Nuclear Instruments and Methods in Physics Research B 268 (2010) 1920–1923

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

A comparative study of PIXE and XRF corrected by Gamma-Ray Transmission for the non-destructive characterization of a gilded roman railing

I. Ortega-Feliu [a,*], A.I. Moreno-Suárez [a,b], B. Gómez-Tubío [a,c], F.J. Ager [a,b], M.A. Respaldiza [a,d], S. García-Dils [e], O. Rodríguez-Gutiérrez [f]

[a] *Centro Nacional de Aceleradores, Avd. Thomas A. Edison, 7, 41092 Sevilla, Spain*
[b] *Departamento de Física Aplicada I, Universidad de Sevilla, Spain*
[c] *Departamento de Física Aplicada III, Universidad de Sevilla, Spain*
[d] *Departamento de Física Atómica, Molecular y Nuclear, Universidad de Sevilla, Spain*
[e] *Departamento de Historia Antigua, Universidad de Sevilla, Spain*
[f] *Departamento de Prehistoria y Arqueología, Universidad de Sevilla, Spain*

A R T I C L E I N F O

Article history:
Available online 25 February 2010

Keywords:
Gilding
Lead segregates
PIXE
RBS
Gamma Transmission
Archaeology

A B S T R A C T

Several fragments of a gilded railing were found in the archaeological excavations carried out in Écija (Spain), among the remains of a collapsed temple. The alloy composition and the gilding procedure used for its manufacture are of interest for a complete archaeological knowledge of the artefact. The common use of IBA techniques directly on the objects for their analysis is not possible due to the thick corroded patinas that they exhibit due to the burial environment. However, non-destructive analyses of a few selected fragments have been done using PIXE and XRF techniques in combination with Gamma-Ray Transmission. Indeed, as was previously shown [1,2], bronze objects can be characterized in a completely non-destructive way using the combination of these techniques. This work, shows the applicability of that method to artefacts made of leaded copper alloy, which is the case of samples studied, for which some problems could arise from the lead segregations present in these kind of alloys. We have found that this railing contains low amounts of Sn and Sb, and that the gilding was most probably obtained using a gold leaf.

1. Introduction

The ancient Roman city whose extension reaches the modern city of Écija (Spain) was founded ca. 14 B.C. by the Emperor Augustus. Between 1997 and 2007, large-scale archaeological excavations were carried out in the *Plaza de España* of Écija. In the course of these works, the remains of a temple's podium were documented. Behind this structure, and in close functional relationship with it, a large ornamental and ritual pool was found. Once the temple collapsed, it became the accidental container of an important number of constructive and decorative elements of this public building. Among the decorative elements documented there, several gilded metal fragments certainly stand out. They were found in 2005 in a very good state of preservation and clear stratigraphical context.

The reconstruction of the piece shows that it was probably part of a gilded railing (*cancelli*), about 1.40 m width and 0.90 m height, belonging to the rear part of the temple (Fig. 1). In the present state of our knowledge, we propose that this is a unique piece, for which no parallel has been found elsewhere in the Roman World. Nevertheless, the iconographical representations on various supports, suggest a more frequent presence of this kind of railing on Roman public architecture, but the poor preservation of metal objects in archaeological contexts has prevented finding similar objects until now. Information about the composition of this object is desired in order to compare it with the rest of the bronze artefacts found in this archaeological site and other places around, and check whether commercial or technological relationships could be established.

In order to complete the archaeological knowledge of the rail, conventional IBA techniques were performed on selected fragments. PIXE spectra with protons and RBS spectra with alpha particles at several energies were acquired on the corrosion patina as well as on the gold layer. XRF analyses were also carried out on the same fragments. Gamma-Ray Transmission combined with XRF and PIXE has proved to be useful in the non-destructive characterization of corroded bronze objects [1,2]. Based on this technique, the gilded roman rail was analysed in order to perform a correction to the composition of the patina, highly altered by corrosion, with the knowledge of the attenuation coefficient of the matrix of the sample.

* Corresponding author. Tel.: +34 954460553; fax: +34 954460145.
E-mail address: iofeliu@us.es (I. Ortega-Feliu).

0168-583X/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2010.02.102

Fig. 1. Picture of the railing remains. An insert shows a small gilded fragment.

The analyses performed on the patina showed that the object was not made of bronze (Cu + Sn), as expected, but a copper alloy was used instead, with very high levels of lead (up to around 70 wt% on the patina) and very little content of tin (less than 1 wt%). In this work, the study of such specific alloy using the mentioned combination of analytical techniques is assessed in terms of their capability and suitability.

2. Analytical techniques

X-ray Fluorescence (XRF) was used to obtain the superficial composition of the samples in a non-destructive way. The experimental setup consisted of a ^{41}Am annular gamma-source (∅ = 2 cm) collimated to 0.8 cm^2, and a silicon drift detector (SDD) manufactured by KETEK. The acquired spectra were fitted with the WinAxil program [3]. For the calibration of the system, certified standards were used. The uncertainties were 3% for Cu and 6% for Pb.

The PIXE technique was performed in a vacuum chamber of the Tandem Pelletron accelerator of 3 MV at Centro Nacional de Aceleradores of Sevilla [4]. Protons of 1 and 3 MeV were used for PIXE analysis of the corroded patina and of the gold layer. X-rays emitted from the sample were detected using a Si(Li) and a LEGe detector placed at 45° with respect to the sample normal. The size of the beam was 0.2 mm^2, and its intensity, 1 nA. The spectra were acquired with 4 μC and fitted using the GUPIXWIN software package [5]. The uncertainties were 3% for Cu and Pb. Also, elemental maps were acquired in a vacuum microprobe chamber with a $4 \times 5\ \mu m^2$ beam of 3 MeV protons. Several maps of the main elements present in the sample were acquired with different map sizes, from $200 \times 200\ \mu m^2$ to $2.5 \times 2.5\ mm^2$. A μ-PIXE spectrum was extracted from a specific area of one of the maps.

The Gamma-Ray Transmission technique (GRT) was used to correct the concentrations of the corrosion patina obtained by PIXE and XRF in order to estimate the volume composition. Our experimental assembly consisted of a ^{241}Am point gamma-source (∅ = 6 mm) suitably shielded and collimated (∅ = 4 mm), and a NaI(Tl) detector surrounded by copper plates that absorb lead X-ray from the shielding. Several points of gamma transmission have been acquired and the mass attenuation coefficient has been calculated for each point. The average value has been used to do the corrections. As in previous cases [1,2], for the GRT corrections, the sample was considered to be a binary compound of copper plus another "element" that includes the rest of the elements in the alloy ("mixture" element). With this hypothesis the mass attenuation coefficient of the "mixture" element is theoretically calculated using the concentrations given by PIXE or XRF in the patina. This coefficient, together with the average mass attenuation coefficient measured by GRT, allows correction of the concentrations of elements in the bulk. The uncertainties were 4% for Cu and 20% for Pb.

The RBS technique was performed on the gold layer with alpha particles of 6 MeV detected with a silicon surface barrier detector at 160° with respect to the incident beam. The current was 1.3 nA, and the accumulated charge, 1.4 μC. The software used for the fitting of the spectra was SIMNRA [6].

3. Results and discussion

Both XRF and PIXE performed on the patina, revealed high levels of lead, instead of tin as would have been expected for a traditional bronze artefact, as it was initially catalogued by the archaeologists. The patina composition obtained by both techniques and in two different fragments of the rail varies considerably due to the high deterioration of the surface because of the corrosion during burial. Fig. 2a shows the contents of the main elements of the alloy, Cu and Pb, obtained by PIXE and XRF (fragments A and B). Thus, the analysis of the patina with these techniques

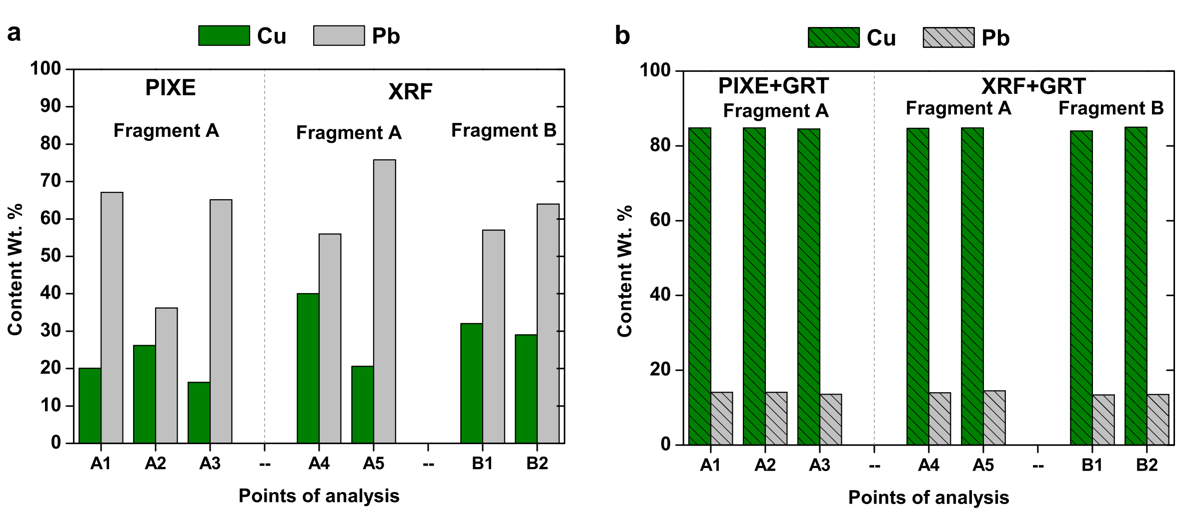

Fig. 2. Contents of the main elements of the alloy, Cu and Pb, obtained by PIXE and XRF of two different fragments of the rail, (a) of the corrosion patina and (b) after applying the GRT correction in order to obtain the core composition. Uncertainties are quoted in the text.