

MICRO-SR-XRF AND MICRO-PIXE STUDIES FOR ARCHAEOLOGICAL GOLD IDENTIFICATION – THE CASE OF CARPATHIAN (TRANSYLVANIAN) GOLD AND OF DACIAN BRACELETS

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Abstract

Trace elements are more significant for provenancing archaeological metallic artifacts than the main components. For gold, the most promising elements are Platinum Group Elements (PGE), Sn, Te, Sb, Hg, Pb. Several small fragments of natural Transylvanian gold - placer and primary - were studied by using micro-PIXE technique at the Legnaro National Laboratory AN2000 microbeam facility, Italy and at the AGLAE accelerator, C2RMF, Paris, France and

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by using micro Synchrotron Radiation X-Ray Fluorescence (micro SR-XRF) at BESSY synchrotron, Berlin, Germany. The goal of the study was to identify the trace elements, especially Sn, Sb and Te. A spectacular application to five Dacian gold bracelets authentication is presented (Sn and Sb traces).

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Introduction

Besides the ratios between the three main components of gold alloys (Au-Ag-Cu), trace elements are very significant for provenancing archaeological metallic artifacts, because the composition of a gold source remains unchanged during the time. The most promising elements are Platinum Group Elements (PGE), Sn, Te, Sb, Hg, Pb [1].

To help Romanian archaeologists in authenticating ancient gold artifacts (jewelry and coins) found on Romanian territory, and in order to answer provenance questions, the Carpathian (Transylvanian) gold source has to be characterized from the elemental point of view. Therefore, Carpathian native gold samples - placer (gold “sand” or nuggets found in river beds) and primary (gold obtained from mining) - have to be measured in order to determine the potential fingerprints of this geological area.

The size of the geological gold samples - especially the ones coming from placers - obtained from the Gold Museum, Brad, Romania, is very small, being of the order of several hundreds μm , both in diameter and thickness. Also the size of samples from archaeological gold objects that can be - at least in principle! - obtained from restoration processes, is in the range of a few hundreds μm . Therefore, to perform authentication and provenance studies, micro-

analytical methods are required. Moreover, since trace-elements are to be sought, the techniques should be sensitive (at least in the $\mu\text{g/g}$ range), and, preferably non-destructive, in order to keep the samples for any further investigations. As a consequence, micro Particle Induced X-ray Emission (micro-PIXE) and micro Synchrotron Radiation X-Ray Fluorescence (micro SR-XRF) were chosen as investigation methods for this study.

Several small fragments of natural Transylvanian gold were investigated by using micro-PIXE at the Laboratori Nazionali di Legnaro AN2000 microbeam facility, Italy and at the AGLAE accelerator, from the Louvre Museum, Paris, France and by using micro SR-XRF at the BESSY synchrotron, Berlin, Germany. The results obtained for geological gold were later used for the authentication of the most spectacular archaeological recovery of the last 100 years in Romania: five huge (approx. one kilo each) spiraled gold Dacian bracelets/armbands.

Experimental

Micro-PIXE measurements on seven Transylvanian native gold samples were firstly performed at the AN2000 accelerator of Laboratori Nazionali di Legnaro, INFN, Italy, in the frame of the European Community FP6 contract EURONS. The experiment was done with a 2 MeV proton microbeam ($9 \mu\text{m}^2$ beam area) [1, 2]. A Canberra HPGe detector (180 eV FWHM at 5.9 keV), covered with a mylar funny filter (52 μm thickness, 11 % hole) to reduce the intensity of the peaks in the low spectral region (below 4 keV) was used. The quantitative processing of the X-ray spectra was performed using the GUPIXWIN software [3]. By using this set-up, Au, Ag and Cu amounts were easily determined; however, the quantification of Sn and Te traces by resorting to the characteristic L X-rays was more delicate, the content in these elements being close to the detection limits.

Further experiments on the same samples were performed by external micro-PIXE at the AGLAE 2 MV Tandem Pelletron accelerator, this time by using a 3 MeV proton beam (100

μm in diameter) [4]. The emitted X-rays were collected by two Si(Li) detectors: the first (10 mm^2 active area) dedicated to the low energy X-rays, and the second (50 mm^2 area) dedicated to the high energy X-rays emitted by the intermediate and heavy elements. The latter detector was covered with a $75\text{ }\mu\text{m}$ Cu foil to reduce the intense Au peaks, and to improve the detection of the K X-rays lines of Te and Sn, trace-elements of interest for this study – see figure 1.

The SR-XRF measurements performed at BESSY Synchrotron Radiation Facility, Berlin, enabled the analysis of a larger number of samples in a very short time. This is due to the high photon flux used to excite the characteristic X-ray, which leads to reduced acquisition time and improved sensitivity for the trace elements of interest. These measurements are also aimed at obtaining a more general characterization of the Transylvanian gold sources, via a large set of analyzed samples. In BESSY experiment, the point spectra for 20 Transylvanian natural gold samples were acquired by using 34 keV excitation energy at the BAM beam-line [5]. The X-ray beam was focused down to $100\times 200\text{ }\mu\text{m}^2$. Characteristic X-rays were collected for 300 s by using a Si(Li) detector covered with a polyethylene filter. Peak contents have been determined by AXIL [6] software and normalized to the integral excitation intensity and detector dead-time. Quantification was done by comparison with pure elemental standards. Second order effects have been taken into account by using the msim5 Monte Carlo simulation program [7].

Results and discussions

The elemental analyses performed on Transylvanian native gold by micro-PIXE lead to the following conclusions: variable and relatively high amounts of Ag (from 8% up to 35%) are present; very low amounts of Cu (from $6200\text{ }\mu\text{g/g}$ down to hundreds of $\mu\text{g/g}$) were put into evidence; traces of Sn ($200 - 600\text{ }\mu\text{g/g}$) are characteristic for placer gold samples – see figure

1; traces of Sb (100 - 250 $\mu\text{g/g}$) and Te (600 – 800 $\mu\text{g/g}$) were found in some primary gold samples. These results are compatible with some minerals typical for Transylvanian native gold [8], such as: petzite (Ag_3AuTe_2), sylvanite ($(\text{Au}, \text{Ag})\text{Te}_4$), jamesonite ($\text{Pb}_4\text{FeSb}_6\text{S}_{14}$), stephanite (Ag_5SbS_4).

The micro SR-XRF measurements confirmed that high Ag amounts and low Cu amounts are to be found in Transylvanian native gold; placer deposits (Valea Arieşului, Valea Pianului) contain as a fingerprint Sn (100-200 $\mu\text{g/g}$), most probably from river bed cassiterite (SnO_2); primary deposits generally present as fingerprints Te (100-1000 $\mu\text{g/g}$) and Sb (50-150 $\mu\text{g/g}$). However, one must take into account the fact that these samples are very inhomogeneous. An interesting case was the one of the primary deposit sample from Roşia Montană, that contains Te (0.25%), Sb (500 $\mu\text{g/g}$), but also Sn (300 $\mu\text{g/g}$). Another primary deposit sample, the one from Valea Morii, showed a relatively large amount of Pb (1%), Sb (250 $\mu\text{g/g}$), traces of Te (50 $\mu\text{g/g}$) and also Sn (200 $\mu\text{g/g}$) – see figure 2.

A spectacular application of the micro-PIXE and micro-SR-XRF studies on native gold was the authentication of some recovered heritage artifacts: five Dacian gold bracelets, currently exhibited at the National Museum of Romania History, Bucharest. These gold multi-spiraled bracelets (see figure 3) were attributed to the classical period of the Dacian civilization (2nd century B.C. - 1st century A.D.), being recovered from the international market of antiquities through a common effort undertaken by the Romanian and German authorities. The artifacts were discovered by archaeological looting in the area of Sarmisegetusa Regia Dacian fortresses in the Orăştie Mountains (UNESCO World Heritage List site), and illegally exported. The bracelets are spiraled (5 – 7 spirals), weighing 800 to 1200 g each. They are 10 to 12 cm diameter, being adorned with stylized palm leaves and with zoomorphic protomes at both ends, being very similar in style with the Dacian silver bracelets previously discovered in archaeological context at Coadă Malului, Senereuş, Orăştie and Herăstrău-Bucureşti [9]. The gold bracelets are the first gold bracelets of Dacian craftsmanship ever found on Romanian

territory, since up to now only silver bracelets were found during the archaeological excavations.

To confirm the authenticity of the bracelets, the analysis of the gold alloy from which they were made was strongly requested. The conditions imposed by the Romanian authorities were: the analyses have to be performed in Romania; no sampling was allowed; nuclear activation of the samples has to be avoided. Therefore, the compositional analysis of the bracelets was performed by X-Ray Fluorescence (XRF) at “Horia Hulubei” National Institute of Nuclear Physics and Engineering, Bucharest, by using ^{241}Am (30 mCi) and ^{238}Pu (10 mCi) radioactive sources, and a HPGe detector – for details, see [10]. A pure gold (99.99%) sample from The National Bank of Romania was used as a standard to extract the 26.4 keV γ peak (from the ^{241}Am source) contribution. In peaks coming from a detector O-ring can be observed in the spectra. The XRF spectrum for bracelet no. 1 is given in figure 4.

The compositional results for the bracelets obtained by XRF are presented in table 1. The numbers are the average of three measurements in different points. Apart for Au-Ag-Cu concentrations, traces of tin, most likely from cassiterite (SnO_2), which is a fingerprint for placer/panned gold were found. Traces of antimony, most probably coming from jamesonite ($\text{Pb}_4\text{FeSb}_6\text{S}_{14}$) and/or stephanite (Ag_5SbS_4), minerals typical for Transylvanian native gold, were also put into evidence. The soil traces in the bracelets cracks turned out to be rich in Ca, most probably due to the fact that the bracelets were buried for a long period of time and not very well cleaned. A relatively different composition for each bracelet was put into evidence.

Comparing the XRF results on bracelets with the micro-PIXE and micro SR-XRF results on Transylvanian gold samples, the conclusion was that the bracelets were made from native Carpathian (Transylvanian) gold (panned mixed with primary) and manufactured using a primitive metallurgy (no intention to refine the native gold). In this way, XRF results strongly support the stylistic arguments regarding the authenticity of the bracelets. Recently, we received from Pieter Meyers [private communication] the results of his LA-ICP-MS (Laser

Ablation Inductively Coupled Plasma Mass Spectrometry) measurements performed in the fall of 2006 on bracelet no. 5; his results are similar to ours. However, he detected as trace-elements - besides Sn and Sb - Pd and Pt, elements that are considered as indicators for placer deposits. The conclusion of his analyses was that the bracelet no. 5 was a genuine ancient artifact, being manufactured mainly from panned gold.

Conclusions

This study demonstrates that micro-PIXE, micro SR-XRF and XRF are useful tools in establishing the authenticity and the provenance of gold ancient artifacts. If micro-sampling is possible during restoration (e.g. from the edges of the objects), micro-PIXE and micro SR-XRF are the perfect choice for analysis, due to their high sensitivity and ability to non-destructively analyze minute samples. However, one has to keep in mind that in general, there are tough regulations regarding gold museum objects, and that is very difficult to take the artifacts out of the museum for investigations. In such cases, in-situ XRF measurements might be a good alternative to answer elemental composition-related questions, even if under these conditions they only give semi-quantitative results for trace elements.

Acknowledgements

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Figure captions

Figure 1 – Micro-PIXE spectrum of a placer gold sample from Valea Arieşului, featuring Sn traces; the spectrum was obtained by placing a 75 µm Cu filter in front of the Si(Li) detector.

Figure 2 – Micro SR-XRF spectrum of a primary gold sample from Valea Morii.

Figure 3 – Bracelet no. 1.

Figure 4 – XRF spectrum of bracelet no. 1.

Table 1 – Elemental composition of the Dacian gold bracelets obtained by XRF

Bracelet no.	Au (%)	Ag (%)	Cu (%)
1	89.85	9.50	0.65
2	78.20	20.30	1.50
3	82.40	16.20	1.40
4	91.50	8.10	0.40
5	92.80	6.90	0.30

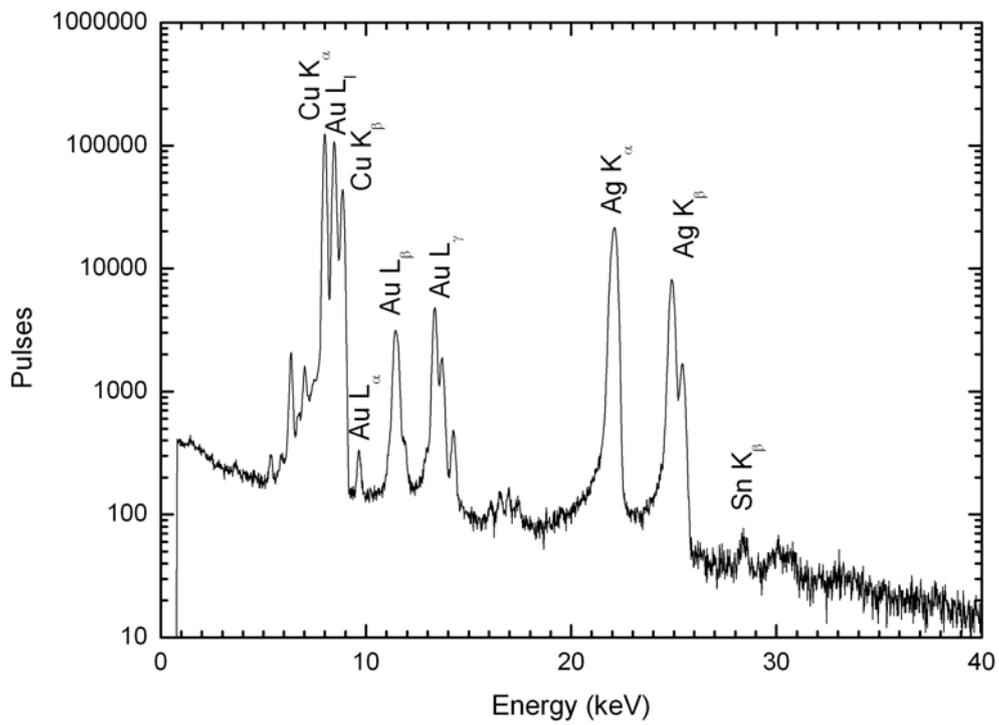


Figure 1

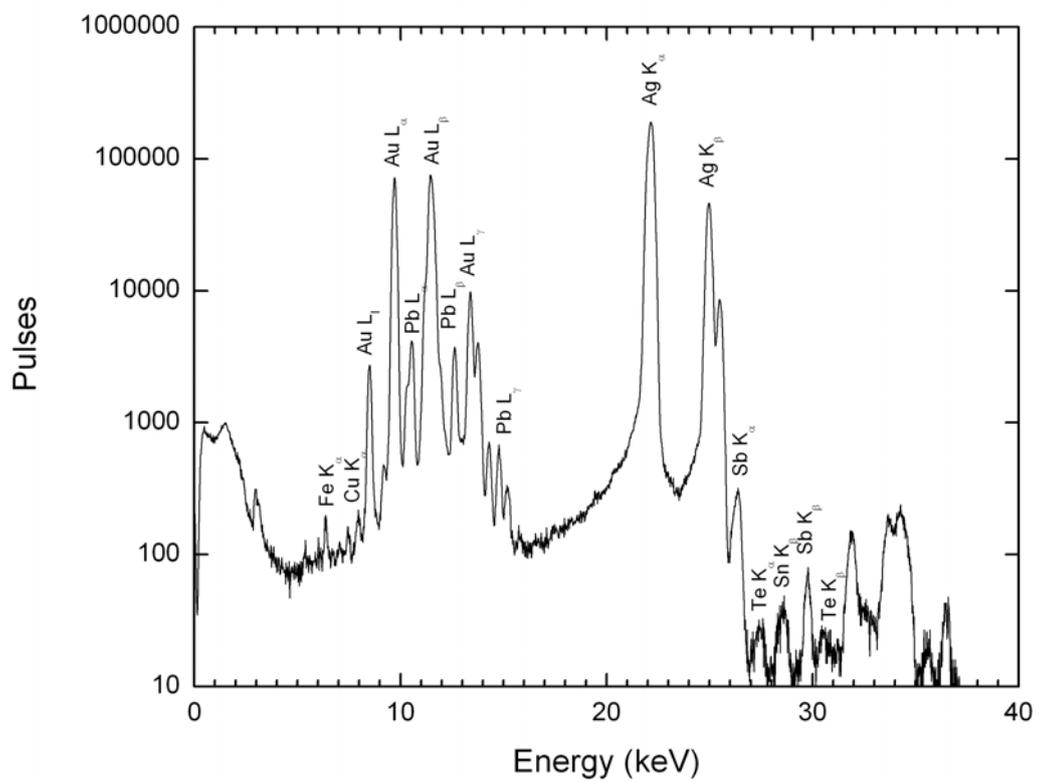


Figure 2



Figure 3

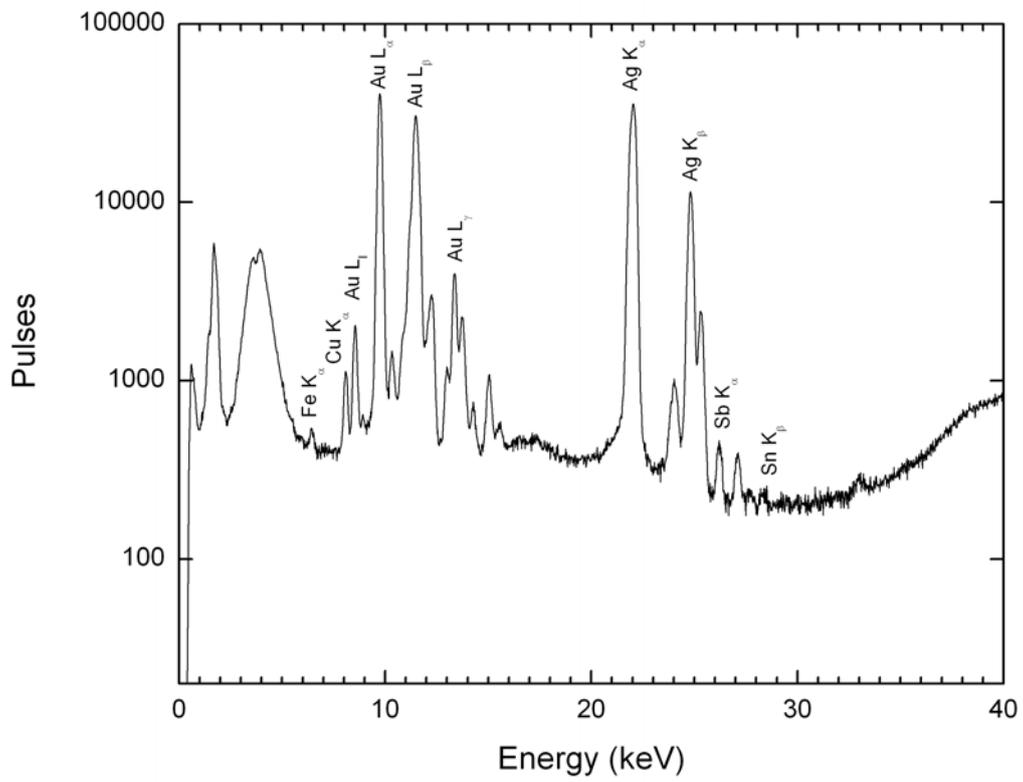


Figure 4