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Micro-EDXRF surface analyses of a bronze spear head: Lead content in metal and corrosion layers

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Abstract

A bronze spear head from Central Portugal dated to Late Bronze Age has been analyzed by non-destructive micro-EDXRF in the metal surface and corrosion layers. The artifact had previously been analyzed using a conventional EDXRF spectrometer having a larger incident beam. The quantification of the micro-EDXRF analyses showed that lead content in corrosion layers can reach values up to four times higher than the content determined in the metal surface. Results obtained with the higher energy incident beam from the EDXRF equipment, although referring mainly to the corrosion layers, seem to suffer some influence from the surface composition of the metallic alloy.

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Keywords: Archaeometallurgy; Micro-EDXRF; Late Bronze Age; Bronze alloy; Lead

1. Introduction

Lead began to be regularly added to bronze (Cu–Sn alloy) during the Late Bronze Age in some "Atlantic" regions. The suggestion made by some studies on ternary ancient bronzes is that no specific lead content was preferred [1–3], the tin content this time was commonly to be around 8–10% for utilitarian artifacts [4].

The knowledge of the lead content in an artifact can be important in order to know if lead was intentionally added to the alloy to improve its casting properties, or if it is present as an impurity resulting from the ores used. A big restrain is how to establish the limit to below which the ternary alloy can be considered natural and above which it can be considered intentional. Some authors have considered lead as being intentionally added to the alloy when present higher than 2% [5,6].

Studies regarding Late Bronze Age metal artifacts from central Portugal revealed that Pb is only present as a minor element in the bronze alloy [7].

Due to the historic/artistic value of many archaeological artifacts, preservation with the minimum change not only in appearance, but also in physical and chemical properties becomes an important concern. Thus, non-destructive analytical technique Energy Dispersive X-ray Fluorescence (EDXRF) spectrometry has had a wide acceptance and applicability in the field of archaeometry. Multi-elemental quantitative analyses made in corroded surface areas of bronze artifacts have shown an increase in tin content when compared to the original alloy [8–10]. But, for ternary bronze alloys, a evaluation of the content of lead in the corrosion surface compared to its content in the metal has not been mentioned often [8,11].

2. Experimental details

2.1. Spear head

The analysed artifact is a socketed spear head which central midrib has a sharp-shaped section. The base of the socket has two rivet holes, one on each side. The object is dated to the Late Bronze Age and was found in Central

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Portugal. The spear head shows a uniform dark patina. Nevertheless, in some areas, more frequently near sharp borders, there is some green and whitish corrosion. In a small area (about $5 \times 1\,\mathrm{mm}^2$) in the base of the socket some corrosion is missing leaving the metallic surface able to be analyzed by micro-EDXRF. This small area was analyzed in three different spots and the results compared with the ones obtained from the corrosion layers.

2.2. *Micro-EDXRF spectrometry*

Micro-EDXRF analyses were made in an *ArtTAX Pro* spectrometer which comprises a low-power X-ray tube with a molybdenum anode. The system includes a set of polycapillary lens that generate a microspot, lower than 100 μm in diameter, of primary radiation [12]. An integrated CCD camera and three beam-crossing diodes provide the control over the exact position on the sample to be analyzed. The X-rays emitted by the sample are collected at 40° by a silicon drift electro-thermally cooled detector with a resolution of 160 eV at Mn-Kα.

To study the heterogeneities over the artifact surface, the spear head was analyzed in eight different spots (Fig. 1), using 40 kV, 0.4 mA and 100 s of tube voltage, current intensity and live time, respectively. The quantification involved the WinAxil software [13], based on the fundamental parameter method [14]. The quantification process uses calibration parameters obtained from the analysis of a reference material (BNF Metals Technology Centre 50.01), having a matrix composition similar to the one of the studied sample.

The accuracy of the method, determined by the quantification of the reference material, was found to be better than 5% for the major elements in the alloy and better than 15% for minor elements. Detection limits [15] were as follows, $\mathrm{Fe} = 69\,\mathrm{mg\,kg^{-1}}$, $\mathrm{Cu} = 119\,\mathrm{mg\,kg^{-1}}$, $\mathrm{Pb} = 156\,\mathrm{mg\,kg^{-1}}$ and $\mathrm{Sn} = 0.15\%$.

2.3. *Energy Dispersive X-ray Fluorescence spectrometry*

EDXRF analyses, published in a previous work [16], were conducted in a *Kevex 771* spectrometer, equipped with a rhodium X-ray tube as the primary excitation source. The system includes several secondary excitation targets and suitable radiation filters that optimize the excitation conditions. The characteristic X-rays (sample spot area close to 3 cm in diameter) are collimated at 90° before being measured in a liquid nitrogen cooled Si(Li) detector with a resolution of 175 eV at Mn-Kα.

The experimental setup involved two different excitation conditions: (1) silver secondary target (35 kV, 0.5 mA and 300 s) to measure Fe, Cu, As and Pb; (2) gadolinium target (57 kV, 1.0 mA and 300 s), to assess Sn and Sb. The spear head was analyzed in three different areas (Fig. 1), to account for possible heterogeneities over the artifact surface. The quantification procedure involved the EXACT computer program [17] based on the fundamental parameter method [14], and uses experimental calibration parameters, calculated through the analysis of a reference material (BNF Metals Technology Centre 50.01). Detailed description of the experimental setup is published elsewhere [18].

The accuracy was found to be better than 2% for the major alloy elements and better than 10% for the minor elements in the alloy. Detection limits [15], were as follows, $\mathrm{Fe} = 84\,\mathrm{mg\,kg^{-1}}$, $\mathrm{Cu} = 112\,\mathrm{mg\,kg^{-1}}$, $\mathrm{Pb} = 131\,\mathrm{mg\,kg^{-1}}$ $\mathrm{Sn} = 47\,\mathrm{mg\,kg^{-1}}$ and $\mathrm{Sb} = 57\,\mathrm{mg\,kg^{-1}}$.

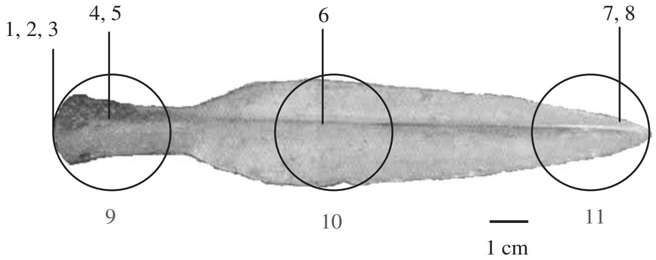

Fig. 1. Image of the spear head with the 8 spots (1–8) analyzed by micro-EDXRF and the 3 areas (9–11) analyzed by EDXRF.

3. Results and discussion

3.1. *Micro-EDXRF analyses*

The results of micro-EDXRF analyses (Table 1) show large differences between the metal surface and different corrosion zones. Since the three analyses made on the metal surface correspond to three spots made on a small area, one should express no surprise in their similar results: 7.8% ± 1.1% for Sn and 2.0% ± 0.4% for Pb. The five analyses on corrosion layers show higher values of Sn and Pb, 30.2% ± 13.2% and 7.9% ± 1.1%, respectively.

Through these analyses one can observe that the Sn contents show different values. In its turn, the Pb content shows much more constant values. Different Sn contents on each corrosion analyses reflect, very probably, different corrosion compounds formed in each area analyzed. Besides this, the analyses show that both Sn and Pb can arise to contents up to four times higher compared to those on the metal surface.

Table 1
Micro-EDXRF analyses of the spear head (in wt%, normalized)

Spot	Description	Cu	Sn	Pb
1	Metal surface	90.8	6.7	2.5
2	Metal surface	90.3	7.8	1.8
3	Metal surface	89.3	8.9	1.8
4	Dark corrosion	55.4	36.8	7.8
5	Green corrosion	51.4	42.1	6.5
6	Whitish corrosion	81.0	10.4	8.7
7	Dark corrosion	67.7	23.1	9.2
8	Green corrosion	54.6	38.4	7.1

Table 2
EDXRF analyses of the spear head (in wt%, normalized)

Area	Description	Cu	Sn	Pb
9	Socket	54.3	39.6	5.4
10	Midrib and blade	62.8	30.4	5.0
11	Tip of the blade	54.5	38.4	5.1

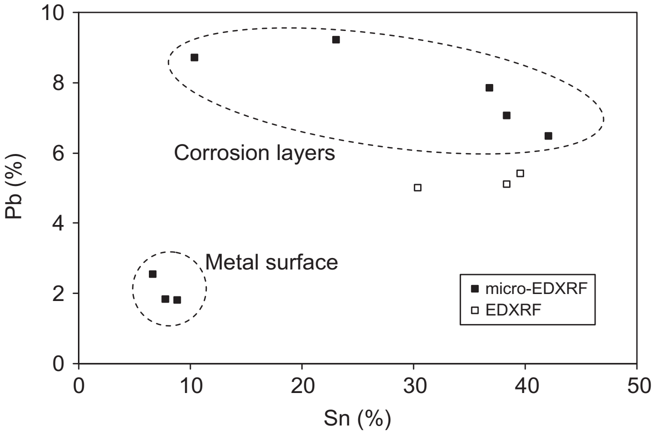

Fig. 2. Results obtained for Sn and Pb in micro-EDXRF and EDXRF analyses of the spear head.

If we consider that the elemental composition given by the metal surface analyses correspond, approximately, to the composition of the original alloy, one can state that the Sn content agrees well with values expected for a common Bronze Age alloy. The Pb content does not by itself, allow one to state if lead is a result of intentional addition or if it is present as a result of ore impurities.

3.2. EDXRF vs. micro-EDXRF analyses

From the EDXRF results (Table 2), [16], it is clear that Sn values (36.1 ± 5.0%) are in agreement to the ones from most of the corrosion areas analyzed by micro-EDXRF (Fig. 2). Meanwhile, the Pb content (5.2 ± 0.2%) seems to be below than the content calculated for the corrosion layers in micro-EDXRF. As for the micro-EDXRF corrosion analyses, the EDXRF Pb values are more constant than the Sn values.

The lower Pb content obtained by EDXRF might be due to the fact that some of the surface metal under the corrosion layer is also being analyzed, since the higher energy of the incident beam results in a larger thickness of the analyzed material.

4. Conclusions

Due to the influence of corrosion layers, the high Pb values (5.2 ± 0.2%) obtained by the conventional EDXRF in the spear head are in disagreement with the Late Bronze Age bronze metallurgy from central Portugal, where low Pb contents are expected. The micro-EDXRF analyses have allowed the characterization of the spear head bronze alloy in a non-destructive way, giving results for the elemental contents in the alloy: 7.8 ± 1.1% for Sn and 2.0 ± 0.4% for Pb.

By comparison of Sn and Pb contents in metal surface and corrosion layers from micro-EDXRF analyses it was demonstrated that their content in corrosion surface can be up to four times higher than in metal surface. It is also interesting to notice that Pb content in corrosion layers seem to show much more stable values than the Sn values in the same corrosion layers. This might happen due to different corrosion compounds formed which also shows different colors.

The depth of penetration of the primary X-ray beam in the conventional EDXRF equipment allows surface metal to be analyzed together with the corrosion layers, resulting in lower contents of Pb than those obtained by micro-EDXRF.

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