

## **NATURAL GOLD COMPOSITION STUDIED BY PROTON ACTIVATION ANALYSIS (PAA)**

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*Abstract:* The minor and trace element concentration of natural gold is essential for provenance studies of gold archaeological artifacts. In this work proton activation analysis is used in order to find what elements can be put in evidence in natural gold. For that purpose some gold nuggets from Romania were used. It was found that PAA is a good supplemental method to neutron activation analysis.

*Key words:* gold, proton activation analysis, archaeological artifacts.

### **1. INTRODUCTION**

The concentration values of minor and trace elements in natural gold from different regions of the terrestrial globe can facilitate both the gold artifact provenance studies, especially of the ancient objects, and to define the genesis of the gold sediments. An international data bank of the natural gold composition would be very useful for the provenance studies and work could be a beginning. For the Romanian history the provenance studies of very old (Neolithic) Romanian gold hoards such as Moigrad and Balaciu (both controversial) as well as the gold Gods found in Calarasi country would be most desirable. But the provenance of gold will also be important for newer artifacts such as the gold Hinova hoard (12th century BC), the Dacian gold coins (ΚΟΣΩΝ), or even Roman gold coins struck after the conquest of Dacia (it is considered that the Roman loot from Dacia included 500000 pounds of gold from which at least 21000000 aurei could be coined [1]).

According to Pernicka [2] the most promising elements for provenance determination are Ag, Cu, Te, Sn and the platinic group of elements (PGE). A previous [3] neutron activation analysis (NAA) on a lot of 15 nuggets from Romania showed that the elements which can be determined by this method in studied gold are: Ag, Cu, Ir, Pt, Hg, Al, Eu and V. The sensitivity for copper of the instrumental NAA is not enough (the limit is 200 – 300 ppm) and this made that

sometimes only the upper limit of copper concentration to be found. Concerning PGE only Ir and Os can be determined by INAA (limit for Ir is about 0,4 ppm), and chemical separation is necessary for platinum determination. Furthermore, Te and Sn have not been seen by INAA. The most productive isotope from the eight tellurium isotopes found in nature which appear in (n, $\gamma$ ) reaction is  $^{130}\text{Te}$ :  $^{130}\text{Te}$  (34.5%)  $\Rightarrow$   $^{131}\text{Te}$  ( $T_{1/2} = 24.8$  min)  $\Rightarrow$   $^{131}\text{I}$  ( $T_{1/2} = 8.05$ d). Even the most intensive  $\gamma$  line (364.5 keV) of  $^{131}\text{I}$  is a difficult to be put in evidence in the gold neutron activation spectrum. Even in more favorable situations it is difficult to go down under a limit of 300 ppm [5]. Tin is also difficult to be seen by INAA, the activation cross sections being very small (under 0.01 barns) for the more abundance isotopes. Platinum was put in evidence by NAA only after chemical separation [4] and only if its concentration is higher than 100 ppm. There was the hope that the platinum limit could be lowered to 2 ppm, such as was reported for the Roman gold coins [6]. So it was expected that PAA has some major advantages in comparison with NAA for compositional analysis of samples with gold matrix.

## 2.EXPERIMENTAL

Twelve nuggets from different Romanian places have been laminated between tantalum foils in order to get a larger surface. Every sample was irradiated at a proton beam of energy  $E_p = 11$  MeV and a current  $I_p \approx 0.3$   $\mu\text{A}$  for about 90 min at the NIPNE.HN Tandem accelerator. After irradiation and a decay time between 24 and 48 hours each sample was recorded at a  $\gamma$  spectrometer with a 50  $\text{cm}^2$  Ge(Li) detector and 2.1 keV resolution for 1.332 MeV ( $^{60}\text{Co}$ ). A cadmium filter of 1 mm thick was used for the first measurements in order to reduce very strong Au-X rays and  $\gamma$ -lines of 77.35 keV ( $^{197}\text{Hg}$ ) and 134 keV ( $^{197\text{m}}\text{Hg}$ ). The later measurements were made without any filter.

Excepting gold (the matrix) the following elements have been seen in the  $\gamma$  spectrum: **Ag**[ $^{109}\text{Cd}$ (453d):88.0(3.9%)/ $^{107}\text{Cd}$ (6.5h):93.1(46%),828.9(0.177%)]; **As**[ $^{75}\text{Se}$ (120d):264.6(57.3%),400.6(11.2%),270.5(24.8%)]; **Cr**[ $^{52}\text{Mn}$ (5.7d):744.1(88%),935.5(94%)]; **Cu**[ $^{65}\text{Zn}$ (244d):1115.5(50.75%)]; **Fe**[ $^{56}\text{Co}$ (77.3d):846.8(100%),1238.3(67.6%)]; **Hg**[ $^{200}\text{Tl}$ (26.1h):368.0(89.3%)/ $^{202}\text{Tl}$ (12d):439.6(91.4%)]; **Pb**[ $^{206}\text{Bi}$ (6.24d):803.0(98.9%),880.9(66.2%)]; **Pt**[ $^{196}\text{Au}$ (6.18d):335.7(88%)/ $^{194}\text{Au}$ (39.5h):328.5(59.1%)]; **Sb**[ $^{121}\text{Te}$ (17d):573.1(80%)/ $^{123\text{m}}\text{Te}$ (119.7d):159.0(84.1%)]; **Sn**[ $^{122}\text{Sb}$ (2.8d):564.0(66%)/ $^{124}\text{Sb}$ (60.4d):602.7(98%),1691.0(45.7%)]; **Sr**[ $^{89}\text{Y}$ (80.3h):388.4(82.5%),484.8(90.6%)]; **Te**[ $^{124}\text{I}$ (4.15d):602.7(62%)/ $^{126}\text{I}$ (12.8d):388.2(34.9%)/ $^{130}\text{I}$ (12.3h):739.4(82.3)]; **Ti**[ $^{48}\text{V}$ (15.97d):938.5(100%),1311.9(97%)]; **Zr**[ $^{90}\text{Nb}$ (14.6h):1129.1(92%)/ $^{92\text{m}}\text{Nb}$ (10.13d):934.5(99.2%)]; **Y**[ $^{98}\text{Zr}$ (78.5h):909.2(100%)]. In brackets are given one or two of the most intensive lines and the emitting nuclide.

### 3.RESULTS AND DISCUSSION

The results are given in Table 1. The first two nuggets belong to the placer deposits and the *Table 1*. Concentration of elements in natural gold samples. The values are in ppm ( $\mu\text{g/g}$ ) if no other indication is given

Source	Ag	As	Cr	Cu	Fe	Hg	Pb	Pt	Sb	Te	Ti	Zr
Valea Ariesului	6.95%	110	n.d.	540	1600	990	170	n.d.	$\leq 13$	33	335	87
Valea Pianului	12.45%	20	n.d.	150	120	390	$\leq 20$	153	79	n.d.	11.6	1.2
Bucium-Izbita	13.95%	55	n.d.	510	110	110	180	n.d.	$\leq 4$	$\leq 15$	0.6	2
Baia de Aries	10.20%	14	n.d.	30	40	280	80	n.d.	3	$\leq 10$	1.8	1.6
Zlatna	27.04%	$\leq 18$	n.d.	50	1500	230	58	n.d.	145	$\leq 80$	2.6	1.3
Ruda-Bran	13.24%	1.46%	5.3	229	2700	950	340	262	560	35	49	n.d.
Valea Morii	18.69%	$\leq 12$	1	60	260	180	115	56	41	$\leq 8$	9.3	1
Musariu-Brad (1)	22.46%	$\leq 10$	n.d.	40	60	229	122	n.d.	32	40	0.6	n.d.
Musariu-Brad (2)	4.90%	28	n.d.	340	6	100	150	58	$\leq 5$	3040	$\leq 0.8$	0.4
Runculet-Straja	22.50%	93	n.d.	60	980	700	125	n.d.	44	300	18	$\leq 0.6$
Rosia Montana	25.65%	$\leq 25$	4.6	25	180	200	450	n.d.	61	180	1.6	n.d.
Bradisor-Brad	8.50%	$\leq 17$	n.d.	200	13	500	36	n.d.	$\leq 6$	230	3.7	$\leq 0.4$

rest to the primary deposits. In comparison with the NAA [3], where parts of the same nuggets were used, these results show some differences which are accounted as a lack of homogeneity. For instance silver show high nonhomogeneities for crystallized nuggets (the also for Musariu – Brad (2) nugget. The concentrations of the rest are in agreement in the limits of  $\pm 30\%$ . Due to the larger masses (at NAA the average weight of the sample was 4 mg, while in PAA a mass of about ten times larger was irradiated) PAA is considered more reliable.

There are only few data one can compare with the Romanian native gold analyses. An analysis of gold from Ras-Shamra, XIV – XII BC [7], most probable natural gold, are given in Table 2 together with present average values  $\langle c \rangle$ . Major differences are seen for copper (one order of magnitude), mercury and tellurium (two orders), etc.

Table 2.- Comparison between presents average concentrations with gold from Ras-Sharma [7].

Element	c[7]	$\langle c \rangle$
Ag	6,2%	15.5%
As	4.7	53*
Cu	0.21%	185
Fe	165	630
Hg	$\leq 3.8$	400

Element	c[7]	$\langle c \rangle$
Pb	54	153
Sb	7	82
Sn	36	n.d.
Ti	0.4	36
Te	$\leq 1.4$	300

\*) Without Ruda-Brad nugget

There is a small probability that minor and trace elements from native gold could indicate the mine from which gold has come. So, two nuggets originating in

the same mine (Musariu-Brad 1 and 2), but coming from different places, differ drastically between them, even an order of magnitude or more. But, some average concentrations might characterize gold from a geographical region. Romanian natural gold has as fingerprint a small concentration of copper, and high concentration of mercury and tellurium. The last element has discovered by F.J.Müller von Reichnstein in Romania at Săcărâmb in 1782 and it is even considered that „only in the ore deposits from Transilvania are found minerals in which tellurium is combined whit gold or silver”, [8]. Also, iridium and osmium (generally PGE) seems to be different in Romanian gold. For instance, the Pietroasa hoard was manufactured from gold in which iridium is found as a solid solution (but iridiosmium inclusions also co-exist) in an average concentration  $\langle c_{Ir} \rangle = 7.8$  ppm [9], very high in comparison with the Romanian native gold ( $\langle c_{Ir} \rangle \leq 0.37$  ppm [3]). When radiochemical separations were made it was seen that  $c_{Ir} \cong 40$  ppb [3]. Finally, it is worth to note that no tin was observed in the Romanian nuggets.

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