PORTABLE X-RAY FLUORESCENCE INVESTIGATION OF CERTAIN BRONZE BEADS OF HOARD TĂRTĂRIA I AND THEIR SPECIFIC CORROSION

R. RADVAN[1], C. BORS[2], L. GHERVASE[1,*]

[1]National Institute of Research and Development for Optoelectronics INOE 2000,
409 Atomistilor St., Magurele, Ilfov County, Romania,
E-mail: radvan@inoe.ro
[*]*Corresponding author e-mail*: ghervase@inoe.ro
[2]National History Museum, 12 Calea Victoriei St., Bucharest, Romania
E-mail: corina.bors73@gmail.com

The paper presents a characterization of certain prehistoric bronze artefacts, part of Tărtăria I hoard (Alba County, Romania), using X-ray fluorescence spectroscopy. Results indicated copper high input at the objects' surface, in green-looking areas, as a consequence of corrosion processes, while darker, brown-looking areas had higher iron levels.

Key words: x-ray fluorescence, bronze alloys, corrosion.

1. INTRODUCTION

In 2012, the construction works of the A1 motorway along the Mureş River valley, Romania led to the discovery and investigation of a new prehistoric site at Tărtăria – *Podu Tărtăriei west*. The archaeological discoveries made here indicate the existence of an important prehistoric habitat characterised by a large quantity of pottery typical for the Basarabi style [1], as well as by a large number of metal objects. In this context, a series of special findings were made, the main ones being two prehistoric metal hoards (named Tărtăria I and Tărtăria II) comprising hundreds of bronze and iron objects. The prehistoric hoard of metal (bronze and iron) objects named Tărtăria I is the largest and most complex find of the Ha B$_3$–C (9th–8th c. BC) period or the so-called Bâlvăneşti-Vinţ series among the discoveries known up to now in Romania, Hungary and Serbia [1]. Ternary alloys of copper with tin and lead were the most often encountered within ancient Europe starting from the Bronze Age [2] until the discovery and use of iron in Europe and on nowadays Romania's territory [3]. Generally speaking, the first Iron Age is characterized by the intrusion of iron in the manufacturing of objects, in detriment of copper alloys.

Several analysis techniques, such as X-ray fluorescence spectroscopy (XRF) [4], Raman spectroscopy [5], laser-induced breakdown spectroscopy (LIBS) [6] are commonly employed in order to evaluate archaeological findings. Due to its non-destructive character, XRF has been widely used in archaeological studies in the recent years, offering qualitative and quantitative information [7–9]. The development of hand-held x-ray fluorescence equipment was a major breakthrough in the field of art and archaeology investigations, allowing *in situ* investigations [10, 11].

Prehistoric and ancient bronzes, buried for a long time in soil, can exhibit different corrosion processes, such as thin corrosion layers or even completely corroded and mineralized objects [12]. Although the terms "patina" and "corrosion" represent the same alteration of the surface of an object, patina generally refers to a smooth, continuous layer which follows the shape of the object, whereas a corrosion layer refers to mineral deposits which do not make up a smooth and uniform layer [13]. Elemental variability, as indicated through XRF, can only be discussed in qualitative terms in the case of objects with patina [14], but yet can provide useful information for researchers, in order to assess surface damage and evaluate the state of preservation of historical bronze objects. Moreover, as stated by Pardini and his co-workers [15], the analysis of the bulk metal and corrosion patina can infer information regarding the origin and dating of an object.

The aim of the paper was to chemically evaluate the corrosion layer of several objects made of ternary bronze alloys by means of X-ray fluorescence spectrometry. The importance of the study comes from the possible information obtained through x-ray fluorescence spectroscopy related to the manufacturing method.

2. MATERIALS AND METHOD

Five bronze objects were included in the study (Fig. 1): three simple beads (preliminary inventory no. 3354, 12223, 12202), a bitronconic bead (preliminary inventory no. 12216) and a group of four "welded" beads (preliminary inventory no. 12230). The beads were not treated in any way and had a highly inhomogeneous surface corrosion layer of variable colors and thickness.

Qualitative XRF analysis was performed using S1 TRACER III-SD energy-dispersive equipment from Bruker Elemental (Germany). The spectrometer is a hand-held unit which incorporates an Rh anticathode, capable of generating maximum 40 kV, 30 μA, 3 W. The parameters set for this study were 40 kV

voltage and 10.60 µA current intensity, 60 s acquisition time. The instrument has a Si drift detector and spot size of 3×4 mm. The spectra were acquired using the S1 PXRF S1 Mode software (Bruker AXS Handheld Inc.) and then processed with Spectra (Artax version 7.4.0.0, Bruker AXS MA). Evaluation of the results was performed based on comparison of raw spectra and net peak count rates. Two measurements were performed for each sample, as indicated in Fig. 1 (white dots): points 3354-1, 12223-1, 12202-1, 12216-1, 12230-1 were in green-looking or light colored areas, while 3354-2, 12223-2, 12202-2, 12216-2, 12230-2 spectra were acquired in darker, brown areas of the objects. The presented results are qualitative, because a quantitative assessment would have required homogenous samples, with flat surfaces. This is not the case for the objects investigated here, which had a visible corrosion layer, of varying thickness, on the surface.
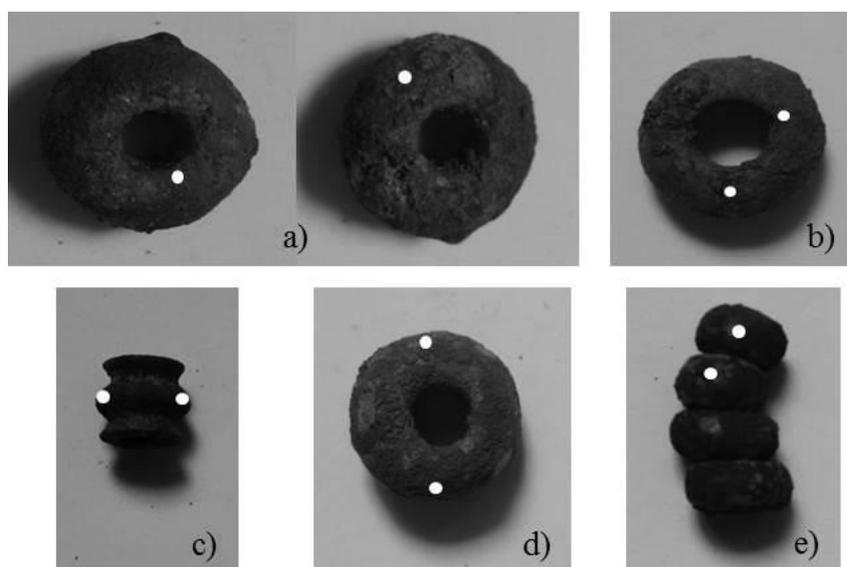

Fig. 1 – Investigated bronze beads: a) object 3354; b) object 12223; c) object 12202; d) object 12216; e) object (group of four "welded" beads) 12230.

3. RESULTS AND DISCUSSION

The recorded XRF spectra of all objects (Fig. 2) suggest that the investigated objects could be a ternary alloy of Cu-Sn-Pb, with various minor and trace elements. All objects had Cu (major), Fe (minor), Sn, Pb, Ag, Sb, Ti, Si (trace) and some minor traces of Al, P, S, P, Ca, Cr, Mn, Au, As.
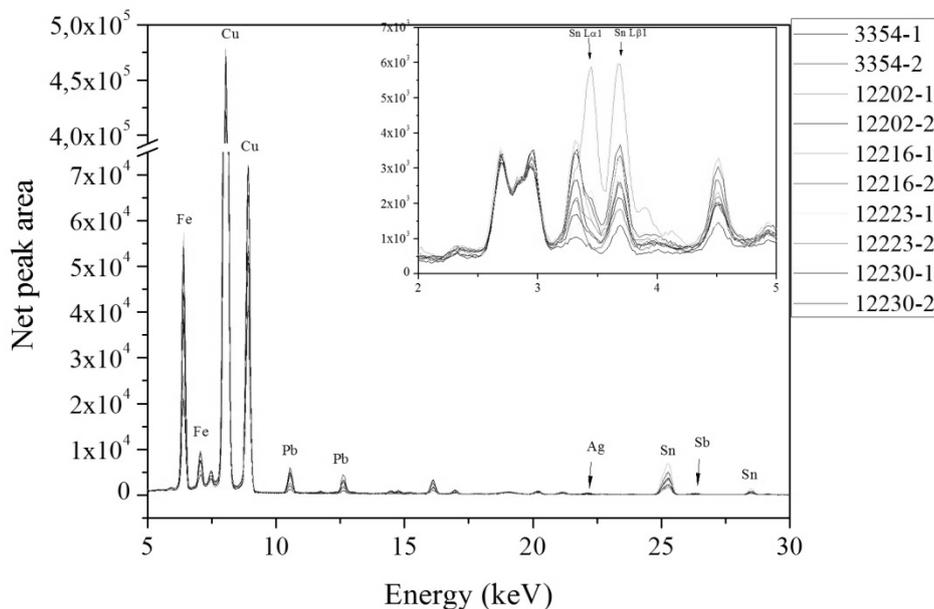
Fig. 2 – XRF spectra of analyzed bronze artefacts.

Figure 3 shows the net peak areas of the main elements found in the objects, normalized with respect to the Rh K_α line of each object. Normalization of the spectra was performed so as to better compare the results and eliminate some of the uncertainty associated with matrix effects. The graphs show important variability both inter- and intra-object, signaling the great influence of the corrosion layer.

In the case of Cu, it appears that measurements taken in green areas (3354-1, 12202-1, 12230-1) had higher intensity than those collected from brown, dark-colored areas from the same samples (3354-2, 12202-2 and 12230-2, respectively). Several literature studies report the formation of copper corrosion products in the case of bronze objects which have been buried in the ground for a long time [12, 14]. These corrosion products can be influenced by the characteristics of the soil. For example, the types of soil, the oxygenation, the moisture level, the groundwater are factors which can induce severe corrosion processes [13]. Thus, the higher Cu intensities found in green areas can be linked not only with the copper from the bronze alloy but also from the copper-based corrosion products, created by decuprification, the shift of the base metals to primary or secondary chemical compounds, such as oxide, carbonates or chloride [16]. Such by-products have different influence on the aspect of the patina: CuO and SnO_2 yield a darker, black

color, Cu_2O gives the corrosion layer a dark brown aspect, while $Cu(OH)_2$ gives a blue-green look [17]. Visual inspection of the beads can suggest that several such oxides could be present at the surface of the beads, as they show both brownish and blue-green areas.

Some of the analyzed spots (3354-2, 12223-1, 12223-2, 12202-1, 12230-2) displayed obvious Sn $L\alpha$ lines. This could mean that for these areas, the tin response also comes from the surface of the objects, which supports the presumption of tin oxides formation in the surface corrosion layer.

In turn, for the areas which had a brown appearance, higher intensities of the Fe lines were detected. High levels of iron can also be related to post-depositional processes due to the soil features, as inferred by Fernandes and co-workers [18]. They studied both corroded and uncorroded bronze alloys and suggested that clay minerals such as illite, could be the source of high iron levels. Another additional source of iron increase could be, according to [19] the selective increase of some elements (such as Fe, Al, Si, Ca or Na) as a result of corrosion processes in copper artefacts. The XRF spectra also indicated that areas with higher Fe content also had higher Si and Ti levels, probably from terrigenous sources. However, the presence of iron with such high intensity might suggest the use of combined iron and bronze in the manufacturing of the objects. This idea can be sustained by literature studies attesting the existence of iron-core objects covered by bronze, such as the wheels of the votive chariot from Bujoru [20] or a series of brooches found in deposits of the Bâlvăneşti-Vinţ series [21].
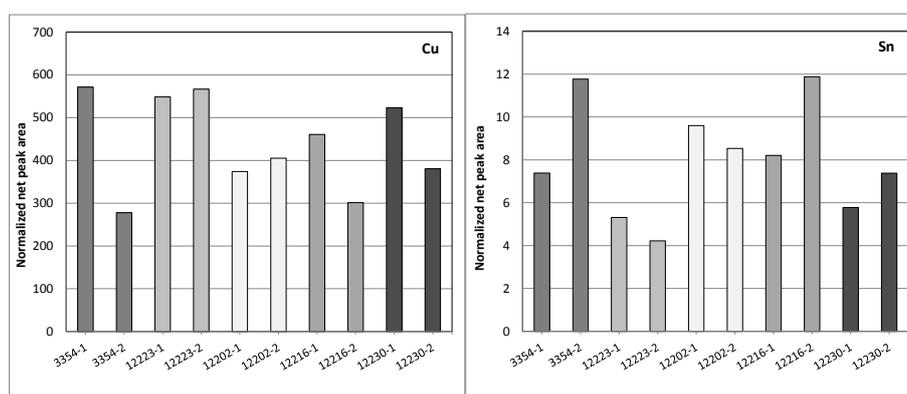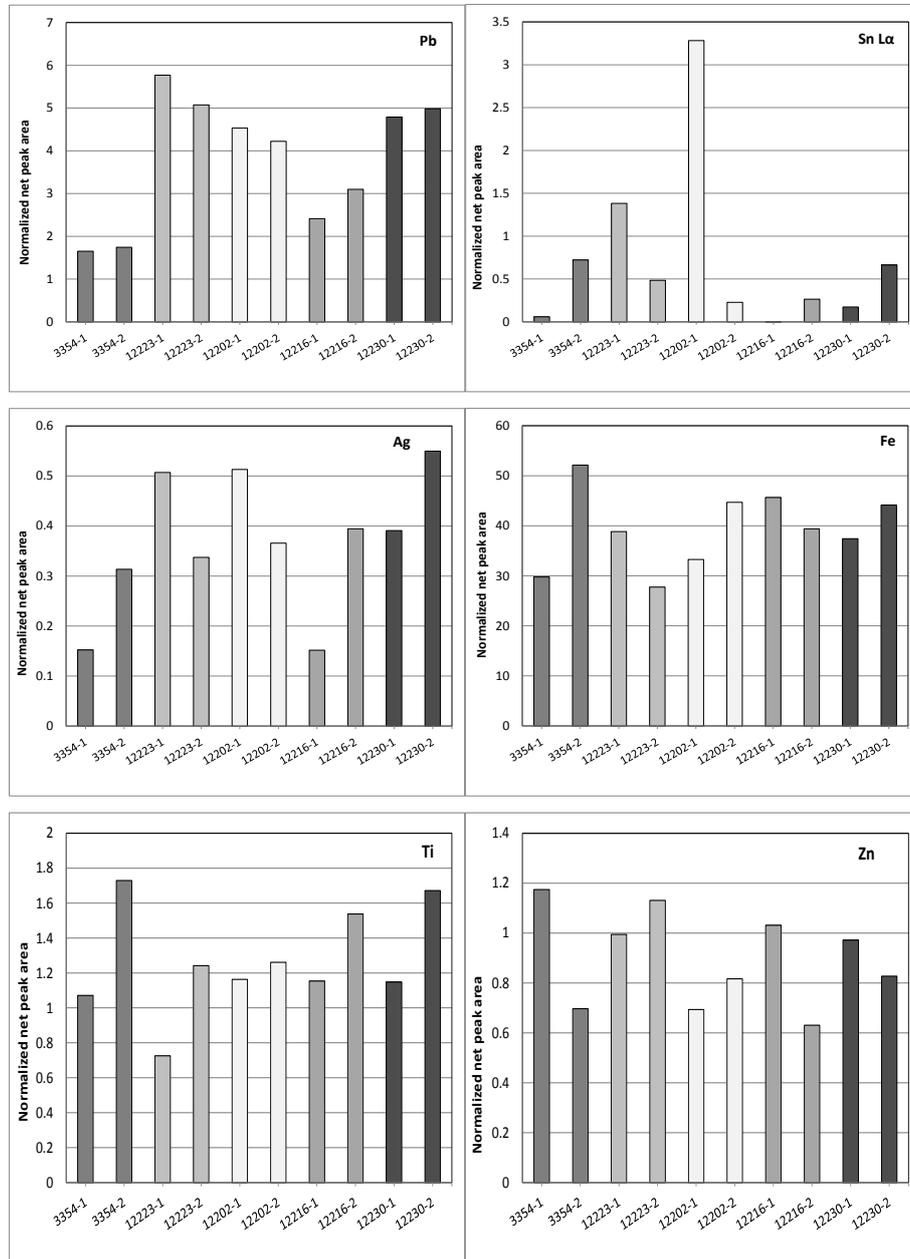

Fig. 3

Fig. 3 (continued) – Normalized net count rates plot
of the main elements detected in the samples.

No apparent correlation could be evidenced between copper and iron intensities, possibly due to the fact that the detected intensities are influenced by the degradation products created at the surface of the objects but also due to additional Fe input from soil and from the neighboring iron-made objects.

XRF data can be further processed to obtain peak ratios, which can help on identifying the layer from which the signal of a certain element comes from. Usually, lower energy characteristic x-rays of an element are more absorbed than its higher energy lines. This means that the Kα line of Cu will be more absorbed than its Kβ line when copper is located deeper within the object. Similarly, lower energy x-rays, such as Pb Mα or Sn Mα are more absorbed than the Pb L α or Sn L α lines, which will be harder to identify if they do not arise from the surface of the object. Moreover, in the case of objects which have clean surfaces, not affected by corrosion/ patina, this approach can be used to identify from which layer comes the characteristic emission of certain elements. Table 1 lists the peak ratios calculated for copper, lead, tin and silver net count rates, as derived from the spectra. The Cu Kα/Kβ ratio showed lower values for the dark, brown-looking areas, which confirm the copper-enrichment in blue-green areas. Lead and tin ratios varied, some of the object showing surface enrichment in lead or tin, while others not. Other authors have also noticed a similar behavior of copper artefacts, which showed relative enrichment or depletion of the major elements, such as Cu, Zn, Pb or Sn [18].

Table 1

Peak ratios of selected elements

Object	Cu Kα/Cu Kβ	Pb Mα/Pb L α	Sn Mα/Sn L α
3354-1	6.415	0.040	0.006
3354-2	6.084	0.038	0.021
12223-1	6.421	0.019	0.075
12223-2	6.318	0.022	0.037
12202-1	6.199	0.018	0.097
12202-2	6.246	0.008	0.011
12216-2	6.201	0.020	–
12216-1	6.194	0.010	0.009
12230-12233-3	6.286	0.014	0.011
12230-12233-4	6.121	0.012	0.031

Results showed great inter and intra-object variability, which can be explained through the important contribution of the natural occurring corrosion processes, altering the surface of the object in a non-uniform manner.

4. CONCLUSIONS

Several beads from the Tărtăria I hoard discovered at Tărtăria–Podu Tărtăriei west site (Alba County), in Romania, were investigated by means of X-ray fluorescence spectroscopy during this study. Results showed a very inhomogeneous response in terms of elemental intensity, from sample to sample, but also within the same object. This response is due to the varying thickness and composition of the corrosion layer created at the surface of the objects. The study reinforces the knowledge regarding the presumed age of the deposit and the manufacturing method of these particular objects, proof of the mixture of iron and bronze at this particular age. Further work should be focused on the comparative evaluation of both corroded and non-corroded objects, so as to clearly differentiate the elements coming from the object from the elements which appear as a consequence of the natural degradation processes occurring during the time the objects is buried in the ground.

REFERENCES

1. C. Borş, L. Irimuş, V. Rumega, S. Dobrotă, C. Rişcuţa, Cercetări Arheologice, **20**, 9-102 (2013).
2. D.A. Scott, *Leaded Bronzes and other Ternary Alloys, in: Ancient Metals: Microstructure and Metallurgy*, vol. 1, Conservation Science Press, Los Angeles, California, 2010.
3. A. László, *Prima epocă a fierului*, in *Istoria Românilor. Moştenirea timpurilor îndepărtate*, vol. 1, Editura Enciclopedică, Bucureşti, 294-326 (2001).
4. A.M.W. Hunt and R.J. Speakman, J. Archaeol. Sci., **53**, 626-638 (2015).
5. M. Sepúlveda, S. Gutiérrez, M Campos Vallette, V. G. Standen, B. T. Arriaza, J.J. Cárcamo-Vega, Heritage Science, **3** (2015).
6. H. Sadek, A. Khedr, M. Simileanu and R. Radvan, Dig. J. Nanomater. Biostruct. **8**, 1357-1363 (2013).
7. M. Mantler and M. Schreiner, X-ray Spectrom., **29**, 3-17 (2000).
8. A.E. Pillay, C. Punyadeera, L. Jacobson and J. Eriksen, X-ray Spectrom., **29**, 53-62 (2000).
9. N. Forster, P. Grave, N. Vickery and L. Kealhofer, X-ray Spectrom., **40**, 389-398 (2011).
10. L. Pappalardo, A.G. Karydas, N. Kotzmani, G. Pappalardo, F.P. Romano and Ch. Zarkadas, Nucl. Instrum. Meth. B, **239**, 114-121 (2005).
11. A. Arafat, M. Na'es, V. Kantarelou, N. Haddad, A. Giakoumaki, V. Argyropoulos, D. Anglos and A.-G. Karydas, J. Cult. Herit., **14**, 261-269 (2013)
12. O. Oudbashi, S.M. Emami, H. Ahmadi, P. Davami, Heritage Science, **1** (2013).
13. D.A. Scott, *Copper and bronze: Corrosion, colorants, conservation*, Getty Publications (2002).
14. P. Colomban, A. Tournié, M. Maucuer and P. Meynard, J. Raman. Spectrosc. **43**, 799-808 (2012).
15. L. Pardini. A. El Hassan, M. Ferretti, A. Foresta, S. Legnaioli, G. Lorenzetti, E. Nebbia, F. Catalli, M.A. Harith, D. Diaz Pace, F. Anabitarte Garcia, M. Scuotto and V. Palleschi, Spectrochim. Acta B, **75-76**, 156-161 (2012).

16. O. Mircea, I. Sandu, V. Vasilache and I.G. Sandu, International Journal of Conservation Science, **3**, 179-188 (2012).
17. G. Arghir, NOEMA. **XI**, 495-513 (2012).
18. R. Fernandes, B.J.H.van Os and H.D.J.Huisman, Heritage Science, **1** (2013).
19. A. Galli, L. Bonizzoni, E. Sibilia and M. Martini, X-ray Spectrom. **40**, 74-78 (2011).
20. E. Moscalu, C. Beda, *Ein Grabhügel der Basarabi-Kultur mit Votivkesselwagen aus Rumänien*, Prähistorische Zeitschrift, **66**, 197–218 (1991).
21. I.A. Aldea and H.I. Ciugudean, *Der dritte hallstattzeitliche Depotfund von Vinţu de Jos*, in T. Soroceanu (Hrsg.), *Bronzefunde aus Rumänien*, Berlin, 213–224 (1995).