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Case study

Unusual coin from the Parabita hoard: combined use of surface and micro-analytical techniques for its characterisation

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Abstract

Out of the staters collection of the National Archaeological Museum of Taranto, during the full examination of about one hundred coins minted by the Greek colony of Taras between the V century BC and the III century BC, our attention has been devoted to a lead coin, which has been regarded for many years as a genuine silver coin. This artifact, entry number 13 in the inventory list for the Parabita hoard, has been studied with the combined use of surface and micro-analytical techniques (SEM, EDX, PIXE, XRD). The joint use of different analytical techniques allowed us to obtain information about the morphology, the structure and the chemical composition of the analysed coin, that revealed a lead core coated with a bi-layer of copper and silver.

Keywords: Great-Greece; South-Italy; V-III century BC; Coin; Micro-analytical techniques

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1. Introduction

The analysis of archaeological objects requires simultaneously non-destructive (the objects are unique and precious), fast (large number of pieces to be analyzed), versatile (samples with different geometry), sensitive (trace elements are often important) and multi-elemental methods [1]. In this context, scanning electron microscopy (SEM) linked to X-ray diffraction (XRD) to obtain information about the morphology and the structure of coins. Proton Induced X-ray emission (PIXE) and energy dispersive X-ray (EDX) microanalysis linked to SEM investigation have been used to determine the chemical composition of the coin.

In this work, the authors, involved in the full examination of about one hundred silver coins coming from collection of the National Museum of Taranto, minted by the Greek colony of Taras between the the V century BC and the III century BC, was attracted by a lead coin which has been regarded for many years as a genuine silver coin. This coin has been classified as entry number 13 in the inventory list for the Parabita (Apulia, South Italy) hoard. Rather surprisingly, the elemental composition of this coin went undetected through several examinations, until the last few years. It was now that in the course of a comprehensive research, performed by the authors, on the silver content of coins minted by the Greek colony of Taras (actually Taranto–South Italy) allowed the identification of lead as the minting metal for this specimen covered by a thin copper/silver patina. The coin is identified by Fischer-Bossert [2] as an unicum because of its being minted with mismatched sides that combine obverse and reverse designs, both pertaining to the Western Greek coinage [3], but not usually paired in regular issues.

It is right to emphasize that all the analysis were performed, maintained in great consideration the elevated historical and artistic value of piece, and, in agreement with the staff in charge of the "Soprintendenza della Regione Puglia", the coin has been analysed any hard cleaning procedure and, for morphological and EDX characterization making use of "low vacuum mode" to avoid charge effect due to pieces more contaminated.

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Fig. 1. Images of the silver- coated "Parabita 13" coin. The coating is still present on the edges.

1.1. The numismatic problem

The Parabita hoard, discovered in the 1948, represent a very interesting numismatic case, among the constituting coins, there is a very rare specimen, the entry number 13 in the inventory list. This coin (showed in Fig. 1) was marked from W. Fischer-Bossert as very interesting for the peculiarity due to the unexpected coupling reverse D/- and obverse R/types never finds up to now in other coins [2]. The coin typology is the following:

- D/Rider crowing horse walking right, dolphin below;
- R/young man on dolphin right holding phrigian helmet, stars on either side, waves below.

The coin is identified as an unicum because of its being minted with mismatched sides that combine obverse and reverse designs. The typology of D/ is known for different series nominally defined *"campano-tarantine"*. Indeed, the reverse of the coin is linked (typologically, but not technically) to a series of Tarentine didrachms minted in the years 333-331/0 BC, the standard weight of which is 7.8 g. The obverse design of the coin belongs to a series of so-called Campano-Tarentine didrachms [4], minted in the middle of the 3rd century BC, not in Taranto, but presumably in Campania or Lucania. The standard weight of this latter series is about 0.8 g lighter than the Tarentine one of the reverse. The specimen Parabita 13 is 8.05 g and consequently, as weight considerations dictate, it was attributed [2] to the heavier (i.e. older) series.

The typology of D/ reminds the woman, head in the emissions of Neapolis. On the contrary, the typology of R/ with the youth onto a dolphin, it is typical of coins minted in Taras.

2. Experimental

A detailed morphological and chemical composition characterisation as well as the microchemical structure of the corrosion products grown on the silver coins was obtained by SEM methods. A scanning electron microscope Jeol JSM 5410-LV coupled to an Oxford Link ISIS 300 Series energy-dispersive spectrometer having a Si(Li) windowsless detector has been used to perform EDX microanalysis. The apparatus allows a resolution of 156 eV. Because the analysed coins are precious historical artefacts and they cannot endure some type of cleaning, SEM observation were performed without any kind of polishing and in the case of elevated contamination due to corrosion, the observation was performed in low-vacuum mode. SEM images have been obtained by backscattered electrons (BSE) with an accelerating voltage of 20 kV and a beam current of 80 μA.

To analyse the coin composition, about 20 area (of about 2000 μm^2) were randomly selected on the two side of coin, X-ray spectra were recorded both at 20 and 30 KV acceleration voltage, the X-ray intensities were converted in wt% atomic concentration by ZAF4/FLS quantitative analyses software support of Oxford-Link Analytical (UK).

The X-Ray spectra have been collected for 200s for every SEM image; this allowed to recognise both the main elements and the trace elements. SEM-EDX analysis is a fast method for element identification and quantization. It allows to obtain the concentration of the element by the relationship:

$$C = C_{\mathrm{st}} \left(\frac{I_{\mathrm{sp}}}{I_{\mathrm{st}}} \right) F_{\mathrm{sp}}$$

where I_{sp} and I_{st} are the intensities of the element in the sample and in the standard respectively, C_{st} is the concentration of the standard and F_{sp} is a factor obtained by the ZAF correction procedure in which ideal flat samples are assumed. In fact, due to electron-sample interactions, there occur processes which influence the production and collection of X-Rays. The ZAF procedure performs a correction for the atomic number effect (Z), the absorption effect (A) and the fluorescence effect (F). Z represents the difference in electron scattering and retardation between the sample and the standard. Loss of X-Rays due to absorption in the sample is represented by (A) and the artificial increase of X-Ray intensity of an element, due to ionization by X-Rays originated by another element, is corrected by (F). Without correction, errors in excess of 10% could result.

Afterwards, an X-Ray dotted map has been acquired for one hour for every chemical element recognized by the X-Ray spectrum. The X-Ray maps are images in which the contrast depends on the punctual presence of the element selected in the X-Ray spectra: the brighter areas correspond to a higher concentration of the element; darker ones correspond to a lower concentration. Several acquisitions were performed on the coin surfaces; in this way, the distribution of elements on the analysed region has been identified and corrosion phenomena were identified. One must mention that the compositions we obtained is relevant only for a thin layer at the surface (tens of micrometers in depth).

The problem of surface enrichments has been considered by collect X-ray spectra at 30 kV acceleration voltage. So, AgKα and AgLα signals referred to CuKα and CuLα signals at 30 kV acceleration voltage have been considered: whereas AgLα radiation (energy 3.0 keV) originates dominantly from a depth of up to 2 μm, the information depth of the AgKα radiation (energy 22.2 keV) is up to 20 μm in a silver–copper matrix owing to its higher energy [5]. Ag-Cu alloys (being Ag w% 98, 95, 90, 80 and 70) have been used in order to determine the calibration curves and information on silver concentration at different depth were obtained. However, the spatial distribution of elements, as we shall see later, excludes the possibility of a process of surface enrichment, as described by Beck et al. [1].

XRD patterns were recorded directly on the silver coin, by multiple scanning using a Rigaku miniflex diffractometer. The