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EDXRF study of Prehistoric artefacts from Quinta do Almaraz (Cacilhas, Portugal)

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Abstract

This paper presents a non-destructive analytical study by secondary target energy-dispersive X-ray fluorescence spectrometry of selected artefacts found during excavations carried out since 1988, at the archaeological site of "Quinta do Almaraz", Estremadura, West Portugal. The analysed collection was composed by metallic artefacts (*fibulae*, fish-hooks, needles, buckle, tweezers, knives, arrowheads), crucibles, slags and metallurgical residues.

The chemical composition of the metallic artefacts have made possible to identify different groups belonging to distinct Prehistoric periods, from the Bronze (bronzes) till the Iron (iron-based alloys) Age. Variation in the Sn and Pb percentages in the bronzes pointed out to the existence of three different metallurgical processes, although they did not present different typological characteristics.

Semi-quantitative analysis on fragments of crucibles have permitted to identify particular metallurgical operations, namely the preparation of gold alloys and the remains of the silver cupellation process, which was introduced in the Iberian Peninsula by the Phoenician [Early Metal Mining and Production, Smithsonian Institution Press, Washington, DC, 1995].

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1. Introduction

The "Quinta do Almaraz" archaeological site is located in Cacilhas (Almada), in front of Lisbon in the Tagus estuary at the western Portuguese Coast. Excavations carried out since 1988 by the *Museu Municipal de Almada* have demonstrated that this particular location has favoured human occupation since an early age, and archaeologists have found remains (thousands) from the Neolithic till the Roman period. The set of the studied artefacts is varied (Fig. 1) and the typological characteristics point out to an exceptional collection in the context of the Late Bronze and Iron Age in the Portuguese territory. Energy-dispersive X-ray

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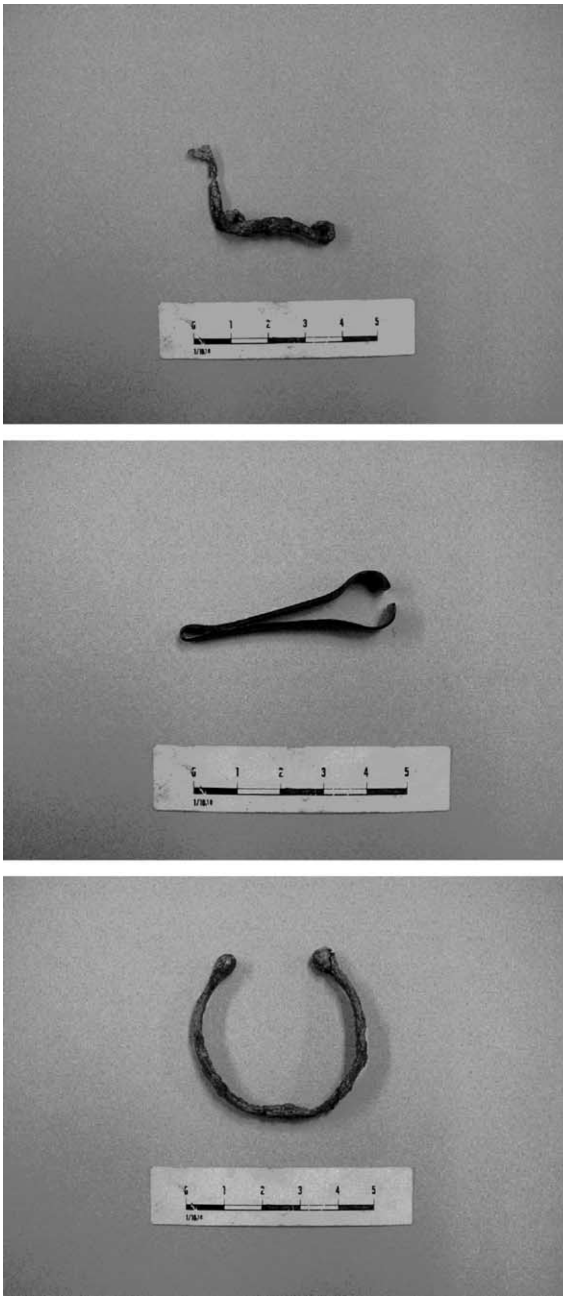

Fig. 1. Examples of metallic artefacts from Quinta do Almaraz.

fluorescence spectrometry (EDXRF) is extremely widely used in archaeometry as a basic method of non-destructive characterisation of metal artefacts. The presence of corroded and patinated metal surfaces and the shape of the artefacts are serious factors that affect the analytical results. In fact, the penetration depth of the incident X-ray beam for copper and iron-based alloys is within the order of not more than several tenths of micra, being the dominant contribution of the detected characteristic X-rays from the corroded/patinated surface [2]. However, the Prehistoric metallurgical evolution can be associated with the emerging of particular types of metals/alloys is easily identified even in the presence of such restrains. Typological characteristics are not sufficient to infer about the recurrent questions: when and by whom an artefact was made. Styles were often copied at different times and distinct locations from their origin, and in such cases, the chemical composition of a given artefact has a primordial role in allocating it to a particular Prehistoric context and in the attribution of a specific technology used in its manufacture. For instance, copper-based metal artefacts with variable percentages of As, Sn, or Pb, that could be intentional, varied with the region (available raw materials) and with the time (evolution of technology).

This work demonstrates the importance of the chemical composition in the archaeometallurgical field. Analysed artefacts could be grouped according to their composition. Analysis of bronze artefacts having the same style evidenced the presence of distinct technologies of manufacturing and a probable distinct origin. Nevertheless, this archaeological site located at the Portuguese coast at the Tagus estuary, was easily accessed by different seafaring travellers and traders. The metal residues in crucible fragments indicated local smelting furnaces and the extraction of silver by cupellation.

2. Experimental

The elemental composition of the metallic artefacts was determined by EDXRF analysis using a commercially available Kevex EDX-771 Analyst System, with a rotating 16-position sample tray. A computer running the WinXRF/ToolBox applications software, which commands the X-ray generator, the detection system and the multichannel analyser, controls the spectrometer. A rhodium anode X-ray tube with six secondary targets and filters produces the primary photon beam. The characteristic X-rays emitted by the samples are collimated at 90° and measured with a Si(Li) detector with a 165 eV resolution and an active area of 30 mm^2. Artefacts were irradiated in different areas using a monochromatic X-ray beam generated by a Gd secondary target and filter, using a voltage of 57 kV and 1 mA current intensity, during 300 s. Spectra were processed using a Gaussian deconvolution that assumes a theoretical relationship among the intensities of X-ray lines within each elemental line series [3]. Elemental concentrations were determined through the EXACT computer program [4], based upon a fundamental parameter method that uses calibration coefficients and accounts for matrix effects. Calibration was performed with standard bronze materials certified by the Bureau of Analysed Samples, Ltd., by using a single calibration coefficient for each element. Crucible fragments were also irradiated in their external and internal surface by using the same excitation conditions to infer about their use in archaeological operations.

3. Results and discussion

3.1. Metallic artefacts

The chemical composition of the analysed artefacts are listed in Table 1 (copper-based

Table 1
Chemical composition of the copper-based metallic artefacts from Quinta do Almaraz

Artefact no.	Description	Cu	Sn	Pb	Fe	Sb	Ni
MMA9605-ALZ1790	Bracelet	94.2	5.21	n.d.	0.55	n.d.	n.d.
MMA9605-ALZ1790C		89.7	9.56	n.d.	0.79	n.d.	n.d.
QA12S-B12NPL5C24D	Fish-hook	98.3	1.24	n.d.	0.50	n.d.	n.d.
QA12S-B12NPL5C24DC		97.4	1.92	n.d.	0.67	n.d.	n.d.
MMA9621-ALZ1798	*Fibulae*	92.9	3.33	0.88	2.74	n.d.	0.13
MMA9621-ALZ1798C		94.3	2.69	0.51	2.37	n.d.	0.13
MMA9622-ALZ1799	*Fibulae* fragments	95.9	2.87	0.73	0.23	0.14	0.11
MMA9622-ALZ1799C	*Fibulae*	89.0	9.33	0.40	1.02	0.16	0.11
MMA4404-ALZ437	Fish-hook	93.3	4.45	1.48	0.66	n.d.	0.12
MMA4404-ALZ437C		92.8	5.0	1.34	0.73	n.d.	0.13
MMA9456-ALZ1765	Arrowhead	94.1	5.34	0.20	0.11	n.d.	0.27
MMA9456-ALZ1765C		87.0	11.75	0.52	0.56	n.d.	0.16
QA12S-B12NPL6C26A	*Fibulae*	91.2	5.19	0.84	2.64	n.d.	0.11
QA12S-B12NPL6C26AC		91.0	4.54	1.37	2.93	n.d.	0.15
QA12S-B12NPL6C26B	Buckle fragment	91.1	7.62	0.42	0.92	n.d.	n.d.
QA12S-B12NPL6C26BC		91.8	7.08	0.30	0.86	n.d.	n.d.
MMA4411-ALZ444	Tweezers	80.4	9.08	9.87	0.33	0.16	0.13
MMA4411-ALZ444C		80.5	9.52	9.37	0.33	0.18	0.11
MMA4410-ALZ443	Small fish-hook	77.2	15.91	6.30	0.62	n.d.	n.d.
MMA4410-ALZ443C		76.8	16.76	5.85	0.63	n.d.	n.d.
MMA9445-ALZ1753	Fish-hook	71.6	14.89	11.96	1.55	n.d.	n.d.
MMA9445-ALZ1753C		69.9	16.47	11.85	1.80	n.d.	n.d.
MMA9446-ALZ1755	Fish-hook	82.0	7.64	9.04	1.14	0.19	n.d.
MMA9446-ALZ1755C		82.6	7.89	8.03	1.32	0.21	n.d.

n.d. – not detected.

Table 2
Chemical composition of the iron-based metallic artefacts from Quinta do Almaraz

Artefact no.	Description	Cu	Fe	As
QA12S-B12NPL6C26D	Knife edge	0.26	99.5	0.22
QA12S-B12NPL6C26DC		0.56	99.1	0.33
QA12S-B12NPL6C26E	Knife hand	0.33	99.4	0.26
QA12S-B12NPL6C26EC		0.78	98.6	0.59
QA12S-B12NPL5C24A	Knife edge	0.17	99.7	0.11
QA12S-B12NPL5C24AC		0.33	99.5	0.20
QA12S-B12NPL5C24B	Ball	0.22	99.5	0.33
QA12S-B12NPL5C24BC		0.44	99.2	0.37
MMA9601ALZ1788	Knife edge	0.54	99.2	0.23
MMA9601ALZ1788C		0.41	99.4	0.18
MMA9437-CACII5	Knife with bronze nails	1.45	98.4	0.20

Codes (A, B, D and E) were attributed to different artefacts with the same number. Code C refers to a second analysis in a different area of the same artefact.

artefacts) and Table 2 (iron-based artefacts). The copper-based artefacts (bronzes) can be gathered in three groups according to their composition. In Table 1 the three different groups of bronze artefacts are separated by lines. Objects of the first group (bracelet and fish-hook) have unexpected low percentages of Sn, in spite of the usual Sn surface enrichment measured in the patina of bronzes [2].

The second group is composed by bronze artefacts with rather different stylistic characteristics (*fibulae*, fish-hook and an arrowhead) also having low Sn percentages, although small percentages of Pb ($<1.5\%$) were measured. During Bronze Age, the addition of Pb was initialised in order to lower the melting point resulting in a more malleable alloy. However, the low contents in Pb indicate that its presence might be due to the type of ore used in the smelting process rather than an intentional addition. This is the case of bronze artefacts of the third group (fish-hook and tweezers) which exhibit significant amounts of lead. The Pb addition could be in this case related to the stylistic specifies of these artefacts, since the addition of Pb can produce breakable alloys.

These different groups correspond to technological productions characteristic of the transition period Chalcolithic to Bronze Age (third to the second millennium) for the first group and Late Bronze Age for the remaining artefacts (XII to VIII century BC).

Iron-based artefacts (Table 2) are more recent and were manufactured during Iron Age, which was introduced in the region by the Phoenician during the VIII century BC.

3.2. Crucible fragments

Comparison of the characteristic X-rays emitted by the irradiation of two crucible fragments (Fig. 2(a) and (b)) in their internal and external surfaces demonstrated that they have been used in smelting. Spectra displayed in Fig. 2(a) shows that the internal surface present significant amounts of Cu, Br, Ag, Bi and Pb. The presence of Ag, together with Bi and Pb points out to a similar extraction process of Ag from jarosites. The most famous ancient mine where jarosites were exploited in the Iberian Peninsula was Rio Tinto, as previously reported [1] and Ag could only be smelted by the addition of Pb (or lead ores). Those minerals have a wide variety of metals, such as the Bi, which on smelting goes off with the silver into the lead. Enrichment in Br is explainable by the high stability of the silver halogenides. Elements like Fe and Zr are due to the crucible raw material composition.

Spectra obtained with the irradiation of the second crucible (Fig. 2(b)) shows the presence on

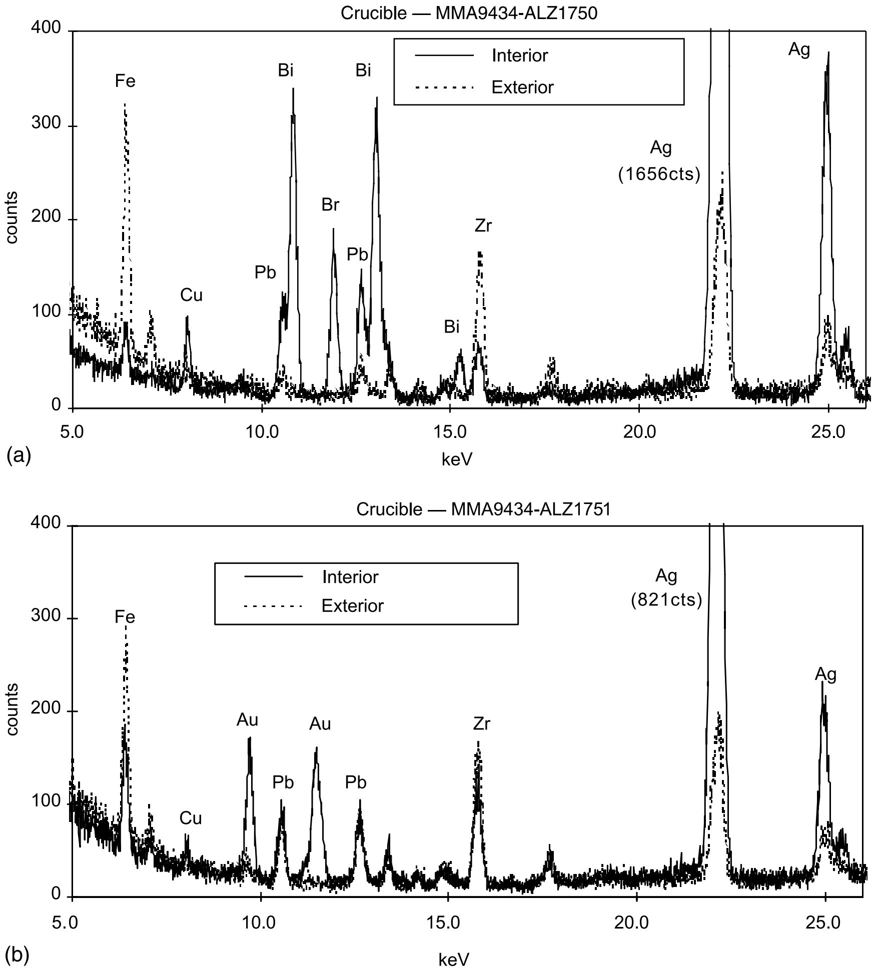

Fig. 2. X- ray spectra emitted by the irradiation of crucible fragments.

its internal surface of Cu, Ag and Au, suggesting that it should has been used for the refining of gold. The ability to refine the gold by separating the silver has very ancient records, namely in Sumeria and Egypt dating back to the third millenium BC, although in Western Europe it has been safely attributed to occur during the first millenium BC [5].

4. Conclusion

EDXRF analysis has demonstrated once more its potential in the answering of relevant questions in the archaeological field. The non-destructive analysis of this unique collection has considerably contributed to the advance of the knowledge in the archaeometallurgy at the Iberian Peninsula. Apparently, two stylistically identical groups of artefacts (groups 2 and 3) co-exist in the same chronological period – Late Bronze Age, but they seem to have been produced with different metallurgical technologies, which may be an indication of their different origins. The semi-quantitative analysis of crucible fragments proved the existence of local furnaces and identified specific smelting processes, particularly the cupellation of Ag not previously testified in Portuguese territory before the Roman period. Iron technology was introduced with the Phoenician settlements during the VIII century BC, amongst them "Quinta do Almaraz".

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