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Micro-XRF analysis of silver "Celtic" coins found in Bulgaria

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A set of 23 silver Celtic-looking coins were analyzed by micro-XRF in order to obtain data about their chemical composition (purity of silver and trace elements content) in relation of the coin type. The aim was either to confirm or reject the hypothesis about ancient imitation of the so-called "Celtic" coins. The results show that very pure silver (approximately 85-93 % Ag), copper and tin as macro-components (%) with traces of iron, gold, bismuth, chromium, nickel, zinc had been used.

Statistical treatment (correlation and cluster analysis (CA), principal component analysis (PCA), and factor analysis (FA)) allowed contextualization of the analytical results and permitted to obtain a better knowledge of the used metal alloys and manufacturing procedure of the investigated Celtic-looking coins. Numismatic expertise was also done and the hypothesis about ancient imitation was confirmed on the basis of the expertise and the elemental composition of the coins.

INTRODUCTION

The Celtic coins and the Celtic-looking coins are subject of a number of numismatic publications. However, archaeometric analyses are almost missing, although, as an exception the articles of Šmit and Kos, 1984 [1] and Šmit *et al.* 2020 [2] may be noticed. In this study, we provide analytical information about the elemental composition of 23 coins in order to draw conclusions about their production technology and authenticity. The determination of the original alloy composition is important not only from numismatic point of view or to confirm or reject the hypothesis about ancient imitation of those so-called "Celtic" coins. By measuring the elemental concentrations, we can assess the genuine fineness of the coins, also. The content of the major elements can provide additional information of the different aspects of the life in past times, social, economic and trade connections, etc. Special attention must be paid when archaeometric analysis of coins made of silver/gold alloys is performed, since they are often subjects of museum exposition and have high aesthetic value.

Although the XRF method is probably the most widely used for the analysis of archaeological samples of various origins, types, and sizes [3-6], without or almost without sample preparation and treatment, its limitations, particularly for the analysis of ancient alloys, are frequently overlooked [7, 8]. The main problem is the well-known phenomenon that archaeological artifacts with high silver content have often surfaces enriched by the noble metal [1, 2, 7, 9-11]. The origin of this enrichment is object of many scientific publications, explaining hypotheses about segregation of the components during casting, abrasion, corrosion products, re-deposition of diagenetic oxides, etc. Detailed explanation of such phenomenon is given, e.g., in Beck *et al. [*7] by the model of the direct enrichment.

X-rays have a low penetration and are mainly suitable for surface analyses. However, depending on the geomorphological conditions of the soils in which the items have been stored for many years, the surface of the metal objects changes, forming a so-called "patina". Historical alloys, such as silver coins, pose several analytical difficulties. When it comes to silver alloys, the patina may contain Ag_2S, Ag_2O, and AgCl, which can lead to uncertainties in the analytic data obtained. Another issue is the effect of metal "leakage" and diffusion over time and space, resulting in the surface of the metal object not being representative of the original metal alloy. Ancient alloys are frequently composed of materials

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or mixtures that are not found in modern alloys. Therefore, the quantification routine must be validated using appropriate certified reference materials. For example, Beck *et al*. [7] used replicas of different composition based on silver-copper alloys ranging from 30 to 80% Ag, and estimation the surface enrichment of Ag.

Besides the XRF technique, other non-destructive methods like PIXE, PIGE, SEM, FNAA, EPMA, LA-ICP-MS are also often applied for archaeometric analyses of silver alloys [see, e.g., 1, 2, 7, 12].

ARCHAEOLOGICAL BACKGROUND

The imitations of *Philip III Aridaeus* have not been the subject of special study in Bulgarian numismatic literature. The data on the known finds of this type of coins found on the territory of the Balkans (and especially of Bulgaria) were summarized for the first time by Konstantin Preda. According to him, they were emitted south of the Danube River, somewhere in the area between Rousse and Veliko Tarnovo. The main part of the imitations of *Philip III Aridaeus* are dated from the middle of the 2nd century BCE to its end [13].

The Celtic-imitation coins and their circulation in the lands on both sides of the Lower Danube were subject to various numismatic investigations (see, e.g., [13-19]). Still, these days, 40 hoards containing late imitations of *Philip III Aridaeus* (and *Alexander III the Great*) are known from the territory of Bulgaria, 11 of them are mixed with other coin types [19, 20]. The hoards were predominantly found in the regions of Rousse and Veliko Tarnovo (northern Bulgaria), while seven were found in the territory of southern Bulgaria [19]. Eleven of the finds also contain the smaller subdivisions of the coins – imitations of drachmas. There are three similar ones known for the territory of Romania, dated generally to the second half of the 2nd century BC [20].

MATERIALS AND METHODS

Materials

The coins, subject of this study, entered the Regional Historical Museum in Shumen as two separate finds from the village of Visoka Polyana. In 2005, the first one was bought by the museum. In the following year, 2006, the museum acquired another find, identical to the first one, with information about the same location. The appearance of the coins (patina, degree of preservation, etc.), as well as the metrical characteristics, allow to assume that they belong to a single hoard.

The coins received at the Shumen museum are of two denominations – imitations of tetradrachms and drachmas, all made of silver and with a slightly scyphate shape (see Fig. 1.).

The larger denomination is represented by eight coins, with weights of 11.98-15.26 g (average 13.81 g) and dimensions within 26.9-31.5 mm. According to the presented images and mostly imitations of inscriptions (in the name of *Philip*), the coins copy the tetradrachms of *Philip III Aridaeus* minted in the Syrian city of Arados [21].

The smaller denomination is represented by 15 coins, weighing 2.42-3.43 g (average 2.99 g) and measuring within 16.3-18.5 mm. While the identification of the larger coins is undisputed, that of the "drachmas" is uncertain. At first sight these should be imitations of drachmas of *Philip III Aridaeus*, made with a badly worn die. A parallel among the discovered and published so far imitations of this type of drachmas (from the territories of Bulgaria and Romania) are those from the village of Urceiu, district Dumbovica, and Optusani, Olt County, Romania [19, 22].

Method

Micro-XRF analysis was carried out using a Bruker M1 MISTRAL spectrometer (Rh-tube, Peltier cooling, 30 mm^2, Si-drift detector (SDD), Mn-K_α resolution 150 eV, collimator 0.1 mm to 1.5 mm). For quantitative analysis, we used a software-integrated fundamental parameters method. This method normalizes each element using the spectrum of a pure element, determines the initial concentration using the fundamental parameters method, and achieves an additional increase in accuracy for certain elements by additional standards. For determination of chemical composition of metal alloys 40 W (40 KV/1.0 mA) tube power and 0.8 mm collimator were used with integration time of 30 sec. To check the uncertainty of the method we measured the MBH-33X GM7 and MBH-33X RB1 metal alloy certified reference materials (CRMs) produced by the MBH Analytical LTD, England and BS SU 936, Brammer Standard Company Inc., USA. Due to weathering and corrosion, all archaeological finds made of silver alloys were subject to alteration, which causes differences between the elemental composition of the bulk and that on the surface. The composition of the corroded outer layer depends on the structure and chemical ingredients of the original alloy, but in general, it consists of silver sulfides, oxides, and chlorides. From an archaeometric point of view, the so-called "patina" may provide important information about the age and burial conditions of the metal artifacts. However, in order to measure the true elemental composition of the bulk using μ-XRF,

all corrosion and contamination products (soil, dust, conservation chemicals) at the measuring points had to be removed. Estimation of the uncertainties is essential to validate the analytical method employed. The SR criterion of McFarren *et al.*1970 [23] can be used to determine the correctness of the data obtained, which, as a result, can be regarded as reliable:

$$SR(\%) = \frac{|C_x - C_w| + 2\sigma}{C_w} . 100$$

where: C_x = experimental value; C_w = certified value; σ = standard deviation.

We used the measurements and reference values for three certified reference materials to compute the criterion's values (see Table 1). In this scenario, the standard deviation of the certified reference material measured by the method utilized must be taken into consideration. This criterion takes into account both the method's uncertainty, as well as the random sampling errors that influence the result's total uncertainty. In every case, the computed values for the SR-criterion are less than 25%, demonstrating the high accuracy and precision of the analytical data obtained in this study (see Table 1).

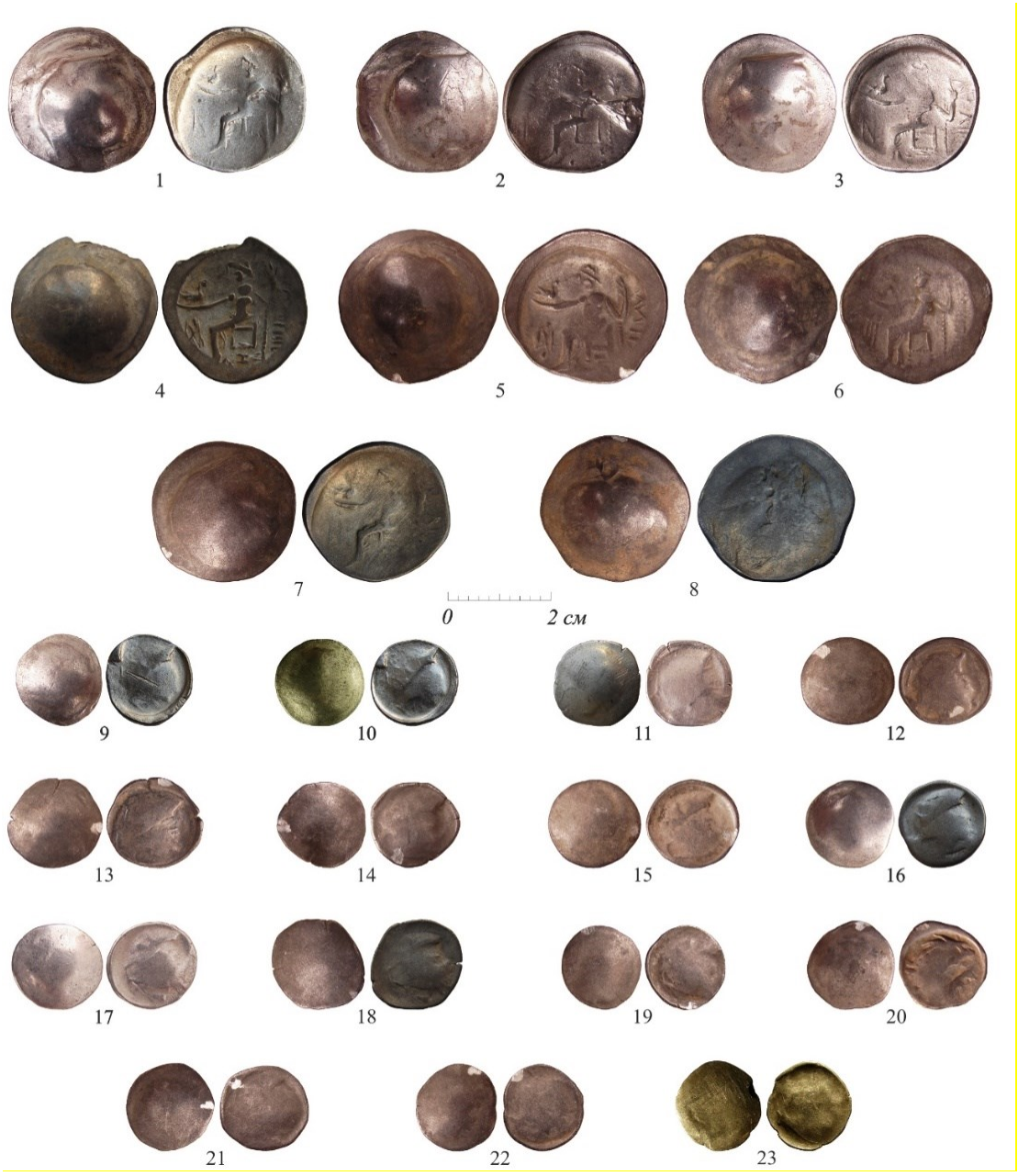

Fig. 1. Illustration of the investigated coins – tetradrachms (1-8) and drachmas (9-23).

Table 1. Comparison of the analytical results of this study to CRMs

Elem.	Certified Reference Materials					
	MBH-33X GM7		MBH-33X RB1		BS SU 936	
	certified	*measured*	*certified*	*measured*	*certified*	*measured*
Sn	10.07±0.06	12.11±0.09	2.137±0.018	1.19±0.06	7.0	6.81±0.02
Pb	1.79±0.03	0.98±0.11	5.02±0.05	5.41±0.06	9.6	10.05±0.05
Zn	1.363±0.015	1.38±0.11	7.95±0.06	6.86±0.09	0.25	0.14±0.09
Fe	0.0178±0.0010	0.020±0.011	0.928±0.011	0.11±0.03	0.003	0.001±0.001
Ni	0.531±0.05	0.551±0.13	0.0539±0.0012	0.05±0.01	0.36	0.255±0.11
As	0.095±0.003	0.084±0.07	0.0030±0.0003	0.021±0.03	0.002	-
P	0.0050±0.0004	0.0035±0.020	0.020±0.002	0.0214±0.002	0.07	0.003±0.001
Co	0.100±0.003	0.008±0.004	0.0558±0.0018	0.061±0.004	0.009	0.006±0.003
Bi	0.098±0.002	0.005±0.002	0.0029±0.0005	0.010±0.001	-	-
Sb	0.111±0.003	0.090±0.09	0.432±0.013	0.471±0.019	0.10	0.80±0.01
Ag	0.0682±0.0016	0.059±0.01	0.0174±0.0018	0.020±0.001	-	-
S	0.0613±0.0016	0.004±0.003	0.0044±0.0008	-	-	-
Te	0.0112±0.0009	-	-	-	-	-
Cu	85.69±0.12	85.55±0.2	83.25±0.16	84.01±0.18	82.5	79.98±1.12
Al	-		0.0048±0.0003	0.004±0.003	0.001	-
Si	-		0.063±0.003	0.024±0.5	0.004	0.001±0.001
S	-		0.0044±0.0008	-	0.007	0.0014±0.047

Table 2: Analytical results of the chemical composition (in weight %)

Lab. code	Cr	Fe	Ni	Cu	Zn	As	Ag	Sn	Au	Pb	Bi
C-1	0.12	0.85	0.071	3.40	0.03	0.08	92.86	0.24	0.96	1.74	<0.002
C-2	0.12	0.77	0.077	3.73	<0.001	<0.001	91.51	0.27	0.89	2.76	0.13
C-3	0.11	0.73	0.079	3.32	<0.001	<0.001	91.08	0.84	0.78	3.12	0.12
C-4	0.12	0.82	0.067	3.93	<0.001	<0.001	91.13	0.70	0.71	2.59	0.09
C-5	0.12	0.73	0.073	4.00	0.06	0.10	89.37	<0.001	0.71	4.78	0.05
C-6	0.13	0.78	0.079	3.79	<0.001	<0.001	92.15	0.37	1.03	1.71	0.09
C-7	0.13	0.77	0.08	4.30	0.05	0.10	91.35	0.61	0.79	2.04	0.08
C-8	0.11	0.79	0.082	3.59	<0.001	<0.001	93.37	<0.001	0.96	0.96	<0.002
C-9	0.12	0.76	0.075	3.38	0.03	0.15	91.42	0.25	0.75	3.21	0.11
C-10	0.12	1.56	0.074	3.84	<0.001	<0.001	85.72	5.92	0.99	1.81	<0.002
C-11	0.13	1.35	0.066	3.15	<0.001	<0.001	87.34	2.89	0.92	3.74	0.12
C-12	0.12	0.93	0.066	2.96	<0.001	<0.001	91.79	0.86	0.74	2.65	0.05
C-13	0.11	1.02	0.075	2.70	<0.001	<0.001	91.89	0.79	0.82	2.75	0.05
C-14	0.10	1.68	0.067	3.12	<0.001	0.08	87.48	4.25	0.80	1.92	<0.002
C-15	0.13	0.91	0.073	2.49	<0.001	0.12	91.64	<0.001	0.72	3.90	0.07
C-16	0.12	1.03	0.077	2.79	<0.001	0.07	92.50	<0.001	0.88	2.59	0.09
C-17	0.12	0.85	0.077	2.36	<0.001	0.24	92.08	0.20	0.78	3.43	0.1
C-18	0.10	3.11	0.067	12.98	<0.001	<0.001	70.80	5.52	1.22	2.20	0.13
C-19	0.13	0.95	0.080	3.31	<0.001	0.06	91.04	1.17	0.74	2.59	<0.002
C-20	0.10	0.97	0.086	3.23	<0.001	<0.001	91.42	0.27	0.80	3.20	0.02
C-21	0.13	0.94	0.078	3.15	<0.001	<0.001	91.15	<0.001	0.82	3.70	0.06
C-22	0.13	0.98	0.071	3.23	<0.001	<0.001	91.76	0.54	0.78	2.50	<0.002
C-23	0.11	1.13	0.083	3.87	<0.001	0.12	86.88	3.51	0.63	3.85	0.06

Sample preparation

A small size spot (about 3 mm^2) of each coin's surface was cleaned with a diamond drill to avoid the effect of patina in the bulk alloy, and the chemical elements were measured for 30 sec on both sides of the coins (to estimate so-called leakage).

RESULTS AND DISCUSSION

The analytical results on the elemental composition of the coins collected in the village of Visoka Polyana are summarized in Table 2. All coins are made of silver alloy, as Ag is the major constituent, with the addition of copper, tin, lead, and other elements in various amounts. The concentrations of silver vary from 85% to almost 93% (average value of 90.3%). The range of the copper content, on the other hand, is between 2.7 and 4.3% except for the sample C-7088, whose level of Cu equals almost 13% (Table 1). The lead content is varying between 2-3%, with an average value of 2.68%. With a high probability, this is due to the presence of lead in the ore (galena with a high level of silver), and this component was not intentionally added to the alloy. It is well known that the melting point of the alloy decreases and the melted metal achieves higher fluidity when the concentration of lead is in the range of 3 and 5%. Therefore, a higher amount of Pb in the silver/bronze alloy creates better properties in the smelted metal and improves the casting process [24]. The Sn content ranges from 6.1% to 0.4%, with an average value of 1.99%. Lead ores include sulfide (galena, PbS) or carbonate (cerussite, $PbCO_3$) with associated sphalerite (ZnS) and copper minerals [25]. All of these silver sources, however, require the cupellation process (oxidative removal of lead as PbO at a temperature of about 950 °C) and are therefore difficult to proceed with.

Statistical treatment of the data obtained

The statistical analyses were performed by the STATISTICA 10.1.0 software package. The analytical data were subjected to correlation, cluster, and factor analysis (principal component analysis). The data were treated by hierarchical cluster analysis, based on the Ward's method algorithm and the squared Euclidean distance. To verify the correct classification, factor analysis (principal component analysis) was also done with a statistical probability of 95% to estimate the similarity of the elemental composition of the analyzed archaeological artifacts. The results are obtained after z-normalization of the data (e.g., [26]).

Statistical estimation shows that there are no significant correlations. The correlations (coefficients up to 0.8) of the cases are as follows: Fe/Sn, Fe/Cu (+); Fe/Ag (-); Ag/Cu (-), Ag/Sn (-); see, e.g., Fig. 2.

The investigated coins form just one major cluster with three sub-clusters and one outliner (coin C-7088), regardless of the scenario applied – using all elements or the microelements only. There are no differences between the type of coins (*drachmas* and *tetradrahcmas*) and their chemical composition of metal alloys used (see Figs. 3a, 3b).

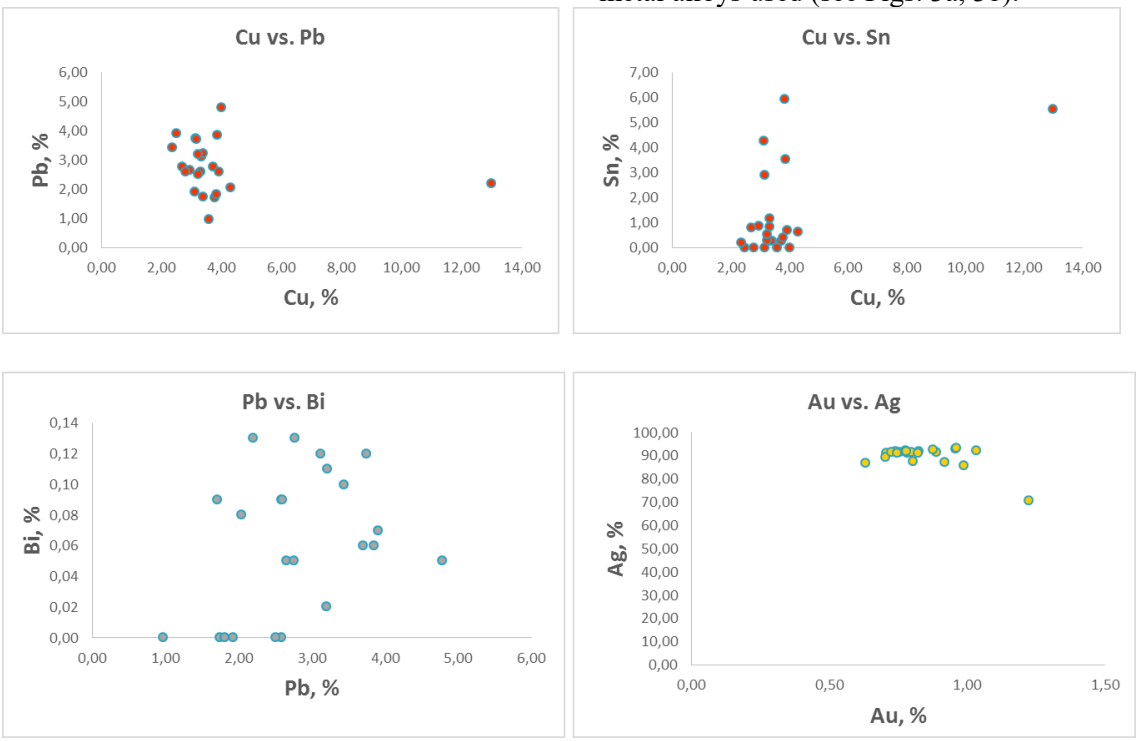

Fig. 2. Bivariate plots of correlations: Cu *vs*. Pb, Cu *vs*. Sn, Pb *vs*. Bi and Au *vs*. Ag.

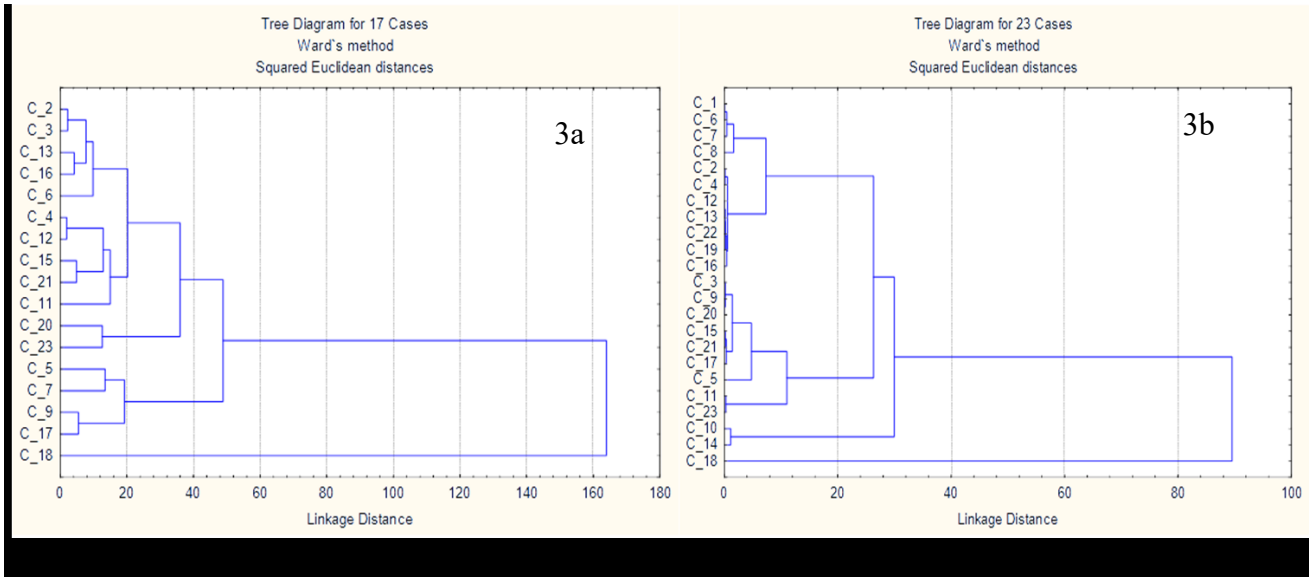

Fig. 3. Dendrograms of the cases using as indicators (3a) all elements and (3b) only macroelements.

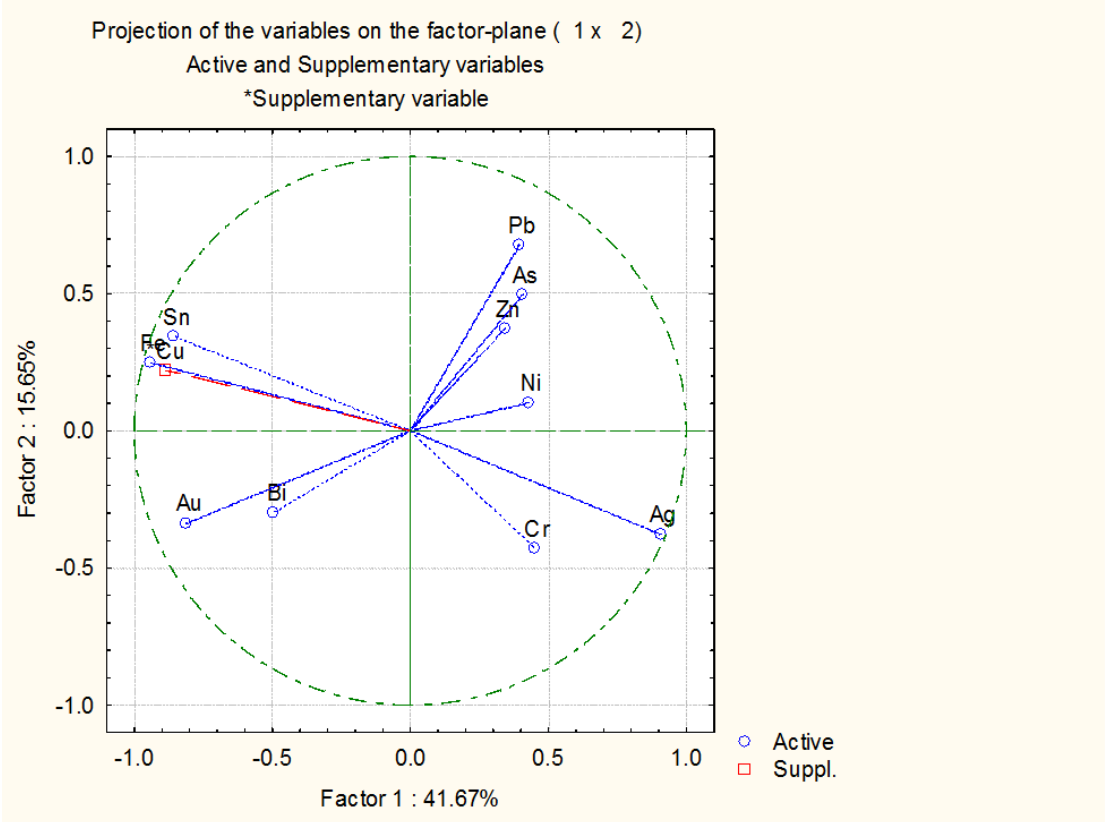

Fig. 4. Two-dimensional plots of the variables (F1 *vs.* F2)

In Fig. 4, a three-dimensional plot shows the obtained cases after factor analysis, FA (principal compound analysis, PCA). Four factors may be extracted. Notably, Factor 4 has the lowest eigenvalue of the vector. Factors 1-3 explained 73.09% of the total variance and are as follows: Factor 1 is a combination of Fe, Cu, Sn (negative), and Ag (positive); Factor 2 is As and Pb (negative); and Factor 3 is Cr and Bi (positive). All of these factors are related to the normal impurities in the ores used, as well as the manufacturing process of the items (cupellation of silver-rich ores). It is interesting to mention again the separation of sample C-18 with a very high amount of Cu.

CONCLUSIONS

By combining numismatic expertise and analysis through the μ-XRF instrumental technique, it is possible to obtain comprehensive information about the investigated coins. Very pure silver

(approximately 85-93 % Ag) along with copper as macro-components (%) and traces of tin, gold, bismuth, chromium, iron, nickel, and zinc had been used for the production of the sampled coins. There are no differences in the chemical composition of the original metal alloy that had been used for the manufacture of drachms and tetradrachms except for one specimen (C-7008). In this way, we may suppose that these coins belong to one treasure, produced from the same ores and by similar technology. The statistical treatment of the data allowed contextualization of the analytical results and permitted a better knowledge of the used metal alloys and manufacturing procedures of the investigated Celtic-looking coins. The analytical results and the numismatic expertise confirm the hypothesis of the existence of ancient imitations of these coins.

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