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Analysis of medieval Serbian silver coins from XIV and XV century by means of wavelength-dispersive X-ray spectrometry

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ABSTRACT

X-ray fluorescence (XRF) spectrometry is known as excellent nondestructive technique for analysis of artifacts, in our case, medieval numismatic coins. Collections of 30 silver coins, owned by National Museum in Belgrade, were investigated during our research. Coins from the historical period from 1389 to 1458 belong to the reign of two Serbian rulers, Stefan Lazarević and Đurđe Branković. The aim of this study was to determine elemental composition of silver coins and to characterize alloys from which the coins were minted. The dominant elements detected in all coins were Ag, Cu, Zn and Pb. In some coins Fe, Si and S were detected as well. Results from quantitative analysis shows that the content of Ag in all investigated silver coins exceed 90%, except in two coins that were assumed to be forged. The concentration of Cu ranged from 3% to 5%, and the contents of Zn and Pb varied around 1%. Characterization of coins provided us information about raw materials and employed metallurgical processes.

1. Introduction

Chemical analysis of medieval coins collection can provide us important information about the origin of the material from which coins are made, or information about the medieval mines, as well as information on the metallurgical processes which were used to obtain alloys. The results of Serbian medieval coins chemical analysis are also of great importance, since no such data were previously available. Furthermore, analysis of the elemental composition of the coins from the numismatic collections can provide information about the medieval monetary system and changes in the economic situation over which the country is going through [10,27,20,28].

Most museums and owners of numismatic collections require the kind of chemical analysis that is non-destructive, which nowadays replaces the older, conventional destructive analytical methods. For many decades the XRF spectrometry appears to be the most suitable for this type of testing [22,21]. This method is fully non-destructive, there is no modification of sample or sample surface, and for this kind of analysis any prior surface treatment is not required [26,12]. The method is fast and it allows determination of a large number of elements, over a wide range of concentrations [8,16]. Therefore, XRF spectrometry is a really suitable technique for rapid qualitative and quantitative multi-elemental analysis.

However, XRF analysis of mediaeval coins has some disadvantages as well. Impurities of the samples, inhomogeneity of the coin, which were usually result of imperfect ancient methods of metal purification and casting, followed by insufficient mixing of molten materials, can influence the final results of the analysis. Problems arising from dents, bulges and the irregular surface of a coin could be overcome by rotation of the sample during analysis, thereby reducing their influence. Additional significant problem may be the corrosion of the coins [23,6,17]. The main reason for this phenomenon is usually chemical composition of the alloy from which the coin was made or because of the environment to which the coin was exposed. For example, Beck and coworkers [2] pointed out that if corrosion of silver coins occurs then the surface layer of a coin could be enriched with silver, since the less precious alloying metals are extracted during corrosion process.

When valuable artifacts, such as mediaeval coins, are analyzed by XRF, we are obliged to accept certain assumptions. We assume that the surface irregularities are eliminated which is achieved by sample rotation during the analysis. If eventual surface corrosion may be present, one should keep in mind that X-rays are passing through it.

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In this research, a selection of 30 coins, which are owned by National Museum in Belgrade-Section of numismatics, were analyzed.

1.1. Historical context

For our investigation of particular interest were the reigns of two Serbian rulers, Stefan Lazarević and Đurđe Branković. The reign of Stefan Lazarević is divided into two periods. In the first period he has ruled (1389–1402) as "knez" (prince) and in the second period (1402–1427) as "despot". The reign of Đurđe Branković is divided into two periods, as well, the first (1402–1412) as "gospodin" (nobleman) and the second period of the reign (1427–1458) as "despot". When reign of Branković ended, Serbia was conquered by Ottoman invaders. From those times only Turkish money was in use in central, eastern and southern Balkan Peninsula.

Since the Roman period, Serbia is known as an area rich in sulfide ore that was successfully exploited and metallurgically processed [25]. Several locations were identified as significant. Mine "Rudnik", which is located in central Serbia, has always been known as location rich in minerals like: sphalerite, galena, chalcopyrite and quartz; from which lead, silver and zinc were exploited. "Rudnik" was mentioned for the first time in 1293 during king Dragutin reign. It is well known that many Serbian rulers minted their money in mint "Rudnik". The tradition of money minting held for decades, until the Turkish invasion. The area of eastern Serbia has numerous mining locations. It is also known as a region rich in copper ores which contained silver as well. Their exploitation was conducted from ancient times until now. Another known mint from medieval times in Serbia was "Smederevo". It was opened during the reign of despot Đurđe Branković in 15th century. Đurđe Branković has raised Smederevo and declared it for a new capital of Serbia. His mint was also located in Smederevo (Fig. 1) [14].

It is known that in the region of Kopaonik, mountain in the southern Serbia (Fig. 1), ore was extracted since Roman times. In 13th century, the medieval town Novo Brdo experienced its blooming and in short timr it became one of the most important mining centers in Serbia and Balkans. Novo Brdo was location known to be rich in Pb–Ag–Zn ores [5]. In that time Novo Brdo mint produced the best and most appreciated silver in the Balkans region [14].

Stefan Lazarević constantly kept Novo Brdo under his control. During his reign mining development was intensified, and it was the main economic activity in those times in Serbia. The "Mining Act", enforced most probably in 1412 by Stefan Lazarević, referred to the legal provisions regulating the life in Novo Brdo, which was considered to be the largest mine in the Balkans in those times [9].

2. Materials and method

2.1. Samples

Selected coins belong to the period from 1389 to 1458. Table 1 contain description of each coin. They were divided into six subgroups based on the monarch and the period when they were minted. Fig. 2 provides pictures of obverse and reverse of all coin groups. Each group belonging to a monarch and year have identification number as well: knez Stefan Lazarević 1389–1402 (S 71.42.1 and S 71.42.6), despot Stefan Lazarević 1402–1427 (S 75.42), gospodin Đurđe Branković 1402–1412 (S 76.45) and despot Đurđe Branković 1412–1458 (S 78.45 and S 79.45). In their diameter, coins vary from 13.09 to 17.26 mm, on average 14.85 mm, although it is difficult to precisely determine the coin diameter because of their irregular shape. The thickness of the coin ranges from 0.35 to 1.22 mm, on average about 0.8 mm, while the mass range from 0.34 to 1.15 g with an average of about 0.8 g. Prior to the XRF analysis, the sample preparation assumed only washing surface of the silver coins with ethanol.

2.2. Experimental

For the coin analysis wavelength dispersive X-ray fluorescence spectroscopy was used. An ARL™ PERFORM'X Sequential X-Ray Fluorescence Spectrometer (*Thermo Fisher Scientific*, *Switzerland*) was equipped with a 4.2 kW Rh X-ray tube, which was able to determine all elements from Be to Am that are covered with our set of crystals: AX03, AX09, AX16C, PET, Ge111, LiF200 and LiF220. For qualitative analysis, spectral recording and data treatment, a software program Thermo Scientific™ OXSAS was used [24].

ARL software program UniQuant was used for quantitative data analysis. UniQuant [31] contains internal standard database, therefore it can be used without previous standard series analysis, since it is a XRF program which works with the advanced Fundamental Parameters Algorithms [3]. Therefore, this program is very useful when standards are available for limited number of elements. For the elements for which one does not have appropriate standard it is suitable to use UniQuant which is able to perform quantification of the whole spectra of qualitatively determined elements. Quantification with UniQuant may include those elements for which the standards are available and those for which one has not an appropriate standard.

Finally, qualitative spectral scans were obtained by using four different crystals (GE111, LiF200, LiF220 and PET), two collimators (0.15 and 0.4) with selected voltage of 50 kV and current of 50 mA. Qualitative analysis with AX03, AX09 and AX16C crystals appeared to be redundant. These conditions are capable to induce X-ray fluorescence of any element present in silver matrix in concentrations of around 1 ppm and higher. During the analysis of the coins elliptical mask was used with a slit of 0.5 mm. Identical conditions, voltage of 50 kV and current of 50 mA, were applied with all used crystals.

For determination of the quantitative composition of the coins, the analysis covered the entire periodic table of elements. Every coin was analyzed in cycles of six measurements.

In ideal case for XRF quantitative analysis a standard that is similar by composition and its density to the investigated sample is required, as well as the same analytical conditions [3,4]. Fortunately, we were able to provide the same analytical conditions and the standard which is by density similar to the investigated samples, but by the composition it has covered only Ag (92,550%) Cu (6,022%), Pb (0,423%) and Au (1,000%) (MBH ANALYTICAL LTD 133X AGQ2 A). The advantage of ARL software program UniQuant is that it allows that it can be checked for accuracy with the available standard, in our case MBH silver standard, and after that, with the same analytical conditions, the unknown samples could be analyzed. Results from UniQuant analysis of silver standard MBH ANALYTICAL LTD 133X AGQ2 A are shown in Table 2.

3. Results and discussion

The analysis of 30 Serbian medieval coins using sequential WD XRF spectrometer provided qualitative spectra shown in the Fig. 3. It can be seen that the Ag was dominant element detected in all coins. Ag was alloyed with Cu and to a lesser extent with Zn and Pb. Impurities of Fe, Si and S were detected only in some coins. Peak from Rh X-ray emission spectrum originates from X-ray tube. Results of quantitative analysis can be seen in Table 2. The content of silver in all samples exceeds 90%, which appeared to be quite