MICRO-SR-XRF AND MICRO-PIXE STUDIES FOR ARCHAEOLOGICAL GOLD IDENTIFICATION

B. Constantinescu[1], R. Bugoi[1], V. Cojocaru[1], R. Simon[2],
D. Grambole[3], F. Munnik[3], F. Herrmann[3], D. Ceccato[4]
1 - Department of Applied Nuclear Physics, "Horia Hulubei" National Institute of Nuclear Physics and Engineering, PO BOX MG-6, Bucharest 077125, Romania
2 - Institute for Synchrotron Radiation, Forschungszentrum Karlsruhe, D-76344, Germany
3 - Institute for Ion Beam Physics and Materials Research, Forschungszentrum Dresden-Rossendorf, PO BOX 510119, Dresden D-01314, Germany
4 - Istituto Nazionali di Fisica Nucleare, Laboratori Nazionali di Legnaro, Padova, Italy

ABSTRACT
For gold, the most promising elements for provenance are Platinum Group Elements (PGE), Sn, Te, Sb, Hg, Pb, but also high melting point elements, such as Ta and Nb. Small fragments of native Carpathian gold - placer and primary - were studied using Synchrotron Radiation X-Ray Fluorescence at ANKA synchrotron. The goal of the study was to identify the trace elements, especially Sn, Sb and Te. The measurements were performed in air by using a 32.5 keV beam to excite the characteristic X-lines in Sn-Sb-Te region. We found Sn to be present in placers, Sb, Te and Pb in primary gold. Native gold nuggets, fragments of objects coming from Visigothic Pietroasa "The Golden Brood Hen with Its Chickens" hoard and small (less than 250 microns diameter) fragments from ancient Dacian and Grek gold coins were analyzed using micro-PIXE technique at the Rossendorf TANDETRON and at the Legnaro AN2000 microbeam facilities. We found Te and Sb in primary gold and Sn and traces of Sb in placers. For Pietroasa hoard, we found Sn in the Oenochoe cup and small fibula, indicating that alluvial gold - probably from Anatolia (Pactolus river) - was used. We also detected Ta inclusions in the large fibula, indicating that Ural Mountains (the only region where Ta and Au minerals are together) gold was (at least partially) used. As concerning the gold coins, two type of Dacian staters were identified: one from remelted refined gold and other from native (alluvial) Carpathian gold. A spectacular application to nine Dacian gold bracelets (armbands), identified as made from native placer and primary Carpathian gold, is also presented.

INTRODUCTION
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 [Pernicka, 1986]. To help Romanian archaeologists in authentication and provenance studies on ancient gold artefacts (jewelry and coins) found on Romania's territory [Bugoi et al, 2005], the very possible use of Carpathian gold must be considered. This analysis involves the compositional study of Carpathian native gold samples – placer (gold sand or nuggets found in rivers bed) and primary (gold obtained from mining), to determine the fingerprints of gold from this geological area. In this paper, the investigation of several small fragments of natural Carpathian gold by using micro Proton Induced X-ray Emission (micro-PIXE) technique at the microbeam facility of Forschungszentrum Dresden-Rossendorf, Germany and by using micro Synchrotron Radiation X-Ray Fluorescence (micro SR-XRF) at ANKA Synchrotron Radiation Facility of the Forschungszentrum Karlsruhe, Germany is presented. The analytical results obtained for the Carpathian gold were applied to the authentication of the most spectacular Romanian archaeological recovery in the last 100 years, the one of nine huge spiraled gold Dacian bracelets.

Inclusions of Platinum Group Elements (PGE) - Ru, Rh, Pd, Os, Ir and Pt - in gold were released into rivers by the decomposition of rocks and occur in placer deposits in the form of grains and nuggets of complex alloys. The melting point of PGE is higher than that of gold; thus, PGE grains remain unchanged during the metallurgical processing of the gold ore. Apart

from PGE inclusions, gold alloys can contain low amounts of high-temperature melting point trace elements, such as Ta, Nb, Cr etc, other potential fingerprints for base metal deposits. The purpose of this Pietroasa hoard study was to obtain relevant information about the metal provenance. Trace elements – such as PGE, correlated with known mines fingerprints can help to identify the ore source. The gold provenance of the objects can lead to further historical conclusions.

EXPERIMENTAL

The micro-PIXE analyses of geological gold samples were performed at the nuclear microprobe facility of the Institute of Ion Beam Physics and Materials Research, Forschungszentrum Dresden-Rossendorf, Germany. The Rossendorf microprobe facility is based on a 3 MV Tandetron accelerator and a Danfysik magnetic quadrupole triplet for beam focusing [Grambole and Herrmann, 1995]. A 3 MeV proton beam was employed; the beam diameter was roughly 150 μm. The total accumulated charge was around 3 μC. The characteristic X-rays were detected by a Si(Li) detector positioned at 120° with respect to the incident beam. A 30 μm thickness Zn absorber was put in front of the Si(Li) detector, to reduce the high contribution of Au L lines. The analysis of the PIXE spectra was performed by using the GUPIX code [Campbell et al, 1995]. Micro Synchrotron Radiation X-Ray Fluorescence Analysis (micro SR-XRF) measurements were also performed for Carpathian gold characterization. Due to the high intensity, tunability and to the radiation polarization of the exciting X-ray beam, better detection limits can be reached. Micro SR-XRF analyses were performed in air at the ANKA FLUO beamline of ANKA synchrotron facility, Karlsruhe, Germany [Buth et al, 2003], by using an incident photon energy of 32.5 keV provided by a Double-Multilayer-Monochromator. The beam was collimated to 93 (h)×116 (v) μm^2. The photon flux was around 10^{10} photons/s. Characteristic X-rays were collected by a Si(Li) detector (135 eV FWHM at 5.9 keV), situated at 90° with respect to the incident X-ray beam. A 1 mm thick Al filter was placed in front of the Si(Li) detector. A video system was used to observe and to select the analytical points on the samples. The SR-XRF data were analyzed by means of the AXIL code [AXIL, 1996].

Five small pieces from five different objects belonging to Pietroasa treasury were also analyzed: the large, the middle and the small fibulae, the dodecagonal basket and a piece of the patera - to be more specific, the central figure representing Cybele. Small fragments (a few square millimetres area) of the original objects were taken by mechanically cutting the artefacts, operation performed during a restoration of the hoard. The micro-PIXE scan measurements and point analyses were done at the nuclear microprobe facility, Dresden - Rossendorf, Germany, and at Laboratori Nazionali di Legnaro, Italy, where a 2 MeV proton beam generated from the AN 2000 Van de Graaff accelerator was used.. The beam diameter was set to 5 μm. The maximum beam current was around 1 nA. To reduce the intensity of the peaks in the low spectral region (below 4 keV), a mylar funny filter (171 μm thickness, 3.3% hole) was employed. The Si(Li) detector employed at Legnaro had a better efficiency in the high X-ray region. Since one of the Pietroasa samples was cracked, spectra for the sample holder and the carbon tape on which the samples were stuck were also acquired in both experiments, in order to subtract the eventual spurious signals coming from the backing.

RESULTS

The micro-PIXE analyses indicated that the Carpathian native gold is characterized by variable high amounts of Ag (from 8% up to 35%), very low amounts of Cu (from hundreds of μg/g up to 1.5%); traces of Sn for placer gold (50 – 400 μg/g); traces of Sb (150 – 800 μg/g) and Te (200

– 1800 μg/g) - for primary gold (see figure 1). These results are compatible with typical minerals for Transylvanian native gold [Berbeleac 1985], such as: petzite (Ag_3AuTe_2), sylvanite (Au, Ag)Te_4, jamesonite ($Pb_4FeSb_6S_{14}$), stephanite (Ag_5SbS_4). The micro SR-XRF measurements confirmed the high Ag and low Cu contents determined by micro-PIXE. The placer deposits from Valea Arieşului, Valea Pianului contain as fingerprint Sn, most probably from river bed cassiterite – see figure 2. The primary deposits present as fingerprints Te (100-1000 μg/g), Sb (50-150 μg/g) and, sometimes, few μg/g of Sn. However, one must keep in mind that the samples are very inhomogeneous. The primary deposit from Roşia Montană contains Te = 0,25%, Sb (500 μg/g), but also Sn (300 μg/g). The primary deposit Valea Morii presents a large amount of Pb = 1%, Sb (250 μg/g), traces of Te (50 μg/g) and also Sn (200 μg/g).

A spectacular application of the micro-PIXE and micro-SR-XRF studies on native Carpathian gold was the one regarding the authentication of some recovered heritage artifacts: nine Dacian gold bracelets exhibited at the National Museum of Romania's History, Bucharest, Romania. The Dacian multi-spiraled bracelets were made of gold (see, for example, figure 7); they belong to the classical period of the Dacian civilization (2nd century B.C. – 1st century A.D.). The bracelets were recovered from the international market of antiquities through a common effort undertaken by the Romanian authorities in collaboration with the German authorities. 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 leafs and with zoomorphic protomes at both ends. There are remarkable analogies with the Dacian silver bracelets [Parvan, 1982]. To confirm the authenticity of the bracelets, the analysis of the gold alloy from which they were made was strongly requested. Taking into account that only non-destructive (and non-sampling!) analyses were allowed by the Romanian authorities, the compositional analysis of the bracelets was performed by Energy Dispersive X-Ray Fluorescence (ED-XRF) at the "Horia Hulubei" National Institute of Nuclear Physics and Engineering, Bucharest, by using Am-241 (30 mCi) and Pu-238 (10 mCi) radioactive sources, and a HPGe detector - see details in [Bugoi et al, 2003]. A pure gold (99,99%) sample from the National Bank of Romania was used to extract the 26.4 keV γ peak (from Am241 source) contribution. An In peak from the detector O-ring can be observed in the spectra. The compositional results obtained by ED-XRF on each bracelet, representing the average of three measuring points are given in table 1; the uncertainties being of the order of 1-2 %, due to the long measurement times (one hour). Taking into account the obtained results, different ingots were used to manufacture each bracelet. The bracelets showed a relatively inhomogeneous composition – this was observed by comparing the results of the measurements in different regions of the same bracelet. For bracelet no. 8, the content of Sn was very high (around 1500 μg/g) – see figure 8; therefore the hypothesis of a deliberate alloying with bronze (approx. 1.5%) of gold is not excluded. Traces of tin – from cassiterite – fingerprint for placer/panned gold were also observed in other bracelets, as well as traces of antimony – most likely from jamesonite and stephanite. Comparing the ED-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 gold - panned mixed with primary - and realized using a primitive metallurgy, with no intention to refine the native gold.

Table 2 summarizes point concentrations for the five Pietroasa hoard analysed samples. To decide if an inclusion is present in a certain area, a correlation between the presence of some elements and their absence in the surrounding must be established. Some point spectra were also acquired in certain zones, to get 'magnified images' of the interesting areas. A first conclusion of these microprobe experiments was that the elemental composition for the five

pieces is strongly different, which is in good agreement with the classification made for the objects taking into account only the stylistic aspects. Thus, the patera is of Greek-Roman style, the dodecagonal basket combines Sassanide (Persian) and Greek-Roman characteristics while the fibulae are of Germanic style (the bird motif). The microscopic concentrations are rather different from the ones obtained by NAA [Besliu et al, 1996]. This fact is not surprising at all, since it is not expected an agreement between the point (the present measurements) and the bulk concentrations of an inhomogeneous alloy determined in [Besliu et al, 1996]. Combining the NAA [Besliu et al, 1996] and Table 1 results, for central figura of the patera (3 P sample) – Pt presence and a Rh – Ir inclusion (Pt can't be detected from a X-ray spectrum in the massive presence of Au) – we can assume an Ural mountains gold provenance. However, in the patera itself (the plate) Pt was not detected [Besliu et al, 1996], so, a re-melting procedure is more credible. Due to the high fineness of gold (~95%), it is likely that gold used to manufacture this object has been obtained by melting some existing jewellery and Roman imperial coins of Mediterranean origin. Analyzing the elemental maps for the large and small fibulae, inclusions of Ta (see figure 9) and Nb were found. As stated in [Barna and Lupei, 1971], the combination Ta – Nb is found in tantalite - columbite type minerals, e.g. in samarskite, mineral which is found in gold ores from the Ural Mountains (Southern region around Samara). These findings confirm the fact that the Germanic 'owners' of the hoard were coming from the region between Caucasus and Ural Mountains in the second half of the IIIrd Century A.D., bringing along their precious jewellery [Ammianus Marcellinus, 1963], and that some of the Pietroasa hoard artefacts – i.e. the fibulae – were manufactured using Ural mountains gold. The Ural mountains hypothesis is also supported by Pt content in large (7 p) and small (10 p) fibulae– see [Besliu et al, 1996] – and the Ru – Os (for small fibula) and Ru – Ir (for middle fibula) inclusions – see Table 2. As concerning the dodecagonal basket, the most important result of these experiments is the finding of small Pd inclusions. The only accessible gold sources with Pd in the IVth Century A.D. were Nubia (Sudan) and Anatolia (Turkey) deposits, intensively used in Egypt (Alexandria) and Syria (Antiochia) workshops -, where Pd was determined in Alexander the Great coins, minted after the Persian Empire conquest (however, we didn't found Pt and Sn traces) and in early Alexandria Byzantine coins. The main composition (Au = 98%, Ag = 1%, Cu = 0.5%) could also suggests a re-melting procedure, probably using Roman imperial coins struck in Oriental provinces . Summarizing the results, we can conclude for the analyzed objects of Pietroasa hoard we have at least four possible gold sources: Southern region of Ural Mountains, Nubia (Sudan) deposits or a Persian source (most likely Pactolus river in Anatolia) and/or various emissions of Roman imperial coins.

CONCLUSIONS

As a general conclusion of this study, all the employed analytical methods - micro-PIXE, micro SR-XRF and ED-XRF – proved their usefulness in authentications of ancient gold artefacts. Due to their excellent performances regarding the detections limits, non-destructivity and lateral resolution, micro-PIXE and micro SR-XRF are the perfect choice for analysis in the case that minute samples are available for elemental analysis. However, in the case that neither sampling is allowed - due to the intrinsic value of the artefacts, nor the transportation of gold objects to an accelerator, in-situ (museum) ED-XRF measurements can be used as a satisfactory alternative to investigate such precious objects. The results obtained by micro-PIXE experiments on gold ancient artefacts, especially the inclusions findings, provided some useful hints regarding the possible provenance of the manufacturing metal. The Pietroasa hoard artefacts were again proved to be of different origins, confirming the stylistic arguments by the different possible gold sources identified: Southern region of Ural Mountains, Nubia (Sudan) deposits, Pactolus river and Roman imperial coins emissions. Further analyses on other artefacts belonging to the same hoard are to be done. However, a correct answer to the question

of the native metal provenance used for each artefact remains a difficult task, taking into account that a complete data bank for the composition of Euro-Asian native gold is not yet available.

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Object	Cu	Ru	Rh	Pd	Ag	Te	Ta	Os	Ir	Au
Central figure of patera	Traces	nd	0.12 %	nd	4.48 %	0.13 %	nd	nd	Traces	95.14 %
Dodecagonal basket	1.25 %	nd	nd	0.35 %	4.95 %	nd	nd	nd	nd	93.35 %
Large fibula	0.13 %	nd	nd	nd	15.35 %	0.31 %	4.93 %	nd	nd	78.82 %
Middle fibula	0.05 %	0.44 %	nd	nd	16.85 %	0.29 %	0.16 %	nd	0.04 %	82.17 %
Small fibula	Traces	1.88 %	nd	nd	8.73 %	nd	39.14 %	0.45 %	nd	49.30 %

nd - not detected Traces – concentrations less than 100 ppm.

Table 1 – Pietroasa hoard samples point concentrations

Bracelet no.	Au (%)	Ag (%)	Cu (%)
1	89.8	9.5	0.6
2	78.2	20.3	1.5
3	82.4	16.2	1.4
4	91.5	8.1	0.4
5	92.8	6.9	0.3
6	92.0	7.1	0.9
7	92.9	6.3	0.7
8	85.0	12.8	2.1
9	87.1	12.2	0.6

Table 2 – Elemental composition of the Dacian gold bracelets obtained by ED-XRF

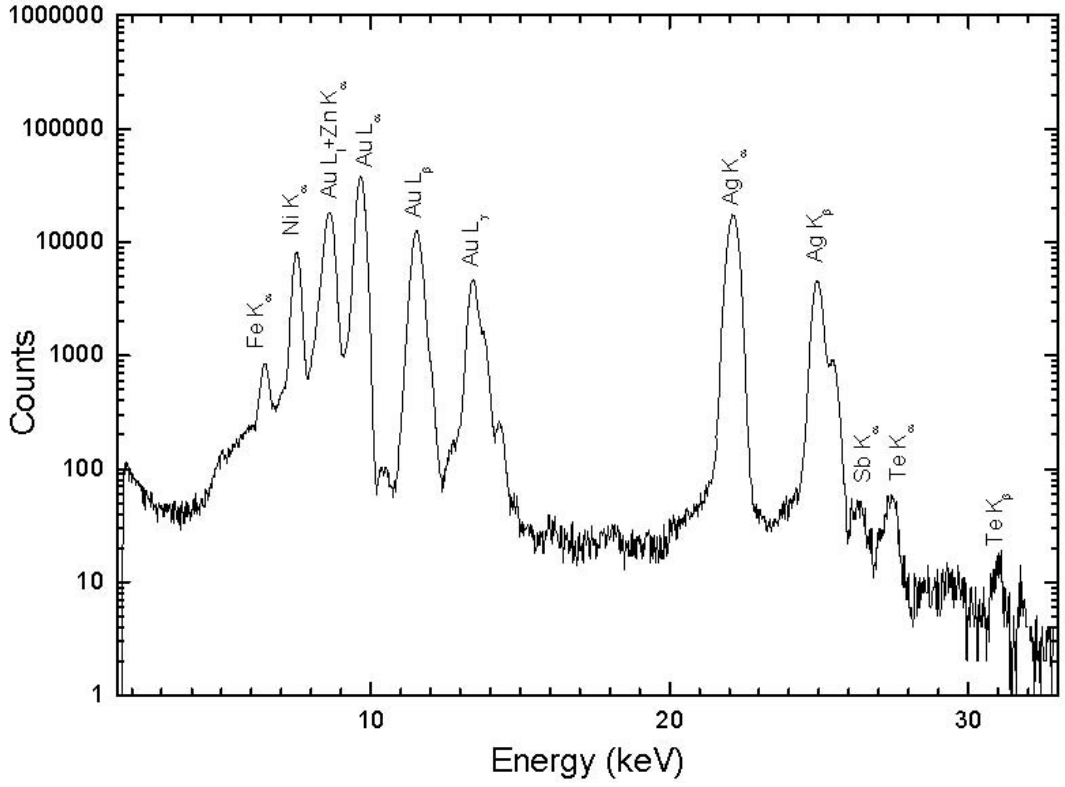

Figure 1. Primary gold sample - Roşia-Montană (micro PIXE) - Sb and Te traces.

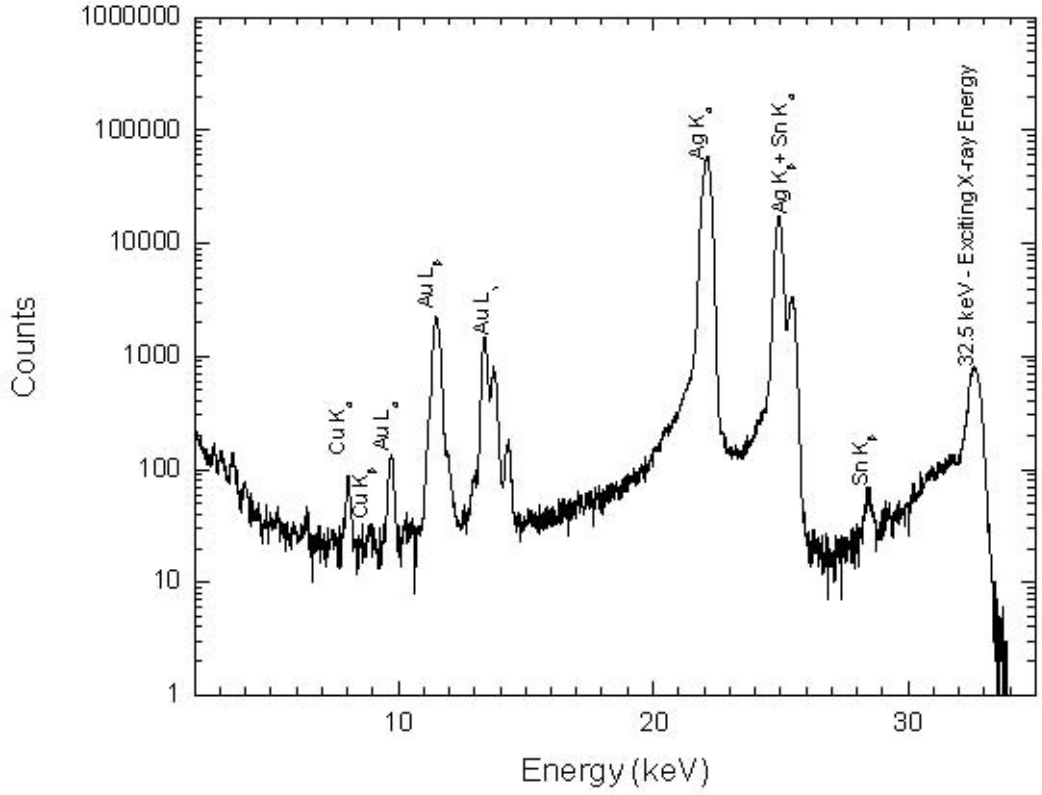

Figure 2. Placer gold (micro SR-XRF) - Valea Arieşului - high Sn content.

Figure 3. Dacian bracelet no. 2.

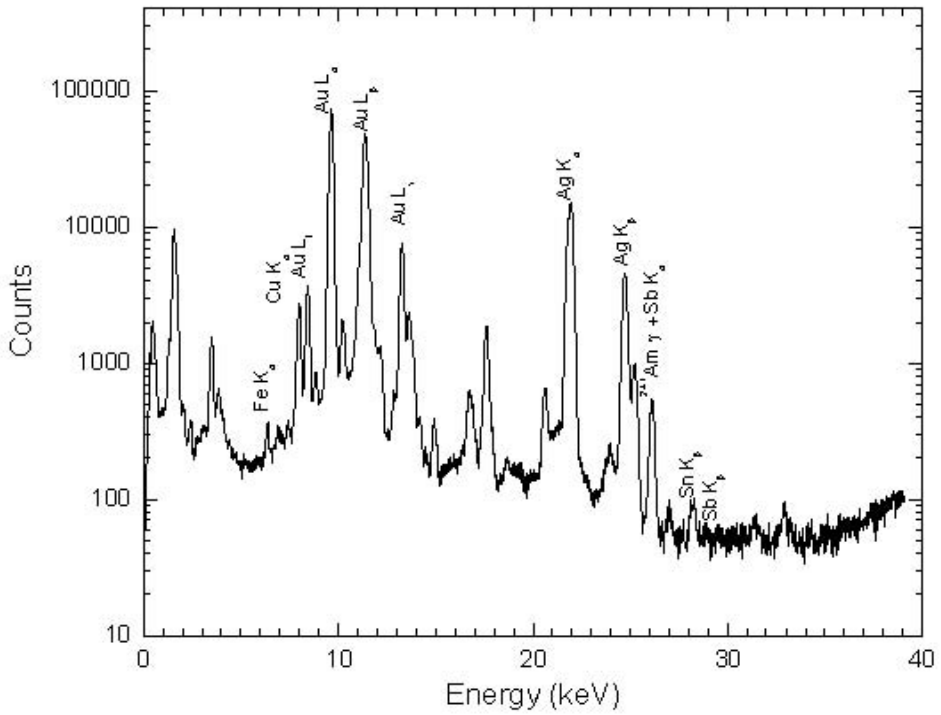

Figure 4. ED-XRF spectrum of bracelet no. 8, featuring high Sn content.

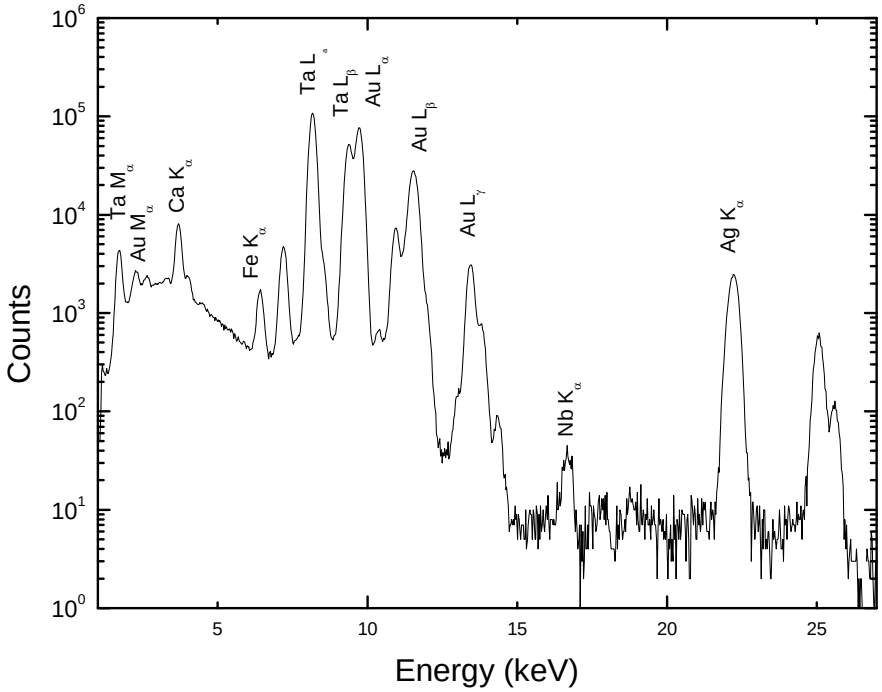

Figure 5 – Micro PIXE spectrum featuring Ta on the Pietroasa small fibula sample

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