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ISSN: 1844-0401

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COMBINED USE OF SURFACE AND MICRO-ANALYTICAL TECHNIQUES FOR ARCHAEOMETALLURGY

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abstract: In this paper, we have analyzed several Romanian coins from early XX century. The differences between them are interpreted considering the particularities of the Romanian coinage manufacturing from that date. The unexpected changes of the alloys' composition, from one year to the next one can be explained by the Romanian specific situations. Our study clearly demonstrates that EDXRF (energy-dispersive X-ray fluorescence) can be used effectively for the nondestructive numismatic analysis; optical microscopy was used for silver coins, being able to observe the presence of copper corrosion products such as cuprite and chloro-argyrite, and the effect of the degradation phenomena on the coin surface. The method can easily be used to analyze coins, indifferently their age, their composition and their state.

received: July 31, 2008 *accepted*: November 10, 2008

1. Introduction

We may say that when numismatists call to analytical physicists it is because they are confronted with problems that traditional methods of numismatics cannot solve. And for more than two centuries, their collaboration was quite intensive and also led to open new ways of investigation for numismatics. Without pondering of any methods, we should like first to present a swift overview of use of metallic analyses in numismatics. Barradon et al.[1] define three directions in the application of scientific methods to coins: analysis of alloys, determination of provenance of the metal and technological studies. For this paper, we will focus on the first one.

The analysis of elemental composition of ancient coins has generated a lot of interest in recent years as it can provide valuable information on different aspects of life, politics, society, religion, art, culture, economy and metallurgy of minting time [2,3].

We will now draw attention to the difficulties encountered by numismatists when they had to draw conclusions from the results of such analyses. One of the most dangerous traps is to

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merge the original composition of the coins and its present composition. Between the minting of a coin and its analysis by modern methods, a lot of years rolled by and the chemical composition of the coin may have suffered important changes. We know, for example, the phenomenon of iron enrichment due to dust incrusted at the surface of the coin, as well as corrosion affecting coins made of copper or of some types of alloys [4]. The precious metal artefacts are characterised by a wide compositional nature that have greatly influenced their chemical stability.

Although various techniques are used for the analysis, EDXRF (energy dispersive X-ray fluorescence) technique is of special interest for the analysis of coins because the technique is not only non-destructive, fast, sensitive, and capable of simultaneous multi elemental analysis, but also ensures that coin can be quantitatively analyzed without damage.

Further merit with EDXRF is that it does not require any special sample preparation as is the case for the techniques like atomic mass spectrometry (AMS) and is also simple compared to particle induced X-ray emission (PIXE) technique.

X-ray fluorescence is probably one of the most widely used methods for elemental analysis of ancient coins [5,6], due to it’s characteristics (non-destructive, the possibility to analyze a great number of elements in a wide concentration range, fast analysis, good analytical parameters, etc). However, one must bear in mind that during totally nondestructive measurements of ancient metals (without any preparation of the sample) the accuracy of the results can be influenced by a number of factors like the existence of corrosion products, surface enrichment or depletion of some elements [7].

In this paper several Romanian coins from early XX century are analyzed, for two of them we have performed an investigation of the corrosion products. The coins have been studied by means of the combined use of optical stereo microscopy and EDXRF technique. These latter analytical techniques have been used to determine the micro-chemical nature and structure of the corrosion for identifying the degradation mechanisms and for tailoring conservation procedures [8,9].

To better understand the results of our work, a short history of Romanian currency (leu) is necessary.

Once the Romanian State Mint came into being on 3.03.1870, the anniversary gold coin of 20 lei and the silver coin of 1 leu were displayed publicly. Those were the first coins to bear the name Leu. The outbreak of the Romanian Independence War [in 1877] triggered a cash crisis that was overcome by issuing mortgage bonds, which represented the first romanian banknotes. Through the new monetary system Romania was connected to the modern european systems and during the four decades [up to 1916] this was the most powerful and stable currency in the Romania's entire economic history of all times and the Leu was one of the most powerful currencies on the european continent. Beginning with the outbreak of the WWI [Aug.1914] and especially after Romania's involvement [Aug. 1916], the Romanian currency entered a new evolution stage. It was the beginning of the first great inflation of the modern Leu, out of the three periods (1916-1926, 1936-1947 and 1990-2000), which came in turn up to the end of the XX century. The inflation during 1916-1926 was the result of high war expenses, important material and humane loss, Romania's external debts, financial obligations imposed to our country by the war winning powers, as well as of the conversion of foreign currencies in provinces joining our country in 1918.

Thus, in comparison to year 1913, in 1918 the Leu value was 3,6 times lower and in 1926 it reached the lowest level, namely a depreciation of 42 times. The inflation "ate" the gold value of Leu (1913 - 97,6%), in 1926 representing only 2,4% of the pre -war value. The monetary reform from 1929 represented the official devaluation of Leu against the pre-war gold Leu. Therefore, the Romanian state contracted a large loan from the foreign banking markets. The official Leu represented only 0,010 grams of gold in comparison to the pre - WWI Leu, which represented 0,3226 grams of gold; one kg monetary gold was established at 111111,11 Lei; this represented a decrease of the Leu value with 32,26 times in comparison to its value in 1913. In the next period, after the global economic crisis between 1929 -1933, the reformed Leu begins to slip slowly into another inflationist period, confirmed in 1936 by the official depreciation of 38%; in 1940, after the outbreak of the WWII, the Leu devaluates with 108% in comparison to the reform value from 1929. But, the most spectacular monetary depreciation – 8532 times – took place between Aug. 1944 and Aug. 1947.

2. Experimental

2.1. Samples

All the coins were collected from various personal collections, including the authors'. From all the coins, for discussion were chosen four, spread over 45 years, all Romanian coins (Figs. 1÷4). Their characteristics are presented in Table 1.

Fig. 1 *Romanian Coin #1 50 bani coin from 1900*

Fig. 2 *Romanian Coin #2 20 lei coin from 1930*

Fig. 3 *Romanian Coin #3 500 lei coin from 1944*

Fig. 4 *Romanian Coin #4 500 lei coin from 1945*

2.2. Apparatus

XRF is a relatively new technique, used in many fields of work: forensic investigation, environmental protection, the control of the contaminated soils and liquids, and many others. XRF has rapidly grown in popularity for heavy metals monitoring. This is happening for several reasons. In contrast with other analytical techniques XRF benefits from simple, essentially hazard-free, sample preparation. It is non-destructive, very rapid and is inexpensive in terms of cost per analysis.

Table 1 Coins' characteristics

Coin	Value (lei)	Diameter (mm)	Color	Inscriptions	Year	Weight (g)
1	50 bani (0.5 lei)	18	Dark silvery	Carol I – King of Romania	1900	2.39
2	20	27	Yellow	Michael I - King of Romania	1930	7.21
3	500	32	Silvery	Michael I - King of Romanians Reverse – Royal effigy	1944	12.13
4	500	30	Yellow	Michael I - King of Romanians Reverse – Royal effigy	1945	10.03

The method allows the determination of the elements "heavier" then Na (Z=11) to U (Z=92). It is a fast, non-destructive method, based on the excitation of each element by an X-ray beam, followed by an emission of a specific X radiation. The apparatus used is a PW4025 – MiniPal – Panalytical type EDXRF Spectrometer.

The XRF determinations have been carried out in Helium atmosphere, for a period of 300 seconds, without any filter, at 16 kV voltage and automatically adjusted current intensity, by the use of a 3.6 μm Mylar tissue.

The surface morphology characterisation of coins has been carried out using an optical stereomicroscope IOR, Romania.

3. Results and discussions

The results obtained for the samples are shown in Table 2, for the major elements; traces of minor elements were also found (Co, Ni, Pb, S and others).

Table 2 The obtained results

Coin \ Element (%)	Fe	Cu	Ag	Zn
Coin #1	0.15	12.60	86.25	–
Coin #2	0.25	75.5	–	22.25
Coin #3	–	12.25	84.0	–
Coin #4	0.35	64.0	–	35.50

The results corresponds to the ages in which they were manufactured (those containing silver – in 1900 – the age of the "gold leu" and 1944 – a period of WWII in which precious metals were used for manufacturing coins; the coins from 1930 (a period of economic depression and 1945 – period at the end of WWII, a difficult economic time for Romania were made from non-precious metals).The presence of iron, mentioned in Table 2 is probably due to patina layer and the conditions they were kept, as the presence of the other minor elements.

In Fig. 5, the surface morphological features observed via optical microscopy are shown. For silver coins, we can observe the presence of copper corrosion products such as cuprite and chloro-argyrite, and the effect of the degradation phenomena on the coin surface. These results indicate that is a film of silver or of other white metals was originally deposited on the coin surface, probably due to the entirely removing or altering by degradation phenomena.

The results indicate that the coin surface is characterised by an external thin region where an appreciably copper core and a low or nil content of Fe and Zn.

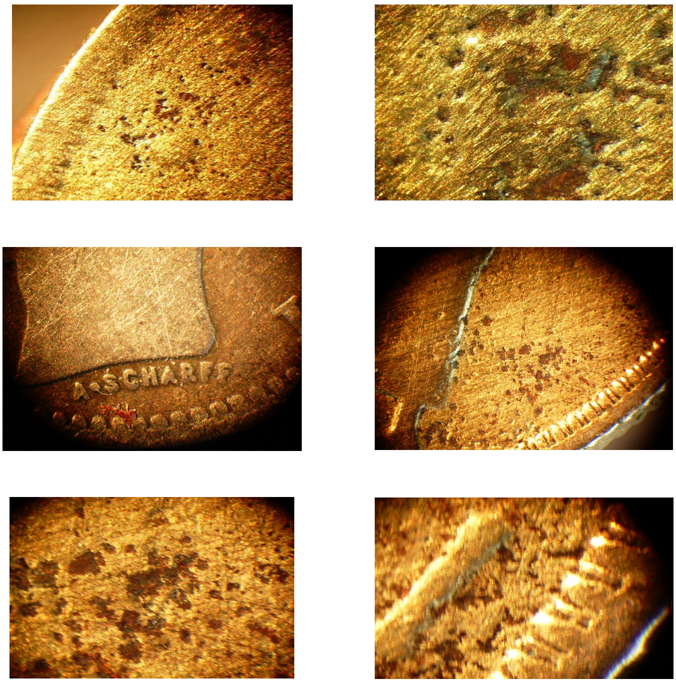

Fig. 5 *The surface morphological features observed via optical microscopy*

The role of the cuprite layer is considered to be acting as an electrolytical membrane allowing the transport of anions such as Cl^{-} and O^{2-}, inward and outward.

The accumulation of chloride ions can be interpreted as an autocatalytic reaction that facilitates the oxidation of copper resulting also in an accumulation of chloride ions and in the formation of cuprite and cuprous chlorides [10]. The Ag-Cu contact induces the less noble metal to become anodic in a couple strongly conductive to corrosion, and a preferential disolution of copper occurs in the less noble anodic areas.

These factors can induce the selective corrosion phenomena of copper by chlorine due to the cyclic reaction that is commonly defined as *bronze disease*. Chlorine also corrodes silver during the archaeological burial in the soil [11]. The presence of the copper islands in the silver aloys is a common feature of the silver-copper alloys, due to the low solubility of silver in copper and vice versa at room temperature. The solubility of copper in silver is about 8-10% at 780ºC (eutectic temperature) and practically nil at room temperature. During the solidification in the Cu-Ag system, each component separates into a nearly pure state and has respective supersaturated solid solution. As a consequence, dispersed copper islands are formed in the silver matrix whose size is influenced by cooling parameters.

Conclusion

The EDXRF investigation was carried out on Romanian coins for the first time. Silver, copper, zinc and iron are found to be the main constituents of the coins and their elemental compositions have been determined. The presence of minor/trace elements like Pb, Co, Ni, and S has also been determined. Our study clearly demonstrates that EDXRF can be used effectively for the analysis of ancient numismatics nondestructively. Further, the present study had managed to correlate the composition of the coins with the period and regimes they were manufactured in.

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