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ELEMENTAL CHARACTERIZATION OF BRONZE AGE COPPER OBJECTS BY MICRO-BEAM MEASUREMENTS

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Abstract. Investigations on the composition of Bronze Age objects recovered from sites in Romania were performed by Synchrotron Radiation X-Ray Fluorescence and micro-Particle Induced X-ray Emission, to compare their elemental patterns with previous results on regional copper sources from Serbia, Bulgaria and Romania. We discuss elemental composition, correlation and profiles in relation with the possible origin of the copper used and the metallic microstructure.

Key words: SR XRF, micro-PIXE, copper, Bronze Age.

1. INTRODUCTION

Trace element analysis proved useful for discussing the provenance of archaeological artifacts, for gold [1], silver [2], obsidian [3] or copper [4]. Previously we have applied this approach in the search of Sb, Sn, Te, Pb in native gold and archaeological artifacts found in Romania (e.g. [5]), or in geological studies [6]. In the case of copper, during the smelting process, siderophile and chalcophile elements (As, Sb, Ag, Co, Ni) are concentrated in the metal, so they are likely to be present in the final artifact as well and they could be adequate indicators of the copper sources [4].

In the present work, we studied a series of Bronze Age copper objects of Transylvanian origin by Synchrotron Radiation X-ray Fluorescence (SR XRF) and micro-Particle Induced X-ray Emission (PIXE), in order to establish a correlation

between their composition and present knowledge on regional copper sources. We attempted a characterization of the samples as complete as possible with the available techniques, also looking for compositional patterns similar with already published data, representing old regional mines in NE Bulgaria (Ai Bunar), Serbia (Rudna Glava, Majdanpek), Hungary and Romania (Baia de Arama, Sasca, Altin-Tepe) [4, 7, 8].

2. EXPERIMENTAL

In the case of archaeological items, there is a trade-off on the non-destructive advantage of the X-ray methods, as sampling might be imposed as a consequence to local legal restrictions of transportation and export for cultural heritage. Then very small samples can be taken from parts with little relevance to the shape or decoration of the object. For bronze objects, one has also to consider an important issue – corrosion, and that most trace elements are enriched in the corrosion layer, due to Cu depletion by oxidation.

In order to obtain a composition close to the one of the bulk, small chips (~200-500μm to mm-size, several chips from the same area, kept in packages P as is) were carefully removed by drilling from previously corrosion cleaned – mechanically polished - areas on the item surface. The largest chips (grains) were chosen for investigation in the experiments, sometimes several different pieces from a package representing one object. The samples studied have been obtained from the History Museum of Arad, via Bucharest University, and from the National Museum of History Bucharest.

The analysis of the samples was carried out by micro-SR XRF at the ANKA/ISS FLUO beam-line in Karlsruhe, Germany, and by micro-PIXE at the microprobes of ATOMKI Debrecen (Hungary) and INFN-LNL, Legnaro (Italy). Previously, the samples (each package) were measured at IFIN, using a portable X-ray spectrometer X-MET 3000TX with a 40kV tube with Rh anode: the detector is a Peltier-cooled PIN silicon diode, resolution 270eV at the MnK_{α} line, and the spot size ~ 30mm^2 [9]. At ANKA, we analysed 12 samples of various copper artifacts (axe, sickle, celt, blade, adornment) and foundry ingots from different deposits (Pecica, Santana, Cicir, Paulis - Arad county and Spalnaca, Alba), and a native copper (Michigan/MIC), a several mm-size, surface-cleaned nugget. At LNL and ATOMKI, we measured by micro-PIXE 30 samples (16 objects), representing 3 bronze deposits [10]: Drajna de Jos, Prahova (votive deposit) – sickles, Spalnaca, Alba (foundry deposit) – cakes, Santana (votive deposit) – celts, knives, and native copper samples: Balan (E Transylvania) and Rudabanya (NW Hungary).

In the micro-SR XRF experiment at the ANKA/ISS FLUO beam-line [11], we performed 1-D scans and obtained fluorescence line profiles with a 32.5keV maximum excitation energy beam and size of 4×10 μm^2. At this energy, the attenuation length of X-rays in copper is ~130μm. The fluorescence signal was

measured with a 50mm^2 high-purity Germanium PGT crystal detector. In-situ software helps in the fast diagnosis of the samples, by on-line analysis based on regions of interest. The deconvolution of the spectra, the identification and fit of the X-ray lines in the spectra and the quantitative evaluation were done using the QXAS (AXIL) software package [12]. A dedicated multi-element standard foil (AXO Dresden), containing Cu (33 ng/mm^2), Fe (33 ng/mm^2), Mo (3 ng/mm^2), Pd (4.9 ng/mm^2), La (35 ng/mm^2) and Pb (29 ng/mm^2) [13] was used for sensitivity calibration. This combination of elements covers most of the spectral region for K-lines, by extrapolation, from Mn to Sn and Sb. The non-linear L-line sensitivity curve for this standard foil contains only 3 points, thus limiting our semi-quantitative evaluation to K-lines only. The samples can be visualized with a microscope/video camera, and the image of the scan area can be recorded as a file. The number of steps (step size ~5-10μm) for the scans was optimized to the actual size and shape of the sample. Exploratory profiling was performed typically by test-measurements in different points chosen on the surface, followed by recording scans of 20s per point. These spectra were then added channel by channel into sum-spectra over the profiles and used as input to the analysis software.

At ATOMKI, the micro-PIXE measurements were carried out at the Scanning Nuclear Microprobe [14], obtaining map- and selected-raster (reduced map) spectra, used a 3MeV H^+ beam, focused to 3×3μm^2, with the intensity of 300–400 pA. The accumulated charge on the samples was 0.5–1.5 μC. The scanned area varied between a few tens of μm^2 to 1×1mm^2, depending on the sample size and structure. The detection stage at ATOMKI consists of a super ultra thin window (SUTW) and a Be-window Gresham Si(Li) X-ray detector, each with an area of 30 mm^2 and resolution 136 eV (at the MnK_α line). The detectors are placed at 135º to the incident beam. In order to reduce the intensity of the CuK peaks and of the pile-up effect, a 250 μm thick kapton absorber foil is used in front of the Gresham Si(Li) detector. This set-up allows the detection of characteristic X-rays for elements with $Z \geq 6$. The spectra were evaluated both with GUPIXWIN [15] and PIXEKLM-TPI [16].

The micro-PIXE analyses at the AN2000 accelerator of Laboratori Nazionali di Legnaro, were carried out in a 2MeV proton micro-beam (9 μm^2 beam area), and beam currents of 400pA to 1nA. The characteristic X-lines were measured with a Canberra HPGe detector (140eV FWHM at 5.9keV). A mylar filter (52μm thick, 11% hole) in front of the X-ray detector was used to reduce the intensity of the peaks in the spectral region below 4keV [17]. Map (sum-) and point-spectra were acquired. The quantitative analysis of the spectra was performed with GUPIXWIN. The experimental choice was mainly imposed by the availability of beam-time at each facility.

Complementary measurements (unfortunately incomplete) on an extended set of copper samples resulted in XRF data (by the IFIN group) and also other techniques like analytical microscopy (XGT-7000), chalcographic studies on polished sections and Pb isotope ratios/LA-ICP-MS [18].

3. RESULTS AND DISCUSSION

Early copper metallurgy appeared in SW Asia in the Neolithic and spread towards present-day Bulgaria, Serbia and Romania, *via* Turkey. Copper could be obtained either from oxidized ores (malachite, azurite, cuprite), from Cu sulfide ores (chalcopyrite, bornite, covellite) or even more composite ores (tennantite /tetrahedrite, fahlore). In the region, copper existed in Romania, in the S-SW e.g. at Ocna de Fier, Sasca, Moldova Noua, in the Nera and Cerna valleys - the Danube gorges (Romanian Banat), at Baia de Arama (Wallachia), Altin-Tepe (Dobrudja), in Bulgaria and Serbia (*e.g*. the Bulgarian ore was of polymetal type, containing Fe, Zn, As, Se, Ni, Ag and Sb [19]). Information on prehistoric copper mining on Romanian territory is scarce, but the presence of archaic cultures and the similar geology (to Serbia) suggest such a possibility at least in the neighbouring Banat. Mining gold, copper or lead in Banat was active by the time of the Roman conquest, but metal extraction traces are proven for more than 150 years before it (e.g. Varad-Coronini, a prehistoric, pre-Dacian and pre-Roman site near Moldova Noua [20]). It is quite probable that such copper sources were used for the production of objects in local workshops.

Our study considers as a working hypothesis that the patterns resulting from published work on regional mines can be identified in Bronze Age objects [4,7,8, 21], and that most likely the manufacturing techniques were not very advanced to change the elemental composition to an unrecognizable extent. We also suppose that the most plausible sources for the copper used should be within a limited close geographical area. The copper sources considered are mines from Banat and the Balkans, e.g. Majdanpek and Rudna Glava in Serbia, Ai Bunar in Bulgaria, or Velem-St.Vit in Hungary. Let us summarize the literature: The copper fraction in the ores is quite variable, but this spread should be hidden by smelting. Considerable variability has been found also for trace-element groups in the samples from the same regional mine. Looking for differences in the composition, we see that SW Romanian copper is a rich Cu-content ore, with significant Fe, and a host of traces. The main difference between Bulgarian and Serbian copper seems to be the absence of Co and Ni in the former. Data for the Hungarian ore [22] are a little too vague, but could be combined with [21]. The presence of Bi, but also the considerable quantities of As and Sb are worth taking into account.

Our samples represent objects found in three geographically distinct regions: Arad County (AR) in Western Transylvania, at the limit to Romanian Banat (Paulis, Cicir, Santana, geographically nearby), Spalnaca in Alba County (AB) in the middle (Transylvania), and Drajna de Jos, in the southern part of Romania (Wallachia), about 70km N of Bucharest.

Most of them are fragments from objects and some are from ingots/cakes.

3.1. SR-XRF RESULTS

Table 1 displays concentration values obtained by SR-XRF for two groups of samples: Arad County (AR) represented mainly by objects and ingots (in italics) from various deposits and a cake from Spalnaca in Alba County (AB). The concentrations were calculated with QXAS with the sensitivity calibration method.

The spectra were fitted in an iterative model taking into account absorption in the copper matrix, with normalization to 100% in each case. The calculations were done for the following cases: no matrix absorption, 100%, 90%, 80% and 70% Cu in the matrix (only P37) and the decision of accept was taken for the case of matching Cu concentration with the absorption model. The absorption correction is expected to influence mostly the low energy estimates (e.g. the As-Pb ratio).

The overall uncertainty limit for the concentration values obtained by SR XRF is < 5 –10% for major elements, <20-30% for minor elements, while the values for traces are indicative, due to all the approximations. Samples P27 and P31 contain a considerable amount of Fe. The estimation is somewhat more sensitive to the absorption model, for Cu and Fe.

The composition of the artifacts shows a great variability of patterns. The samples contain Co, most of them Ag, but some of them also contain more exotic traces: Se, In, Bi. We identified various patterns: copper and tin bronze (Cu-Sn: Cu ~85–95%, Sn ~5–10%; actually tin bronze is defined in literature in the classical sense as an alloy containing more than 1% Sn). Co content in the order of ~0.01–0.1% points most likely to a Serbian mine [8], but could also represent local or Hungarian sources. Previously we have found such an example in a set of extra-Carpathian Bronze Age objects (Celt axes and sickles [5]), and different patterns for all the other objects.

Table 1

SR XRF data: composition in wt% (QXAS estimates)

sample	Cu	Sn	Sb	Fe	Ni	Zn	As	Pb	Ag	Co	Se
P10 (AR)	95.7 (97.9)	<0.01	<0.01	3.2 (1.5)	0.2	0.4 (0.4)	<0.01	0.1	0.01	0.3	<0.01
P17 (AR)	91.7 (93.2)	0.01	<0.01	4.4 (5.6)	2.0 (0.6)	0.3 (0.3)	0.3 (0.1)		0.01	1.2	<0.01
P17b	97.8	<0.01	0.03	1.0	0.4	0.3	0.2	0.01	0.01	0.2	
P1 [a] (AR)	96.0 *94.34* (92.4)	2.6 *4.9* (7.1)	0.06 *0.07*	0.2 *trace* (0.4)	0.3 *0.21*	0.4 *0*	0.1 *0.47* (0.1)	<0.01 *0*	0.01 *0.01*	0.1 *0*	<0.01
P31 (AR)	87.4 (96.8)	<0.01	<0.01 (2)	10.5 (0.3)	0.2	0.3	0.02	0.02	<0.01	0.2	
P27 (AR)	82.8 (89.8)	0.06 (7.7)	0.01	15.6 (1)	0.2 (0.5)	0.3	0.05 (0.2)	0.3 (0.2)		0.2	
P14 (AR)	92.8 (93.6)	0.01 (4.4)	<0.01	5.1 (1)	0.3 (0.3)	0.3	0.03 (0.5)	0.1 (0.2)	<0.01	0.2	

Table 1 (continued)

P16 (AR)	92.3 (88.3)	4.5 (9.6)	0.1	1.3 (1.4)	0.4 (0.2)	0.4	0.1 (0.3)	0.4 (0.3)	0.01	0.2	0.01
P19 (AR)	91.7 (84.5)	5.2 (14)	0.4 (0.5)	0.4 (0.2)	0.4 (0.2)	0.3 (0.2)	1.1 (2)		0.01	0.2	<0.01
P12 **PIXE** (AR)	87.9 **98.46** (89.3)	7.9 **0.5** (9.1)	0.2	1.0 **0.53** (1)	0.3 **0.19**	0.4	0.6 **0.08** (0.3)	1.0 **0.22** (0.2)	0.07	0.2 **0.02**	0.04
P3 (AR)	88.4 (74.7)	5.7 (20)	0.1	0.7 (0.9)	0.8 (0.4)	0.3	0.4 (0.6)	3.0 (3.7)	0.03	0.3	<0.01
P37 [b] *84.83* **PIXE** **86.16** Sn **15.78** point (85.5) (AB)	70.9	<0.01 **0.22** **79.17**	1.7 *0.36* **3.28** **3.48** (5.3)	24.1 *0.29* **0.08** **0.36** (6)	0.6 **6.8** **0.2** (0.7)	0.2 *0.13*	2.2 **3.25** **0.48** (2)	*0.35* **0.07** **0.51**	<0.01 **0.076**	0.4 **0.015** **0.014**	*0.04*
MIC	99.1	<0.01	<0.01	0.2	0.2	0.3		<0.01	<0.01	0.2	

[a] (*in italics*) spectral analysis on a sample from the same axe by S. Junghans et al (Stuttgart, 1968)
[b] (*in italics*) old chemical analysis on an ingot from the same deposit, by O. Helm (1895)
[a,b] data from [10]; micro- PIXE results added in **bold**, X-met results in parantheses

We have also added to the table the only analysis results found in literature [10]: a measurement on the Paulis axe (P1, the only EBA artifact in the study) and on an ingot from the Spalnaca deposit (P37). The values obtained by us are in reasonable agreement for P1. The Spalnaca samples come from different items – the deposit consists of about 1000-1200kg pieces, various objects, fragments and ingots (also an antimony ingot), kept in museums in Aiud, Bucharest, Cluj-Napoca, Alba Iulia (Romania) and Budapest (Hungary) [10]. The main difference in the two results is the significant amount of iron (~20%) determined in this work. The cake from Spalnaca has a very heterogeneous composition, high concentration of Sb, and a strong variation in Sn in the analyzed area. This find can be related to early "Hungarian" antimony-bronze artifacts, in agreement with theories regarding the development of BA cultures and their migration trends in the region.

As an illustration, figure 1 displays a spectrum for a Cu-Sn/Pb Santana sickle (P3) and a set of normalized profiles for sample P10 (Santana ingot). Due to the lower statistic, the elemental correlations obtained from experimental intensity profiles (K_α, L_α-lines) give mostly qualitative information.

Sample P10 is interesting as it contains traces of Bi and In; As is at the detection limit level. The presence of Br in axe P1, and ingots P17 and P37 is also worth mentioning. However, there is no Br in P17b (same ingot as P17). Whether Br could be a trace element of interest for the localization of the copper source should be still proven.

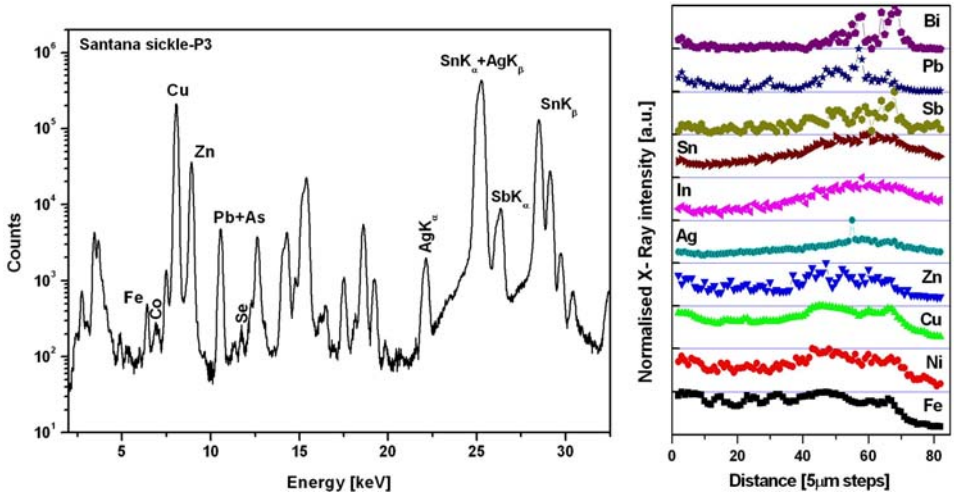

Fig. 1 – SR XRF results: P3 (Santana sickle) sum-spectrum –left; Intensity profiles for ingot P10 (Santana): correlations In-Sn (Ag,Sb) and Cu-Fe(Ni) are evident.

Samples P3, P12, P16, P19 show compositional patterns generally similar to the one reported for Serbian copper (Majdanpek) [4,8].

We note the constant presence of Fe in all samples and the relatively high content of Fe in the cakes and in P27 and P31. This is related to the polymetal type of the ore used; we do not think that Fe was added intentionally.

Keeping in mind the used approximations, the possible sources of error and the spread in the results, we still consider as fairly plausible the connection of the samples studied with the sources mentioned above. We note that most objects (axe P1, sickle P3, blade P12, disk P19, adornment P16) are of Cu-Sn type (associated with Sb!). Sn added to copper improves the hardness of the metal, which is consistent with the usage of the first three objects as tools. The exceptions, celts P14 and P27, and spearhead P31 are impure copper with high Fe content.

According to the LA-ICPMS data on some of these objects, reported in [18], P1 and P17 are grouped on the same line (linear fit), by the Pb isotope ratio dependence ($^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$. Cake P37, disk P19 and sickle P3 are situated on a parallel line, on the same isochrone (same geological age of the ore); P10 (the only sample containing traces of Bi) and P31 are totally independent outliers. In the same work, several samples from local Romanian sources (Ocna de Fier, Moldova Noua – from Romanian Banat, Baia de Arama in Wallachia, Baia de Aries and Deva in Transylvania) were also analyzed. P1 and P17 results fit the Banat isochrone line with Ocna de Fier/Dognecea copper (P1 practically coincides with Ocna de Fier).

Table 1 contains in parantheses the XRF data measured on the content of the packages (as a shallow layer of grains) and thus a good approximation for the average composition. The uncertainty of the measurements is 10% [9].

The global composition is fairly well reproduced by the SR XRF results (averages over profiles along the surface) and the PIXE map data (averages of the map surface). However, the point/selected-raster data are meant to be used only in the study of micro-inclusions.

3.2. RESULTS BY MICRO-PIXE

The micro-PIXE results show a large spread, and it is difficult to extract conclusions on a global composition of the objects. We have two choices: a statistical discussion or we can look more at the traces, their spatial distribution and correlations. As a direct discussion is too difficult, we will refer in the following only to a few aspects related to the Drajna set and the native copper samples.

We found Pb micro-inclusions in the Balan (E Transylvania) native copper (Fig. 2a) and Hg (but no Sb) micro-inclusions in the Rudabanya (NW Hungary) sample – possible fingerprint elements for these ores. More generally Pb is correlated with Sn, as e.g. in the Drajna sample maps (e.g. P62, Fig. 2b), where we see obvious Cu-Ni and Sn-Pb correlations, the two being complementary. Ni is an impurity in the copper mineral, while Sn and Pb are alloying elements.

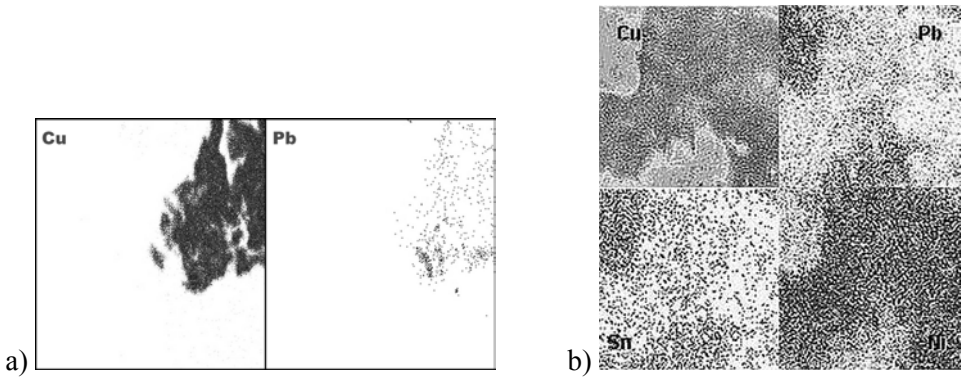

Fig. 2 – a) Localised and distributed Pb in native copper (Balan); b) sickle P62 Drajna correlations: Cu/Ni and Sn/Pb are complementary (the darker, the higher concentration).

The Cu contents measured are grouped between 70–80% and 80–90%, completed by Sn to roughly 100% (Cu-Sn bronzes). Sb is present in some samples, ~1%, as a rule, Ag ranges up to 1%, and so does Bi, Br. Hg is rare, but is present in the Rudabanya native copper and in some Drajna sickles. Br is present in the Balan copper. A group of sickles contain As and Pb as minor elements (e.g. P45, 51, 61–62). The trace element patterns of fragments for several Drajna sickles (*e.g.* P39–P45 contain Se and Co, no Se for P≥ P46) match both patterns from Serbia (Co), and Bulgaria (Se) or a mix of them [4,7,8], suggesting re-melting of old

objects. The presence of Bi traces in a few objects from Drajna (P44, 46–62) and Santana blade P12 suggests that they contain partly Alpine Copper [21].

For an overview of the data, rather than giving a lengthy table of results, we show the frequency distributions for various major, minor and trace elements for the Drajna set in Fig. 3.

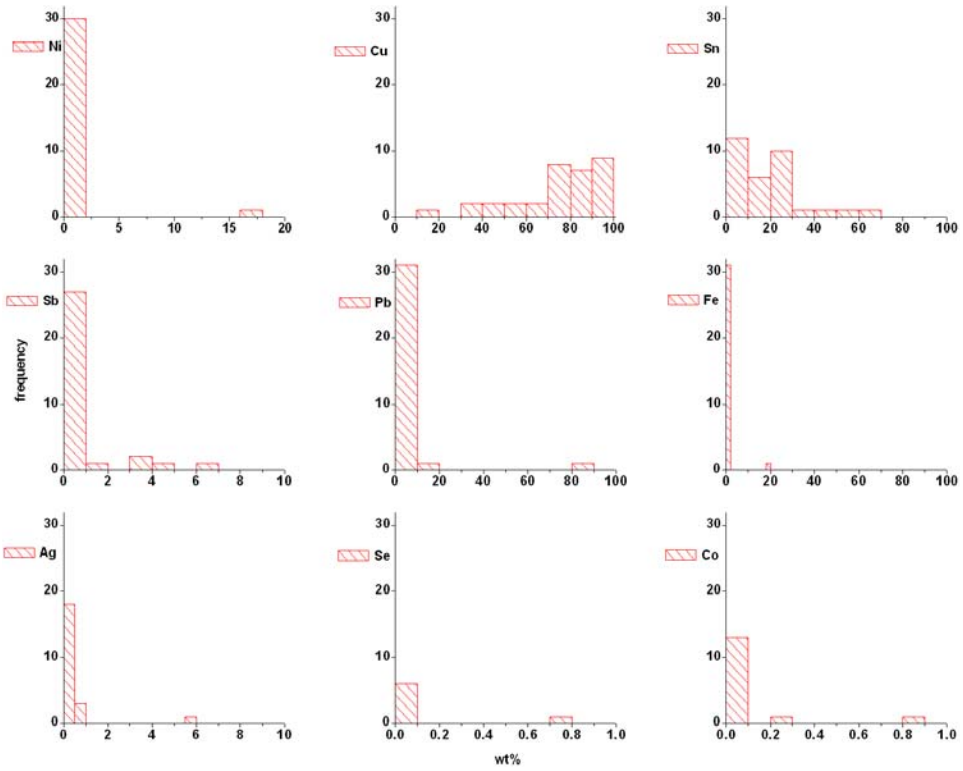

Fig. 3 – Frequency distribution of objects vs concentration in wt% for major (Cu, Sn), minor (Ni, Fe, Sb, Pb) and trace (Ag, Se, Co) elements in the Drajna set.

A somewhat more elaborate approach gives the plot from fig. 4, obtained by applying statistical analysis (a combination of Cluster Analysis (CA) and Discriminant Analysis (DA) [23]) to the same set of data. Cluster Analysis grouped the PIXE (map) measurements into four clusters. Group 1 contains only two measurements, Balan and P42L1, with overwhelming Pb content (centroid concentration 83.15%), and was excluded from further analysis. Stepwise Discriminate Analysis (DA) placed correctly (some superposition of group 3 and 4) 88.38% of the objects in the three remaining groups. It also indicates that As, Pb and Sb are involved in the grouping. The plot shows the final result of applying DA to the 3 clusters mentioned above. From the Pearson correlation coefficient matrix of concentration values, DA estimates in the first order, strong anticorrelation of

Cu with a series of (alloying) elements Sn, As, Sb, Pb, positive strong correlation within each pair of the alloying elements, and a weak positive correlation of Cu with Ni. The grouping pattern can be seen as well, from the loading of factor F1, which describes 99.6% of the total variance (positive high loading for Cu, negative loading for Sn, Pb, Sb, As). On the F1 axis, increasing from left to right we find the samples with increasing Cu content (less Sn, less mechanical strength). This result reflects the correlation matrix picture: group 2 is dominated by the behaviour of the alloying elements (Sn, Sb, Pb, As), while group 4 is dominated by the copper content; thus, group 2 is characterized by centroid concentration values of 43.7% Cu, 40.1% Sn, 3.0% Sb, 5.6% Pb, 1.6% As, while the group 4 includes softer bronze items (Cu 91.8%, 7.0% Sn, 4.1% Pb). No significant correlation can be defined for group 3 (centered on zero). Even this discussion should be taken with caution, as we can see that in some cases different measurements for the same object occur in different groups/clusters (e.g. P51 in groups 2 and 3, or P44 in all three groups). This shows that actually we might either measure by micro-PIXE (even mapping) insignificant areas and we probe too deep into the structure for a statistical analysis (the objects are to a too inhomogeneous, due to the metallurgical process itself). The observed grouping cannot be used for provenance.

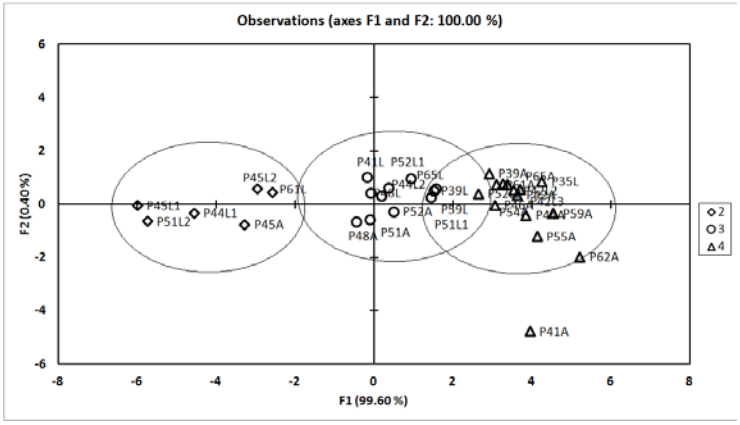

Fig. 4 – Statistical Analysis (Discriminant Analysis) applied to the Drajna set.

4. CONCLUSIONS

XRF and PIXE compositional screening can help in the evaluation and classification of copper objects: can identify rare traces accurately and give some clues regarding the inner structure of the material by elemental mapping or profiling. Thus, we could identify trace elements like Co, Se, Bi, Hg, Br - possible indicators of certain metal sources.

- Most copper objects from the SR XRF study can be connected with possible local (Ocna de Fier, P1) or to Serbian copper (P3, P12, P16, P19), due to the presence of Co.
- We identified Hg in a Rudabanya (Hungary) native copper sample and Br traces in the Balan sample (a Transylvanian source).
- We identified the presence of Bi in a set of Drajna sickles, partly superposed with a set containing Hg; this suggests partly use of remelted Alpine and maybe also Hungarian copper (and probable commercial links with the region).
- Hg, Bi, In, Ag and Br seem to be worth searching for in further studies.

Micro X-ray techniques can describe the local composition of the objects, the local inhomogeneity in their structure and put in evidence the presence of trace elements in the copper (Sb, Co, Ag, Se) used in the manufacture of various objects. Averaged over a sufficient area, they can give an accurate global composition of the material.

We can suggest possible sources for some items, mainly for early objects made of impure copper, less for later bronzes, due to material mixing.

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