DETERMINATION OF PLATINUM CONCENTRATION IN GOLD MATRIX BY NEUTRON ACTIVATION

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INTRODUCTION

The determination of platinum concentration in a sample with a high amount of gold is a difficult problem. Even more difficult is to finde the platinum concentration in a gold matrix. Nevertheless the problem is important at least in archaeology and geochemistry investigations. Platinum has six stable isotopes, all of them having moderate values of the neutron activation cross section. One hour irradiation of platinum in a reactor gives for the stable isotopes ^{190}Pt, ^{192}Pt, ^{194}Pt, ^{196}Pt and ^{198}Pt a production factor of 0.07, 0.03, 0.08, 3.0 and 100.0 respectively. The only nuclei which deserve to pay attention are the last two. ^{197}Pt is not very convenient having the most intensive gamma-line at 77.46 keV (21 %) that is in the X-ray region and a relatively short half-life (18.3 h).

The most productive is ^{199}Pt with a short half-life (30.8 min) and not very intensive gamma-lines (542.7 keV has 16.4 %), but it is β^--decaying in ^{199}Au ($T_{1/2}$ = 3.15 d). This seems to be a good alternative. Unfortunately in neutron irradiation ^{199}Au is also coming on the other way (Figure 1).

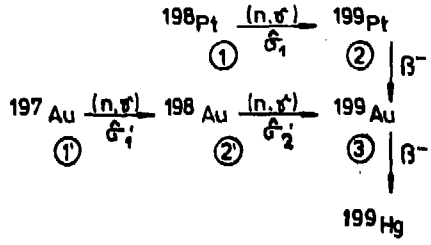

Figure 1

The idea of the work consists in the pre-irradiation separation as far as possible of platinum of its matrix and to find the most favorable irradiation conditions of the separate sample in order to get a high ratio of activities

$$A_{199}/A'_{199}$$

were by prime is indicated the interference chain initiated by ^{197}Au.

EXPERIMENTAL

Chemical separation. The pre-irradiation separation was made by means of many step organic solvent extraction technique, followed by ion exchange procedure. The tests were made with gold and platinum metals irradiated at the neutron fluxes in such a way to create balanced activity tracers ^{198}Au and ^{199}Pt (or ^{197}Pt). After irradiation the samples were mixed up, completely dissolved in aqua regia and separated.

Counting was done using a 50 cmc coaxial Ge(Li) detector and a 4096 channel pulse-hight analyzer. System resolution is better than 2 keV fwhm at 1.33 MeV γ-ray. The detector was placed in a low background protection which reduces the background around 100 times. In order to keep a constant geometry all samples were measured at the same volume (12 ml). The separation scheme is summarized graphically in Figure 2. The solvent extraction was repeated four times. The aqueous phase of the fourth extraction was heated to dryness and the residue was dissolved in 3 ml of 3N HCl. The solution was then passed through a small (0.5 cm diameter) column with 0.25 g Dowex 2 x 10 (200 - 400 mesh) ion exchange resin at a flow of 12 drops/min and washed with 50 - 125 ml solution of HCl conc.(10 %) + acetone (90 %) at the same flow rate.

If the initial ratio Pt/Au = 1, after the first and fourth solvent extraction steps it becomes in aqueous phase 200 and 4000 respectively. In this time the platinum concentration is reduced to 80 %. After the ion exchange procedure the ratio becomes Pt/Au = 10^5 and the total recovery of platinum is found to be (68 ± 3) %.

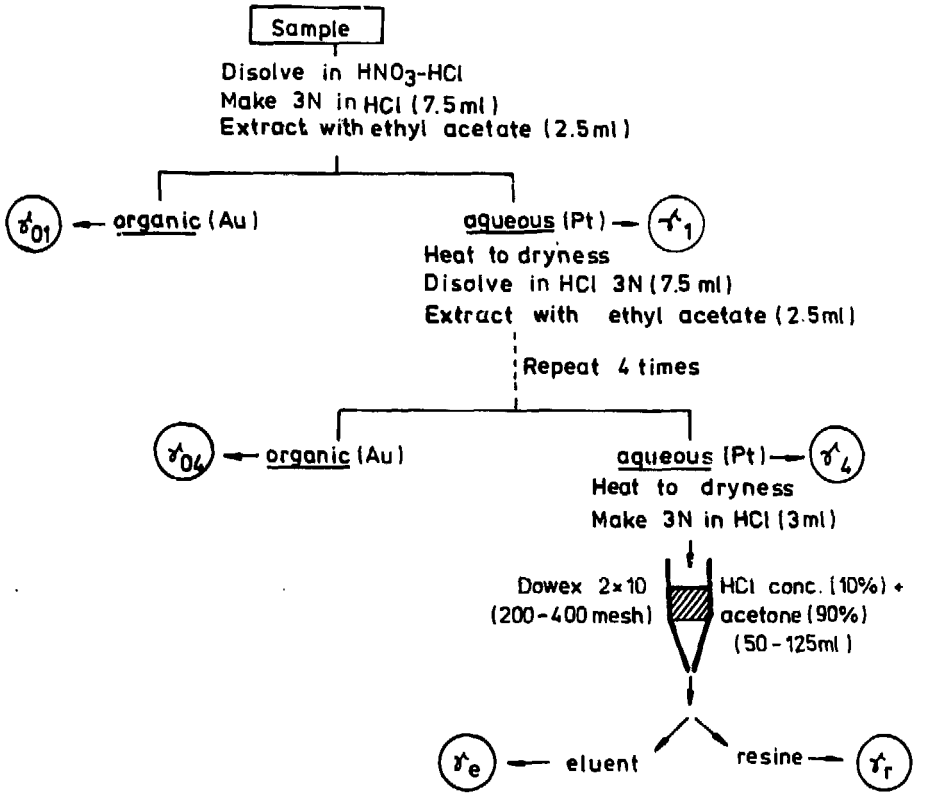

Figure 2

Irradiation parameters. The irradiation time and the neutron flux have to be properly chosen in order to make the ratio of the ^{199}Au activity coming from platinum (Λ_{199}) to the ^{199}Au activity coming from gold (Λ'_{199}) as high as possible. One can find that at the end of neutron irradiation (see Fig.1):

$$\Lambda_{199}(o) = n_{Pt}\,\hat{\sigma}_1\,\phi\;\frac{1}{\lambda_3-\lambda_2}\left[(1-e^{-\lambda_2 t})-\frac{\lambda_2}{\lambda_3}(1-e^{-\lambda_3 t})\right]$$

$$\Lambda'_{199}(o) = n_{Au}\,\hat{\sigma}'_1\,\hat{\sigma}'_2\,\phi^2\;\frac{1-\lambda'_2}{\lambda'_2}\left[\frac{1}{\lambda_3}(1-e^{-\lambda_3 t})+\frac{1}{\lambda_2-\lambda_3}(e^{-\lambda'_2 t}-e^{-\lambda_3 t})\right]$$

In these equations

$$\hat{\sigma} = \sigma_{th} + (\phi_{epi}/\phi_{th})\,I$$

where I is the integral resonance.

The ratio $\Lambda_{199}/\Lambda'_{199}$ vs. the irradiation time is given in Figure 3. The curves 1, 2 and 3 are calculated for a flux of 10^{11}, 10^{12} and 10^{13} n cm^{-2} s^{-1}, respectively. The lower neutron flux the higher the ratio $\Lambda_{199}/\Lambda'_{199}$, but a too low flux can give an insufficient detection limit for platinum. For a necessary fluence it is better to chose a lower neutron flux. At the gamma-spectrometer used in this work the detection limit is of 35 ng Pt for an irradiation time of 3 h and a measuring time of 10000 s. With a reduction of gold concentration by 10^5 times and a $\Lambda/\Lambda' = 8$, an amount of 3 mg gold will give a correction of only 10 % in the γ-line of 158.4 keV (^{199}Au). This correction is found by aid of the ratio (area of 158.4 keV γ-line)/(area of 411.8 γ-line) of a standard of gold irradiated in reactor together with the investigated samples.

RESULTS AND DISCUSSION

Nuggets of gold from different placers of the Apuseni Mountains (Romania) and from Romanian rivers have been used as samples. The mass of the samples was between 3 and 5 mg.

In order to observe by aid of ^{198}Au tracer the reduction of gold along the platinum separation process the samples were irradiated at a low neutron fluence

(6.10^{13} n cm^{-2}). The recovery of platinum was found using a combination of platinum and gold with a mass ratio Pt/Au ~1/1000 which was processed in the same way with the investigated samples. The resins on which platinum was retained were irradiated a time of 20 hours at a thermal neutron flux of 1.1 10^{11} n cm^{-2} s^{-1} (thermal column of the VVR-S reactor).

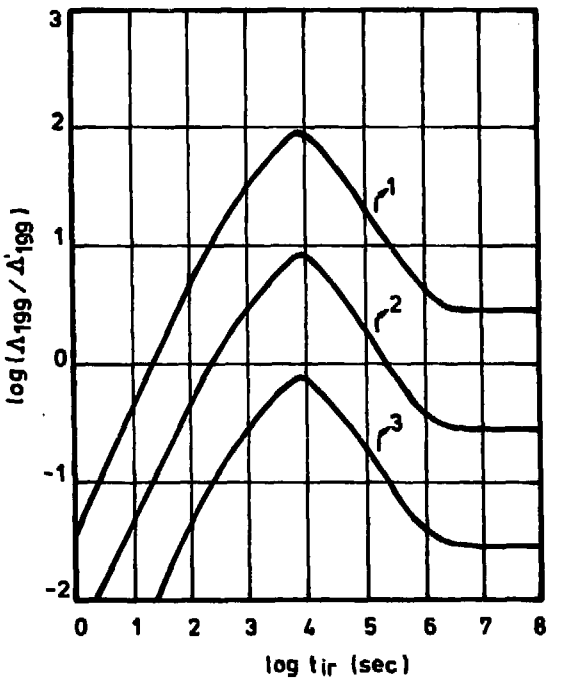

Figure 3

Counting was done after a decaying time of 6 days in order to get a low ^{24}Na and ^{82}Br activities coming from resin. Concentrations of platinum between 0 and 460 ppm with an average of 270 ppm were found in the investigated nuggets.

Interferences. The interference of ^{47}Sc (159.4 keV) coming from $^{46}Ca(n,\gamma)^{47}Ca$ (β^-) is not possible, calcium being not retained by the resin. Also the reactions (n,p) and (n,α) which produce ^{47}Sc are excluded since thermal neutron fluxes were used. Nevertheless tin by the ^{117m}Sn (14 d) isotope which has only a γ-line (158.4 keV) can interfere with ^{199}Au. Its presence can be put in evidence counting either 158.4 keV γ-line after the decay of ^{199}Au (ca. 30 d) or 592 keV γ-line of the ^{113}Sn (115 d) isotope and doing the necessary corrections. A tin standard was irradiated together with the resins on which platinum was absorbed in order to find the ratio of the areas A(158.4 keV)/A(592 keV) coming from tin. In our samples no tin interferences was found.