THE ANALYSIS OF TRACE ELEMENT CONCENTRATION IN ANCIENT OBJECTS BY NEUTRON ACTIVATION ANALYSIS

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Introduction

Neutron activation analysis is commonly used to determine trace element concentrations in ancient objects in order to evaluate their origin. At the Reactor Laboratory trace elements have been analyzed from some copper and brass objects and also from samples of old ceramics.

Because of its sensitivity neutron activation analysis is a suitable technique for the analysis of small amounts of materials. The sample size has to be small when rare and hence valuable objects are analyzed.

Sample preparation

Copper and brass objects

In the analysis of metal objects the sample preparation was carried out in the following way: The samples were taken by drilling a 4 mm deep hole with a steel drill 3 mm in diameter. The first millimeter was removed before taking the sample so as to avoid possible contamination caused by the altered surface layer. The samples of some milligrams were dissolved in quarz ampoules with ultrapure HNO_3 and diluted to 200 μl in order to avoid self absorption during irradiation. The brass samples did not dissolve in HNO_3 and therefore HCl was added drop by drop until the sample was completely dissolved. A reagent blank was also prepared. The standard was prepared of liquid solutions of the appropriate elements.

Ceramic samples

The ceramic samples were homogenized in an agate mortar. About 80 mg of the samples and the same volume of standards were weighed into small polyethylene capsules (0.5 ml in volume). Two of the standards were rock standards made by the Geological Survey of Finland, while the other two were artificial silicon-based standards made in the Reactor Laboratory.

Analysis

Irradiation of the samples and standards took place in a research reactor Triga Mark II in Otaniemi, Espoo, where the neutron flux varied from 10^{12}—10^{13} n/cm² s depending on the irradiation position.

The samples were measured with a γ-spectrometer which comprises a sample changer, a Ge(Li)-detector and a multichannel analyzer (Vänskä et al., 1981).

The spectrometer was equipped with an on-line microcomputer which computes the elemental concentrations of the samples immediately after the measurement has ended.

Copper and brass objects

The standards and samples were irradiated for 30 h in the central tube of the reactor. After the irradiation the samples were transferred into polyethylene capsules using a Pasteur pipette. This was done in order to lower the background activity and to improve the geometry of the measurement. The samples were measured 5 days and 13 days after irradiation for one hour. The blank contained small peaks of ^{51}Cr, ^{60}Co, ^{187}W, ^{198}Au and ^{122}Sb these corresponding to negligible concentrations as compared to the results reported. Co is an exception because of a high ^{60}Co background in the Laboratory. A little cobalt is also found by a (n, α) reaction from copper. The effect of these errors was corrected in the results which are shown in Table 1.

Ceramic samples

Three separate irradiations were performed to analyze 30 elements from the ceramic samples.

Table 1. Concentration in μg/g.

Sample	As	Ag	Sb	W	Au
Brass ring		464	1360	<20	15
Copper ring	280	35		110	0.018
Sword	137	4.6	66		0.24
Knife	1090	90	1290	<3	1.2
Plate		551	1896	33	9.0

	Cr	Co	Ni	Zn
Brass ring	59	55	658	59700
Copper ring		5.5		5.5
Sword		24	270	8.8
Knife		<10	95	1600
Plate	252	161	6830	<150

Table 2. Trace element concentration of short-lived nuclides.

Sample No.	V μg/g	Al %	Mn %
1	101	10.6	0.37
2	93	9.4	0.21
3	129	8.4	0.16
4	135	10.4	0.16
5	100	8.8	0.16
6	145	10.3	0.12
7	134	10.6	0.11
8	91	8.4	0.29
9	109	9.8	0.19
10	102	9.7	0.52

Table 3. Average detection limits for whole rock and till samples.

Element	Detection limit (ppm)	Element	Detection limit (ppm)
Na	250	Sn	100
Sc	0.5	Sb	0.1
Cr	40	Cs	0.6
Fe	2500	Ba	80
Co	2.5	La	1.5
Ni	40	Sm	0.05
Zn	100	Lu	0.05
As	1	Hf	2
Se	4	Ta	0.5
Br	0.6	W	2
Rb	15	Au	0.003
Mo	1.5	Th	0.4
Ag	3	U	0.3

The short-lived nuclides V, Al and Mn were measured after a 20 s irradiation in a thermal flux of $1.2 \cdot 10^{12}$ n cm^{-2} s^{-1}. The cooling and measurement times were two minutes. The results of these elements are in Table 2.

Sodium and potassium were analyzed using an irradiation time of 5 hours. The samples were measured after two days for 20 minutes. These nuclides could also be analyzed after epithermal irradiation but the sensitivity is better in the above procedure.

The rest of the elements were analyzed using epithermal irradiation which improves the sensitivities above all of As, Br, Mo, W and Au. This method reduces the total activity of the sample which is mainly due to the ^{24}Na-activity. The detection limits of some till samples can be seen in Table 3. The detection limits were calculated applying the definition of Currie (1968).

In the Reactor Laboratory epithermal irradiation has been routinely used to analyze exploration samples for mining companies (Rosenberg et al., 1982). The ceramic samples were analyzed in the same way. The samples and the standards were irradiated for 25 hours. After 5 days the samples were measured for 20 minutes. Some of the results have been collected in Table 4. The other elements gave only determination limits.

Activation analysis is a moderately accurate technique the relative error being of the order of ± 10 %.

Discussion

The copper ring was found at the Suovaara stone age site in Polvijärvi, Finland. It has been described by Taavitsainen (1982). The copper ring seems to have a very high degree of purity. The trace element composition is characteristic of pure natural copper. The ring contains As and therefore the region of the Urals, USSR, is thought to be the most probable area of origin and not the area of Eastern Karelia, where the object was found. The sword is probably from Northern Germany. The origin of the other objects has not yet been determined.

The ceramic samples were found in Harjavalta, Finland. It is quite obvious that the determination of the origin of these objects will require additional work. Comparing for instance the elemental concentrations of the samples with the clay used in different areas can be a start in solving this problem.

Table 4. Trace element concentration of ceramic samples.

Sample	Na %	K %	Br	As	Sc	Ba	Cs	Rb
1	0.81	3.16	6.5	2.9	24	2170	6.2	148
2	0.65	3.36	7.3	2.3	23	1300	9.5	191
3	0.67	2.64	7.0	4.3	20	860	7.5	147
4	0.87	3.11	3.7	4.2	25	1110	9.2	179
5	0.81	2.56	10.0	1.6	18	1230	8.7	166
6	0.75	2.94	4.8	3.7	20	1580	9.7	186
7	0.79	3.17	4.9	4.1	22	940	9.9	192
8	0.70	2.38	5.8	3.5	16	690	7.7	148
9	0.77	3.04	5.2	3.7	19	1180	9.1	197
10	0.66	2.65	8.4	3.1	20	2750	9.7	184

	Cr	Ni	Fe	Co	La	Sm	U	Th
1	138	62	74800	30	56	7.3	6.8	24
2	129	97	70600	36	58	8.0	6.4	22
3	449	158	67000	32	59	6.9	3.5	18
4	153	57	77400	28	62	7.3	5.0	24
5	91	34	51300	21	51	6.4	4.9	23
6	123	66	60600	21	49	6.2	4.6	20
7	105	61	68000	26	63	7.9	4.8	24
8	799	174	61400	34	56	7.1	4.1	16
9	126	91	59900	34	59	7.9	5.1	20
10	116	52	61200	29	62	8.7	6.4	21

Concentrations in $\mu g/g$.

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