ARCHAEOMETRICAL STUDIES ON MEDIEVAL SILVER COINS AT THE BUCHAREST TANDEM ACCELERATOR

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Abstract

The analysis of archaeological objects requires simultaneously, non-destructive, fast, versatile, sensitive and multielemental methods. The purpose of our work is to help Romanian curators to identify objects provenance (workshops, technologies, mines) and to explain commercial, military and political aspects. Medieval Moldavian (XIV-XVI Centuries) silver coins (groschen) were studied to determine the evolution of the coinage (debasement, metal sources, minting technologies). For these coins, two methods were used: 3 MeV protons PIXE (Proton Induced X-ray Emission) and ^{241}Am source based XRF (X-Ray Fluorescence). XRF was used to determine the heavier elements concentrations. Comparing the trace elements results (Bi, Pb, Zn, Au, Sb) obtained on these samples with the ones on coins from the neighbouring countries (Hungary, Poland, Tatar Khanate, Bohemia) we concluded that a lot of Moldavian emissions were made by melting foreign coins, probably obtained as customs taxes. For some coins, the Hg presence is an indication of the use of local silver ores to manufacture local money. The relationship between the silver content of the coins and the military conflicts during various periods is discussed.

1 INTRODUCTION

The trace element composition of archaeological metallic objects may reveal information on the ore sources (mines), on the manufacturing processes (e.g. metallurgy) and on trade routes. The noble metals artifacts play a special role not only because of their value, but also because they are very stable against corrosion. This means that very old artifacts are relatively well preserved and can be easily analyzed nondestructively using surface techniques such as PIXE and XRF (the analyzed depth is in the range of some tens of micrometers). [1, 2, 3] When dealing with coinages the main questions are the evolution of the fineness, the debasement process, as well as the ore supplies issue.

Our purpose was to help Romanian curators to perform a thorough study on the Moldavian Medieval silver coins - groschen - that circulated during the late Middle Age on the Moldavian territory. The elemental composition of these coins lead to different historical hypotheses regarding the manufacturing process and a close connection between the economical life of those ages and the corresponding historical events was revealed.

2 EXPERIMENTAL

Our study was an extensive one: around one thousand medieval coins being analysed during the last three years in our laboratory. For the non-destructive analysis of the samples, two analytical methods were used: 3 MeV protons PIXE and ^{241}Am source based XRF. For in vacuum PIXE, we used a proton beam obtained from the Bucharest 8 MV FN High Voltage Tandem. The coins were in vacuum analyzed with a 3 MeV proton beam impinging at 45° to the surface. A Canberra GL0110P – Low Energy Germanium Detector (100 mm^2 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. We routinely used a 0.8 mm diameter beam and a constant proton dose, each acquisition taking roughly 10 minutes.

XRF measurements were done with a spectrometer consisting of a 30 mCi ^{241}Am annular gamma source and a Si(Li) vertical detector. XRF was used to determine the heavier elements concentrations, such as Ag, Sn, Sb.

PIXE was employed to determine elements with $20 \le Z \le 40$ and Au, Hg, Pb, Bi (using L rays) because of its high ionization cross section, with sensitivities of around 5 ppm. For elements with $41 \le Z \le 60$ (Ag, Cd, In, Sn, Sb especially), XRF was used as a complementary technique, because of its higher sensitivity for higher Z elements. XRF is simpler and cheaper than PIXE, but longer acquisition times are required. The sensitivity in our case is 20-30 ppm (for Ag region). A drawback of the XRF method using an ^{241}Am source is the complicated spectrum of the source.

Quantitative results were obtained using modern coins with known elemental composition. Dedicated home-made software was employed to infer the quantitative results.

The overall uncertainty for the PIXE method 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 – see above) The errors are 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. [4, 5]

In the case of silver matrix, the exact values of trace elements concentrations are not relevant, only the bare presence and the order of magnitude of the concentrations being indicators of the possible ore source.

The melting technologies were not very advanced, so the resulting alloy was strongly inhomogeneous. As a consequence, we have noticed serious differences between the average compositions of both sides of the coins.

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 possible hypothesis is 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 as PIXE and XRF were necessary, to confirm or to infirm this hypothesis. Many types of silver Medieval coins were analysed: Moldavian, Bohemian, Hungarian, Tatar, Walachian and Polish, coined between the XIVth and XVth century and the results of different coins groups were compared. An example of a spectrum is shown in figure 1 (a Petru I Musat silver 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 just traces of earth oxides to be found on the coins. (the analyzed coins are precious historical artefacts and they were not thoroughly cleaned).

To review the main types of studied coins in a synthetic mode, a list of average composition with respect to the country is given in Table 1.

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 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 (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 monetary emissions that took place during that period contained an increasing amount of copper. By contrast, Walachia's political and economical situation was much stable, and the determined silver content of the corresponding coins is high and relatively constant. For Hungarian coins (see also table 1), one can notice great variations of the composition. 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 de Luxemburg, a king with a quiet reign. For Polish coins, we remark a source for the silver, with Au as fingerprint and traces of Sb. The region of mining was Silezia (Schlesien). For Bohemian coins, the silver alloy is characterized by the lack of Au and the presence of Zn. Metallifer Mountains is 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 Tatar coins, one can notice the relatively high amount of silver with high gold content. Bi is found sometimes as trace elements. 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 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 Ag content for the period when Moldavia was under Poland suzerainty and relatively lower Ag content for the periods of alliance with Hungary).

It is worthwhile mentioning that during the Moldavian conflicts with Poland, the commercial links were interrupted. As a consequence, Bogdan III and Stefanita, two Moldavian princes from the first half of the XVIth century, had tried to coin money from local silver ores, which were very poor in silver. 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 Hg (up to 10%).

Table 1 – Upper and lower limits of the determined elements

Country	Cu(%)	Zn(%)	Ag(%)	Au(%)	Pb(%)	Bi(%)
Bohemia (1360-1380)	2.0…6.0	0.1…0.4	90.0…97.0	n.d.	0.3…4.0	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.
Tatar Khanate (XIVth Century)	2.0…22.0	n.d.	75.0…97.0	0.4…0.8	0.4…1.7	0.2…1.0
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
Hungary Sigismund de Luxemburg (1385-1400)	1.0…27.0	n.d.	70.0…97.0	0.1…0.3	0.2…1.5	n.d.
Walachia (1370-1400)	2.0…16.0	n.d.	0.5…1.2	0.5…1.2	0.5…2.3	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.
Moldavia Petru I (1380-1390)	50.0…60.0	n.d.	35.0…48.0	0.1…0.3	0.4…1.7	0.1…0.2
Moldavia Petru I (1380-1390)	70.0…78.0	n.d.	19.5…28.0	traces	0.3…0.8	0.1…0.3

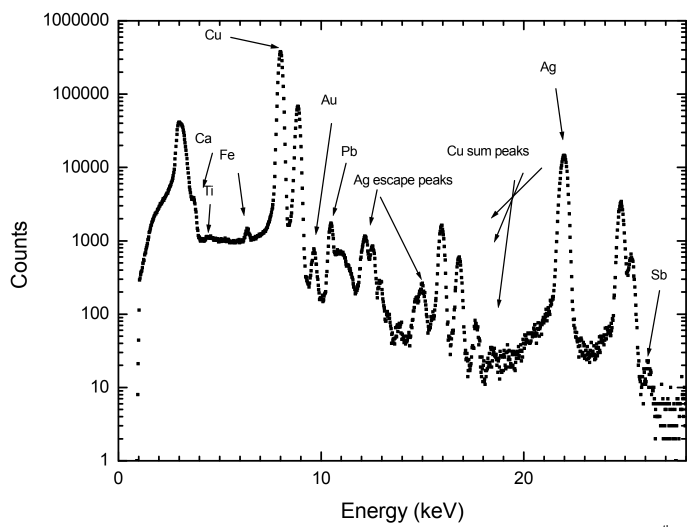

Figure 1 Petru I Musat silver grosch, Corlateni hoard, Moldova, XIVth century

4 CONCLUSIONS

The present work helped the curators 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 our PIXE and XRF measurements. A guess of the ore source was 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. A detailed archaeological paper is under progress, containing historical conclusions.

5 REFERENCES

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