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Technical note

An Energy-Dispersive X-Ray Fluorescence Spectrometry and Monte Carlo simulation study of Iron-Age Nuragic small bronzes ("*Navicelle*") from Sardinia, Italy☆

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ABSTRACT

A spectrometric protocol combining Energy Dispersive X-Ray Fluorescence Spectrometry with Monte Carlo simulations of experimental spectra using the XRMC code package has been applied for the first time to characterize the elemental composition of a series of famous Iron Age small scale archaeological bronze replicas of ships (known as the "*Navicelle*") from the Nuragic civilization in Sardinia, Italy. The proposed protocol is a useful, nondestructive and fast analytical tool for Cultural Heritage sample. In Monte Carlo simulations, each sample was modeled as a multilayered object composed by two or three layers depending on the sample: when all present, the three layers are the original bronze substrate, the surface corrosion patina and an outermost protective layer (Paraloid) applied during past restorations. Monte Carlo simulations were able to account for the presence of the patina/corrosion layer as well as the presence of the Paraloid protective layer. It also accounted for the roughness effect commonly found at the surface of corroded metal archaeological artifacts. In this respect, the Monte Carlo simulation approach adopted here was, to the best of our knowledge, unique and enabled to determine the bronze alloy composition together with the thickness of the surface layers without the need for previously removing the surface patinas, a process potentially threatening preservation of precious archaeological/artistic artifacts for future generations.

1. Introduction

Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF) is a non-destructive analytical technique with wide applications in several research areas including the Cultural Heritage/Conservation Science one [1–17]. Performing quantitative EDXRF analyses on archaeological and Cultural Heritage metallic artifacts is, however, particularly challenging due to their complex multi-layered internal structure. "Layers" may include: a) the original metal and/or alloy substrate (gold, silver, bronze etc.); b) surface patinas enriched in corrosion products (sulphides, oxides and/or chlorides compounds) due to attack by agents present both in the atmospheric and/or burial environments; c) protective treatments applied in past conservation interventions; d) soil derived incrustations from the archaeological burial environment [10–14]. In cases where the layered structure is not homogeneous, the separation between two or more adjacent layers is not well defined and/or when the layers are very thin, meaningful results on the bulk metal composition are even more difficult to obtain. In order to estimate layers thickness and composition in such multi-layered metal objects, a method based on estimating changes in the theoretical ratios of selected fluorescence line intensities due to the attenuation of the layers crossed by the radiation has been recently proposed [4,7,18,19]. However, this method strongly depends on the specific XRF setup used. In the aforementioned studies, for instance, a monochromatic X-Ray beam obtained by placing a filter at the output of the X-Ray tube has often been used: this setup, though, affects the quality of the results. Moreover, in some of these studies, the metal objects were subjected to a pre-analysis cleaning treatment to remove any surface corrosion patina and/or of protective layer present, a practice not always feasible when dealing with precious and unique artistic and/or archaeological objects. The methodological approach proposed in the current study involving Monte Carlo simulation tests does not require any constraint on the setup or on the XRF excitation spectrum nor it requires pre-treatment by potentially damaging cleaning procedures [4,7].

In this study, the EDXRF/Monte Carlo Simulation protocol has been tested on a series of Iron Age (900–600 BCE) small-scale bronze replicas of ships, called "*Navicelle*" from the Nuragic civilization in Sardinia, Italy.

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Other examples of the application of Monte Carlo simulation to XRF analyses can be found in the literature [20–25], but the Monte Carlo used here shows some innovative features allowing the production of a high quality spectrum in just a few minutes (see Materials and methods section).

From an archaeological point of view, these bronzes has been usually associated with sacred sites this testifying their close, religious links with the sea which was a typical trait of the Nuragic culture in the island [26]. The "*Navicelle*" were probably used as lucernas (small lamps) in ex-votos offerings. Only a total of 150 Nuragic authentic "*Navicelle*" artifacts have been so far discovered in Sardinia but, due to their high artistic as well as archaeological significance, the commerce of these unique artifacts in local antiques fairs has been thriving for quite a long time thus stimulating the growth of a well-developed forgery industry. Despite their significance, no systematic material study has been ever carried out to shed light on their raw material provenance, production technology and objects authenticity. Aim of this work was therefore two-folded: a) to test the applicability of combining EDXRF data with Monte Carlo simulations in determining the bronzes bulk composition without the need for removing the alloy's bronze corrosion and/or protective patina; b) to provide compositional data on the unique Nuragic artifacts by nondestructive EDXRF spectrometry.

2. Materials and methods

Three "Navicelle" were selected for investigation: 2 boats (boat n. 1347 from an unknown locality in Sardinia and the so-called and famous "Re Sole" boat from the Badde Rupida Nuragic monument in Padria (Sassari), Fig. 1a and b) which are stored at the G.A. Sanna Museum in Sassari and 1 boat (boat n. 36/41 from Bultei, Northern Sardinia) which is stored at the National Archaeological Museum of Cagliari, Italy.

EDXRF analyses were performed using a portable X-Ray instrumentation formed by a SDD detector coupled with a DSP Multichannel analyzer (1-2-3 system manufactured by Amptek) and an Ag-anode X-Ray tube (mini-X manufactured by Amptek). Both detector and X-Ray tube are freely positionable, allowing to select the best geometrical setup for the analysis. However, the more common setup is formed by the detector placed vertically, 2–3 cm far, from the sample surface with the X-Ray tube forming an angle with the detector of about 30°, still 2–3 cm far from the sample surface. This position is preferable to the more standard 45°- 45° configuration, because it allows to minimize the effects due to surface roughness. No collimation was used on the detector, while the X-Ray tube used a 1 mm wide collimator. The spot size was about 2 mm. Each measurement lasted about 4 min. A Monte Carlo model of the sample analyzed was then built assuming the two and/or three multilayered structure previously mentioned, although other type of structures were also tested. Our approach was based on the use of a Monte Carlo simulation (MC) following a probabilistic simulation of the X-Ray interaction with matter. Usually several millions of photon interactions need to be simulated before a good simulation of real experiments can be produced. The general aim of MC codes in the context here examined is to simulate a wide variety of X-Ray experimental set-ups: this lack of specialization, however, has the drawback that, in order to achieve an adequate simulation of a XRF analysis, a considerable amount of simulation time, (in the order of several hours or days) is usually required. To overcome this problem, several specialized MC codes have been developed. These codes are able to perform simulations only for a reduced set of X-Ray experiments, i.e. at energies <100 keV. This limitation, however, does not introduce a true restraint on the XRF experiments that can be performed, which are typically run at energies around 40–50 keV in most applications, particularly in the Cultural Heritage/Conservation Science sector. Using the aforementioned specialized codes, the speed of the simulation run can be dramatically increased: in fact, a XRF analysis can be adequately simulated in just a couple of minutes. This time is comparable to the experimental acquisition time and therefore the simulation can be regarded as being performed in real time. Two of such fast and specialized MC codes are readily available [27–32]. The first one was developed specifically for XRF experiments, while the second one can be also used to simulate radiographic, CT and phase contrast simulations. Both codes are based on the *Xraylib* database [33,34]. In the current study, we used the second one, called *XRMC* [31]. Before running the simulation, MC codes require a detailed description of both sample's composition and structure. From the point of view of the authors, one of the most critical parameter in this respect is the X-Ray spectrum emitted by the source. Here we have used the real spectrum emitted from the source, corrected for attenuation effects due to ambient air as well as to the presence of the detector windows. Its correctness has been tested on several reference samples. The quality of the simulation is assessed by comparing,

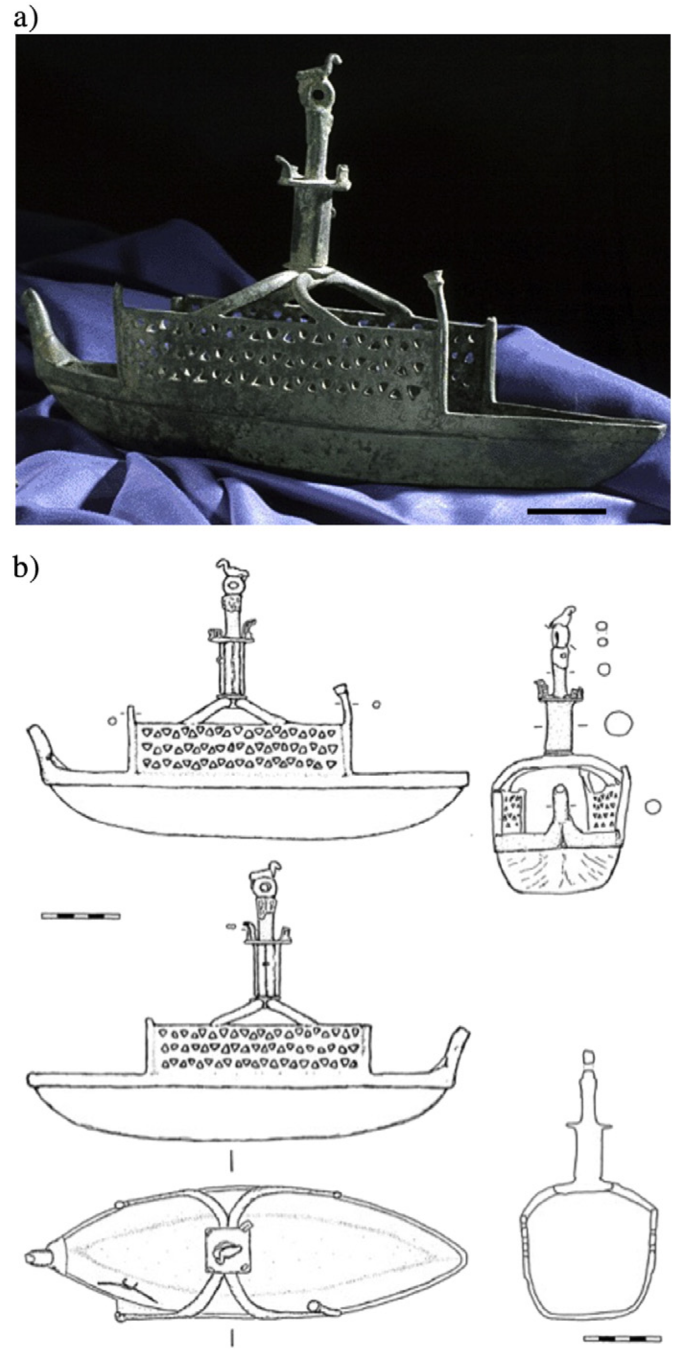

Fig. 1. Iron-Age bronzes from Sardinia, Italy: a) "*Navicella*" Re Sole, Padria, Sassari, scale bar = 4 cm; b) "*Navicella*" Re Sole, Padria, Sassari, archaeological drawing, scale bars = 6 cm.