošković Institute Tandem Accelerator Facility using ion micro beam. Rutherford Backscattering Spectroscopy (RBS) was performed as well on selected samples. SEM-EDX investigations of cross-sections along with the surfaces were also performed.

In this work we report and discuss the results obtained by the three X-ray methods and RBS for major (gold, silver, copper) and minor elements on different threads like stripes, wires and “srma” (metal thread wrapped around textile yarn).

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1. Introduction

Metal threads are part of the historical Croatian textiles of great value, used usually for decoration of festive folk costumes and liturgical vestments (Fig. 1). Textiles containing metal threads are inevitable items of cultural, social and religious life, representing something festive, expensive and worth of respect [1]. Primarily, metal threads have been abundant and frequently used on liturgical vestments, giving all the splendour and grandeur to the clothes, worn during the celebration of the holy Mass. Metal threads were also used in the Croatian festive folk costumes worn for the special ceremonial occasions, such as the uniform for the “Sinjska Alka”, an equestrian competition inscribed in the UNESCO Intangible Cultural Heritage list in 2010.

Historically, metal threads were primarily made of gold, silver or copper alloys, but recently aluminium is mostly used. Aluminium has silver shine that can replace and imitate silver and after a special procedure can even get a gold colour [2,3].

The oldest metal threads were narrow stripes, cut from a hammered foil and directly incorporated in textile (Fig. 2a). Later on the technology evolved to production of combined textile metallic yarns and metal wires. Combined textile metallic yarn was made of metal stripes or just one spiral wrapped around the textile yarn, which represent the core, called “srma” (Fig. 2b). This increased flexibility and even allowed different applicability. Metal wires with circular cross section were produced by drawing a metal rod through progressively smaller holes (Fig. 2c) [4–6]. All the three types of metal threads analysed in this study are from various Croatian museums from all regions and include different textile items such as liturgical vestments and folk costumes.

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Fig. 1. Historical textile from which some samples of metal threads were taken: a) Folk costume (apron), Osijek, beginning of the 20th century; b) Liturgical vestment (antependium), Novigrad, 19th century.

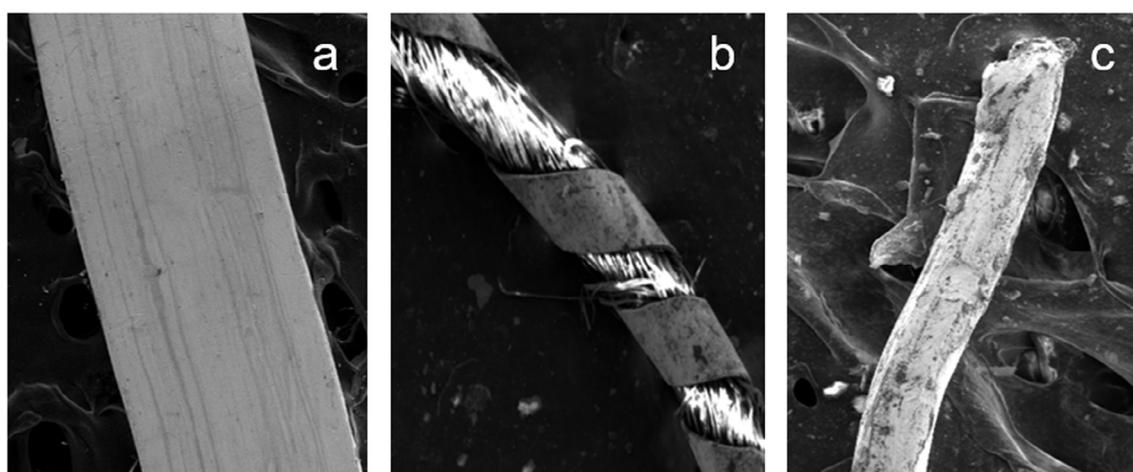


Fig. 2. Backscatter images of three different types of the metal threads investigated by SEM-EDX: a) narrow stripes; b) combined textile metallic yarn ("srma"); c) metal wire.

The study is focused on elemental analysis of the collected samples using X-ray Spectroscopy techniques: (i) Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX) [6–8], (ii) X-ray Fluorescence Spectroscopy (XRF) [9–11] and (iii) Particle Induced X-ray Spectroscopy (PIXE) [12,13], together with Rutherford Backscattering Spectroscopy (RBS). These X-ray Spectroscopy techniques are very common for elemental analysis of cultural heritage samples, while RBS can give additional complementary information on the layered structure of such materials. The result of this study could provide valuable information about the ancient manufacturing techniques and appropriate treatment for cleaning and conservation [3,9,14,15].

2. Experimental

2.1. Material and methods

Forty samples of the metal threads from historical textiles, liturgical vestment and folk costumes were analysed. Samples taken out of the liturgical vestments are from the area of Dalmatia, Central Croatia and North-West Croatia, and folk costumes from the area of Dalmatia and East Croatia. The oldest samples, from 17th and 18th century, are from liturgical vestments of the treasure of the Zagreb Cathedral. Croatian festive folk costumes, such as those related to the "Sinjska Alka", are from the 19th and 20th century [1]. Sampling was performed with special permission of restorers and

conservators, their supervision and cooperation in such way that the valuable historic textile is not damaged.

SEM-EDX analysis was performed at the Faculty of Textile Technology using Tescan MIRA Field Emission (FE) SEM, with the operating voltage 20 kV and working distance 25 mm. The spectra were acquired by Bruker Quantax EDX system with XFlash[®] SDD detector capable to detect elements from boron to uranium. For each sample surface analysis was performed at several points and the average concentrations have been reported. Samples were also measured at cross sections, in which case several points were selected at the central part of each cross section and again the average concentrations have been reported.

XRF measurements were performed at the Croatian Conservation Institute using Artax spectrometer, manufactured by Bruker and equipped with an Rh anode X-ray tube. The voltage used was 50 kV, electron beam current intensity of 0.7 mA, with a collimated X-ray beam of 0.6 mm. X-rays were detected by the XFlash[®] SDD detector, capable to detect elements from potassium to uranium.

PIXE measurements were performed at the Ruđer Bošković Institute ion microprobe facility, which is described in detail elsewhere [16]. The 1 MV Tandetron accelerator provided 2 MeV proton beam which was focused by a triplet magnetic quadrupole lens system to a 2 μm spot size and raster scanned over selected sample areas. A rectangular or squared scan patterns were used with a different size (between $100 \times 100 \mu\text{m}^2$ and $1.3 \times 1.3 \text{mm}^2$) and a variable number of pixels (up to 128×128). PIXE spectra

were collected using Si(Li) detector placed at 135° relative to the beam direction at a distance of approximately 2 cm from the target. The X-ray energy resolution was about 160 eV (for the Mn $K\alpha$ line). Data were digitally recorded with the SPECTOR data acquisition software [17,18] in a list file which can be replayed off-line. Afterwards, collected data were analysed with the GUPIX-Win software [19] in iterative matrix mode and using normalization to 100 wt%. The calibration of the analytical system was tested by measurements of National Institute of Standards & Technology (NIST) standard reference materials SRM[®]620 (soda-lime flat glass) and SRM[®]1107 (UNS 46400 naval brass).

RBS measurements were performed in standard vacuum scattering chamber using a circular 1.6 MeV proton beam of 3 mm in diameter delivered by the 1 MV Tandetron accelerator at the Ruđer Bošković Institute. Backscattered proton spectra were measured by silicon surface barrier detector placed at the scattering angle of 165° . Afterwards, the collected data were analysed with the SIMNRA simulation software [20].

3. Results and discussion

First samples were analysed qualitatively with XRF and quantitatively with SEM-EDX. On some samples high differences between XRF qualitative and SEM-EDX quantitative data were observed. For example, XRF spectrum of a particular sample (S11, wire from the “Sinjska Alka” uniform) showed very high Cu $K\alpha$ intensity and very low Ag (K and L) intensities, while on the same sample SEM-EDX showed very high Ag L X-ray intensity and very low intensity of Cu $K\alpha$ (Fig. 3). Such difference in the results could be attributed to different depth penetration of X-rays (100–200 μm) and electrons (0.5 μm) in metals and a layered structure of such a sample, having in mind that average width was 500–700 μm for investigated metal stripes, 200–400 μm for metal stripes in “srma” and 70–100 μm for wires.

Because of these large deviations, all the samples were additionally measured by micro-PIXE technique with 2 MeV protons having penetration depth in metal of about 20 μm . Figs. 4–6 show comparative results for Au, Ag and Cu concentrations obtained by PIXE and SEM-EDX. The figures show large differences between

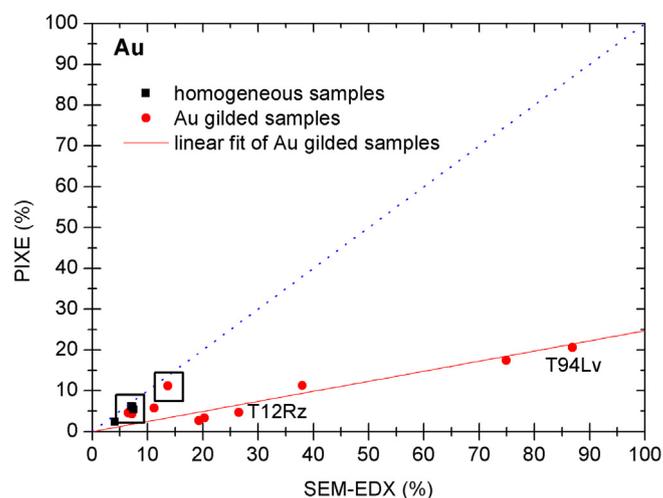


Fig. 4. Comparative results for Au weight concentrations obtained by PIXE and SEM-EDX. Diagonal line would correspond to homogeneous samples. Several Au gilded samples marked within black squares could be characterized as almost homogeneous due to the very thin gilded layer.

PIXE and SEM-EDX concentration results for many samples. Since the analysis was performed on the assumption of homogeneous samples, we can conclude that only those results close to diagonal lines could correspond to actually homogeneous samples. In case of Au (Fig. 4) almost all SEM-EDX results are higher than PIXE results which can be explained by the assumption that Au layer is present above the bulk Ag. The sample with the largest gold concentration of about 90 wt%, as reported by SEM-EDX, would correspond to the gold layer thickness similar to the 20 keV electron range in gold, which is approximately 0.5 μm [21]. Moreover, Troner et al. [8] indicated that the characteristic X-rays are principally generated at a depth of about two-thirds of the maximum penetration depth. Hence, in the first approximation the thickness of gold layer for the other samples can be estimated following the red line at Fig. 4, from the samples with the thinnest Au gilded layer on the left to the ones with the thickest Au gilded layer on the right. The

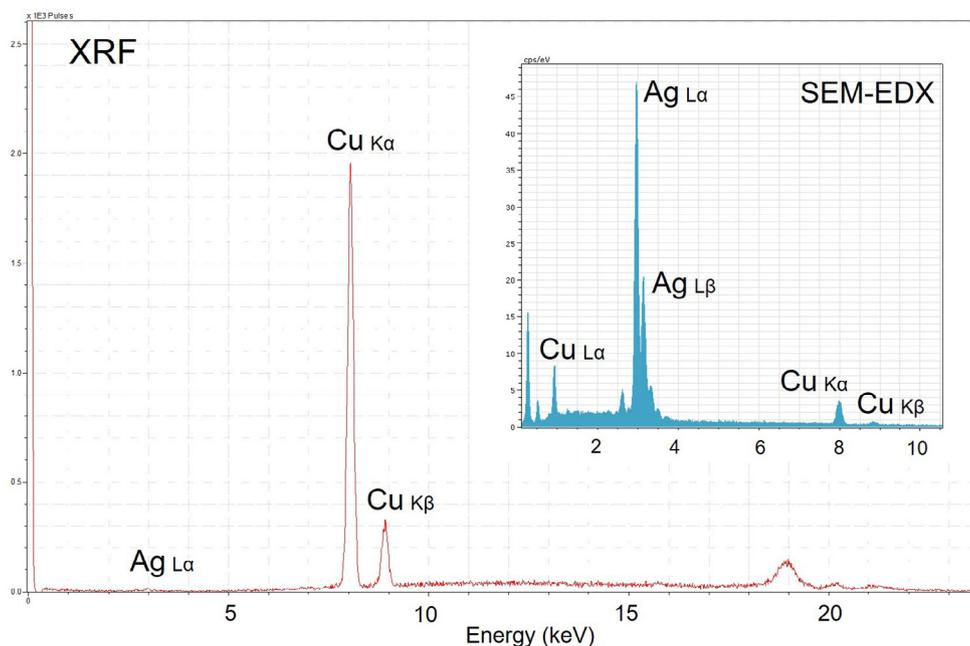


Fig. 3. XRF and SEM-EDX spectra of sample S11.

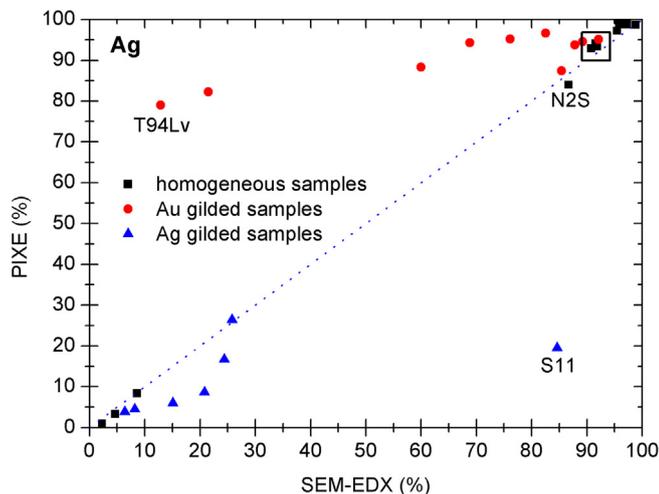


Fig. 5. Comparative results for Ag weight concentrations obtained by PIXE and SEM-EDX. Diagonal line would correspond to homogeneous samples. Four homogeneous samples within black square contain low concentration of Au.

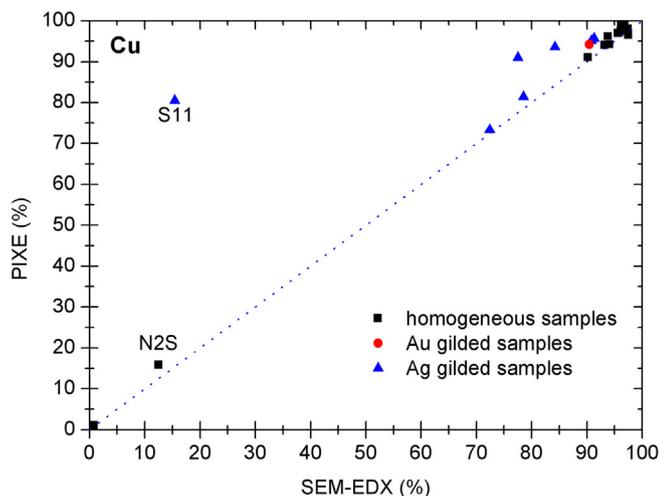


Fig. 6. Comparative results for Cu weight concentrations obtained by PIXE and SEM-EDX. Diagonal line would correspond to homogeneous samples.

assumption of the layered structure of most gold containing samples is also confirmed at Fig. 5 showing increased PIXE concentrations of Ag compared to SEM-EDX results for Au gilded samples. Fig. 6 shows comparative PIXE and SEM-EDX results for Cu. As it can be seen, most samples seem to be homogeneous, but a number of samples shows increased PIXE concentrations, which in combination with Fig. 5 can lead to the conclusion that those are Ag gilded Cu metal threads.

Silver layer thickness in the case of copper cored threads could be estimated from Cu $K\alpha$ and Cu $K\beta$ intensity ratios in related XRF or PIXE spectra. On the sample S11 (marked at Figs. 5 and 6) we performed further GUPIX analysis assuming layered sample with Ag on the top. It resulted with the Ag layer of $314 \mu\text{g}/\text{cm}^2$ (which would correspond to $1.75 \cdot 10^{18}$ at/cm² or about 300 nm of pure silver) on the top of Cu bulk. Following the same procedure, additional GUPIX analysis of the sample T94Lv (narrow metal stripe from liturgical vestment of the treasure of the Zagreb Cathedral) marked at Figs. 4 and 5, resulted with the Au layer of $440 \mu\text{g}/\text{cm}^2$ (which would correspond to $1.34 \cdot 10^{18}$ at/cm² or about 230 nm of pure gold) on the top of Ag bulk. Overall, the surface gold layer existence could be assumed mostly on the silver core threads with

the exception of only one copper core thread (red dot at Fig. 6). At the other hand, the surface silver layer is related exclusively to the copper core threads.

In order to further clarify this issue, we performed additional studies: (i) some samples were cut and cross sections measured with SEM-EDX; (ii) RBS measurements were performed on selected samples.

SEM-EDX analysis of cross sections confirmed our assumptions of the presence of the layered structures on many samples. As illustration, Table 1 shows results obtained for major elements by PIXE, SEM-EDX and SEM-EDX cross section measurements for two already discussed critical samples assuming homogeneous elemental distribution.

SEM images of metal threads cross sections showed that the thickness of the gold and silver layers is not uniform but may vary significantly due to imperfect manufacturing [22], considerable wear, and/or unsuitable cleaning methods. However, in most cross section SEM images the layer structure could not be clearly observed and distinguished from the bulk. Also, SEM revealed small cracks in the metal surface, in particular in the thin gold layers, which is in the agreement with reported correlation between the micro-structure parameters (dislocation density, crystallite size and planar defects) and the metal-threads manufacturing procedures [14].

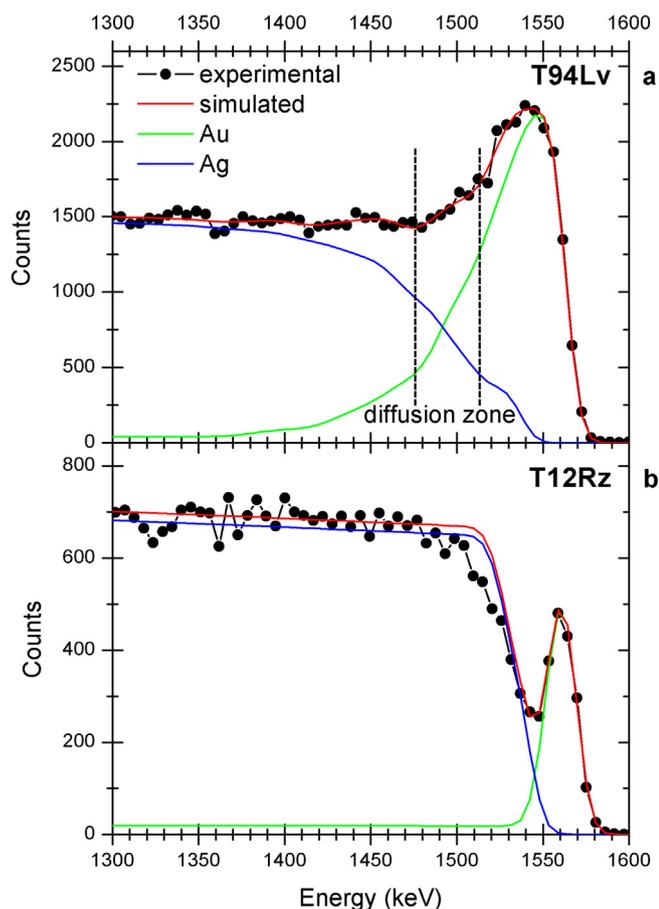
RBS measurements were performed on selected samples to assemble additional information on their layered structure and to determine the thickness of the gilded layer. To ensure better flatness, samples were fixed on the carbon tape. The RBS measurements were performed with 1.6 MeV protons in order to reduce possible contribution of the elastically scattered protons from carbon backing having strong resonance at 1.734 MeV. Fig. 7 shows RBS spectra obtained from two samples taken from liturgical vestment of the treasure of the Zagreb Cathedral, also marked at Fig. 4. Measured RBS spectrum at Fig. 7a corresponds to the sample T94Lv (narrow metal stripe), while Fig. 7b corresponds to the sample T12Rz (metallic yarn from “srma”). According to SIMNRA analysis, the thickness of the gilded layer at T94Lv varies between $1.35 \cdot 10^{18}$ at/cm² and $1.42 \cdot 10^{18}$ at/cm² as measured on both sides of the stripe. Under assumption of pure gold gilded layer that would correspond to the thickness between 230 and 240 nm, confirming previous GUPIX result. However, the SIMNRA simulation showed that the gilded layer was not pure gold but gold-silver alloy. As it can be seen from Fig. 7a, the proper fit of the sample T94Lv required the use of several layers with different Au/Ag concentrations. This is in agreement with the comment of Balta et al. [13] who reported that the interface between gold and silver in such samples is not sharp due to atomic diffusion resulting in silver migrating into the gold layer and vice versa. In that respect, between the surface and the Ag bulk there should be about 100–150 nm thick “diffusion layer” with similar weight concentrations of gold and silver, marked at Fig. 7a as “diffusion zone”. At the other hand, the sample T12Rz has much thinner Au-Ag layer of about 90 nm and atomic diffusion is not prominent. In general, RBS analyses showed that thickness of Au/Ag layers on Ag core of the narrow metal stripes is between 80 and 240 nm, and from 90 to 150 nm for the metallic yarns from “srma”. Also, it is worth to mention that in the case of the metal yarns with thinner gilded layer, SIMNRA simulations resulted with the gilded layer of the approximately same weight concentrations of gold and silver, corresponding to the 12-karat gold.

Regarding the analyses of the homogeneous metal threads, gold is present in only four samples taken from the Split festive folk costumes. Au concentration in these samples, showed at Fig. 4 and marked within black square at Fig. 5, varies between 2 and 8 wt %. Silver containing alloys (Fig. 5) are divided in two main groups: one with low Ag concentrations related to the copper alloys, and

Table 1

Comparative results obtained for major elements by PIXE, SEM-EDX and SEM-EDX cross section measurements assuming homogeneous elemental distribution for two samples.

| Sample | Method | Au (wt%) | Ag (wt%) | Cu (wt%) |
|--------|-----------------------|----------|----------|----------|
| T94 Lv | PIXE | 20.6 | 79.0 | 0.4 |
| | SEM-EDX | 86.9 | 12.9 | 0.2 |
| | SEM-EDX cross section | 0.3 | 99.6 | 0.1 |
| S11 | PIXE | 0 | 19.5 | 80.5 |
| | SEM-EDX | 0 | 84.6 | 15.4 |
| | SEM-EDX cross section | 0 | 0.3 | 99.7 |

**Fig. 7.** RBS spectra obtained on the samples taken from liturgical vestments of the treasure of the Zagreb Cathedral: a) T94 Lv (narrow metal stripe); b) sample T12Rz (metallic yarn from “srma”).

the other representing the silver alloys. This group could be subdivided to the almost pure silver (Ag concentration >98 wt%) and gold containing Ag alloys marked within black square at Fig. 5. One remaining sample contains about 15 wt% of Cu besides the Ag (marked as N2S at Figs. 5 and 6). The similar grouping could be observed for the copper containing alloys. Two distinct groups can be identified at Fig. 6: the one with low Cu concentrations (related to the silver alloys) and the other representing Cu alloys. The second one could be subdivided in almost pure copper (Cu concentration >95 wt%) and the ones with the low Ag and Au concentrations. Between stands the sample N2S. Overall, all homogeneous samples showed very strong correlation between the concentrations of gold, silver and copper as determined by PIXE and SEM-EDX ($R^2 > 0.9$).

Also, in some metal threads several trace elements were quantified by PIXE and SEM-EDX. As example, Zn and Sn were found in the concentrations up to 5 wt%, while Ti and Fe in concentrations less than 0.1 wt%.

4. Conclusion

Selected metal threads from the historical Croatian textiles have been analysed for the first time by the three X-ray methods (SEM-EDX, XRF and PIXE) and RBS. XRF provided fast qualitative analysis for selection of the samples, while SEM-EDX and PIXE delivered complementary quantitative results of the surface and the bulk elemental composition. In addition, RBS gave valuable information on the layered structure of gilded metal threads.

In the case of gold and silver gilded samples, SEM-EDX and PIXE showed diverse results due to different depth penetration in metals and layered structure of the probe used. More reliable analysis of the gilded samples required SEM-EDX measurements of cross sections and RBS analyses as well. The surface gold layer was found mostly on the silver core threads with the exception of only one copper core thread, while the surface silver layer is related exclusively to the copper core threads.

Silver and copper were the most widely used for the homogeneous metal thread production. Only four silver alloys contain gold in rather small concentrations.

Presented analysis of metal threads gave us valuable information about the old manufacturing techniques. For example, the presence of “diffusion layer” between the Au/Ag surface and the Ag bulk in analysed “srma” samples indicates that the possible methods used for gilding were either firegilding or diffusion bonding [13]. Such information is useful for selecting appropriate treatment for cleaning and conservation.

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