

PHYSICAL METHOD & INSTRUMENTATION

SOME CONSIDERATIONS ON X-RAY FLUORESCENCE
USE IN MUSEUM MEASUREMENTS –
THE CASE OF MEDIEVAL SILVER COINS

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Abstract. The purpose of this paper is to give a general layout for the potential applications of Energy-Dispersive X-Ray Fluorescence (ED-XRF) technique for ancient silver coins characterization, using *in-situ* (in museums) measurements. Examples concerning originality testing, provenance (mines, workshops) identification, counterfeits selection, historical studies (manufacturing technologies, commercial, military and political relationships) are given. Two study cases of medieval coins are described: German *brakteaten pfennige* and Moldavian *groschen*. Other analysis methods and their use in the study of medieval coins are illustrated with the example of Particle Induced X-ray Emission (PIXE) technique.

Key words: ED-XRF, archaeometry, silver coins, PIXE, provenance.

1. INTRODUCTION

The Energy-Dispersive X-ray Fluorescence (ED-XRF) method is a fast, cheap and reliable analytical tool. It does not require sampling or complicated sample preparation, the equipment is relatively simply to operate and presents the advantage to be easily transported or designed in a portable form, to allow *in-situ* measurements (*e.g.* in museums or historical, archaeological or architectonic sites). Some experimental results obtained at the National Museum of Romania’s History based on these latter advantages – transportability and portability – are the main issues of this paper.

Archaeological and art objects are unique (even ancient coins belonging to the same emission), so a rigorous standardization of their measurements is quite impossible. However, a dedicated detailed procedure for one type of objects and a particular ED-XRF spectrometer can be elaborated if a certain laboratory is interested in a specific case.

The noble metals artifacts play a special role in archaeometry not only because of their value, but also because they are very stable against corrosion. This means that these objects are relatively well preserved and they can be easily non-destructively analyzed using surface techniques such as ED-XRF – the analyzed depth is in the range of some tens of micrometers, and up to one hundred microns.

This paper intends to explain what should be expected from ED-XRF archaeometrical analyses and two applications using this technique *in-situ* (inside the museum) on medieval silver coins from the National Museum of Romania's History in Bucharest are given.

2. ARCHAOMETRICAL APPLICATIONS OF ED-XRF

The elemental composition provided by ED-XRF can be used for the following archaeometrical purposes:

- Originality testing – for example, it is known that modern silver obtained through electrolysis contains no gold traces; as a consequence, the counterfeits of ancient silver coins do not contain gold at trace level; Greek–Roman bronze (Cu–Sn) objects, which always contains lead in variable amounts, can be faked by using modern brass alloy (Cu–Zn);
- Provenance – minor and trace elements determined through elemental analysis can be used for ore and/or workshop identification;
- Conservation – protective measures can be decided on compositional basis; *e.g.*, anticorrosion treatments for less noble metal objects;
- Restoration – it is better to have the elemental composition of a deteriorated object, in order the use similar or compatible materials to accomplish a good restoration;
- Historical studies – based on the elemental composition determined through ED-XRF, different conclusions regarding the manufacturing technologies, commercial, military and political relationships between ancient populations and/or trade routes can be revealed; for example, selection of the high-purity silver coins from adulterated silver plated (using edge measurements) and /or silvered items belonging to similar official emissions is possible.

To apply this analytical method in a museum, for a multidisciplinary team (archaeologist-physicist) it is necessary to have some basic knowledge of the general XRF theory – see [1] and to have an ED-XRF spectrometer. The excitation of the characteristic X-rays can be made either using a radioactive source (*e.g.*, ^{241}Am or ^{238}Pu) or a low power X-ray tube, while the detection is usually made with a solid state detector – either a liquid nitrogen cooled semiconductor detector (Si(Li) or low energy HPGe) or a Peltier cooled detector (*e.g.* Si PIN).

The following operations must be performed in order to analyze an archaeological item:

- sample “preparation” – for silver and less deteriorated bronze coins a superficial cleaning using alcohol on a cotton piece is sufficient;
- calibration of the ED-XRF spectrometer – for the tube excited ED-XRF spectrometer with secondary target excitation, see [2]. Potential certified reference materials are modern silver and copper (bronze) coins from special emissions with declared elemental composition. In general, for any metallic sample, pure metal or alloys foils can be used, *e.g.*, from Goodfellow Metals Ltd or Advent Research Ltd;
- routine check of the ED-XRF spectrometer (before each round of measurements of minimum 10 samples) [3];
- repeatability test – based on [4, 5];
- reproducibility test (for each general type of samples) – based on [4, 5].

3. EXPERIMENTAL RESULTS

Due to their high resistance to oxidation, silver artifacts are easily to analyze. Only a smooth mechanical cleaning (*e.g.*, using pure alcohol on a cotton wad) is necessary to remove the eventual organic and inorganic impurities (dust, soil remnants from the archaeological site, etc.). The eventual presence of a black-grey coloured oxide submicronic layer on the silver coins (the silver passivation phenomenon which prevents the in-depth oxidation development) cannot affect the absolute compositional results more than 1 to 5%, depending on the atomic number Z of the element. Due to the relative inhomogeneity of silver alloys coupled with possible different local wearing, a correct analysis must include a large area on both sides of the coin and mini- or micro- examinations (analysis with adequate collimators, or analysis performed with Proton Induced X-ray Emission (PIXE) and/or the microbeam variant (micro-PIXE), which can add more information on microstructural compositional and wearing aspects). Edge analysis using adequate collimators could give valuable information about the eventual plating (*e.g.* bronze core mechanically covered with thin – tens of micrometers silver foils – see [6]).

One should also mention that iron traces in silver/bronze coins are partially due to dust impurities which never can be avoided.

To obtain more information regarding the elemental structure of coins, other techniques can be used as well:

- Micro-PIXE to detect plated coins, especially if cracks or holes are visible – see [7];
- Rutherford Back-Scattering (RBS) to determine the layer structure of silvering including the eventual adhesive alloy;

- PIXE to detect metallic trace elements, such as: Ni, Bi, Zn, As, Sb, which are fingerprints for different silver mines – see below.

The ED-XRF measurements described in this paper were performed with a spectrometer consisting of a 30 mCi ^{241}Am annular gamma source and a Canberra Si(Li) vertical detector (200 eV FWHM at 5.9 keV). For *in-situ* National Museum of Romania's History measurements, the gamma source excitation was chosen in favor of the X-ray tube variant due to the less restrictive radioprotection regulations, the ^{241}Am source being transported out of the museum and back to the institute every day after the measurements.

In the case of coins, previous studies have shown that the chemical composition of the silver alloys can be regarded as being characteristic of the various mintages of the period. These characteristics can originate from the different ores and from the manufacturing process used for the silver production. For a statistical evaluation of the data a representative number of coins are required as untypical values influence the interpretation of the analytical results.

As the medieval silver coins are surface-corroded, a major disadvantage of ED-XRF is its relatively low information depth, which is a function of the energy of both the primary and the fluorescence radiation and also of the chemical composition for the specimen itself. Applied to corroded objects non-destructively, it has to be considered that the results obtained from the surface do not represent the chemical composition of the core. Owing to corrosion processes the base components of the alloy will be oxidized and dissolved. Consequently, the surface of the coin will be depleted of these elements and an enrichment of the noble constituents of the alloy will occur. For example, in [8], the in-depth composition variation for some corroded silver coins, using 3 MeV proton PIXE at LARN, Namur, Belgium accelerator was studied. After mechanical polishing, it was observed that a depletion of the silver content from 93.3% at the surface to 82.5% after a 100 microns layer was removed, and an enrichment in copper from 6.1% to 17% for the same analyzed depths.

Most of the measurements were performed with ED-XRF, in order to determine some trace elements (less than 0.1% content); few representative samples from the analyzed batches of coins were measured using in-vacuum PIXE at the Bucharest 8 MV FN High Voltage Engineering Corporation Tandem. The coins were in vacuum analyzed with a 3 MeV proton beam impinging at 45° to the target surface. A Canberra GL0110P – Low Energy Germanium Detector (100 mm² area, 10 mm thickness, 0.075 mm Be window thickness, energy resolution 160 eV FWHM at 5.9 keV, 500 eV FWHM at 122 keV), perpendicularly oriented to the proton beam direction recorded the X-ray spectrum emitted by the samples. A 0.8 mm diameter beam and a constant proton dose were used, each acquisition taking roughly 10 minutes.

The overall uncertainty for the ED-XRF and PIXE measurements was 5% for major elements; 5–10% for minor elements and 15% for trace elements (only for

PIXE) – major elements are those contributing more than 10% to overall composition, minor elements 0.1–10% and trace elements less than 0.1%, down to detection limits. The uncertainties were not only statistical; they also originate from the roughness of the coin surface, from the chemical corrosion, and/or the wearing of the objects, altering the accuracy of the results. In the case of silver matrix, the exact values of trace elements concentrations were considered of being not relevant, only the bare presence and the order of magnitude of the concentrations indicating the possible ore source. The melting technologies were not very advanced, so the resulting alloy was strongly inhomogeneous. As a consequence, serious differences between the average compositions of both sides of the coins were noticed.

4. ILLUSTRATIVE EXAMPLES

When dealing with coinages the main questions are the evolution of the fineness, the debasement process, as well as the ore supplies issue [9].

A very interesting case was the one of the *brakteaten pfennige* (one side thin foil coins), minted by the medieval German princes and bishops (Xth – XIIth centuries). The National Museum of Romania's History has some hundreds of such coins in its collections, and a quick sorting of them was necessary. A way of solving this problem was to use *in-situ* ED-XRF measurements.

Very few coins were high fineness silver coins – see Fig. 1, for which the following composition: Ag = 96%, Au = 0.75%, Pb = 0.65%, Cu = 2.05% was determined. However, most of the coins were silvered coins, with either copper – see Fig. 2, or bronze or leaded bronze (Pb = 65%, Cu = 22%, Sn = 12%, Sb = 0.4%) core – see Fig. 3, being covered with a very thin silver layer. This thin silver layer contains a lot of mercury, which probably remained from the extraction process of silver through amalgamation. A possible explanation for these numerous silvered coins can be the fact that the old German silver mines were probably exhausted during XIth century, only in the XIVth century being discovered new mines in Saxony (*e.g.*, Freiberg and Schneeberg). However, during this period (Xth – XIIth centuries) the construction of the great cathedrals had started, and there was a high need for money; therefore, a strong debasement of these silver coins took place.

A more extensive study was performed on the medieval silver coins named *groschen* that circulated during the late Middle Age on the Moldavian territory. Approximately one thousand of medieval (XIVth–XVIth centuries) silver *groschen* were studied to determine the evolution of the coinage – debasement, metal sources, minting technologies. Two analytical methods were used: ^{241}Am source based ED-XRF and, only for some representative exemplars, 3 MeV protons PIXE.

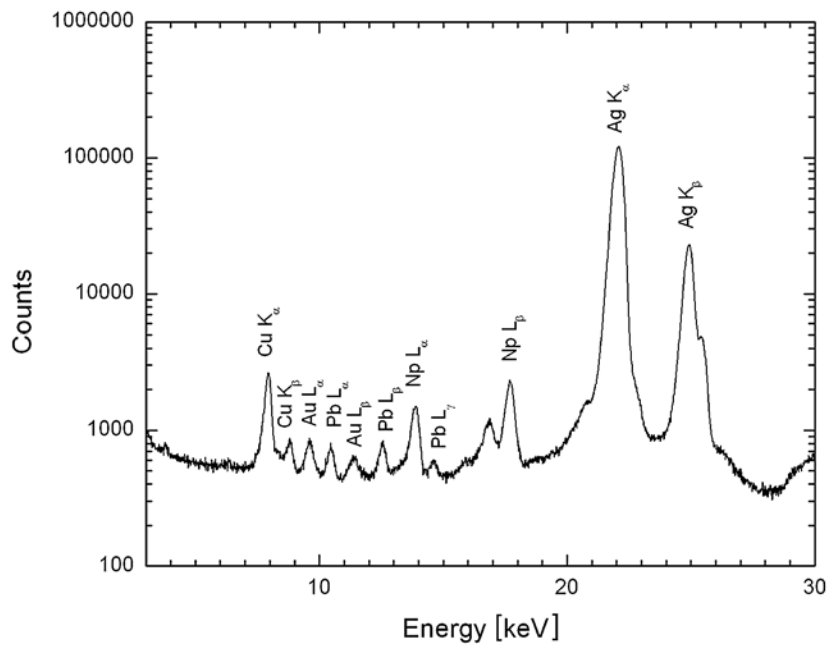


Fig. 1 – High fineness silver *brakteate pfennig* XRF spectrum (Np L lines come from the ^{241}Am excitation source).

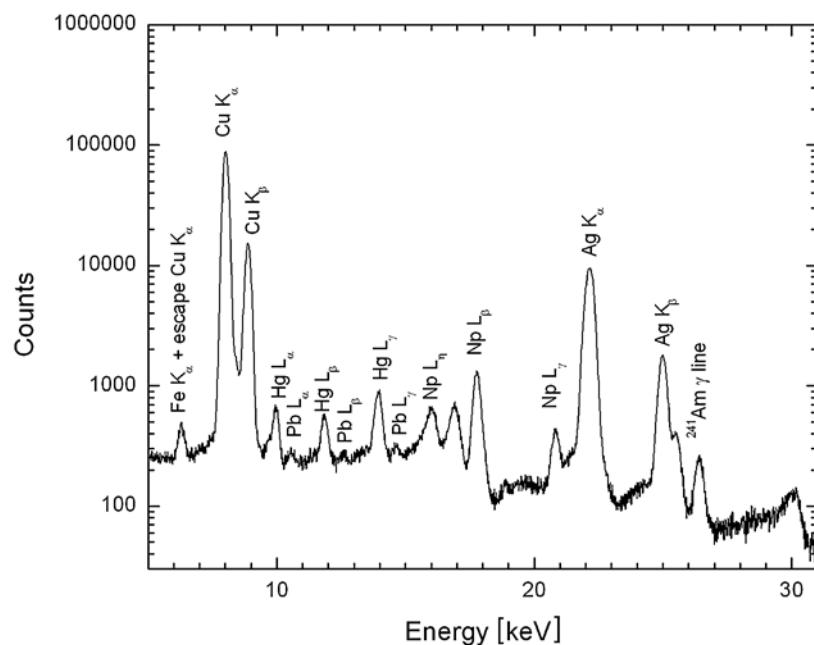


Fig. 2 – XRF spectrum of a silvered copper core from a *brakteate pfennig* (Np lines come from the ^{241}Am excitation source).

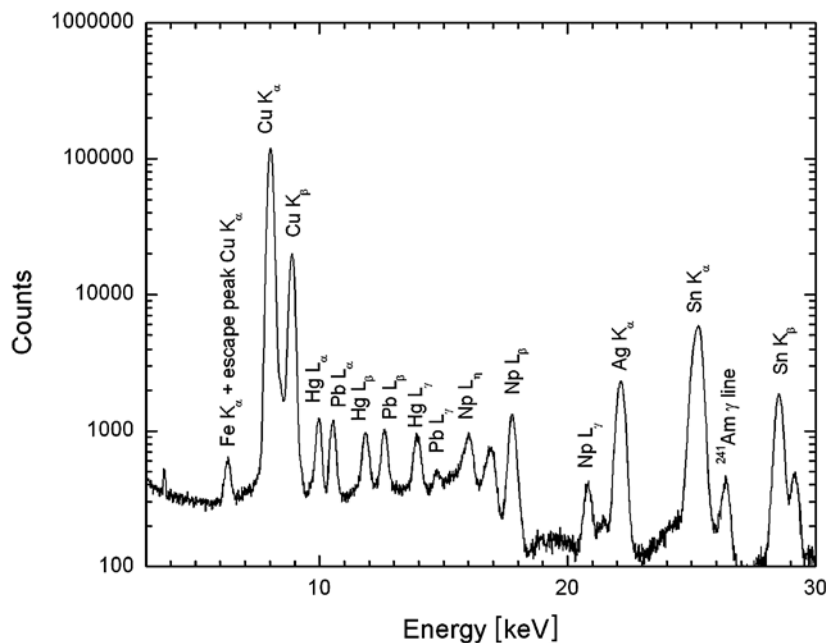


Fig. 3 – XRF spectrum of a silvered bronze core from a brakteate pfennig (Np L lines come from the ^{241}Am excitation source).

The fundamental historical problem that raised this study was the fact that Moldavia is a region where there are no silver mines. One possible hypothesis was that the first monetary emissions of Moldavian Medieval princes were made using foreign coins, taken as customs taxes and from commercial exchanges, which were melted and reused. The physicist non-destructive analytical methods, such ED-XRF and PIXE were necessary, to confirm or to infirm this hypothesis. Many types of silver medieval coins were analyzed: Moldavian, Bohemian, Hungarian, Tatar, Walachian and Polish, all coined between the XIVth and XVth centuries and the results of different coins groups were compared. Two examples of spectra are shown in Fig. 4 (ED-XRF spectrum of an Alexandru cel Bun *grosch*) and Fig. 5 (PIXE spectrum of a Petru I Mușat *grosch*).

In order to establish a connection between the coins and the silver ore sources, the following trace elements were considered: Au, Bi, Pb, Zn and Sb. The content of Ag and Cu was very variable even for different emission of the same ruler, Ag/Cu ratio being an indicator of the debasement (inflation). Ca, Ti, and Fe, although determined, were not taken into account in the provenance analysis, since they are probably just traces of earth oxides to be found on the coins (the analyzed coins are precious historical artifacts and they were not thoroughly cleaned, excepting the alcohol wipe cloth rubbing).

Gold, being a noble metal is not affected when silver is purified by amalgamation or cupellation. It remains in the silver with its original proportion

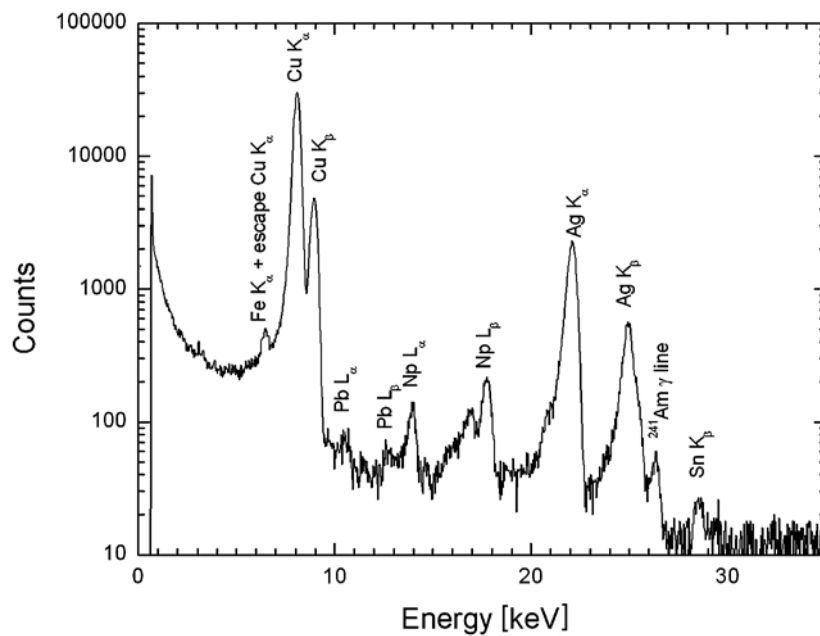


Fig. 4 – XRF spectrum of an Alexandru cel Bun (XVth Century) *grosch* (Np L lines come from the ^{241}Am excitation source).

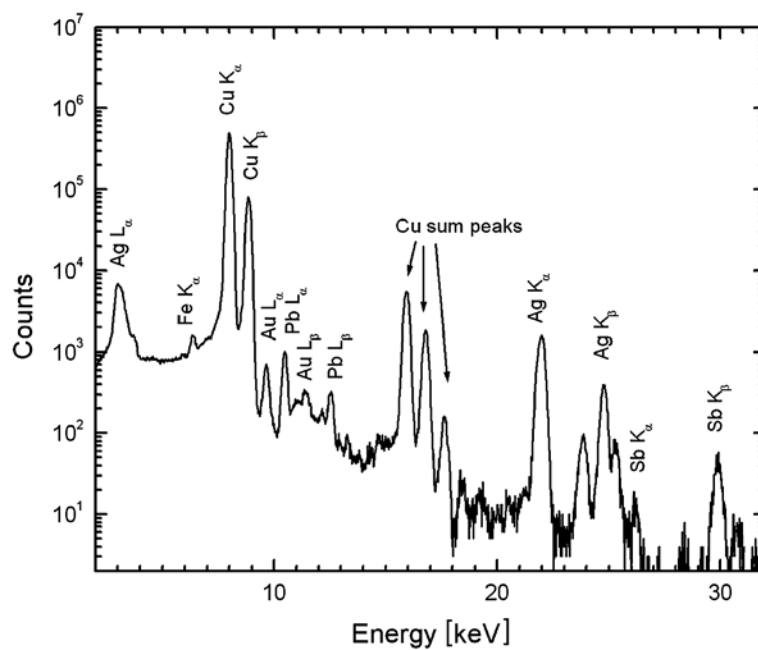


Fig. 5 – 3 MeV p PIXE spectrum of a Petru I Musat XIVth Century *grosch*.

unchanged. Since the gold most probably originates in the silver ores, it can be measured to explore the possible sources of the silver.

An interesting fact connected with the manufacturing technology is observed addition of relatively low amount of Pb (around 1%) in a copper matrix in order to lower the melting point of the alloy. A much lower content of lead can be attributed to the imperfections in the metallurgical process (such a low amounts could not be refined in the purifying procedure).

A low amount of Cu (up to 1%) plays the role of hardener for the silver alloy, while a higher amount indicates a difficult economical situation. In this way, the ratio Ag/Cu reflects the economical and political situation of the corresponding epoch. A nice example is the comparison between the two historical Romanian regions: Moldavia and Walachia. During the XIVth century, the Moldavian princes passed through a very difficult period (many conflicts with the neighboring Poland and Hungary and Tatar invasions). As a consequence, the monetary emissions that took place during that period contained an increasing amount of copper (copper proportion in Moldavian coins emitted during the XIVth century increased from 19% to 78%, while the silver proportion decreased correspondingly, from 79% to 19%). By contrast, Walachia's political and economical situation was much stable, and the determined silver content of the corresponding coins was high and relatively constant (from 80% up to 97%). For the Hungarian coins, great variations of the composition were noticed, not only regarding the major elements proportion (Cu and Ag), but also for trace elements presence and proportion, such is the case for Au, Pb, Bi and Sb. As possible sources for the silver ore, one can indicate Transylvanian ones (Bi, Pb and Sb as trace elements) for Maria reign (anarchy, civil war, conflicts with Austria). Transylvania and Croatia mines (little gold) were used by Sigismund of Luxemburg, a king with a quiet reign. For Polish coins, a silver source with Au as fingerprint and traces of Sb was put into evidence, silver ore being mined most likely from Silezia (Schlesien). For Bohemian coins, the silver alloy is characterized by the lack of Au and the presence of Zn (0.1%...0.4%). Metallifer Mountains was the closest and the most probable silver ore source. Both Poland and Bohemia had peaceful and economical flourishing history during the XIVth century, fact that explains the high and relatively constant silver content of the coins (average silver content was 95%). Tatar coins were characterized by a relatively high amount of silver (75%...97%) with a high gold content (0.4%...0.8%). Bi was found sometimes as trace element (0.2...1.0%) in Tatar coins. The main silver source was very likely a Middle-Eastern one.

Petru I was the first Moldavian prince who struck a local coin, as a sign of the country independence. The silver content is very different for the three monetary emissions that took place: the average silver content was around 20%, 48% and 70%, respectively. The precious metal was most likely obtained by melting foreign silver and copper coins (for some of coins, copper was even the main element, reflecting a high debasement). One can find coins with composition

similar to the foreign ones, depending on the military alliances and commercial exchanges typical for the respective period (high Ag content for the period when Moldavia was under Poland suzerainty and relatively lower Ag content for the periods of alliance with Hungary). As a consequence, the historian hypothesis that the Moldavian coins were obtained by melting foreign coins obtained as taxes or through commerce was confirmed.

It is worthwhile mentioning that, in the XVIth century, during the Moldavian conflicts with Poland, the commercial links were interrupted. As a consequence, Bogdan III and Ștefăniță, two Moldavian princes from the first half of the XVIth century, had tried to coin money from some local silver ores, which were very poor in precious metal. Since the local craftsmen did not master very well the amalgamation processes, the refinement of the ore was very crude, and these coins feature a remarkably high content in other metals and a clear Hg presence – see Fig. 6.

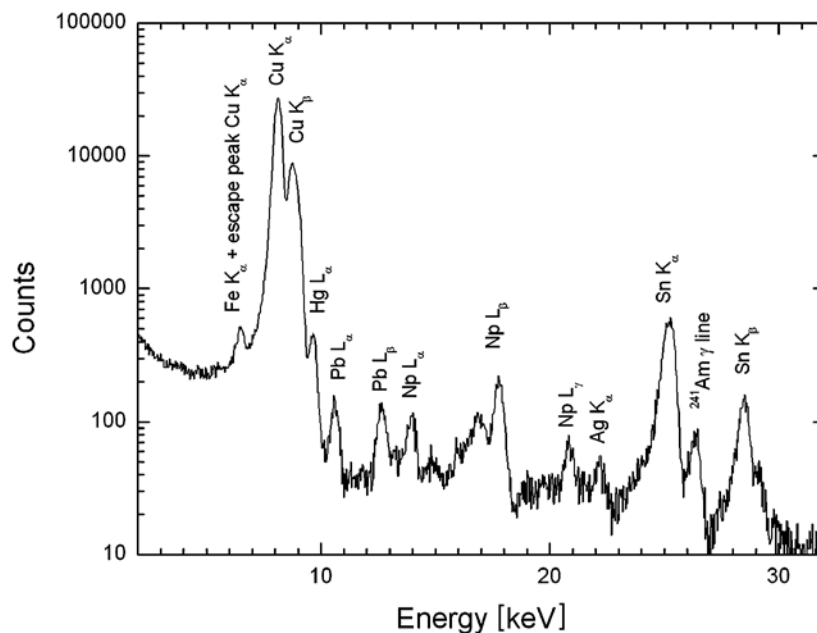


Fig. 6 – Ștefăniță (XVIth Century) *grosch* XRF spectrum (Np L lines come from the ^{241}Am excitation source).

5. CONCLUSIONS

The present studies demonstrated the utility of ED-XRF technique (*in-situ* ED-XRF completed by PIXE) for solving specific museums problems related to classification, authentication and characterization of ancient silver coins. A fast

selection of medieval German *brakteaten pfennige* was performed as a first example. The present work also helped the numismatists to demonstrate that a classification of the Moldavian medieval coins with respect to the contemporary foreign coins is possible, explaining the circulation of money as a function of the international relationships and wars. The thesis of melting foreign coins to produce local money stands, as it was proven by the above-described ED-XRF and PIXE measurements. A guess of the ore source is possible using the determined minor and trace elements. The presence of Hg in the late Middle Age Moldavian coins indicated the attempts to use the local ores, poor in silver. The potential of ED-XRF technique for specific museums studies was clearly demonstrated, having as a first result the decision of the cultural Romanian authorities to acquire a transportable (or portable) ED-XRF facility dedicated to circulate in Romanian museums for compositional analysis of metallic objects and painting pigments.

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