MEDIEVAL SILVER COINS ANALYSES BY PIXE AND ED-XRF TECHNIQUES

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This paper presents some applications of *Particle Induced X-ray Emission* (PIXE) and *Energy-Dispersive X-Ray Fluorescence* (ED-XRF) for the characterization of some medieval silver coins: Moldavian *groats* and *bracteate pences*. The elemental composition measurements were performed in connection with more comprehensive historical and numismatic studies. Aspects related to manufacturing technologies, commercial, military and political relationships, provenance (mines, workshops) identification were revealed as a consequence of the undertaken analyses.

Key words: PIXE; ED-XRF; silver coins; elemental composition.

1. INTRODUCTION

The elemental composition of archaeological metallic objects (trace-elements determination including) may reveal interesting clues regarding the manufacturing process (metallurgy), the employed ore sources (mines), the ancient trade routes or the political and economical connections between ancient populations.

Analytical techniques based on the quantitative characteristic X-rays measurements – such as *Particle Induced X-ray Emission* (PIXE) and *Energy-Dispersive X-ray Fluorescence* (ED-XRF) – can be successfully applied to provide answers regarding the elemental composition of ancient metallic artifacts; most often, these measurements were successfully used for the study of coins [1–4]. PIXE and ED-XRF measurements provide elemental information regarding the first tens of micrometers of the analyzed object; this information is meaningful in the case of noble metal artifacts, mainly because the corrosion phenomena are rather limited for this particular type of samples.

In the case of coinages, the main questions that arise in the minds of historians and numismatists are the following: which was the evolution of the fineness? was there any debasement process? can we obtain any information regarding the manufacturing technology? which was the source of precious metal from which the coin was manufactured?

The present paper describes the results of the fruitful collaboration established during the last years in the field of archaeometry between "Horia Hulubei" National Institute for Nuclear Physics and Engineering and the National Museum of Romania's History. An extensive campaign of PIXE and ED-XRF measurements took place; a very large number of medieval silver coins that circulated on the Moldavian territory during the late medieval period (XIV^{th}–XVI^{th} centuries) – the so-called Moldavian *groats* and numerous German *bracteate pences* dating from the X^{th}–XII^{th} centuries were investigated. As a consequence of the elemental composition measurements, several important historical conclusions were obtained. They are related to the following aspects: fineness evolution, manufacturing technology, connections between the economical and the political events that took place in Moldavia history and the neighboring kingdoms during the XIV^{th}–XVI^{th} centuries period.

The data regarding the Moldavian mint alloys are rather scarce in the literature; the interest for this numismatic issue has only risen during the last decade. Some examples can be found in [5] – where data on the Moldavian monetary mint struck at the end of the XIV^{th} century (the reign of Petru I, Ştefan I and the beginning of Alexandru I's reign) or the beginning of the XVI^{th} century (Bogdan III monetary issue) are presented; in [6] the data are limited to the second half of the XV^{th} century coinage only. In any case, the information extracted from the above-mentioned preliminary studies led to the conclusion that the Medieval Moldavian monetary system was a dynamic and complex one, its evolution being influenced not only by economical factors, but also by political ones. As a consequence, this monetary system has to be studied in connection with the evolution of the monetary systems of the two greatest powers neighboring Moldavia: the Hungarian and the Polish kingdoms. Therefore, a thorough and more systematic analytical investigation of the Moldavian medieval coinage and of the contemporary coinages from the neighboring countries was started, in order to fully understand the dynamics of these closely interconnected monetary systems.

2. EXPERIMENTAL

All analyzed coins belong to the numismatics collections of the National Museum of the Romania's History in Bucharest; the PIXE and ED-XRF measurements took place at "Horia Hulubei" National Institute for Nuclear Physics and Engineering.

The non-destructive analysis of the coins was performed by employing two analytical methods: 3 MeV protons PIXE and ED-XRF based on a ^{241}Am source.

PIXE measurements were done in vacuum; the 1 mm diameter proton beam was obtained from the Bucharest 8 MV FN HVEC Tandem accelerator of the "Horia Hulubei" National Institute for Nuclear Physics and Engineering. A Canberra GL0110P – Low Energy Germanium Detector (100 mm^2 area, 10 mm thickness, 0.075 mm Be window thickness, energy resolution FWHM of 160 eV at 5.9 keV, FWHM of 500 eV at 122 keV), perpendicularly oriented to the proton beam direction was used for the detection of the characteristic X-rays emitted by the coins. The data acquisition was made for a constant proton dose, the measurements for each coin lasting roughly 10 minutes.

The ED-XRF measurements were made with a spectrometer consisting of a 30 mCi ^{241}Am annular gamma source and a Si(Li) vertical detector (FWHM of 180 eV at 5.9 keV). ED-XRF spectra were acquired for half an hour.

The quantitative results were obtained by using as standards modern coins with known elemental composition.

ED-XRF, being a much simpler and cheaper analytical method than PIXE, was routinely used for coins analysis, while the PIXE measurements were done just in selected cases.

The overall uncertainties for the determined concentrations was 5% for major elements; 5–10% for minor elements and 15% for trace elements (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 estimated uncertainties are not only statistical; they also originate from the roughness of the coin surface, from the chemical corrosion, and/or the wearing, altering the accuracy of the results.

In the case of silver matrix, the exact values of trace elements concentrations were considered of being not of very much importance, only the bare presence and the order of magnitude of the concentrations being taken as indicators of the possible ore sources.

Since the melting technologies were not very advanced, it was expected that the coins alloy to be relatively inhomogeneous. As a consequence, as a final result for each analyzed artefact the average of the concentrations for each side of the coins was taken.

Two examples of typical spectra are shown in Fig. 1 (the PIXE spectrum of a Petru I Musat groat) and in Fig. 2 (the ED-XRF spectrum of an Alexandru cel Bun groat).

The results of the analyses are summarized in Table 1, where a list of the average composition with respect to the country is given; the comparison between the different groups of coins is thus facilitated.

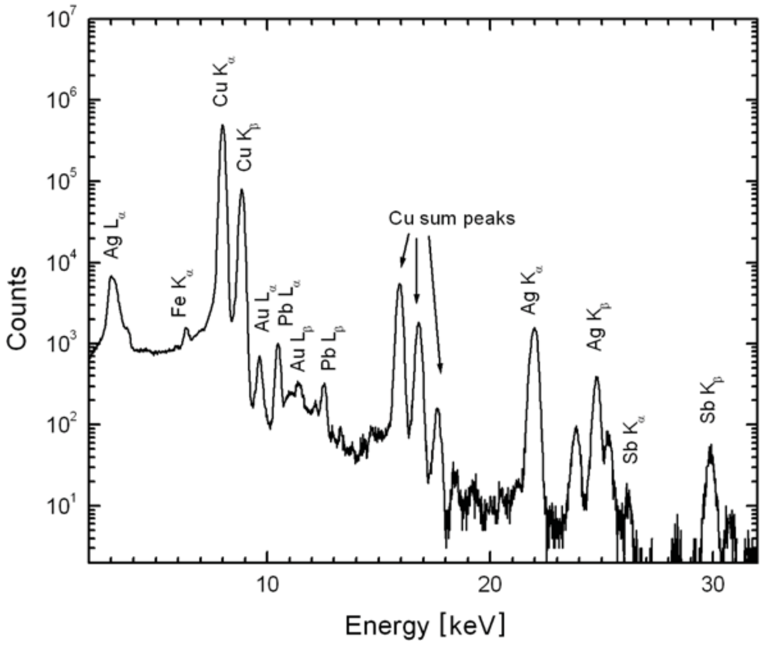

Fig. 1 – PIXE spectrum of a Petru I Musat *groat*.

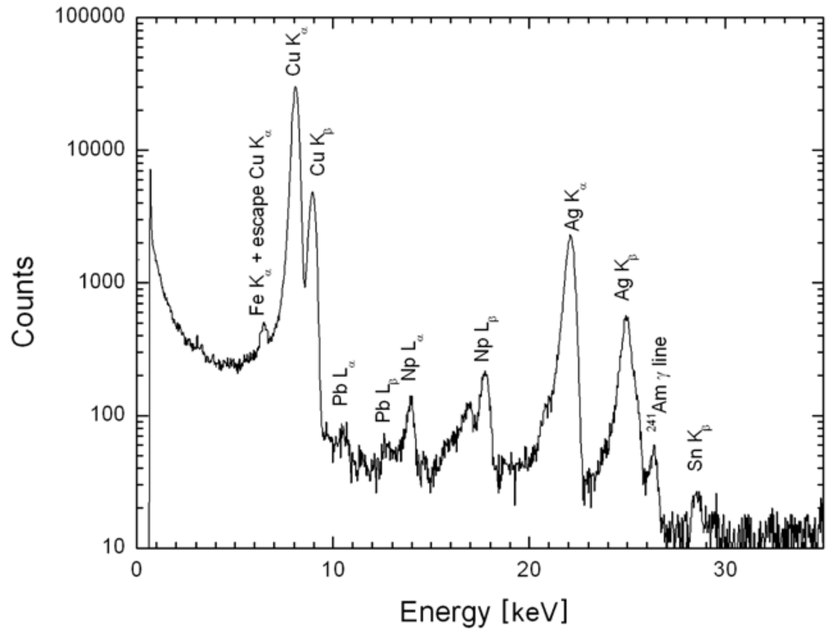

Fig. 2 – ED-XRF spectrum of an Alexandru cel Bun *groat* (Np L lines come from the ^{241}Am excitation source).

3. RESULTS AND DISCUSSIONS

The fundamental historical problem that raised this study was the fact that Moldavia is a region where there are no silver mines. One historical hypothesis was that the first monetary issues of the Moldavian medieval princes were made by using foreign coins, taken as customs taxes and from commercial exchanges, which were melted and re-used. The physical non-destructive analytical methods – ED-XRF and PIXE – were thus necessary to confirm or to infirm the above-mentioned hypothesis.

The analyzed silver coins – approximately one thousand – Moldavian groats, but also many other types of contemporary silver coins that circulated that period in the neighbouring countries: Hungary, Poland, Bohemia, Golden Hoard, Wallachia – were all minted during the XIVth-XVIth centuries.

The content in silver and copper was very variable even for different issues of the same ruler; the Ag/Cu ratio can be considered as an indicator of the debasement–inflation.

Three types of mint, all with the same legend, but in different alloys were put into evidence for the Moldavian silver groats:

- silver (for numismatists, the word “silver” designates the alloy which comprises over 50% Ag);
- billon (for numismatists, the word “billon” designates the alloy which comprise under 49.9 % Ag);
- copper or, more rarely, bronze (Cu-Sn alloy) – in any case, with an Ag content below 3%.

This situation is, undoubtedly, a “notable exception” for the entire wide-world medieval numismatics. It has to be noticed that the simultaneous presence of all the above-mentioned issues would have blocked the whole economic and social mechanism of the Moldavian state, due to the fact that nobody would have had accepted coins with the same nominal value, but with a reduced content of precious metal. In such a situation, the main loser would have been the state itself, which would have lost not only an essential instrument for the internal as well as for the external policy, but also the biggest part of the precious material stock, which would have been detained by particulars or would have left the country, back to the state income coming back – through fiscal or customs mechanisms – only the bronze coins. An explanation has therefore to be found for those different issues – and the most likely explanation was that these different coinages were successive in time.

Ca, Ti, and Fe, although determined through the ED-XRF and PIXE measurements, were not taken into account for further numismatics analyses, since they were considered as coming just from the traces of earth oxides to be found on the coins surfaces. Their presence in the spectra was due to the fact that the analyzed coins are museum artefacts and that they were not thoroughly cleaned – except for alcohol wipe cloth rubbing.

An interesting fact connected with the manufacturing technology is the observed addition of relatively low amount of lead (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 low amounts could not be refined in the purifying procedure).

A low amount of copper (up to 1%) plays the role of hardener for the silver alloy, while a higher amount is a debasement indicator – the ratio Ag/Cu reflecting the economical and political situation of the corresponding epoch. A pretty good example for this issue is the comparison between the two historical Romanian regions: Moldavia and Wallachia (see Table 1). During the XIVth Century, the Moldavian princes passed through a very difficult period (many conflicts with the neighbouring Poland and Hungary and Tatar invasions). As a consequence, the issues that were struck during that period contained an increasing amount of copper. By contrast, Wallachia's political and economical situation was much stable, and the determined silver content of the corresponding coins was high and relatively constant. For the Hungarian coins, one can remark big variations in the composition (see also Table 1).

Table 1

Upper and lower limits of the determined elements in the medieval *groats* (n.d. means "not detected")

Country	Cu (%)	Zn (%)	Ag (%)	Au (%)	Pb (%)	Bi (%)	Sb (ppm)
Bohemia (1360–1380)	2.0…6.0	0.1…0.4	90.0…97.0	n.d.	0.3…4.0	n.d.	n.d.
Poland (1370–1390)	2.0…4.0	n. d.	94.0…98.0	0.3…0.7	0.7…1.3	n.d.	250
Golden Horde (XIVth Century)	2.0…22.0	n.d.	75.0…97.0	0.4…0.8	0.4…1.7	0.2…1.0	n.d.
Hungary Maria (1380–1385)	22.0…42.0	n.d.	55.0…75.0	0.2…0.5	0.5…2.8	0.1…0.2	200
Hungary Sigismund of Luxemburg (1385–1400)	1.0…27.0	n.d.	70.0…97.0	0.1…0.3	0.2…1.5	n.d.	n.d.
Wallachia (1370–1400)	2.0…16.0	n.d.	80.5…97.0	0.5…1.2	0.5…2.3	n.d.	n.d.
Moldavia Petru I (1375–1380)	19.0…37.0	n.d.	60.0…79.0	0.3…0.7	0.3…1.3	n.d.	200
Moldavia Petru I (1380–1385)	50.0…60.0	n.d.	35.0…48.0	0.1…0.3	0.4…1.7	0.1…0.2	160
Moldavia Petru I (1385–1390)	70.0…78.0	n.d.	19.5…28.0	traces	0.3…0.8	0.1…0.3	n.d.

Au, Bi, Pb, Zn and Sb were the trace-elements considered as being relevant for the trials of identifying the silver ore sources. In particular, 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 unchanged. Since gold most probably originates from the silver ores, it can be measured to explore the possible sources of the silver.

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 (with very small gold content) were used by Sigismund of Luxemburg, which had a very long and troubled reign. For the Polish coins, the trace-elements indicate a source with Au and Sb traces as fingerprint – the most likely region of mining this kind of silver was Silesia (Schlesien). For the Bohemian coins, the silver alloy is characterized by the lack of Au and the presence of Zn. 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. For the Tatar coins, one can notice the relatively high amount of silver with high gold content. Bismuth is found sometimes as trace-elements in those coins. The main silver source was very likely in this case a Middle-Eastern one.

Petru I was the first Moldavian prince who struck a local coinage. The silver content was very different for the three monetary issues that took place during his reign: the average silver content was around 20%, 48% and 70%, respectively. The precious metal was most likely obtained by melting down foreign silver and copper coins (for some coins, copper is 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 silver content for the period when Moldavia was under Poland suzerainty and relatively lower silver content for the periods of alliance with Hungary). As a consequence, the supposition that the Moldavian coins were obtained by melting foreign coins obtained as taxes or through commerce was confirmed.

An important contribution of the performed analysis analyses regards the understanding of the technology used in the Moldavian monetary workshops during XIVth–XVIth centuries. It is worthwhile mentioning that, during the Moldavian-Polish conflicts, the commercial links were interrupted. As a consequence, Bogdan III and Ştefan IV, two Moldavian princes from the first half of the XVIth century, had tried to strike coins with very poor content in precious metal. The refining technologies of silver alloys were compatible to those used in more advanced countries from Central Europe, but probably the political will to constantly respect the legal standards was missing. Moreover, the external aspect of the coins was improved through the additional silvering. In certain cases, the analyses have highlighted the use of amalgamation technique (Ştefan IV).

Another study case was the one of the *bracteate pence* – a one side thin foil coins minted by the medieval German princes and bishops during the Xth–XIIth centuries. The National Museum of Romania's History has some tens of such coins in its collections, and a quick sorting of them was necessary. A way of solving this problem was to use the ED-XRF measurements. Very few coins were high fineness silver coins – see Fig. 3, for which the following average composition was determined: Ag = 96.00%, Au = 0.75%, Pb = 0.65%, Cu = 2.05%.

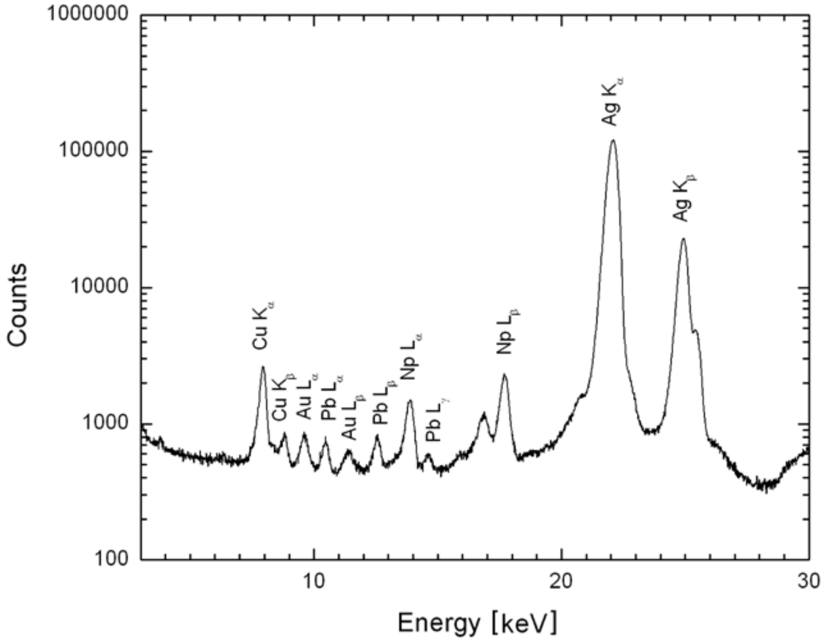

Fig. 3 – ED-XRF spectrum of a high fineness silver *bracteate pence* (Np L lines come from the ^{241}Am excitation source).

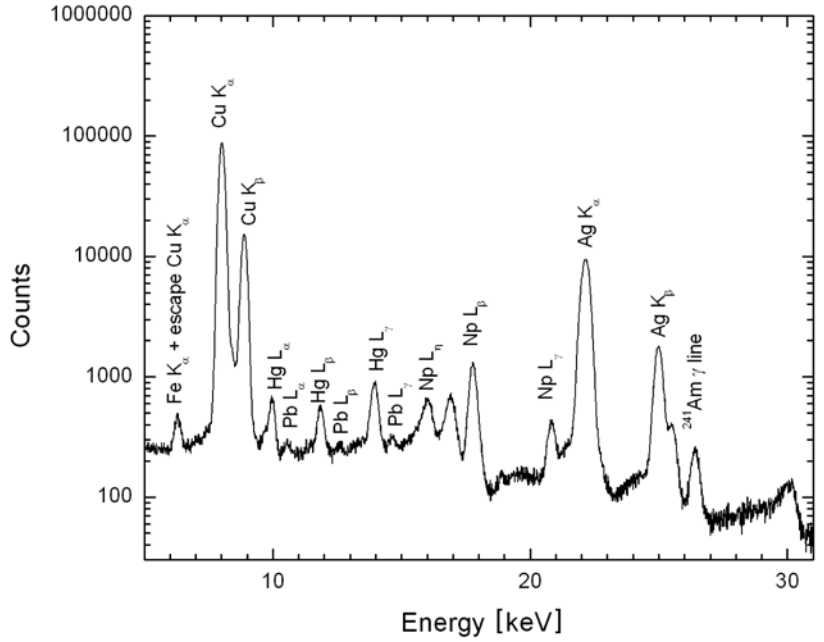

Fig. 4 – ED-XRF spectrum of a silvered copper core from a *bracteate pence* (Np lines come from the ^{241}Am excitation source).

However, most of the coins were silvered coins, with either copper – see Fig. 4, or bronze or leaded bronze (Pb = 65%, Cu = 22%, Sn = 12%, Sb = 0.4%) core – see Fig. 5, being just covered with a very thin silver layer. This thin silver layer contains a lot of mercury. This element is not a remnant of the silver extraction process, but, more likely just the indicator of an amalgamation silvering processing.

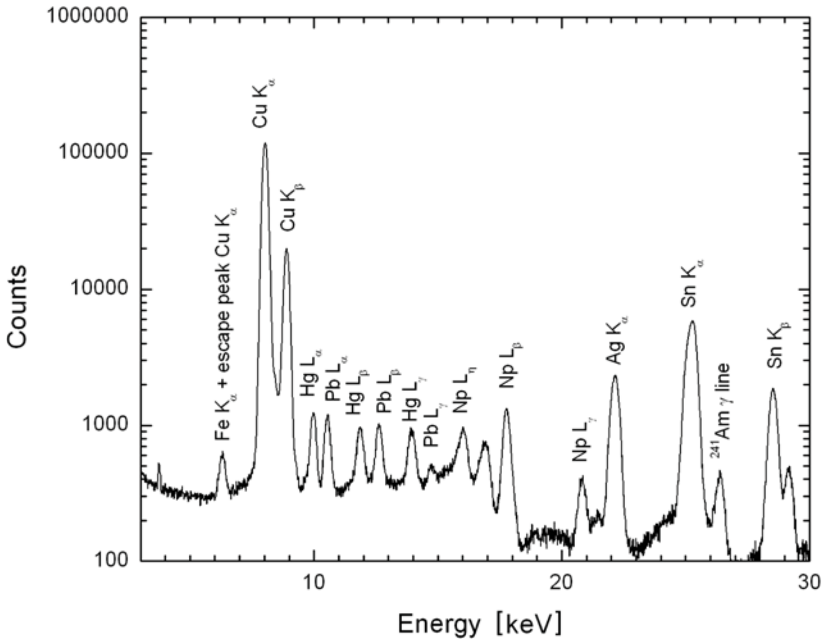

Fig. 5 – ED-XRF spectrum of a silvered bronze core from a *bracteate pence* (Np L lines come from the ^{241}Am excitation source).

A possible explanation for the apparition of this high number of silvered coins can be the fact that the old German silver mines ores were probably exhausted during XIth century, and just only in the XIVth century new mines in Saxony (*e.g.* Freiberg and Schneeberg) were discovered. However, during this period (Xth–XIIth centuries) the construction of the great cathedrals had started, and there since was a high need for currency, a strong debasement of the original silver coins took place.

4. CONCLUSIONS

PIXE and ED-XRF measurements were used for the elemental characterization of the different types of medieval coins – the Moldavian *groats* and the German *bracteate pences*. The analyses helped the Romanian 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 political relationships existing by that epoch. The thesis of melting foreign coins to produce local money was confirmed, being supported by the reported PIXE and ED-XRF measurements. The use of different silver ore sources was put into evidence by using the information provided by the minor and trace-elements concentrations that were determined in different types of coins. The presence of mercury in the late Middle Age Moldavian coins indicated the use of silver amalgamation metallurgical procedure.

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