The Archaeometric Characteristics of Some Ancient Medical Instruments from the Moesia Inferior Roman Province, Revealed by SEM/EDX and μ-FTIR

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Our study focuses on four ancient medical instruments, two of iron, from the Noviodunum-Tulcea archaeological site and two of bronze, one was from Ibida-Tulcea and the other from Tomis-Constanta. Being analyzed by SEM/EDX and μ-FTIR, we found a series of archaeometric characteristics of the corrosion crusts and of the metallic core. The recorded data were correlated with those resulted from previous systematic researches made in Dobrogea (the Moesia Inferior Roman province), which revealed the habits and crafts of the population inhabiting that region during the 2-4th centuries AD.

Keywords: iron and bronze artifacts, medical instruments, corrosion crust, archaeometry, SEM-EDX, μ-FTIR

While buried underground, ancient objects of copper and iron alloys are affected by degradation, a chemical modification occurring in the composition materials (by processes of chemical, electro-chemical and/or micro-biological corrosion processes, sometimes assisted by thermal processes which happened before those objects were discarded, such as incineration or burning, for various reasons). The effects of degradation are often assisted by pedological erosion processes and by structural-functional deterioration that modifies the physical state of artifacts [1, 2]. Those two cumulative effects, depending on the composition of the alloy and the degree of wear before discarding the object, cause major modifications, often irreversible ones, both in the structure and in the morphology of artifacts, leading to shape loss and, implicitly, to a loss of historic signification [3-9].

By corroborating the two techniques, SEM/EDX and μ-FTIR, we found three groups of structural components in the metallic bulk structure (with or without the core):

- those from the patina resulted after manufacture until abandonment (products of chemical and electro-chemical corrosion as coatings of oxides and rarely of stable sulphuric compounds);
- those resulted right before abandonment, under the influence of the chloride anion in the damp environment and of other oxi-anions (carbonate, sulphate, nitrate, phosphate etc.), which formed hydrated salts or hydroxo-compounds, prone to dissolution with material losses, or to forming zonal mole-shaped nodes [1-6, 9];
- finally, those resulted after abandonment, in the stratigraphic succession (the evolutionary profile of the soil) of the archaeological site structure, by contamination with the surrounding environment, based on processes of monolithization, mineralization, segregation, re-crystalization/structural reformation.

Those structural components are very important elements in the evaluation of certain archaeometric characteristics, such as traces of fingerprints, or bone fragments, textile fibers, coating structures, shells, other micro-biologic formations (resulted from metabolism, from common activities, or from fragments of materials from their structure), or the distribution of the chemical components on the surface and in the volume of the alloy etc. [1-7].

In any study on archaeological artifacts it is important to establish the patrimonial elements (authenticity, origin, the nature of the material, the manufacture conception and technology, the aging patina/historical imprint, utility, the distribution area, the age/dating, placement/systematic classification of typology etc.) and also the patrimonial functions (aesthetic-artistic, historic-documentary, technical-scientific, social-cultural, administrative and economic and most of all the spiritual function, that develops the domain/direction, the absolute degree of novelty etc.).

Therefore, one must identify certain attributes involved in their authentication [10-14]. Moreover, the experiment data obtained during the scientific investigation of metallic artifacts by co-assistance and corroboration of various techniques, may result in important contributions to one of the three domains: archaeo-metallurgy, archaeometry or historiography [15-18] and, in the case of medical instruments, there is a fourth domain, that of archaeo-medicine.

The discovery of specific instruments implies the existence of certain ancient medical practices and that calls for complex evaluations of the use and also of the commercial relationships existing in ancient times. That involves certain modern non-invasive analytic techniques, corroborated with historiography data.

We know that ancient Roman medicine represented a science that developed with the contribution of certain civil practitioners, acting especially in urban areas, but also military ones [19-21]. They were instructed preferentially in renown Greek centers, but also in various areas of the Roman Empire, but many inherited their knowledge from father to son [22].

During medical interventions they frequently used various devices and equipment, which were essential and were manufactured by doctors or by specialized craftsmen

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on their behalf. Historical documents, be they literary, archaeological, or others, are not, unfortunately, very generous and neither do they provide enough support to current researches, by offering a precise typology for every instrument they discover during digs.

In Romania they discovered many ancient medical instruments, especially in the sites in Dacia, such as that of Ulpia Traiana Sarmizegetusa, which were made of bronze, silver or bone [23]. Roman surgery used a wide variety of instruments, but the main categories were: scalpels with a bronze handle and an iron blade, various types of probes, spatulas, spoons, needles, forceps, tweezers, hooks, suction cups, syringes etc. [19].

In Moesia Inferior, which comprises Dobrogea (Romania) and the north-eastern part of Bulgaria, during archaeological digs they discovered several types of medical and pharmaceutical instruments and also medicine recipients made especially of bronze. Based on the analysis thereof, but also on the study of inscriptions, they proved the existence of several disciples of Hippocrates in old centers within that province, such as: Histria, Tomis, Marcianopolis, Odessos, Dionysopolis [19, 24].

Those instruments could also be used in other domains, especially in cosmetic activities or for personal hygiene.

From the instruments discovered in Dobrogea we analyzed many tweezers and spatulas made of copper alloys and a series of scalpels, together with fragments of instruments made of iron alloys, in order to establish their state of conservation, the chemical composition of the alloys and the manufacture technology employed.

The present paper contains the results of the SEM-EDX and micro-FTIR analyses for some of those instruments, representative for the two types of materials, bronze and iron, in a conservation state that allowed precise indication of their use. We found several archaeometric characteristics in regard to the type and the process used in the alloy, the manufacture of the instrument and the evolution of the corrosion crust composition and of the composition of the metallic core while buried.

Experimental part

Materials

From the objects discovered in Moesia Inferior by our team we chose two instruments of bronze and two of iron, to study their archaeometric characteristics:

-Iron Surgical knife (registered as S1, without inventory number), with preserved 41 mm handle and part of the 31.30 mm blade, strongly corroded (fig. 1).

-Iron Spatula (registered as S2, without inventory number), preserved as a 65 mm long fragment with a visible 8.20 mm paddle, and a ligula 4.60 mm in diameter (fig. 2).

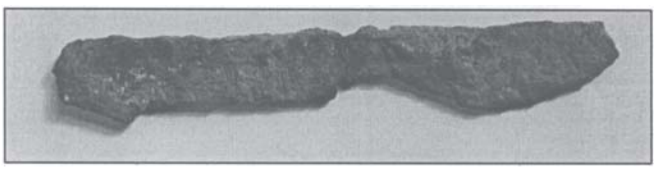

Fig. 1. Iron surgical knife, (S1)

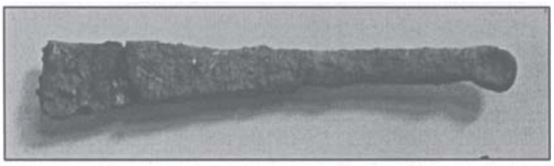

Fig. 2. Iron spatula, (S2)

-Scalpel fragment (registered as S3, inv. no. 40344), 51.64 mm long and 10.65 mm wide, with a median fin, broken at both ends (fig. 3).

-Spatula- probe (registered as S4, inv. no. 31980), with one kernel shaped end, 3.45 mm in diameter and 12.20 mm in length, and a paddle shaped one, 51.20 mm long and 9.45 mm maximum width. The maximum length of the item is 152 mm (fig. 4).

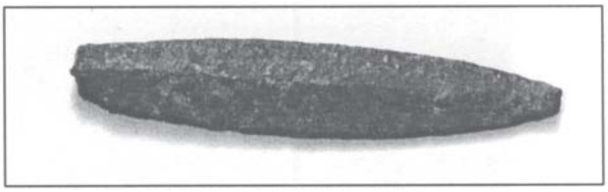

Fig. 3. Scalpel fragment, (S3)

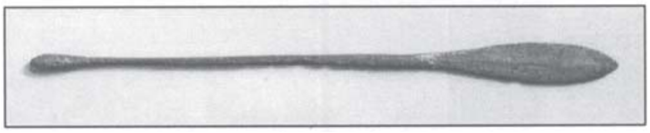

Fig. 4. Spatula-probe, (S4)

The SEM-EDX Analysis

We used a VEGA II LSH SEM scanning microscope, made by TESCAN, The Czech Republic, coupled with a Quantax QX2 EDX detector, made by Brüker/Roentec, Germany.

Sample analysis was performed at a 500x magnification, with a 30 kV acceleration tension and the working pressure below $1x10^{-2}$Pa. The image obtained was constituted by scattered electrons (SE).

The technology, together with the visualization of the micro photogram allows image rendering with atom mapping on the analyzed surface and, based on the X rays spectrum, we could determine the elementary composition (in gravimetric or molar percentages), of a certain structure, or of a selected area and we could evaluate variations in composition along a vector in the area or section under analysis.

The micro-FTIR Analysis

The Spectra were recorded by a FTIR spectro-photometer, coupled with a Hyperion 1000 microscope, both made by Brüker Optic, Germany.

The FTIR spectro-photometer was a Tensor 27 model, suited mostly to close IR measurements. The standard detector was a DLaTGS type, which covered the 4000-600 cm^{-1} spectral domain in our analyses. The Tensor was completely controlled by the Opus software, which records interactive video data and uses spectrum libraries specific to the type of material. The microscope was fitted with a 15x lens.

The equipment used for analysis was installed in the Scientific Investigation and Cultural Heritage Conservation Laboratory within the Platform for Interdisciplinary Formation and Research - ARHEOINVEST at "Al. I. Cuza" University, Iasi.

Results and discussions

For the medical instruments under study, we focused on the effects of decay underground, the composition of alloys and the manufacture technology.

The surgical knife (S1) and the spatula (S2) were characterized by complex structures with interrupting foils, as observed in the SEM images (figs. 5 and 6). The degradation processes, that is, the chemical alteration and physical deterioration while the objects lay buried underground, formed a surface crust with a rough and non-

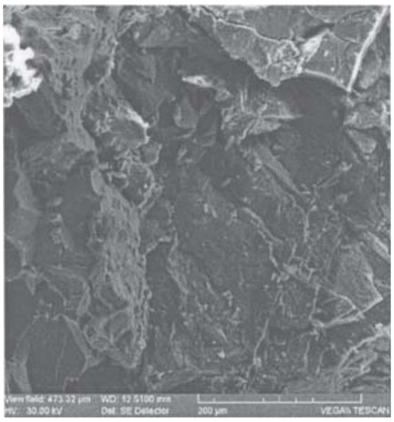

Fig. 5. SEM image of an area from the surface of the iron surgical knife (S1)

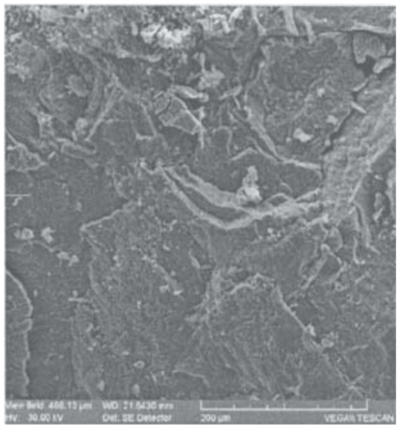

Fig. 6. SEM image of an area from the surface of the iron spatula (S2)

homogeneous look, where the corrosion products were irregularly and chaotically distributed. Part of the degradation processes products was lost by division and erosion, which led to the loss of certain parts in areas on the surface of the artifacts.

As regards the composition, based on the EDX spectra (figs. 7 and 8), we determined the elements corresponding to alloy - Fe, C and contamination elements from the environment - Al, Si, P, Ca and O (tables 1 and 2).

The two iron objects were made by striking (forging).

The scalpel fragment (S3) and the spatula-probe (S4) have distinct compositions and structures, attributed to two different manufacture technologies and the instruments were cast and polished.

The SEM image of the scalpel fragment (fig. 9) reveals a non-homogeneous structure, because of the irregular spread of the alloy components, the partial solubility and the imperfections in the corrosion products (irregular pitting, micro-crevasses and nano-nodes, or moles). The external surface had a dark green, discontinuous superficial crust, composed of the alloy corrosion products. The basic elements in the composition of the alloy were Cu, Zn and Sn, and the ones resulted from contamination were Fe, Cl,

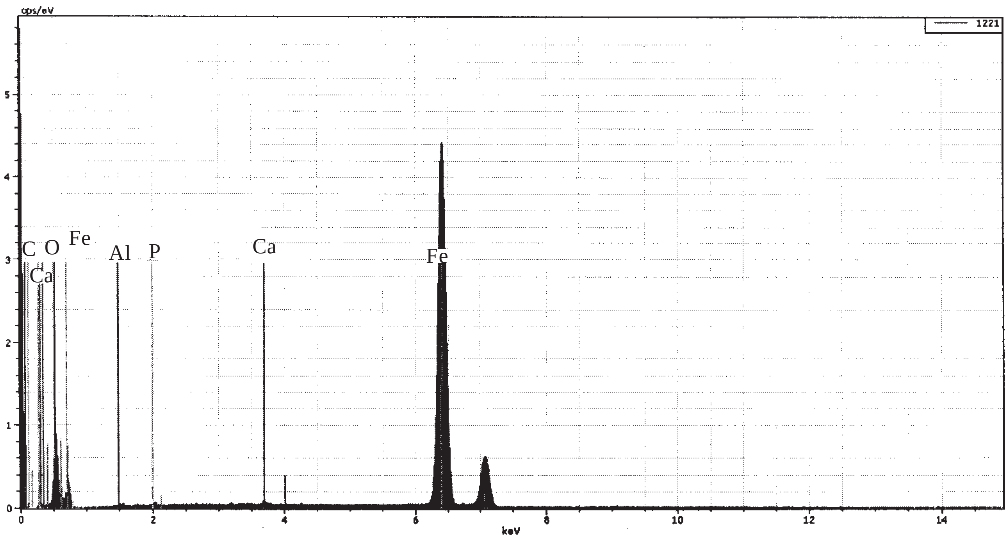

Fig. 7. EDX spectrum of the iron surgical knife (S1)

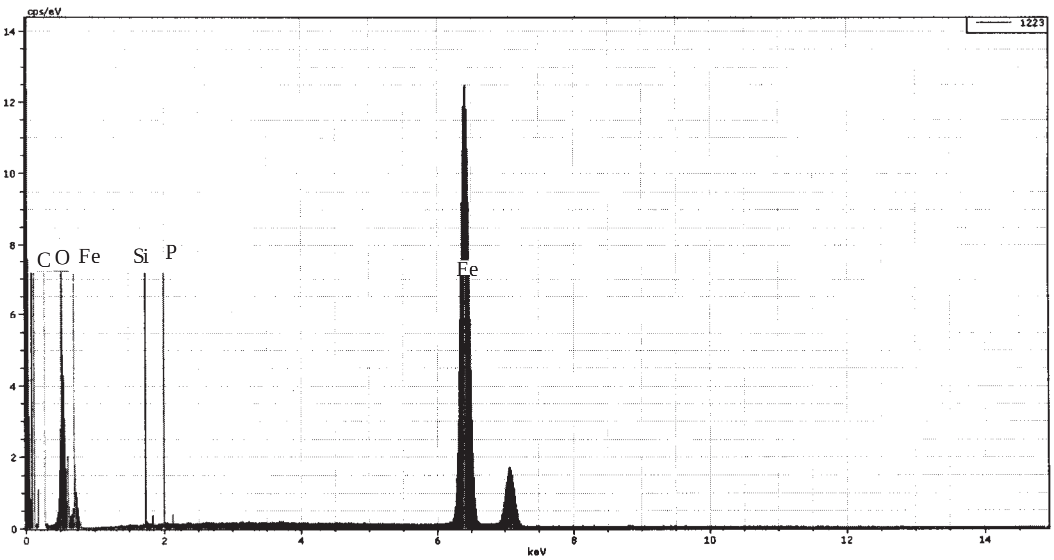

Fig. 8. EDX spectrum of the iron spatula (S2)

Table 1
ELEMENTAL COMPOSITION OF THE IRON SURGICAL KNIFE (S1)

Element	[norm. Wt.-%]	[norm. Wt.-%]	Error in %
Carbon	0.695616	2.35952	0.261755
Iron	84.22624	61.44417	2.395493
Phosphorus	0.44224	0.581697	0.06155
Calcium	0.603535	0.613521	0.057233
Aluminum	0.705444	1.065195	0.09273
Oxygen	13.32692	33.93589	2.135049
	100	100	

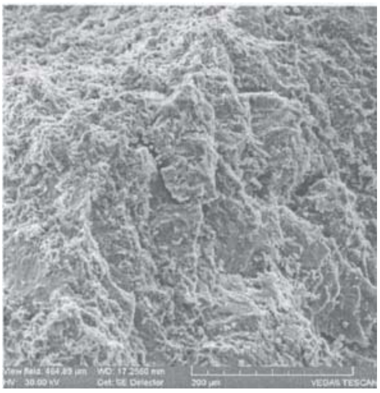

Fig. 9. SEM image of an area of the scalpel fragment (S3)

Table 2
ELEMENTAL COMPOSITION OF THE IRON SPATULA (S2)

Element	[norm. Wt.-%]	[norm. Wt.-%]	Error in %
Carbon	0.57294	1.758924	0.160406
Iron	79.28432	52.34851	2.246004
Phosphorus	0.180247	0.214581	0.038424
Silicon	0.332171	0.436111	0.048769
Oxygen	19.63032	45.24188	2.615988
	100	100	

Table 3
ELEMENTAL COMPOSITION OF THE SCALPEL FRAGMENT, (S3)

Element	[norm. Wt.-%]	[norm. Wt.-%]	Error in %
Copper	63.16515	43.4479	1.927983
Zinc	5.31682	3.554021	0.220338
Tin	2.544338	0.936843	0.149858
Iron	0.49578	0.388033	0.054529
Chlorine	18.79607	23.17379	0.83214
Carbon	2.258549	8.219204	1.852268
Oxygen	7.423294	20.28021	2.146935
	100	100	

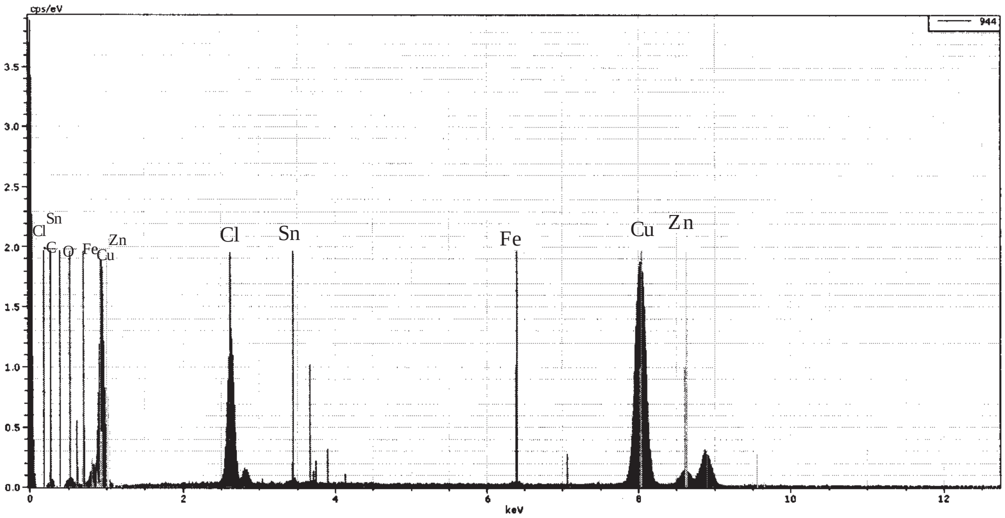

Fig. 10. EDX spectrum of the scalpel fragment (S3)

C and O (table 3). They were evaluated according to the EDX spectrum in figure 9.

The SEM image of an area on the surface of the spatula-probe (S4), presented in figure 11, the morphology of the item indicating a casting process followed by polishing, the surface structure being relatively smooth. The item was in a good conservation state . According to the EDX spectrum in figure 12, the alloy contained as basic elements Cu and Sn, and as impurities Pb, Al, C and O (table 4), which were both from the basic ore and from contamines in the environment.

Based on the specific group vibrations, the μ-FTIR analysis determined the nature of the corrosion products in the surface structures [25-27].

Table 5 lists the main spectral columns, with representative peaks for every object under analysis.

We noted a good correlation between the elements identified by SEM-EDX and the compounds revealed by the μ-FTIR analysis.

The corrosion crusts on the iron artifacts were discontinuous, with products formed in three phases: first the ferrous hydroxide $Fe(OH)_2$ was formed and the hematite α-Fe_2O_3, then the goethite α - FeOOH and the lepidocrocite γ-FeOOH and in the last phase, the magnetite Fe_3O_4, which is electrochemically inert [12, 13].The corrosion crusts of the bronze medical instruments contained chemical compounds such as: oxides (CuO, Cu_2O, Fe_2O_3, Fe_3O_4, SiO_2 etc.), carbonates and basic hydrated sulphates ($CuCO_3{\cdot}Cu(OH)_2$, $CuSO_4{\cdot}3Cu(OH)_6$ etc.), hydroxoclorides ($Cu_2(OH)_3Cl$, $CuCl_2{\cdot}3Cu(OH)_2$ etc.) and others. They formed while the objects was buried in the archaeological site, due to processes of degradation and segregation occurring from the surface inside and from the inside to the surface. The first are influenced by both the composition of the alloy and the processes of manufacturing and by the effects of the burial environment. The later can either form layered structures, known as the Liessegang effect [1-3], on the surface of the object, based on hydrogels of Sn(II) and Zn(II) with membrane level activity and continuous coating-generative structural reformation for periodic osmotic processes. The ones in second group are influenced by the nature and the

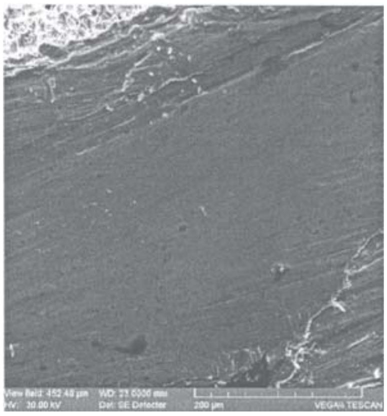

Fig. 11. SEM Image of an area on the surface of the spatula-probe, (S4)

Table 4
ELEMENTAL COMPOSITION OF THE SPATULA-PROBE (S4)

Element	[norm. Wt.-%]	[norm. Wt.-%]	Error in %
Copper	88.05616	79.8799	2.441481
Tin	4.906632	2.382661	0.203218
Lead	2.50136	0.695909	0.111946
Aluminum	0.090344	0.193019	0.035286
Carbon	0.694925	3.335223	0.265527
Oxygen	3.750583	13.51329	0.788404
	100	100	

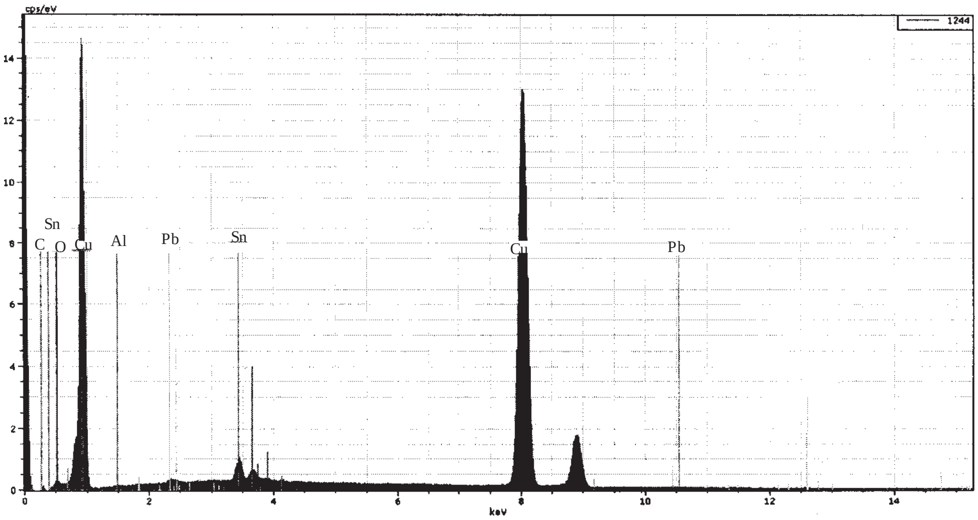

Fig. 12. EDX Spectrum of the spatula-probe (S4)

Table 5
THE REPRESENTATIVE PEAKS AND THE SPECTRAL COLUMNS OF THE COMPOUNDS IDENTIFIED IN THE CRUST OF THE OBJECTS

Ion type	Spectral columns (cm^{-1})	The peaks present in the analyzed objects (cm^{-1})	The analyzed object
carbonate	670-745; 800-890; 1040-1100; 1320-1530	724.44; 1442.14	S1
		878.68; 1340.63; 1497.43	S3
		743.63; 1073.33; 1412.08	S4
dibasic or diprotic orthophosphate	830-920; 1600-1900; 2150-2500; 2750-2900;	1682.90; 1795.85;	S1
		1729.58	S2
chloride	610-630; 900-1050	1030.91	S3
Stagnate	600-700	654.75	S3
		671.34	S4
Silicate	860 – 1175	888.10	S2
aluminate	800 – 920	870.14	S1
		890.65	S4
aquo- and hydro-compounds, coordination water	2550-3500	2930.84; 3281.19	S1
		2635.40; 2862.28; 3241.59	S3
		2856.09; 2926.29; 3378.44	42
physically bound waters	3500-4000	3508.74	S2
		3527.45	S3

composition of the chemical components in the structure of the basic alloy, as well as by their way and degree of dispersion in the volume phase. For example, we know that zinc, iron and other very active metals in copper alloys, segregate in time from the volume phase to the surface, where, after processes of dissolution, they disperse in the burial environment, or by monolithization, form a complex crust on the surface of the object. Copper alloys that contain Zn and Fe diminish in time their concentration of those elements, the variation being directly proportional with the age of the alloy.

Conclusions

The structural, compositional and morphological analyses of ancient metallic medical instruments, by nondestructive techniques, such as scanning electronic microscopy (SEM-EDX) and μ-FTIR, reveal the conservation state, the quality of the alloys, the object manufacture technology and the evolution of the deterioration and degradation effects during burial in the archaeological site and they also attest the existence of medical practices in certain periods and in a certain area, as in the case of the medical instruments from the 2nd - 4th century AD, discovered in Dobrogea (Romania).

Similar objects, as utility and age, found in the same archaeological site, reveal a lot regarding chemical alteration and physical deterioration processes by their state of conservation when uncovered. By comparing the experiment data from the analysis of the corrosion crusts resulted during the burial period we noted clear differences between the poor state of the iron objects (the surgical knife and the spatula), which are less resistant to the chloride anion and the relatively better state of the bronze objects (the scalpel fragment and the spatula-probe).

Based on our results from the SEM-EDX and the μ-FTIR analyses, we highlighted the compositions and structures of the two types of alloys (iron and bronze). The manufacturing procedure was different according to the instrument type (the iron instruments were made by two distinct forging procedures and were subsequently processed by striking, while the bronze ones were made by casting and polishing). Moreover, we learned the chemical composition and the distribution components in the volume phase of the alloy and the corrosion crusts, both as regards the basic alloy components and the impurities from the ore, or those inserted by contamination in the archaeological site.

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