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Simple methods for characterization of metals in historical textile threads

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ABSTRACT

Characterization of metal threads on historical textile materials is important for preservation of valuable cultural heritage. Obtained results dictate decisions on cleaning, conservation and restoration steps. The most important part of characterization is chemical analysis of originally applied materials, since this enables understanding the nature of chemical and physical degradation and determines the cleaning methods. Methods applied should be non-destructive and sensitive enough to detect trace elements in small sample amounts. The goal of this research was to describe the most useful procedures for fast and simple determination of specific metals of interest. Therefore we propose application of scanning electron microscopy equipped with EDS detector (SEM-EDS) for sample surface analysis and inductively coupled plasma-optical emission spectroscopy (ICP-OES) for chemical analysis of metals threads. For quality insurance reasons, a comparative method applied for chemical analysis was atomic absorption spectrometry (AAS). This combination of methods has proven to be very useful in analysis of historical samples, since SEM-EDS was a simple and non-destructive method which provided information on chemical composition of sample surfaces, while ICP-OES and AAS enabled the full insight into the average chemical composition of samples. Nevertheless, both ICP-OES and AAS were destructive methods which demanded dissolving of samples prior to the analysis. In this work nine different metal fibers collected from historical textile materials were characterized. Proposed methods enabled obtaining information on sample constitution, morphology, topology and chemical composition.

1. Introduction

The most important step during textile conservation is identification of materials originally applied in order to understand the nature of gradual chemical and physical degradation [1]. The threads applied on historical textile materials were made from metals in combination with vegetable or animal fibers (cotton, silk, wool and flax). Metal fibers were manufactured by drawing a metal wire to the required diameter, or by beating a thin sheet and then cutting to the required thickness [2,3]. The average width of metal strips was between 0.20 and 0.30 mm, and the average thickness varied between 0.005 and 0.030 mm. The metals most commonly used were gold, silver, copper, and their combinations or alloys [3]. The typical metal thread consisting of metal fiber wounded around the textile yarn is shown in Fig. 1.

Dust, soil particles, fats, oils, calcareous deposits and corrosion products of alloying elements can cover the surface of historical material leaving stains and damage of textile material. Additionally, alloying elements will dissolve under inappropriate cleaning procedures causing more significant problems to textile conservators. Therefore the determination of alloying compounds present as minor or trace elements is a crucial step in chemical analysis for preserving valuable historical materials.

While investigating deeply into the nature of historical fibers and metal threads many modern analytical procedures may be applied. The most appreciated are time of flight secondary ion mass spectrometry (ToF-SIMS), inductively coupled plasma-optical emission spectrometry (ICP-OES) and scanning electronic microscope (SEM) [2,4,5]. Since very small changes in the concentration of alloying component have the significant impact on the property of materials, it is crucial to have a high degree of precision while measuring the trace and minor components in the presence of other macro compounds in historical metal fibers. Special problem lays within the fact that valuable golden or silver materials are available for the analysis in very small sample amounts. Secondly, only accurate analytical methods may provide information on different metal corrosion processes which occur during prolonged contact with different physical, chemical and biological agents [6–9]. For simultaneous determination of many metals present in the same sample, inductively coupled plasma optical emission spectrometry

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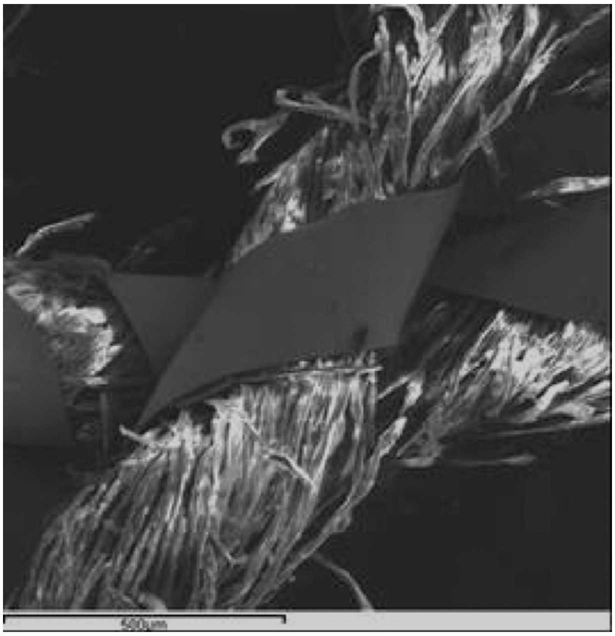

Fig. 1. SEM microphotograph of metal fibers wounded around the historical textile yarn.

is much more appropriate than analytical absorption spectrometry, since AAS is a single element method for metal analysis [10–13]. Secondly, SEM-EDS can be applied as a non-destructive method allowing the sample to be returned to the original material after the analysis [14–17]. The drawback of SEM-EDS is the fact that results present the average chemical composition of only a specific analyzed part of the sample surface [18,19]. Nevertheless, this information is useful in complete characterization of materials, providing the insight into the layer composition, morphology and topology of samples and into the corrosion processes. The combination of SEM-EDS and ICP-OES has been applied for characterization of variety of different metal samples [20–26], but not for the analysis of historical metal threads until now, according to our findings. Some authors have recommended an electron probe micro-analysis using a set of wavelength dispersive spectrometer for metal threads investigation, although the availability and accessibility of such equipment can be a problem [27–32]. Recently, Auger electron spectroscopy (AES) has been applied to characterize the layer structure of some metal threads, but it is also a destructive technique with the inconvenience of demanding ultra-high vacuum [33]. The external differential – PIXE technique is also recommended as an efficient and non-destructive tool for the characterization of the structure of ancient metal threads. In contrast to EDX and XRF, this method allows the detection of the layer structure and, in contrast to AES, it is non-destructive for samples [34]. The condition of investigated samples will depend on the quality of material, natural aging processes and the physical, chemical and biological conditions and pollutants in which they have been in contact to [35]. Therefore, the conservation and restoration of such items is a very complex problem. One of the most critical parts of conservation work is a delicate cleaning step. Many concerns about the safety of the cleaning methods and their long-term effects on metal threads arise during conservation treatment. The biggest concern is that all treatments that involve liquid reagents can produce irreversible changes to the organic fibers inside the metal filaments. Therefore, this is one of the most important and most irreversible processes which has to take into consideration the type of object, the composition of materials and the state of conservation. Materials and methods applied for cleaning which are suitable for metal filaments may be harmful to core yarns or to the ground materials (textile, glass, metal or wood). Therefore a compromise must be made in order to preserve all components of the treated object. Since cleaning of the textile is such a difficult task, new techniques are developing in order to find more appropriate and more efficient methods without causing damage to valuable historical samples. Recently some authors proposed avoiding the wet cleaning and replacing it with a laser cleaning process [36]. Laser has been considered to be a promising cleaning technique because it is a controllable monochromatic energy source which can remove the surface contaminants precisely and selectively [37]. Nevertheless, in all cases the previous chemical characterization and analysis of metal composition is needed. Historical textile materials employing metal's threads are usually in a poorer condition than those which do not contain metals because of the extra stress from the high mass of material and multiplicity of degradation and corrosion processes [38–43].

Therefore the goal of this research was to apply the combination of scanning electron microscopy equipped with the EDS detector (SEM-EDS), atomic absorption spectrometry (AAS) and inductively coupled plasma-optical emission spectroscopy (ICP-OES) for detection of metals in nine different metal items collected from Croatian textile historical materials.

2. Experimental

2.1. Instrumentation

Chemical analysis was performed using an axially viewed Thermo Elemental "IRIS Intrepid II" XSP, Duo (Thermo Electron Corporation). The instrument was equipped with a standard one piece extended torch with a quartz injector tube, autosampler AS ASX-510. The ICP-OES operating parameters were: RF power of 27 MHz, plasma power 1150 W, plasma flow 25.0 L/min, Ar flow 0.5 L/min. Sample introduction system used was a cyclone spray chamber and a concentric nebulizer, with sample flow of 2.40 mL/min and rinse time of 20 s. All the measurements were done in triplicates. For the comparison of the results, a second independent method was applied: metals detected in sample solution by ICP-OES were additionally checked in the same sample solution by flame atomic absorption spectrometer (AAS), AA-6800, Shimadzu. Working parameters of AAS are listed in Table 1 [38]. Scanning electronic microscope "TESCAN VEGA TS5136LS" with the EDS detector was applied for the monitoring of the sample morphology and the determination of major sample components. SEM-EDS instrumen-

Table 1
AAS standard conditions and LODs of Cu, Cr, Mn, Mo, Ni, Si and Sn.

Parameter	Cr	Cu	Mn	Mo[a]	Ni	Si[a]	Sn
λ (nm)	357.9	324.8	279.5	313.3	232.0	251.6	286.3
Slit (nm)	0.7	0.7	0.2	0.7	0.2	0.2	0.7
Relative noise	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Characteristic concentration (μg/mL)	0.078	0.077	0.052	0.67	0.14	2.1	3.2
Linear area (μg/mL)	5.0	5.0	2.0	40	2.0	150.0	400.0
LOD (μg/mL)	0.3	0.15	0.15	4.50	0.60	0.90	15.0

[a] Nitrous oxide/acetylene mixture.

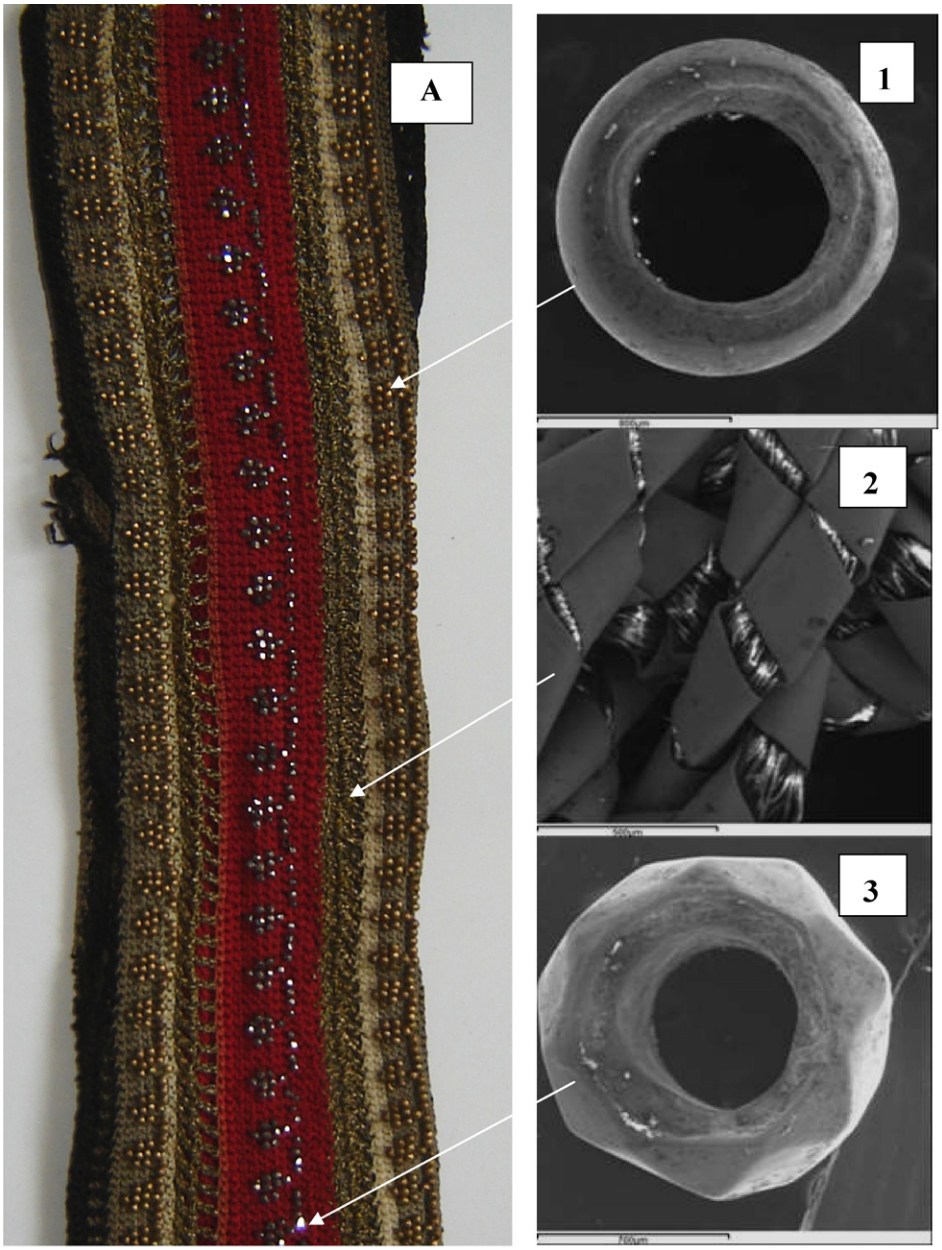

Fig. 2. SEM microphotographs of metal items collected from material A: (1) metal pearl golden colour, (2) metal fiber and (3) metal pearl silver colour.

tal parameters were: working distance of 25 mm, energy 20 eV, magnification 1000–10,000×, detectors used were the back scatter and the detector of secondary electrons, with the collection time of 30 s. The operating parameters of Sputter Coater SC 7620 applied for coating of samples with thin layer of Au/Pd were: power of 230 V (12 A), target Au/Pd, target distance 45 mm, power supply output 800 V, resolution 15 s, pump rate 25 L/min, sputtering rate 6 nm/min, coating thickness 1–20 nm, coating uniformity > 10%, gas medium Ar.

2.2. *Reagents and solutions*

All the reagents (nitric acid) and 1000 μg/mL standards (Al, As, Be, Bi, Ca, Co, Cr, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Si, Sn, Tl) used for this research work were of p.a. grade, supplied by Merck, Darmstadt, Germany and by Perkin Elmer (Cd, Cu, Hg, and Zn). Ultra pure nitric acid supplied by Merck, Darmstadt, Germany and ultra pure water produced by NIROSTA were used in ICP-OES analysis.

2.3. *Samples*

In this work all samples of metal threads were taken from damaged areas of historical textiles, when possibly, normally consisting of threads measuring 5–7 mm in length and in few micrograms per sample (0.00100–0.30000 g of thin metal thread filaments per sample). The historical materials were received for the chemical analysis tanks to the courtesy of two professors from the Faculty of Textile Technology, University of Zagreb, Croatia: Prof. Dr. sc. Ljerka Bokić, and Prof. Dr. sc. Maja Andrassy. The samples are dating from the 18th and 19th century. They were all collected from nine different Croatian historical textiles: national costumes (samples A, C and D), decorative materials (samples B and E) and uniforms (samples F and G). Two different metal items were analyzed: seven metal fibers from samples A to G, and two metal pearls from sample A. Tested materials are presented in Figs. 2–4. They were first studied in order to determine their morphological characteristics (such as type of thread, the twisting of the metal strip, the colour and the ori-

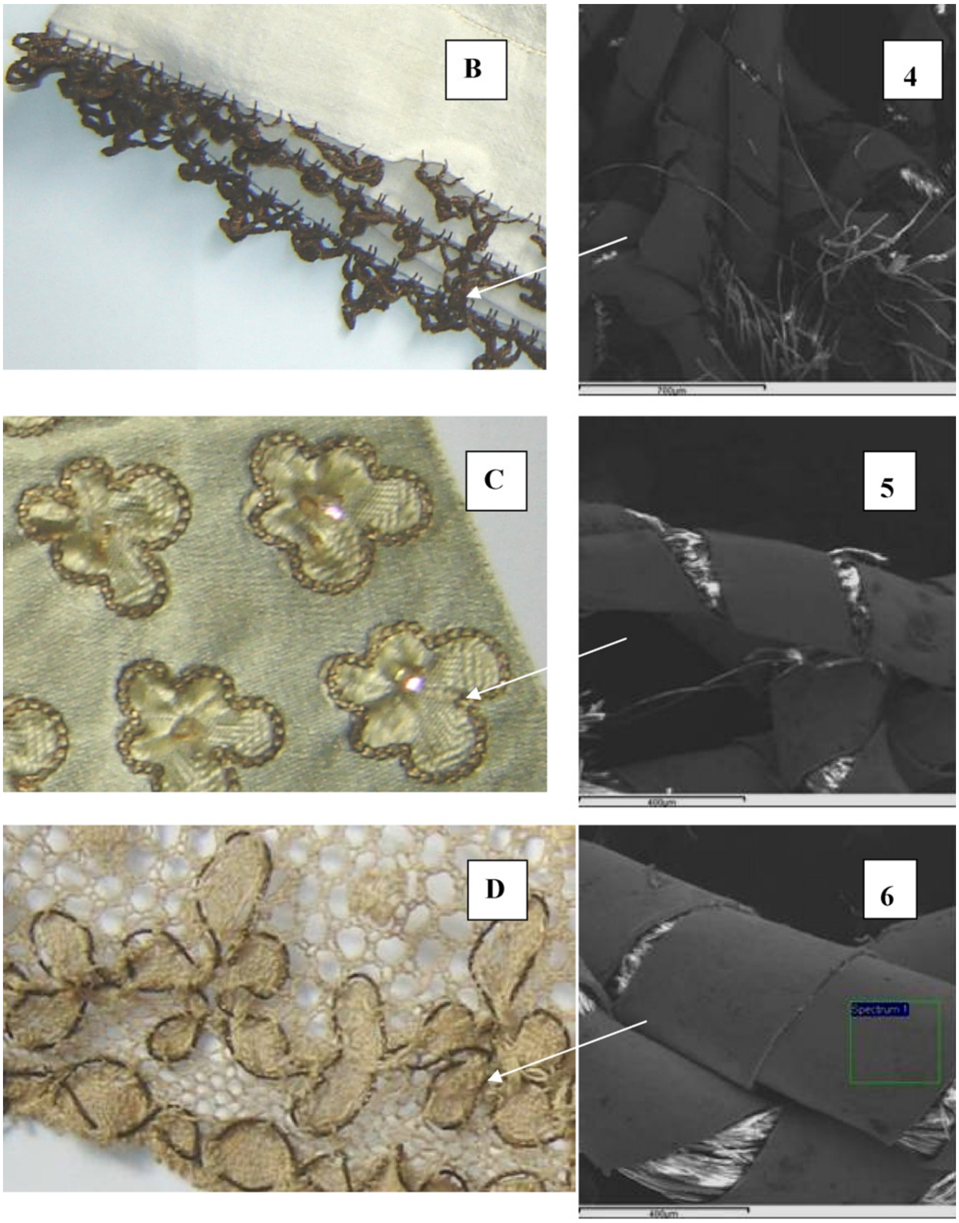

Fig. 3. SEM microphotographs of metal items collected from materials B, C and D.

gin of the inside core yarns). Afterwards they were analyzed by SEM in order to measure the width of the strip and to detect corrosion and degradation processes on metal surfaces. The EDS was used to obtain information on chemical composition of sample surface.

For the ICP-OES and AAS analysis, metal samples were dissolved in 1 M nitric acid. SEM-EDS analysis was performed on metal threads and on the core fibers separately: inner fibers were coated with thin gold/palladium layer by SC7620 Sputter Coater Quorum, and the characterization of threads was done by SEM-EDS. In addition, inside textile cores made of organic natural polymer fibers (cellulose or proteins) were after coating with Au and Pd analyzed by SEM microscopy.

3. Results and discussion

Since only accurate analysis can provide information on chemical composition of metal threads, very important part of analysis was the determination of the limit of detection (LOD). In this work limits of detection for ICP-OES were determined for all elements of interest on several emission lines. The LODs of chosen lines expressed as three times the standard deviation of the blank solution (1 M nitric acid) are presented in Table 2. In the same table, the experimental LODs are compared to the literature data (LOD lit.), and they show the expected disagreement, due to the significant matrix effects. Limits of detection of the AAS method are presented in Table 1.

Table 3 shows the elemental composition of samples investigated obtained after multi-elemental axially viewed ICP-OES and single element AAS analysis. The axial configuration of the ICP-OES was chosen due to many advantages [10–13]. The results of the chemical analysis present an average chemical composition of metal items calculated after ICP-OES and AAS analysis of triplicates. As it can be clearly seen from Table 3, metal samples 1, 2, 4, 5, 6, 7, 8 and 9 collected from historical textiles are copper alloys, while sample 3 is a steel material. All the RSD were in the range of 1.2–3.9%. Unfortunately, both of those methods are destructive and they demand a prior degradation of all samples. The important difference between those two analytical methods is that AAS

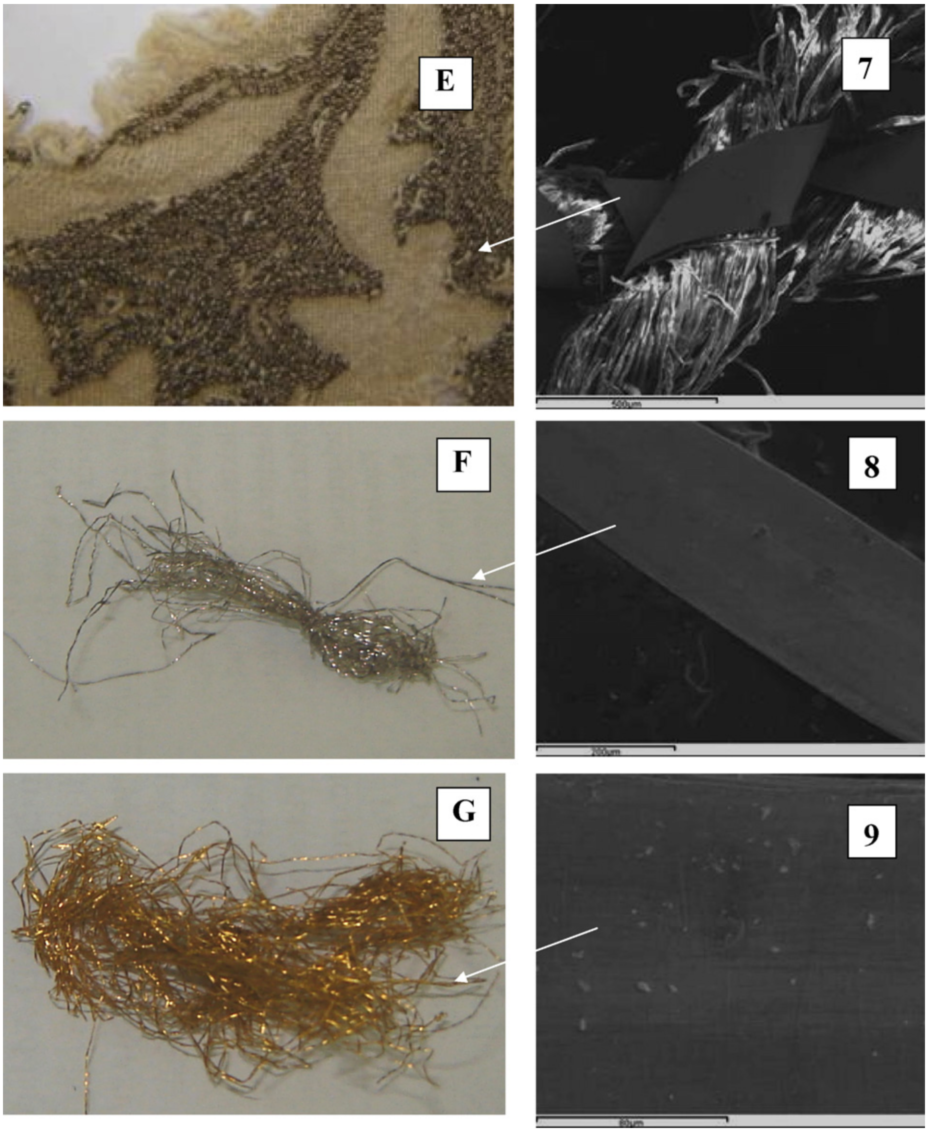

Fig. 4. SEM microphotographs of metal items collected from materials E, F and G.

is a single element method, while ICP-OES is a method for simultaneous determination of many elements in the same sample, which enables fast and precise analysis of alloys. Secondly, limits of detection in ICP-OES are much lower than in AAS, which is extremely important in cases of historical samples in which minor and trace elements have to be determined in very small sample amounts available for the analysis. Therefore, the best choice is to perform a fast prescreening by ICP-OES, and then to confirm the presence of some elements of special interest by independent method like AAS. In cases of more complicated samples which contain traces of analyte, the better choice would be GF-AAS, a method for single element analysis, but with limits of detection lower that in AAS and ICP-OES.

As a contrast to previously mentioned analytical methods (AAS, GF-AAS, ICP-OES) which enable performing a full chemical analysis, scanning electron microscope equipped with the EDS

Table 2
ICP-OES limits of detection of investigated elements on all tested lines, experimentally calculated (LOD) compared to literature data (LOD lit.) [55].

Element	λ (nm)	LOD (mg cm^{-3})	LOD lit. (mg cm^{-3})	Element	λ (nm)	LOD (mg cm^{-3})	LOD lit. (mg cm^{-3})
Al	237.312	9.7	1.0	Mn	257.610	0.6	0.1
Al	396.152	10.1	1.0	Mo	202.030	0.3	0.5
As	193.759	4.6	2.0	Ni	231.604	0.4	0.5
Au	191.964	100.7	1.0	Pb	220.353	3.6	1
Au	191.964	22.4	1.0	Sb	206.833	3.1	2
Bi	223.061	6.2	1.0	Si	212.412	2.3	10
Cd	226.502	0.2	0.1	Sn	189.989	1.5	2.0
Co	228.616	0.3	0.2	V	311.071	3.3	0.5
Cr	205.552	0.3	0.2	W	207.911	5.3	1.0
Cu	324.754	5.4	0.4	W	224.875	0.6	1.0
Fe	259.940	3.2	0.1	Zn	206.200	0.8	0.2

Table 3
Chemical composition of metal items from historical textiles after ICP-OES and AAS analysis expressed in mass percentages (wt%).

Sample	Mass percentages (wt%)											
	Ag	Al	Au	Cu	Fe	Mn	Ni	Pb	Sb	Si	Sn	Zn
1	0.01	0.02	[a]	Rest	0.15	[a]	0.05	0.66	[a]	0.87	0.22	12.9
2	0.12	[a]	0.02	Rest	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]
3	[a]	[a]	[a]	[a]	Rest	[a]	0.03	[a]	[a]	0.95	[a]	[a]
4	0.22	[a]	[a]	Rest	[a]	[a]	[a]	[a]	[a]	1.38	0.02	0.02
5	0.68	[a]	[a]	Rest	[a]	[a]	0.25	0.05	0.05	1.48	[a]	0.10
6	1.20	[a]	[a]	Rest	0.35	0.03	0.29	0.11	[a]	1.03	0.02	0.23
7	0.16	[a]	[a]	Rest	[a]	[a]	[a]	[a]	[a]	0.75	0.64	[a]
8	4.00	[a]	[a]	Rest	[a]	0.14	5.33	0.07	[a]	1.00	0.02	[a]
9	[a]	[a]	9.79	Rest	[a]	0.34	10.7	0.11	[a]	0.92	[a]	0.13

[a] All other elements investigated were below the limits of detection (<LOD).

detector (SEM-EDS) is able to perform an analysis of sample surface [44,45,25]. It is important to emphasize that the electron cloud of SEM-EDS penetrates only into few micrometers of the investigated sample surface. Therefore the results of qualitative and quantitative SEM-EDS analysis cannot be comparable to the results of ICP-OES or AAS. But when all of those results are combined, they provide the full insight into sample chemical composition, morphology and structure. Such information may be very valuable in analysis of historical samples [46–54]. This approach is a novelty in this field, since until now only SEM-EDS analysis was recommended as a non-destructive approach for historical threads analysis. According to our findings it is better to use few micrograms of samples and destroy them in order to have the full insight into the real chemical composition of samples, than to have only SEM-EDS semi-quantitative data (quantitative data of surface of the sample), and then to ruin the sample afterwards during the conservation procedure.

The results of SEM-EDS analysis of metals analyzed in our research are presented in Table 4 and in Fig. 5. SEM-EDS results were sometimes in good agreement with the ICP-OES and AAS average chemical composition results (samples 1, 3, 4, 5, 6 and 7), but there are also exceptions (samples 2, 8 and 9). As was previously mentioned, SEM-EDS analysis is the chemical analysis of a sample surface. Therefore the quantitative SEM-EDS results of samples which have silver of gold layers on the surface of threads will give much higher quantities of those metals, than are present in the average chemical composition obtained after ICP-OES and AAS analysis. Only with samples that have unified chemical composition through their cross-section, SEM-EDS and ICP-OES (AAS) results will be perfectly comparable. In other cases remarkable differences will occur. Very nice example for this is sample 9: if we look closely to the SEM-EDS result we can see that the sample 9 is almost pure gold (69%), and the rest is copper (29.4%) and nickel (1.6%) alloy. But the results of a real average chemical composition obtained by ICP-OES and AAS reveal that gold actually does not overcome 10% (it is 9.8%), and there are also other alloying elements present in the copper alloy other than nickel of 10.7% (manganese 0.34%, lead 0.11%, silica 0.9% and zinc 0.13%). This can additionally be explained when we look closely to the SEM microphotograph of the sample, which reveals a thin gilded layer on the surface of a copper metal thread. The same situation occurs with sample 2 (Cu alloy with Au and Ag outer layers) and sample 8 (Cu alloy with Ag layer on the surface of the thread).

From the presented results of analyzed samples it can be clearly seen that the combination of SEM-EDS and ICP-OES is extremely useful in the analysis of valuable historical samples. The results of ICP-OES and SEM-EDS should be combined in order to obtain a complete picture of the sample investigated. This statement can be confirmed by the analysis of reference materials. For the purpose of quality assurance, two reference materials were analyzed by SEM-EDS after ICP-OES and AAS chemical analysis: a pure copper sample, and a silver alloy containing defined amounts of copper and lead. Reference materials were analyzed 11 times (the same as

Table 4
SEM-EDS results expressed in mass percentages (wt%), $n = 11$.

Sample	Mass percentages (wt%)						
	Ag	Al	Au	Cu	Fe	Ni	Zn
1	–	4.03	15.67	Rest	–	–	11.97
2	82.99	–	17.01	–	–	–	–
3	–	–	–	0.15	Rest	–	–
4	2.02	–	2.72	Rest	–	–	–
5	6.34	–	–	Rest	–	–	–
6	15.54	–	–	84.46	–	–	–
7	–	–	–	100.0	–	–	–
8	45.96	–	–	45.91	–	3.03	–
9	–	–	68.97	29.43	–	1.60	–

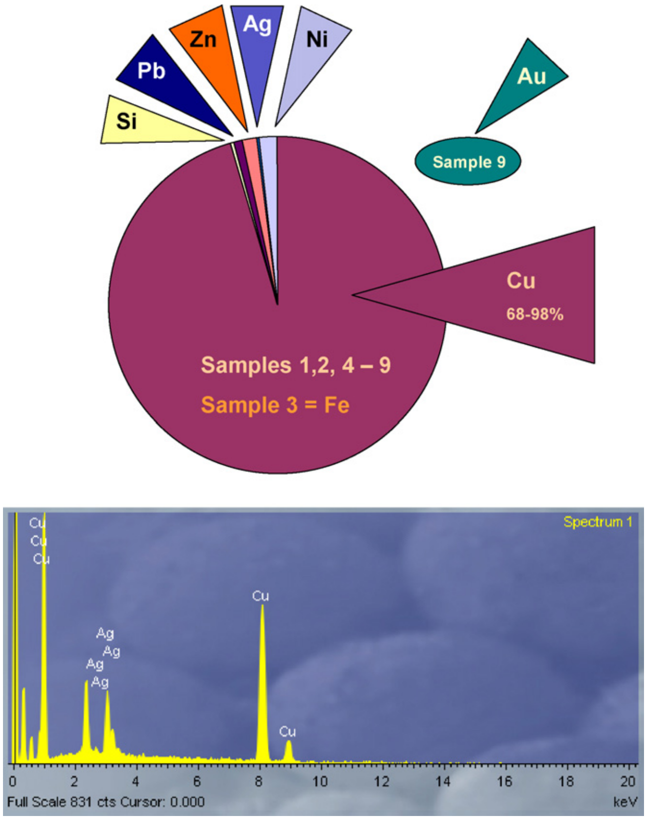

Fig. 5. The average presentation of SEM-EDS results of historical samples and the typical SEM-EDS spectra of sample 6.

Sample description

SILK, Historical material A;
Metal items analysed:
1- metal pearl (Cu),
2 - thread (Cu, Ag),
3 - metal pearl (Fe)

SILK, Historical material B;
Metal items analysed:
4- thread (Cu, Ag)

FLAX, Historical material C;
Metal items analysed:
5 - thread (Cu, Ag)

FLAX, Historical material D;
Metal items analysed:
6 - thread (Cu, Ag)

COTTON, Historical material E;
Metal items analysed:
7- thread (Cu, Ag)

COTTON, Historical material F;
Metal items analysed:
8- thread (Cu, Ag)

COTTON, Historical material G;
Metal items analysed:
9- thread (Cu, Au)

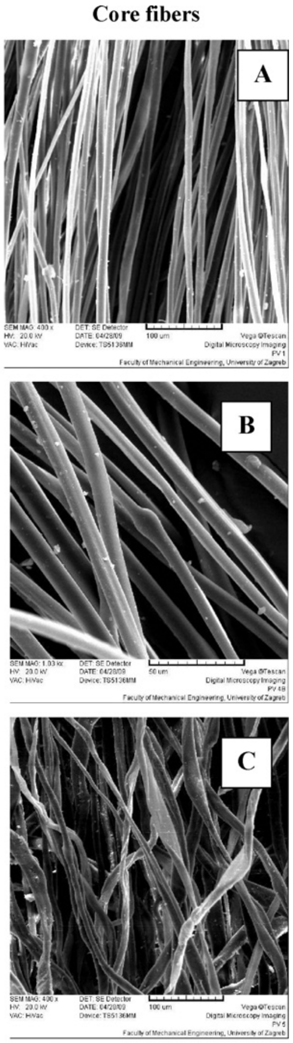

Fig. 6. SEM microphotographs of inside core yarns of textile materials, 400×. A: silk from samples 1 and 2; B: flax from samples 3 and 4; C: cotton from samples 5 to 7.

the original historical samples), and their RSD were much better due to the uniformity of the alloys (up to 0.2%).

In this paper SEM was additionally applied for the identification of textile fiber yarns in the core of samples. Such analysis enables identification of the present fiber. In order to obtain clear and nice figures, the textile fibers were previously pre-coated with a thin layer of Au and Pd. The results are shown in Fig. 6. As it can be clearly seen from this figure, the textile fibers which were present in the core of metal threads were made of silk (samples 1–2), flax (samples 3–4) and cotton (sample 5–7).

4. Conclusions

Characterization of metal items on historical textile is important part in preservation of historical and cultural heritage. Corrosion products of alloying elements covering the surface of historical material can leave stains, but in some cases can even cause degradation and damage to valuable historical material. Additionally, alloying elements present as minor or trace compounds in the alloy can dissolve under inappropriate cleaning procedures and will cause more degradation and staining. Therefore the chemical analysis and determination of alloying compounds is crucial step in preserving valuable historical materials. This work showed that inductively coupled plasma-optical emission spectrometry and scanning electron microscope equipped with EDS detector may be easily applied in this purpose. ICP-OES can be recommended as a choice for multi-elemental determination of metals in sample solutions with high precision. It offered the possibility of determining the trace elements and the bulk elements in the same sample. SEM-EDS analysis showed the possibility of monitoring different coatings on metal samples, detecting their dimensions and performing the elemental EDS analysis of different components. The combination of both methods enabled the complete characterization of historical metal fibers.

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