Analysis of corrosion products in some metallic statuettes of the Museum of Archaeology and Ethnology (MAE-USP)

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ABSTRACT

The recent acquisition of a sealed chamber with controlled humidity by the Museum of Archaeology and Ethnology of the University of São Paulo (MAE-USP) requires new methods for conservation and restoration of metallic objects in its collection. To establish new procedures for the identification of corrosion mechanisms and agents in the exhibition environment, and to set up new standards for conservation of the museum’s collection, Proton Induced X-Ray Emission (PIXE) elementary analysis of some metallic objects is in progress, using the external beam facility at LAMFI. The first analysis involved metallic objects from the collection of MAE, two African statuettes “male Edans” from the Ogboni Secret Society, of the Ilobu-Iorubá ethnic group, one pectoral adornment from the Chimu culture, Peru and one anthropomorphic pendant from the Tairona culture, Colombia. The in air non destructive PIXE analysis allowed identifying major and some secondary components in the alloys and in the corrosion products on the samples, data that were used to identify the corrosion sources and to set up the exhibition environment.

1. INTRODUCTION

Due to the artistic and/or the historical value, the chemical characterization of cultural heritage items should be analyzed with non-destructive methods. The ion beam analysis of organic and volatile samples, archaeological pottery artifacts and paintings are now possible at the external beam facility of the LAMFI-USP (Laboratório de Análise de Materiais por Feixes Iônicos). This facility opens new possibilities for analysis of large art objects, which are not compatible with the high vacuum environment of a regular target chamber.

The PIXE analysis, which is a highly sensitive and non-destructive IBA method, allows the identification of the major and minor components of the alloys (tens of ppm). When operated
in an external beam facility, PIXE analysis is suitable for artistic and archaeological artifacts not measurable in the standard high vacuum environment of the analytical IBA chambers. Open air PIXE analysis was employed to analyze valuable samples from the collection of the Museum of Archaeology and Ethnology of the University of São Paulo (MAE-USP). The recent acquisition of a sealed chamber with controlled humidity by the Museum required setting up new methods for conservation and restoration of metallic objects in the collection, pointed to an initial characterization of some pieces of the museum’s collection. The characterization of the corrosion products of some metallic statuettes from the African and pre-Colombian collection of MAE will allow the identification of the corrosion mechanisms and the corrosion agents in the exhibition environment [1], as well as helping with the conservation of the museum’s collection.

2. EXPERIMENTAL

The open air PIXE analysis involved two ethnological metallic statuettes from the African collection, one pectoral adornment and one anthropomorphic pendant. The African statuettes were two "male Edans" from the Ogboni Secret Society, of the Ilobu-Iorubá ethnic group [2]. The pectoral adornment was from the Chimu culture, Peru that resided in the north coastline from 1000 to 1470 d.C. The anthropomorphic pendant is from the Tairona culture, Colombia.

Optical inspection with a stereoscopic lunette showed that all samples had corrosion products with different structures and colors covering the metallic objects.

2.1. Samples

Figure 1 and 2 show the samples mounted in the external beam setup for PIXE analysis.

![Figure 1. Samples analyzed with PIXE technique "male Edans" statuettes (A and B) right and left, respectively.](image)
2.1.1. PIXE Analysis

PIXE measurements were performed at LAMFI using a 2.4 MeV proton beam exited through a 50µm thick Kapton foil. Due to the 10mm air path and the Kapton exit window the final beam energy was approximately 1.0 MeV. For X-ray detection an XR-100CR (Si-PIN, FWHM 220eV@MnKa) detector was mounted on a water-cooled aluminum base. The X-ray detector was placed at 12 mm from the target at an angle of 135 degrees to the incident beam. Typical beam currents used to analyze the statues were a few nA keeping dead time and pulse pile-up within low and acceptable limits. The acquisition time was set to 1200 seconds for each sample. The presence of the argon X-rays from the air worsen somewhat the detection limits for Cl and K, Kα lines. However the same Ar signal was used to check the experimental reproducibility since its intensity is proportional to the distance between the exit window and the target.

The integrated charge on the target during the analysis was determined indirectly by measuring scattering events on a thin gold foil inside the chamber. The elastic peak of Au in the energy backscattered spectra was used to normalize the X-ray spectra and to calculate the actual integrated charge on the target.

3. RESULTS AND DISCUSSION

Figure 3 shows the PIXE energy spectra measured (normalized to the charge) from statuette A, using a 2.4MeV (effective 1.0MeV) proton beam. A qualitative analysis of a spot without any visible corrosion (black line) showed Cu and Zn as the main components of the alloy with Pb in a smaller quantity. Elements such as Al, Si, S, Cl, K, Ca, Fe, Ni and Sn were measured in smaller amounts. The analysis of corrosion products on the ear (blue line) and on the forehead (green line) of the same statuette indicated a higher relative mass concentration of Zn than Cu, in opposition to the alloy at the base, indicating a probable selective corrosion. The presence of sulphur in some of the examined spots suggested the existence of sulphides.
or sulphates of copper or/and zinc. It is worthwhile to remember that low Z elements such as C, N and O are not visible in PIXE measurements.

Figure 3. – PIXE energy spectra for the metallic statuette A showing the detected elements in comparison with different point in the statuettes

In statuette B, the PIXE spectra (figure 4) showed that the main components were Cu, Zn and Pb in the corrosion free region, while sulphur was found in smaller amounts on the spots indicated by the green line. The analysis of the grayish colored spots on this statuette indicated the presence of lead and its carbon/oxygen compounds, which was confirmed by a Raman analysis [4]. X-Ray lines of sulphur were also observed, indicating the presence of sulphide or sulphate compounds similarly as in statuette A. The relative mass of sulphur increases in the corrosion products on the back and on the buttocks (black and red lines) of this statuette, in comparison with its forehead (green line), indicating a probable presence of lead sulphate.

In statuette C, the anthropomorphic pendant, the PIXE spectrum showed that the main components of the alloy were Cu and Au. Other elements such as S, Cl and Fe were also found when the black patina of the statuette was analyzed, but in smaller amounts. The pectoral adornment was covered with corrosion products with different colors. PIXE analyses were done at 5 points with different colors, two at the front (P1, P2) respectively black and white, and two at the back (P4, P5) respectively greenish and brownish. The X-ray spectra showed that the main component of the alloy is Cu. Other elements like Si, S, Cl, Fe and As were also found. Arsenic could be the indication of environmental contamination.
The calculated concentrations measured with PIXE are summarized in tables 1 to 3. The values for these concentrations are proportional to the peak areas normalized to the charge and the detector yield curve. Due to many uncertainties in the measurements (local composition variations, surface roughness, variable detector-sample distances, etc) the overall uncertainty is estimated to be 15%.

**Table 1. Relative mass concentrations (%) at different points on the African statuettes.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Statuette A base</td>
<td>0.15</td>
<td>1.65</td>
<td>0.69</td>
<td>0.57</td>
<td>0.51</td>
<td>1.53</td>
<td>56.7</td>
<td>33.1</td>
<td>4.10</td>
</tr>
<tr>
<td>Statuette A arm</td>
<td>0.08</td>
<td>0.76</td>
<td>0.36</td>
<td>0.20</td>
<td>0.33</td>
<td>1.00</td>
<td>42.3</td>
<td>43.2</td>
<td>1.29</td>
</tr>
<tr>
<td>Statuette A forehead</td>
<td>0.13</td>
<td>0.98</td>
<td>0.49</td>
<td>0.25</td>
<td>0.46</td>
<td>0.94</td>
<td>33.1</td>
<td>62.2</td>
<td>0.92</td>
</tr>
<tr>
<td>Statuette A ear</td>
<td>0.12</td>
<td>0.80</td>
<td>0.81</td>
<td>0.18</td>
<td>1.63</td>
<td>0.84</td>
<td>24.0</td>
<td>69.9</td>
<td>1.27</td>
</tr>
<tr>
<td>Statuette B forehead</td>
<td>0.14</td>
<td>4.22</td>
<td>0.27</td>
<td>0.06</td>
<td>0.23</td>
<td>0.09</td>
<td>20.3</td>
<td>2.57</td>
<td>69.5</td>
</tr>
<tr>
<td>Statuette B back</td>
<td>0.17</td>
<td>2.47</td>
<td>0.57</td>
<td>0.27</td>
<td>0.49</td>
<td>0.18</td>
<td>37.8</td>
<td>3.66</td>
<td>51.7</td>
</tr>
<tr>
<td>Statuette B buttocks</td>
<td>0.11</td>
<td>0.81</td>
<td>0.46</td>
<td>0.32</td>
<td>0.73</td>
<td>0.56</td>
<td>74.8</td>
<td>9.63</td>
<td>11.6</td>
</tr>
</tbody>
</table>

Figure 4. – PIXE energy spectra for the metallic statuette B showing the detected elements in comparison with different point in the statuettes.
Table 2. Relative mass concentrations (%) at different points on the anthropomorphic pendant

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Statuette C front</td>
<td>0.06</td>
<td>0.20</td>
<td>0.20</td>
<td>0.04</td>
<td>0.20</td>
<td>39.0</td>
<td>0.33</td>
<td>58.2</td>
<td></td>
</tr>
<tr>
<td>Statuette C black part</td>
<td>0.20</td>
<td>4.17</td>
<td>2.84</td>
<td>0.24</td>
<td>0.11</td>
<td>0.17</td>
<td>40.0</td>
<td>1.61</td>
<td>44.5</td>
</tr>
</tbody>
</table>

Table 3. Relative mass concentrations (%) at different points on the pectoral adornment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si</th>
<th>S</th>
<th>Cl</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample D P1</td>
<td>0.16</td>
<td>6.38</td>
<td>15.5</td>
<td>0.08</td>
<td>0.57</td>
<td>67.4</td>
<td>0.52</td>
<td>0.59</td>
</tr>
<tr>
<td>Sample D P2</td>
<td>0.10</td>
<td>1.18</td>
<td>6.95</td>
<td>0.27</td>
<td>0.19</td>
<td>87.2</td>
<td>0.04</td>
<td>0.43</td>
</tr>
<tr>
<td>Sample D P4</td>
<td>0.05</td>
<td>0.63</td>
<td>0.82</td>
<td>0.09</td>
<td>0.44</td>
<td>95.0</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>Sample D P5</td>
<td>0.08</td>
<td>1.06</td>
<td>4.13</td>
<td>0.09</td>
<td>0.27</td>
<td>89.0</td>
<td>1.11</td>
<td></td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

The LAMFI external beam setup was used for the first time to analyze archaeological artifacts from the metallic collection of the MAE-USP. The in air and non-destructive PIXE analysis allowed the detection of major and secondary component in the alloys and the positive identification of most of the corrosion products on these samples. The PIXE results are being used to help MAE identifying the corrosion mechanisms and the corrosion agents in the exhibition environment and to set up a new standard for conservation of the museum’s collection work.

ACKNOWLEDGMENTS

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REFERENCES