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ARCHAEOMETALURGICAL EVALUATION OF TWO SPEARHEADS FROM THE BRONZE AGE

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Abstract

The paper presents the results of the conjoint MO, SEM-EDX and micro-FTIR analyses conducted on two spearhead discovered in Stuhuleț and Huși (Vaslui County, Romania), attributed to the Bronze-Age Sabatinovka culture, in order to authenticate and establish the state of preservation, and to establish the manufacturing technique (the archaeometalurgical procedure) and the provenance of the raw materials, based on the chemical composition.

Keywords: *Spearheads; Bronze; Archaeometallurgy; OM; SEM-EDX; micro-FTIR*

Introduction

The systematic study of complete or fragmentary metallic artifacts, from various historical periods, is meant to establish the alloy composition, to clarify both the processes of corrosion and other processes that affected the state of preservation during uselife and underground lying, by ascertaining the nature, structure and distribution of compounds formed in the corrosion [1].

After manufacture, bronze ancient artifacts develop a superficial layer of compounds, from the primary or noble patina (cuprite and sulphide), then a ceramic coating of malachite, which also has protection and aesthetic functions, and towards the end of the uselife, just before discard, the primary patina is affected by the appearance of compounds from the group of oxyhydroxides and of unstable basic chlorides and carbonates, and the secondary or poor patina appears [1-3].

While buried underground, these are subjected to progressive processes of degradation, chemical changes incurring in the component materials both by processes of chemical corrosion, electrochemical and/or microbiological, sometimes assisted before abandonment by thermal processes, such as incineration or firing, for various reasons, and processes of mineralization, segregation, diffusion and monolithization. The latter lead to the incorporation into the corrosion layer of the two patinas of microstructures originating from the lying environment (wood fragments, textile fabrics, leather, bone, nummulites, ceramics, other

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metals, etc., but also soil elements). They form the tertiary or vile patina, formed in the archaeological site and dependent on its aggresivity. In the soil, the processes of degradation are often accompanied by pedological processes of erosion and functional-structural deterioration that alter the physical state of the artefacts [2-4]. The cummulative effect of the environmental factors from during the four stages (manufacture, use, discard and lying), can be correlated with the endogenous parameters of the artefact (the alloy composition, the provenance of raw materials, the archaeometalurgical procedure for manufacturing the alloy, and the technology for processing the artefact, the amount of wear incurred before discard, etc.). They often involve major, sometimes irreversible, changes both in the structure and the morphology of the artefact, altering its shape and, implicitly, its historical significance, as for instance in the case of items without a metallic core [3–10].

The study analyses two spearheads discovered in different areas of Vaslui County, Romania, attributable to the Sabatinovka culture. The two items were analysed using the non-invasive techniques OM, SEM-EDX and micro-FTIR, in order to do an archaeometallurgical assesment on the basis of the chemical composition, crusts corrosion morphology and of the alloys. Based on these results the making technique and the source of raw materials were established.

Experimental part

Those two pieces taken into analysis are spearheads, discovered in Stuhuleț and Huși, Vaslui County, Romania (Fig. 1), and specific to the Sabatinovka culture.

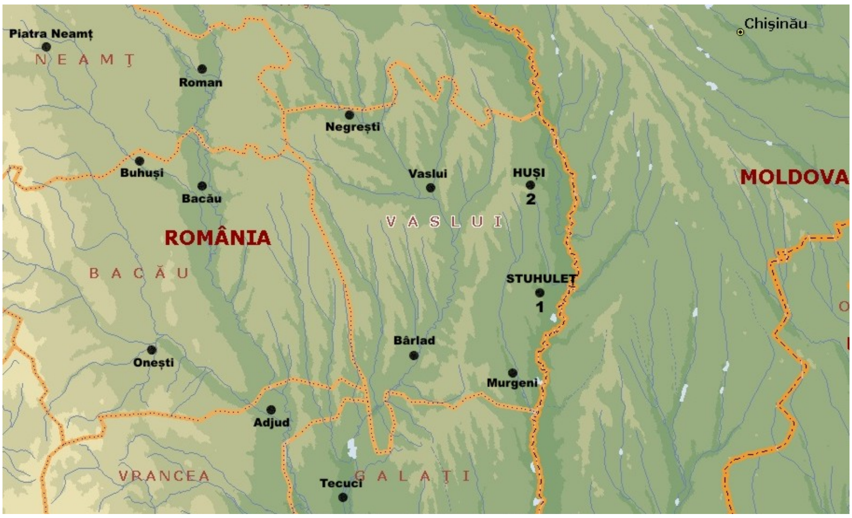


Fig. 1. The geographical location of the discoveries in Vaslui County, Romania: 1- Stuhuleț; 2- Huși, [11]

The spearhead from Stuhuleț, named S1 (Fig. 2), part of a deposit of bronzes found in the Museum of History in Vaslui [12].

The piece has a total length of 19.0 cm, the length of the sheath in 7.9 cm, the length of the blade is 13.5 cm, and its maximum width is 4.3 cm. The thickness of the wall of the shaft tube is 2.0 mm. The mouth of the tube is straight and round in shape. The tube is short, conical and extends along the blade as a rib that tapers towards the tip of the blade. The rib, which also serves to strengthen the blade, is round. The blade is leaf-shaped, uniform, and with a sharp tip. The slight bents are probably due to the discovery processes or agricultural operations, and were straightened with great care by hitting. Right under the mouth of the shafthole, there are two fastening orifices positioned opposite from each other, on the same vertical imaginary line with the blade. A small casting gap is found on the side of the tube. The nobile patina is found on one of the sides, light green towards the tip and dark green over the entire shaft tube. The poor and vile patina found on the other side of the spearhead were removed. The spearhead from Stuhuleț is of the Dremajlovka type, specific to the Sabatinovka culture, and represents the most western discovery of this type of weapon, being the only discovery of this kind in the area between the Carpathians and the Prut River.

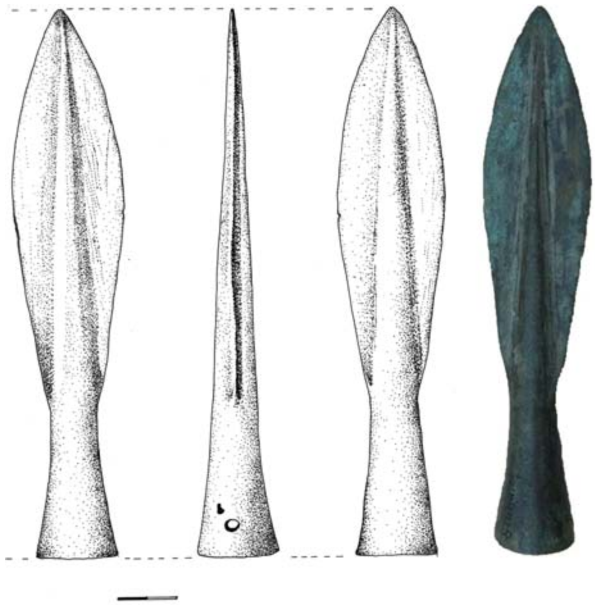


Fig. 2. Images of the spearhead from Stuhuleț – S1

The second piece, the spearhead from Huși (Vaslui County, Romania), named S2 (Fig. 3), is likewise from the collections of the Museum of History in Vaslui, but her shape differs quite a lot from the first one [13].

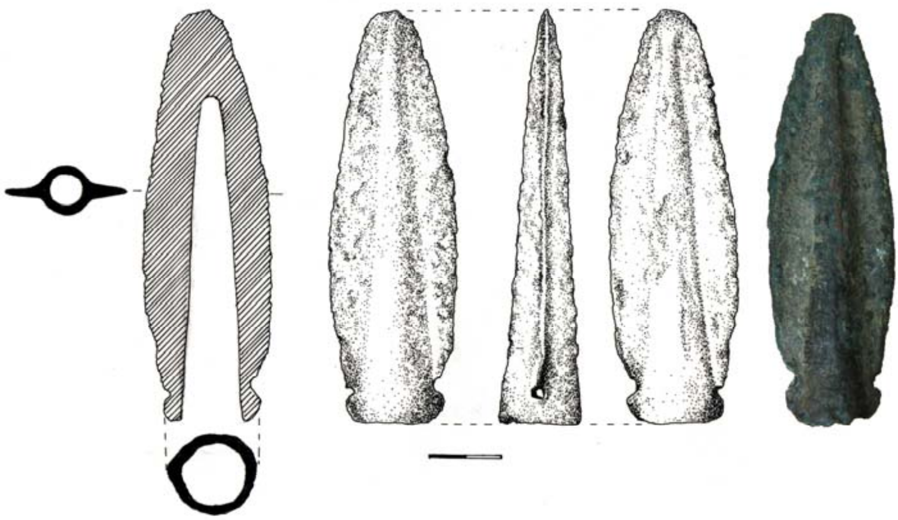


Fig. 3. Images of the spearhead from Huși – S2

The piece is 11.6cm in length, the length of the shafthole is 9.4cm, the length of the sheath is 1.4 cm, the length of the blade is 10.2cm, the maximum width of the blade is 3.4 cm, the diameter of the shaft tube is 2.2 cm, the thickness of the shaft-tube wall is 4.0mm, and the thickness of the blade is 3.0mm. The weapon was casted in a bivalve mould (molds and stone shells). Burrs are visible along the edges of the tube, which proves that shells were used for recasting. The artefact is strongly corroded; approximately 90% of its surface is covered by oxidation blots. The shaft tube is very short, with relatively thick walls. The tube runs along the blade up to near its tip. Two fastening orifices are found on the sides. The blade is leaf-shaped, narrow and long. The two edges of the blade are slightly asymmetric: one edge is widest at the middle part of the length, while the other is widest in the section from the middle towards the base. The tip of the spearhead is round.

The spearhead from Huși is of the Krasniy Mayak type, specific to the Sabatinovka culture, and constitutes, as in the case of the piece from Stuhuleț, an isolated find for the area east of the Prut.

Optical microscopy analysis

For analysis a Carl Zeiss Axio Imager A1m optical microscope was used, fitted with a video camera and co-assisted by a computer. The samples were analysed by reflexion at different magnification factors (50X and 100X). This technique provides information both on the crusts resulting from the alteration of the basic alloy and on those resulted by incorporating and monolithization processes of elements from the archaeological site (identifying the commonalities or differences in terms of aspect, colour, homogeneity of chemical compounds derived from primary, secondary or tertiary patina).

The SEM-EDX analysis

The analyses employed a scanning electron microscope (SEM), Vega II LSH model produced by Tescan, connected to a Quantax QX2dispersive X-raydetector (EDX) produced by Bruker/Roentec (Germany).The microscope, controlled entirely through a computer, has an electron gun with tungsten filament, and can achieve a resolution ranging from 3nm to 30kV, with magnifications between 30X and 1,000,000X in resolution operating mode, with an acceleration voltage from 200V to 30kV, and a scanning speed between 200 ns and 10 ms per pixel. The operating pressure is less than 1×10^{-2}Pa. The resulting image can be constituted by secondary electrons (SE) or backscatter electrons (BSE) at magnification between 200X and 1000X.

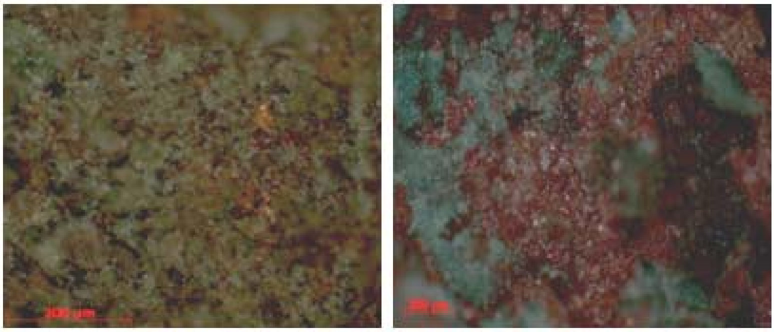
The Quantax QX2 is an third-generation, X-flash type, EDX detector used for qualitative and quantitative micro-analysis.

The micro-FTIR analysis

The spectra were registered using a FTIR spectrophotometer type TENSOR 27 coupled with a HYPERION 1000 microscope, both produced by Bruker Optic, Germany. The TENSOR 27 is most adequate for measurements in the near-IR spectrum. The standard detector is DlaTGS, which covers the 7500–370cm^{-1} spectral range, and which works at room temperature. The working resolution is 4cm^{-1}, though it can reach 1cm^{-1}. The TENSOR 27 is fitted with a He–Ne laseroperating at a wavelength of 633nm and delivers an output of 1mW, in a RockSolid alignment of the interferometer. The signal-to-noise ratio of the TENSOR 27 is very high. The equipment is fully controllable through the OPUS software (OPUS/VIDEO for interactive video acquisition). Transmission and reflexion modes of operation are both available. The MCT type detector is cooled with liquid nitrogen (-196°C).The spectral range in which the samples were analysed is 600–4000cm^{-1}.

Results and discussions

It can be observed in the microphotographs of the two spearheads from Stuhuleț and Huși, obtained through OM for representative areas on their surface (Fig. 4), the corrosion crusts, which are found on the entire surface of the pieces, as well as cracks that lead to scaling. Also formations of corrosive-products congruents, with an un-uniform zonal distribution, such as structures de cuprite, malachite, azurite, nantokite, brochantite etc., can be observed.



a b

Fig. 4. OM images of the two pieces: a – S1; b – S2

The formation of uniform and compact crusts — containing structures specific to the primary patina (grey-green and brown-red), but also to the secondary or poor one (blue, black and grey), and, respectively, the tertiary or contamination one, formed during the underground lying through monolithisation in the corrosion crust (black and grey) can also be observed.

In the SEM image of the surface of the two artifacts (Figs. 5 and 6), the morphology and distribution of corrosion products can be distinguished. The EDX spectrum has evaluated the elemental composition of corrosion products present.

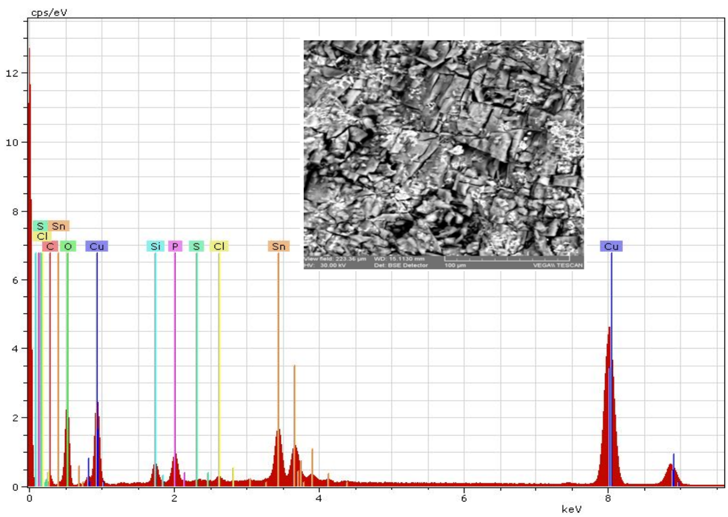


Fig. 5. The SEM microphotography and the EDX spectrum for S1

Thus, from the EDX spectrum for the spearhead from Stuhuleț (Fig. 5) were determined beside the basic elements of the alloy (copper, tin and sulfur), which proves that it was elaborated by pyrometallurgical processes of polysulfide ore rich in Cu and Sn, components of corrosion and contamination products, during the time that the two artifacts were buried underground such as: Si, P, Cl, C, and O (Table 1). This indicates that the piece suffered corrosion and segregation processes under the influence of a very aggressive buried environment very aggressive rich in oxygen, phosphates, carbonates and silica (quartz microcrystal).

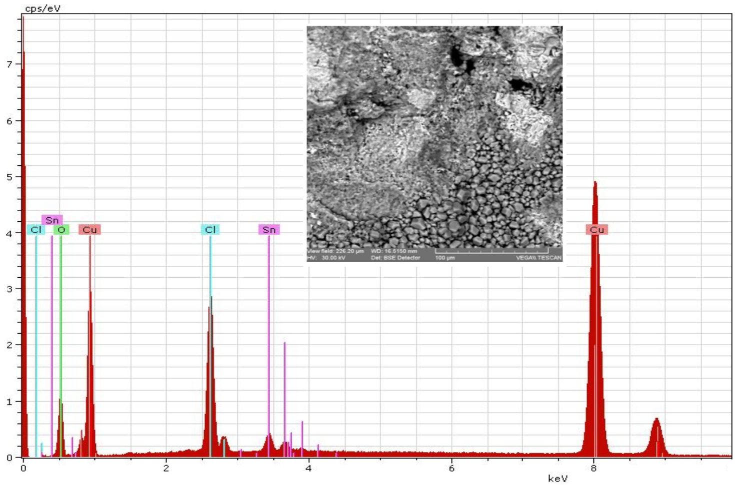


Fig. 6. The SEM microphotography and the EDX spectrum for S2

The EDX spectrum for Huşi spearhead (Fig. 6), reveal the presence of only Cu and Sn in the alloy and proves that it was elaborated by melting brasen and tin nuggets, while the composition of the corrosion crust, which containing only Cl, C and O, shows that the site was less aggressive (Table 1).

Table 1. The chemical composition of the surface structures

Samples	Elemental composition — weight percent (%)							
	Cu	**Sn**	**Si**	**P**	**Cl**	**S**	**C**	**O**
S1	38.987	12.944	2.026	2.598	0.311	0.204	1.014	41.916
S2	58.401	4.550	-	-	13.502	-	0.893	22.653

By comparing the spectral bands obtained from the micro-FTIR analysis of the corrosion products from the two spearhead with those available in spectra libraries and specialised works [14–18], it was possible to identify the main corrosion and contamination products formed on the surface of the two artefacts.

Thus from both artefacts were registered specific peaks to the ion chloride in the spectral domains 610–630cm^{-1} and 900–1050cm^{-1}, ion carbonate (1320–1530cm^{-1}) and oxides (600-700 cm^{-1}). For the Stuhuleț spearhead were identified also ion peaks: silicate (860–1175cm^{-1}), phosphate (2750–2900cm^{-1}) and sulphate (960-1030cm^{-1}).

Based of these micro-FTIR peaks, through corroboration with the elemental analysis from the EDX spectra, it was shown that the corrosion crusts of the two spearheads contain:

- oxides: tenorite - CuO, cuprite - Cu_2O, cassiterite – SnO_2 and quartz – SiO_2;
- basic carbonates, phosphates and sulphates: malachite - $CuCO_3{\cdot}Cu(OH)_2$, hydroxi-orthophosphate - $Sn(OH)(PO_4)$, brochantite - $CuSO_4{\cdot}3Cu(OH)_2$,
- hydroxochlorides: paratacamite - $Cu_2(OH)_3Cl$, atacamite - $CuCl_2{\cdot}3Cu(OH)_2{\cdot}nH_2O$ and others.

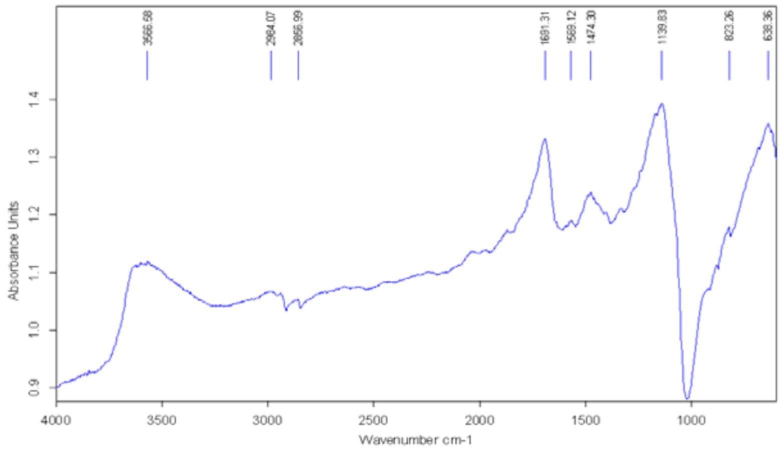


Fig. 6. Micro-FTIR image for sample S1

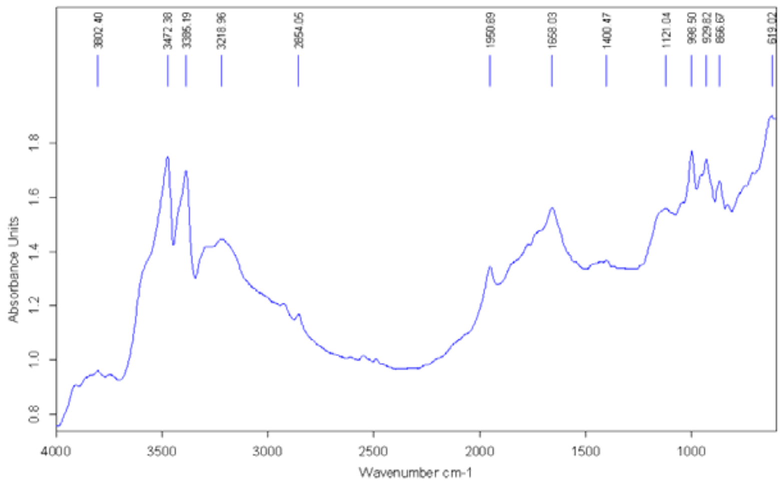


Fig. 7. Micro-FTIR image for sample S2

They were formed through redox, acid-base and complexation reactions, which took place on the surface of the alloys during the four stages passed by the artifact (manufacture, use, discard, lying), followed by segregation and incorporation of microstructures from the archaeological site during the contamination period. The first are influenced both by the composition of the alloy and the physical-mechanical and metallurgical processes employed during manufacturing, and by the aggressiveness of the environment during the first three stages. The second group of chemical compounds from the corrosion crust, formed during lying, are influenced by the nature and composition of the alloy, as well as by the compounds in the first two patinas (primary and secondary), by the manner and extent of dispersion in the volume phase, over the surface of the item. A number of corrosion crusts identified in limited areas, across the surface after being extracted from the site, displayed stratified structures, known as Liesegang patterns [19–23]. These stratified structures were harder to identify in the case of the spearhead from Stuhuleț because the hydroxy- and chloro-apatite coatings had non-membranous activity (since they were more porous), thus preventing the structural reformation of the congruent layers, which were present as thin overlapping membranes interspersed by empty layers, as they were rough (Fig. 8).

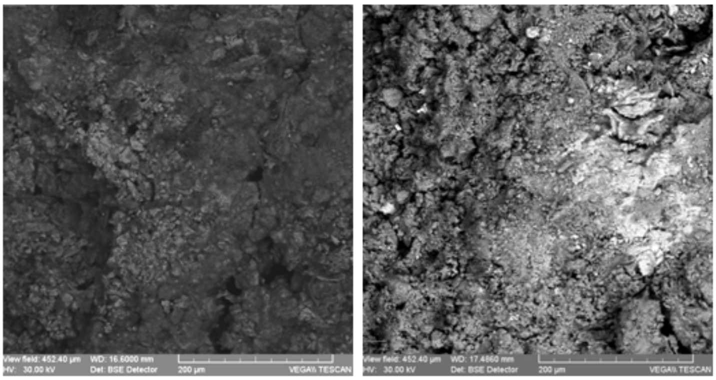


Fig. 8. SEM microphotography of the corosion crust of Stuhulet spearhead

Conversely, in the case of the spearhead from Huși, these stratified structures formed on the basis of Sn(II) hydrogels, which have membranous coatings activity and continuous structural reformation of the thin congruous layers through cyclic osmotic processes, in the form of thick stratified structures (Fig. 9).

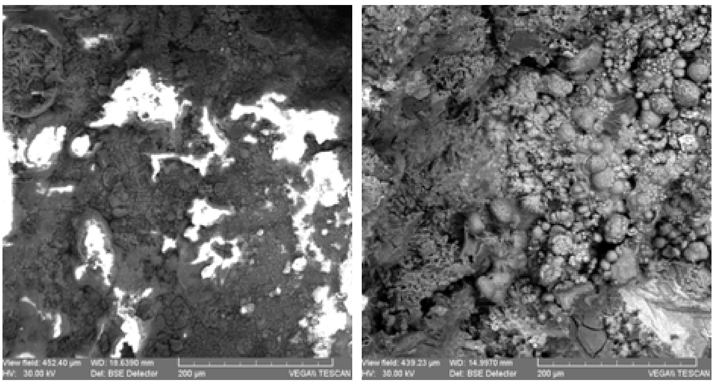


Fig. 9. SEM microphotography of the corosion crust of the Husi spearhed, with restructurated formations

Conclusions

Based on the results obtained by corroborating the results of the OM, SEM-EDX and μ-FTIR analyses on the base alloy and the compounds from the corrosion crusts of the two spearheads, the following conclusions can be drawn:

- the spearhead from Stuhuleț was made by casting in bivalve moulds or shells from siliceous rocks of a bronze alloy elaborated from polysulphides rich in copper and tin originating from the Western Carpathians;
- the spearhead from Huși was similarly made by casting in bivalve moulds or shells from siliceous rocks, but of a bronze alloy elaborated from copper and tin nuggets originating from ores located in the Western Carpathians or from Altântepe in Dobrudja;
- the presence of burrs and casting holes shows that the moulds had wear from previous uses;
- in the case of the spearhead from Stuhuleț, the four contexts (manufacture, use, discard, lying) through which the item passed took place in more aggressive environments, in the presence of oxygen and anions: chloride, sulphate, phosphate, carbonate, and silicate;

- the presence of the phosphate anion and of the chlorides, in a slightly basic environment, lead to the development of coatings over the structures of the primary and secondary patinas, with a semi-membranous (porous) effect, the corrosion crusts being in the form of thin rough membranes, overlapping and interspersed by empty layers;
- conversely, the presence of Liesegang rings in limited areas of the spearhead from Huși was due to the formation over the primary and secondary patinas of coatings with continuous membranous and structural reforming activity of the thin congruous layers through cyclic osmotic processes, in the form of thick layers;
- the shape of the items and the composition of the alloy shows that the two spearheads are specific to the Sabatinovka culture, specifically the Dremajlovka type in the case of the Stuhuleț spearhead, and the Krasniy Malik in the case of the Huși spearhead, both representing the westernmost and only discoveries of this type of weapon in the area between the Carpathians and the Prut River.

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