

Conservation State Assessment and Determination of Certain Archaeometric Characteristics for Two Bronze Items from the Early Hallstatt Period

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In our paper we presented the results of an analysis we performed by using the coroboration of OM, SEM-EDX and micro- FTIR techniques on two archeological artifacts, representing a spear head and a razor blade, which were found by accident in Boldesti-Vatra Satului, in district Todiresti, Iasi county. They were dated as belonging to the early Hallstatt, Gáva-Holíhrady culture (XII-X century BC). The experiment data were enough for the evaluation of the conservation level and the determination of some archaeometrical characteristics, which lead to the determination of the way they were manufactured, their use, their abandonment and their discovery.

Key words; bronze, early Hallstatt, Gáva-Holíhrady culture, conservation state, archaeometric characteristics, OM, SEM-EDX and micro-FTIR

The archeological collection of the “Mihai Constantin” School Museum of the High School “Ion Neculce” from Targu Frumos, Iasi county, contains a number of important materials, among which two are some very interesting artifacts, representing a spear head and a razor blade which were discovered by chance, around the center of Boldesti village, Todiresti district, Iasi county (fig. 1) [1]. They were dated as belonging to the early Hallstatt, Gáva-Holíhrady culture, which belongs to Granicesti Cultural Group from Suceava plateau. (XII-X century BC) [2, 3].

The most similar artifacts, typologically and cultural-chronologically, can be found among the bronze artifacts from Transylvania, which were dated at the beginning of the iron age (early Hallstatt) within the Carpathian area of: Cincu, Galospetreu, Gusterisa II, Suseni, Spalnaca II, Zlatna II [4] and Valcele II [5], although they were spread over a wider area [6].

Such bronze items are associated with Gava-Holíhrady communities (XII-X century BC), with polished and

grooved black pottery, that, during several periods of time, was also found in the eastern Carpathian territories belonging to the Granicesti, Corlateni and Chisinau cultural groups.

The study of the physico-mechanical deterioration and chemical degradation phenomena of the ancient bronze artifacts is a very complex task [7].

The archaeological bronze has a very complex composition of the corrosion products, resulted from the reactions with corrosion agents (of chemical, electrochemical or microbiological nature), or by contamination in the soil underground [8-13]. For the pieces of ancient bronze, both the ones with metallic bulk and the ones without it, coming from disturbed sites or not, three types of products can be differentiated in the structure of the archaeological patina: the first ones resulted from the corrosion processes, the other ones from the acid-base processes, mainly through hydrolysis and ionic exchange, and the last ones from the processes of contamination



Fig. 1. Geographical localization of the discoveries

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(diffusion, segregation, deposition, etc.) [14-18]. These products are formed in different types, being characteristic to certain types of patina: the oxides and sulphides, formed since the utilization period, constitute the primary patina; the halogenides, ox hydroxides, carbonates, sulphates, phosphates etc., resulted in the last period of utilization and in the first step of pedological period, define the secondary patina; finally those resulted from physical processes of diffusion-segregation-deposition-recrystallization are forming the contamination patina [19-21].

In order to determine their conservation degree and some of their archaeometrical characteristics needed to determine the ore, the manufacturing technology used to produce them and their path from manufacturing to discovery, the bronze archeological artifacts were chemically analyzed. We checked the allotropic phases from the metallic core and we also analyzed the nature, morphology and the distribution of the structural components from the surface [14, 17, 22].

In that regard the two archeological artifacts were analyzed both at the level of their metallic core and in certain areas of their surface. We used non-invasive techniques, such as Optical Microscopy (OM), micro-FTIR and Scanning Electron Microscopy (SEM), coupled with EDX detection.

Experimental part

The *spear head*, with inventory number 134/1972 (fig. 2), is of filiform type, well sharpened, slightly asymmetrical with rounded wings towards the base and with a visible median rib, which branches towards the tube and presents traces of burrs on its rib. The tube has two perforations of a maximal diameter of 5mm and a depth of 60mm, which allow to be caught in the shaft. On the sides of the wings could be noticed longitudinal abrasion traces, attrition traces and material losses.

The spear head has a length of 161mm, with a blade of 105mm and the tube used to fix it on the wooden bail is 56mm. The maximal width of the blade is 45mm and the tube diameter is 25mm. Its total weight is 146.412g.



Fig. 2. Images of the faces and of the edges of the spear head

The *razor blade* with inventory number 135/1972 (fig. 3), is slightly curved, with a triangular section, with a non-callous edge, with one single edge and with a perforation ($\varnothing = 3.8 - 4\text{mm}$) for fixing it to the bail with a rivet.

On the blade we noticed longitudinal abrasion traces, which were done while sharpening the razor when it was being used, or by those who discovered the artifact. On the right edge, towards the tip, we noticed material loss, which

appeared due to a manufacturing imperfection or during use.

The artifact is 139mm long, 18mm wide and its blade is of 3 mm. It weights 26.022g.



Fig. 3. Images of the faces and of the edges of the razor blade

The objects were analyzed by OM, SEM-EDX and micro-FTIR, without sampling.

a. The optical microscopy analysis

The surface microstructures were studied with a Carl Zeiss Axio Imager A1m optical microscope, at 100X magnifications, to which we attached an AXIOCAM camera, and we used dedicated software for data recording and processing.

b. The SEM-EDX analysis

We used a scanning electron microscope, model SEM VEGA II LSH, made by TESCAN, coupled with an QUANTAX QX2 EDX detector, manufactured by Bruker/ROENTEC Germany.

The Quantax QX2 is an EDX detector used for qualitative and quantitative micro-analysis. The EDX detector is the third generation, the X-flash, that does not require liquid nitrogen cooling and is about 10 times faster than the conventional Si (Li) detectors.

The technique we used (micro-photogram viewing, imaging plays mapping (layout)) investigated the surface atoms and we obtained an X-ray spectrum based on elemental composition determination (gravimetric or molar percentage of a microstructure or a selected area and assessment of its composition variation ordered along a vector in the area or section we analyzed).

c. micro-FT-IR analysis

The spectra were recorded with a FT-IR spectrophotometer coupled with a HYPERION 1000 microscope, both from Bruker Optic, Germany.

The TENSOR 27 FT-IR spectrometer is an advanced flexible desktop instrument suitable for routine applications, as well as for laboratory research. The TENSOR 27 is designed for measurements mainly in the mid-infrared region. The standard detector is a DLATGS which covers a spectral range from 4000 to 600 cm^{-1} and works at room temperature. The resolution is normally 4 cm^{-1} but it can go up to more than 1 cm^{-1} .

Analyses were performed in the Laboratory of Scientific Investigation and Conservation of Cultural Heritage in the Platform of Interdisciplinary Training and Research, „Al.I. Cuza” University of Iași.

Results and discussions

The artifacts were analyzed by three different non-invasive techniques, which, corroborated together allowed



Fig. 4. Optical microscope images 100X:
a - the spear head and b - the razor blade

us to determine the chemical composition of the base alloy, the manufacturing method and the modifications of the items, from the structural and compositional point of view, both at the surface and inside. We aimed to determine some archaeometric characteristics, involved in the evaluation of their contexts from manufacturing up to their discovery. We took into account three types of compounds from the utilization period of time (primary patina) up to the moment of the abandonment (secondary patina) and from the moment of burial to the discovery (contamination patina or the corrosion, monolithic and mineralization bulk, etc.).

The microscopic analysis revealed a green corrosion crust with unequal distribution and microstructures incorporated from the archeological site (fig. 4).

The specimens were analyzed by SEM-EDX, both in the structure of the metallic core, to determine the basic elements from the alloy used during the manufacturing process and on the surface, to point out the corrosion products and the contamination with structural elements (figs 5 and 6).

Thus, by EDX we determined the elemental composition of the core alloy, which contained Cu, Sn, Pb, Ni and Fe, as well as several contamination elements from the archeological site or from the molding shapes, such as Si, Al, Na, K, Ca, Mg, Cl, S, C and O. The core alloy compositions of the metallic core of the two artifacts are presented in table 1, in weights percents.

The obtained values rank the two artifacts in the category of the complex bronzes, medium alloyed, of good

quality, soft and easy to manufacture. The stanium bronzes and a Pb content of up to 2-3% together with the Ni and Fe microelements offer them constant mechanical properties and they were improved by shaping through beating or splintering, becoming resistant to corrosion in an acid environment [11, 17, 22].

The absence of the Fe in the metallic core is explained through its migration in the artifact during its underground stay, from the volume phase of the artifact towards the surface. There, through oxidation and dissolution a part migrates in the composites from the contamination patina, and a part segregate under the influence of the underground water in the soil [14, 15-17, 19, 20].

This phenomenon occurs in all the Copper-based alloys that contain Fe and Zn as alloy elements, or as microelements derived from the ore. These two active metals, due to their negative electrode potentials, in contact with the Cu positive potential segregate towards the surface of the object, especially after the action of the chloride anion through microcracks (anodisation) which plays an important electrolytic part, creating pitting microcells that force the migration of the Fe^{2+} and Zn^{2+} towards the surface [11, 14, 15, 17, 22].

The presence of the Fe and of the S in the surface structures (table 2) prove that the artifacts were obtained from polysulphurous ores and copper nuggets.

The presence of the oxygen in the interior structures of the bronzes prove that during the processing of the alloy the refinement was very weak or lacked completely and that during the micro-pitting corrosion processes, as a

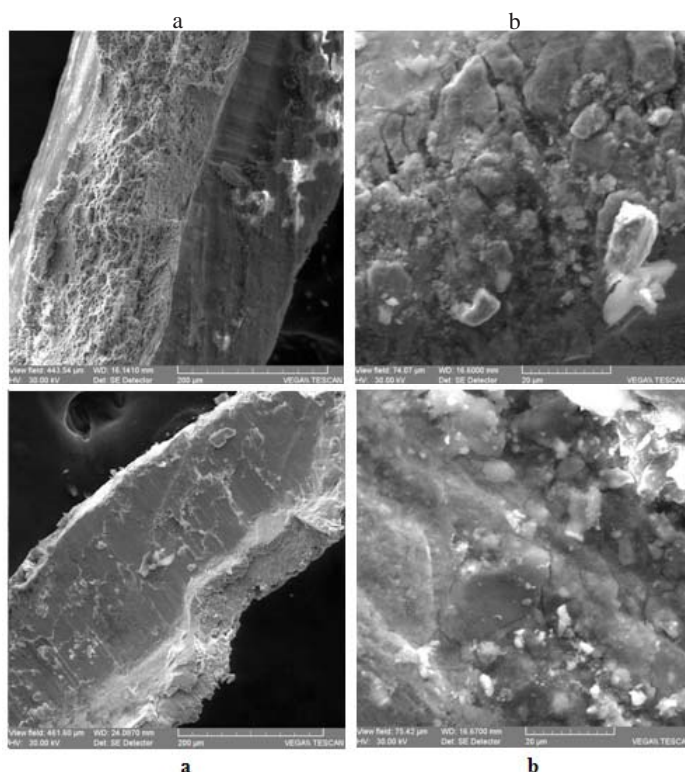


Fig. 5. SEM images for the spear head
a - in the core at a 500X magnification, b - on the surface on a 3000X magnification

Fig. 6. SEM images for the razor blade
a - metal core 500X; b - on surface 3000X

Table 1
CHEMICAL COMPOSITION OF THE METALLIC CORE

Artifact	Elemental composition – weight percent (%)				
	Cu	Sn	Pb	Ni	O
Spear head	84.475	4.907	4.821	0.780	5.017
Razor blade	84.341	6.508	3.596	0.694	4.861

Table 2
CHEMICAL COMPOSITION OF THE SURFACE STRUCTURES

Artifact	Elemental composition – weight percent (%)															
	Cu	Sn	Pb	Ni	Fe	P	Mg	O	C	S	Cl	Na	K	Ca	Al	Si
Spear head	61.956	6.484	2.053	0.593	0.327	0.061	0.395	21.499	3.251	0.583	1.533	-	-	-	0.674	0.593
Razor blade	47.267	4.282	2.129	0.443	0.613	-	0.796	25.717	6.353	1.768	2.075	2.442	0.859	1.314	1.058	2.885

consequence of the Fe and Ni chloride segregation, the chlorine anions were substituted with hydroxide anions, which together formed porous structures, irregularly distributed, depending on areas with a minimal resistance to corrosion resulted after the thermal processes of smiting/forging.

Also, the presence of Sn in the tin dioxide detected in the surface structures proved that after the lenticular segregation in certain crevasses, the aggressiveness of the chlorine anion and of the hydroxide anion in the presence of the admitted oxygen turned it into tin dioxide. The microscope was able to detect it as very thin traces.

All the elements from the core of the pieces can be found in the corrosion crust, but in very small percents (table 2).

The chemical composition of the surface structures is in correlation with the corrosion products types, formed both in the utilization and in the abandonment periods of time, but also during the underground stay. Through OM we could identify the microcrystallines of cuprite, sulphure, nantokite, azurite, atacamite and paratacamite, which explains why next to the alloy elements there was sulphur, carbon, chlorine and oxygen. The rest of the elements, Na, K, Ca, Al and Si, considered as contaminants, resulted either from the molding shapes (stone shapes or from mixtures based on loess) for the object, or from the archeological site. They appeared in the surface structures from diffusion, osmosis, segregation, mineralization and monolitization, under the form of aluminosilicates and carbonates.

Type structure/compound	Theoretical spectral bands (cm ⁻¹)	Peak present in analyzed artifact (cm ⁻¹)	Artifact
Cuprite	620-650	621	1
		-	2
Cassiterite	600-800	-	1
		762.86; 792.55	2
Sulphate (Brochantite/Antlerite)	960-1030; 1040-1210;	995.97; 1059.99	1
		1066.57	2
Carbonate in Malachite (a) and calcite (b)	1320-1530	1397.33 (a); 1462.32 (b)	1
		1334.99 (a); 1442.55 (b)	2
Chloride in Atacamite/Paratacamite	831-999 (4 high peaks) 2450-2560 (3 medium peaks)	933.12; 2500.37	1
		835.44; 921.63; 2551.74	2
Hydroxide anion	1550-1675	1551.57; 1670.20	1
		1551.77; 1591.89; 1670.20	2
orto-phosphate dibasic or diprotic	1600-1900; 2150-2500;	-	1
		1800.98; 2433.83	2
silicate	670-745; 860-1175	1171.94	1
		681.38; 1112.41	2
aluminate	800-920	863.71	1
		892.60	2
acvo and hidroxo-complexes, water of coordination	2550-3500	2857.52; 2927.93; 3231.44; 3380.10; 3468.34	1
		2934.08; 3456.26	2

Table 3
REPRESENTATIVE PEAKS AND SPECTRAL BANDS OF THE IONS IDENTIFIED IN THE ANALYZED ARTIFACTS

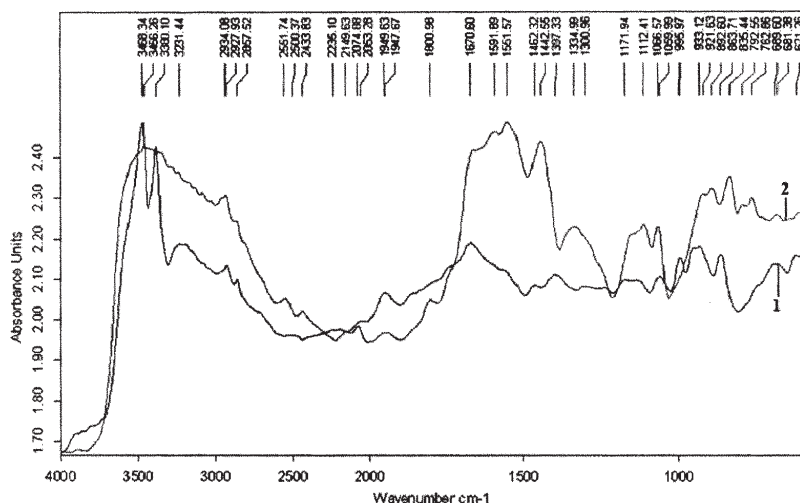


Fig. 7. The micro-FTIR Spectra for the spear head (1) and for the razor blade (2)

The composites were identified also through the comparison of the spectral bands obtained by micro-FTIR analysis, which were compared to those from the spectra libraries and from relevant scientific publications (fig. 7 and table 3) [18, 23, 24].

Because the artifacts were aggressively cleaned when discovered, only a part of the corrosion and contamination compounds were found in an adequate quantity to determine the FTIR, their majority being microscopically identified in the structure of the residual patina which remained after the cleaning processes.

Table 3 presents the main spectral bands of the compounds from the surface of the artifacts, both those of the base alloy and those originated through contamination.

Conclusions

Based on the results obtained by corroborating the OM, SEM-EDX and micro-FTIR techniques we may assert that the two bronze artifacts we investigated were obtained by casting and polishing, from alloys based on Cu, Sn, Pb, Ni and Fe, where Ni, Fe and Sn suffered, in time, strong segregation processes towards the surface. On the surface we found the basic corrosion compounds from the primary and secondary patina of the alloy elements, but also compounds from the tertiary and the contamination patina.

The metallic core of the items had extremely fragile areas, with a porosity distributed depending on the centers of weak resistance points resulted during manufacturing and utilization and also from corrosion processes. There are also small areas of missing material, aggressively cleaned areas and others types of areas.

On the surface, under the microscope, we found both the compounds of the alloy elements, mostly as a residual patina (remained after the inappropriate cleaning) and those from the contamination. The composition and the degree of conservation of the two structural elements (the metallic core and the crust and the corrosion products from the surface) prove the considerable age of these pieces. The presence of Ni and Fe, together with Cu, Sn and Pb, in the composition of the alloy reveal the fact that the raw material could be obtained from the ores extracted from the mines in the Oriental Carpathians, especially from the Balan area [18, 21].

We cannot excluded the possibility that the bronze from some artifacts could originate from recycling faulty items [25-28], by recasting and mixing, so that the elemental "patterns" of the deposits, of the ores and the previous alloy "networks" were mixed. Thus, we determined a very large and uncertain area of origin, since the ancient natural resources were exploited and transformed.

The information we obtained completes the information about the Hallstatt bronzes from the eastern side of the Carpathians. We intend to add that to a larger data base with similar relevant information.

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