Mass-resolved ion scattering spectrometry for characterization of samples with historical value

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Abstract

The layer-by-layer atomic composition of major elements (Cu, Ag, and Au) in the medieval Venetian coin has been measured by mass-resolved ion scattering spectrometry (MARISS) using 1 keV Ne+–He+ mixed ion beam for both controlled erosion of the sample (up to 0.3 μm in a depth) and simultaneous generation of analytical signals. Quantification was carried out by calibration using pure standard materials. It was shown that the surface of the coin is significantly enriched in silver (ca. 80 at.%), whose content tends to decrease inward the coin. Formation of the Ag-enriched layer (or surface depletion in copper) could be caused by the environment the coin was exposed to for many centuries.

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1. Introduction

In the field of cultural heritage, elemental analysis of numismatic objects is a well-established tool [1] to identify the manufacturer, to recognize the provenance, and even to reveal adulteration. One of the main difficulties here comes from the uniqueness of samples of an historical value that rarely fit analytical purposes. At present, ion-beam techniques such as particle induced X-ray and gamma-ray emission, and Rutherford backscattering spectrometry have proven to be the most suitable techniques for near-surface (down to several micrometers in depth) non-destructive atomic identification and testing of such objects [2–4] (to name but a few works).

A number of papers related to application of XPS [5], Auger electron spectroscopy [6] and SIMS [7] in archaeometry of old coins and alloys have been published. These methods have a very low information depth (about several nanometers) and can give useful information about surface enrichment or depletion. Low-energy ion scattering (LEIS) [8–10] is able to probe the outer atomic layer of a surface. As a rule, quantification in LEIS is performed by the use of calibration standards [11,12]. In contrast to SIMS, the yield of scattered ions is not sensitive to the “matrix effect,” at least for metal alloys. LEIS sputter depth profiling is also possible [13,14]. The additional mass analysis of the scattered ion species simplifies LEIS peak identification and eliminates the overall ion
background related to sputtering of the target materials under dynamic bombardment conditions [15–17]. Wittmaack denoted this technique as the mass-resolved ion scattering spectrometry (MARISS) [15].

Generally, LEIS belongs to the high-technology sectors, such as industrial catalysis, semiconductor fabrication, electron emitter manufacturing, etc. [18,19]. However, it is of interest to apply MARISS for characterization of rare numismatic objects, either. The goal of the present work was to investigate low-energy (1 keV) backscattering of Ne$^+$ and He$^+$ ions from a medieval Venetian coin. Here we report our results of MARISS elemental identification and depth profiling of the coin with appropriate calibration of surface atomic concentration and depth of analysis.

2. Experimental

We studied a medieval “denaro” [20] issued by the Doge Enrico III (ca. 1056–1125). The coin was minted out of silver or “billon” (silver–copper alloy); its surface looked clean enough, without a visible presence of the patina. Before introduction into the analytical chamber, the coin was only rinsed with ethanol, and obviously no surface mechanical polishing was done.

For standard references, polycrystalline pure silver, copper, and gold samples by Goodfellow were used. The densities of these materials are listed in Table 1. The bulk atomic density, $\rho_a$, was derived from the mass density using the well-known expression [21], and then the surface atomic density, $N$, was estimated as $N = \rho_a^{2/3}$.

Table 1

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>29</td>
<td>47</td>
<td>79</td>
</tr>
<tr>
<td>Atomic weight (amu)</td>
<td>63.54</td>
<td>107.9</td>
<td>197</td>
</tr>
<tr>
<td>Mass density (g/cm$^3$)</td>
<td>8.92</td>
<td>10.5</td>
<td>19.3</td>
</tr>
<tr>
<td>Atomic density ($\times 10^{22}$, atm/cm$^3$)</td>
<td>8.45</td>
<td>5.86</td>
<td>5.90</td>
</tr>
<tr>
<td>Surface atomic density ($\times 10^{15}$, atm/cm$^2$)</td>
<td>1.93</td>
<td>1.51</td>
<td>1.52</td>
</tr>
</tbody>
</table>

Details of our system and MARISS measurements have been reported in our previous publications [17,21–23]. In brief, a monoenergetic inert gas ion beam (without mass separation) was produced by an electron-impact ionization source IQE 12/38. The incident ions were directed at a fixed incident angle $\psi = 60^\circ$ with respect to the sample surface. The ions backscattered at the angle $\theta = 2\psi$ (specular reflection) were mass and energy analyzed by the Hiden EQS 1000. All measurements were performed using the “in-plane” geometry within a small solid angle of acceptance ($\Delta\Omega \sim 10^{-4}$ sr). The operating pressure in the analytical chamber was $(3–5) \times 10^{-7}$ Pa, the residual gas atmosphere was controlled by the same Hiden EQS 1000 Analyser. The depth of sputter craters was determined by a Tencor Stylus Profiler P-10.

With our backscattering geometry, the classical laws of energy and momentum conversation prohibit binary elastic scattering of a projectile from a surface atom lighter than the projectile. Hence, we cannot monitor oxygen, nitrogen, and other light surface impurities with only Ne$^+$ primary ions. In order to be able to analyse light species as well, we used a mixed He$^+$–Ne$^+$ ion beam along with an accurate mass separation of scattered ions and consecutive registration of both He$^+$ and Ne$^+$ energy distributions. In this way, total concentration of the residual surface contaminants (with the exception of hydrogen) was estimated to be less than 1 at.% for all pure standards. The assessment of the surface cleanliness from positive and negative secondary ion mass spectra, measured by the same Hiden EQS 1000 Analyser, confirmed the MARISS results.

3. Results and discussion

The MARISS spectra of $^{20}$Ne$^+$ ions scattered from pure Cu, Ag, and Au standard samples are shown in Fig. 1. No refinement or correction were applied to the experimental results, since the spectral background is efficiently eliminated by mass separation. The measurements were carried out under steady-state bombarding conditions, when the surface of the samples was sputter cleaned, and the scattered ion intensities were stabilized (the ion dose was above $5 \times 10^{16}$ cm$^{-2}$).

The main characteristics of the spectra are summarized in Table 2. The relative peak energies approximately correspond to those calculated via the binary elastic collision model. It is known [8–10] that the ion-scattered intensity of the $i$-element on a surface, $I_i$, is
related to its surface atomic concentration $N_i$ by the following equation:

$$I_i = I_0 Y_i N_i.$$  \hspace{1cm} (1)

Here, $I_0$ is the ion-beam current and the elemental sensitivity or the scattered ion yield $Y_i$ can be represented by \cite{8,21}

$$Y_i = P^+_i \frac{d\sigma_i}{d\Omega} \Delta\Omega T_i R_i C,$$  \hspace{1cm} (2)

where $P^+$ is the ion-survival probability, $d\sigma/d\Omega$ is the differential scattering cross-section, $\Delta\Omega$ is the analyzer’s solid acceptance angle, $T$ is an apparatus coefficient, $R$ is a factor that accounts for the surface roughness and related shadowing ($R = 1$ for a flat surface), and $C$ is a constant, depending on the method of the intensity measurement (peak height, peak area, or first derivation peak-to-peak).

It is conventional to determine the elemental sensitivity by calibration with respect to pure standards. The values of $Y_i$ estimated in our study for 1 keV $^{20}$Ne$^+$ ions scattered at 120$^\circ$ from pure Cu, Ag, and Au are presented in Table 2. The calibration procedure is only valid if $Y$ is independent of the atomic concentration in a given matrix and is not sensitive to the “matrix effect.” The recent LEIS round robin experiment for the example of the Cu$_{0.55}$Pd$_{0.45}$ alloy \cite{12} has shown that the quantitative composition analysis can be performed by this method with a reasonable accuracy and reproducibility. We have demonstrated \cite{24} that MARISS enables to quantify precious ternary alloys as well.

If no “matrix effect” is involved, one finds from Eq. (1) that for the $i$-element in a standard sample and a sample of interest (unknown), both of which are probed under identical experimental conditions, the surface atomic densities, $N_{\text{std}}$ and $N_{\text{unk}}$, should be related by

$$N_{\text{unk}} = N_{\text{std}} \frac{I_{\text{unk}}}{I_{\text{std}}} C_{18}/C_{19} = I_{\text{unk}} Y.$$  \hspace{1cm} (3)

It is important that the quantification procedure per se is independent of the nature and the number of other atomic species on the probed surface. The relative surface atomic density of the $i$-element in a multi-component sample can be calculated as

$$\gamma_i = \frac{(I/Y)_i}{\sum_{j=1}^{k} (I/Y)_j} \times 100 \text{ at.\%},$$  \hspace{1cm} (4)

where $k$ is the number of atomic species in the sample, and $\sum_{j=1}^{k} \gamma_j = 100 \text{ at.\%}$. During sputter depth profiling of the coin, we measured consecutively 23 sets of Ne$^+$ and He$^+$ scattered ion spectra. Fig. 2(a–b) displays such spectra registered at the beginning (Start) and at the end (End) of the experiment. In Fig. 2a, it is possible to discern (i) three pronounced peaks related to $^{20}$Ne$^+$ ions scattered from Cu, Ag, and Au atoms; (ii) the lengthy background, which we attribute to $^{20}$Ne$^+$ scattering from a small amount of common surface contaminants.

### Table 2

$^{20}$Ne$^+$ scattered from the Cu, Ag, and Au pure standards (Fig. 1)

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative peak energy, $E/E_0$</td>
<td>0.377 ± 0.005</td>
<td>0.56 ± 0.01</td>
<td>0.74 ± 0.01</td>
</tr>
<tr>
<td>Peak intensity, $I$ ($\times 10^3$, cps)</td>
<td>8.1 ± 0.2</td>
<td>3.2 ± 0.1</td>
<td>2.2 ± 0.1</td>
</tr>
<tr>
<td>Relative elemental sensitivity, $Y/Y_{Cu}$</td>
<td>1</td>
<td>0.51 ± 0.05</td>
<td>0.345 ± 0.04</td>
</tr>
</tbody>
</table>
(Na, Al, Si, Cl, etc.) and (or) to the re-ionized neon atoms scattered from the major elements in deeper layers; and (iii) the narrow peak near zero energy caused by the primary ions, which were initially implanted and then re-emitted. In Fig. 2b, one can find $^4\text{He}^+/\text{O}$, $^4\text{He}^+/\text{Cu}$, $^4\text{He}^+/\text{Ag}$, and $^4\text{He}^+/\text{Au}$ scattered peaks and “zero-energy” self-sputtered helium peak. The intensity of the $^4\text{He}^+/\text{O}$ peak is very low (at the level of background), and its value has remained practically unchanged during depth profiling. The quantification of the surface oxygen content by LEIS is complicated [9], and cannot be performed in a direct and straightforward way, particularly under dynamic bombardment conditions. To compare our $^4\text{He}^+$ spectra with those measured in LEIS experiments of CuO sample [25], we roughly estimate the oxygen concentration ca. 5–7 at.%. The total amount of different impurities and residual contaminations in the near-surface layers of the coin is estimated to be less than 10–15 at.%. Such an uncertainty hinders but does not preclude quantification of $^{20}\text{Ne}^+$ spectra by Eq. (4).

The results of quantitative MARISS depth profiling of the coin are presented in Fig. 3. The statistical variation between three probes taken in different points was within $\pm 20\%$. The depth scale in Fig. 3 was derived from the total depth of the sputter crater $Z$ and the bombardment time $T$ assuming that the erosion rate is $V_{\text{sp}} = \frac{dZ}{dt} \sim Z/T$. This expression is not completely precise for the samples with variable elemental composition versus the depth. However, for ternary precious alloys the uncertainty $\Delta V_{\text{sp}}$ should not exceed 15–20%. Initial and ion-induced surface roughness can also complicate converting of the sputtering time into the sputtering depth, in particular for an object with an unpolished surface. We estimate the average sputtering velocity to be $2.4 \pm 0.8$ nm/min. We did not carry out long sputter cycles, which could damage the coin.

Fig. 3 exhibits a clear Ag-surface enrichment (ca. 80 at.%), which evidently decreases inward the coin. On the contrary, the Cu-atomic concentration tends to increase when the depth of sputtering increases. It is a common knowledge that the surface composition of numismatic objects can be affected by the environment they were exposed to during many centuries of
their long lifetime. Since copper is more oxidizable than silver, a contact with a corrosive environment (SO₂, sweat, moisture, etc.) leads to formation of copper oxides, which then can be removed by friction or dissolution. Such processes cause the formation of a surface layer enriched in silver, which is revealed in our experiment.

4. Summary

We have determined the layer-by-layer atomic composition of major elements (Cu, Ag, and Au) in the medieval Venetian “denaro” by low-energy MARISS. The quantification was carried out using the elemental sensitivities estimated for pure standard references. Sputter depth profiling (up to 0.3 μm) was performed using 1 keV Ne⁺–He⁺ mixed ion beam for both controlled erosion of the sample and simultaneous generation of analytical signals. It was shown that surface of the coin is significantly enriched in silver, whose content tends to decrease inward the coin. The formation of Ag-enriched layer (or surface depletion in copper) could be explained by the influence of the environment the coin was exposed to.

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References