Contribution of Microchemical Surface Analysis of Archaeological Artefacts

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Abstract

Museum CIRTA of the town of Constantine has a collection of more than 35000 coins and statuettes going back to Numide, Roman, Republican, Vandal and Byzantine times and is struck in the name of the cities, of the kingdoms and the empires. Surface analysis of these coins gives information about the chemical composition and leads to recommendations for restoration and preservations. This work is a contribution of microchemical surface study of coin with the effigy of the Numide King Massinissa (Constantine between 3rd and 2nd century before Jesus Christ). The photographic and scanning electron microscopy coupled with energy dispersive spectrometry (SEM + EDS) and diffraction of X–ray (DRX) was used. The optic microscopy (OMP) and SEM pictures of coins showed heterogeneous surface. Scanning electron microscopy coupled with energy dispersive spectrometry identified three basic metals copper (46.06%), antimony (17.74%) and lead (12.06%), (Weight Percentage). The DRX identifies stages (copper and lead) and their crystalline oxides Bindheimite (Pb2Sb2O7) and Bystromite (MgSb2O6) on the coin’s surface.

Keywords: MEB, EDS, DRX, Lead, Copper

1. Introduction

The thorough knowledge of a work of art or an archaeological object, under its various aspects, like the structure or the chemical composition of constitutive materials is a precondition to any applied research, in industry, in history of art or in archaeology, like with any intervention in conservation or restoration. Museum CIRTA of the town of Constantine has a collection of more than 35000 coins and statuettes going back to Numide, Roman, Republican, Vandal and Byzantine times and is struck in the name of the cities, of the kingdoms and the empires. One of the first works [1] was carried out to study the techniques used by Greeks to produce schemes on Attic vases and the chemical composition of the black gloss. Many analytical methods have been used to identify the chemical composition of archaeological artefacts [2, 3]. The common techniques were oriented to the bulk chemical

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determination and to the structural features. The thorough knowledge of the surface characteristics of an archaeological object, under its various aspects, like the structure or the chemical composition of constitutive materials is a precondition to any applied research, in industry, in history of art or in archaeology and is required to any intervention in conservation or restoration. A few analytical techniques such as x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS) and glow discharge optical emission spectrometry (GDOES) [4-14] are not destructible. These techniques complement the bulk analytical investigations and help us to build our past. The combination of XPS, scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), inductively coupled plasma mass spectrometry (ICPMS) and x-ray diffraction (XRD) were also used to shed light on the manufacturing techniques and the effects of ageing on some silver Republic Roman coins [15]. Analysis included SEM, EDS and XRD were used to study several bronze and lead objects recently discovered at Venetic-Roman site of Monte Calvario di Auronzo, in the Italian eastern Alps [16]. The XRD and EDS coupled with SEM were largely used to characterize namely cross-sectional elemental distribution. The identification of patina in chemical and structural nature is often performed by X-ray diffraction XRD.

This work is a contribution of micro chemical surface study of coin with the effigy of the Numide King Massinissa (Constantine between 3rd and 2nd century before Jesus Christ). Surface analysis of these coins gives information about the chemical composition and leads to recommendations for restoration and preservation [17]. Need for integrity preserving of the coin led us to privilege the nondestructive methods. The photographic and scanning electron microscopy coupled with energy dispersive spectrometry and diffraction of X-ray was used. In order to preserve all the information registered above it, the analyses were carried out on the rough coin without making to the surface any polishing.

2. Experimental

The photographic pictures were carried out using a Leica MDa-1274684 camera (Audio Visuel University Mentouri Constantine, Algeria). SEM coupled with the EDS were carried in the Center of Electronic scan microscopy and microanalyses (CEMBA), using a Joel JSM 6301F microscope with field effect coupled with the EDS (University of Rennes I, France). DRX has been carried on a D8 Advance Siemens diffractometter equiped with a geometry BRAGG-BRENTANO goniometer and provided with a copper anticathode (\( \lambda = 1,5401 \text{ Å}, I = 30 \text{ mA} \) and \( V = 40 \text{ kV} \)). Sweeping was made between 10 and 70° with a step of 0.02.

3. Results and discussion

3.1. Photography

The study of the photographic pictures of the Numide coin, in direct or shaving light, shows the large effigy and the bearded effigy of King Numide Massinissa with the glance directed towards the left and symbols to the top of the head, on the place (Avers). On the back of the part (Revers) is observed an attached horse, galloping towards the left with a small head countermarked on the side of the horse and with the lower part a too unobtrusive biliter legend to be deciphered (Figure 1). The coin is dark gray colour, with a diameter measurement 25 mms and its aspect is hardly preserved.

3.2. SEM picture

The choice of the analyzed points is motivated by the search for the matrix composition and the elements identification that constitute its skates. The MEB picture of the coin is represented on the figure 2. Four points (A, B, C and D) with the nuances going of the dark gray to the white were chosen for the elementary analysis carried on the protecting patina of the coin surface. The image MEB shows irregularities and roughness on the surface and visible advanced corrosion phenomena. The contrast colours indicate diversity in chemical composition of the coin.
3.3. EDS analysis

The spectrum of the microanalysis (EDS), in the dark gray point A, is represented on the figure 3. The microanalysis show the elements peaks: copper, magnesium, antimony, lead, iron, chlorine, oxygen and carbon. Peaks energies $E = 8.04; 8.90; 0.92$ and $0.94$ keV are ascribable to the under layers $K\alpha_1; K\beta_1; L\alpha_1$ or $L\beta_1$ of copper, respectively [5]. Peaks with $E = 10.44; 10.55; 12.61; 12.62; 2.48$ and $2.58$ keV, are ascribable to energies of under layers $L\alpha_2; L\alpha_1; L\beta_1; L\beta_2; M-V$ and $M-IV$ of Lead, respectively [18]. Peaks of carbon, oxygen, antimony, magnesium, iron and chlorine are observed. Copper is the most abundant element with 62.99% (wt) and lead is only at 2.15% (wt). The table 1 includes the results of the EDS elementary analysis of the Numide coin. In the point A, the results show that the surface consists mainly of copper and antimony with respective weight percentage 62.99% and 7.15%. Magnesium and iron are observed with small mass percentages going from 3.23 to 0.55%. The second analysis was made in the point B (grey area). On the EDS spectrum, the peaks of elements: copper, antimony, lead, iron, oxygen and carbon are observed. A new peak at energy 1.73 keV of $K\alpha_1$ or $K\alpha_2$ is ascribed to silicon element. This microanalysis shows that the chemical composition of the patina is mainly rich of copper (53.41%) and antimony (25.02%) and relatively poor of lead and iron (Table 1). A microanalysis made in the light grey point C (Figure 2, Table 1) gives the same elements observed earlier on the EDS spectrum of point B. The copper remains majority with 52.08% (wt), the lead’s concentration increases by +6.77% and the antimony’s one decreases by -8.01% (wt).
The last analysis was carried on the white point D (Figure 2). The EDS spectrum shows the main peaks of elements: lead, copper, carbon, oxygen, silicon, potassium and antimony. The iron was not detected in this point (Figure 4). In this point, the EDS analysis shows an important variability in surface composition. There is an inversion in the concentrations of the lead and the copper. The lead became majority with 22.81% (wt) against 10 and 2 %, founded previously. On the other hand, the percentage of the copper decreased (15.77% against 53.41 and 52% in points B and C (Table 1). The silicon gets incrusted as sand’s grains in joints and gaps on the coin’s surface. The other detected elements (oxygen, chlorine, magnesium, carbon) are exogenous elements and result from the ground contagion.

Table 1: EDS microanalysis of the Numide coin.

<table>
<thead>
<tr>
<th>Element</th>
<th>A (% wt)</th>
<th>B (% wt)</th>
<th>C (% wt)</th>
<th>D (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>62.99</td>
<td>53.41</td>
<td>52.08</td>
<td>15.77</td>
</tr>
<tr>
<td>C</td>
<td>12.32</td>
<td>05.29</td>
<td>14.08</td>
<td>25.53</td>
</tr>
<tr>
<td>O</td>
<td>12.16</td>
<td>06.97</td>
<td>08.44</td>
<td>24.67</td>
</tr>
<tr>
<td>Mg</td>
<td>03.23</td>
<td>06.06</td>
<td>02.91</td>
<td>/</td>
</tr>
<tr>
<td>Sb</td>
<td>07.15</td>
<td>25.02</td>
<td>17.01</td>
<td>11.65</td>
</tr>
<tr>
<td>Pb</td>
<td>03.15</td>
<td>02.22</td>
<td>09.99</td>
<td>22.81</td>
</tr>
<tr>
<td>Fe</td>
<td>00.55</td>
<td>00.38</td>
<td>00.62</td>
<td>/</td>
</tr>
<tr>
<td>Cl</td>
<td>00.31</td>
<td>/</td>
<td>00.69</td>
<td>/</td>
</tr>
<tr>
<td>Si</td>
<td>/</td>
<td>00.18</td>
<td>/</td>
<td>01.08</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td>99.49</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

In summary, analysis made in the four points of the Numide coin give a weight average concentration of copper (46.06%), antimony (14.20%) and lead (9.54%), (Table 2). These values seem to indicate that the matrix of the Numide coin is constituted by a ternary alloy Cu-Pb-Sb with 60.71% of copper, 23.38 % of antimony and 15.89 % of lead (relative composition). The other elements revealed by the elementary analysis are exogenous and result from the contagion by the ground where the coin was found.
Table 5: Average concentration of elements analyzed by EDS in the Numide coin

<table>
<thead>
<tr>
<th>Elements</th>
<th>% wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>46.06</td>
</tr>
<tr>
<td>Sb</td>
<td>14.20</td>
</tr>
<tr>
<td>Pb</td>
<td>09.54</td>
</tr>
</tbody>
</table>

3.4. DRX analysis

DRX gives diffraction peaks of the lead metal: $d_{\text{hkl}} = 2.84; 2.46; 1.74; 1.492$ and $1.237 \text{ Å} (d_{\text{hkl}} = 2.86; 2.47; 1.74; 1.49$ and $1.42 \text{ Å}$, Fiche ASTM N° 4 – 686 [19] and lines of copper metal. $d_{\text{hkl}} = 2.087; 1.807; 1.287$ and $1.089 \text{ Å} (d_{\text{hkl}} = 2.09; 1.81; 1.28$ and $1.09 \text{ Å}$, Fiche ASTM N° 4 – 836 [19]. The hydroxide mixed lead and antimony, Bindheimite ($\text{Pb}_2\text{Sb}_2\text{O}_7$) [20-21] is identified with $d_{\text{hkl}} = 3.0; 1.85$ and $2.61 \text{ Å}$, Fiche ASTM N° 18-687 [19]. The Bystromite ($\text{MgSb}_2\text{O}_6$) is the second phase identified with $d_{\text{hkl}} = 3.32; 2.57$ and $1.73 \text{ Å}$, Fiche ASTM N° 15 – 684 [19].
4. Conclusion

The elementary analysis made in four points of the Numide coin’s surface, indicate the presence of the three elements copper, antimony and lead. The average concentrations of these elements seem to indicate that the matrix of the coin is constituted by a ternary alloy Cu-Pb-Sb of relative composition with 60.71% of copper, 23.38% of antimony and 15.89% of lead (relative composition). The iron, the magnesium, the potassium and the other detected elements are exogenic and coming from a ground contamination. They are impurities naturally present in the environment of burying coin. The DRX study identified the metallic phases copper and lead and the crystalline oxides bindheimite (Pb$_2$Sb$_2$O$_7$) and bystromite (MgSb$_2$O$_6$). The presence of the antimony, in this last mixed oxide, is explained by its fault of the matrix towards the surface.

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