

Article

Monte Carlo Simulations of ED-XRF Spectra as an Authentication Tool for Nuragic Bronzes

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Abstract: The high artistic and cultural relevance of particular objects, in this case from the Nuragic civilization, have stimulated the growth of a forgery industry, replicating small bronze boats (*navicelle*), statues (*bronzetti*), and other objects. It is often the case where the forgeries are of such quality that it becomes difficult to distinguish them from authentic artifacts without a proper chemical analysis. In this research, a Monte Carlo simulation algorithm for X-ray interactions with matter is used to obtain the chemical composition from the bulk of each object from a set of five. The method employed has the advantage of being completely nondestructive and relatively fast. The objects' chemical composition and morphology were compared with the data available from authentic artifacts so their authenticity could be inferred. Four of the five objects are likely to be authentic, where two of them could be associated with a Sardinian origin.

Keywords: X-ray fluorescence; Monte Carlo simulations; nuragic; bronzes; authentication



Citation: Nocco, C.; Brunetti, A.; Barcellos Lins, S.A. Monte Carlo Simulations of ED-XRF Spectra as an Authentication Tool for Nuragic Bronzes. *Heritage* **2021**, *4*, 1912–1919. <https://doi.org/10.3390/heritage4030108>

Academic Editor: Chiara Soffritti

Received: 21 July 2021

Accepted: 17 August 2021

Published: 19 August 2021

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1. Introduction

The Nuragic civilization was a mostly pastoral and agricultural society, which is considered native from the island of Sardinia, located in the Mediterranean basin [1,2]. The Nuragic civilization, contemporary to the construction period of the so-called *Nuraghi*, spans from between about 1700 and 1200 BCE. In this period, their metallic production was modest and uniform in a topological perspective. It was only later, during the Late Bronze Age (LBA) 1200–950 BCE and Early Iron Age (EIA) 950–600 BCE in Sardinia, that metallurgical production significantly increases [3,4].

Nevertheless, Nuragic people excelled in metalsmithing, leaving a vast amount of objects behind [5,6]. Many of these objects (e.g., *Navicelle* and *Bronzetti*) have a high artistic and archaeological significance, fueling the commerce of such pieces and, consequently, stimulating the growth of a well-developed forgery industry [7].

Distinguishing fakes from originals is not a trivial task. The chemical composition of artifacts has long been used as a parameter to either authenticate or trace their origin [7,8]. This can be achieved through a variety of analytical techniques, and Energy-Dispersive X-ray Fluorescence (ED-XRF), being easy to use, portable, and nondestructive, has become a staple in the field [9,10]. However, when dealing with metallic artifacts, it is often the case where these objects are found heavily corroded, sometimes with its original shape unrecognizable [11].

The corrosion layer(s) formed through centuries or millenia present a different composition from the bulk material, understood as the artifact's real composition. Therefore, for authenticity studies, ED-XRF analysis requires the removal of the protective patina, given the multi-layered structure presented by such objects (bulk → corrosion layers → protective

coating/paraloid), avoiding any bias introduced by the superimposing layers [10]. Nevertheless, even the smallest damage can be considered unacceptable when dealing with archaeological materials, and a complete nondestructive approach is needed.

Previous attempts to estimate different artifacts' layers thickness and composition in a nondestructive approach have been performed by measuring changes in the theoretical ratios of specific fluorescence lines [12–14]. This method works well for samples where the layering structure is rather simple and where the bulk matrix can be estimated to a certain extent. For overly complex structures, with several layers, simulating the X-ray response with a Monte Carlo algorithm can provide better results [7].

In this scope, the present research made use of a Monte Carlo protocol, simulating experimentally acquired ED-XRF spectra. The information obtained was combined with data from authentic Nuragic metallurgy manufactures to test the authenticity of a group of apprehended objects, with no archaeological background, in a completely noninvasive approach.

2. Materials and Methods

The investigated set of objects consists of five bronze artifacts. All of them are believed to be of Nuragic origin and are out of archaeological context. They are part of a larger set of over 430 pieces, from a preventive seizure by part of the local police—*Nucleo Tutela Patrimonio Culturale* of the Carabinieri. They are under tutelage of the local governmental authorities—at the *Soprintendenza Archeologia, belle arti e paesaggio per le province di Sassari e Nuoro*—who kindly provided the objects for investigation. Among the objects, there is one *bronzetto* and one *navicella* (Figure 1).



Figure 1. Set of studied samples. 1–3—daggers, 4—*Bronzetto*, and 5—*Navicella*. Scale = 10 cm.

The experimental ED-XRF spectra were obtained with an XG-Lab ELIO™ instrument. The spectrometer was equipped with a 25 mm² active area and 12 μm Be window silicon drift detector (SDD) detector. The X-ray tube had an Rh anode and was capable of operating from 10 to 50 KV and from 5 to 200 μA. The spectra were acquired with an accumulation time of 60 s and with the voltage and current set to 40 KV and 60 μA, respectively. The distance between the spectrometer head and sample was kept constant to 1 cm.

XRF spectra simulations of all experimental spectra were performed with a modified version of the XRM C package [15] available at [16], version 6.4.1. This package is based on the *xraylib* database [17] and is capable of simulating complex geometrie, as well as up to any order of photoelectric interaction. A threshold was set at the third order, as errors in the atomic parameters accumulate with a growing interaction order and may result in a loss of significance. This methodology has already been extensively used with archaeological manufactures [7,18–20].

The XRF spectrometer used does not allow for changing the tube-detector geometry; therefore, the X-ray tube profile used for the simulations was deconvolved from a blank spectrum, taken from a 2 cm thick piece of plexiglass under the same previous working conditions. The detector response was modelled as well to accurately reproduce the experimental setup response. The objects were simulated as a bi-layered or triple-layered structure accordingly. The digital model, representing the analytical volume of the sample is a stack of finite parallel layers, each with an associated composition and thickness.

Each experimental XRF spectrum is simulated independently. An initial guess model is created based on careful visual inspection of the sample and any other analytical data available prior to the simulations (e.g., Raman spectroscopy data). The model is updated iteratively after each simulation (changing the number of layers, their composition, thickness, and ordering) until a match is obtained with the experimental spectrum, with a sufficiently low chi-squared error.

The final model that outputs a near-perfect reproduction of the experimental spectrum can be considered to represent the real structure of the sample. A similar approach that also uses iterative simulations for quantification analysis can be found in the literature [21]. Figure 2 shows a block diagram of the simulation phase.

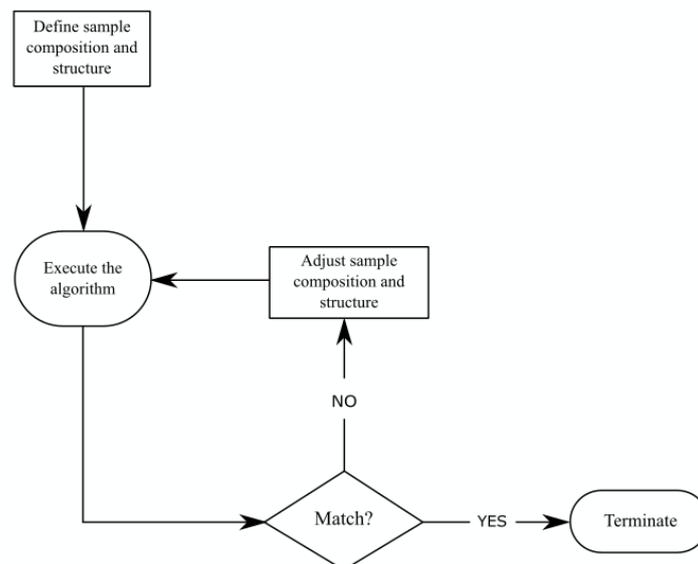


Figure 2. Block diagram of the simulation procedure.

Each simulation took approximately 6 minutes, varying according to the sample complexity. The simulations were run on a Dell XPS 14 L421X laptop (3rd generation Intel Core i7-3537U processor and 8 GB DDR SDRAM). The final models—obtained at the end of the iteration process (Figure 2)—were re-run a few more times to ensure their repeatability, yielding a standard deviation of less than 1%, calculated on the chi-squared difference between each simulation and the previous run. The inheritant errors of the algorithm itself are better described elsewhere [17].

3. Results and Discussion

3.1. Daggers

The simulated spectra for daggers 1 and 2 are shown in Figure 3. A total of four spectra from different spots were taken from dagger 1, and three were taken from dagger 2. The daggers match morphologically to known authentic ones, having parallels with daggers from *Pirosu-Su Benatzu*, *Su Monte*, and *Complesso Nuragico di Albini* [5,6].

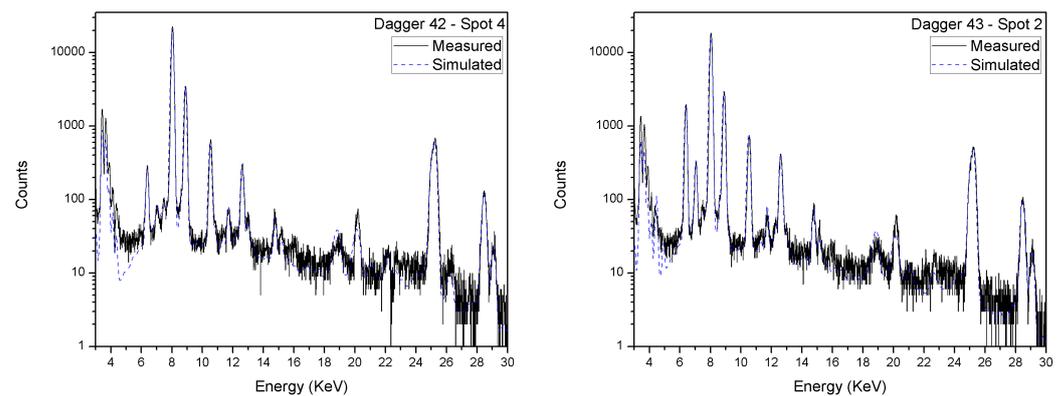


Figure 3. Simulated and experimental spectra for daggers 1 and 2.

Figure 4 shows a scatter plot between Pb and Sn for all samples. Both daggers were simulated as bi-layered structures and were revealed to be made of a leaded bronze alloy with a high tin content. They also presented small varying quantities of As and Fe (As 1.505–2.7%–Fe 0.25–2.5%), commonly occurring in Sardinian copper ores [22]. The patina thickness could be estimated and ranged from 24 to 38 μm . Small quantities of Ag, Ni, Bi, and Sb could be detected in the dagger 1 bulk composition.

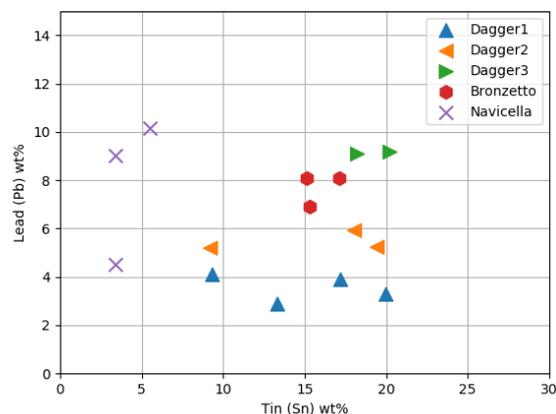


Figure 4. Tin and lead scatter plot for all samples.

Ancient Sardinian copper deposits provided several tons of malachite, azurite, pyrite, chalcopryrite, covellite, chalcocite, enargite, and tennanite copper ores [2,5]. Therefore, locally smelted copper ingots could likely present high quantities (several ppm's) of Bi and Sb as well as considerable amounts of Pb (≈ 2 wt%) and several hundreds of ppm of Fe (chalcopryrite— CuFeS_2 —has 36.87 wt% of Fe). As a matter of fact, Fe content in a total of 14 copper ingots fragments—some clearly identified as oxhide ingots—has been reported as 0.175 ± 0.267 wt% [5] and 0.02 wt% in a few other oxhide ingots [2]. In any case, the weight percentage of Fe present in the final bronze object is a result of mixing tin and copper ingots—or using a copper–tin ingot—so the Fe origin may not be directly linked to the ore itself.

The presence of Fe in ancient bronzes is rather common in such low percentages and can also come from the flux added during the smelting process [23,24]. Its quantity can be used as a sign of technological level and skill of the metalworker, where low amounts (around 0.3 wt%) are signs of a more efficient smelting process [24] and consistent with Early Iron Age bronzes from within the Mediterranean [25]. This element has been reportedly found in few *Navicelle* and other Nuragic artifacts [7,19,25,26].

The tin content detected is considerably high, being unusual for objects related to Nuragic workshops, and is hardly reported in the literature passed a threshold of around

15 wt%. Nevertheless, Robbiola et al. [11] reported the chemical composition of a Cu–Sn alloy axe (among other objects) from the Western France Bronze Age as containing 22 wt% Sn, and an ingot containing 18.2 wt% Sn, demonstrating that a considerably high quantity of Sn is not necessarily an indicator of forgery.

Lastly, Ag (as impurity) and As, detected in dagger 1, are also reportedly found in several other authentic objects, such as the four daggers and one spatula from *Monte Baranta*; the *Maracalagonis* sword [5]; a bronze bun-ingot [6]; and some *bronzetti* preserved at Musei di Providence, Detroit [27].

No impurities were detected in dagger 2 with the proposed methodology. However, the average composition obtained, very similar to dagger 1, can still be used in favor of its authenticity, having As and Fe to relate its origin to the same origin as several other authentic Nuragic objects.

It must be taken into consideration that such assumptions take previously acquired data as an anchor, which may be biased, as no details on how the chemical composition of most of these objects was obtained. Furthermore, it must be taken into account that objects were often re-used and melted together through time, so different origin ores may end up in a same object.

Dagger 3 not only has fewer parallels in the literature considering its morphology (only a couple were found [6,28]) but also presented a slightly different composition from the previous two daggers. It is made of a Cu 69.30%–Sn 20.20%–Pb 9.20% bronze alloy, with Fe and As impurities (0.20 wt% and 1.20 wt%, respectively). Lead in such quantities is common in Nuragic bronzes from the Iron Age (900–600 BC) [7] but is hardly found together with the corresponding tin quantity. Its composition may suggest an original manufacture, either Nuragic or imported, if the product was re-melted and re-used. The corrosion patina thickness observed is compatible with Robbiola's Type I, characteristic of quaternary bronzes.

3.2. Bronzetto

The *bronzetti* are the most typical Nuragic manufactures, widely known and widespread. They represent a series of activities intrinsic to the nuragic culture and are commonly found in votive, ritualistic, and/or religious contexts [29]. The *Bronzetto* (Figure 1) herein investigated is a classical representation of an archer and appears heavily corroded. Parallels can be drawn with some archer *bronzetti* depicted in Lilliu's catalogue and Moravetti et al.'s work [6,27]. For the application of the MC protocol, three spots were analyzed: two taken in the vicinity of each other and one in a region presenting clear visual signs of oxidation.

The average composition obtained demonstrates that *bronzetto* no. 4 is made of a leaded bronze alloy with high tin content (Cu 72.9%–Sn 15.8%–Pb 7.7%); see Figure 4. As and Fe are present in small quantities, similar to those observed in the daggers (As 1.9–2.85%–Fe 0.4–1.35%), which can be characteristic of Sardinian mineralization [5]. Lead, even that commonly present in authentic *bronzetti*, is reported in much lower quantities.

The chemical analysis of a set of 12 *bronzetti* from the National Archaeological Museum in Cagliari (Sardinia, Italy) reports Pb contents between 0.06 and 0.99 wt%, and only one *bronzetto* having 6.50 wt% Pb in its composition [5]. Concerning Sn, the reported amount varies from 5.9 to 13.1 wt%. No amount of As is reported in this set of 12 *bronzetti*. It is important to mention that, within this set of objects, most are from the same location, with only one third having an unknown origin.

Furthermore, another set of 31 fake *bronzetti* were also chemically characterized by Atzeni et al. [5]. Their chemical composition varies significantly, as expected, presenting Zn concentrations ranging from 0.1 to 10.8 wt%, with an average value of 3.90 wt% and a standard deviation of 2.68. The Sn content averages 5.56 wt%, with a maximum of 13.20 wt%, and the Pb content averages 4.10 wt%, with a maximum of 10.30 wt%. The Fe content reported in the fakes is consistent and averages 0.45 wt%. No amount of As is reported in any of the 31 fakes.

3.3. Navicella

The *navicelle*, small bronze boats, from an archaeological perspective, are usually associated with votive or religious practices (as the *bronzetti*), testifying to the religious link of Nuragic people with the sea and its traits. They were used probably as small lamps (lucernae) in ex voto offerings [7,30].

The *navicella* (Figure 1) had three spots investigated with the proposed methodology. The spots are shown in Figure 5: two spectra were acquired from its left side (one in a darker spot, probably an encrustation or oxidation—spot 2) and one from the bottom lower part of the boat—spot 3.

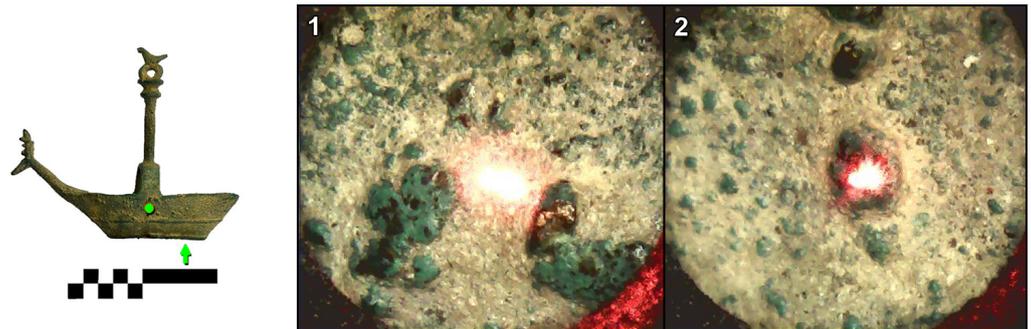


Figure 5. Micrographs of spots 1 and 2 investigated in the navicella.

The alloy used to make this *navicella* is somewhat unusual in an archaeological perspective. It contains Cu, Sn, Pb, Fe, and Zn in significant quantities. Averaging the concentrations obtained with spots 1 and 3, the alloy is a Cu 77.25%–Sn 3.4%–Pb 6.75%–Fe 6.4%–Zn 5.5%. What stands out is the unusual presence of Zn, commonly associated with forgeries.

The difference in Pb and Fe contents between spots 1 and 3, namely 9.0 wt% and 9.6 wt% for the former and 4.5 wt% and 3.2 wt% for the latter, respectively, suggests that the object was cast upside-down. Heavier elements tend to migrate by gravity during the casting process resulting in a Cu–Pb segregation. This is due not only to a gravity gradient but also to the inherent low-miscibility between the two metals [31].

Spot 2 presented significantly less Fe content than spot 1, a small quantity of As (0.10 wt%) and 2 wt% more Sn than spots 1 and 3. It also presented considerably more Zn than the other analyzed spots and a higher content of copper in the corrosion layer. Zinc is reported in some Cypriot bronzes from 11th to 8th centuries BC, but in percentages never exceeding 1 wt%, suggesting that the use of Zn was not intentional [32]. Lastly, although Zn sulphides can be associated with *Montevecchio's* galena (Sardinia) [33], it is very unlikely that such high percentages (≈ 5.5 wt%) in a final product would derive from the ore at that time.

Concerning the authenticity of the object, although it matches the typology of some other nuragic *navicelle* described in Lilliu's catalogue [27], it is clear from the chemical composition that this *navicella* is a later reproduction. Zn was very unlikely to be used as an intentional alloying element during the Nuragic Bronze Age or Iron Age, and high contents of this element are usually a sign of falsification [5]. Moreover, the excessive amounts of Zn are also compatible with that of several fake bronze figurines listed in Atzeni et al.'s work (Chapter 1, section L [5]).

4. Conclusions

The proposed methodology was tested as an authentication tool to nondestructively investigate archaeological bronzes, obtaining their bulk composition without cutting, scratching, or damaging the objects. Furthermore, with the chemical composition of the artifacts and with enough geological data, it is possible to suggest the origin of the object if they are an authentic Nuragic manufacture rather than imported.

By tracing parallels with known authentic object's morphology and composition, available from catalogues, it was possible to reach a conclusion regarding the authenticity of most of the objects investigated. Daggers 1 and 2 are very likely original manufactures of Nuragic origin; while dagger 3 may be an original manufacture, it is hard to ascertain if it has a Sardinian origin. The *bronzetto* analyzed fits with the daggers, and even if the origin of the object cannot be asserted, it is very likely that this *bronzetto* is an authentic one. Lastly, regarding the *navicella*, the excessive presence of Zn attests against its authenticity.

The Monte Carlo protocol described in this work and previously applied to other archaeological objects has proven to be effective. It provided useful information regarding the bulk material of heavily corroded objects without the need for sampling. Lastly, it was demonstrated to be a powerful tool when used together with traditional XRF spectrometry, further increasing this technique's applications by overcoming one of its limitations.

Author Contributions: Conceptualization, A.B. and S.A.B.L.; data curation, C.N.; formal analysis, C.N. and S.A.B.L.; investigation, C.N.; methodology, A.B. and S.A.B.L.; project administration, A.B.; resources, A.B.; software, A.B.; supervision, A.B.; validation, C.N. and S.A.B.L.; visualization, S.A.B.L.; writing—original draft, S.A.B.L.; writing—review and editing, C.N. and A.B. All authors have read and agreed to the published version of the manuscript.

Funding: This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska–Curie grant agreement No. 766311 and from FAR 2019, FAR 2020, and the FSC 2014–2020 project by Regione Autonoma della Sardegna, "Sviluppo di una metodologia spettroscopica integrata e innovativa per la caratterizzazione di bronzi antichi" (RASSR79938, CUP J81G17000140002).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data generated in this study is available upon request.

Acknowledgments: The authors thank the Soprintendenza Archeologia, belle arti e paesaggio per le province di Sassari e Nuoro for providing the samples; Anna Depalmas for providing an archaeological background support; Alba Canu, from Li Punti restoration laboratory, for providing the instrumentation and space for the XRF analysis; and Gianluigi Marras for kindly taking care and tutelage of the samples.

Conflicts of Interest: The authors declare no conflict of interest.

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