ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
MATHEMATICS, PHYSICS, THEORETICAL MECHANICS
FASCICLE II, YEAR XI (XLII) 2019, No. 2
DOI: https://doi.org/10.35219/ann-ugal-math-phys-mec.2019.2.05

SURFACE AND ELEMENTAL ANALYSIS OF 20TH CENTURY ROMANIAN COINS USING SEM-EDX TECHNIQUE

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Abstract
The cooperation between scientists and numismatics is needed because there is a practical requirement to extract all the information from materials in order to accomplish a complete research. In this paper several Romanian coins from early 20th century are analysed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) in order to determine the micro-chemical nature and structure in order to establish the conservation state and manufacturing method. The results indicated that the coins were authentic and for some cases mechanical evidences were presented, suggesting pre-heating before minting. Generally, the metallic samples were relatively well protect against the aggressive external factors but, due to the natural corrosion process, many corrosion products were formed on the metallic surface.

Keywords: Romanian coins, SEM-EDX, microstructural analyses, composition, numismatics, coinage.

1. INTRODUCTION

Nowadays, due to the technical evolution, several analytical techniques have been developed having high sensitivity, precision and a non-destructive character, characteristics that facilitate the analysis of heritage objects, that includes numismatic collections.

Such techniques that respect these strict conditions are: energy dispersive X-ray fluorescence (ED-XRF) [1-4], scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX) [3-5], vibrational spectroscopy methods [5,6], optical microscopy [7], particle induced X-ray emission (PIXE) [3,4,7].

ED-XRF proved to be an affordable non-destructive sensitive technique used for many applications in various domains [8,10,11]. Scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX), represents a technique very often chosen to analyze mainly the microstructure of artifacts, because the X-rays are not affecting their basic structure. Beside the fact that it needs no sample preparation, it can determine chemical elements (from Z=11 up to 92, heavier than Na) both qualitatively and quantitatively with a good precision and sensitivity, in a short time and with low costs [4,7-9].

SEM permits the visualization of the surface morphology and topology with the help of the secondary electrons [6]. EDX analysis is based on X-ray fluorescence that is probably one of the oldest and widely used methods for elemental analysis of coins [1], but with various applications in many other domains such as forensic, environment, health, archaeology and many others [9,12]. The analysis is based on the excitation of the elements in a sample using an incident electron beam, followed by the emission of a characteristic X-ray radiation with a specific wavelength, that allows the identification of each element, and a specific intensity that allows the determination of the element concentration.

Because SEM-EDX is a surface method (1-5 µm depth of penetration) and has a non-destructive character, some errors can appear mainly because of the existence of the corrosion products or any surface treatments.

Due to the fact that numismatics has a high survival rate, coin chemical composition and surface study can be used to enrich the knowledge about coinage production regarding the methods that have been used and the origin of the materials used in that period. Other information that can be discovered from studying numismatics refers to: politics, life, society, economy, metallurgy, religion, art, culture, clothing, traditions or architecture [9]. Also, the results can be used to determine the authenticity, the conservation state and if any treatments were applied [6].

Regarding the monetary history, in Romania at the middle of the 19th century, the currency was characterized by monetary anarchy and speculation. This was a consequence for the absence of a national currency, in that period existing more than 80 types of foreign currencies in use. When finally the Romanian monetary system was applied in 1870, it was the most stable and powerful currency in Europe. The first coin named "leu" were a 20 "lei" coin – a gold coin, and 1 "leu"– a silver one. In 1877 the first Romanian banknotes appeared as a consequence of the Romanian Independence War. This was the situation until Romania was involved in the World War I in 1916 which drove our country to the first great inflation of the modern "leu". Nevertheless, the most impressive currency depreciation (8532 times) occurred between August 1944 – August 1947 [9,13].

The fundamental aim of this paper was to identify the microstructure, microchemical nature, manufacturing process and present state of conservation of some Romanian coins from 20th century using SEM-EDX technique.

2. EXPERIMENTAL

Analyzed coins

The coins subjected to this study are originated from the beginning of the 20th century, from Romania. On a time scale the oldest ones are from 1906 (5 and 10 "bani"), 20 and 100 "lei" from 1943, 500 "lei" from 1945 and the most recent is 100.000 "lei" from 1946. The coins belong to author's private collection and they are presented in Fig. 1. Some physical characteristics of coins are presented in Table 1. In order to obtain accurate results, the coins were cleaned with alcohol and dried using hot air.

Fig. 1. Both sides of the investigated 20th century Romanian coins

Table 1. Characteristics of the examined Romanian coins

Sample	**5 “bani” 1906**	**10 “bani” 1906**	**20 “lei” 1943**	**100 “lei” 1943**	**500 “lei” 1945**	**100000 “lei” 1946**
Dimension (*mm*)	18	21	25	27	30	36
Thickness (*mm*)	1.10	1.32	1.56	1.76	1.79	2.38
Diameter center hole (*mm*)	0.3	0.4	-	-	-	-
Weight (*g*)	2.44	3.89	5.88	8.39	9.98	25.08

Method of analysis

This experiment was performed in the Electron Microscopy Laboratory, using a scanning electron microscope Model Quanta 200 (Philips FEI Company) equipped with an energy dispersive X-ray spectroscopy module. For the analyzed coins the following settings were used: 15 kV as accelerating voltage (EHT) at a working distance (WD) ranging between 8.9-10.3 mm and a probe current < 100 nA. The EDX system uses a Silicon Drift Detector (SDD). All the samples were analyzed in high vacuum (HiVac) mode (60 Pa chamber pressure), at a magnification of 250X up to 500X.

3. RESULTS AND DISCUSSION

In Figs. 2-6, it is presented a selection of micrographs and spectra obtained for each analyzed coin by SEM-EDX. Every coin was analyzed on a clean surface and on a part that presented corrosion in order to highlight the differences.

5 “bani” and 10 “bani” coins from 1906

These coins are the oldest in this analysis set and the only ones having a hole for a practical purpose. The surface morphology of the *5 “bani”* coin, presented often corrosion products and fine lines (*Figure 2a*). This type of lines are named slip bands, and demonstrates that the coin was cold–worked [5].

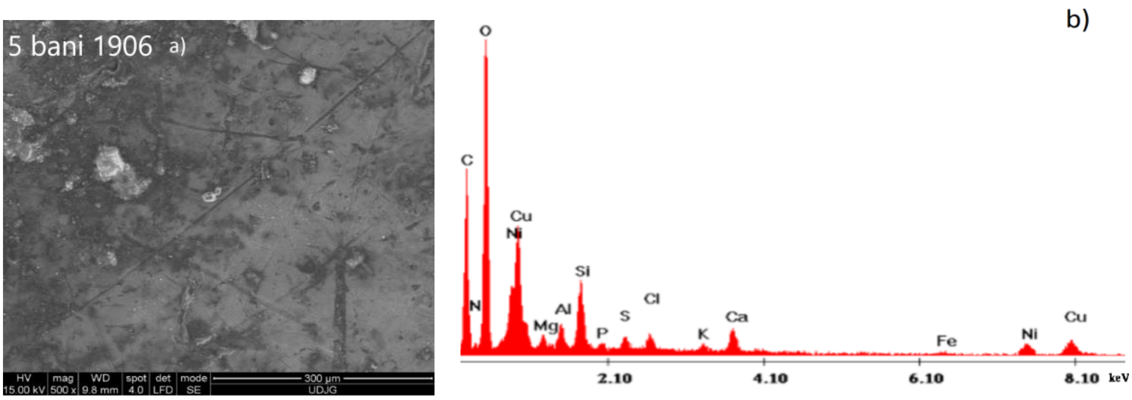

Fig. 2. 5 “bani” coin (1906): a) Surface SEM micrograph, b) Elemental composition obtained by SEM-EDX analysis

Besides the C and O, the elemental composition (*Figure 2b*) presented Cu (38.97 wt.%) and Ni (14.32 wt.%) as major elements, and traces such as Cl (1.09 wt.%), Ca (1.64 wt.%), Al (1.19 wt.%) and Si (3.56 wt.%).

20 "lei" coin from 1943

The coin surface of *20 "lei"* from 1943 (Fig. 3a) was very difficult to be studied due to the aggressive corrosion phenomenon. Besides C and O, the major element identified was Zn in proportion of 47 wt.% (Fig. 3b). The corrosion products presented as trace elements such as Al, Ni, Si, Cl, K and Co (less than 1 wt.%) and Ca (2.67 wt.%) (Fig. 4). Calcium was identified in low concentrations and this could be attributed to the sedimentary layer on the surface of the sample.

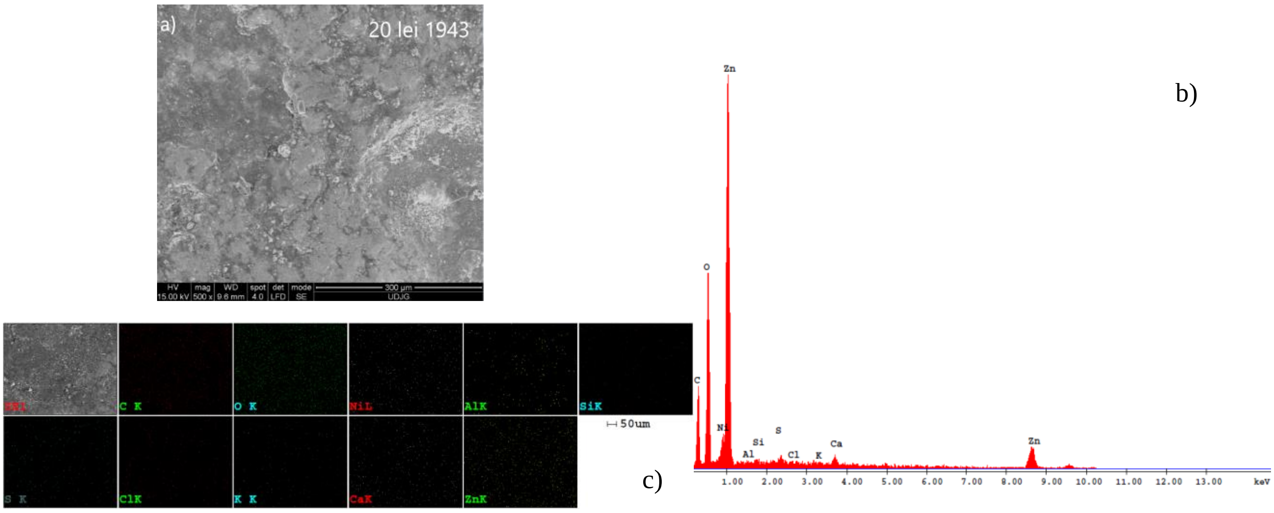

Fig. 3. 20 "lei" coin (1943): a) Surface SEM micrograph, b) Elemental map and c) Detail of EDX spectrum

EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Elem	Wt %	At %	K-Ratio	Z	A	F
C K	24.53	46.09	0.0565	1.1006	0.2093	1.0003
O K	25.17	35.50	0.0864	1.0794	0.3177	1.0009
AlK	0.15	0.12	0.0007	1.0022	0.4890	1.0003
SiK	0.29	0.23	0.0018	1.0325	0.6131	1.0004
S K	1.00	0.70	0.0081	1.0181	0.8021	1.0007
ClK	0.84	0.53	0.0070	0.9724	0.8601	1.0005
CaK	1.10	0.62	0.0106	0.9966	0.9584	1.0043
ZnK	46.92	16.20	0.4082	0.8665	1.0040	1.0000
Total	100.00	100.00				

EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Elem	Wt %	At %	K-Ratio	Z	A	F
C K	23.79	42.03	0.0614	1.0875	0.2374	1.0004
O K	32.33	42.87	0.1126	1.0666	0.3262	1.0007
SiK	0.16	0.12	0.0011	1.0184	0.6383	1.0004
S K	0.41	0.27	0.0034	1.0050	0.8211	1.0010
ClK	0.27	0.16	0.0023	0.9602	0.8777	1.0014
K K	0.15	0.08	0.0013	0.9631	0.9476	1.0039
CaK	2.67	1.41	0.0255	0.9840	0.9672	1.0040
ZnK	40.21	13.05	0.3447	0.8537	1.0042	1.0000
Total	100.00	100.00				

Figure 4. 20 "lei"coin (1943): examples of elemental composition (wt.%) *obtained by EDX analysis applied on coin surfaces affected by corrosion*

100 "lei" coin from 1943

SEM images of *100 "lei"* coin from 1943 illustrate some corrosion marks (Fig. 5a) and few small pinches like possible material defects appeared (Fig. 5b). The scratches existing on the sample surface could amplify the pitting process.

The corrosion products can be seen in Fig. 5a, and Fig. 5b showed the lines corresponding to the coinage process. The elemental analysis revealed the presence of the major elements Ni (85.38 wt.%), Fe (2.88 wt.%), C (9.25 wt.%) and O (2.49 wt.%). In addition, in some areas, low contents of Si, Al, P, S, Cl, Ag, Ca and Co were observed (Fig. 5c).

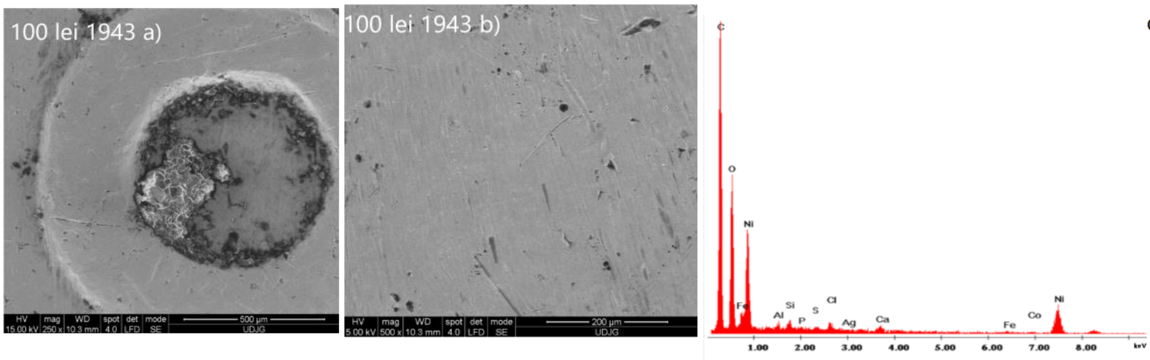

Fig. 5. 100 “lei” coin (1943): a) SEM micrograph of coin surface (250X); b) SEM micrograph of coin surface (500X); c) Detail of EDX spectrum

500 “lei” coin from 1945

The micrography from Fig. 6a illustrated fine scratches, twin lines and some corrosion products [14-16]. The surface illustrated also the presence of strain and twin lines and some corrosion products. The surface presents the same slip lines like on the *5 “bani”* coin surface. This also indicates a cold worked-coin. The main elements presented in the metal composition of the coin are: Cu (52.48 wt.%), Zn (23.22 wt.%) and C (18 wt.%) and O (4.61 wt.%). In certain micro-areas of the coin were found traces of Mg, Al, Si, S, Cl, K, Ca and Ti (Fig. 6b).

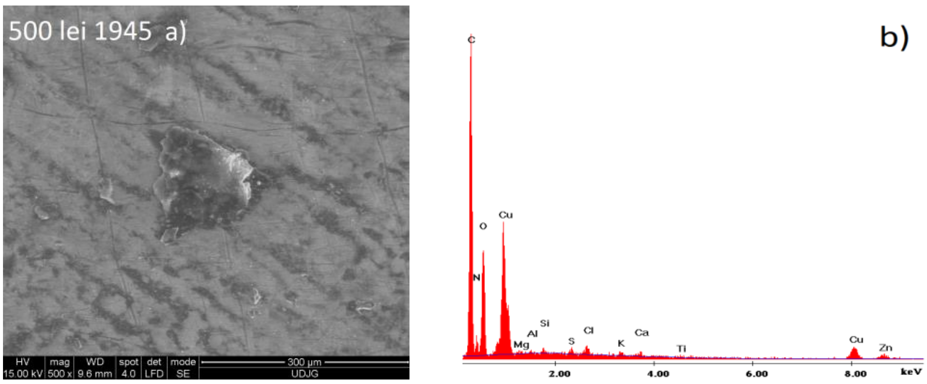

Fig. 6. 500 “lei” coin (1945): a) Surface SEM micrograph, b) Detail of EDX spectrum

100.000 “lei” coin from 1946

In this case the analysis was carried out to establish the authenticity of the silver coin. The surface did present some clear traces of coinage. Twin bands can appear in the microstructure of different alloys, such as silver-cooper, because at first are hot-worked and then annealed. If the twin bands are slightly curved is suggested that the coin was cold-worked after the final annealing or they are just hot-worked. In Fig. 7a it can be seen the slip lines that have remained from the final hammering. Furthermore, the evidences of mechanical operations along with annealing treatment are presented. This fact may suggest that the primary silver was preheated before minting.

The elemental content (Fig. 7b) revealed the presence of Ag (85.19 wt.%), Cu (3.37 wt.%) and C (7.25 wt.%) and O (3.10 wt.%). Al, Mg, Si, S, Cl and Ca were found as traces. The presence of Cl element can be attributed to copper corrosion products such as cuprites (Cu_2O) and chlorargyrite (AgCl) [9]. And due to the fact that silver combines with sulphur results silver sulphide (AgS) which is black coloured.

The trace elements can be used for the identification of the ores from which silver was extracted. The lack of Pb suggests that the silver is not extracted from lead ores, like it was used to in ancient times. Adding 3 - 4 % of copper to silver is a common practice from the ancient times since the third millennium BC in Mesopotamia. The copper content increases the mechanical properties and the strength of silver and also is a cost saver [5]. According to the SEM-EDX results, silver was the main element of the coin's alloy. A concentration that exceeds 85 wt.% indicates a high purity and also good skills in the silver extraction from ore.

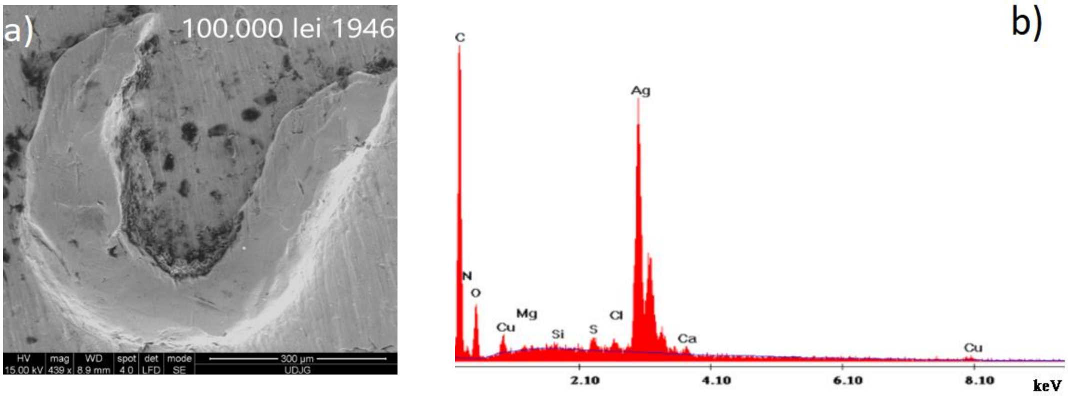

Fig. 7. 100.000 "lei" coin (1946): a) Surface SEM micrograph, b) Detail of EDX spectrum

Using SEM-EDX were obtained information regarding chemical composition and superficial morphology in order to establish their conservation state and their process of manufacture. The results of the analysis depended on: manufacturing methods, cooling rate, alloy's nature and metal impurities. The morphology of all studied coins which are made of alloy illustrate specific curved twin bands formation during the hot-working and annealing treatment. The fine and slip bands from the surface of the majority studied coins are the result of the cold-worked treatment. From micrographs and EDX spectra a naturally corrosion process was remarked when the coins were only exposed to elements such as air. Although, silver as a noble metal it is not completely resistant to corrosion. On the other hand, results from microanalysis could help us to validate the authenticity of the *100.000 "lei"* coin from 1946, the silver coin. The results of this study improved our knowledge about Romanian coins from that period.

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