PRELIMINARY IN-SITU STUDY OF THREE FLAGS FROM THE NATIONAL HISTORICAL MUSEUM, WITH X-RAY FLUORESCENCE

OLTA ÇAKAJ[1], ERANDA GJEÇI[1] , FREDERIK STAMATI[2]

[1]Departmet of Physics, Faculty of Natural Sciences, University of Tirana

[2]National Historical Museum, Tirana

e-mail: olta.cakaj@fshn.edu.al

Abstract

The objects of this study are three flags from the National Historical Museum. The renaissance çeta flag, one-year Independence's anniversary (28.11.1913) flag and the "Dëshira" (Desire) Albanian society in Sofia flag needed immediate restoration and this process begins with the chemical elemental analysis of the flags' fabric. To complete this task, for the first time in Albania, a non-destructive in-situ μ-XRF device from the Department of Physics was used. The major elements in these flags resulted Fe, Sb, Sn, Cu, while Zn, Ni and Pb were detected in quantities less than 10%. A distinct element of the "Dëshira" ("Desire") Albanian society flag's fringes is Au, giving them the characteristic yellow colour; while the high percentage of Ag in the letters cannot fully originate from the device target, making it a possible element of the sewing threads.

Key words**:** *Flag, Albania, μ-XRF, non-destructive in-situ analysis, restoration.*

Përmbledhje

Në qendër të këtij studimi janë tre flamuj nga Muzeu Historik Kombëtar. Flamuri i çetave rilindase, i një-vjetorit të Pavarësisë (28.11.1913) dhe ai i shoqërisë shqiptare "Dëshira" në Sofie kishin nevojë të menjëhershme për restaurim dhe ky proces nis me analizën e elementëve kimik të copës së flamujve. Për të realizuar këtë detyrë, për here të pare në Shqipëri, u përdor pajisja jo shkatërruese e analizës μ-FRX në vend, nga Departamenti i Fizikës.

Elementët kryesorë (maxhorë, mbi 10%) në këta flamuj rezultuan Fe, Sb, Sn, Cu, ndërsa Zn, Ni dhe Pb u detektuan në sasi më të vogla se 10%. Një element dallues i thekëve të flamurit të shoqërisë shqiptare "Dëshira" është Au, i cili i jep atyre ngjyrën e verdhë karakteristike. Ndërsa përqindja e lartë e Ag tek shkronjat nuk mund të vijë plotësisht nga target-i i pajisjes, duke e bërë atë një element të mundshëm të fijeve të qepjes.

Fjalë kyçe: *Flamur, Shqipëri, μ-FRX, analizë jo shkatërruese në vend, restaurim.*

Introduction

Flags have been used all over the world for thousands of years to identify people, places, cultures, and beliefs. From earliest times, cloth banners were used in the East. However, in the West, the first flaglike objects were vanilloids, carved staffs used to protect and bring victory to the bearer. The soldiers of ancient Rome, for example, carried standards ornamented with eagles. Later, in the XII and XIII centuries, the Christian crusaders introduced banners to identify their armies in battle. In particular, they used the Christian cross, which today appears on European flags in various guises (as the St. George cross, the saltire, the Greek cross, the off-centre Scandinavian cross, etc).

Islam also has a long history of flags, dating back to its earliest founding dynasties: red for the Khawarij; white for the Umayyad; black for the Abbasid; and green for the Fatimid (Islamic tribes / dynasties). Later, just as the cross had been used to rally Christendom, the crescent was displayed to unite the Muslim world. Today, the symbol of the crescent, and the ancient dynastic colours of Islam, still dominate the flags of the Arab nations.

In medieval Europe, banners, pennants, and coats of arms were used to identify monarchs, families, cities, and regions. Many of these heraldic designs still appear on European flags. But it was not until the XVII century that official national flags began to emerge. Some were the result of political unions, such as the Union Flag (also called the Union Jack) of Great Britain, adopted in 1606. But many had their origins in banners of political groups fighting for nationalist causes. The most famous of these is the tricolour, which became a

powerful symbol of freedom during the French Revolution of 1789, and since then has influenced the design of countless national flags across the globe.

From the XVIII century onward, many countries in all continents fought to free themselves from centuries of colonial rule by the Western European nations. In the XIX century, new-born South American republics celebrated their new-found freedom with flags that reflected both their past struggles and their optimism for the future. In the XX century, many former British colonies achieved independence; some retained the Union Jack on their flags and others created vibrant new designs based on their indigenous cultures.

Today, the flags of the world provide a fascinating document of each country's national identity: from past struggles to current political alliances; beliefs, whether religious or secular; even art and culture. For example, in Eastern Europe, we find that flag designs are often based around the colours red, blue, and white, which date back to the pre-Communist Russian tricolour, revived again after the collapse of the Union of Soviet Socialist Republics. In Arabic countries, the design of a white or red crescent moon and stars on a green background is prevalent, referring to Islamic religious beliefs in this part of the world. And in Africa, during the 1960s when many new flags were established as countries became independent, various designs featuring the colours red, yellow, and green, remind us of Africa's history of resistance to colonialism. (Prendi, 1982; Crampton, 1989; Edelman, 1991; Greig, 2015)

Caring historical and symbolic importance, the flags of this study needed immediate restauration at the National Historical Museum. In order for this restoring process to be in accordance with the flag's chemical composition, due to production materials and their degradation, the non-destructive in-situ μ-XRF (micro X-ray fluorescence) analysis were irreplaceable. In this case, two conditions were mandatory, the flags should not get damaged and the metal elements should be determined without sampling. XRF meet both conditions, unlike the other spectroscopic methods such as XRD (X-ray diffractometry), FTIR (Fourier-transform infrared spectroscopy), Raman spectroscopy, etc. Publications about chemical analysis of flags with physical methods are very few, in this way this article can be used as a guide to other case studies. (Nature Publishing Group, 1960; Carter, 1978; Potts & West, 2008; Muthu, 2017; Berns, 2019; Vilá et al, 2020)

Materials and methods

There are three flags at the centre of this study, conserved at the National Historical Museum. The flag of the renaissance çeta, the flag of one-year Independence's anniversary (28.11.1913) and the flag of "Dëshira" (desire) Albanian society in Sofia had immediate need to be restored in order for the degradation process to be stopped. The first step to archive this is the metal elements analysis with non-destructive in-situ μ-XRF. The measurable elements of the μ-XRF device are from Mg to U, 1ppm limit of detection, 1ppm-99.999% analysis range, 20 sec test time used in this study (up to 60 sec for this device), 128eV energy resolution, fast SDD detector, 9000mAh rechargeable lithium battery-up to 12 hours work time battery. (Nature Publishing Group, 1960; Carter, 1978; Potts & West, 2008; Vilá et al, 2020)

The flag of the renaissance çeta (patriotic squads) was taken from the Historical Museum of Erseka in 1981 to be exhibited in the National Historical Museum (figure 1a). According to the ethnographer, Abas Dojaka, this flag could have belonged to Mihal Grameno's or Petro Nini Luarasi's çeta.

The flag of the one-year Independence's anniversary was taken from the Dedej masjid in Tirana, during the time when all religious institutions were closed (figure 1b, photo of flag and its analysis). Since then, it was kept in the Institute of History-Linguistics' ethnographic fund, until it was transferred in the National Historical Museum in 1981. Based on its writings, linguist think it was used in the area between Tirana and Mat river. In the Dedej masjid the flag was placed in a frame and hung on the wall, where the lower part was discoloured and damaged from the sun. There is no official documentation of both these flags' origin.

During the last years of the XIX century the Albanian patriotic activities in Sofia reached a political and spiritual peak, with the formation of "Dëshira" ("Desire") society on January 1, 1893 (figure 2). The first symbol of this society was its name, the second its official foundation on August 15, 1896 (the Saint Maria day) and the third one was the society's flag. In 1904 the Albanians living in Sofia were asked to contribute in order to cover the flag's production cost. For this purpose, 45 gold napoleons were collected; although there is no documentation about the flag's designer, Polikseni Luarasi was the one who embroidered it in silk (1.5kg weight).

The flag has the spear socket on the left side and eight threads for hanging it on a rod on the upper side. Its field is divided into two equal parts, one red and the other white according to literature but in reality, the colours have charged into creamy yellow and beige. The idea of the two fields was given by the Bulgarian government. Red is the national colour symbol, while white is for education. Today's official two-headed eagle was embroidered in the middle of the flag. At that time, the eagle form was not officially approved among patriots, still under the influence of Turkey, everyone composed it according to their idea of greatness. Yellow and heavy fringes hanged on the flag's sides which, together with two tassels on top, are considered to be golden. Under the eagle was written with yellow and bright metallic threads: *SHOQERIA E SHQIPETARVET DESHIRE; FILLUAR ME 1 KOLLOZHEG 1893 NE SOFJE*. In 1930, a representative delegation of the Albanian society "Dëshira" came to Tirana from Sofia, bringing along the flag, handing it over to King Zog, whom ordered the donation of the flag to the National Historical Museum. The representative delegation followed the itinerary Bilisht - Korçë - Librazhd - Elbasan - Durrës, arriving in Tirana on March 28 and being received by King Zog on March 31. The event was covered in various periodicals such as "Gazeta e Korçës" and "Gazeta Shqipëtare".

a) 

b) 

b) 

Figure 1. Photo of the: a) renaissance çeta's flag, b) one-year Independence's anniversary flag (b) below, while being analysed).

Figure 2. Photo of "Dëshira" (desire) Albanian society in Sofia flag.

On table 1, the flags' dimensions are listed. These three flags were produced using silk.

Table 1. The three silk flags of this study and their dimensions.

Flag	Dimensions (width x height)
The flag of the renaissance çeta	75cm x 65cm (+10cm fringes)
The flag of one-year Independence's anniversary (28.11.1913)	65cm x 55cm
The flag of "Dëshira" (desire) Albanian society in Sofia	110cm (+8cm fringes) x 100cm (+2□8cm fringes)

Silk is composed by protein fibres and is the strongest natural textile in the world. This is one of the main reasons why this material was used in the flags' production while the threads used to sew the flags are a good indicator of their historical period. The main damage sources of a flag's degradation are wind, light exposure, temperature and humidity fluctuations, various pests.

Human used wild silk in order to produce basic fabrics while cultivation of domestic silk dates in China back in 6500 B.C. Silk was highly prized by Westerners as far back as Roman times but the popularity of this rare and expensive substance only grew during the Medieval period. By the XI century A.D., silk production was widespread throughout Europe. The thickness of silk fibres' is 8-15 μm; elongation until rupture is 25%, while in wet conditions fibres expand up to 32% before breaking.

Silk is composed of:

- Fibroin, a complex protein made up of long chains of amino acids including glycine, alanine, and serine; approximately 75% of silk weight.
- Ash of silk fibroin, around 0.5%.
- Sericin, acts as glue to hold the fibroin fibres together; approximately 22.5% of silk weight.
- Fat and wax; approximately 1.5%.
- Mineral salts containing Ca, K, Fe; approximately 0.5% of silk weight.

Fibroin and sericin give silk its desired physical and chemical properties, such as mechanical strength, smoothness and capacity to reflect light. (Lambert & Wilson, 2016; Muthu, 2017; Berns, 2019)

Results and discussions

In figure 3 and tables 2, 3, 4 the results obtained with the μ-XRF device are presented, correspondently the red field spectre analysed in the third flag and the chemical composition along with the standard deviations for all flags.

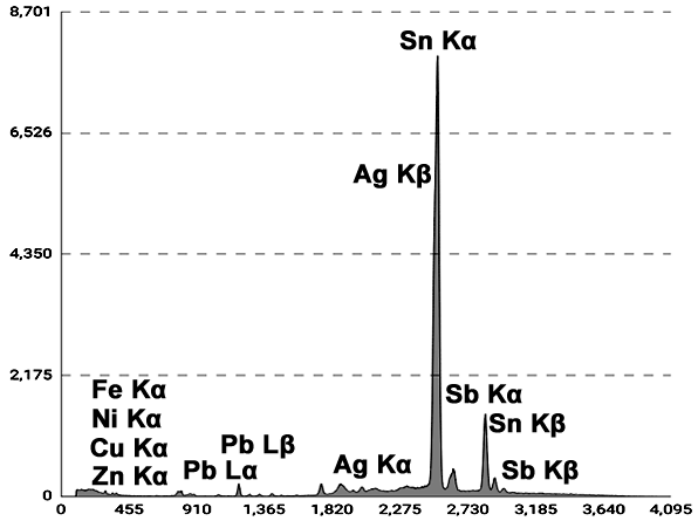


Figure 3. The μ-XRF spectra of red field analysed in the "Dëshira" (desire) Albanian society flag.

Table 2. μ-XRF results with standard deviations of different components on the renaissance çeta's flag; Fe, Sb, Cu, Ag, Sn, Zn, Ni, and Pb.

Analysed spots	Red field	Eagle	Black fringes	Red fringes	Primer
Fe (%)	48±1.5	33.1±1.7	48.1±1.9	55.6±2.1	48.9±1.8
Sb (%)	34.2±1.3	46±2.1	34.6±1.1	22.2±1.1	31.9±1.5

Cu (%)	2.1±0.03	2.7±0.02	2±0.03	3.2±0.04	2.4±0.03
Ag (%)	5±0.2	5.7±0.2	5.3±0.2	4.7±0.3	5.4±0.2
Sn (%)	5.7±0.2	8±0.7	6.6±0.2	3.6±0.09	5.9±0.2
Zn (%)	2.4±0.05	3.9±0.03	1.1±0.02	5.2±0.1	2.8±0.06
Ni (%)	2.6±0.08	0.6±0.01	2.3±0.07	4.4±0.16	2.7±0.08
Pb (%)	-	-	-	1.1±0.03	-

Table 3. μ-XRF results with standard deviations of different components on the one-year Independence's anniversary flag; Fe, Sb, Cu, Ag, Sn, Zn and Ni.

Analysed spots	**Red field**	**Eagle**	**Eagle's beak**	**Primer**
Fe (%)	46.3±1.3	34±1.6	43.9±1.2	52.5±1.8
Sb (%)	39.4±1.2	52.4±1.9	43.6±1.2	30.9±1.1
Cu (%)	2.1±0.03	2.3±0.02	1.9±0.03	3±0.04
Ag (%)	3.3±0.2	3.8±0.1	3.4±0.2	3.6±0.2
Sn (%)	3.1±0.01	4.8±0.1	3.6±0.1	3.2±0.02
Zn (%)	2.8±0.06	2.5±0.02	1.5±0.02	3.4±0.09
Ni (%)	3±0.1	0.2±0.01	2.1±0.06	3.4±0.1

Table 4. μ-XRF results with standard deviations of different components (divided into three sections) on the "Dëshira" ("Desire") Albanian society's flag; Fe, Sb, Cu, Ag, Sn, Zn, Ni, Pb and Au.

Analysed spots	**Yellow fringes**	**Writing**	**Red field**	**Primer under red field**	**Black eagle**

Fe (%)	-	12.4±0.7	29.3±1.5	32.2±1.9	64±2.4
Sb (%)	19.1±0.9	0.6±0.01	3.5±0.2	0.8±0.01	2.4±0.1
Cu (%)	55±1.3	0.5±0.01	0.7±0.01	6.1±0.4	1.4±0.01
Ag (%)	4.8±0.2	77±2.3	4±0.1	4.6±0.3	3.9±0.1
Sn (%)	-	8.2±0.2	59.2±1.1	51.6±2.1	27±1.3
Zn (%)	-	0.4±0.01	1.6±0.04	1.9±0.03	0.7±0.01
Ni (%)	-	0.5±0.02	1.4±0.05	1.8±0.07	0.2±0.01
Pb (%)	-	0.4±0.01	0.3±0.01	1±0.02	0.4±0.01
Au (%)	21.1±1	-	-	-	-

The above tables show the analysis of the main parts of each flag. The results of other elements analysed in the third flag are as follow:

- the white fabric under the red field, the white field, the primer under the white field and the white primer had a variation of Fe from 21.7% to 29.7%, Sn from 22.6% to 44.1% and Cu from 19% to 39.7%; other elements such as Sb, Zn, Ni and Pb were detected in less than 2%;
- the various elements of the eagle, such as its claws and beak, different grey parts of the its wing, contained Fe 24.7% - 60.7%, Sn 29.2% - 63.1%, Sb 4% - 7.5% and less than 3.3% of Cu, Zn, Ni, Pb.

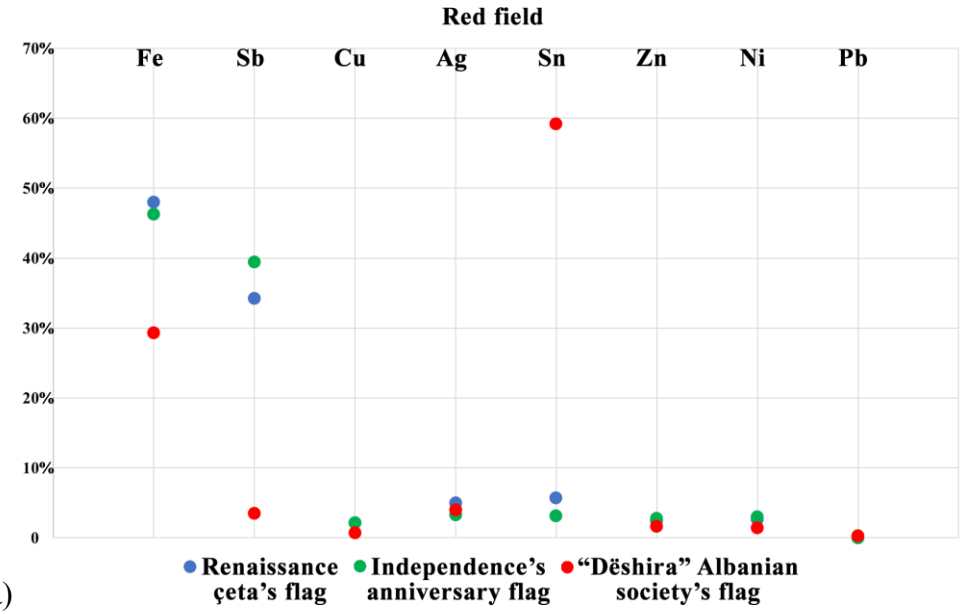
Non-destructive in-situ μ-XRF is an irreplaceable analytical method for culture heritage objects. From the above results both the renaissance çeta and the on-year Independence's anniversary flag contain elements above 10% such as Fe, Sb and Cu, Sn, Zn, Ni with a percentage below 10%. In the red fringes of the firs flag also Pb was detected with a concentration of 1.1% ± 0.03%.

In the case of the "Dëshira" ("Desire") Albanian society flag the elements with a content above 10% are Fe, Sn and Cu only in the case of the white field, white primer, white fabric under red field and primer under white field. The elements resulting with a percentage below 10% are Sb, Zn, Ni and Pb. The

fringes are composed by Cu, Au and Sb while the letters on the flag contain Ag, Fe, Sn as major elements and Sb, Cu, Zn, Ni, Pb as minor ones.

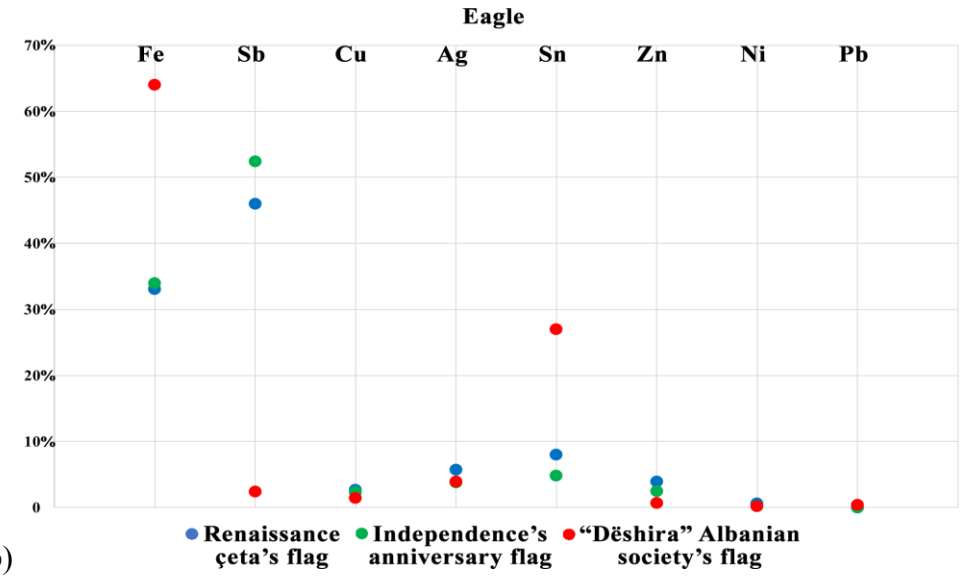
Ag spectra lines come from the μ-XRF device target, but it can also originate from the flag's fabric. This cannot be distinguished in the case of the detected percentage between 3 and 6%. (Potts, 2008)

Figure 4 a), b), c), show the composition comparison (Fe, Sb, Cu, Ag, Sn, Zn, Ni, Pb) between the red field, the eagle and the primer for all flags.



a)

b)



c)

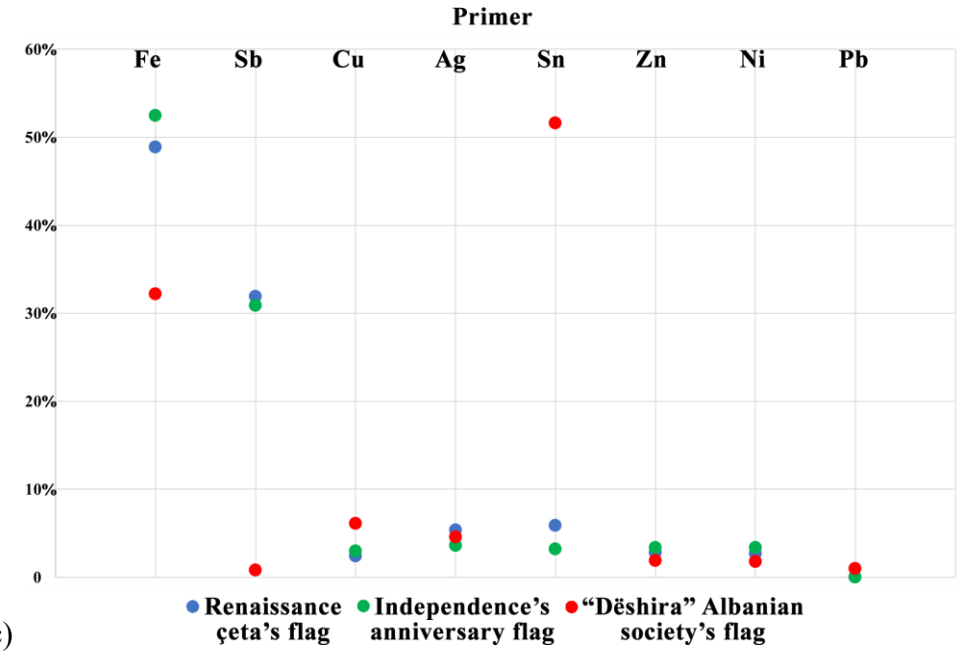


Figure 4. The composition comparison (Fe, Sb, Cu, Ag, Sn, Zn, Ni, Pb) between the red field, the eagle and the primer for all flags.

According to the graphics of figure 4, the variation in Fe, Sb and Sn percentages in the red field, eagle and primer are easily visible. Being the main detectable elements of the above flags' parts, this difference in percentages can provide information regarding the various materials and production techniques used, taking into account the different flags' origin.

One basic component of animal fibres, such as silk, is amino acid which contains the (NH□) and (COOH) groups, all elements non-detectable with the μ-XRF device. Elements such as Fe, Sb, Sn, Cu, Au, Ag, Zn, Ni and Pb might originate from the silk colouring process, from threads' colours used for sawing or from contamination. The μ-XRF results are normalized, meaning the sum of the detected elements percentages must be 100%. In the case of non-detectable light elements, such as C, O, H, N, their content is added to the major detectable elements. This means that the results of table 2, 3 and 4 should be taken into consideration as relative amounts, rather than absolute ones, in samples that contain light elements.

μ-XRF results helped to identify the metal elements present in these flags, which can damage the silk and alter its properties. In order to correctly restore such important objects of our cultural heritage, further investigations, with complementary methods, are necessary.

Conclusions

The μ-XRF analytical method was performed for the first time in Albania, on material such as flags' fabric. The major elements in the renaissance çeta and the on-year Independence's anniversary flags are Fe and Sb, while the "Dëshira" ("Desire") Albanian society flag contains in high percentage Fe, Sn and in few cases Cu. Also, elements such as Zn, Ni and Pb were detected in quantities less than 10%, in all the flags.

A distinct element of the "Dëshira" ("Desire") Albanian society flag's fringes is Au, giving them the characteristic yellow colour; while the high percentage of Ag in the letters cannot fully originate from the device target, making it a possible element of the sewing threads.

The XRF analytical method provided information concerning especially metal elements during a non-destructive procedure. These metal elements can damage the flags' silk. However, they will undergo various complementary investigation methods, in order to correctly restore them.

Acknowledgements

We are very thankful to the National Historical Museum for making the flags available for us and to the Department of Physics, Faculty of Natural Sciences for allowing the in-situ analysis with the μ-XRF device.

References

B. Lambert, K. A. Wilson, *Europe's rich fabric - The consumption, commercialisation, and production of luxury textiles in Italy, the low countries and neighbouring territories (XIV-XVI centuries)*, Ashgate Publishing Limited, pp. 107-158, 2016.

Ch. Greig, *The Directory of Flags - A guide to flags from around the world*, The Ivy Press, pp. 6-11, 2015.

D. V. Edelman, *The fabric of history*, Sheffield Academic JSOT Press, pp. 103-115, 1991.

F. Prendi, "The prehistory of Albania. Cambridge Anicent History", vol. 3, part. 1, chapter V in: *The prehistory of Balkans, The Middle East and Aegean World X to XVIII century B.C*, Cambridge University Press, pp. 187-237, 1982.

J. Carter, "Conservation and restoration of the "Bowman" flag", AICCM Bulletin, vol. 4, no. 4, pp. 33-37, 1978.

J. F. Vilá, M. d. P. Piana, M. P. Tamborini, N. Gáname, G. Canosa, "Electron microscopy contribution to the restoration of the oldest historical flag of Entre Ríos, Argentina", Microscopy and Microanalysis, vol. 26, pp. 67-68, 2020.

Nature Publishing Group, "Restoration of a Silk Flag", Nature no. 188, pp. 1155, 1960.

P. J. Potts, M. West, *Portable X-ray fluorescence spectrometry capabilities for in situ analysis*, The Royal Society of Chemistry, 2008.

R. S. Berns, Principles of colour technology, Wiley, pp. 1-16, 111-144, 2019.

S. S. Muthu, *Textile science and clothing technology*, Springer, pp. 57-96, 2017.

W. G. Crampton, *Flag - Discover the story of flags and banners, their history, their meanings and how they are used*, A Dorling Kindersley Book, pp. 16-25, 1989.