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Microprobe study of Portuguese ancient silver coins of uncertain provenance

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Ion Beam Analytical (IBA) techniques such as Particle Induced X-ray Emission (PIXE) and Elastic Backscattering Spectrometry (EBS) are finding increasing applications in the study of ancient coins [1] because they are non-destructive and can determine the coin chemical fingerprint down to the ppm range, which in some cases can be related with the ore provenance or the metal purification process, thus giving information about the fabrication period. In ancient coins, surface inhomogeneities created by centuries of corrosion growth, require a micro beam to characterize them. The analysis of μ-PIXE and μ-EBS spectra taken simultaneously allows to differentiate the superficial corrosion layer from the bulk, giving elemental surface composition distribution and elemental depth profiling, respectively. Using 1.0 and 2.0 MeV proton beams from the nuclear microprobe (resolution 3×4 μm^2) located at the Ion Beam Laboratory at CTN (Sacavém - Portugal), this approach was used to try to clarify about the authenticity of two XVI century Portuguese 91.6%wt silver (stipulated by decree of law) coins (Fig. 1) as the stylistic analysis by numismatic experts was not conclusive. Three coeval genuine Portuguese coins were also studied and served as a comparison.

2D-PIXE maps (as shown in Fig. 2) were acquired for all coins, followed by point analysis (3×4 μm^2) in areas with thicker (higher Fe and Br content) and thinner (higher Ag and Cu content) corrosion layer.

Figure 3 shows fitted μ-PIXE and μ-EBS spectra taken simultaneously using a 1.0 MeV proton beam. These fits performed on all five coins showed that:

a) major elements Ag and Cu: genuine coins have ≈95 wt% in Ag and ≈5 wt% in Cu homogenously distributed, while the two coins of uncertain provenance show ≈70-80 wt% in Ag and ≈20-30 wt% in Cu;
b) trace elements Au and Bi (which are related with ore provenance): not detected on all coins, but when detected the concentration is around 0.05 wt%;
c) trace element Pb (which is related with Ag refining process): detected on all coins, with ≈0.2 wt% quantified.

From these results it was not possible to give a definite answer about the authenticity of the two coins of uncertain provenance. The low content in Ag is very uncommon in ancient coins, even more knowing that Ag-Cu alloys get surface enriched in silver, as observed for the genuine coins. However, in terms of trace elements, data are consistent with genuine coins.

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[1] Guerra, M.F. *et al., Nucl. Instr. and Meth. in Phys. Res. B,* **240**, 505-511, 2005.

Figure 1. Obverse and reverse of the two analyzed coins of uncertain provenance. Left panel: Portuguese 5 Reais of King Manuel I (1495-1521); Right panel: Portuguese XXXX Reais of King Filipe I (1580-1598).

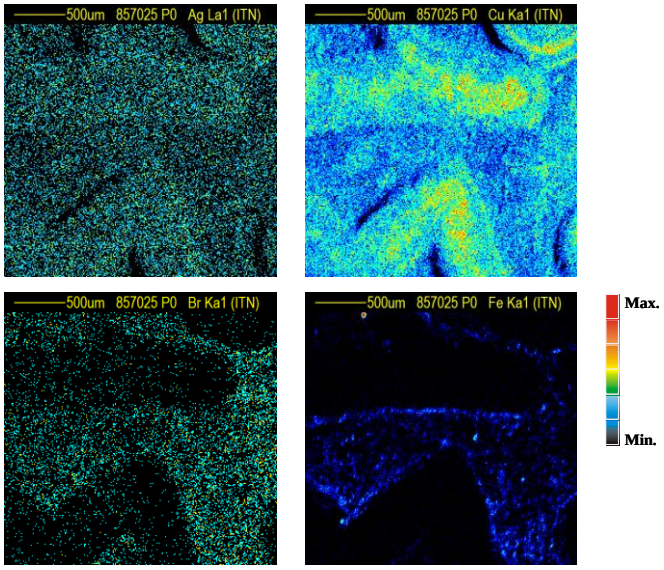

Figure 2. 5 Reais of King Manuel I coin: 2D-PIXE maps of Ag, Cu, Br and Fe (2640×2640 μm^2).

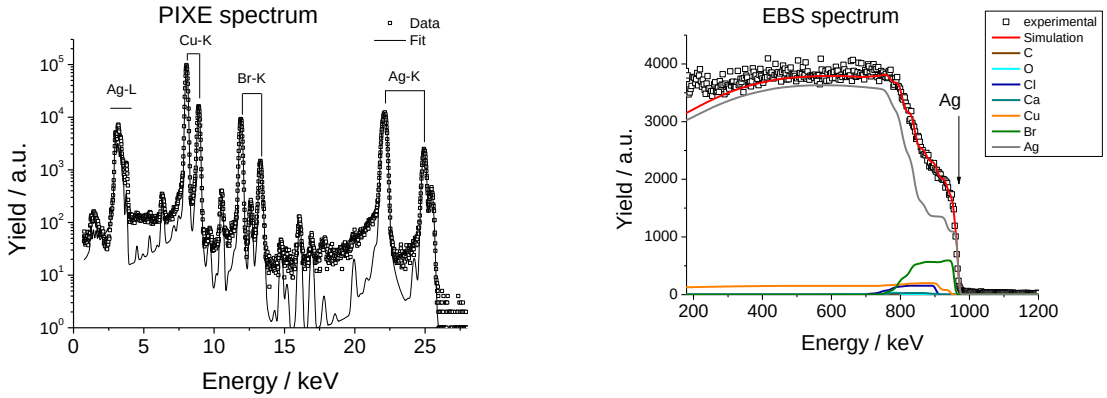

Figure 3. Fitted μ-PIXE and μ-EBS spectra, acquired on a corroded area of the 5 Reais coin using a 1.0 MeV proton beam. PIXE spectrum clearly shows the presence of Br in this area while the EBS spectrum fit ascertains the corroded area thickness (signal from Br layer results in the lower surface layer signal of Ag).

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