ANALYSIS OF FINDS (INGOTS AND SCRAP) FROM THE PRODUCTION CENTERS NEAR ZLATAR, PRESLAV DISTRICT AND NOVOSEL, SHUMEN DISTRICT (BULGARIA) (PART I)

Stella DONCHEVA[*]
Nina ARCHANGELOVA[**]
Ákos CSEPREGI[***]
Anikó ANGYAL[****]
Zita SZIKSZAI[*****]

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Rezumat: *Istoria cercetărilor metalurgiei a demonstrat faptul că determinarea caracterului aliajului pe baza elementelor chimice este o sarcină simplă în investigarea metalurgică istorică. Este greu de clarificat din ce depozit de minereu a fost extras metalul. Cuprul și alte minereuri din fiecare zăcământ, pe lângă componenta principală cuprul, conțin și multe alte elemente care formează o varietate de combinații calitative și cantitative. Metalul extras din minereu dublează elementele care se află în el. Prin elementele care compun metalul, combinația generală a elementelor minereului poate fi stabilită cu suficientă acuratețe. Găsirea sursei materiei prime este mai importantă decât determinarea tipului de aliaj. Apoi, sunt dezvăluite rutele comerciale pe care metalul și produsele sale au fost difuzate în diferitele comunități și culturi. Astfel, se restabilește relația dintre comunitatea metalurgiștilor, intermediari și consumatorii produselor.*

Grupul de lingouri, ca una dintre principalele materii prime pentru producție, precum și produsele separate ca rebuturi, care se constituie în a doua materie primă importantă, reprezintă un subiect nu mai puțin interesant. Dimpotrivă, generează întrebări fundamentale cu privire la întregul proces de producție, la etapele și succesiunea proceselor sale. Printre principalele sarcini care pot fi rezolvate cu rezultatele cercetării compoziției elementare a

[*] Stella DONCHEVA: Shumen University, Shumen; e-mail: s.doncheva@shu.bg.

[**] Nina ARCHANGELOVA: Shumen University, Shumen; e-mail: n.arhangelova@shu.bg.

[***] Ákos CSEPREGI: Institute for Nuclear Research (ATOMKI)/University of Debrecen, Debrecen; e-m

[****] Anikó ANGYAL: Institute for Nuclear Research (ATOMKI), Debrecen; e-mail: angyal.aniko@atomki.hu.

[*****] Zita SZIKSZAI: Institute for Nuclear Research (ATOMKI), Debrecen; e-mail: szikszai.zita@atomki.hu.ail: csepregi.akos@atomki.hu.

întregului set de produse se numără originea metalului și modalitățile de ajungere a acestuia în atelierele centrelor de producție din vecinătatea orașului Preslav. În plus, pot fi determinate principalele metale și aliaje utilizate la fabricarea acestor produse, precum și compoziția și principalele elemente de aliere din aliaj, care determină caracterul acestuia. Principalele rezultate oferă un punct de plecare pentru analiză în aceste direcții, iar acumularea unei baze de date extinse va permite concluzii mai complete și definitive.

Abstract: *Determining the character of the alloy based on the chemical elements is a simple task in historical metallurgical research. It is difficult to clarify from which ore deposit the metal was extracted. Copper and other ores from each deposit, in addition to the main component-copper, also contain many other elements that form a variety of qualitative and quantitative combinations. The metal extracted from the ore duplicates the elements that are in it. By the elements composing the metal, the general combination of the elements of the ore can be established with sufficient accuracy. Finding the source of the raw material is more important than determining the type of alloy. Then, the trade routes along which the metal and its products traveled in the different communities and cultures are revealed. Thus, the relationship between the community of metallurgists, middlemen and consumers of the product is restored.*

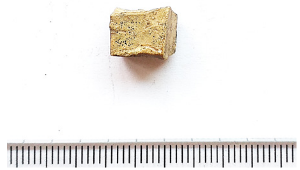
The group of ingots, as one of the main raw materials for production, as well as the products set aside for scrap, which is the second important raw material, is no less an interesting topic. On the contrary, it poses fundamental questions concerning the entire production process and its stages and sequence of processes. Among the main tasks that can be solved with the results of the research of the elemental composition of the entire set of products are the origin of the metal and the ways of its arrival in the workshops of the production centers in the vicinity of Preslav. In addition, the main metals and alloys used in the manufacture of these products can be determined, as well as its composition and the main alloying elements in the alloy, which determine its character, can be determined. The main results do provide a starting point for reasoning in these directions, and the accumulation of an extensive database will make the conclusions even more complete and definitive.

According to the study of selected materials received from the archaeological investigations of the production centers in the vicinity of the capital Preslav, carried out at the Institute for Nuclear Research in Debrecen, only those originating from the complexes near Zlatar (Preslav district) and Novosel (Shumen district) are presented here. These represent two of the three metalworking centers known for the Balkan area for jewelry production in the 10th century. The finds from Zlatar are predominant, so our attention will be directed to them first. This also implies the larger number of objects belonging to the two main groups of materials, tracing the path of production activity in art metal workshops – the ingots and rejected products, the so-called scrap metal (**Tab. I**). Selected samples of the finished product were investigated in several successive projects before, and the results of PIXE analyzes have found a place in prestigious international publications[1].

[1] DONCHEVA *et alii* 2021a, p. 71–98; DONCHEVA *et alii* 2021b, p. 191–208.

Table I

Sample No	Dimensions /cm/	Weigth /g/	Object	Alloy	Main elements obtained after PIXE, sorted by quantity above and about 1%	Image
ZLT 6	8,5/0,3/0,3	4,06	scrap	lead brass	Cu, Zn, Pb	
ZLT 8	1,6/0,8-1,6/0,2-0,7	8,84	Pour lip	multicompo-nent	Cu, Pb, Sn, Zn, Sb	
ZLT 9	3,5-4/1,1-1,3/0,2-0,3	4,17	Pour lip	cooper	Cu, Pb, As, Ag	
ZLT 10	6,5/0,6-1,4/0,2	5,58	Pour lip	brass	Cu, Zn, Pb, As	

Sample No	Dimensions /cm/	Weigth /g/	Object	Alloy	Main elements obtained after PIXE, sorted by quantity above and about 1%	Image
ZLT 17	2,4/0,7-1/0,6	7,47	Pour lip	lead	Pb, Cu, Sn, Sb	
ZLT 19	4/0,5/0,5	8,48	Ingot	lead	Pb, Sb, Cu	
ZLT 20	1,8/1/1	13,49	Ingot	lead	Pb, Sb	
ZLT 21	1,1/0,7/0,6	5,37	Ingot	lead	Pb, Sb, Cu	

Sample No	Dimensions /cm/	Weigth /g/	Object	Alloy	Main elements obtained after PIXE, sorted by quantity above and about 1%	Image
ZLT 22	2,2/1,3/1,2	9,21	Pour lip	lead	Pb, Sb, Cu	
ZLT 23	1,8/1,6/0,1-0,3	2,12	Waste product	lead	Pb, Sb, Cu, Zn	
NVS 2	2,5/1,3-1,5/0,5	18,73	Ingot	lead	**Pb, Sn, Sb**	
NVS 3	5,1/0,5-1,3/0,2	4,45	Pour lip	lead brass	Cu, Zn, Pb	
NVS 5	3-3,2/0,5-0,6/0,3-0,4	6,68	Ingot	tin-lead bronze	Cu, Sn, Pb	

Sample No	Dimensions /cm/	Weigth /g/	Object	Alloy	Main elements obtained after PIXE, sorted by quantity above and about 1%	Image
NVS 18	4,2/0,4-0,7/0,2-0,6	7,63	Ingot	lead	Pb, Sb	
NVS 21	3/1,5/0,2-0,3	11,43	Ingot	lead	Pb, Sb	
NVS 22	1,3/0,7/0,6	4,27	Ingot	lead	Pb, Cu, Sb	
NVS 24	2,1/0,4-0,6/0,3-0,4	3,69	Ingot	lead	Pb, Sb, Cu	

Determining the alloy based on the chemical elements is a simple task in historical metallurgical research. It is difficult to clarify from which ore deposit the metal was extracted. Copper and other ores from each deposit, in addition to the main component-copper, also contain many other elements that form a variety of qualitative and quantitative combinations. The metal extracted from the ore duplicates the elements that are in it. From the elements composing the metal, the general combination of the elements of the ore can be determined with sufficient precision[2]. Finding the source of the raw material is more important than determining the type of alloy. Then, the trade routes along which the metal and its products traveled in the different communities and cultures are revealed. Thus, the relationship between the community of metallurgists, traders and consumers of the product is restored.

The group of ingots, as one of the main raw materials for production, as well as the products set aside for scrap, which is the second important raw material, is no less an interesting topic. On the contrary, it poses fundamental questions concerning the entire production process and its stages and sequence of processes. Among the main tasks that can be solved with the results of the research of the elemental composition of the entire set of products are the origin of the metal and the ways of its arrival in the workshops of the production centers in the vicinity of Preslav. In addition, the main metals and alloys used in the manufacture of these products can be determined, as well as its composition and the main alloying elements in the alloy, which present its character, can be determined. The main results do provide a starting point for reasoning in these directions, and the accumulation of an extensive database will make the conclusions even more complete and definitive (**Tab. IIa-c**).

Objects found at the production center near Zlatar, Preslav district

The predominant alloy in the group of objects measured is **lead**. The extraction of lead became very easy from its ore galena (lead sulfide). Only one incomplete roasting of galena is sufficient for the two parts (roasted and unroasted) to interact and for a certain amount of metallic lead to flow from the ore[3]. This can be done by heating galena in an ordinary, open fire fanned by a natural air current. Galena melts at 1135°C, partially sublimating as early as 755°C. When galena is heated in the presence of air, it begins to oxidize from 360°C upwards. By blowing the molten lead with air at a temperature where the lead oxide that forms melts and can be skimmed off, the conversion to dross or oxide of all the lead can take place. This process was used in ancient times for the separation of lead from the precious metals contained in it by the process of cupellation.

Six out of a total of 10 objects present this second main alloy for the production of articles in art metal complexes, after the alloy of bronzes (**Fig. 2, 18, 20, 21–24**). Models were mainly cast from lead, on which the finished products were subsequently obtained from bronze and, less often, from silver alloy.

[2] CHERNIH 1972, p. 60.
[3] TRIFONOV 1950, p. 72–74.

Table IIa

Cbm.	Conc (wt%)											
Object	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Ag**	**Sn**	**Sb**	**Pb**	**Alloy**
Zl 6	0.038	0.014	0.342	0.006	0.136	69.551	27.440	0.184	0.078	<LOD	<LOD	2.296	lead brass
Zl 8	0.024	0.010	0.412	0.019	0.075	79.292	4.384	0.199	0.078	6.628	0.307	8.770	multicomponent
Zl 9	0.028	0.007	0.249	0.007	0.064	98.542		0.427	0.212	<LOD	<LOD	0.690	cooper
Zl 10	0.022	0.008	0.107	<LOD	0.039	77.613	21.322	0.239				0.650	brass
Zl 17	0.015	0.007	0.198	<LOD	0.010	1.305	0.096		0.029	0.560	0.234	98.492	lead
Zl 19	0.017	<LOD	0.063	<LOD	0.009	0.329	0.012		0.023		0.612	99.145	lead
Zl 20	<LOD	<LOD	0.043		0.011	0.097			<LOD		0.796	99.1	lead
Zl 21	0.009	<LOD	0.051	<LOD	0.010	0.223	0.018		<LOD	0.102	0.565	99.245	lead
Zl 22	0.011	<LOD	0.041		0.008	0.198	<LOD		0.031		0.428	99.447	lead
Zl 23	<LOD	0.009	0.051		0.011	0.864	0.244		<LOD		0.773	98.896	lead
Ns 2	0.014	<LOD	0.049		0.007	0.284			<LOD	2.546	0.729	97.282	lead
Ns 3	0.018	0.012	0.325	0.007	0.056	80.518	14.046	0.187	0.073	1.897	<LOD	3.831	lead brass
Ns 5	0.024	0.012	0.098	0.015	0.035	89.246		0.388	0.049	7.442	<LOD	4.409	tin-lead bronze
Ns 18	0.015	<LOD	0.080	<LOD	0.010	0.204	0.013				0.705	99.059	lead
Ns 21	0.013	<LOD	0.040		0.009	0.178	0.009		<LOD		0.586	99.272	lead
Ns 22	0.015		0.047	<LOD	0.010	2.926	0.080		0.029		0.849	98.423	lead
Ns 24	0.013	0.008	0.036	<LOD	0.013	0.519	0.033		<LOD		0.577	99.362	lead

Table IIb

	Fit.error (%)											
Object	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Ag**	**Sn**	**Sb**	**Pb**
Zl 6	5.82	12.19	1.21	28.9	2.32	0.15	0.23	6.85	25.36			1.85
Zl 8	8.46	16.81	1.08	9.37	3.63	0.13	0.51	10.53	21.98	2.55	17.32	0.62
Zl 9	7.76	22.22	1.49	24.68	4.8	0.14		3.22	15.32			4.45
Zl 10	9.23	20.69	2.66		6.26	0.16	0.28	4.93				4.62
Zl 17	20.47	37.14	1.88		15.81	0.6	3.16		32.86	8.83	13.33	0.13
Zl 19	20.59		4.81		19.77	1.46	17.24		37.74		8.94	0.15
Zl 20			6.23		14.93	2.81					7.57	0.15
Zl 21	39.92		5.96		19.52	1.91	12.96			35.63	9.69	0.15
Zl 22	26.22		5.23		17.15	1.62	46.93		24.77		9.23	0.11
Zl 23		35.01	5.98		17.53	0.78	1.7				8.35	0.15
Ns 2	28.76		5.82		27.34	1.58				4.35	9.96	0.15
Ns 3	14.2	16.47	1.6	30.46	6	0.17	0.38	10.6	34.91	7.87		1.84
Ns 5	9.39	14.93	2.97	10.4	7.76	0.15		4.35	32.4	2.89		1.27
Ns 18	24.52		3.96		18.19	1.93	16.61				8.89	0.15
Ns 21	27.52		7.42		20.79	2.18	24.04				9.75	0.15
Ns 22	24.82		6.75		21.27	0.53	5.31		39.37		8.55	0.16
Ns 24	24.41	33.21	8.02		13.06	1.02	6.93				9.02	0.16

Table IIc

	LOD (wt%)											
Object	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Ag**	**Sn**	**Sb**	**Pb**
Zl 6	0.003	0.003	0.005	0.005	0.004	0.016	0.028	0.059	0.022	0.030	0.057	0.092
Zl 8	0.003	0.003	0.006	0.004	0.005	0.017	0.024	0.150	0.013	0.095	0.060	0.054
Zl 9	0.004	0.003	0.006	0.004	0.054	0.016		0.029	0.035	0.066	0.077	0.146
Zl 10	0.004	0.003	0.006	0.004	0.004	0.020	0.034	0.028				0.103
Zl 17	0.005	0.004	0.004	0.004	0.003	0.003	0.004		0.009	0.095	0.026	0.033
Zl 19	0.006	0.005	0.004	0.004	0.003	0.003	0.004		0.013		0.026	0.065
Zl 20	0.006	0.005	0.004		0.003	0.003			0.013		0.052	0.054
Zl 21	0.007	0.006	0.005	0.004	0.003	0.003	0.004		0.010	0.085	0.066	0.032
Zl 22	0.005	0.004	0.003		0.003	0.002	0.003		0.010		0.025	0.052
Zl 23	0.007	0.005	0.004		0.003	0.002	0.004		0.011		0.044	0.031
Ns 2	0.007	0.006	0.004		0.003	0.002			0.013	0.116	0.067	0.036
Ns 3	0.005	0.006	0.007	0.005	0.006	0.020	0.031	0.095	0.033	0.176	0.107	0.101
Ns 5	0.004	0.003	0.007	0.003	0.005	0.010		0.087	0.022	0.107	0.063	0.128
Ns 18	0.006	0.005	0.004	0.004	0.003	0.003	0.004				0.053	0.045
Ns 21	0.007	0.006	0.005		0.003	0.002	0.004		0.016		0.060	0.044
Ns 22	0.007		0.005	0.004	0.004	0.006	0.006		0.015		0.092	0.053
Ns 24	0.006	0.005	0.005	0.003	0.003	0.003	0.004		0.014		0.051	0.070

One part of the finds consists of ingots of finished metal from which the mentioned articles were cast. For example, among the investigated finds, four are identified as lead ingots (Zl. 17, 19, 20, 21), one is a melt separated for recycling (Zl. 22) and one is a scrap model (Zl. 23). Among these six finds, the leading element is *lead Pb* in its maximum values of 98–99% (**Fig. 4**). Despite the similarity, some slight deviations from these indicators are also observed. For example, two objects show a value of 98.492 and 98.896% (Zl. 17, Zl. 23), while the rest have a value above 99%, i.e. almost pure lead alloy-from 99.1 to 99.447% (Zl. 20, Zl. 22).

A natural impurity of lead ores is *antimony Sb*. Its values enter the lead alloy directly from the raw material and do not depend on the content of the main element lead Pb (**Fig. 14**). The amounts of antimony Sb in the group vary from 0.234 to 0.796%, and in the first case the lead Pb is 98.492% (Zl. 17), and in the second–99.1% (Zl.20), (**Fig. 15, 26**). At alloy values above 99%, antimony Sb amounts to 0.428% (Zl. 22), 0.565% (Zl. 21) and 0.612% (Zl. 19).

An indicative element for lead ores is *silver (Ag)*, which also inserted lead in alloys (**Fig. 13**). Its content in the analyzed group of subjects is barely noticeable, and somewhere below the permissible minimum of registration in the study (**Fig. 16**). Its values are only 0.023% (Zl. 19)-0.031% (Zl. 22), and in three items it does not even reach these amounts (Zl. 20–21, Zl. 23). This comes to show only one thing, namely the very well purified alloy from which silver was previously extracted by the method of cupellation and subsequent refining of the metal, considered the main method of mining and obtaining pure silver from its main carrier-lead ores. Metallic lead is obtained by roasting the ores and subsequent reduction with carbon in shaft furnaces. The melting point of lead is 327°C, but melting requires at least 800°C for the lead to become liquid. Lead ores contain rock impurities (silicates), which at the high temperature of the reduction react with part of the lead oxide and form lead silicate, which passes into the slag. In addition to this method, known as the frying-reduction method, a frying-reaction method is also applied. With it, the ore is fried in a lack of oxygen so that part of the silphite remains unchanged. The temperature is then raised and the air purge is stopped.

Crude lead contains silver, copper, arsenic, antimony, tin, bismuth, etc. It undergoes refining. The copper is separated as the melt cools to near the melting temperature, where the copper crystallizes, trapping small amounts of lead in a corresponding inter-metallic compound. The remaining elements are oxidized by blowing air and float to the surface. Pure silver is relatively rare in nature, and where it is found, its quantities are scarce and do not give the opportunity to talk about silver extraction from its natural minerals. Therefore, lead ores are the main source of obtaining this valuable metal both in ancient times and today.

The other impurity that naturally occurs in lead ores and enters the alloy subsequently is *copper Cu* (**Fig. 3**). Here, unlike antimony, the copper content in the alloy is directly proportional to the percentage amount of lead (**Fig. 17**). That is why the values are the highest in those items where the lead Pb is 98%. So, for example, with lead of 98.492% stands above one percent copper, i.e. 1.305% (Zl. 17); and at 98.896% Pb-0.864% Cu (Zl. 23). For the rest of the samples, the ratio is the same. Where the lead is above 99%, the copper content varies with its percentage and ranges from 0.097% (Zl. 20) to 0.329% (Zl. 19) (**Fig. 32–34**).

An optional element for lead alloys is *tin Sn*. Usually, it is either absent or its values are insignificant and in most cases are below the permissible minimum, therefore they are not taken into account in the analysis of the elemental composition (**Fig. 6**). However, here, in one of the samples, the *tin Sn* values are above the expected level, reaching up to 0.56% (Zl. 17) (**Fig. 22, 34**). In this case, the alloy is defined as tin-lead. Of the remaining examples, there is only one more where the content of tin Sn is recorded, but its value is smaller-0.102% (Zl. 21) and one cannot speak of an alloy influenced by tin.

The presence of *zinc Zn* in the lead alloy is not a natural impurity in the lead alloy, but usually enters together with the copper (**Fig. 5**). Sometimes, when the values are greater, its presence is an indicator of the addition of scrap recycled metal, but in this case the reason for the zinc to be reported is rather the former. Therefore, its values are tied to those of the amounts of copper in the alloys of the individual objects, i.e. where there is a high percentage of copper Cu in the lead alloy, there the presence of zinc is most noticeable 0.244% Zn-0.864% Cu (Zl. 23); 0.096% Zn–1.305% Cu (Zl. 17) (**Fig. 23, 32–33**). And in the ingot with a copper content of 0.097%, the presence of zinc in the alloy (Zl 20) is not even recorded.

The rest of the measured elements-*chromium Cr, manganese Mn, nickel Ni* have values of 0.01% and below (**Fig. 7–8, 11**). In some cases, the amounts are so minimal that they fall under the so-called permissible minimum and were not measured as such (**Fig. 18–20**). Their presence in the lead alloy is the result of entry from the original ore sources. The situation is similar with the recorded values of *iron Fe*, which is a natural impurity of lead ores (**Fig. 9, 21, 37**). Its amounts average 0.04% (Zl. 20, 22)-0.05% (Zl. 21, 23). Somewhere they reach up to 0.063% (Zl. 19) and at most up to 0.198% (Zl. 17). The iron values are also an indicator of the reduction conditions during the melting and casting of the alloys. The low amounts are an indication of the very good conditions of preparation and implementation of this process (**Fig. 35**).

The remaining four objects analyzed in the course of the study are made of alloys of different composition, generally defined as **bronze alloys**. The first of them (Zl. 6) is a representative of *brass alloys*. The Cu content of the copper base is very low–69.551%. On the other hand, the amounts of zinc Zn are very high and reach 27.44% (**Tab. II**). That's why the alloy is brass. The elevated lead Pb values of 2.296% precisely identify the object's alloy as *lead brass* (**Fig. 5, 23**). The amounts of *arsenic As* of 0.184% enter from the raw material-the copper ores. They are also indicative of their origin (**Fig. 12**). It is accepted that the limit concentration of arsenic As in the alloy should be 1% to talk about of artificially obtained bronze[4].

Silver Ag has values of 0.078%, which defines it, along with other trace elements such as *nickel Ni and cobalt Co*, with amounts of 0.136% Ni and 0.006% Co respectively as an indicator of the origin of the copper raw material (**Fig. 10–11, 13**). The value of *iron Fe*, which also enters the alloy from the starting material, is 0.342%. Its low values are indicative of the good conditions provided during the entire reduction process and prove its origin (**Fig. 36**).

Another one of the samples was identified as *brass* (Zl. 10). In it, *copper Cu* is 77.613% Cu, and *zinc Zn*–21.322% (**Fig. 5, 32–33**). Here the *lead Pb* is 0.650%, which

[4] RINDINA, RAVICH 2012, p. 5.

does not define the alloy as lead brass, but rather as a relatively pure zinc alloy. *Silver Ag, tin Sn and antimony Sb* were not registered during the elemental composition analysis, and the amount of *cobalt Co* was below the permissible minimum registration, therefore it was not reported. Of the important trace elements, the percentage content of *arsenic As* is elevated-0.239% (**Fig. 12**). Other elements indicative of raw material sources were also recorded, such as *nickel Ni*-0.039%, *manganese Mn*-0.008% and *chromium Cr*-0.022% (**Fig. 29, 31, 37**). The *arsenic As* increases the hardness of the metal, and the nickel Ni holds the arsenic in the alloy, which can volatilize when heated, making the alloy suitable for quenching and tempering. *Iron Fe* amounts of 0.107% Fe were introduced from the starting materials.

In both examples of brass alloys, additional significant amounts of *zinc Zn* have been added, which, unlike most of the trace elements discussed, is not present in the copper ores, or if there are traces of it, they are insignificant and cannot be registered in the study of the composition of the alloy (**Tab. II**). In the first case (Zl. 6) it is a bronze wire obtained from a metal to which a considerable amount of zinc and lead has been added to improve the casting properties of the alloy and to obtain a color resembling gold. In the second sample (Zl. 10), which is part of a foundry system, recycled metal was added in which the zinc content was significant. Subsequently, when the metal is melted and the scrap scraps are placed in the smelter, zinc falls into the alloy and determines the properties characteristic of brass alloys in the finished products. Undoubtedly, the craftsmen preparing the alloys well understood what amount of ligature was necessary to obtain a metal of the desired qualities.

One of the objects-part of a funnel system ("tree") subjected to analysis shows belonging to the so-called *"pure" copper* (Zl. 9). The base content of 98.542% *Cu* is the highest compared to all samples examined. *Tin Sn and antimony Sb* fall in the column below the permissible minimum and are not registered. *Lead Pb* is 0.69% and in this case is a natural impurity of the natural copper ore (**Fig. 3–4, 17, 34**). One part of the *silver Ag*-0.212% enters from the ore, and another part is the accompanying element Pb. Indicative of the source of raw material are the amounts of *arsenic As*-0.427%, which in these values fall into the alloy from the copper ore (**Fig. 12, 26**). Contrary to most expectations, arsenic As does not readily volatilize from copper, even when the temperature reaches several hundred degrees. In the smelting of copper ores, on the contrary, arsenic is released very efficiently. Therefore, this element can be a good indicator of natural copper[5].

It should be added *nickel Ni*-0.064%, *manganese Mn*-0.007%, *cobalt Co*-0.007% and *chromium Cr*-0.028%, which are natural impurities of "pure" copper (**Fig. 29–30**). *Iron Fe*-0.249% also belongs to the elements accompanying the copper ore, and its low values are an indicator of the excellent reduction conditions provided during the entire process of melting and casting of the metal (**Fig. 27, 35**). Likewise, cobalt Co is always low because, unlike nickel Ni, it often precipitates as carbonate. For the same reason, gold Au is low, while silver Ag is reaching a percentage level. Thus, the pattern of low cobalt Co, antimony Sb and gold Au combined with high silver Ag and/or arsenic As can be considered as an indication of native copper (**Fig. 24,**

[5] PERNICKA 1999, p. 163–171.

26, 30, 36). Unfortunately, such a clear pattern is rarely found[6]. Concentrations of all impurities are usually low and it can be difficult to decide whether the copper is natural or smelted. Nevertheless, the trends are clear.

The variety of alloys used in the complexes of workshops near Zlatar is supported by another common alloy, which is the so-called *multicomponent alloy*. As the name indicates, its composition is determined by two or more alloying elements. A representative of the alloy is a piece of a funnel system (Zl. 8) set aside for scrap. Its composition is identical to that of the group of objects that flew away with it. Therefore, analyzing the elemental composition of such foundry remains is also important for the overall picture of the alloys prepared by the ancient masters. *The copper base Cu* is 79.292%, which is much smaller compared to, for example, the previous sample analyzed (**Fig. 3, 34**). This is due to the significant amounts of the three alloying elements of the bronze alloy-*lead Pb, tin Sn and zinc Zn*. The most significant is the amount of *lead Pb*–8.770%, which was artificially added to the molten alloy (**Fig. 17, 35–36**). It is followed by *tin Sn*–6.628% and *zinc Zn*–4.384%, which also enter the smelter, but not alone, but rather with the added scrap (**Fig. 22–23, 33**). Multicomponent alloys are known to be composed of both raw material additions and scrap, the latter source being the determining factor. For casting and stamping, multi-component alloys obtained by mixing scrap from different sources were used[7].

In this order, the amounts of the remaining elements are determined by the base and alloying attachments of the alloy. For example, *antimony Sb* of 0.307% is mainly an accompanying element of lead Pb (**Fig. 14–15, 25**). The minimum amounts of *silver Ag*-0.078% enter both through lead Pb and copper Cu (**Fig. 13, 16, 24, 36**). *Arsenic As*-0.199% falls not only through the copper, but also from the recycled metal added to the alloy (**Fig. 12, 26**). The same applies to the other trace elements *nickel Ni*-0.075%, *cobalt Co*-0.019%, *manganese Mn*-0.01% and *chromium Cr*-0.024% **(Fig. 8, 10–11, 18–20**). *Iron Fe* is 0.412% and enters mainly through the copper ore, and part of it also from the recycled metal (**Fig. 9, 21, 27–28, 35, 37**).

Copper refining is done to reduce impurities of bismuth Bi, arsenic As, sulfur S, even when they are in an amount not greater than 1–2%, which reduce technical qualities. In the Middle Ages, the method of refining melting was used, in which melting and blowing alternated with abundant access of air. In the latter, the impurities contained in the raw copper are oxidized and removed either by flying out or by producing slag. Thus zinc Zn, lead Pb, arsenic As and antimony Sb for the most part fly off, and iron Fe, nickel Ni, the remaining zinc Zn pass into silicates, giving slag. The copper oxide is removed by sprinkling a layer of charcoal on top of the refractory metal bath and stirring for up to an hour with raw wooden sticks. Through dry refining, it is impossible to completely remove the impurities or separate the precious metals, therefore certain amounts remain in the alloy and are registered in the analysis of the elemental composition of the products obtained from it.

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6 PERNICKA 1990, p. 21–129.

7 AVILOVA 2010, p. 5–14.

Objects found at the production center near Novosel, Shumen district

The examined small group of finds from the production center near Novosel shows a more compact picture (**Tab. I**). Here, the variety of alloys is not so great, but the number of objects is also not great (**Tab. II**). However, the results provide insight into some of the popular alloys used in the casting process. Out of a total of seven examined objects, five were cast from **lead alloy** (Ns. 2, 18, 21–22, 24) (**Fig. 2**). Some differences are also observed among it. Thus, for example, in one of the samples (Ns. 2), the *lead base* Pb is 97.282%, in contrast to the other samples, where it is 98 and above all over 99% Pb (Ns. 18, 21, 24) (**Fig. 4**). The deviation in the given example is due to the increased content of *tin Sn*–2.546%, the values of which indicate its artificial addition in the alloy (**Fig. 6, 22, 33–34**). The sample is an ingot with a rectangular cross-section and oval edges, with signs of chipping at one end, i.e. in the process of work certain quantities of metal were separated from it and added to the alloy prepared for remelting. The high value of tin Sn also indicates that the ingot was cast on site, in the workshop itself, and in the process of its preparation a certain amount of tin was deliberately added to improve the properties of the raw material. Half of a mold for shapes identical to the present one, found at the production center near Zlatar attests to the casting of ingots on site. Undoubtedly, such tools were also used in the other complexes where such activity was carried out.

The *antimony Sb* value is 0.729% Sb, which is due to its entry from the lead ore, in which antimony is a natural impurity (**Fig. 14–15, 25–26**). An important observation is the fact that the amounts of *silver Ag* are not high and even fall below the permissible limits of a study in which no values were noted not only for this sample but also for two more belonging to the lead alloy group (Ns. 21, 24). This mainly shows one thing-the very good purification of the alloy and the separation of impurities in it, among which *silver Ag* is one of the most important (**Fig. 13, 16, 36**). Purification is carried out in the processes of cupellation and subsequent refining carried out during the preparation of the raw material. The mentioned processes were carried out where the main lead substrate was mined. In the studies of the three known production centers in the vicinity of Preslav, no traces of metallurgical activity have been found so far, which suggests that such activity was not carried out in these places.

Of the trace elements in the lead alloy, which can be a starting point for reasoning in the direction of the origin of the raw material and its deposit, the values of *copper Cu*-0.284% Cu, minimal amounts of *nickel Ni*-0.007%, somewhat *chromium Cr*-0.014% are indicative. (**Fig. 3, 7, 11, 31, 37**). The indicators of *iron Fe* are also a factor-0.049% Fe, especially with their minimal amounts, which, in addition to being a natural impurity, are also an indicator of the very good reduction conditions implemented during the preparation and implementation of the entire process of melting and casting the metal (**Fig. 9, 21, 25, 27–28**).

The representatives of the lead alloy that we mentioned show relatively similar parameters, in contrast to one of them (Ns. 22). The *lead base Pb* in it is 98.423%, and the content of *antimony Sb*, influenced by it-0.849% (**Fig. 15**). In contrast to the first example and those mentioned similar to it in terms of the amount of *silver Ag*, here it has been reported and is 0.029% (**Fig. 16, 36**). Indicators of elements such as *zinc Zn*, which is 0.08% and is missing in the first sample, as well as *nickel Ni*-0.01% Ni and *chromium Cr*-0.015% show an increase (**Fig. 5, 18, 20**). The *iron Fe* of 0.047% Fe is similar in amount and is a consequence of the lead ores and possibly some added recycled metal (**Fig. 9, 27–28**). Reason to assume such is the content of *copper Cu*, which is close to 3%, i.e. 2.926% (**Fig. 3, 17, 29, 31**). There is no way that such amounts of copper are a natural impurity to the raw material. The high value is a consequence of added "pure" copper or of recycled metal in which the content of copper and that of zinc, which is not a natural impurity of lead ores, is accounted for in the analysis.

The use of different sources of metal is also attested by the remaining three samples (Ns. 18, 22, 24). The *lead base* in all three is similar and ranges from 99.059% (Ns 18) to 99.362% (Ns. 24), which is practically a "pure" lead alloy (**Fig. 4, 17, 32, 36**). In view of these values, the amounts of *antimony Sb* from 0.577% to 0.705%, which is positively correlated with lead, are also based on these values (**Fig. 15**). Silver Ag values that were not reported or fell below the acceptable assay minimum also support the general picture. *Tin Sn*, unlike the first sample (Ns. 2) was not reported. *Zinc Zn* was found in minimal amounts – from 0.009% (Ns 21) to 0.033% (Ns. 24), *nickel Ni* also-0.009%, 0.01 and 0.013% (**Fig. 11, 20, 31, 37**). In one of the samples (Ns. 24) *manganese Mn*-0.008% was found (**Fig. 19, 29–30**). In the other two examples, its content is below the permissible minimum and was not counted numerically in the study. The amounts of *chromium Cr* are similar-0.013-0.015% (**Fig. 7, 18**). A greater variation in percentage content in the three samples shows the *copper Cu* content of 0.178% (Ns. 21), 0.204% (Ns. 22) and 0.519% (Ns. 24) entering the alloy of the three ingots as a natural impurity from lead ores (**Fig. 3, 17, 22, 34–35**). The differences suggest different sources of raw material supplied to metalworking workshops in the form of ingots.

The presence of two sources of raw material-ingots and scrap-is confirmed by the study of the elemental composition of the two **copper alloy** objects. One of them is an ingot (Ns. 5) and the other a caster "tree", part of the caster system in the foundry case, by which the molten metal reached the negative impressions in the sand mold of the case (Ns 3). The ingot is made of *tin-lead bronze. The copper base Cu* is 89.246% (Ns. 5), (**Fig. 3, 32, 36**). The main alloying additives of the alloy are tin and lead, and their values are greatly increased. *Tin Sn* is 7.442%, and *lead Pb*–4.409%, which also determines the name of this alloy (**Fig. 22, 33–34**). Both metals are artificially added to the alloy. The expected amount of antimony Sb that would have entered through the lead is below the permissible minimum and is not accounted for. *Silver Ag*, on the other hand, is 0.049%, which is present but at a low percentage, indicating its entry as a natural impurity from the copper ore into the alloy rather than through lead (**Fig. 13, 16, 24, 36**). The latter testifies also to the relatively "pure" metal of the alloying lead plug added during the preparation of the alloy.

Arsenic As is an important trace element providing a starting point for raw material sources. Its value is significant-0.388% and indicates both its entry from copper ores and the addition of a certain amount of recycled metal containing arsenic, the so-called arsenic bronze, from which a significant part of the chronologically earlier metalwork products were cast (**Fig. 12, 26**). An important relation to the deposit of copper ores is given by the amounts of nickel and cobalt. *Nickel Ni* is 0.035%, and *cobalt Co* is 0.015% (**Fig. 10–11, 20, 31**). *Manganese Mn*-0.012% and *chromium Cr*-0.024% should be added to them, which are also decisive for the overall picture of the starting raw materials (**Fig. 18–19, 29**). The low values of *iron Fe*-0.098%

also define it as a natural impurity of the ore and an indicator of the very good reduction conditions during the preparation and melting of the metal, without the separation of slags and overburning of the metal (**Fig. 9, 21, 25, 28, 37**).

Bismuth Bi, arsenic As and lead Pb have the most harmful effect on copper. Thus, 0.01% Bi and more than 0.1% Pb make copper brittle when hot (forging and rolling), and arsenic As, although it does not affect the ductility and strength of copper, even in amounts of 0.01% reduces electrical conductivity by 3%. An admixture of nickel Ni makes copper more ductile, a little tin Sn and zinc Zn, and also manganese Mn and aluminum Al make casting easier and do almost no harm.

In the workshop, the ingots were separated. At the same time, a part of the metal was remelted and used to cast finished products, another part served as raw material for obtaining blanks-sheets, strips, rods, wires. Casters have noticed that ingots cast from highly burned metal have a coarser structure than ingots cast from metal at less heat. Strong heating leads to the destruction of the particles of isomorphous impurities, as a result of which they come out of the crystallization process. Low heating and low casting temperature contribute to the intensification of the processes of "non-spontaneous" crystallization and the obtaining of a fine-grained structure in the castings.

Impurity-free alloys have a columnar structure. The formation of the crystallization structures, in addition to the composition, can also be influenced by the conditions of casting and cooling. By changing these conditions, a different construction of the ingots can be obtained and the ratio between the main structural zones can be influenced. Rapid cooling, high preheating of the metal, elevated casting temperature and relaxed casting promote the formation of columnar crystals throughout the thickness of the ingot, called transcrystallization. Transcrystallization is characteristic of copper and its other alloys (brass, tin bronze, etc.). Such a structure of the ingots is the reason for their destruction during casting, and also during the subsequent processing under pressure.

The fragment of the funnel system (Ns. 3) was cast, together with the rest of the articles on it, subsequently separated, from *leaded brass*. The *copper base Cu* in this case is much lower–80.518%, which is a consequence of the high values of *zinc Zn*–14.046%-the main alloying additive of the alloy (**Fig. 3, 5, 32**). Besides the addition of zinc Zn, high values of *lead Pb*–3.831% and of *tin Sn*–1.897% were recorded in the study (**Fig. 22–23, 33**). The presence of lead, the two metals with relatively high values, is explained by their artificial addition to the alloy, which in all probability happened not so much with their individual addition, as with their entry from scrap recycled metal into the smelter. The content of *silver Ag*-0.073%, as well as *arsenic As*-0.187% are also confirmation of what was said (**Fig. 13, 16, 26**). The latter are also an indicator of ore deposits, but with the addition of recycled metal, their diagnosis becomes vaguer and more conditional. The admixture of lead, the concentration of which is high (up to 1–2%), improves the casting qualities of the metal compared to pure copper. Arsenic and antimony have such an effect. Metallurgists-casters obviously knew the properties of copper obtained from different ores: carefully selected copper minerals (malachite, azurite) or from unrefined polymetallic ores[8].

[8] TEREHOVA 1975, p. 37.

The amounts of *nickel Ni*-0.056% and *cobalt Co*-0.007% are also trace elements important in research in this direction (**Fig. 10–11, 20, 31**). *Manganese Mn*-0.012% and *chromium Cr*-0.018% are indicative in the same respect (**Fig. 7–8, 18–19, 30**). The many and varied elements recorded in the alloy analysis are indicative of the use of recycled metal. *Iron Fe* values are slightly elevated-0.325%, which is indicative of both their natural admixture of ore sources and added scrap (**Fig. 9, 27–28, 35**). However, the indicators show the presence of good reduction conditions in the melting and casting of the metal in the mold, from whose funnel system the present object is also.

With the exception of gold and platinum, the majority of metal artifacts used in antiquity and the Middle Ages were obtained from the smelting of metal-bearing ores, which produced various metals and alloys. One of the first tasks of archaeological chemistry is to trace these metal objects back to their ore sources using the analyzes of the so-called "trace elements", which is a direct method of reconstructing ancient trading patterns. Thus, the use of the term "trace element" is for an element in the alloy that is not deliberately added and which is contained in and is characteristic of the ore from which the metal is derived[9]. Such a "trace element" can be from a fraction of a percent to several tens of percent, and the question of its deliberate addition or accidental fall into the alloy continues.

There are different opinions about the nature of the early processes for obtaining metal alloys. The main thing is that the metal alloys were obtained by the careful mixing of the molten metals. Others suggest that compositional control is achieved by successive additions of relatively pure alloying elements to the alloy. Between these two opinions there is a third, which is that the control over the content of the alloy was already carried out when the ores, mined from different geographical regions, were mixed together, before their smelting. Thus, a proper balance of the composition in the final metal is achieved. Work processes for the preparation of the final metal products further complicate the picture, such as the introduction of high-temperature processes, which may in turn require the additional addition of pure metals. Adding to this the almost invariable practice of adding recycled metals, as well as post-deposit corrosion resulting from electrochemical modification of the composition, the situation is further complicated. The current interdisciplinary study is a small step towards the clarification of all these processes that accompany the products from the production centers for artistic metal in the vicinity of Preslav-the result of the combined efforts of researchers from different fields of knowledge.

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[9] POLLARD, HERON 2008, p. 193.

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Fig. 1. Administrative positioning of the production centers of metal art near Zlatar and Novosel (Bulgaria).

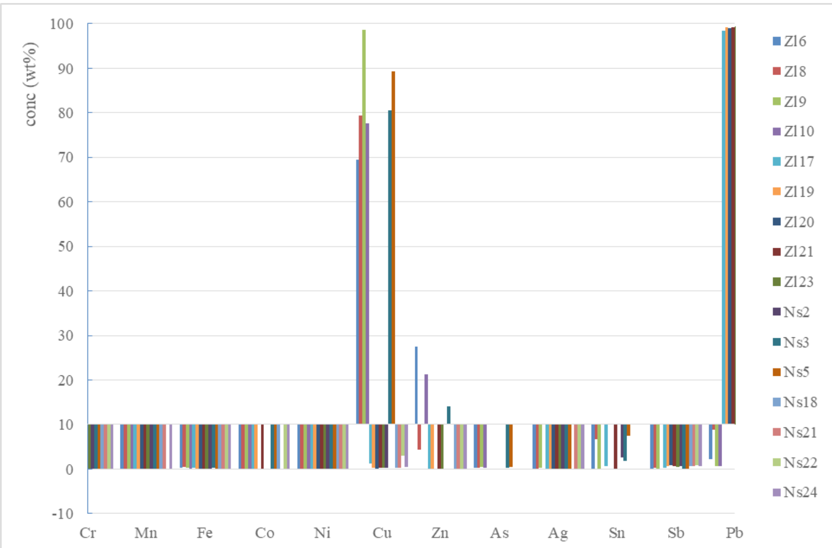

Fig. 2. Elemental composition of artifacts of non-ferrous metals found on the centers of metal art in Zlatar and Novosel.

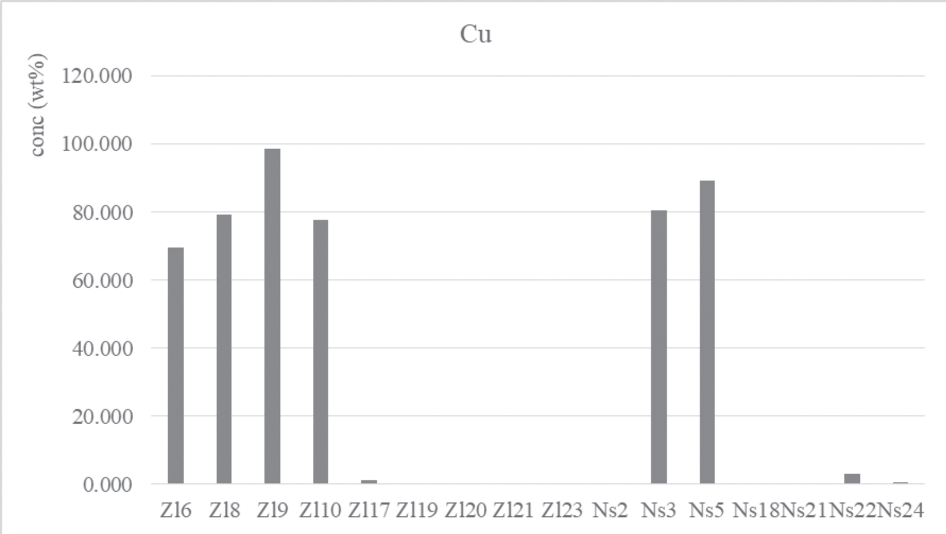

Fig. 3. Concentration of copper (Cu) in artifacts of non-ferrous metals found on the centers of metal art in Zlatar and Novosel.

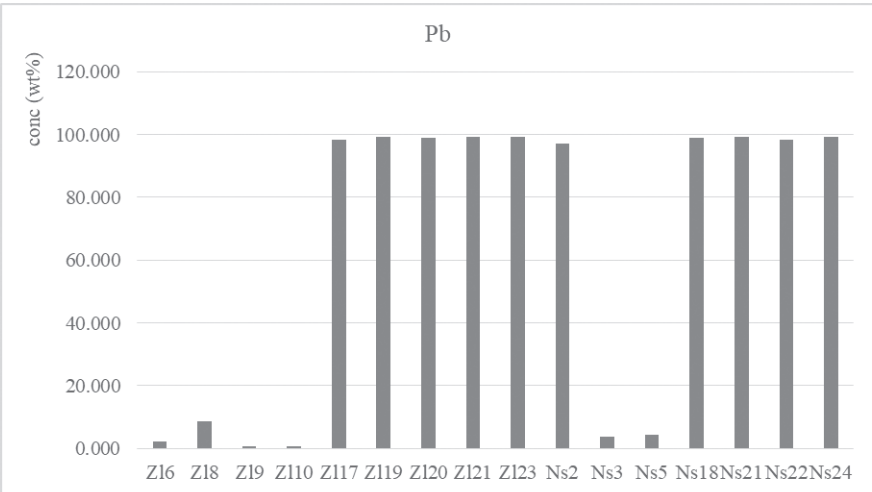

Fig. 4. Concentration of lead (Pb) in artifacts of non-ferrous metals found on the centers of metal art in Zlatar and Novosel.

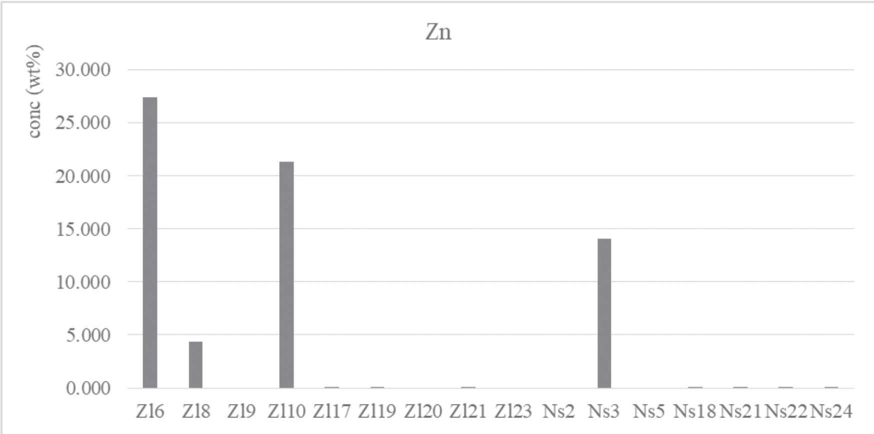

Fig. 5. Concentration of zinc (Zn) in artifacts of non-ferrous metals found on the centers of metal art in Zlatar and Novosel.

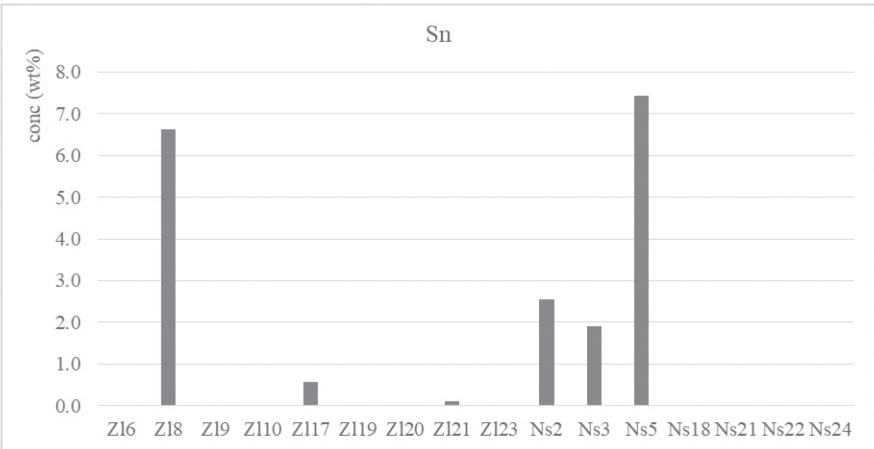

Fig. 6. Concentration of tin (Sn) in artifacts of non-ferrous metals found on the centers of metal art in Zlatar and Novosel.

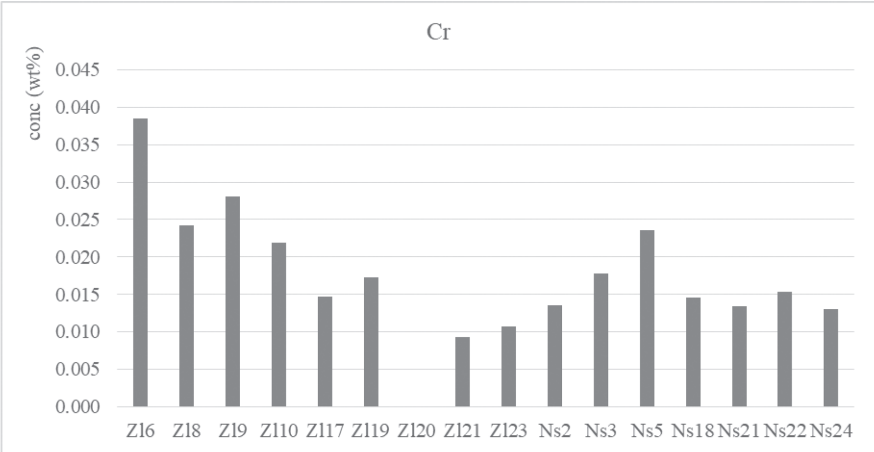

Fig. 7. Concentration of chromium (Cr) in artifacts of non-ferrous metals found on the centers of metal art in Zlatar and Novosel.

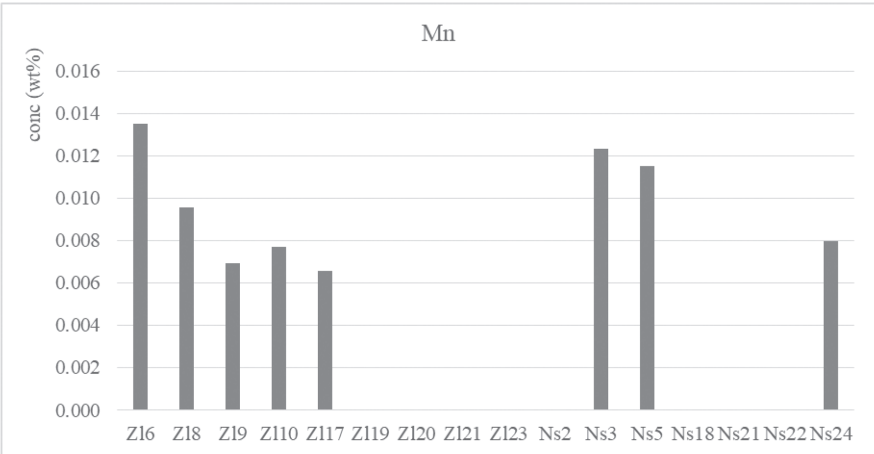

Fig. 8. Concentration of manganic (Mn) in artifacts of non-ferrous metals found on the centers of metal art in Zlatar and Novosel.

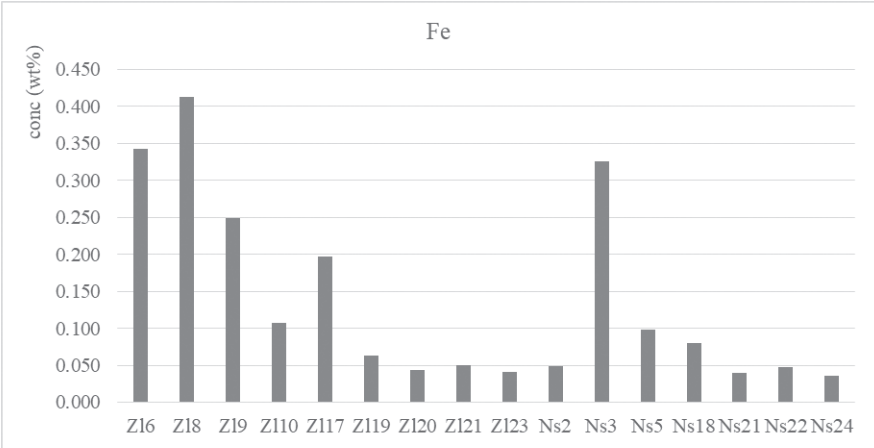

Fig. 9. Concentration of iron (Fe) in artifacts of non-ferrous metals found on the centers of metal art in Zlatar and Novosel.

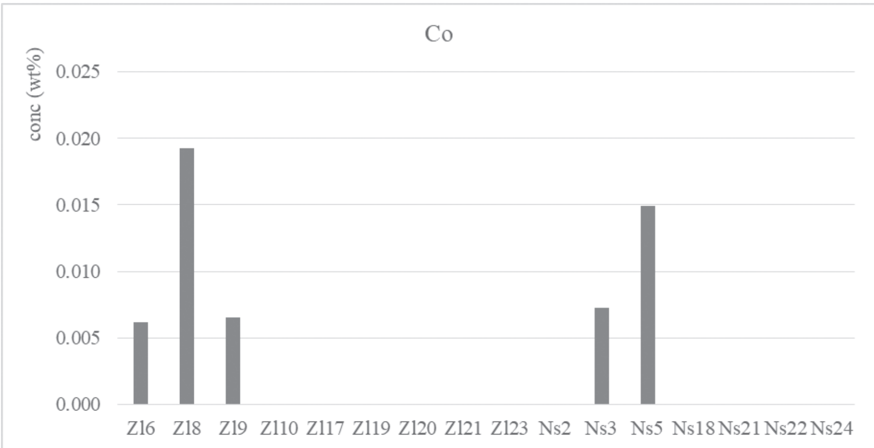

Fig. 10. Concentration of cobalt (Co) in artifacts of non-ferrous metals found on the centers of metal art in Zlatar and Novosel.

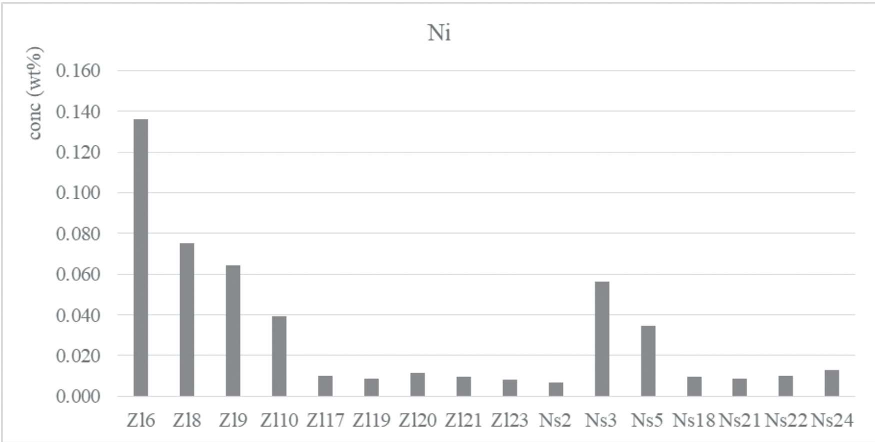

Fig. 11. Concentration of nickel (Ni) in artifacts of non-ferrous metals found on the centers of metal art in Zlatar and Novosel.

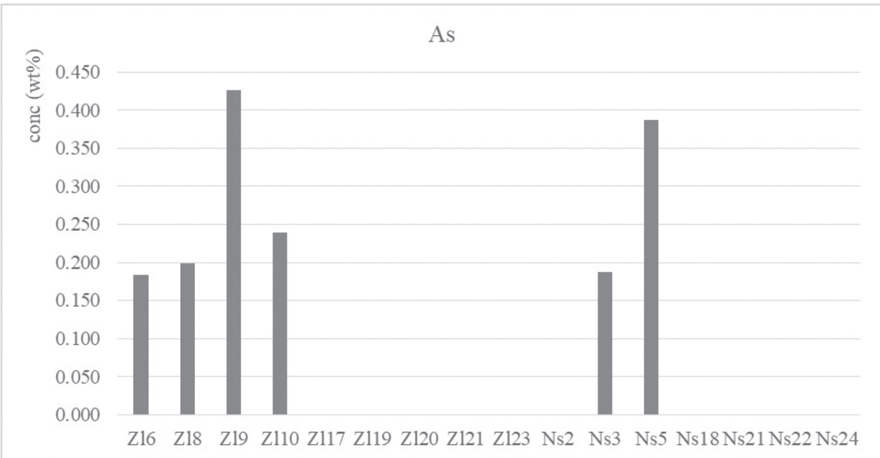

Fig. 12. Concentration of arsenic (As) in artifacts of non-ferrous metals found on the centers of metal art in Zlatar and Novosel.

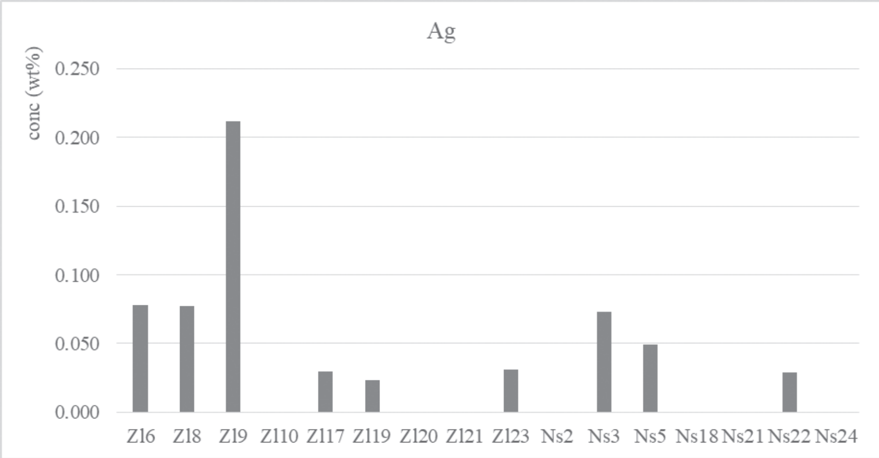

Fig. 13. Concentration of silver (Ag) in artifacts of non-ferrous metals found on the centers of metal art in Zlatar and Novosel.

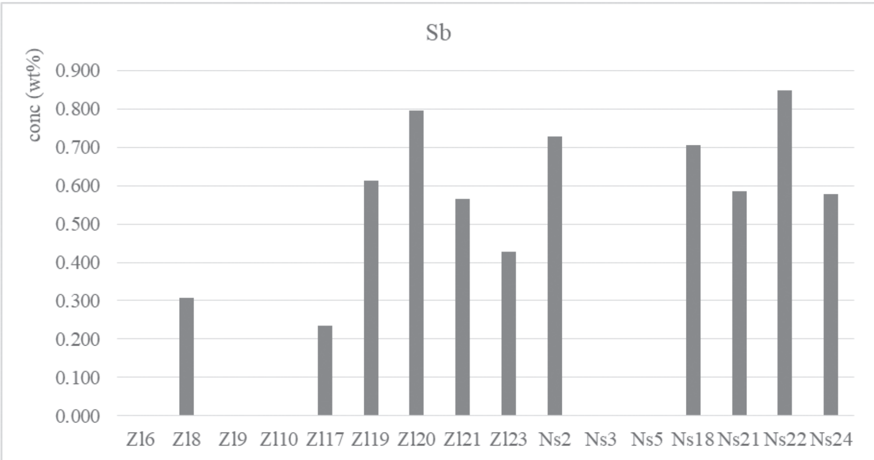

Fig. 14. Concentration of antimony (Sb) in artifacts of non-ferrous metals found on the centers of metal art in Zlatar and Novosel.

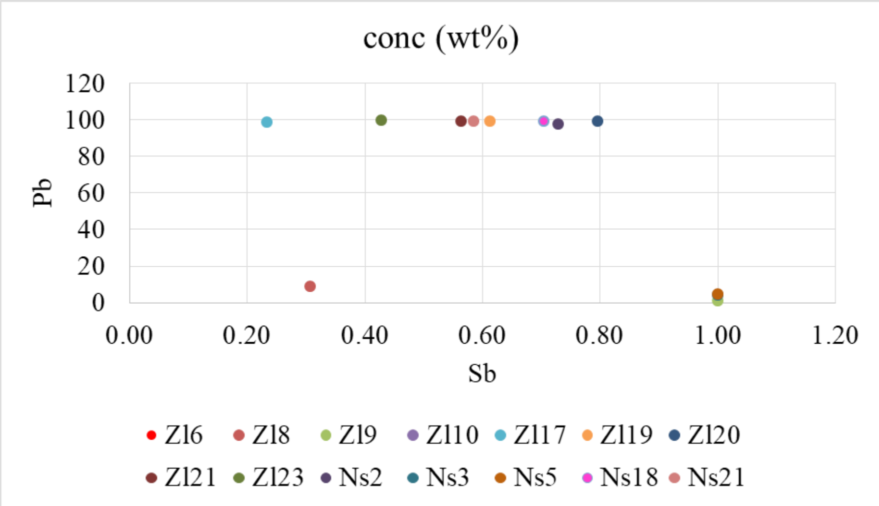

Fig. 15. Scatter graph of the concentration of antimony and lead (Sb-Pb) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

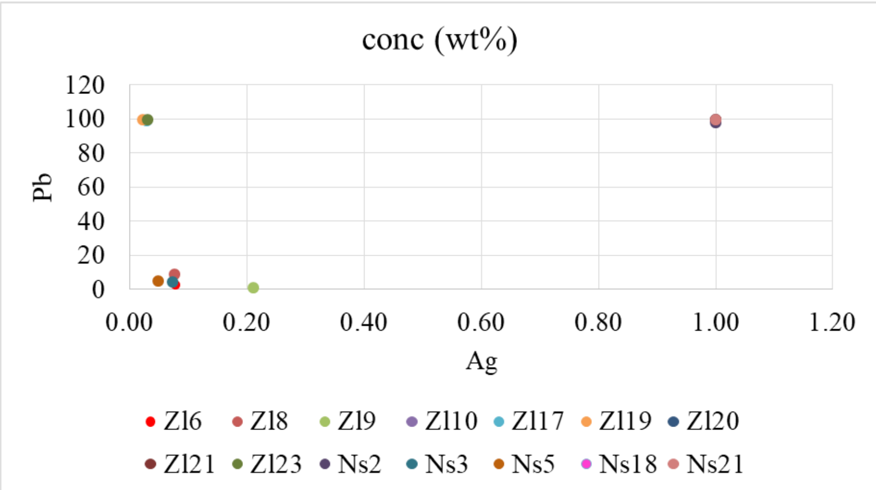

Fig. 16. Scatter graph of the concentration of silver and lead (Sb-Pb) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

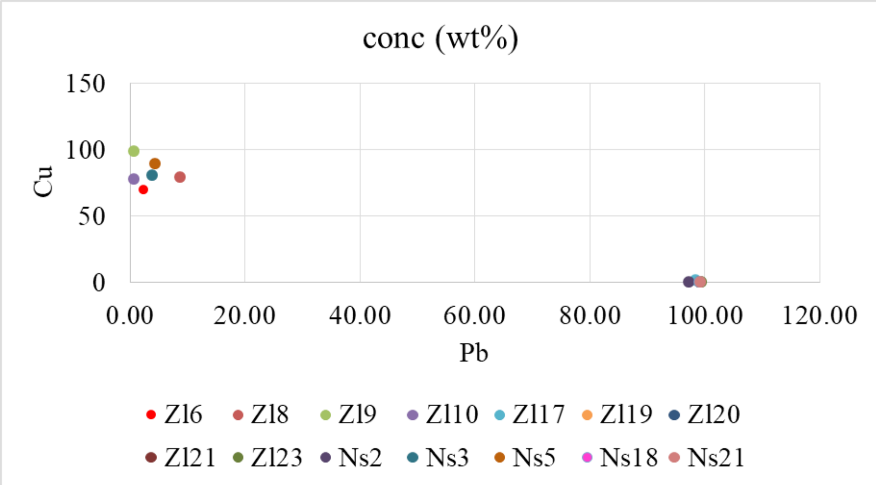

Fig. 17. Scatter graph of the concentration of lead and copper (Pb-Cu) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

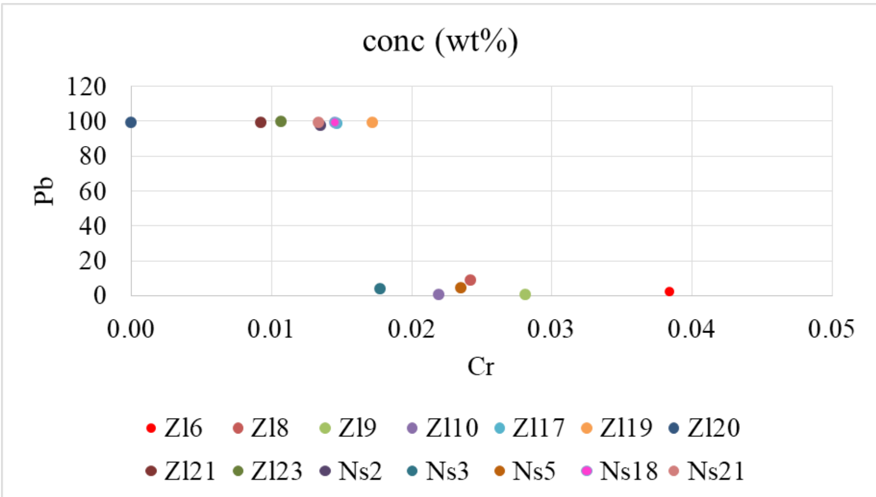

Fig. 18. Scatter graph of the concentration of chromium and lead (Cr-Pb) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

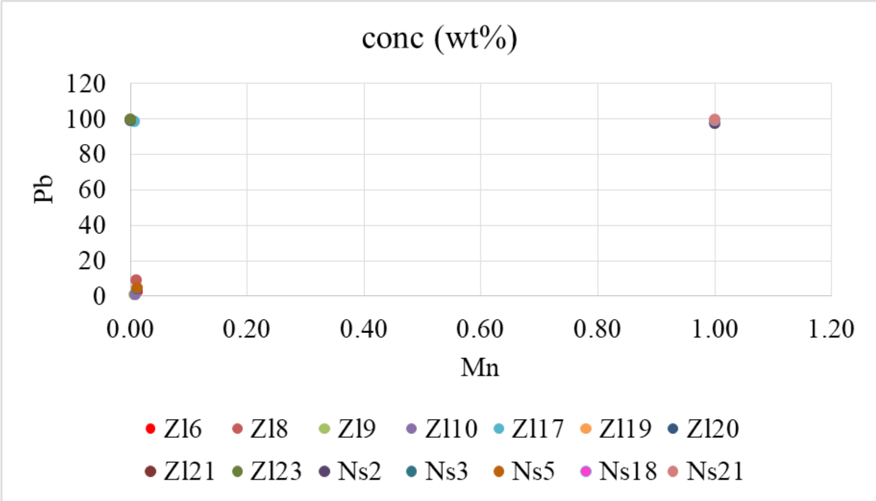

Fig. 19. Scatter graph of the concentration of manganic and lead (Mn-Pb) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

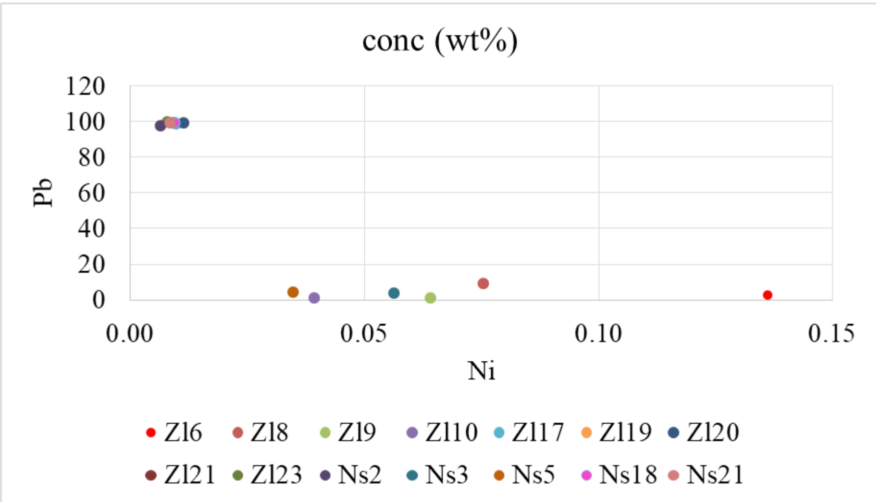

Fig. 20. Scatter graph of the concentration of nickel and lead (Ni-Pb) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

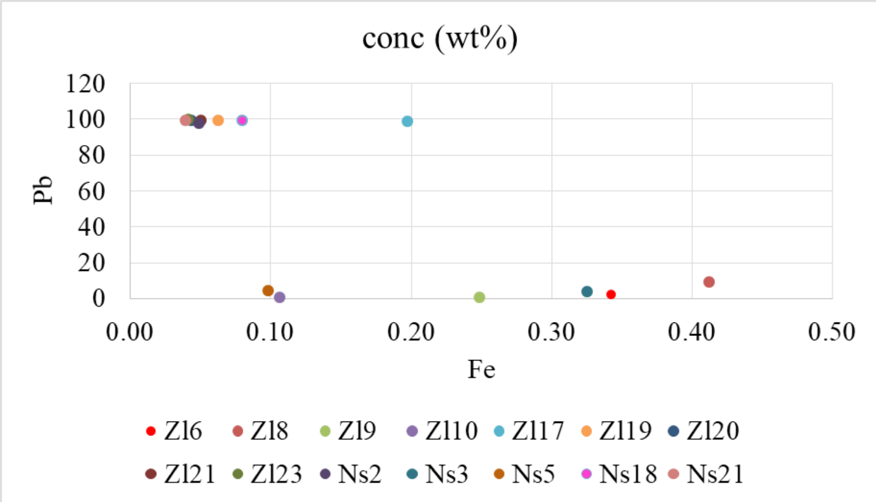

Fig. 21. Scatter graph of the concentration of iron and lead (Fe-Pb) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

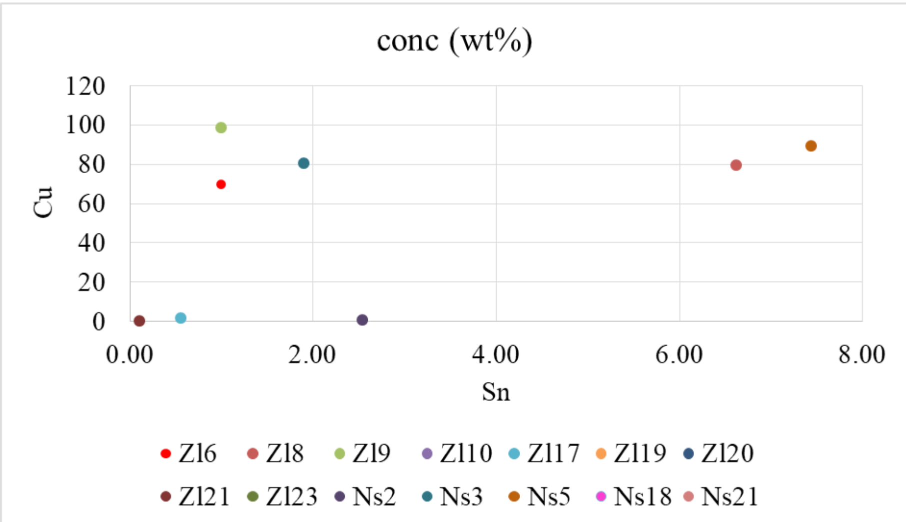

Fig. 22. Scatter graph of the concentration of tin and copper (Sn-Cu) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

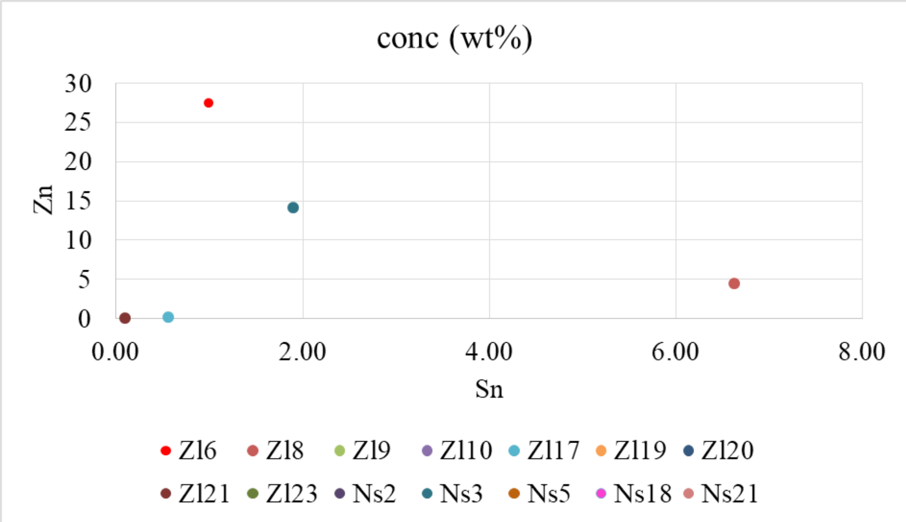

Fig. 23. Scatter graph of the concentration of tin and zinc (Sn-Zn) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

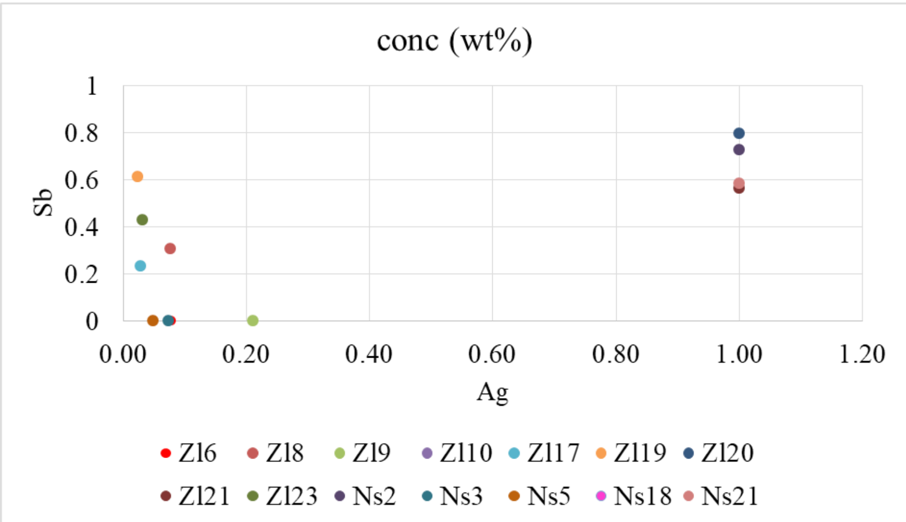

Fig. 24. Scatter graph of the concentration of silver and antimony (Ag-Sb) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

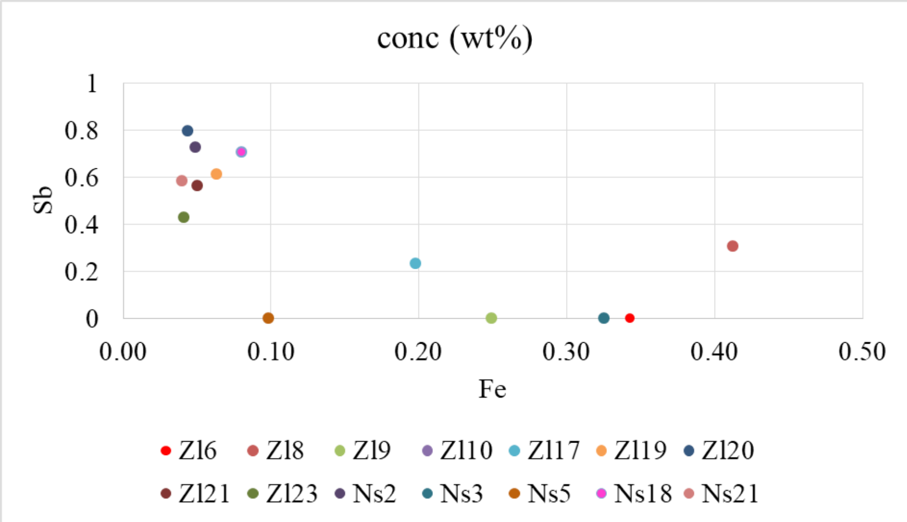

Fig. 25. Scatter graph of the concentration of iron and antimony (Fe-Sb) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

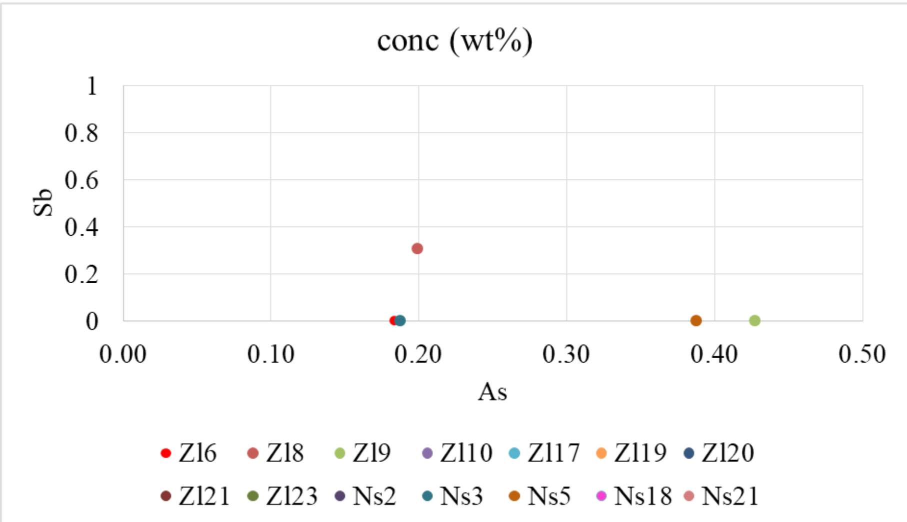

Fig. 26. Scatter graph of the concentration of arsenic and antimony (As-Sb) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

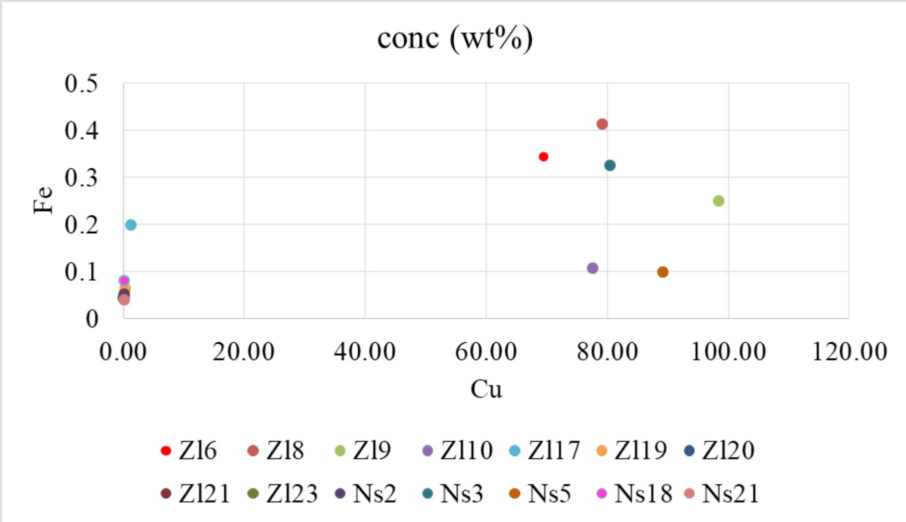

Fig. 27. Scatter graph of the concentration of copper and iron (Cu-Fe) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

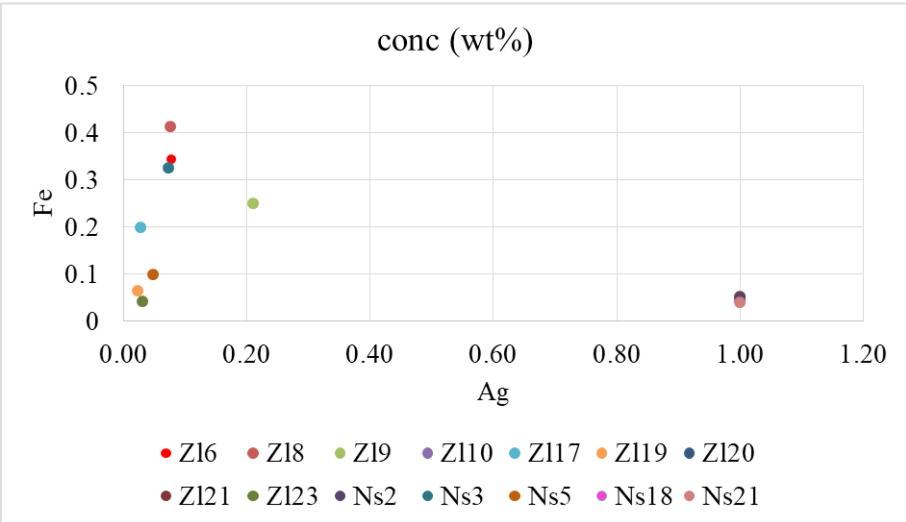

Fig. 28. Scatter graph of the concentration of silver and iron (Ag-Fe) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

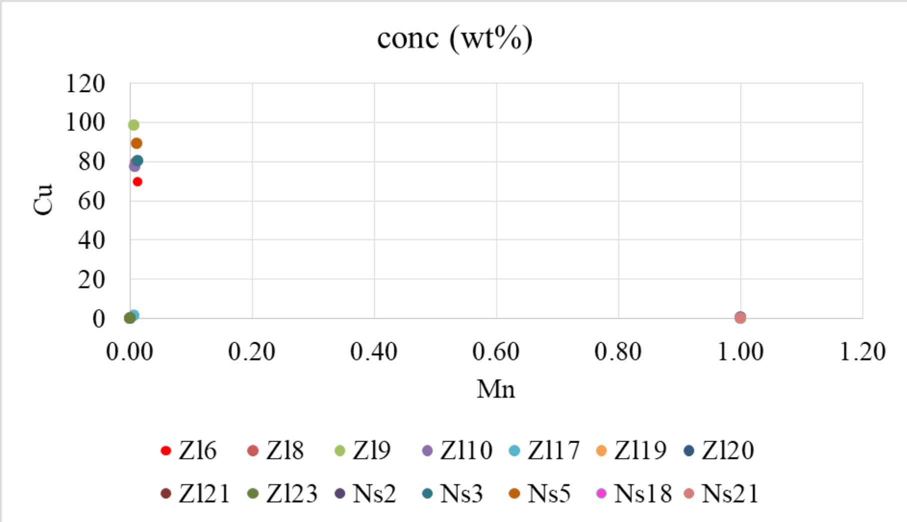

Fig. 29. Scatter graph of the concentration of manganic and copper (Mn-Cu) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

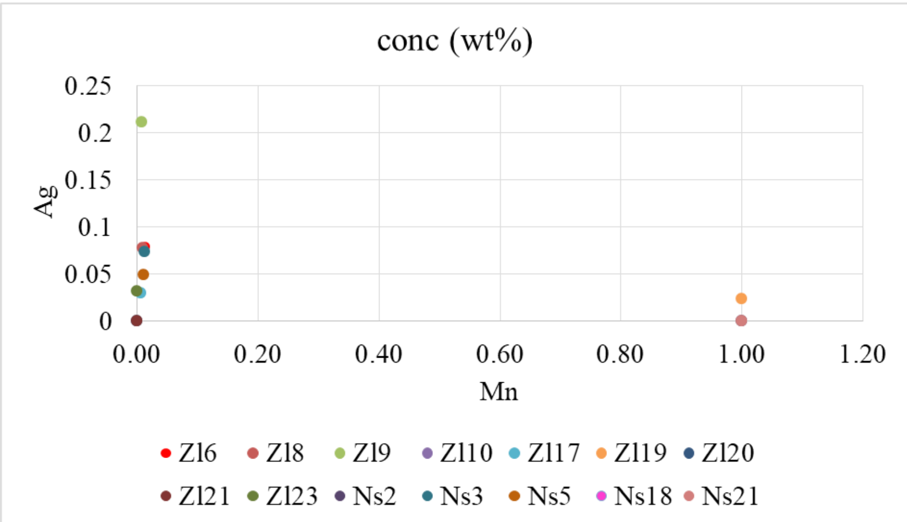

Fig. 30. Scatter graph of the concentration of manganic and silver (Ag-Mn) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

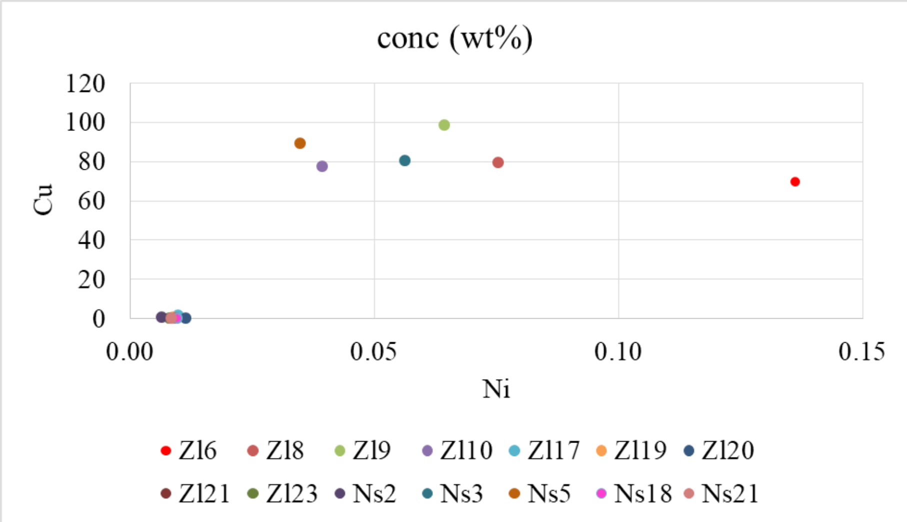

Fig. 31. Scatter graph of the concentration of nickel and copper (Ni-Cu) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

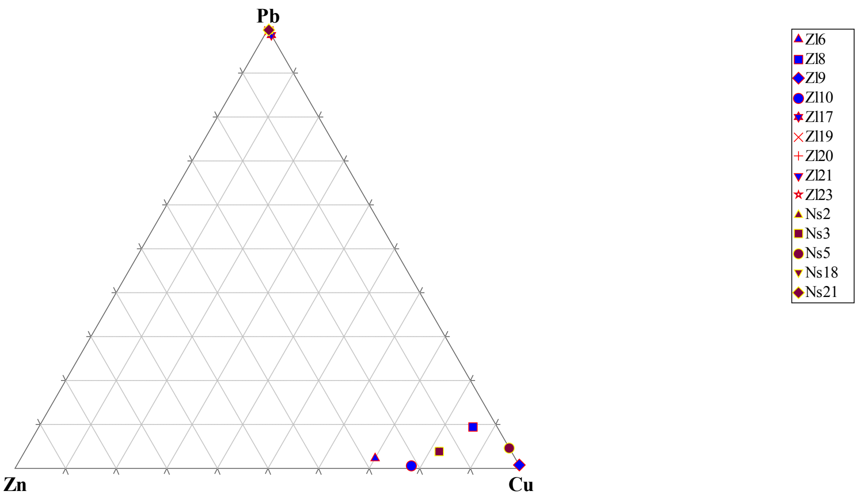

Fig. 32. Triplot of the concentration of zinc, copper and lead (Zn-Cu-Pb) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

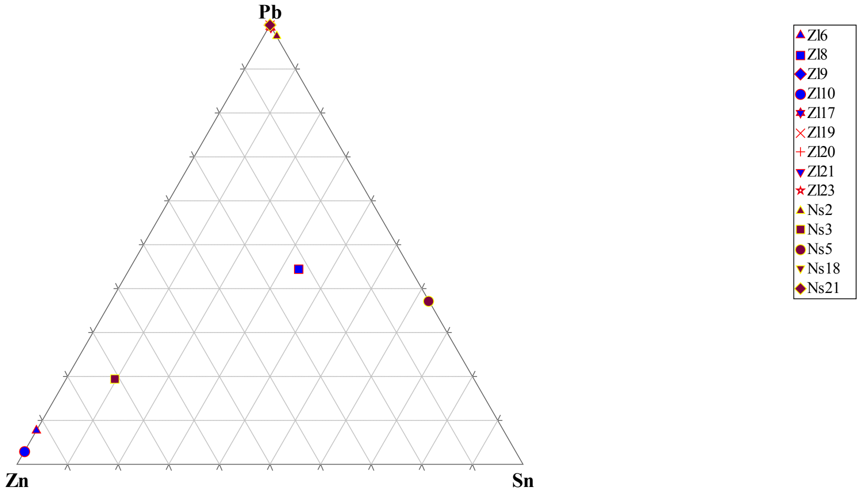

Fig. 33. Triplot of the concentration of zinc, tin and lead (Zn-Sn-Pb) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

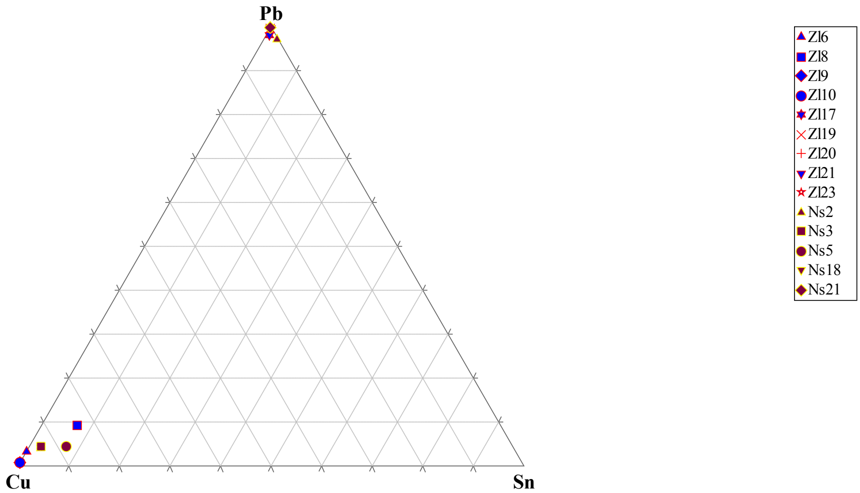

Fig. 34. Triplot of the concentration of copper, tin and lead (Cu-Sn-Pb) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

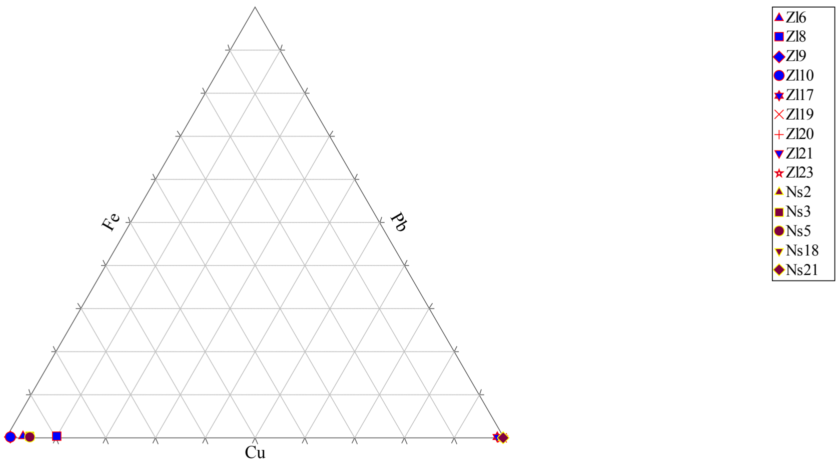

Fig. 35. Triplot of the concentration of copper, lead and iron (Cu-Pb-Fe) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

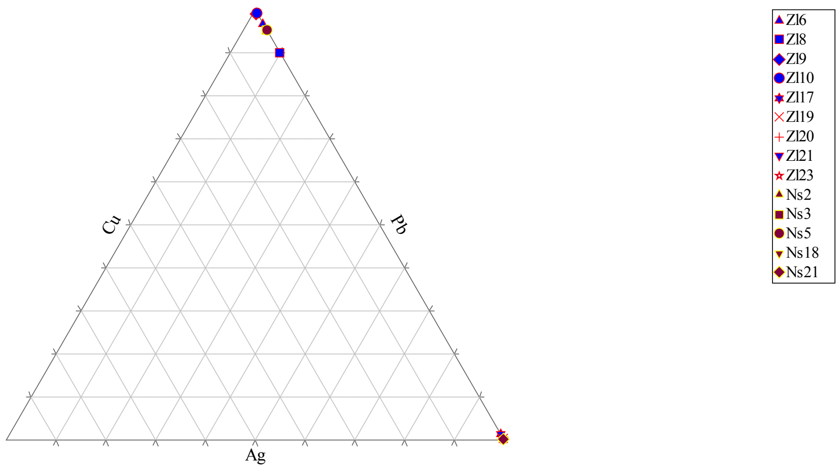

Fig. 36. Triplot of the concentration of silver, lead and copper (Ag-Pb-Cu) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.

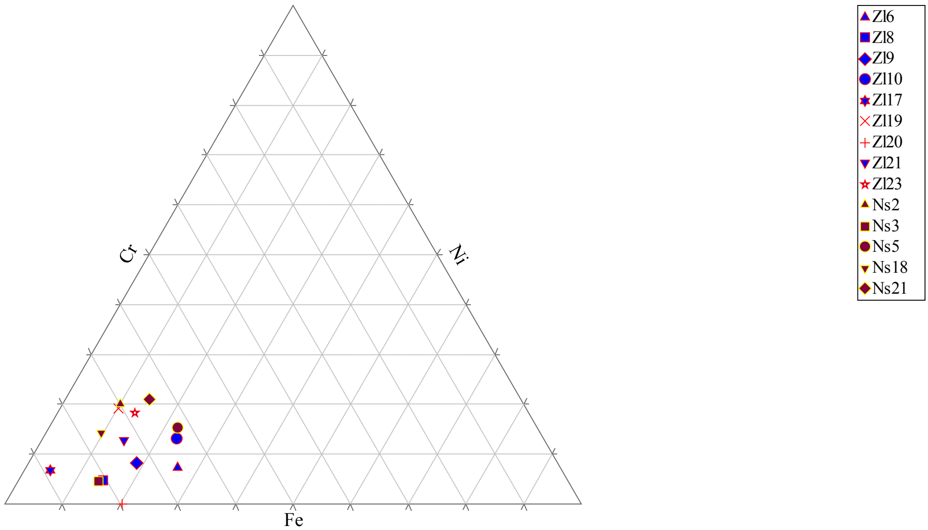

Fig. 37. Triplot of the concentration of iron, nickel and chromium (Fe-Ni-Cr) in non-ferrous metal artifacts found at the production centers of metal art in Zlatar and Novosel.