

MONOSTANDARD ACTIVATION ANALYSIS OF PREHISTORIC COPPER OBJECTS

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INTRODUCTION

Investigation on the composition of metallic prehistoric objects has become more and more systematic in the last years. Among these the analysis of copper objects has to answer a series of questions concerning the ancient mining and production of metal. The most used method for the investigation of prehistoric copper objects was spectral analysis. By its means tens of thousand of objects were analyzed at Stuttgart Museum [1] and at the Institute of Archaeology of the USSR Academy of Science [2]. The sensitivity reported in ref. [2] is about an order of magnitude higher than that obtained at Stuttgart.

It is to suppose that the neutron activation analysis (NAA) can be as simple as the spectral analysis but allowing probably lower detection limits, an advantage which ought not to be ignored. In order to demonstrate the possibilities of NAA on copper objects and to compare them with those of spectral analysis, especially from the point of view of detection limits, eleven Eneolithic copper axes and other three objects have been chosen as investigation objects. Nine of these axes are adze-axes (cross-axes). The idea was to simplify as far as possible the method of analysis. With that end in the view the monostandard activation analysis was used [3]. The resonance integrals used in this work were weighted average calculated on the basis of data from Gryntakis' and Kim's compilation [4].

EXPERIMENTAL

Fragments from the investigated objects were cut with a special knife of hard steel resulting samples weighting between 2 and 20 mg. After a careful washing in pure alcohol each sample was wrapped up in a pure aluminum foil. These samples, the neutron flux standard, a nickel and two copper standards were placed together into a quartz ampoule which was heat sealed. Irradiation was performed at the VVR-S reactor of the IPNE from Măgurele at an average thermal flux of $9.5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ for 96 hours. The two copper standards were pure metallic "Analar" copper with weights of 2 and 23 mg. Since their masses are more or less equal to the minimum and maximum masses of the investigated samples, the specific activity ratio gives an indication of self-shielding effects of neutron flux and decaying gamma-rays in solid samples. Both the calculations [5] and the experimental data show effects smaller than 5 %.

After irradiation each sample was unwrapped, put in a clean vial and counted at a gamma spectrometer with a large Ge(Li) detector with 1.8 keV fwhm for 1.33 MeV gamma-ray and 4096 channel analyzer. The counting was performed beginning with the 6th day after the end of irradiation. The concentration of nickel was measured by means of ⁵⁸Co (71.3 d) isotope produced by ⁵⁸Ni(n,p) reaction, using the nickel standard. A correction was made for the contribution of the ⁶³Cu(n, α)⁶⁰Co reaction when the concentration of cobalt was determined. This has been done by means of a pure copper standard irradiated together with the investigated samples.

The results obtained by monostandard NAA are given in Table 1. All the isotopes measured here have long half-lives (more than 27 days) excepting ⁷⁶As (1.096 d) and ¹⁹⁸Au (2.697 d). These two isotopes, especially ⁷⁶As, have to be counted during a few days from the end of irradiation. The area of 279.17 keV (²⁰³Hg) photopeak was corrected for the interference given by the gamma-ray of 279.5 keV (25 %) emitted by ⁷⁵Se, using for this the area of the 135.9 keV (58 %) gamma-line of the same nuclide.

Since lead and bismuth cannot be analyzed by NAA followed by gamma-ray spectroscopy, all the objects but nrs. 11 and 13 were investigated by aid of an X-ray spectrometer with a Si(Li) detector having a resolution of 180 eV for K-Mn. No lead and bismuth could be detected at a concentration detection limit of 0.01 %.

DETECTION LIMITS

The sensitivity that can be reached in the instrumental NAA depends to a great extent on the purity of copper. Copper itself has two natural isotopes, ⁶³Cu and ⁶⁵Cu, with abundance of 69.1 % and 30.9 %, respectively. In a reactor neutron flux they give (n, γ), (n,p), (n, α) and (n,2n) reactions. All resulting nuclides but ⁶⁰Co have quite short half-lives and 6 days after the end of irradiation ⁶⁴Cu (12.7 h) activity diminishes 4×10^{-4} times (⁷⁶As activity decreases only a factor of 0.02) and the sample can be counted. An element present in the sample in a high concentration or/and large activation cross section can mask an other isotope with a small rate of accumulation. The situation is worse when the last one emits only one γ -ray.

The limits of detection estimated in INAA are given in Table 2. The smallest concentration which could be measured by spectral analysis [2] for more than 1200 samples are also given for comparison in Table 2. It can be considered that the smallest determined concentration is quite close of the detection limit. Some values in Table 2 for NAA are taken on a similar ground.

For manganese the detection limit was determined by 1 min irradiation of a copper sample (10 mg) at the rabbit system of VVR-S reactor (2×10^{12} n cm⁻² s⁻¹), using a decaying time of 1 h and a counting time of 1000 s.

By means of INAA a number of 12 elements could be determined in a long irradiation run, the same number as in spectral analysis. Six elements have a detection limit an order of magnitude higher in INAA in comparison with spectral analysis and only three have a lower detection limit (Fe, Ni, Sn). If the irradiation time is increased 4 times, only tin remains with a lower detection limit. Furthermore, other three elements are seen with high sensitivity (Hg, Cr, Se), which are not reported in spectral analysis.

Table 1. Concentration in mg/kg (if no other specification) of trace elements in prehistoric copper objects

No.	Inv. No.	Ag	As	Au	Co	Cr	Fe	Hg	Ni	Sb	Se	Sn	Zn
1	MNH14050	311	57	7.0	1.3	n.d.	120	2	20	74	52	n.d.	≤12
2	MNH15887	16	14	0.4	0.4	211	400	12	40	23	15	0.13%	42
3	MNH32041	860	1.76%	1.8	n.d.	n.d.	n.d.	n.d.	30	0.17%	≤2	n.d.	n.d.
4	MNH15916	22	4	1.2	0.1	8	60	0.4	40	2	3	n.d.	11
5	MNH14049	45	160	1.3	0.1	n.d.	≤50	6	50	50	8	n.d.	16
6	Coll. Aparu	1140	120	9.4	n.d.	n.d.	≤100	2	230	31	21	n.d.	12
7	MNH54045	32	32	0.8	n.d.	-	≤20	1	30	3	n.d.	n.d.	11
8	MNH54751	24	26	0.7	n.d.	786	26	6	80	17	1	n.d.	11
9	MNH14066	14	7	0.2	2.7	-	60	2	120	2	13	n.d.	16
10	MNH15917	9	53	0.3	0.2	-	≤20	0.3	70	4	2	n.d.	13
11	Link I 65	31	8	2.1	0.2	3	32	0.6	90	1	22	n.d.	18
12	MNH39258	95	1.56%	4.9	1.4	n.d.	60	1	60	14	40	n.d.	16
13	Awl I 33	52	2	1.1	0.9	≤2	n.d.	4	150	1	39	n.d.	5
14	Rus/80 SIII	470	0.10%	0.6	0.3	25	n.d.	1	130	54	23	n.d.	5

Table 2. Detection limits in mg/kg obtained in instrumental neutron activation analysis (INAA) and spectral analysis (SA)

Element	INAA	SA	Element	INAA	SA
		[2]			[2]
Ag	5	1	Mn	5	100
As	7	70	Ni	20	5
Au	0.2	10	Pb	-	1
Bi	-	5	Se	0.3	-
Co	0.2	10	Sn	80	50
Cr	3	-	Sb	0.4	15
Fe	26	10	Zn	2	30
Hg	0.3	-			

DISCUSSION

A number of 38 adze-axes found on the territory of Bulgaria has been analyzed by Chernyh [2] and all of them are framed in the six groups defined by him, the majority being in the first group. In our case only two axes can be included in the first group, three in the second group, but the rest of four cannot be placed in any of the Chernyh's group. This fact demonstrates that these groups are not enough to characterize the copper objects from Eneolithic.

One can see that the two axes have a high concentration of arsenic (between 1 and 2 %) indicating an arsenical bronze ($c_{Sn} < 0.4$ %) [2] produced deliberately in order to change the metallic properties of copper. It is interesting to try some suppositions on the nature of mineral, which inserted arsenic in the alloy. In bronzing a high concentration of arsenic could be obtained by adding sulfarsenide minerals, such as energite or tennatite, or sulfide minerals such as orpiment or realgar.

In sulfoarsenides arsenic, antimony and silver are geochemically associated, that is a certain ratio exists between their concentrations. As Goffer shown [6] the concentration ratios As/Sb and As/Ag for copper objects found in the Dead Sea area are correlated. From the plot 11.6 of ref. [6] one can infer that the correlation is

$$\langle c_{As} \rangle = 128(\langle c_{Ag} \rangle)^{1.78} = 17(\langle c_{sb} \rangle)^{1.5}$$

where the elemental concentration is expressed in per cent. This correlation agrees very well for the axe no. 3, but not for the axe no. 12. On the Romanian territory enargite and tennantite were identified in many places [7].

In conclusion it can be said that monostandard INAA is a rather simple and reliable method. It has sensitivity higher than spectral analysis, the processing of the spectra can be performed by means of a computer and an average counting time of 1 h seems to be enough for a satisfactory statistics. Furthermore, it is not necessary to do any chemical processing on the sample, except maybe a slight etching and washing before, or even better after irradiation. It is also an advantage that the sample is not destroyed. In this way it can be preserved or, if it is necessary, analyzed again by NAA or some other method. All these advantages represent good premises for the prospect of studying many thousand of archaeological copper objects found on Romania territory.

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