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INTEGRATED ANALYTICAL STUDY FOR THE SOMES METALIC ARTEFACT DISCOVERI IN IBIDA SITE, ROMANIA

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ABSTRACT

The paper presents the results of the analyses conducted using the SEM-EDX and micro-FTIR co-assisted techniques, on several metallic artefacts unearthed during the excavations at the (L)Ibida archaeological site in Slava Rusă, Tulcea County, Romania, that took place between 2001 and 2008. The data produced is of use in identifying several archaeometrical structural and compositional features which allow for the identification of the origin of the ores, of the alloy type, and of the manufacturing technology. A series of new data is thus produced, that can consolidate the three databases of scientific conservation of metallic artefacts (i-archaeometallurgy/archaeometry/historiography, ii-museum exhibiting, iii-itinerate/transfer/exchange/trade).

KEYWORDS: metal, SEM-EDX, micro-FTIR, archaeology

1. Introduction

The investigation of metallic artefacts requires a close collaboration between specialists from various domains of study: archaeology, history, chemistry, physics, metallurgy, geology, etc. They seek to establish: the nature of the material, the manner of processing the raw material, the manufacturing of the object itself, the subsequent preserving and restoring activities the object underwent.

To these purposes, they most often employ interdisciplinary methods of analysis, such as optical microscopy, scanning electron microscopy (SEM) alongside an EDX detector, micro-FTIR, calorimetry by reflexion, etc. [1].

The present study will provide the results of the SEM-EDX and micro-FTIR analyses performed on several objects discovered during the excavation conducted between 2001 and 2008 at the *(L)Ibida* archaeological site from Slava Rusă, Tulcea County, Romania.

As with any valuable cultural heritage asset, metallic artefacts can "travel", from the manufacturer who created them to the museum which exhibits them, by one of the following routes:

- Normal route of artworks, with a range of specific contexts (creation, acquisition, classification, display, preservation/ restoration, etc.);

- abandonment route, with contexts of creation, acquisition, use, loss of use functions, abandonment, archaeological discovery, preservation/restoration, ranking, showdown, etc.;

- concealment and oblivion route (especially for hoards), with contexts of creation, acquisition, use, loss of use functions, abandonment, archaeological discovery, preservation/restoration, display etc.;

- route through theft, with contexts of creation, acquisition, use, loss of use functions, abandonment, archaeological discovery, preservation/restoration, display or reuse etc.;

- route through falsification, reproduction/ copying, destruction, etc. with contexts of creation, acquisition, use, unlawful/illegal activities and their discovery, recovery of heritage functions, reintegration by display setup;

- route by disaster (earthquake, flood, fire, volcanic eruption, landslide, crash, etc.), with contexts of creation, acquisition, use, loss of use functions, abandonment, archaeological discovery, preservation/ restoration, display;

- Route by plagues (cholera, health disasters etc.), with contexts of creation, acquisition, use, loss of use functions, abandonment, archaeological discovery, preservation/restoration, display;

Some routes may modify a series of heritage elements (patina, share value, conservation status, etc.) as well as the main heritage function, the aesthetic and artistic.

An outline of areas of interest, the purpose of conservation and scientific activities integrated bronze artefacts in accordance with codes of ethics, is shown in Figure 1.

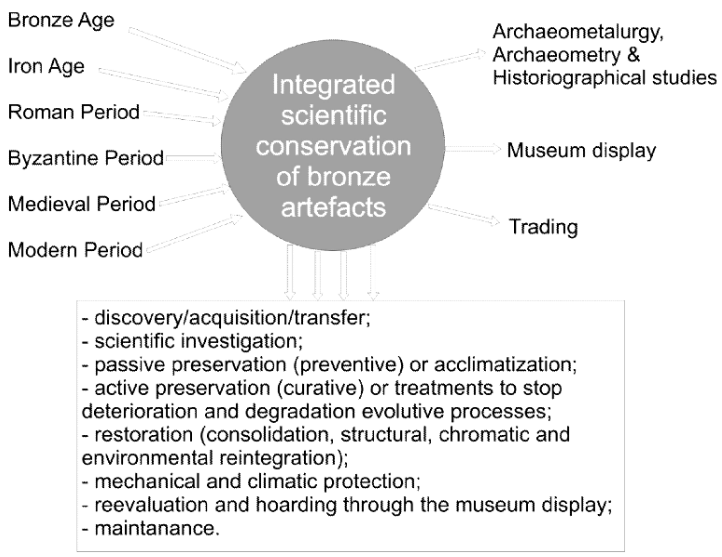

Fig. 1. *Scheme of the areas of interest (left), goals (right) and specific integrated scientific conservation activities (bottom) of ancient bronze artefacts*

For the value of a piece of bronze coming from archaeological sites there are some basic steps to be followed, namely [1, 2, 3]:

-excavation;

-cleaning;

-scientific investigation;

-the coherent reconstruction of the shape from fragments;

-completion of form and ornament;

-mechanical and climatic protection by coating;

-display and maintenance.

Depending on the circumstances and purposes, these steps may be detailed or developed with other activities or interventions.

2. Materials and methods

The artefacts selected for investigation have been discovered by the specialists from the Institute of Eco-Museal Research in Tulcea, the Institute of Archaeology in Iasi, and the Institute of Anthropology in Bucharest, during the archaeological diggings of the *Ibida* site at Slava Rusă [4].

They are presented in Figure 2 and consist of:

-*haft – P1* (Figure 2a), discovered at *Ibida* in 2006, G Curtain wall, S3, survey C1, inventory no. 48237. The item is 44mm in length, rectangular, and ends with a pommel with a diameter of 8mm. At approximately 32.6mm from the end with the pommel, the handle has two diagonal asymmetrical incisions, and at 5.75mm from them another two very fine incisions. The weight is 6.47g. On the side to which the blade was attached, two rivets were preserved; they are positioned at approximately 25mm from each other, and most probably were part of the fixing mechanism.

-*blade of pocket-knife – P2* (Figure 2b), discovered at *Ibida* (*passim*), Nichifor donation, inv. no. 40344. The length is 51.64mm and the maximum width is of 10.65 mm. The weight is 5.52g. Only the blade is preserved, without the handle. Unfortunately, neither the connecting mechanism has been preserved. The piece was dated between the 2nd and 4th century A.D.

-*fragment of knife - P3* (Figure 2c), discovered at *Ibida* in 2002, G Curtain wall, S1, square 24, -1.50m, on the level (north of the wall), inventory no. 45889. The length of the blade is of 48.83 mm, and the width at the base is 24.70mm. A 19.40mm fragment of the haft has been preserved. The rivet fixating the blade to the handle can still be observed. The weight is 17.44 g. Given the current shape of the blade, its original length was probably around 130mm. The artefact was dated between the 4th and 6th century A.D.

Fig. 2. *Items discovered during the archaeological diggings at (L) Ibida (Tulcea County): a. Haft, inv. no. 48237; b. Blade of pocket-knife, inv. no. 40344; c. Fragment of knife, inv. no. 45889; d. Scissors, inv. no. 31978; e. Pincers, without inventory number; f. Fragment of knife, without inv. number*

-scissors – P4 (Figure 2d), inventory no. 31978. The two blades have been preserved almost entirely. The length of the piece is 67.87mm, the width is 23.84mm, and the weight is 13.49g.

-pincers – P5 (figure 2e), discovered at Tufani, without an inventory number. The artefact survived entirely, and it is composed of a 6.58mm-wide metal band, with the arms of 55mm each, curly, and with a coil with a diameter of 9.87mm. The piece weights 5.56g.

-fragment of knife – P6 (Figure 2f), discovered at Noviodunum in 2007, without an inventory number. A 31.30mm fragment of the blade has survived, as well as a 41mm of the handle. Only one edge was usable, and the maximum width of the blade is of 15.21mm. The weight of the artefact is 6.12g.

The SEM-EDX and micro-FTIR methods were employed to investigate the above-mentioned archaeological pieces, in order to identify the materials used in their manufacturing.

a. SEM-EDX analysis

A SEM (model VEGA II, produced by the Czech TESCAN company) electronic scanning microscope was used co-jointly with an EDX detector (QUANTAX QX2 type, produced by the BRUKER/ROENTEC in Germany).

This method, alongside the visual inspection of the micro-photogram, allows for the mapping (deployment) of the atoms from the investigated area, while alongside the X-ray spectra it allows for the determining of the elemental composition (in gravimetric or molar percentages, of a micro-structure or of a selected area) and the assessment of the compositional variation along a vector running across the investigated area or section.

b. Micro-FTIR analysis

The spectra were recorded using TENSOR 27 FT-IR spectrophotometer, coupled with a HYPERION 1000 microscope; both pieces of equipment were produced by Bruker Optic, Germany.

The FT-IR spectrophotometer is a TENSOR 27 model that is most appropriate for near-IR (NIR) measurements. The standard detector is the DlaTGS, which covers the spectral range 400–600cm^{-1} and which works at room temperature. The resolution is in most cases of 4 cm^{-1}, but it can reach up to 1 cm^{-1}.

The equipment used for the investigation was made available by the Laboratory for Scientific Investigation and Conservation of Cultural Heritage Items within the Interdisciplinary Research Platform in the Field of Archaeology – *ARHEOINVEST* from the "Alexandru Ioan Cuza" University of Iasi.

3. Results and discussions

Following the SEM-EDX analysis of the structures from the surface and the cross-section, the elemental composition, in mass percentages, of the objects found during the archaeological excavations, was established (Table 1). On the basis of these results, it was possible to establish the nature of the

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materials used in manufacturing the objects. Thus, in the P1 haft and in the P5 pincer the main elements are copper and zinc, while in the P2 blade of pocket-knife, alongside copper and zinc, tin is also present.

The P3 fragment of knife, the P4 scissors and the P6 fragment of knife, all have iron in their composition.

Table 1. *Chemical composition of investigated items*

Index	Item/ Inv. no.	Elemental composition – mass percentages (%)													
		Cu	Sn	Zn	Fe	O	C	S	P	Cl	Na	K	Ca	Al	Si
P1	**Haft/ 48237**	63.659	-	14.743	0.752	8.463	9.639	-	-	0.299	-	-	-	1.149	1.295
P2	**Blade of pocket-knife/ 40344**	83.191	2.544	5.317	0.496	6.673	0.900	-	-	0.879	-	-	-	-	-
P3	**Fragment of knife/ 45889**	-	-	-	54.489	31.730	5.466	-	-	-	3.606	0.559	1.209	1.796	1.144
P4	**Scissors/ 31978**	-	-	-	67.129	30.478	0.501	0.328	0.327	-	-	-	0.329	0.591	0.317
P5	**Pincer/ w/o inv. no.**	75.877	-	16.719	-	4.939	2.465	-	-	-	-	-	-	-	-
P6	**Fragment of knife/ w/o inv. no.**	-	-	-	84.226	13.326	0.696	-	0.442	-	-	-	0.604	0.705	-

Iron, just like copper, is the main metal to be found in processed alloys that is often corroded while lying buried. The processes of chemical alteration, monolithisation, and mineralisation occurring *in situ* means that the following elements should also be present: C, O, Si, Al, Cl, etc. [3, 5, 6].

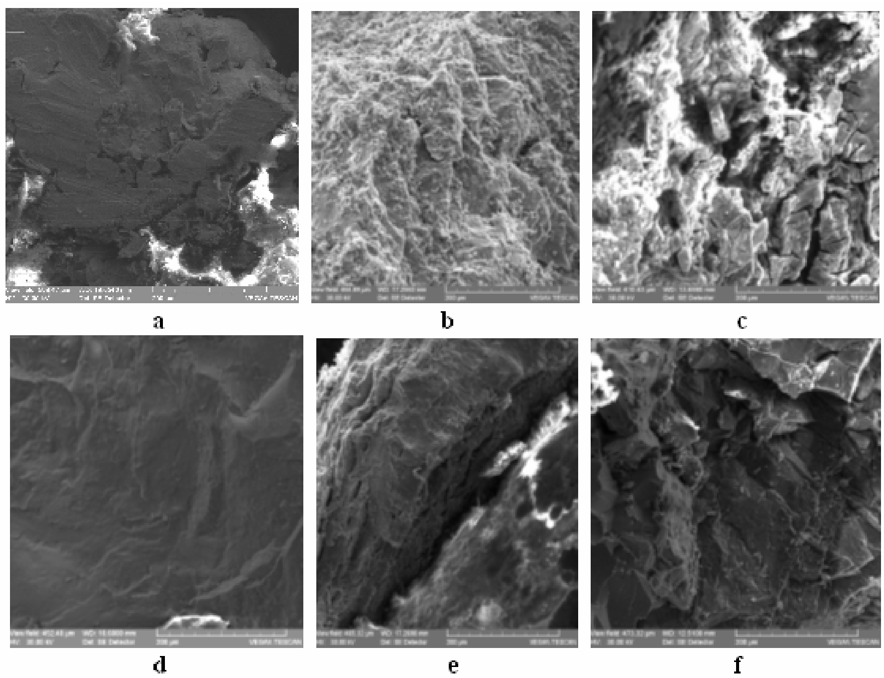

Fig. 3. *SEM images of investigated objects:*
a. Haft, inv. no. 48237; b. Blade of pocket-knife, inv. no.40344; c. Fragment of knife, inv. no.45889; d. Scissors, inv. no. 31978; e. Pincers, without inventory number; f. Fragment of knife, without inv. number

In our case, the following contaminants were identified: C, O, Si, Al, Na, K, Ca, S, P and Cl.

Because of the interaction between the soil and the metallic pieces, processes of chemical, electro-chemical, biological, etc. corrosion occur. The altered metal alloy presents on its surface a crust; nonetheless, the mechanism by which this crust is formed cannot be generalised for all types of artefacts. This crust can be thin, smooth and with a homogenous structure, or thick, rugged and with a non-homogenous structure. Significant similarities or differences can be found on objects of the same type, historical period, manufacturing technology, etc. [5, 6, 7, 8]. In the SEM images (Fig. 3), the internal structure of the analysed samples can be observed. Using the micro-FTIR analysis based on group characteristic vibrations, the nature of the corrosive products from the surface structures has been confirmed.

By comparing the obtained spectral bands with the ones from spectra libraries and from the dedicated literature [9, 10], the main components formed on the surface of the objects were identified; they constituted the residual patina which remained after the cleaning operations. Table 2 (Annex 1) presents the main spectral bands, with the representative peaks and their corresponding ions.

4. Conclusions

On the basis of the results obtained by corroborating the results of the SEM-EDX and the micro-FTIR analyses we can conclude that objects P1, P2 and P5 are made from copper-based alloys, while P3, P4 and P6 are made from iron. The objects suffered from prolonged processes of segregation towards the surface of the active metals, and deteriorated, from the surface towards the interior, by redox, acidic-basic and complexing processes assisted by monolithisation by the inclusion of contaminating elements. These features prove the considerable age of these artefacts. Oxide compounds (CuO, Cu_2O, Fe_2O_3, Fe_3O_4, SiO_2, etc.), hydrated basic carbonates ($CuCO_3 \cdot Cu(OH)_2$, $CuSO_4 \cdot 3Cu(OH)_6$, etc.), chlorine compounds ($Cu_2(OH)_3Cl$, $CuCl_2 \cdot 3Cu(OH)_2$, etc.) and other compounds were formed by the alteration processes caused by the underground lying environment [5, 6].

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Annex 1

Table 2. *Representative peaks and spectral bands of the ions identified in the analyzed objects*

Spectral bands (cm^{-1})	**Functional group**	**Peak present in analyzed objects** (cm^{-1})	**Analyzed objects**
670-745; 800-890; 1040-1100; 1320-1530	Carbonate ion	724. 1378.1465	P1
		1340. 1497	P2
		1413. 1482	P3
		1462. 1515	P4
		723. 1376. 1465	P5
940-1120	Orto-phosphate ion	1001	P3
830-920; 1600-1900; 2150-2500; 2750-2900;	Orto-phosphate dibasic ion	1719. 1896. 2304. 2851	P1
		1675. 2635. 2307. 2862	P2
		1753.	P3
		1613. 1676. 2829	P4
		1743. 2851	P5
570-680; 960-1030	Sulphate ion	618	P3
600-660; 610-630; 900-1150	Chloride ion	965. 1126	P1
		640. 929	P4
600-700	Tin ion	654	P2
		698	P4
860 – 1175	Silicate ion	889	P1
		1130	P2
		1044	P3
		1036. 1123	P4
		887	P5
		888	P6
800 - 920	Aluminate	889	P1
		878	P2
		865	P3
		837	P4
2550-3500	Aquo and hydroxo-compounds. water of coordination	2636. 2920. 3278	P1
		3241	P2
		2999. 2585. 3173	P3
		3318. 3374. 3040. 2950	P4
		3329. 2955. 2922	P5
3500-4000	Waters related physically	3603	P1
		3527	P2
		3651	P3
		3509	P4
		3508	P6