IRINA FIERASCU[1]
RADU CLAUDIU FIERASCU[2]

Scientific paper
UDC:620.183.19

Research on the degraded artifacts for the development of new protection methods

The history of metals and metal artefacts is closely related to the history of mankind. The discovery of metals and metalworking are important factors that led to the development of human civilization. Even though the metals are considered stable materials, once in contact with the environment, they gradually deteriorate and the deterioration rate depends on every metal/alloys characteristic. That is why the restorer/conservator of metallic artefacts should have knowledge from diverse areas (metalworking techniques, history of metalwork, history of art, archaeology, corrosion of metals, scientific research methods and others). The paper presents some aspects regarding the steps involved in the restoration and conservation of some selected artifacts, from the point of view of researchers in the field of materials science and chemistry.

Key words*: archaeometallurgy, artefacts, protection methods*

INTRODUCTION

Archaeometallurgy is considered to be the first well-developed area of archaeometry, appearing out of application of some physic-chemical methods in the area of cultural and historical research (Rehren, 2008). The born of a new scientific field can be traced back to 1958, when the journal *Archaeometry* established, and over the years, archaeometallurgy evolved in a recognized and important sub-field.

The metals and metal objects played a very important role in the development of human civilizations; its role is even reflected in the names of the archaeological periods (*Copper Age*, *Bronze Age*, *Iron Age*). Metallurgy can be traced back aprox. 8000 years ago, when the first gold objects were manufactured (Cramb, n.a.). From the metals known in our days, only 24 were known before 19th century, and 12 were discovered in the 18th century. Therefore, from the first use of metals (gold and copper) until the end of the 17th century, only 12 metals were known. From these metals, arsenic, antimony, zinc, bismuth and platinum, were discovered in the thirteenth, fourteenth and in the 16th century. The rest of the metals, known as *Metals of Antiquity* are: *Gold* (6000BC), *Copper* (4200BC), *Silver* (4000BC), *Lead* (3500BC), *Tin* (1750BC), *Iron* (1500BC) and *Mercury* (750BC) (Cramb, n.a.).

Author's address: [1]The National Institute for Research & Development in Chemistry and Petrochemistry – ICECHIM Bucharest & Politehnica University of Bucharest, Romania, [2]The National Institute for Research & Development in Chemistry and Petrochemistry – ICECHIM, Bucharest, Romania

Paper received: 11.01.2013.

The history of metals is closely linked to that of coins. Nowadays, archaeologists and numismatics agree that the coins were invented independently at three different locations between 700-600 BC (Lydia, India and China), and then spread all over the Eurasian continent (Howgego, 1995).

The most threatening factors that can affect the metal artefacts are the atmospheric and mechanical factors (Curkovic et al., 2010). Even though metals seem to be protected from the action of biodeteriogens, the literature describes several fungi that are able to cause undesirable effects on metals (NPS, 1998) In our days, the main method of protecting the metal artefacts is the use of coatings (such as waxes, acrylic resins and other corrosion inhibitors); some biological treatments based on the capacity of fungal strains to create a stable layer on the surface of the artefacts are also studied (Joseph et al., 2012a; Joseph et al., 2012b).

Our goal in this paper is to present some aspects regarding the way we think a study on metal artefacts should be carried out, from the preliminary analysis to the selection of best-fitted coatings.

MATERIAL AND METHODS

Metal artefacts

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

Analytical methods

When speaking of rapid and non-destructive characterisation of any material (and especially materials with historic value), the most useful technique is XRF (X-ray Fluorescence), which is widely employed for the analysis of elemental composition in materials.

The X-ray fluorescence analyses presented in this paper were performed using an EDXRF spectrometer, PW4025 MiniPal 2, PAnalytical.

The morphological characteristics of the analyzed coins were recorded with a metallographic microscope (IOR, Romania, x 20÷80). For the FTIR analysis we used a Tensor 37 FTIR spectrometer (Bruker).

Figure 1 - The analyzed coins (1 to 6)

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

Coin	Inscriptions	Diameter (mm)	Weight (g)
1	50 BANI 1900/ Carol I rege al Romaniei (Carol I king of Romania), portrait	18	2.3942
2	10 BANI 1867/ Royal effigy	30	9.9363
3	Portrait (Dionysos right wreathed in ivy), Herakles standing left, holding club and lion's skin, Greek letters	33/30 (ellipsoidal)	16.6959
4	EIN KREUZER 1816/ Imperial arms surmounted by the Austrian imperial crown	26	7.7782
5	Diademed female head right, illegible	23	7.2868
6	10 BANI – illegible/illegible	22/4	3.9332

RESULTS AND DISCUSSIONS

Previously (Dumitriu et al., 2011) we proposed a synthetic approach for this type of artefacts, adapted in figure 2.

In the present paper we will discuss the results obtained on our artefacts in steps 1 and 2, and some solutions for step 5.

The first step involved the visual and microscopical (figure 3) examination of the artefacts. 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).

After the visual investigation (table 1), two of the analysed coins presented illegible inscriptions. After the microscopical investigations, those inscriptions could be read, offering important information: on the surface of coin 5, we were able to distinguish the inscription *ΜΕΣΑΜ-ΒΡΙΑΝΩΝ* either side of Athena Alkidemos advancing left. On the front of coin 6, the year 1905 could be read and on the verso, the inscription *Romania*.

Step 2 of the process involved the identification of the metals (alloys) of the coins. The results obtained are presented in figure 4 and table 2.

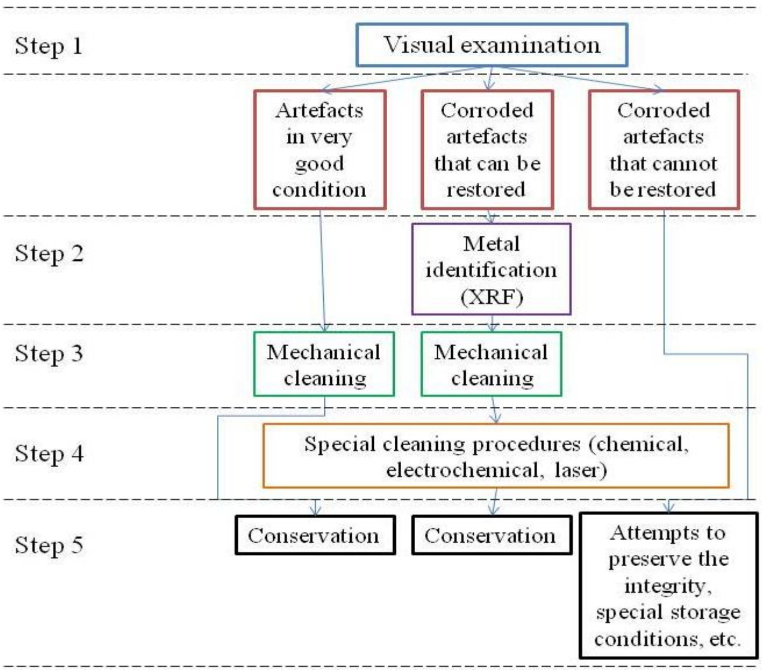

Figure 2 - Schematic representation of the approach on restoration/conservation of the coin artefacts (Dumitriu et al., 2011)

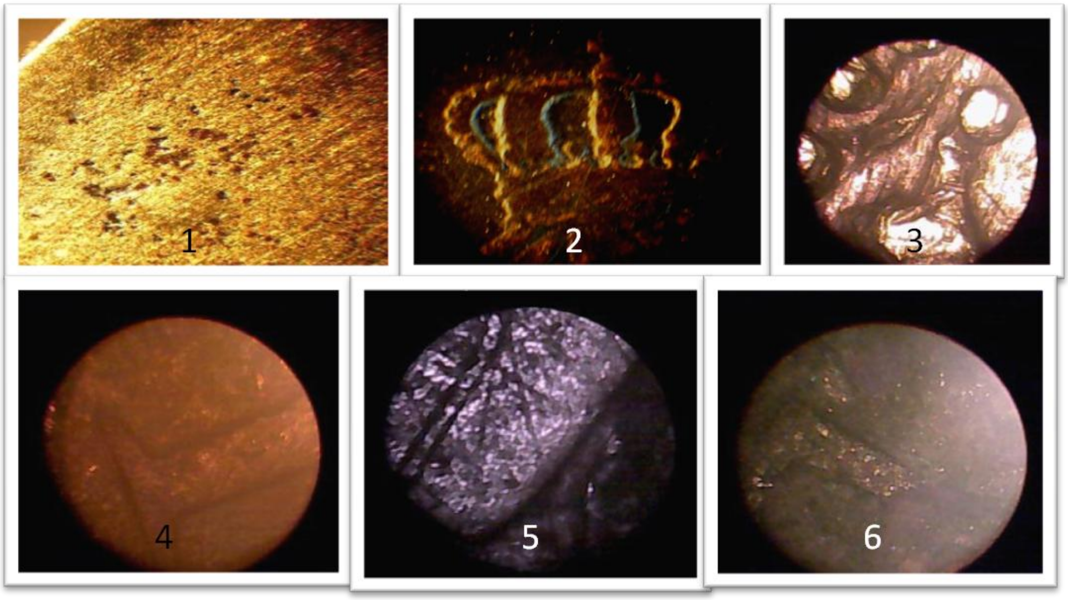

Figure 3 - Microscopical images of the analysed coins

Table 2 - Composition of the coins (XRF)

Coin	**Composition (element) %**					
	Cu	**Ag**	**Zn**	**Sn**	**Ni**	**Fe**
1	12.6	86.25	-	-	-	-
2	89.52	-	0.9	3.85	-	-
3	0.3	93.52	-	-	-	-
4	96.9	-	-	-	-	-
5	13,4	-	-	33,5	-	18.52
6	69.6	-	-	-	23.21	-

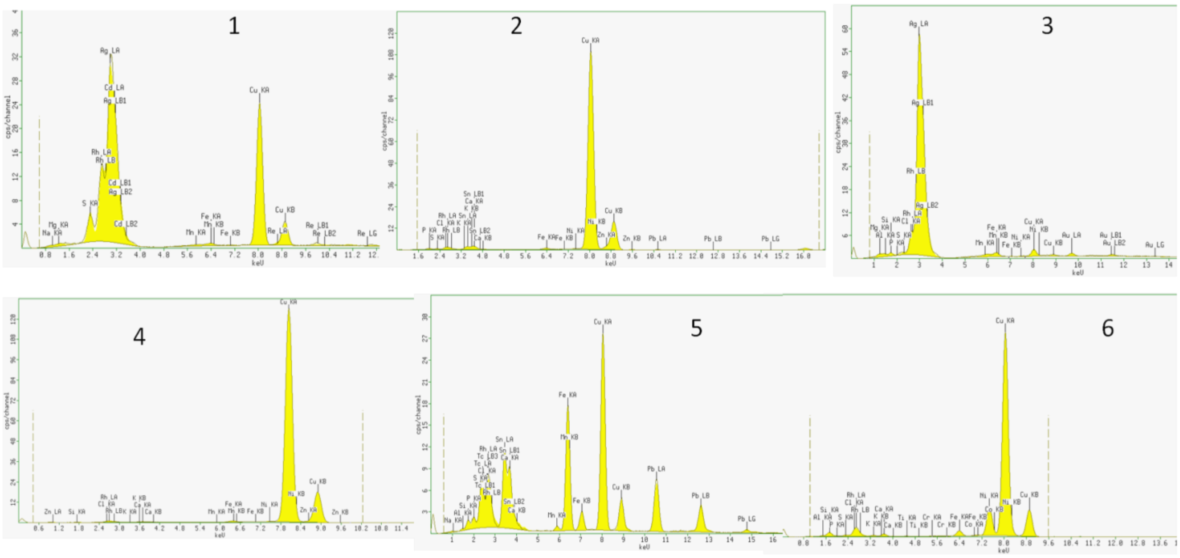

Figure 4 - EDXRF spectra of the analyzed coins

Traces of other elements were found on the surface of the coins (Fe, Co, S, Na, Ca and others). 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 (Ion et al., 2008; Fierascu et al., 2008; Fierascu et al., 2009, Dumitriu et al., 2011).

From steps 1 and 2 some conclusions can be drawn: coin 1 (Romanian coin) is made of silver, as it belongs to the *golden era* of the Romanian coin (a booming economic period); the other two Romanian coins (2 and 6) are made of copper alloys (Cu/Sn/Zn and respectively Cu/Ni) due to their low value (Fierascu et al., 2009); coin 4 (well-known in Romania) is the basic monetary unit of the Austrian Empire and is made of copper. The coin was issued up to 1852 wearing the same year (1816) (van Wie, 1999).

Coins 3 and 5 are, at first sight, Greek coins from the beginning of our era. Coin 5 is made of bronze and the alloy, the inscriptions and other details (diameter and weight) provides information on the authenticity of the coin. This seems to be a *Mesembria*, a Greek currency from 3rd-2nd century BC (Dumitriu et al., 2011).

Coin 3 is in a much better state of preservation (due the metal from which it was made, much less prone to oxidation). Diameter, weight, composition of the coin (silver) and details on the surface of the coin (blows on the coin, model of the letters) all lead to the conclusion that the currency is a *Tetradrahma* of Thasos (2nd-1st century BC) (Dumitriu et al., 2011).

Step 5 of the process requires the formation of transparent films in order to prevent contact with the atmosphere.

A coating suitable for coins (and other metal objects) should:

- be as inert as possible (will not react with the metal);
- be reversible (can be easily removed with solvents - so no mechanical action);
- be transparent, colorless, preferably as little gloss (matte)
- isolate the artefact from the rest of the environment;
- to age as hard as possible, without releasing corrosive products.

Our experience suggests some solutions:

- polyvinyl alcohol - water

The use of polyvinyl alcohol is hampered by the difficulty to form the film on the surface of the material and by the long evaporation time of the solvent used (water). 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 figure 5a). Removing the film can be done mechanically. Another disadvantage of the use of PVA is its biodegradability, the film needing restoration over time. 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 (figure 5b).

Polystyrene – solvent toluene

Coating (figure 5c) meets the requirements for conservation of metals and can be removed using toluene. However the last two solutions posses problems regarding the toxicity of the solvents used.

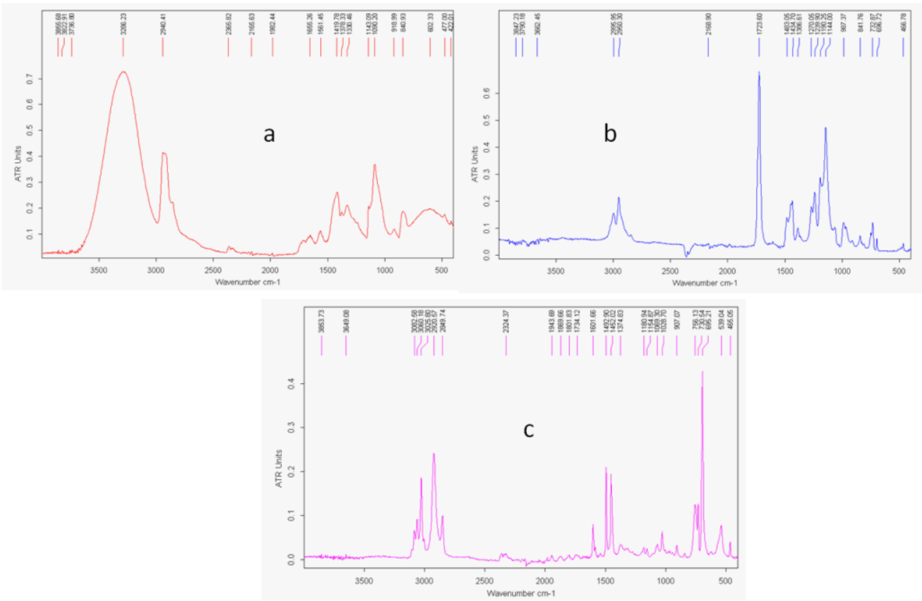

Figure 5 - FTIR spectra of the realized coatings

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 (coins). In order to illustrate the principles involved in the process, six coins were selected, of various composition, ages and corrosion degrees.

Following the scheme presented any coin artifacts can be approached for the restoration and conservation. Also, using the visual examination (weight, dimensions, morphological characteristics), corroborated with the metal/alloy 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 not genuine.

The paper also suggests the use of some protective coatings, however this area of research will be further detailed in future papers.

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