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Elemental characterisation of a collection of metallic oil lamps from South-Western al-Andalus using EDXRF and Monte Carlo simulation^{*}

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Abstract. This study is part of a wide-scale research on metal production in South-Western al-Andalus during the Islamic period, under the project “DE RE METALLICA - DEfining and REdiscovering MEtallurgy and Trade in AL-Andalus (8th–13th centuries AD): Leaping into Innovative Comprehensive Archaeometric Approaches”. In particular, this paper presents the results of the elemental analysis carried out on a group of six Islamic oil lamps found at different sites in Southern Portugal, spanning from the 10th to the 13th centuries AD. Due to the exceptional historical value of these artefacts, the analyses were carried out according to a completely non-destructive approach that combines Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF) with a Monte Carlo (MC) simulation code named X-ray Monte Carlo (XRMC). This novel and ground-breaking approach has proven to be especially suitable for non-destructive analysis of artefacts with a multi-layered structure, such as archaeological metals, being able to estimate the composition of the original alloys and to characterise the structure and composition of each layer superimposed to the bulk with no need of removing samples or cleaning the artefacts’ surface from corrosion compounds. The application of the EDXRF/MC analytical protocol revealed that the six oil lamps selected for this paper are covered by a structure composed of three different layers (protective layer + corrosion patina + alloy). The bulk metal is a copper-based alloy with a great variability in terms of Fe, Zn, Sn, As, and Pb, likely suggesting either the use of scrap metals as raw material or the indiscriminate addition of different kind of minerals. With regard to the objectives of this paper, EDXRF/MC protocol successfully allowed to estimate the chemical composition of the six oil lamps in a completely non-destructive way, thus representing a viable compromise between the necessity to ensure their physical integrity and the need to obtain reliable analytical data able to address historical issues.

1 Introduction

Portable Energy Dispersive X-ray Fluorescence (EDXRF) is a simple and non-destructive technique widely used for estimating the elemental composition of ancient metal alloys. If compared with other analytical techniques that also provide compositional data (*i.e.* Particle-Induced X-ray Emission, Instrumental Neutron Activation Analysis, Inductively Coupled Plasma Mass Spectrometry, Atomic Absorption Spectroscopy, etc.), EDXRF brings together a number of advantages, since: a) theoretically, it does not require any sample preparation; b) analysis can be made directly on the object, thus with no constraints relative to dimensions and weight of the artefact to analyse; c) the

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equipment can be easily transported, providing *in situ* analysis; d) it is a fast technique, thus allowing to analyse a great amount of artefacts in a relatively short time; and e) once the equipment is purchased, it is a relatively inexpensive technique, not requiring the use of consumable resources. All these factors are particularly relevant in Cultural Heritage and their combination has been a crucial element for the extensive adoption of handheld and portable EDXRF devices in the analysis of artefacts with historical and archaeological value [1–5].

As for metal, EDXRF has demonstrated to be a very useful tool able to provide, for example, a better understanding of ancient technologies [6], enabling the identification of craft production processes and technological systems [7,8], the definition of trade routes and contact networks [9,10], the availability of raw materials or the occurrence of recycling practices [11]. Accordingly, a correct estimation of the original alloy composition is crucial to obtain reliable and consistent data to be used to address historical issues. However, performing quantitative EDXRF analyses on archaeological metals is a complex process. Due to the reduced X-ray penetration depth [12–14], quantitative EDXRF data could be affected by the most superficial layers generally made up of compounds resulting from alteration and corrosion processes formed when a metal remains buried for hundreds or thousands of years [15–17]. In this regard, if one looks into the cross section of a metal recovered during an archaeological excavation or exhibited in a museum, a very complex stratified structure consisting of the original alloy, the corrosion patina, the soil-derived crust and/or the artificial protective layer can be generally observed. The non-removal of these superficial compounds lets the chemical contamination which limits the acquisition of trustworthy compositional data of the original alloy. This is the reason why the vast majority of the studies investigating the bulk composition are performed according to (micro-) destructive and (micro-) invasive approaches aimed at putting the underlying metal in sight.

This paper reveals the elemental composition of six metallic oil lamps from South-Western al-Andalus, also known as Gharb al-Andalus, corresponding approximately to modern South of Portugal, by means of an *in situ* and non-destructive approach combining EDXRF spectrometer, for acquiring the data, and X-ray Monte Carlo (XRMC), *i.e.* a Monte Carlo (MC) software developed for simulating X-ray imaging and spectroscopy in heterogeneous samples, for its processing. Because of their function, *i.e.* to make light in the darkness, and regardless of the material with which they were produced, *i.e.* clay, glass or metal, the Islamic religion regarded oil lamps as objects owning a strong symbolic value and a considerable evocative charge, as also reminded in the Qur'an [18,19].

Since the oil lamps analysed in this paper remained buried for centuries, they were subjected to surface alteration processes that led to the formation of outer layers with a different chemical composition than that of the original alloy. Moreover, once recovered, each artefact has undergone a conservation treatment that was completed with the application of a protective layer (Paraloid B-72). Due to the impossibility of mechanically removing these outer layers, an accurate estimation of the bulk composition would be rather problematic to obtain with traditional approaches, since the presence of compounds from the alteration layers would have affected the quantitative results. Accordingly, since the EDXRF/MC spectrometric protocol applied in this paper has already proved to be able to determine the composition of the bulk metal, as well as the structure and the composition of the superimposed layers with no need to remove them, it was regarded as the analytical tool most appropriate for evaluating the elemental composition of the six oil lamps selected in this study.

The overall goal of this paper was to determine the type of alloy used in the production of the oil lamps, seeking also to understand whether a common production technology, namely a typical chemical pattern, might be revealed inside a type of artefacts not very widespread in Southern Portugal and found in some of the most important urban centres from Gharb al-Andalus, such as Mértola, Silves, Cacela, and Faro.

2 Materials and methods

2.1 Materials

The six oil lamps (fig. 1) selected for analysis were found at different sites in Southern Portugal (fig. 1) and are attributed to a period between the 10th and the 13th century AD [20,21]. In this study, the oil lamps are identified through their laboratory reference numbers, from C1 to C6.

C1 is a zoomorphic-shaped oil lamp with incised decoration. The artefact, currently stored at the National Museum of Archaeology of Lisbon (MNA35037), has unknown provenance. It belonged to the personal collection of the Portuguese King D. Luís I (1838–1889) [22], having been recently considered as a replica produced in the late 19th century [23]. C2 was recovered at Quinta da Fidalga (Cacela) and was incorporated in the National Museum of Archaeology of Lisbon in 1896 (MNA17027) [22,24]. The oil lamp has two beaks, one of them lost. C3 was found at the site of Quinta da Judiária (Faro) and is stored at the Archaeological Institute of the University of Faro (TJG.HM/87-lab37) [20]. C4 and C5 are from the castle of Silves [25,26]. C4 is an open oil lamp with two beaks, while C5 is a fragment corresponding to an oil lamp bird-shaped handle. Finally, C6 is a fragmented oil lamp found in Mértola.



Fig. 1. Oil lamps from unknown site (C1), Quinta da Fidalga (C2), Quinta da Judiária (C3), Silves (C4 and C5), and Mértola (C6). Location of the archaeological sites from where the oil lamps came from (A).

2.2 Methods

EDXRF analyses were performed using a Bruker TRACER III-SD handheld spectrometer (fig. 2(a)) equipped with a rhodium anode tube and a Silicon Drift Detector. The operating conditions were 40 kV, 3 μ A current with an Al/Ti filter (304.8 μ m Al/25.4 μ m Ti), and 120 seconds acquisition.

Data processing and quantification was accomplished through both an empirical calibration and the XRMC software. As for the former, quantification by empirical calibration was developed just for having a constant control over the data obtained through the EDXRF/MC protocol. For this purpose, five standards from certified reference materials BCR-691 [27] were used following the approach described in [28]. Regarding the latter, quantification was performed with the XRMC software, *i.e.* an MC simulation algorithm based on the Xraylib X-ray database [29] allowing to characterise in almost real-time both the structure and the elemental composition of each layer from a multi-layered artefact. When compared with more traditional quantification methods [30,31], the main advantage of the EDXRF/MC protocol relies in the fact that it provides the elemental composition of the original alloy with no need of removing the corrosion patina which generally covers this sort of artefacts (fig. 2(b)).

The EDXRF/MC protocol has already been described in more details in previous papers [32–35]. In the case of the six oil lamps, the EDXRF/MC analysis was performed as follows: before starting with the simulation, the experimental setup of the X-ray spectrometer was characterized by introducing in the software different types of information about, for example, X-ray tube and detector position and composition, thickness of the detector and spectrometer windows. Afterwards, the real X-ray tube emission was determined with direct measurements of both the beam and the five standards from certified reference materials BCR-691 [27], also used for the empirical calibration. At the end of this procedure, the error of the chemical composition of the reference samples was estimated to be less than 5% for the major chemical elements. The detection limit was fixed at around 10–20 ppm.

After analysing the six oil lamps by EDXRF, the quantitative estimation of the composition and the characterisation of the structure of both the bulk metal and the superimposed layers was based on a two-steps procedure. First, the guess data of the structure and the elemental composition of the real sample were determined based on the type of patina/corrosion layer (estimated by a visual inspection or by another type of measurement) and on the bulk composition (estimated by the XRF measurements). Second, the measures were simulated and the obtained spectra were compared to the measured ones. Then, the difference between simulated and measured spectra was evaluated by a visual approach and/or, for a finer estimation, by a chi-squared test. If the estimated error was lower than a pre-established threshold, the simulation ended and the structure/composition used for the simulation were regarded as the best representation of the real sample. Contrariwise, the structure and/or composition of the sample were changed and a new simulation was performed. It should be stressed that for each point analysed, several sample configurations were tested at the level of number, composition, and thickness of the different layer in order to find the best-fitting parameters.

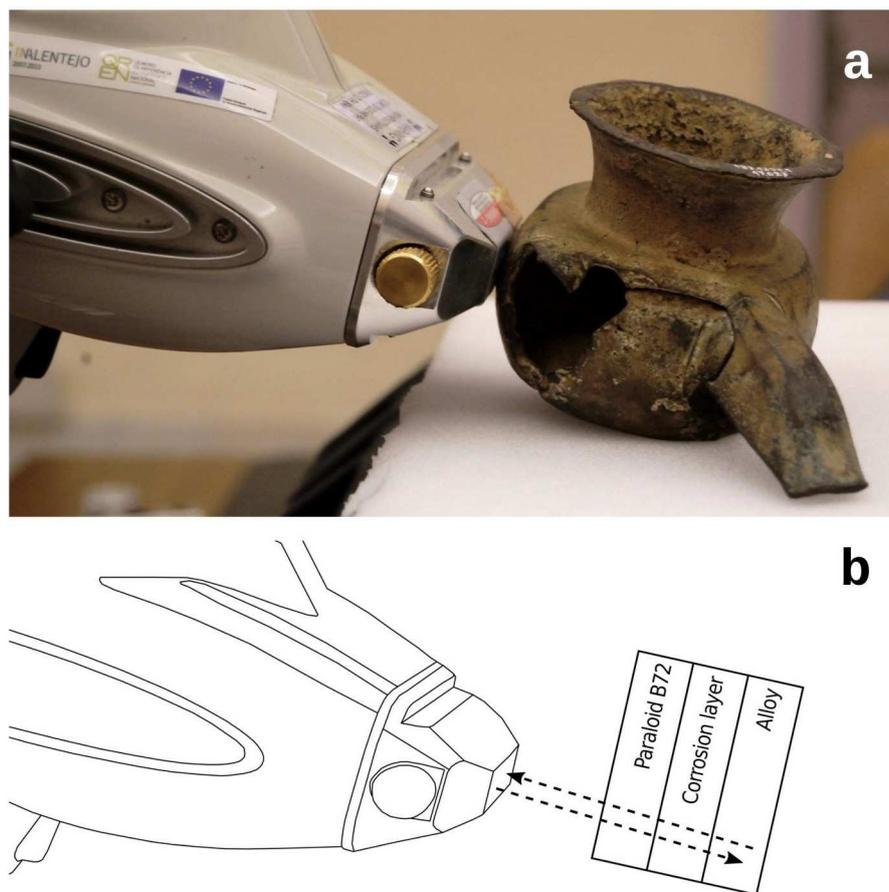


Fig. 2. Equipment set-up while analysing oil lamp C2 (a). Schematic representation showing the multi-layered structure of the oil lamps, highlighting the capability of MC simulation in estimating the thickness and the composition of the different layers (b).

However, by adopting the EDXRF/MC protocol, some limitations capable of preventing a good estimation of the alloy composition may be considered as well, mainly as consequence of: a) the density and the structure of the corrosion layer, especially if the superficial patina appears to be too thick, thus not allowing the X-ray radiation from the alloy to reach the detector; and b) the presence of rough/irregular surfaces, which can introduce disturbing and uncontrollable effects, thus making a good fitting difficult between the experimental and the simulated spectra. If for the first point a valid solution does not exist yet, for the second one, the disturbing effects have been reduced efficiently with the implementation of an MC algorithm able to simulate rough surfaces [36].

Finally, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) was also performed with a Hitachi S3700N interfaced with an energy-dispersive spectrometer (EDS) Bruker XFlash 5100 Silicon Drift Detector, with a 129 eV energy resolution at Mn $K\alpha$. SEM-EDS allowed to identify the occurrence of micro-inclusions in the metal and to monitor the variations in composition between the external layers and the bulk alloys in small areas free of corrosion compounds.

3 Results and discussion

As already mentioned, the MC data processing provides information on the elemental composition of the original alloy and on the composition and thickness of the superimposed layers. In the case of the oil lamps analysed in this paper, the MC algorithm determined a structure consisting of three different layers: a) a Paraloid B72 layer applied on the surface of the metals for consolidation and protection of the objects against degradation mechanisms; b) a corrosion layer consisting of copper oxides; and c) the bulk alloy. It is important to stress that even if the two external layers do not contribute with characteristic peaks to the XRF spectrum, data about their composition and thickness can be deduced by comparing the spectrum background region between the simulated and the experimental spectra. This means that even elements with no detectable fluorescence photons (low- Z elements) contribute to the background as well [37].

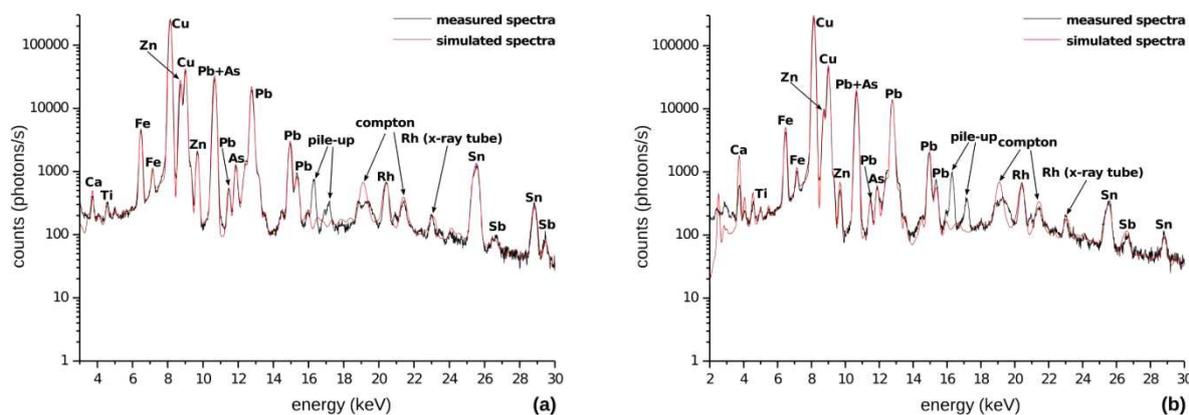


Fig. 3. EDXRF and Monte Carlo simulation spectra of C4/2 (a) and C5/1 (b).

Table 1. Quantification of the elemental composition of the oil lamps analysed by XRF (wt%). Three points of each object were analysed. Error margin to be considered: about 5% of the estimated concentration for elements with relative concentration higher than 1 wt%, and 10% of concentration error for lower concentrations. n.d.: not detected.

ID	Fe	Cu	Zn	As	Ag	Sn	Sb	Pb
C1/1	1.7	81.2	16.3	0.1	0.05	0.2	0.05	0.4
C1/2	1.4	83.5	14.6	0.1	0.05	0.1	0.05	0.2
C1/3	1.2	82.5	15.5	0.08	0.02	0.4	n.d.	0.3
C1 average composition	1.43	82.4	15.47	0.09	0.04	0.24	0.03	0.3
C2/1	0.3	81.65	3.1	5.5	0.1	0.1	0.15	9.1
C2/2	0.1	79.05	2.65	5.25	0.15	0.1	0.05	12.65
C2/3	0.3	72.05	2.65	5.7	0.15	0.1	0.1	18.95
C2 average composition	0.23	77.58	2.8	5.49	0.13	0.1	0.1	13.57
C3/1	10.0	58.58	3.0	0.1	0.02	1.0	n.d.	27.3
C3/2	10.0	49.19	3.0	0.1	0.01	0.4	n.d.	37.3
C3/3	7.1	51.64	4.1	0.1	0.01	1.2	n.d.	35.85
C3 average composition	9.03	53.14	3.37	0.1	0.01	0.87	n.d.	33.48
C4/1	1.05	78.05	5.75	2.5	n.d.	4.15	0.15	8.35
C4/2	1.05	77.1	6.1	2.1	n.d.	3.15	0.1	10.4
C4/3	1.0	77.15	6.5	2.85	0.1	5.0	0.3	7.1
C4 average composition	1.03	77.43	6.12	2.48	0.03	4.1	0.18	8.62
C5/1	n.d.	89.80	2.0	1.0	n.d.	0.6	0.2	6.4
C5/2	1.0	86.15	3.05	1.0	n.d.	0.3	0.1	8.4
C5/3	n.d.	90.6	2.0	1.0	n.d.	0.8	0.2	5.4
C5 average composition	0.33	88.85	2.35	1.0	n.d.	0.57	0.17	6.73
C6/1	1.7	68.3	9.8	n.d.	n.d.	5.5	n.d.	14.7
C6/2	1.55	67.6	10.1	n.d.	n.d.	5.0	n.d.	15.75
C6/3	1.55	67.05	10.0	n.d.	n.d.	5.9	n.d.	15.5
C6 average composition	1.6	67.65	9.97	n.d.	n.d.	5.47	n.d.	15.32

The EDXRF spectra, measured (black line) and simulated (red line), of C4/2 (a) and C5/1 (b) are shown in fig. 3. In both cases, the three-layered structure (protective layer + oxide patina + original metal) is confirmed. Quantification based on empirical calibration carried out on these points provided the following results: C4/2 consists of 1.4% Fe, 79.6% Cu, 4.5% Zn, 3.65% As, 7% Pb, 3.65% Sn, and 0.2% Sb; C5/1 is composed of 1.1% Fe, 84.98% Cu, 1.9% Zn, 1.4% As, 9.61% Pb, 0.8% Sn, and 0.2% Sb. Since these data reproduce the composition of the artefacts without removing the effects of the corrosion patina, their variation with respect to the data obtained through the EDXRF/MC protocol can be attributed to the contamination from the outer layers.

The composition of the six oil lamps, as established by processing the data with the XRMC software, is shown in table 1. An error estimation of 5% for major elements and 10% for minor elements (> 1%) should be considered. Since it was supposed that the oil lamps, as well as an archaeological metal in general, usually do not have a homogeneous composition, and in order to have data statistically more representative of their real composition, table 1 reports the results obtained on three different points for each artefact.

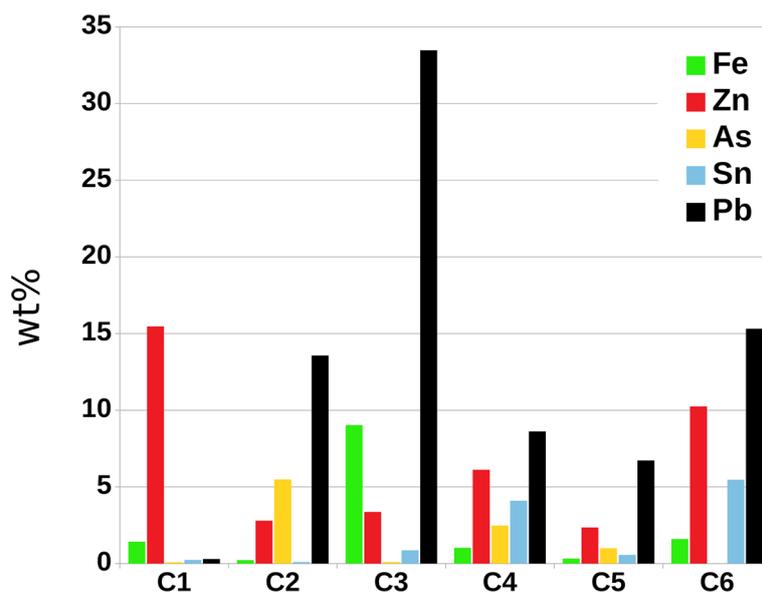


Fig. 4. Histogram showing the variability of the main elements alloyed with Cu.

According to the results, the oil lamps can be grouped as follows [38]: a) C1 is a rather pure brass alloy (Cu+Zn) with minor elements, *i.e.* Fe, As, Ag, Sn, Sb, and Pb, not exceeding 2.2% in total; and b) C2 to C6 are a leaded brass alloys (Cu+Zn+Pb) with a pronounced variability of both major and minor elements (fig. 4).

Tin, for example, ranges from 0.1% (C2) to 5.47% (C6). According to Craddock [39], Islamic metalworkers did not commonly use tin as a deliberate additional alloying element, due to the fact that this element was not available in most of the Islamic world. Indeed, as for as al-Andalus, the exploitable tin mines closest to Southern Portugal are located in the north-western region of the Iberian Peninsula and at the time were no longer accessible to Moors due to the Christian Reconquest of Western Iberia. Accordingly, the low Sn amount could actually be the consequence of a decrease in tin supply and the low tin amount detected in the six oil lamps could be the result of the random mixing of scrap bronzes during the production process. In fact, each time a metal containing Sn is melted down, tin progressively decreases through volatilization, thus leading to the production of increasingly tin-poorer alloys [40].

Large differences in the Zn content have been detected as well, with values ranging from 2.35% (C5) to 15.47% (C1). From the EDXRF/MC protocol point of view, the systematic occurrence of Zn is a novelty when compared with previous case studies adopting the same quantitative approach [41–43]. Indeed, the presence of Zn represented a hard task due to, on the one side, an anomalous change of the Zn-*K* peaks and the simultaneous presence of intense Cu-*K* peaks on the other. In order to overcome this constraint, different quantitative approaches have been used and only a very complex combination of the composition, density and thickness of the different layers allowed to obtain a perfect reproduction of experimental spectra. Based on the zinc concentration, 5 oil lamps out of the 6 can be considered as low brass alloys (average zinc content < 10%) and only C1 contains a noticeably elevated concentration of zinc (15.47%).

Figure 5(A) shows the plot of Sn against Zn. Based on the Sn/Zn ratio three different groups can be observed. The first group (C2, C3, and C5) contains less than 1% Sn and between 2 and 4% Zn. In the second group (C4 and C6), Sn ranges between 4 and 6% and zinc between 6 and 10%. Finally, C1 shows a Sn/Zn ratio completely different to the rest of the oil lamps analysed.

If the Pb variable is introduced in this analysis, the previous trend appears to be confirmed (fig. 5(B)). Actually, lead occurs in 5 of the 6 oil lamps with percentages high enough to affect the mechanical behaviour of the alloys. Pb tends to be inconsistent in C1, likely representing an accidental incorporation from the ores used to produce the objects. High leaded alloys should be expected for this kind of objects: indeed, in micro-structural terms, the addition of lead to a copper alloy lowers its melting point and increases the fluidity of the molten metal, thus being the most adequate solution for casting complex shapes. On the other side, though, lead is insoluble in copper alloys, forming segregations dispersed throughout the metal (fig. 6) making the alloy weaker and more susceptible to breakages if intensely forged and hammered.

The random and unpredictable distribution of Sn, Zn, and Pb also extends to other elements, namely Fe (from 0.23% in C2 up to 9.03% in C3) and As (not detected in C6 up to 5.49% in C2). This meaningful compositional variability could be explained with an indiscriminate mixing of recycled artefacts and scrap metals, and/or with the random addition of minerals during the production process. With regard to this last aspect, even if no data on mineral extraction sites active during the Islamic period in South-Western al-Andalus are not yet available, it should be noted that Southern Portugal is rich in mining resources, especially pyrite (FeS₂), sphalerite (ZnS), and galena (PbS) [44].

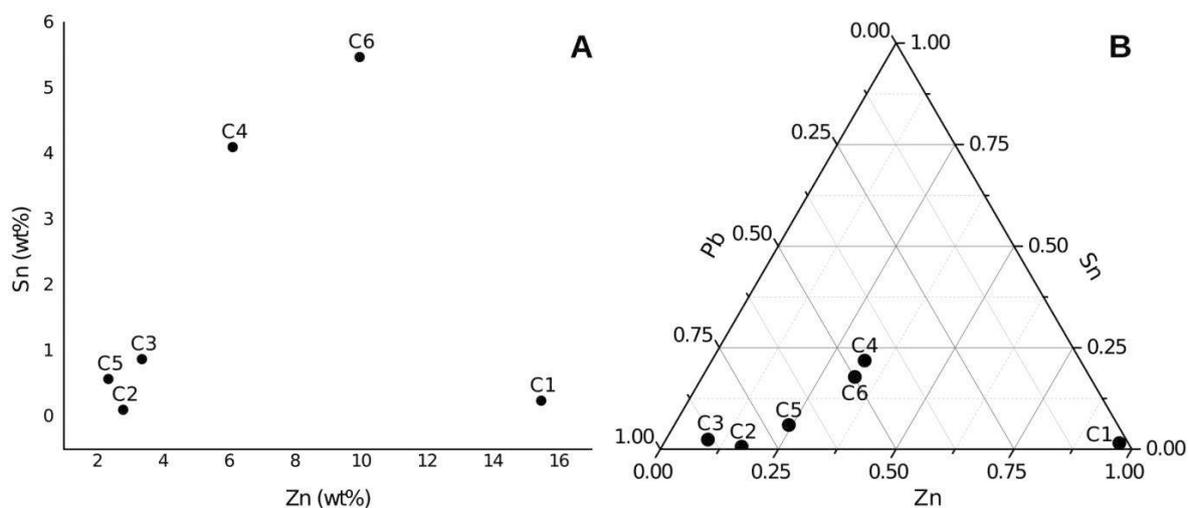


Fig. 5. Diagram of Zn against Sn for the six oil lamps (a) and ternary plot of Zn/Sn/Pb (b).

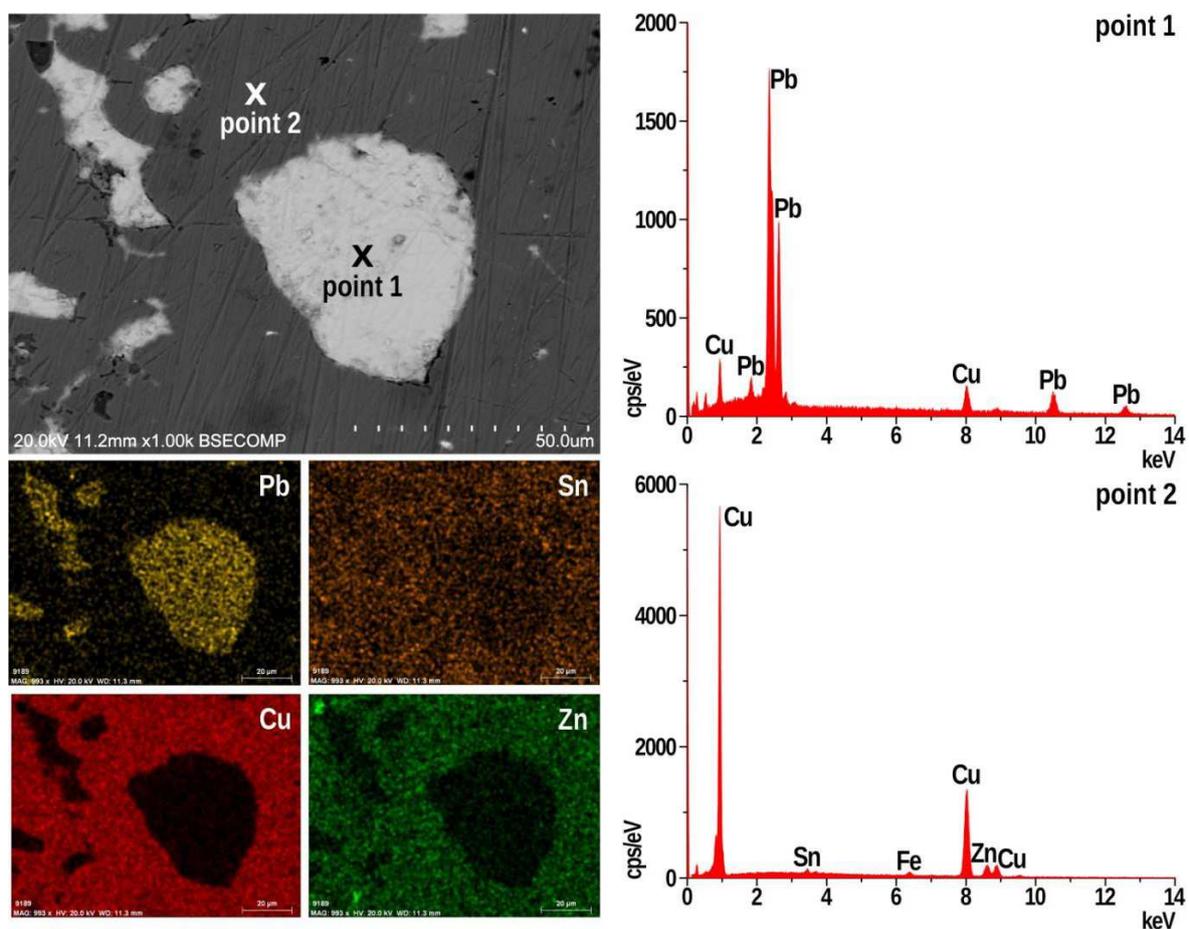


Fig. 6. SEM/EDS image of Pb rich inclusions are very common in all the artefacts analysed and due to their low miscibility in molten alloy, they are clearly visible as globular shaped inclusions irregularly dispersed in the alloy.

According to the data, one can state that despite the oil lamps' unique morphological features, the technology employed for their production was not linked to specific and predefined chemical patterns, thus suggesting that the metalworkers that produced these objects were not able to have full control over the metallurgical processes, whether they used fresh minerals or recycled scrap metals.

In a broader framework, the rarity with which metallic oil lamps are documented in South-Western al-Andalus, especially when compared with more common clay types [23,45,46], could also suggest that, notwithstanding the remarkable social value and aesthetic qualities of this kind of artefacts, they could be used, in turn, as scrap metals like any other metallic typology, thus explaining the few specimens known in the region. For example, recycling practices have already been recognized in Madinat al-Zahra (Cordoba, Spain) [47] and it should not be excluded that scrap metals were indiscriminately used as raw material for the production of new objects, regardless of the social position of the owners and/or the function of the artefacts. Finally, it should be also noted that C1—considered by [23] as a late 19th-century replica—stands out clearly from the rest of the collection, especially with regard to the occurrence of Zn and Pb, being the first much higher and the second much lower than in the rest of the oil lamps.

4 Conclusions

When dealing with archaeological metals, and to shed light on issues related to production technology, EDXRF analysis should be carried out on the original alloy of the artefact, removing the contamination of the superimposed layers, *i.e.* corrosion patina, products applied during restoration, incrustations, etc. For this purpose, unlike traditional quantitative methods that require sampling or mechanical removal of the outer layers, the EDXRF/MC protocol is able to cut out the effects of chemical elements that are not part of the bulk metal, thus allowing a completely non-destructive analysis.

In this paper, EDXRF/MC protocol appeared to be an appropriate approach to analyse six unique Islamic oil lamps from Southern Portugal for which sampling was not allowed. XRMCA algorithm has been used as data processing and quantification tool, enabling to obtain an accurate reproduction of the measured spectrum with a good characterisation of the analysed areas, both in terms of composition and structure. The six oil lamps were modelled as multi-layered objects formed by three layers: a) a Paraloid B72 layer; b) a patina/corrosion layer; and c) the bulk metal.

The results show that artefacts are copper-based metals with a strong variability of elements like Fe, Zn, Sn, As, and Pb. The random distribution of these elements could be related to the likely use of scrap metals or could be explained with the mixing of certain types of ores locally available. In any case, the compositional fluctuation revealed by the data suggests that no particular concerns existed as far as the mechanical properties of the final alloys.

In summary, the data reported in this paper confirm the reliability of EDXRF/MC protocol to analyse *in situ* and non-destructively multi-layered metal artefacts, while also representing a very important contribution for improving our knowledge on Islamic metallurgy from the most Western region under the Islamic influence, *i.e.* South-Western al-Andalus.

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