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Energy dispersive X-ray fluorescence spectroscopy/Monte Carlo simulation approach for the non-destructive analysis of corrosion patina-bearing alloys in archaeological bronzes: The case of the bowl from the Fareleira 3 site (Vidigueira, South Portugal) ☆

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ABSTRACT

Energy dispersive X-ray fluorescence (EDXRF) is a well-known technique for non-destructive and in situ analysis of archaeological artifacts both in terms of the qualitative and quantitative elemental composition because of its rapidity and non-destructiveness. In this study EDXRF and realistic Monte Carlo simulation using the X-ray Monte Carlo (XRMC) code package have been combined to characterize a Cu-based bowl from the Iron Age burial from Fareleira 3 (Southern Portugal). The artifact displays a multilayered structure made up of three distinct layers: a) alloy substrate; b) green oxidized corrosion patina; and c) brownish carbonate soil-derived crust.

To assess the reliability of Monte Carlo simulation in reproducing the composition of the bulk metal of the objects without recurring to potentially damaging patina's and crust's removal, portable EDXRF analysis was performed on cleaned and patina/crust coated areas of the artifact. Patina has been characterized by micro X-ray Diffractometry (μXRD) and Back-Scattered Scanning Electron Microscopy + Energy Dispersive Spectroscopy (BSEM + EDS). Results indicate that the EDXRF/Monte Carlo protocol is well suited when a two-layered model is considered, whereas in areas where the patina + crust surface coating is too thick, X-rays from the alloy substrate are not able to exit the sample.

1. Introduction

The quantitative characterization of the chemical composition of metal alloys in archaeological bronze artifacts by physical–chemical techniques is of utmost importance towards the identification of ancient production technologies, historical trade routes, raw material sources (Cu, Sn, Pb) and more precise dating of the objects under investigation.

With the development of miniaturized X-ray detectors and tubes, allowing the production of hand-held portable spectrometers and in-situ fast and affordable measurements, X-ray fluorescence spectroscopy has become a routine technique in the non-destructive analysis of archaeological alloys and metal art objects [1–5].

Once spectra have been obtained quantitative XRF analyses of the detected elements are a rather complex operation since many parameters should be well known and kept under control. Moreover, a correct quantification requires an accurate estimative of background and/or a precise determination of the geometry of the experiment, taking into account also the roughness of the sample surface. Quantitative elaboration of the spectra is usually done with reference standards. However, algorithms able to describe the phenomena using measured parameters can also been used [6–8].

In this paper, we apply X-ray Monte Carlo (XRMC) codes [8] for the quantification of spectra acquired on a proto-historic bronze from southern Portugal. These are probabilistic simulation algorithms used in a number of research areas to solve high dimensional problems that cannot be accomplished in an analytical way.

In the case of X-ray interactions with matter, Monte Carlo simulations generate random (both in energy and direction) photons. Usually the majority of these photons do not reach the detector and so a large number of photons must be generated. In fact, a long time of simulation is required and a good statistic spectrum can last up to days before to be generated. However, there are some techniques called variance reduction techniques, which speed up the simulation forcing the detection of each generated photons [8].

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For this purpose, two fast Monte Carlo codes have been developed for this kind of application in order to simulate a good quality spectrum in a couple of minutes, the same order of time required by the measurements [8–12]. Both of them are based on a constantly updated X-ray database, called Xraylib [13,14].

One of the main limits in obtaining reliable analyses of archaeological bronze alloy composition is the roughness of the surface [8,15,16] together with the almost ubiquitous development of oxidized corrosion patinas with variable thickness usually composed by Cu-based oxides [17]. Moreover, on top of these patinas, a layer of encrusted mineral material from the soil where the object had been buried is often present. The application of Monte Carlo simulations can represent a useful analytical tool to overcome all of these constraints.

In fact, if the patina and the soil-derived crust are not previously removed, chemical analysis of the object usually reflects the composition of these components and not that of the original alloy. Cleaning and removal of both patina and soil layer before is therefore a necessary, albeit unwanted, practice in order to obtain the composition of the bulk of the metal.

The key idea of this paper is to construct a model of the experiment as well as one of the sample multilayered structure and then run iteratively the Monte Carlo until the simulated spectrum is an almost perfect reproduction of the measured spectrum. When this is obtained the sample is perfectly determined both in chemical composition and structure.

The advantage of this method is not only that the background is not removed (and so one of the main sources of error is removed) but also that structural information of the bronze object surface (i.e. thickness of corrosion/encrusted layers) may also be modeled considering the artifact as having a multilayered structure [18].

To test the feasibility of the application of a combined Monte Carlo simulation/X-ray Spectrometry approach in archaeometry research, in this study we have combined portable EDXRF with Realistic Monte Carlo simulations using the fast X-ray interaction XRMC software package to investigate a unique archaeological bronze object displaying a well formed corrosion patina and soil derived surface crust.

2. Materials and methods

2.1. The bowl

The bowl analyzed in this paper was part of a grave goods discovered in an Iron Age burial (Fig. 1) recently excavated in the site of Fareleira 3 (Beja, Southern Portugal). In the sepulture, an adult male skeleton was inhumed in fetal position and lateral decubitus, with the head facing west and the feet in the opposing direction. The grave goods consist of both metal artifacts and pottery: with regard to the first, beyond the bowl, two iron spearheads, a bi-metallic (iron and bronze) knife, a fibulae and other undefined artifacts were recovered. Pottery was constituted by three wheel-made cups placed at the feet of the dead.

The bowl is the most interesting object of the grave goods, both for the rarity with which this typology appears in the south of Portugal and for its state of conservation, being the only complete specimen from this region.

From a morphological point of view, it is a large (Ø cm 32) undecorated and hemispherical beaten Cu-based object, with opposed handles fixed with three rivets at the body of the recipient. One of the handles is lost. The bowl from Fareleira shows very interesting parallels with similar objects from eastern Mediterranean [19]. Based on typological features alone, it may be attributed to the Orientalizing Period, namely to the VII century BC [20].

2.2. EDXRF and Monte Carlo simulation

The XRF experiments performed here are based on the portable XRF system, composed by an Amptek MiniX X-ray tube equipped with Ag anode, 50 kV max, 200 μA max. The X-ray detector was an X-123 SDD by Amptek, coupled to a DSP Multichannel Analyzer, with a resolution of 140 eV at Mn Kα FWHM 5.9 keV. Acquisition time was 120 s. The detector was placed orthogonally to the sample surface while the X-ray tube was at 30°. Certificated bronze sample was used for the calibration. All measurements were carried out under ambient air.

Monte Carlo simulation codes used in the present study are fully described in Ref. [8].

Margin of error to be considered for the chemical composition are: <2.00 wt.% for the major elements (>5.030 wt.%); <5.00 wt.% for the elements between 1.00 and 5.00 wt.%; <10.00 wt.% between 0.50 and 1.0 wt.%; and <50% between 0.10 and 0.50 wt.%.

2.3. μXRD and BSEM–EDS

In order to characterize the patina, μXRD and BSEM–EDS have been utilized as auxiliary analytical methods. For μXRD, a commercial BRUKER D8 Discover System with the DAVINCI design with a Cu Kα source operating at 40 kV and 40 mA and a LINXEYE™ 1-dimensional detector was used. The sample scraped from the oxidized corrosion patina of the bowl was deposited onto a flat zero-background sample holder and irradiated through a 0.6 mm slit. The micro beam was achieved using a Göbel mirror and a 1mm collimator.

The angular range (2θ) was scanned from 3° to 70° at a step size of 0.02° with a counting time of 1 s/step. Evaluation of X-ray diffractograms was made by using the routines of the Diffrac. EVA

Fig. 1. Archaeological burial site with bronze bowl in its original position.