European Journal of Science and Theology, March 2009, Vol.5, No.1, 25-34

SURFACE AND ANALYTICAL TECHNIQUES STUDY OF ROMANIAN COINS

Radu-Claudiu Fierascu[1, 2*], Irina Dumitriu[1, 2], Mihaela-Lucia Ion[3], Adrian Catangiu[2] and Rodica–Mariana Ion[1, 2]

[1] *National Research & Development Institute for Chemistry and Petrochemistry – ICECHIM, Bucharest, Spl. Independentei, 202, sect. 6, Romania*
[2] *Valahia University, Targoviste, 2 Carol I Bd, Romania*
[3] *University of Bucharest, Art History Faculty, 36-46, M. Kogalniceanu Bd, Romania*

(Received 10 November 2008, revised 15 December 2008)

Abstract

Archaeometallurgy is the study of metalworking structures, tools, waste products and finished metal artefacts, from the Bronze Age to the recent past. It can be used to identify and interpret metal working structures in the field and, during the post-excavation phases of a project, metal working waste products, such as slags, crucibles and moulds. The technologies used in the past can be reconstructed from the information obtained. Scientific techniques are often used by archaeometallurgists, as they can provide additional information.
In this paper, we have analyzed several Romanian coins from XIXth-early XXth 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.

Keywords: EDXRF, optical microscopy, coins, Archaeometallurgy

1. Introduction

It has become quite apparent in the recent years that natural sciences such as Chemistry, Physics, Earth sciences, Biology and their associated technologies increased their role for the study and preservation of our historical patrimony. The dialog and the experience exchange between Science and Theology can only improve our knowledge.

A new scientific field, which combines the technologies of many disciplines, has progressively grown in importance: Archaeometry. And it should be pointed out that the relevance of the contribution of Science for the overall knowledge and for the conservation of the Cultural Heritage is widely acknowledged by the community of 'humanists' themselves. It is worthwhile mentioning - as a striking example bearing witness to this - that just below the Louvre, the French Ministère de la Culture has installed a very well equipped

* E-mail: radu_claudiu_fierascu@yahoo.com, fax: +40213163094

laboratory, including among other instrumentation a particle accelerator! Conversely, scientific institutions are increasingly aware of the importance of putting top technologies at disposal of the world of art and archaeology.

A review book has been recently published concerning radiation in art and Archeometry [1] where a chapter is devoted to the 'X-ray fluorescence (XRF) application to the study and Conservation of Cultural Heritage' and a second one to the analysis of coins and other metalwork using XRF, PIXE and activation analysis [2].

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 [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 merge the original composition of the coins and its present composition. Between the minting of a coin and its analysis by modern methods, many 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 fast, sensitive and capable of simultaneous multi-element analysis, but also ensures that coin can be quantitatively analyzed without damage.

Further merit of 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 earliest and most widely used methods for elemental analysis of ancient coins [5, 6]. This is related with the characteristics of the method like non-destructive nature, 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 non-destructive 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, etc. [5-7]

In this paper, several Romanian coins from XIXth-early XXth century are analysed, by means of the combined use of optical stereo microscopy, and energy dispersive X-ray fluorescence (EDXRF) technique. This latter analytical technique has been used to determine the micro-chemical nature and structure of the corrosion for identifying the degradation mechanisms and for tailoring conservation procedures [8-15].

The case study is on Romanian coins, but the method of analysis, once perfected, can be easily applied to other fields, such as Biblical archaeology. Our group performed some studies on religious objects [16], but mainly on paper artefacts. From the perspective of Biblical archaeology, the study of metal artefacts (icons, vessels, coins, etc) is of much greater interest. This is why, in order to establish a working method, we performed the present study, obtaining satisfying results.

2. About Romanian currency

In order, to better understand the results of our work, a short history of Romanian currency (***leu***) is necessary.

At the middle of the XIXth century, Moldavia and Wallachia were ruled by monetary anarchy and coin speculation, which hindered the normal development of economic activities. There was no national currency; over 80 types of foreign currencies were in use on the Romanian market, having different values and exchange rates and creating great computation difficulties. The Romanian *leu*, an imaginary computation unit, was divided into 40 *parale*/pennies and one penny [named in Romanian language *para* (pl. *parale*)] into 3 *bani*; the subdivisions were represented by Turkish coins with close values.

Through the new monetary system Romania was connected to the modern European systems and 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 World War I (August 1914) and especially after Romania's involvement (August 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 XXth century. The inflation between 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.

After the global economic crisis between 1929-1933, the reformed Leu begins to slip slowly into another inflationist period; in 1940, after the outbreak of the World War II, the Leu devaluates with 108% in comparison to the reform value from 1929. During the war, the inflation increased 4-6 times. But, the most spectacular monetary depreciation -8532 times in comparison to 1938 - took place between August 1944 and August 1947. Therefore, the bank issued banknotes of 10000 lei, 100000 lei, 1000000 lei and in July 1947, the highest banknote of 5000000 lei.

	(a)
	(b)
	(c)
	(d)
	(e)
	(f)

Figure 1. Romanian coins used for the study (see Table 1): (a) coin #1, (b) coin #2, (c) coin #3, (d) coin #4, (e) coin #5, (f) coin #6.

3. Experimental

3.1. Samples

All the coins were collected from various personal collections, including the authors' ones. From all the coins, for discussion were chosen six, spread over 75 years, all Romanian coins (Figure 1). Their characteristics are presented in Table 1.

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
#5	10 bani (0.1 lei)	30	Dark brown	10 bani – 1867 Royal effigy	1867	9.9363
#6	5	20	Copper brown	Michael I King of Romanians Reverse – Royal effigy	1930	12.13

3.2. 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. 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. Appropriate sensitivity (lower limits of detection, LLD), analysis accuracy and reproducibility are critical when considering an analytical technique. In addition, a system should be robust, offer straightforward calibration and be easy to use.

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 (an X radiation with a specific wavelength). In the case of a typical XRF system, the photons emitted by the X-ray source are absorbed in the first 10–100 μm of the object surface, depending on the density of the material and on the X-ray beam energy.

By XRF it can be determined the elements in a concentration range from 100 mg/kg to 100%.

The apparatus used is a PW4025 – MiniPal – Panalytical type EDXRF Spectrometer (Figure 2).

Figure 2. PW4025 EDXRF spectrometer.

The XRF determinations have been carried out in Helium atmosphere, for a period of 300 seconds, without any filter, at proper voltage and current intensity for each element, corresponding to the calibration curve, by the use of a 3.6 μm Mylar tissue. The concentrations were calculated automatic by the spectrometer’s software.

A calibration curve was produced for 15 samples (with composition close to the one of the coins) whose metal concentration had been determined by the ICP-AES method. The resulting correlation factor (over 0.999) and the correlation with inductively coupled plasma – atomic emission spectrometry (ICP-AES) determination permitted us to assume an acceptable reliance for the EDXRF method. Later, a comparison was made for 32 samples analysed by the ICP-AES and EDXRF methods, and the results were very good. For the ICP-AES determinations, we used an ICP-AES spectrometer Varian, Liberty 110.

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

4. Results and discussion

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 coins' composition determined by EDXRF.

Coin	Element (%)				
	Fe	**Cu**	**Ag**	**Zn**	**Sn**
#1	0.15	12.60	86.25	-	-
#2	0.25	75.5	-	22.25	-
#3	-	12.25	84.0	-	-
#4	0.35	64.0	-	35.50	-
#5	0.29	84.2	-	1.3	5.99
#6	0.29	86.8	-	7.54	-

The results can be easily correlated with the ages in which they were manufactured (those containing silver – in 1900 – the age of the 'gold leu' and 1944 – a period of World War II in which precious metals were used for manufacturing coins; in the second case silver was probably used also due to it's great value - 500 lei. The coins from 1867 (the beginning of the coinage in Romania), 1930 (a period of economic depression) all being also of small value, and 1945 (even if it represents a great value it was made in period at the end of World War II, a difficult economic time for Romania) were made from non-precious metals.

The major elements detected are those involved in the coins' alloy, while the presence of iron as a minor element, 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 Figure 3, the surface morphological features observed via optical microscopy are shown. For silver coins (Figure 3a-3c) and for copper coins (Figure 3d and 3e) we can observe the presence of what we suppose to be copper corrosion products such as cuprite and chloro-argyrite (supposition based on the chlorine detection by a semi-quantitative XRF analysis, performed on the coins) and the effect of the degradation phenomena on the coin surface.

The results indicate that the coin surface is characterized by an external thin region where an appreciably copper or silver core and a low or nil content of Fe and Zn. One can also observe the copper or silver core (depending on the coin's composition).

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.

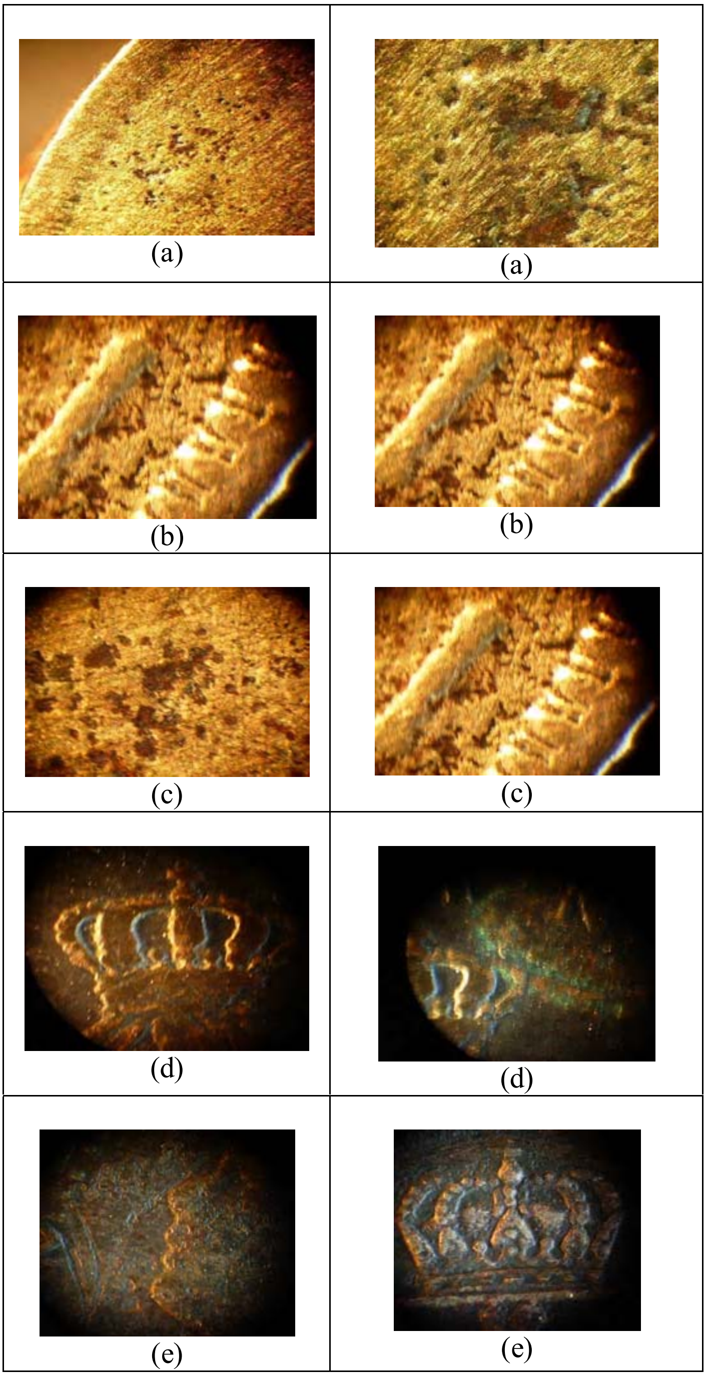

Figure 3. The surface morphological features observed via optical microscopy (see Table 1): (a) coin #1, (b) and (c) coin #3, (d) coin #5, (e) coin #6.

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 [17].

The Ag-Cu contact induces the less noble metal to become anodic in a couple strongly conductive to corrosion, and a preferential dissolution 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 [18].

The presence of the copper islands in the silver alloys is a common feature of the silver-copper alloys, due to the low solubility of silver in copper and vice versa at room temperature [19].

The solubility of copper in silver is about 8-10% at 780º C (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. Therefore, dispersed copper islands are formed in the silver matrix whose size is influenced by cooling parameters.

The precise identification of the corrosion products is to be made based on our previous experience [12] and will be the subject of another study.

5. Conclusions

The combined EDXRF-optical microscopy investigation was carried out on Romanian coins. 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. We established experimentally the use of EDXRF for the analysis of the coins (by the comparison with ICP-AES). Further, the present study had managed to correlate the composition of the coins with the period and regimes they were manufactured in.

References

[1] D.C. Creagh and D.A. Bradley (Eds.), *Radiation in Art and Archeometry*, Elsevier, Amsterdam, 2000.

[2] J.-N. Barrandon and M.-F. Guerra, *Physics in Numismatics*, in *Survey of Numismatics Research*, IAPN, Berlin, 1997, 825.

[3] M. Hajivaliei, M.L. Garg, D.K. Handa, K.L. Govil, T. Kakavand, V. Vijayan, K.P. Singh and I.M. Govil, Nucl. Instr. and Meth. B, **150** (1999) 645.

[4] J. Condamin and M. Picon, *Changes suffered by coins in the course of time and the influence of these on the results of different methods of analysis*, in *Methods of Chemical and Metallurgical Investigation of Ancient Coinage*, E.T. Hall & D.M. Metcalf (eds.), Royal Numismatic Society, London, 1972, 49.

[5] F. Schweizer, *Analysis of ancient coins using a point source linear X-ray spectrometer: a critical review*, in *Methods of Chemical and Metallurgical Investigation of Ancient Coinage,* E.T. Hall & D.M. Metcalf (eds.), Royal Numismatics Society, London, 1972, 153.

[6] M. Cowell, Royal Numismatics Society Special Publication, **30** (1998) 448.

[7] G.E. Gigante, S. Ridolfi, P. Ricciardi and M. Colapietro, *Cultural Heritage Conservation and Environmental Impact Assessment by Non-destructive Testing and Micro-analysis*, A.A. Balkema Publishers, London, 2005, 1-11.

[8] R.M. Ion, M.L. Ion, R.C. Fierascu, I. Dumitriu, F. Rugina, S. Cosulet and V.I.R. Niculescu, *Studii de arheometrie asupra unor artefacte ceramice din patrimoniul muzeal românesc*, Proc. of 5th Int. Simp. Mechatronics and mechanical engineering, microtechnologies and new materials, Valahia University, Targoviste, 2007, 33-41.

[9] R.-M. Ion, P. Zaharia, R.C. Fierascu, I. Dumitriu and N. Ion, *Analysis of stainless steel samples by energy dispersive X-Ray fluorescence (EDXRF) spectrometry,* Proc. of International Conference on Advanced Technologies and Materials, Vol. I, Dunarea de Jos University, Galati, 2007, 145-146.

[10] R.-M. Ion, M.L. Ion, R.C. Fierascu and I. Dumitriu, *Alloy design of ductile phosphoric iron: ideas from archaeometallurgy,* Proc. of International Conference on Advanced Technologies and Materials, Vol. II, Dunarea de Jos University, Galati, 2007, 141-144.

[11] R.-M. Ion, R.C. Fierascu, I. Dumitriu and C. Bercu, *Instrumental characterization of clay by XRF, XRD and FTIR,* Proc. of International Conference on Advanced Technologies and Materials, Vol. II, Dunarea de Jos University, Galati, 2007, 491-493.

[12] R.M. Ion, D.Boros, M.L. Ion, I. Dumitriu, R.C. Fierascu, C. Radovici, G. Florea and C. Bercu, Metalurgia International, **13(5)** (2008) 61.

[13] R.M. Ion, M.L. Ion, R.C. Fierascu and N.Ion, *Energy dispersive X-ray fluorscence (EDXRF) analysis of steels with implications in archaeometallurgy*, Proc. of 5th Int. Simp. Mechatronics and mechanical engineering, microtechnologies and new materials, Valahia University, Targoviste, 2007, 41-50.

[14] R.M. Ion, I. Dumitriu, D. Boros, D. Isac, M.L. Ion, R.C. Fierascu and A. Catangiu, Metalurgia International, **13(8)** (2008) 43.

[15] R.-M. Ion, D. Boros, M.-L. Ion, I. Dumitriu, R.C. Fierascu, C.Radovici and C. Bercu, *Compositional analysis of the iron ores from ancient archaeological site Covasna,* Proc. of 6th Int. Simp. Mechatronics and mechanical engineering, microtechnologies and new materials, Valahia University, Targoviste, 2008, 21-25.

[16] R.M. Ion, M.L. Ion, V.I.R. Niculescu, I. Dumitriu, R.C. Fierascu, G. Florea, C. Bercu and S. Serban, Romanian Journal of Physics, **53(5-6)** (2008) 781.

[17] L. Robbiola, J.M. Blengino and C. Fiaud, Corros. Sci., **40** (1998) 2083.

[18] D.A. Scott, *Metallography and microstructure of ancient and historic metals*, The Getty Conservation Institute, Los Angeles, 1991, 37.

[19] A. Addicks, *Silver in industry*, Reinhold, New York, 1940, 405.