# SUPPORT MATERIALS IN ARCHAEOMETALLURGY. COIN ANALYSIS

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**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. In this paper, we have analyzed several Romanian coins from early XX century. Our study demonstrates that EDXRF (energy-dispersive X-ray fluorescence) can be used effectively for the nondestructive numismatic analysis; optical microscopy was used, being able to observe the presence of 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.*

**Keywords**: archaeometallurgy, EDXRF, coin artefacts

## 1. Introduction

A new scientific field, which combines the technologies of many disciplines, has progressively grown in importance: Archaeometry. 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 [1-3].

The development of non-destructive physical methods of analysis has opened new windows for the study of archaeological objects. The data obtained by the application of these methods can help the archaeologists to answer specific questions concerning dating, technology, provenance and authenticity of the objects that the traditional methods cannot solve. X-ray fluorescence is probably one of the earliest and most widely used methods for elemental analysis of ancient coins [1,2]. This is related with the characteristics of the method like

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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 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, etc. [1–3].

In this paper, several Romanian coins from XIX$^{th}$-early XX$^{th}$ 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 [4-7].

## 2. Experimental

### 2.1. Samples

All the coins were collected from various personal collections, including the authors' ones. From all the coins, for discussion were chosen nine, spread over 76 years, all Romanian coins (Figure 1). Their characteristics are presented in Table 1.

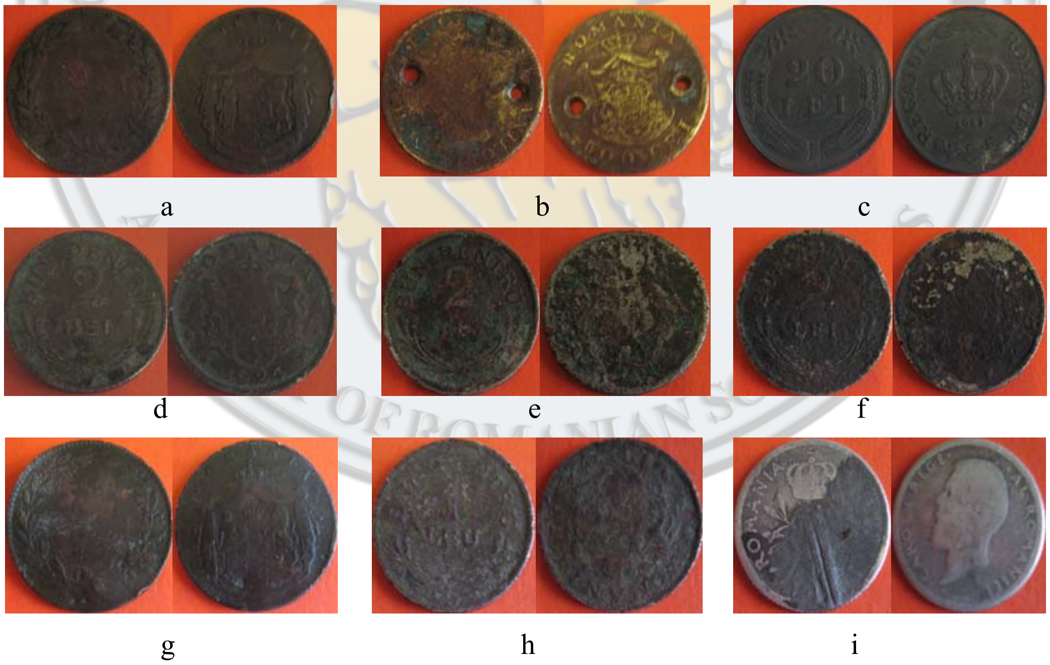



**Fig. 1.** The coins analyzed in the study. (**a** – coin #1, **b** – coin #2, **c** – coin #3, **d** – coin #4, **e** – coin #5, **f** – coin #6, **g** – coin #7, **h** – coin #8, **i** – coin #9)

**Table 1)** Characteristics of the analysed coins

| *Coin number* | *Weight (g)* | *Diameter (mm)* | *Front inscription* | *Back inscription* | *Colour* | *Observation* |
|---|---|---|---|---|---|---|
| 1 | 9.2612 | 30 | 10 bani 1867 | Romania – Royal effigy | Dark brown | - |
| 2 | 9.4345 | 30 | Romania – 500 lei – Royal effigy | Michael I king of Romanians Michael I portrait | yellow | Green and reddish stains, probable year - 1940 |
| 5 | 6.0202 | 26 | 20 lei | Romanian Kingdom 1943 | Dark silvery | - |
| 6 | 7.0072 | 25 | Good for 2 lei | Romania 1924 Royal effigy | Reddish | Green stains |
| 12 | 6.3554 | 25 | Good for 2 lei | 1932 unreadable | Silvery | Green stains– probable year-1920 |
| 13 | 6.3132 | 25 | Good for 2 lei | unreadable | Silvery | Black stains– probable yaer - 1920 |
| 15 | 4.6419 | 25 | 5 bani 1867 | Romania – Royal effigy | Black | Stained, deformed |
| 29 | 3.2695 | 21 | Good for 1 leu | Romania 1925 | Probably brown | Fully stained |
| 30 | 2.3695 | 18 | Romania 1913 5 bani | Carol I rege al romaniei | argintiu | Pata pe aprox 50% din fata |

## 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. 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. 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).

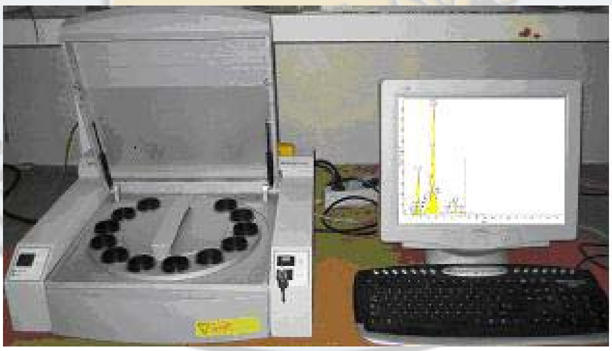


**Fig. 2.** PW4025 EDXRF spectrometer.

The XRF determinations have been carried out in Helium atmosphere, for a period of 300 seconds, without any filter, at 30 kV and automatic current intensity, by the use of a 3.6 μm Mylar tissue. The concentrations were calculated automatic by the spectrometer's software.

Due to the semiquantitative characteristic of the method used, it must be remembered that the results will be affected by the patina layer. However, the major constituents will clearly gave the composition of the coin, while the minor and trace elements are important in order to draw conclusions regarding the corrosion phenomenon that appears on the coins, correlated with the environment the coins were kept.

The surface morphology characterisation of coins has been carried out using an optical stereomicroscope Carl Zeiss Jena.

## 3. Results and discussions

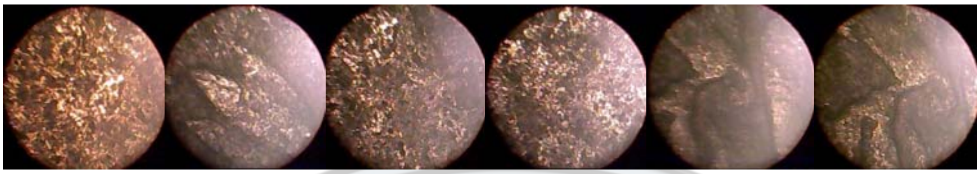
In Table 2 are presented the results obtained for the coins analyzed, showing only major constituents.

**Table 2)** Major constituents of the analyzed coins (EDXRF results)

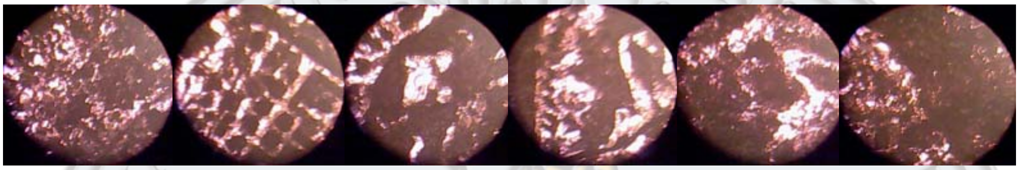
| *Coin* | *Cu (%)* | *Sn (%)* | *Zn (%)* | *Ni (%)* | *Pb (%)* | *Ag (%)* |
|---|---|---|---|---|---|---|
| 1 | 88.4 | 5.3 | - | - | - | - |
| 2 | 74.4 | - | 24.3 | - | - | - |
| 3 | - | - | 85.1 | - | - | - |
| 4 | 74.9 | - | - | 9.54 | - | - |
| 5 | 66.6 | - | - | 11.2 | - | - |
| 6 | 69.3 | - | - | 16.6 | - | - |
| 7 | 79.1 | 7.5 | - | - | - | - |
| 8 | 58.8 | - | - | 4.48 | - | - |
| 9 | 5.64 | 14.2 | - | - | 6.11 | 58.5 |

From the EDXRF results the coins can be divided in five categories, according to their alloy composition: copper/tin alloys, copper/zinc alloys, zinc coins, copper/nickel alloys and silver-based alloys. The minor and trace elements discovered (Na, Al, Si, Cl, sometimes Fe) have two explanations: some of them are native in the ores, others are due to the corrosion products appeared on the surface of the coins (Cl, S) [8, 9].

In figure 3 are presented some representative surface characteristic obtained by optical stereomicroscopy for the five groups of coins.



a



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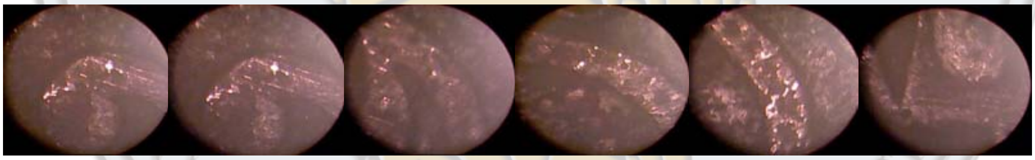

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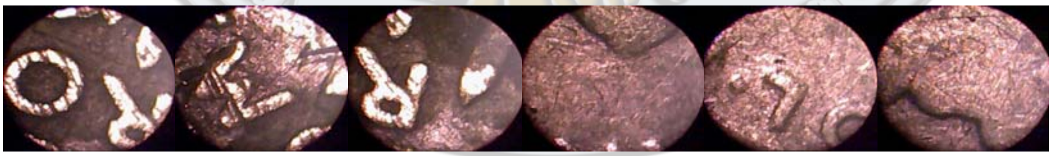

e

**Fig. 3.** Surface characteristics of the analysed coins obtained by stereomicroscopy. a) Cu/Sn alloys – coin #7, b) Cu/Zn alloys – coin #2, c) Zn coins – coin #3, d) Cu/Ni alloys – coin #4, e) Ag – based alloy – coin #9;

From the surface characteristics, 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. One can also observe the metal core.
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 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 [11].
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 [12].
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 [13] and will be the subject of another study.

## Conclusions

The combined EDXRF-optical microscopy investigation was carried out on Romanian coins. Silver, copper, zinc and tin 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, Cl 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.
The use of EDXRF for the study of coin artefacts looks promising, and our group hopes to establish a proper procedure for the analysis, restoration and conservation of the metal artefacts in generally and of the coin artefacts, especially.

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