Characterization of Mercury Gilding Art Objects by External Proton Beam

V. Corregidor1, L.C. Alves1, N.P. Barradas1, M.A. Reis1, M.T. Marques1, J.A. Ribeiro1
1. Unidade de Física e Aceleradores, LFI, ITN, E.N.10, 268-953 Sacavém, Portugal
2. CEFUL, Av. Prof. Gama Pinto, 2 1649-003 Lisboa, Portugal
3. CFAUL, Av. Prof. Gama Pinto, 2 1649-003 Lisboa, Portugal
4. Casa Museu Dr. Anastácio Gonçalves, Av. 5 de Outubro, 6-8, 1100-065 Lisboa, Portugal
5. IMC, Palácio Nacional da Ajuda, 1349-021 Lisboa, Portugal

Introduction

The fire gilding is one of the methods used by the ancient goldsmiths to obtain a rich, metallic glow and durable golden appearance in ornamental objects. This layer is characterized, among others, by its thickness (several microns), a Hg content (between 0-21%) and a diffusion profile depending on the temperatures achieved during the process.

Gilded sacred art objects dated from the XVI to the XVIII centuries, belonging to the Casa-Museu Dr. Anastácio Gonçalves Collection (Lisbon) were analyzed using the external ion microprobe at Nuclear and Technological Institute, Lisbon.

The average concentration of homogeneous areas were calculated with GUPPI, DATPIXE and NDF codes showing very similar results.

The NDF code was used for RBS spectra fitting and sample composition determined in a self-consisting way with PIXE data simulated by means of LibCPXE code, an open-source library for multilayered samples which can work jointly with the NDF code.

The process of gilding

A mixture of 1 part of Au to 8 part of Hg is added into a crucible and then heated. The metals form a silvery amalgam that is poured into a vessel of water. After that, it is squeezed through a fabric to remove the Hg excess.

The surface to be gilt is prepared with an acid solution. (1) The amalgam is applied to the surface with a hard brush (2) and then put onto a hot charcoal fire (3). The time (few minutes) and temperature (250-300 °C) were crucial and usually judged by the goldsmith experience when the amalgam changes color from gray to dull yellow. At this stage around 2/3 of mercury is volatilized.

Then, the object is burnished (4) to compress the porous structure until create a smooth and brilliant surface.

Experimental

1. X-ray: Si Bruker SDD, 145 eV resolution at 45° and 2.8 cm distance, with 350 µm Mylar foil.
2. micro-camera
3. 1940 keV proton beam extracted through a 100 nm thick SiN window. Current: 200 pA
4. RBS: Surface barrier detector at 47° and 2.2 cm distance.

Normal incidence. Detectors in the IBM geometry.

Controlled helium flow.

Codes for data analysis: GUPPI, DATPIXE, NDF and QXAS. All compositions are in weight percent.

Results

Reliquary, CMAG 1194

When a flat surface with a homogeneous composition is analyzed, the codes used to calculate the concentration shown slightly different results. They can be related with calibration issues.

Ostensorium, CMAG 1164

The monestence is made of silver and the rays are made of a Ag-Au-Cu alloy (80%, 12%, 3% respectively).

Ciborium, CMAG 1180

The inside of the cup and the cover are completely girt. The internal part of the cup has an average composition of 25% of Ag, 70% of Au and 15% of Hg. A silver layer over the base of the ciborium has Au-rich regions.

The composition was calculated assuming multilayered structure using LibCPXE-NDF codes.

Conclusions

When a homogeneous area of analysis is considered, the average composition obtained with the GUPPI, DATPIXE and NDF codes is quite similar. Efforts related to finer detector calibration, stability of the He flow control and data base consistency issues should be done to overcome these slightly differences.

In some particular cases the simultaneous fitting of the RBS and the PIXE experimental data reveals that the inhomogeneous composition observed in the PIXE maps are mainly due to superficial inclusions which are Au reach with a diffusion profile into the silver object.

Different Hg and Au/Ag ratio contents have been found in the reliquary and ostensorium pieces dating from different centuries and proveniences.

In the silver parts of the ciborium, which is partially fire-gilded, some traces of Hg and Au were found, related with the manufacture process.