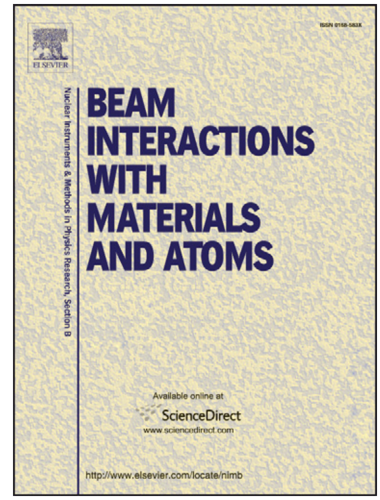

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Late Bronze Age Hoard studied by PIXE

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Abstract

The hoards of metallic objects belonging to the Late European Bronze Age can be interpreted differently depending on the type, number and composition of the artefacts. PIXE analysis has been performed in nine items from the Hoard of Freixanda in Portugal comprising 4 socket axes, a palstave axe, a ring, a chisel, a dagger, and a casting debris. Besides the composition of the main matrix elements, that is Cu and Sn, the amount of trace elements of interest like, As, Pb, Ni and Ag has been determined using this ion beam technique. The high tin content alloy and the high purity of the metals from the Freixanda hoard are characteristic of the Portuguese and Spanish Late Bronze Age metallurgy, supporting the idea of a regional production.

1- INTRODUCTION

Metal hoards are of the most peculiar cultural features of the so called *Late Bronze Age* (13^{th} - 8^{th} c. BC) in Western Europe. These accumulations of goods show great variability both in their content (the sort of objects they include) and in the type of places where they can be found. They are mostly located outside of settlements, forming isolated contexts, therefore their chronology and functionality must be deduced from the constituents of the deposit itself. It is necessary to evaluate the kind of objects which are present (ornaments, weapons, tools or any combination thereof), their amount (from a couple to several hundreds) and their state of conservation (broken, incomplete fragments, unused objects), as well as the location chosen for the deposition (places of passage, rivers, landmarks, near settlements…). Historically, according to which variables are considered, the interpretations of the nature of the hoards have been different, giving rise to a wide debate about the topic, still raging nowadays [1,2]. A first distinction is usually made between ritual and non-ritual (utilitarian) hoards. Especially significant are also the so-called “founders' hoards” which include broken pieces (scraps) and casting residues.

The present work is aimed at investigating the features of the Freixanda hoard (Ourém, Santarém; Portugal), adding the elemental analysis of the objects to the archaeological facts for the interpretation of this particular site. With these data, it is possible to evaluate the degree of homogeneity or heterogeneity of the metal, to relate composition with typology and function, and to identify which objects constitute truly singular artefacts. This can provide information that would allow the classification of the hoard as being the result of an accumulative process of different objects, or if, on the contrary, it corresponds to a more specific production. At the same time, the compositional analysis would provide us with additional data in order to study the Freixanda hoard in the framework of the Late Bronze Age (LBA) metal productions in Portugal and, by extension, in the Iberian Peninsula and the so-called Atlantic Europe.

The Freixanda Hoard

The hoard was first described in 1970 by Brandão [3]. It was discovered by chance during agricultural works in a vineyard, some 500 m from the Nabão river. The location where the hoard was found does not have any particular geographical feature since it is on the slope of a gentle hillside, and no specific landmarks or containers for the multiple elements were identified.

It comprises 9 pieces (Fig.1, Table I): 4 double-looped socketed axes, a single-looped unifacial palstave, a dagger, a chisel, a pair of tongs and a melting lump, amounting for a total weight close to 4.4 kg. The pieces are complete, with three exceptions: one of the axes has its socket broken close to the rim, and is missing both loops as well; another axe is also missing one loop, and the dagger has its point broken. Several pieces show clear signs of use and appear worn or modified, like the dagger or the cutting edge of the socketed axe number 3. The most remarkable piece is the pair of tongs, of uncommon typology for this period and of exceptionally large size (28.1 cm long). The single looped unifacial palstaves have a geographical distribution concentrated essentially in the North and centre of Portugal, being absent from the neighbouring Spanish regions, and nevertheless appearing as a unique sample in the deposit of Monte Sa Idda in Sardinia. The occurrence of one in this hoard gives an element of local or regional production to the finding. The double looped socketed axes have different morphologies: two of them present a smooth body and the two others feature a double groove. These double looped socketed axes, which are predominant in the Portuguese area, are found as well in Galicia and also frequently appear in France and England.

Given the features described above, the deposit has been attributed to the smelters type [1], i.e. it is interpreted as metal collected by a caster craftsman to be used as raw material: there are worn pieces, with some cracks, and there is also a bulk of raw metal. Furthermore, the collection includes a pair of tongs which could very well be a tool for the metallurgical work.

Finally, the site has no apparent connection with ritual activities, and no contemporary site in the surrounding area is so far known.

2- PIXE ANALYSES OF THE BRONZES

The pieces were analysed at the CMAM Accelerator Laboratory of the Universidad Autónoma de Madrid, furnished with a 5 MV Cockcroft-Walton electrostatic accelerator [4,5]. One of the beam lines [4] is equipped with an Oxford quadrupole doublet and delivers the beam in air through a ultrafine Si_3N_4 (silicon nitride) window, 200 nanometre thick, in such a way that at four millimetre from the Si_3N_4 window, even if diffused in its travel through the air, the ion beam has a nearly Gaussian spatial distribution with a FWHM of 40-50 µm. Prior to the analyses the objects were cleaned in selected areas to remove the corrosion layer. Spot measurements were performed on the bronzes; no beam scanning was done. The X-rays were collected, quite traditionally, by two detectors located on either side at 45º from the sample surface. A 30 mm^2 Ge(Li) detector with helium flow in front and collimated to 1 mm diameter detected the low Z elements. A 80 mm^2 Si(Li) detector, with a 15 µm Co filter in front of it to attenuate the copper contribution to the detector energy spectrum, detected medium and high Z elements. A beam of 3MeV protons was used with currents around 3 nA and measurement times of 600 s. The PIXE spectra were processed with the GUPIX package [6], with the assumption that targets were thick and homogeneous. The list of samples with their measurements is given in Table I, together with the sample composition. The analytical procedure has been checked with the help of two bronze standards, and the results of the PIXE analysis reproduced very well the certified values, as seen in the example of Fig. 2.

Composition

All the pieces are made of a tin-bronze (Cu-Sn) alloy, with percentage over 10% Sn. Almost all of them can be classified as High Tin Bronzes, featuring percentages over 14% Sn, according to the average value of the two measurements carried out on each sample (Fig.3). The variability of the analytical results in different areas of a given piece is the result of the chosen conditions for the acquisition of data. During the cooling stage of the casting process in a mould, the Cu-Sn alloys generate distinct metallic phases with different proportions of tin, giving rise to the typical dendritic structures. This segregation can be reduced or eliminated through re-crystallization of the metal via an annealing heat-treatment, but if the alloy is too rich in Sn the formation of two different phases (alpha and delta) cannot be avoided, as the maximum solubility of Sn in Cu at the solid state is about 14-15%. Beyond this percentage, eutectic alloys are always found [7]. Because the PIXE analysis is performed in a very small area, it is very sensitive to this formation of segregations, a fact pointed out by Northover and Rychner [8] as occurring specially in Sn-rich bronzes, like the objects from the Freixanda hoard. The same phenomenon was described in the study of the LBA weapons hoard of Puertollano [9], which, as in our case, was also analysed in individual spots using a PIXE external beam with a 3 mm^2 area. Consequently, it is advisable to perform more than one analysis if the beam is small and the bronzes under scrutiny are rich in tin.

The only discordant objet from the general homogeneity in composition of the hoard is the pair of tongs, with a significantly lower content of tin (11.6%).

Impurities

Regarding impurities, it must be noted that the presence of elements other than the main alloy constituents is very scarce in the metal objects from the LBA in the Iberian Peninsula [10], in opposition with what happens in other Central European and Atlantic areas where, at some stages, As, Sb, Ag or Pb appear in excess of 0.5%, being able to reach even values over 1% [11, 12].

Following this trend, the high purity of the metals from the Freixanda hoard is characteristic. The impurity model distinguishes itself by the presence of Pb, Ni and As in the majority of the pieces, while Fe and Sb appear only sporadically. In no case have been Zn and Co detected. The only object where the sum of all the minor elements exceeds 0,5% in weight is the knife, but never reaching 1% and on account of a higher content in As for this piece, compared with the axes (Fig.4). The other object that steers away from the typical values for this hoard is the pair of tongs, but this time because the purity of the metal is higher due to the absence of As, Ag and Pb. In this case, the only element detected as an impurity has been Ni.

It is worth mentioning that the Fe impurities are extremely low. In the majority of pieces it is below the detection limit, suggesting a metallurgy that would precede the technological change in the furnaces introduced by the Phoenician colonization in the Peninsular South [13]. As explained by Craddock and Meeks [14], a low amount of Fe impurities is a distinctive trait of a primitive metallurgical technology, without formation of slag.

The melting lump

Its composition and shape prevent its classification as a fragment of ingot, which are of plano-convex section and usually made of copper. The elongated shape of the lump, with a narrowing towards one end, as well as its width and thickness, suggest that it could be a scrap of metal, the consequence of an unsuccessful cast in a mould. Its weight of 173g is clearly insufficient for an axe or a chisel, but it could be adequate for the dimensions of a knife. As it is a full-formed alloy, a plausible option would be that of a metallic mass created by the re-melting of scraps or objects. One of the consequences of the re-melting of such a metal is a reduction of the volatile impurities (As, Sb, Pb, Zn) while the concentration of Ni and Ag remains stable [15]. There is also a small loss of the alloyed tin [16].

Although in our particular case we can't really know what the original metal was, assuming rough features similar to those of the other metallic elements of the hoard, it can be noticed that the metallic lump lies in the lower part of the scale for concentration of impurities, specially regarding As and Pb, whereas regarding Ni and Ag it stands in an intermediate-high position (Fig. 4). Additionally, its percentage of tin is lower than the average for the rest of the hoard, although it must be noted that in this particular case only one analysis was performed on the piece, thus the possibility of the existence of metallic phases richer in tin can't be discarded until results of the metallographic study are available. Therefore, given its composition and morphology, it seems only plausible to assume that this piece of metal was obtained through a process of re-melting of bronze objects.

3- COMPARISON WITH THE COLES DE SAMUEL HOARD.

There are not many elemental analyses of Portuguese hoards that could be used as a comparative tool, but, fortunately, the Coles de Samuel hoard, which contains a number of objects similar to those found in Freixanda, was studied some time ago [17] using Optical Emission Spectroscopy. This hoard, as in the case of Freixanda, included 4 double-looped socketed axes, a single-looped unifacial palstave and a chisel, in addition of 6 sickles and 6 open armrings [1]. Barring the differences between the analytical techniques and the precision of the results, a general comparative study can be performed between the materials with a similar typology.

With the exception of a socketed axe featuring higher levels of concentration of As and Pb impurities, amounting to 1.3% in weight, both collections of materials show similar characteristics, all of them being tin-bronzes with a tendency towards high values of Sn (>12%). The only significant difference is the average value of Sn, being lower in the Coles de Samuel hoard (12.5%) compared with the Freixanda (13.9%), but in agreement with the values obtained for the metallurgy of Baioes (13 ± 0.3% Sn) [10]. These differences can be attributed to the different analytical techniques used.

4- CONCLUSIONS

The typology of the objects contained in the Freixanda hoard suggests that we stand in front of a recollection of artefacts manufactured inside the boundaries of a specific geographical area, with no elements that can be considered exotic or foreign. The compositional analyses validate the hypothesis of local productions with low concentrations of impurities, typical for the Portuguese and Spanish LBA, in contrast with the productions from other Atlantic regions. On this regard, the Freixanda hoard features a manufacturing technology similar to that of the contemporary hoard of Coles de Samuel, also in Portugal. Despite the relative compositional homogeneity, it is possible to single out the pair of tongs, which would be a tool of the metalworker, from the rest of the collection, which would be considered as the metal cache of a founder´s hoard. The amount of wear and tear of the material, as well as the broken parts, together with the presence of a metallic mass that could be the result of metal recycling would support this interpretation. Furthermore the location of the finding, in an unremarkable location and without traces of ritual use, would point in the same direction. The absence of Pb as a constituent of the alloy and the low levels of Fe impurities indicate a metallurgical technology previous to the Phoenician influence in the Iberian Peninsula.

References

[1] R. Vilaça, Depósitos de bronze do território português. Um debate em aberto, Conimbriga anexos 5 (2007) 1-148.

[2] S. Needham, When expediency broaches ritual intention: the flow of metal between systemic and buried domains, J. Roy. Anthrop. Inst. 7-2 (2001) 275-298.

[3] D.P. Brandão, Achados de cobre e de bronze na regiao de Leiria, O Arqueólogo Portugês IV 324.

[4] O. Enguita, M.T. Fernández-Jiménez, G. García, A. Climent-Font, T. Calderón and G.W. Grime, The new external microbeam facility at the 5 MV Tandetron accelerator laboratory in Madrid: beam characterisation and first results, Nucl. Instr. Meth. B 219-220 (2004) 384-388

[5] A. Climent-Font, F. Pászti, G. García, M.T. Fernández-Jiménez and F. Agulló, First Measurements with the Madrid 5MV Tandem Accelerator, Nucl. Instr. Meth. B 219-220 (2004) 400-404.

[6] J. L. Campbell, T.L. Hopman, J.A. Maxwell and Z.Nejedly, The Guelph PIXE software package III: Alternative proton database, Nucl. Instr. Meth. B 170 (2000) 193-204.

[7] R.F. Tylecote y J.P. Northover: Metallographic study, in The Petters Late Bronze Age Metalwork, ed. by S.P. Needham (British Museum Occasional Paper 70, 1990) 89-97.

[8] P. Northover, V. Rychner: Bronze Analysis: experience of a comparative programme, In L´atelier du bronzier en Europe du XX au VIII siécle avant notre ère. Actes du colloque international Bronze´96 Neuchâtel et Dijon, I ed. by C. Mordant, M. Pernot, V. Rychner (Paris, CTHS 1998) 19-40.

[9] I. Montero, M. Fernández, B. Gómez and Mª A. Ontalba, Espadas y Puñales del Bronce Final: el depósito de armas de Puertollano (Ciudad Real), Gladius XXII (2002) 5- 28.

[10] Elin Figueiredo, R.J.C. Silva, J. C. Senna-Martinez, M. Fatima Araujo, F.M. Braz Fernandes and J. L. Ines Vaz, Smelting and recycling evidences from the Late Bronze Age habitat site of Baio˜es (Viseu, Portugal), Journal of Archaeological Science 37 (2010) 1623-1634.

[11] P. Northover, The metallurgy of the Wilburton hoards, Oxford Journal of Archaeology 1-1 (1982) 69-109.

[12] B. Rohl and S. Needham, The circulation of metal in the British Bronze Age: the application of lead isotope analysis (British Museum Occasional Paper 102, 1998).

[13] A. Orejas and I. Montero: Colonizaciones, minería y metalurgia prerromanas en el levante y sur peninsulares, Treballs del Museu Arqueològic d´Eivissa i Formentera 47 (2001) 121-159.

[14] P.T. Craddock and, N.D. Meeks, Iron in ancient copper, *Archaeometry*, 29-2 (1987) 187-204.

[15] R. F. Tylecote, H. A. Ghaznavi and P. J. Boydell. Partitioning of trace elements between the ores, fluxes, slags and metal during the smelting of copper, Journal of Archaeological Science, 4 (1977) 305-333.

[16] S. Rovira and I. Montero, Natural tin-bronze alloy in Iberian Peninsula metallurgy: potentiality and reality, in, *The problem of Early Tin*. Acts of the XIVth UISPP Congress Liege (2-8 september 2001) ed. by A. Giumlia-Mair and F. Lo Schiavo (BAR Int. Series 1199, 2003) 15-22.

[17] A. Coffyn, Le Bronze Final Atlantique dans la Péninsule Ibérique (Diffusion de Boccard, Paris 1985).

Figure Captions

Figure 1. The collection of metal objects found on the site of Freixanda (Portugal).

Figure 2. Results of PIXE analyses of a bronze standard compared to the certified values.

Figure 3. Stack plot for the major components, Cu and Sn, of the Freixanda artefacts. Labels on the X-axis are references explained in Table I.

Figure 4. Stack plot for the trace components, Fe, Ni, As, Ag, Sb and Pb, of the Freixanda artefacts. Labels on the X-axis are references explained in Table I.

Table Captions

Table I. List of results for the PIXE measurements performed on the Freixanda objects, including reference codes for the figures and the elemental concentrations.

Table II. Results of compositional analyses of the Freixanda artefacts compared with the results from similar objects from the site of Coles de Samuel. The number of valid measurements for each element is indicated (Valid N).

Table I

Object	**Measuring spot**	**Code**	**Cu [%]**	**Sn [%]**	**Fe [%]**	**Ni [%]**	**As [%]**	**Ag [%]**	**Sb [%]**	**Pb [%]**
Socketed axe # 1	Edge	ax1e	84.55	14.97		0.048	0.100	0.074	0.073	0.186
	Butt	ax1b	83.25	16.11		0.033	0.127	0.139		0.345
Socketed axe # 2	Edge	ax2e	85.07	14.83		0.060		0.037		
	Butt	ax2b	85.32	14.48	0.061	0.043	0.038	0.037		
Socketed axe # 3	Side	ax3s	86.39	13.30		0.050	0.118	0.037	0.048	0.060
	Side Edge	ax3se	86.88	12.75	0.016	0.054	0.121	0.046	0.058	0.081
Socketed axe # 4	Edge	ax4e	85.80	13.77	0.016	0.048	0.134	0.050	0.055	0.123
	Crack	ax4c	83.78	15.90		0.057	0.124	0.047		0.097
Palstave	Edge	pse	86.34	13.29		0.057	0.193	0.036		0.083
	Butt	psb	86.39	13.16		0.050	0.160	0.087	0.071	0.075
Chisel	Body	csbd	83.52	16.08		0.057	0.116	0.096		0.130
	Butt	csbt	86.46	13.13		0.061	0.163	0.034	0.055	0.102
Tongs	Ring	tgr	88.40	11.58		0.019				
Dagger	Point	dgp	87.32	12.04	0.067	0.038	0.311	0.045		0.179
	Handle	dgh	83.99	15.14		0.038	0.519	0.065	0.058	0.197
Melting Lump	Body	mlp	86.79	12.89		0.049	0.036	0.075	0.086	0.075

Table II

	Freixanda			**Coles de Samuel**		
Element	*Valid N*	*Mean*	*St. Dev.*	*Valid N*	*Mean*	*St. Dev.*
Fe	4	0.040	0.027	0		
Co	0			0		
Ni	16	0.048	0.011	6	0.026	0.017
Cu	16	85.64	1.50	6	85.07	1.91
Zn	0			5	0.007	0.008
As	14	0.162	0.122	6	0.317	0.340
Ag	15	0.060	0.030	6	0.042	0.012
Sn	16	13.96	1.43	6	12.47	1.33
Sb	8	0.063	0.012	6	0.053	0.023
Pb	13	0.133	0.078	6	0.163	0.264


0 1 2 3 4 5 6 7 8 9 10
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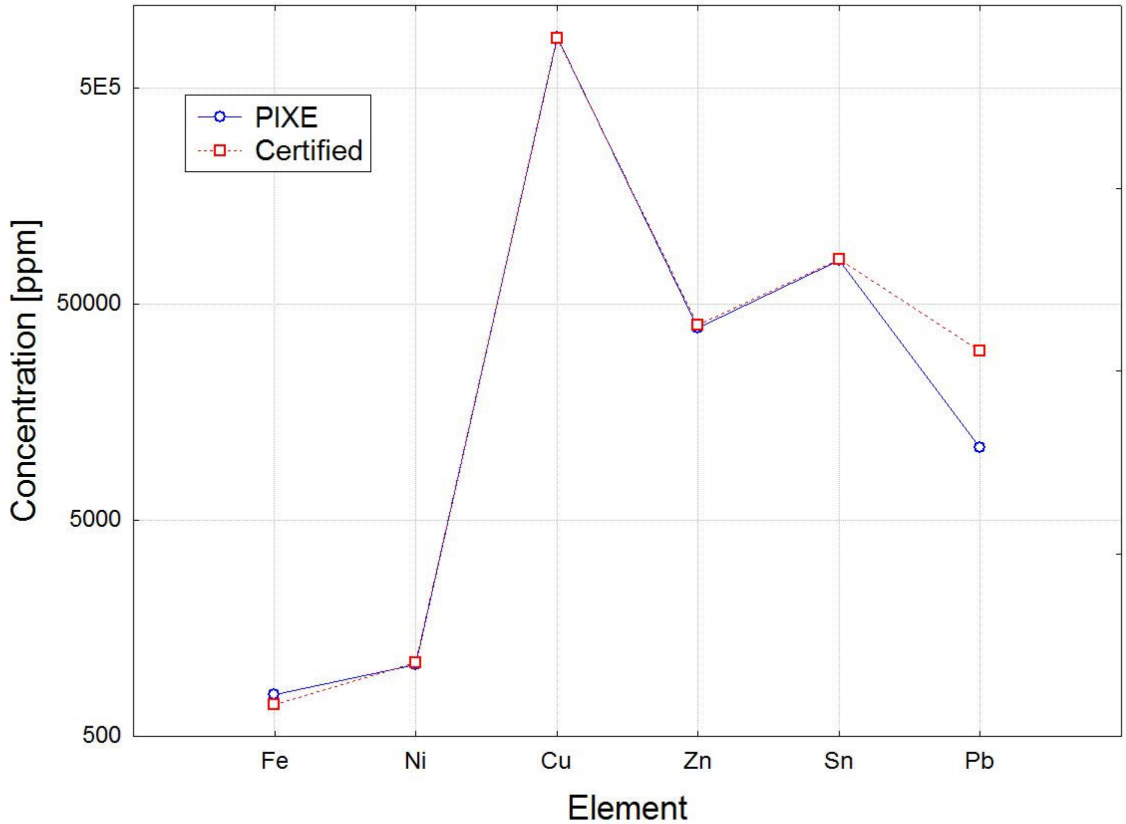
FIGURE 1



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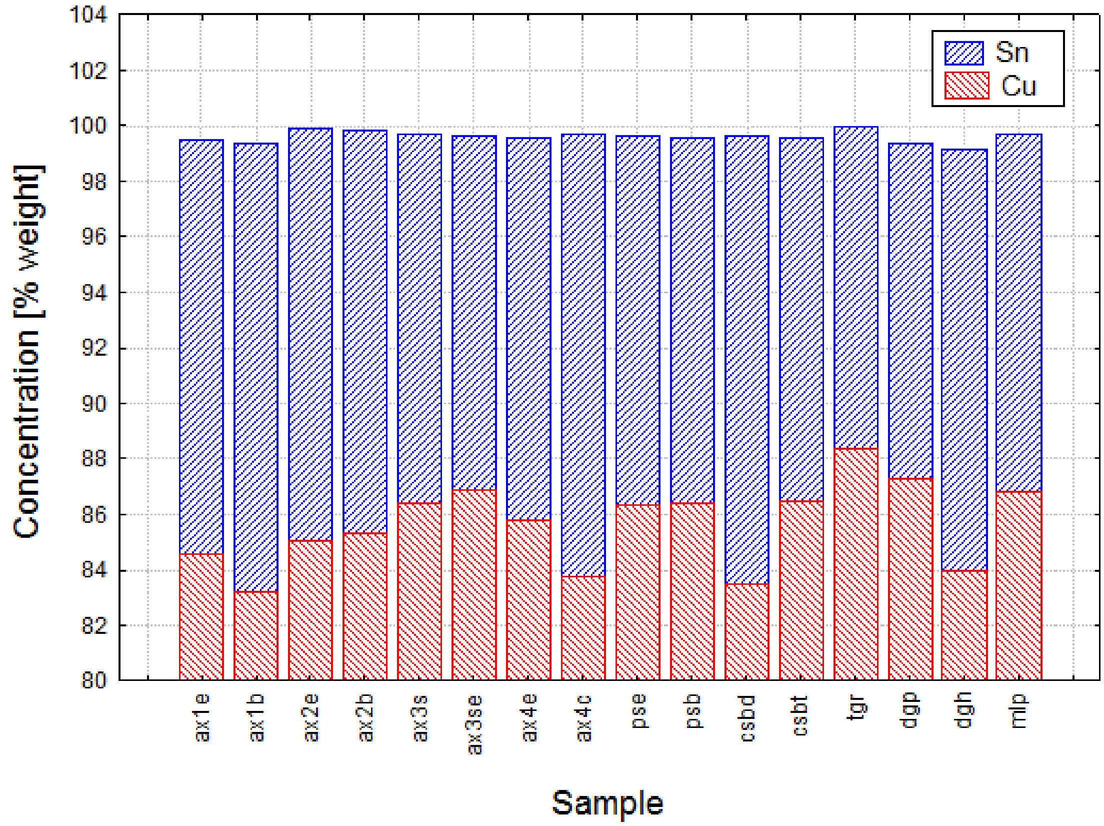
PIXE
Certified
Concentration [ppm]
Fe
Ni
Cu
Zn
Sn
Pb
Element

FIGURE 2



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90
88
86
84
82
80
Concentration [% weight]
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Cu
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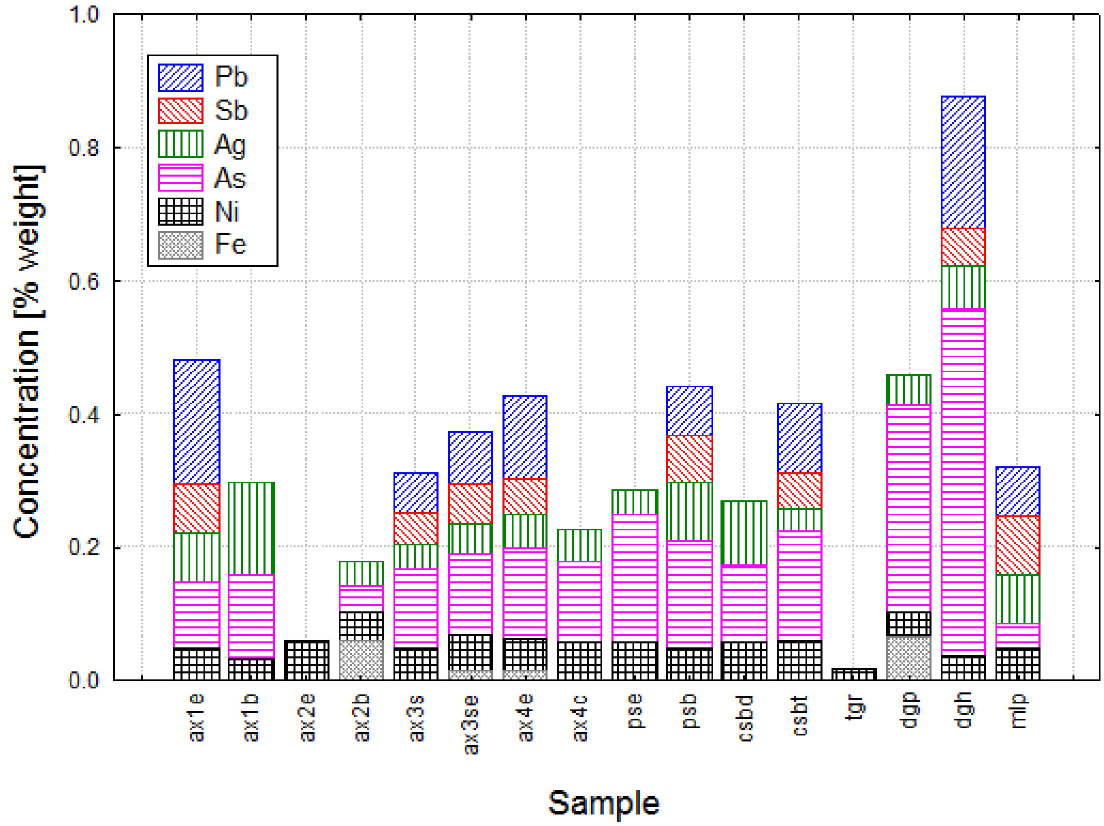
ax1b
ax2e
ax2b
ax3s
ax3se
ax4e
ax4c
pse
psb
csbd
csbt
tgr
dgp
dgh
mlp
Sample

FIGURE 3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0.6
0.4
0.2
0.0
Pb
Sb
Ag
As
Ni
Fe
ax1e
ax1b
ax2e
ax2b
ax3s
ax3se
ax4e
ax4c
pse
psb
csbd
csbt
tgr
dgp
dgh
mlp
Sample

FIGURE 4

Keywords : Micro-PIXE, Metallurgy, Bronzes