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First attempt to obtain the bulk composition of ancient silver–copper coins by using XRF and GRT

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ABSTRACT

Archeological silver–copper pieces often show surface enrichments in silver, either intentional or fortuitous. When this happens, non-destructive techniques like PIXE (Proton Induced X-ray Emission) and XRF (X-Ray Fluorescence) are not sufficient to access the whole bulk pieces because their penetration depths are typically of a few tens microns. If the archeological pieces cannot be cut or polished, it is necessary to apply other non-destructive techniques to access the bulk pieces. That way, archeological bronze pieces have been successfully studied combining XRF (or PIXE) with GRT (Gamma-Ray Transmission).

In this work, the bulk composition of five silver Roman coins have been indirectly measured by combining XRF and GRT. These results were compared with previous works made by our group using the same coins by direct means of PIXE and XRF, so the accuracy of this indirect method could be tested.

1. Introduction

The archeological silver–copper pieces sometimes can have a surface enrichment of silver [1–15]. This enrichment can reach some hundreds of microns in depth [16] so it is not possible to determinate the fineness of the pieces by superficial techniques like XRF or PIXE because their penetration depths are shorter [3,4,17–20]. In these cases it is necessary to combine those superficial techniques with other techniques that allow in-depth analysis. Thus, the combination of XRF (and PIXE) with GRT has been successfully used in archeological bronzes [22,23]. Therefore, the combination of XRF with GRT has been used in the present work to study the bulk composition of silver–copper Roman coins.

It is important to note that the bulk composition of the coins used in the present work was already studied by micro-XRF and micro-PIXE in a previous investigation [16]. With this knowledge, the results obtained in the present work can be compared with the previous ones, checking in that way the feasibility of the combination of XRF and GRT.

2. Materials and methods

2.1. Coins

A set of six Roman Republican coins from 211 BC to 86 BC (four denarii and two victoriati) [16] were analyzed in the present work (Table 1). The classification of the coins was done according to Crawford [24]. Their surface elemental compositions were determined by means of XRF; meanwhile the GRT technique was used to correct in depth (volume) the concentration of the surface compositions obtained by XRF.

All coins except the one named N1 were cut in halves. In a previous work [16], a cross-section of each coin was polished with a diamond solution up to 1 μm and then analyzed by micro-PIXE and micro-XRF (direct bulk measurements).

2.2. Experimental

The experimental conditions of XRF, micro-XRF and micro-PIXE can be found elsewhere [16], so only a short description of XRF will be given here. The surface of the coins were measured by XRF using a portable X-ray tube with a W anode and a 12.5 μm thickness Be window. Its output was filtered with a 1 mm thick aluminum foil and the analyses were performed at 30 kV and 590 μA. A silicon drift detector (Ketek) with a 8 μm thickness Be window and a Zr

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Table 1
Set of six Roman Republican coins analyzed [16].

Coin	Reference	Monetary valor	Date (BC)
N1	Cr. 218	Denarius	147
N2	Cr. 350	Denarius	86
N8	Cr. 113	Denarius	206–195
N9	Cr. 114	Denarius	206–195
N10	Cr. 53	Victoriatus	211
N11	Cr. 83	Victoriatus	211–210

internal collimator was used. The acquired XRF spectra were analyzed using the WinQxas software [25]. Certified standards with similar compositions to these coins have been used to calibrate the system.

The experimental GRT setup consisted of a ^{241}Am (principal photon energy 60 keV) point gamma source (6 mm diameter) properly shielded with Pb and collimated (4 mm diameter), and a shielded NaI(Tl) detector surrounded by copper plates to absorb Pb X-rays from the shielding. A Canberra 2020 amplifier and a Canberra S100 multichannel analyzer were connected to the detector and the spectra were acquired with Genie-2000 software [26]. The same points analyzed by XRF were measured by GRT. The mass attenuation coefficient (μ) needed for the GRT correction was calculated for each point (Eq. (1)) and its average values were then used to make the corrections in depth,

$$\mu = -\frac{1}{\rho x}\ln\left(\frac{I}{I_0}\right) \quad (1)$$

where I_0 is the intensity of the incident photon beam, I is the intensity of the transmitted photon beam, x is thickness of the point analyzed and ρ is the mass density of the sample. The mass density ρ was obtained by an experimental method based in the principle of Archimedes and using a He pycnometer [27].

The samples were considered to be a binary compound of silver (first element) and a mixture of all other elements present in the alloy (second element called "mixture element"). Under this hypothesis [21,22], the mass attenuation coefficient of the mixture element ($\mu_{mixture}$) was theoretically calculated using the concentrations C_i given by XRF in the surface (Eq. (2)).

$$\mu_{mixture} = \frac{\sum_{i\neq Ag}\mu_i C_i}{\sum_{i\neq Ag} C_i} \quad (2)$$

Then the average mass attenuation coefficient (μ) measured by GRT allows us to correct the concentration of the elements in the bulk. If a binary alloy of silver and the other elements (mixture) is considered, the final bulk concentration of silver is given by Eq. (3).

$$C_{Ag} = \frac{\mu_{mixture} - \mu}{\mu_{mixture} - \mu_{Ag}} \quad (3)$$

It is important to note that the density of the coins has to be determined accurately for a proper combination of XRF and GRT, which is no an easy work when the coins are very porous.

3. Results and discussion

The XRF results of the surface of the coins given by Ager et al [16] were corrected in depth by using GRT and both are shown in Table 2 ("surface" from [16] and "bulk" from this work). The average mass attenuation coefficient μ used for each coin is given in Table 3. When the surface results from [16] are compared with the bulk results obtained in this work it is clear that the combination of the techniques XRF + GRT always predicts surface enrichment in silver since the elemental composition of the bulk (XRF + GRT) is lower than the elemental composition of the surface (XRF). In addition, Ager et al [16] demonstrated that not all coins had surface enrichment in silver: the three denarii (N2, N8 and N9) were homogeneous pieces as shown in Figs. 1 (coin N2) and 2 (coin N8), meanwhile the two victoriati (N10 and N11) presented a surface enrichment in silver as shown in Figs. 3 (coin N10) and 4 (coin N11).

The micro-PIXE and micro-XRF Ag and Cu results of the bulk composition of the coins from [16] and the indirect results of the bulk composition made by combining XRF and GRT are shown in the Table 4. By comparing both results two main conclusions can be extracted:

Table 2
Mean concentrations and standard deviations obtained by XRF [16] of the surface of the coins (surface) and of the bulk composition of the coins indirectly obtained by combination of XRF and GRT (bulk).

Coin		Concentrations (wt. %)									
		Ag	Au	Cu	Fe	Zn	Pb	Bi	Hg	Mn	Br
N1	Surface	97.8 ± 0.9	0.25 ± 0.25	0.13 ± 0.05	0.7 ± 0.4	0.033 ± 0.010	0.05 ± 0.03	0.02 ± 0.02	–	0.02 ± 0.05	1.0 ± 0.5
	Bulk	83 ± 3	2.2 ± 0.6	1.2 ± 0.2	4.9 ± 0.9	0.27 ± 0.05	0.45 ± 0.10	0.16 ± 0.04	–	0.12 ± 0.04	7.5 ± 1.4
N2	Surface	97.9 ± 0.5	0.28 ± 0.02	1.1 ± 0.3	0.08 ± 0.03	0.017 ± 0.011	0.51 ± 0.14	0.08 ± 0.02	0.011 ± 0.007	–	–
	Bulk	90 ± 7	1.4 ± 1.0	5.4 ± 3.8	0.44 ± 0.34	0.10 ± 0.08	2.5 ± 1.8	0.37 ± 0.27	0.05 ± 0.05	–	–
N8	Surface	97.5 ± 1.6	0.6 ± 0.4	1.0 ± 0.6	0.048 ± 0.010	0.037 ± 0.019	0.5 ± 0.5	0.04 ± 0.04	0.003 ± 0.006	0.23 ± 0.30	0.04 ± 0.05
	Bulk	86 ± 5	4.7 ± 2.0	5.2 ± 1.9	0.36 ± 0.14	0.25 ± 0.10	2.11 ± 0.86	0.13 ± 0.06	0.009 ± 0.007	0.78 ± 0.40	0.14 ± 0.07
N9	Surface	98.3 ± 0.4	0.9 ± 0.3	0.56 ± 0.03	0.067 ± 0.014	0.024 ± 0.005	0.16 ± 0.02	0.03 ± 0.02	–	0.005 ± 0.006	0.02 ± 0.02
	Bulk	90 ± 5	5.0 ± 2.5	3.3 ± 1.6	0.39 ± 0.19	0.15 ± 0.07	0.91 ± 0.45	0.36 ± 0.08	–	0.03 ± 0.02	0.08 ± 0.06
N10	Surface	95.5 ± 1.5	0.28 ± 0.03	3.8 ± 1.5	0.046 ± 0.008	0.024 ± 0.005	0.34 ± 0.06	0.069 ± 0.012	0.005 ± 0.006	0.003 ± 0.005	–
	Bulk	60 ± 6	2.6 ± 0.5	32.8 ± 5.3	0.44 ± 0.08	0.23 ± 0.05	3.10 ± 0.58	0.64 ± 0.12	0.04 ± 0.01	0.03 ± 0.01	–
N11	Surface	94.2 ± 0.6	0.49 ± 0.04	4.8 ± 0.6	0.11 ± 0.07	0.031 ± 0.008	0.29 ± 0.06	0.026 ± 0.005	0.010 ± 0.007	0.009 ± 0.006	0.02 ± 0.02
	Bulk	64 ± 3	3.1 ± 0.3	30.3 ± 2.1	0.70 ± 0.06	0.19 ± 0.02	1.81 ± 0.20	0.16 ± 0.02	0.07 ± 0.01	0.059 ± 0.009	0.10 ± 0.01

Table 3
Average mass attenuation coefficients of the coins used in the present study.

	N1	N2	N8	N9	N10	N11
μ (cm^2/g)	5.22 ± 0.14	5.49 ± 0.35	5.42 ± 0.14	5.543 ± 0.088	4.32 ± 0.43	4.424 ± 0.071