# A synthetic approach into the restoration and conservation of metal artifacts (coins)

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Using analytical and optical techniques we have studied some metal artifacts (coins). All the coins have been provided from private collections, varying their composition, manufacturing year and historical value. Most metal objects studied show evidence of the passage of time and requires a broad characterization, to adapt restoration procedures. The metal artifacts, especially the coins, offer very interesting information about the cultural and economic habits of the past civilizations. The restoration procedures have to take into account the composition, structure, state of the artifacts, as well as the aesthetic needs, in order to offer some valuable artifacts for the cultural heritage.

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## 1. Introduction

The trace of old civilization can be evaluated through the artifacts they left behind [1-3]. In order to keep those artifacts available for the generations to come, it is important to restore and/or conserve theme. Metal artifacts are, perhaps, expose to deterioration more than any other type of artifacts [4]. The atmospheric and mechanical factors, together with the lack of knowledge in their manipulation can lead to unrepairable damages [5].

In order to perform a restoration on a metal artifact, the first and most important step is to determine the composition of those artifacts. X-ray fluorescence is a highly versatile method, successfully used in most of the world's archaeometallurgy laboratories [6-8], as well as for the study of many other types of materials [9, 10]. The optical methods (metallurgical microscopy) can be used for the visualization of the details on the artifacts, as well as for the visual identification of corrosion on the surface of the artifacts [11].

The analysis of ancient coins can offer informations on the trading patterns of ancient people, as well as information on the coins' authenticity [12].

Once the composition of the coins is established, the best methods for their restoration and conservation can be chosen [13, 14].

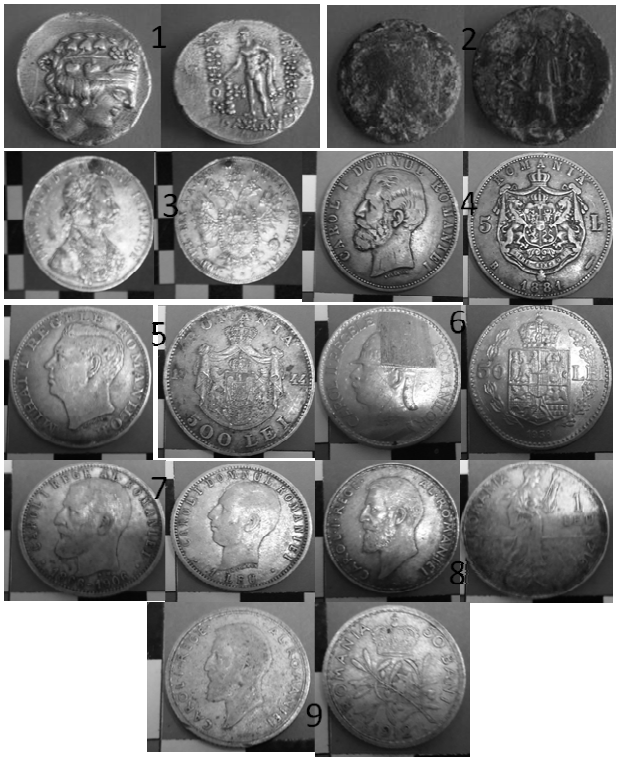



*Fig. 1. The coins analysed (1-9).*

## 2. Materials and methods

### 2.1. Coins

All the analyzed coins are from private collections. The coins are presented in figure 1, and their characteristics in table 1.

*Table 1. Characteristics of the analysed coins (the number in table corresponds with the number on fig. 1)*

| No. | Inscriptions | Diameter (mm) | Weight (g) |
|---|---|---|---|
| 1. | Portrait (Dionisos Dionysos right wreathed in ivy), Herakles standing left, holding club and lion's skin, Greek letters | 32 | 16.6959 |
| 2. | Diademed female head right, *ΜΕΣΑΜ-ΒΡΙΑΝΩΝ* either side of Athena Alkidemos advancing left | 23 | 7.2868 |
| 3. | FRANC-IOS-I-D-G-AVSTRIAE IMPERATOR, portrait / LOD ILL REX A A 1883 HUNGAR BOHEM GAL (4) crowned double-headed Imperial eagle | 40 | 13.7568 |
| 4. | CAROL I DOMNUL ROMANIEI, portrait/ ROMANIA 5 L 1881, royal effigy | 37 | 24.6422 |
| 5. | MIHAI I REGELE ROMANILOR portrait/ ROMANIA 1944 500 LEI, royal effigy | 32 | 11.8247 |
| 6. | CAROL II REGELE ROMANILOR portrait/ 50 LEI 1938, royal effigy | 24 | 5.857 |
| 7. | CAROL I DOMNUL ROMANIEI 1 LEU portrait / CAROL I REGELE ROMANIEI 1866-1906, portrait, royal effigy | 23 | 4.9505 |
| 8. | CAROL I REGE AL ROMANIEI, portrait / ROMANIA 1 LEU 1914 peasant spinning | 23 | 4.9905 |
| 9. | CAROL I REGE AL ROMANIEI portrait / ROMANIA 50 BANI 1912, crown and olive branch | 18 | 2.477 |

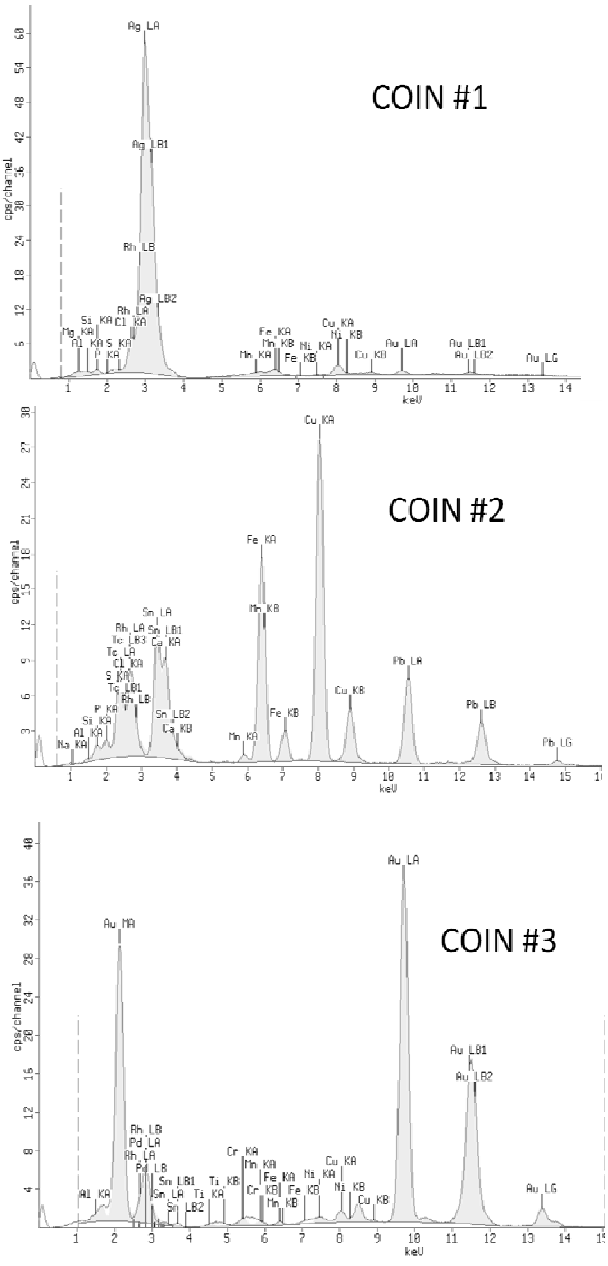
### 2.2. Apparatus

The X-ray fluorescence analysis was performed using an EDXRF spectrometer, PW4025 PAnalytical. For the FTIR analysis we used a Tensor 37 FTIR spectrometer (Bruker).

The morphological characteristics of the analyzed coins were recorded with a metallographic microscope (IOR, Romania, x 20÷80).

## 3. Results and discussions

The results obtained through EDXRF analysis (in figure 2 are presented the EDXRF spectra of the coins) allows us to perform a classification of the coins, by the metal or alloy they are composed of (Table 2).



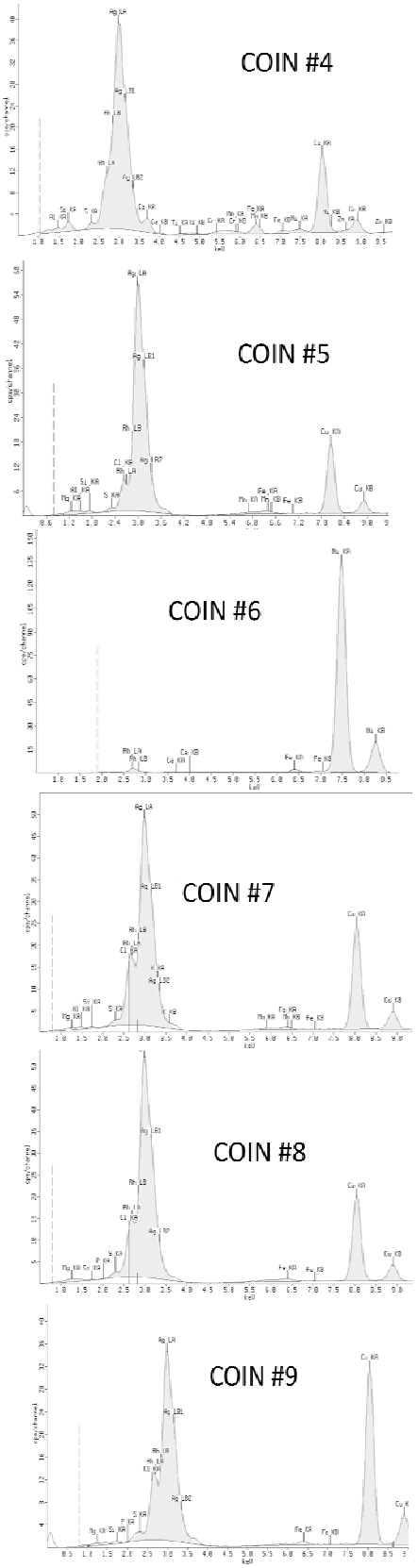



*Fig. 2. The EDXRF spectra of the analyzed coins*

*Table 2. Composition of the coins (by EDXRF)*

| Coin | Coin composition |
|---|---|
| 1. | Ag (93%), minor elements |
| 2. | Cu (13.4%), Sn (33.5%), Fe (8.61%) other minor elements |
| 3. | Au (80%), other minor elements |
| 4. | Ag (89%), Cu (9%), other minor elements |
| 5. | Ag (71%), Cu (25%), other minor elements |
| 6. | Ni (98%), other minor elements |
| 7. | Ag (86%), Cu (13%), other minor elements |
| 8. | Ag (85.2%), Cu (11.7%), other minor elements |
| 9. | Ag (83%), Cu (13%), other minor elements |

The presence of minor elements in the results can be explained either as corrosion products or as elements native in the ores from which the metals were extracted (as previously presented by our group [15-19]).

As a second step in the characterization of the coins studied, some morphological characteristics of the coins were recorded using the metallographic microscope (Fig. 3).

Those results are important both in therms of corrosion patterns (that can be observe) and in therms of surface characteristics of the coins (shape of the letters, a better image of the inscriptions on the coin, and others). Based on corroborated EDXRF-metallographic microscopy results, the authenticity of the coins can be evaluated (considering the alloys or metals they are manufactured from and the surface characteristics).

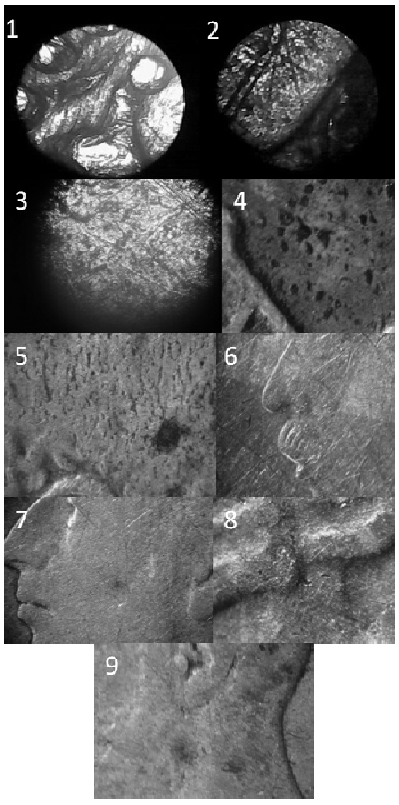



*Fig. 3. Morphological characterisation of the analysed coins*

The corroborated results (EDXRF and morphological) allows us to interpret the small stains as corrosion products [15-18]. The coins #1, #3 and #6 are the "cleanest" artifacts. The coins made of alloys (especially the bronze one) are damaged by corrosion.

Using those techniques, some supplementary conclusions can be drawn regarding the authenticity of the coins. Thus, considering the composition, weight and dimensions, as well as some surface characteristics (shape of the letters), we can state that the first two coins are Greek coins. Coin #1 it is a tetradrachm, from Thasos area ($2^{nd}$-$1^{st}$ century B.C.). Coin #2 seems to be a *mesembria*, Greek coin from $3^{rd}$ – $2^{nd}$ century B.C.

Coin #3 is a gold 4 ducat coin from the time of the Austro-Hungarian Monarchy (1867-1918).

The other coins (4-9) are all Romanian coins. Coin #4 is one of the first coins issued in the Romanian Kingdom, minted in Bucharest. Prior to this date (1867-1881), some coins were issued under official country title *Principality of Romania.* Coin #7 is a *1 leu* coin issued in 1906, minted in Brussels. Coins 8 and 9 are issued in 1912 and respectively 1914, first one minted in Hamburg (coin has 102 dents on the edge and so can be distinguished from the coins minted in Brussels that has 106 dents) and the second one minted in Brussels. All these coins belong to the era of Carol I, first king of Romania, and they are made from Ag-Cu alloy.

Coin #6 is a *50 lei* coin, issued in 1938 and minted in Bucharest, during the reign of Carol II. These coins were made of nickel (aprox. 98%) and were withdrawn from circulation with the start of World War II, due to the necessity of nickel in the arms industry.

Coin #5 is a *500 lei* coin, issued in 1944 and minted in Bucharest, during the second reign of Mihai I. Even if it is made of an Ag-Cu alloy, the percent of silver is much reduced compared with the other coins analyzed (the percent of silver is around 70%) [19].

In order to clean the coins, we are proposing some methods based on a chemical approach [14]:

- *Electrochemical cleaning*

Cleaning of metal objects by electrolytic reduction is one of the most effective methods of restoration.

The essence of the technique is to create an electrolytic cell in which the artifact serves as the cathode. Reduction occurs at the cathode and liberates hydrogen. In the reduction process, some positively charged metal ions on the surface of the artifact are reduced to metallic state in situ. In addition, chlorides and other anions are extracted from the sample and migrate to the positively charged anode.

- *Galvanic cleaning*

Galvanic cleaning is a electrochemical reduction method without using a power source. Basically, the object is wrapped in aluminum foil and then inserted into the 5-10% solution of sodium hydroxide, sodium carbonate 15-20% or 5% sodium bicarbonate. Treatment may last from several days to several weeks. On objects made of copper alloys, method cannot be successfully applied, because cleaning is too violent, resulting in damage to objects.

- *sodium sesquicarbonat cleaning*

Sodium sesquicarbonat $Na_3H(CO_3)_2$ is a double salt composed of sodium bicarbonate and sodium carbonate. The term is also applied to the equimolecular mixture of the two salts.

Cupric chloride appeared on articles of copper and its alloys are insoluble and cannot be removed by washing. When bronze or other copper alloys are placed in a 5% solution of sodium sesquicarbonat, hydroxyl ions chemically react with the alkaline solution of copper chloride to form soluble salts. In practice, this solution is rarely applied, because reactions take place over a long period (several days to months).

Restoration of metal objects does not stop the production of various corrosion products. Thus, once restored, the objects re-enter the natural cycle of formation of corrosion products. To prevent them and preserve objects restored is necessary to form transparent films, to prevent contact with the atmosphere.

From our work, we are proposing some films to be used for the conservation of coins:

- *polyvinyl alcohol - water*

Polyvinyl alcohol raises some issues that stand in the way of its use as a coating material in the conservation of metals: it is difficult to form the film on the surface of the material and the evaporation of the solvent used (water) takes a long time. These problems can be removed by evaporation to the point where the viscosity of PVA is very high, followed by formation of the film (the FTIR spectra of the film formed on the surface of the coin is presented in Fig. 4).

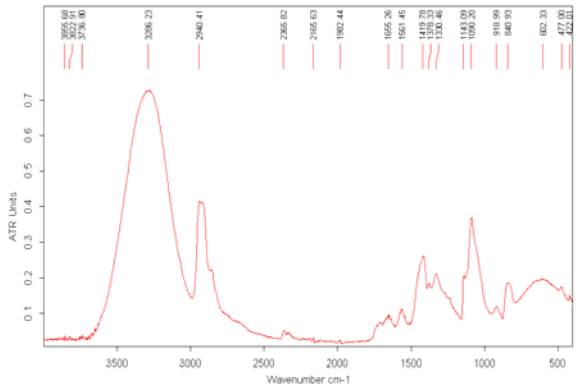



*Fig. 4. IR spectrum of the film created*

Removing the film created is done mechanically. Another disadvantage of the use of PVA is that it is biodegradable and will degrade over time. The film should be restored after several years.

The advantage of using PVA is the solvent (water), which poses no problems of toxicity.

- *Poly(methyl methacrylate), solvent acetone: toluene - 1:3, toluene or chloroform.*

The film can be very easily created, is a very good isolator and it is easy to remove using the proper solvents.

- *Polystyrene – solvent toluene*

Coating meets the requirements for conservation of metals and can be removed using toluene.

All these methods were tested, together with other possibilities (like natural resins), but those films has a yellowish color.

From the work carried, we can suggest a synthetic approach regarding the coin artifacts, presented in figure 5.

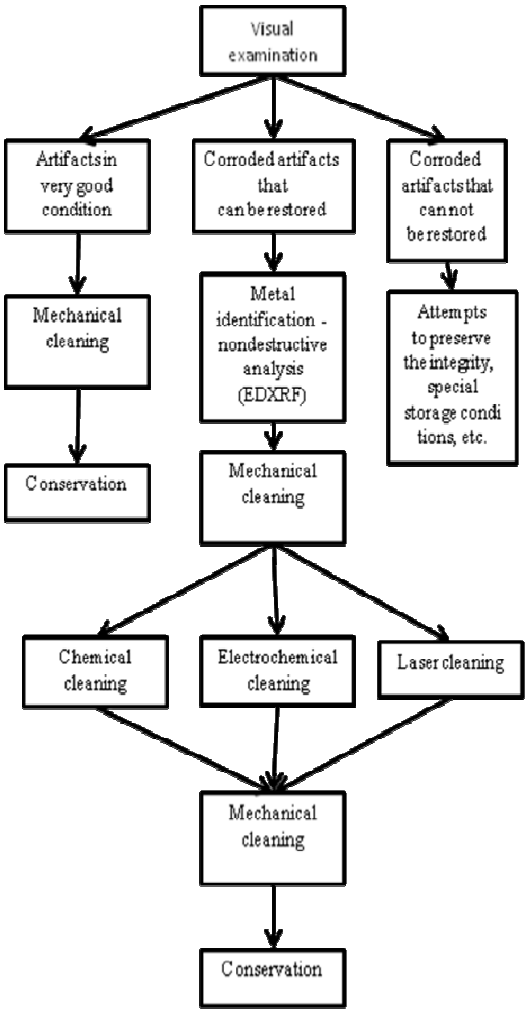



*Fig. 5. Schematic representation of the approach on restoration/conservation of the coin artifacts*

## 4. Conclusions

In the present work we presented some aspects regarding the preliminary analysis and the steps involved in the restoration and conservation of some metal artifacts. For the preliminary analysis, nine coins were selected, of various composition, ages and corrosion degrees.

Following the scheme presented in figure 4, any coin artifacts can be approached for the restoration and conservation. Also, using the visual examination (weight, dimensions, morphological characteristics), corroborated with the metal identification, some judgments regarding the authenticity of the coins studied can be made. If the alloys or the morphological characteristics (shape of the embossed letters and others) are not consistent with the known data, it is pretty safe to say the coins are fake.

**Aknowledgemets**

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