The Determination of Gold in Assay Process
by Thermal Neutron Activation Analysis

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試金工程中의 金의 熱中性子에 依한 放射化分析

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Abstract

12 samples from an assay process chain were submitted to qualitative and quantitative neutron activation analysis for the determination of gold. Gold was detected and quantitatively determined in three samples after a chemical separation consisting of solvent extraction and precipitation steps. Recoveries ranged between 81.0 and 93.6% and results of duplicated determinations were reproducible. Quantitative data were obtained from gamma-spectrometric photopeak-area counting.

Interference from fast neutron reactions was negligible.

要　旨

試金工程의 試料中의 金의 定性 및 定量을 熱中性子에 依한 放射化分析으로 試圖하였다.

回收率은 81.0～93.6%이고 結果는 再現性이 좋았다. 定量的 結果는 γ-Spectrometric photopeak-area counting으로 얻었으며 速中性子反應으로 因한 干涉은 無視할 수 있었다.

1. Introduction

Gold in ore is determined by dry assay method one of the typical flowsheet being shown in Fig. 1.

Considerably losses of gold in sample during the fusion and cupellation steps have been reported in several cases when certain elements are associated in the ore. But there is also the possibility of losing gold during the other steps of this process such as mixing, molding, and when slag off as shown in Fig. 1. It was, therefore, thought of interest to control stepwise this possible loss of metallic gold. Although the accuracy of the quantitative analysis by radioactivation analysis is inadequate to replace the classical method of routine gold assay process, its sensitivity

appears so high that it is indicative for the control and the development of the classical assay process.

In this paper a trial to investigate any loss or gain of gold through the assay process; reagents as well as parts of the apparatus, by qualitative and quantitative radioactivation analysis was therefore discussed. The nuclear data for gold being extremely favorable, great sensibility can be obtained by this method.

2. Nuclear data [1~7]

The nuclear data in connection with the radioisotopes encountered in this work are shown in Table I. It appears that in our experimental conditions the influence from interfering fast-neutron reactions can be neglected as the sample does not contain enough Hg to be detected and

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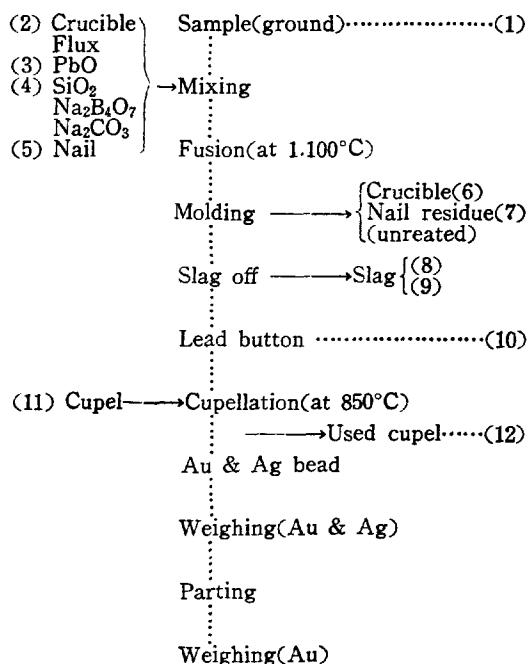*** Taejon Mineral Laboratory

also as it is very improbable to have isotope build up by(n,p) reaction s. Futhermore Pt seems not to be present in the sample. The secondary reaction: $Pt^{197} \xrightarrow{\beta^-} Au^{197}$ (n, γ) Au^{198} is anyhow negligible when irradiating for 15 min. or 6 hrs. at a thermal neutron flux of $10^{12} n/cm^2$ sec.

The decay scheme of gold-198 is given in Fig. 2.

The calculated sensitivities, in gram element detectable, are summarized, together with the irradiation times, in Table II.

It appears from Table II that the activation analysis technique is particularly suitable for the determiantion of trace amounts of gold, as sensitivity is extremely high.

Fig. 1 A typical assay flowsheet

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(2) Crucible⎫   Sample(ground)·····················(1)
    Flux    ⎪        ⋮
(3) PbO     ⎪
(4) SiO₂    ⎬  →Mixing
    Na₂B₄O₇ ⎪        ⋮
    Na₂CO₃  ⎪
(5) Nail    ⎭  Fusion(at 1.100°C)
                     ⋮
                                  ⎧Crucible(6)
                     Molding ────→⎨Nail residue(7)
                     ⋮            ⎩(unreated)

                     Slag off ───→Slag⎰(8)
                     ⋮                ⎱(9)

                     Lead button ·····················(10)
                     ⋮
(11) Cupel───→Cupellation(at 850°C)
                     ⋮   ────→Used cupel·····(12)
                     Au & Ag bead
                     ⋮
                     Weighing(Au & Ag)
                     ⋮
                     Parting
                     ⋮
                     Weighing(Au)
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3. Experimental

3.1 Irradiation and counting facilities

Powered samples, sealed in pharmaceutical-type gelatine capsules, were irradiated in nylon "rabbits" in the pneumatic transfer system or in the rotary specimen rack of the TRIGA MARK II nuclear reactor of the Atomic Energy Research Institute of Korea. The former system permits irradiation at a thermal neutron flux of about $1.3 \times 10^{12} n/cm^{-2}$ sec^{-1} (at full power of 100 Kw) and delivery to a hood in the hot laboratory within two seconds after the end of irradiation. The neutron flux in the rotary specimen rack is $0.7 \times 10^{12} n/cm^{-2}$ sec^{-1}.
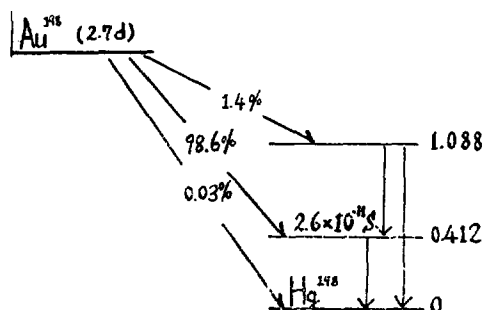

Fig. 2 Decay scheme of Au^{198}

Table II Calculated sensitivity in gram element detectable by the reaction $Au^{197}(n, \gamma)$ Au^{198}

(abundance=100% cross-section=98b

neutron flux=$10^{12} n/cm^2 sec.$)

Irrad. time	Calculated Sensitivity(g)
5 min	3×10^{-8}
15 min	1.2×10^{-8}
1 hr	3.2×10^{-9}
6 hr	5.4×10^{-10}
24 hr	1.3×10^{-10}

Table I Nuclear data

(n, γ)	Nuclear Reaction	Ab. %	$T\frac{1}{2}$	Cross Section barns	γ-Radiation Energies	Remarks on Influence
Interfering Reaction	Au^{197} (n, γ) Au^{198}	100	2.7d	98	0.412, 1.088, 0.676	Main Reaction
	Hg^{198} (n, p) Au^{198}	10.02	2.7d	—	//	Negligible
	Au^{198} (n, γ) Au^{199}	—	3.15d	3.5×10^4	0.158, 0.05	//
	Pt^{196} (n, γ) Pt^{197} $\xrightarrow{\beta^-}$ Au^{197} (n, γ) Au^{198}	—	2.7d	98	0.412, 1.008, 0.676	//

Samples were then treated chemically and measured with a 2″×2″ NaI(Tl activated) crystal coupled to RCL-256-channel pulse height analyzer. Flux monitoring during irradiation was done with gold foils, weighing between 0.1 and 0.2 mg, taped to the central inner side of the cap of the nylon rabbit, or plastic container which positions are closest to the sample. All irradiations were normalized to a neutron flux of 1.3×10^{12}n/cm²sec for the pneumatic transfer system and 0.7×10^{12}n/cm²sec for the rotary specimen rack.

The activity of the gold monitoring foils was determined by well type gamma counting.

3.2 Preparation of samples

Known amounts of 12 samples were chosen from the assay process chain(Fig. 1) and were then analysed to test the general applicability of the radiochemical separation procedure. Every sample to be determined was ground to a fine powder with a clean agate mortar and pestle. The sample No. 10–lead button- was ground to fine particles with a iron file. The weighed samples were placed in gelatine capsule(pharmaceutical) which were individually wraped with clean tissue paper, and irradiated in the "Rabbit" and or plastic container together with a weighed gold monitoring foil during a period,calculated to given

optimum sensitivity for the gold concentration under consideration.

3.3 Radiochemical separation procedure[6~12]

The irradiated sample(0.2—0.6g) was transfered from the gelatine capsule to a nickel crucible, and was fused with about 0.5g of Na_2O_2 and 25 mg of Au carrier, as $AuCl_3$ soln. After cooling the crucible, the solidified melt was dissolved by 5ml of c-HCl, transfered to a 250ml beaker under addition of 20ml of aqua-regia and then heated to dryness on the hot plate. The residue was dissolved again by addition of 2ml of c-HCl, further diluted with 15ml of 10%-HCl and filtered.

The filtrate was transfered to a 200 ml separation funnel, containing 15ml ethyl acetate. After extraction, it was back-extracted with 10ml of $0.33 N-NH_4 OH$. Then the aqueous-phase was heated to dryness in a 250ml beaker on the hot plate. The residue was dissolved by addition of 2ml of aqua-regia, evaporated, dissolved with another 20ml of 4N-HCl and heated gently in the presence of 10ml of 5%-Hydroquinone solution, thus precipitating elementary gold from its salts. After heating 20min., the solution was diluted with 20ml of H_2O, cooled and filtered through a Whatman No. 42 filter paper on a glass filter.

The filter paper was completely ignited in a porcelain crucible to obtain gold sponge. The elementary gold was weighed in a counting vial to determine the chemical recovery and counted with the 256-multichannelanalyzer.

3.4 Sample counting[13.14]

Samples and standards were checked for radiochemical identity and purity by half-life measurements and by gamma spectrometry.
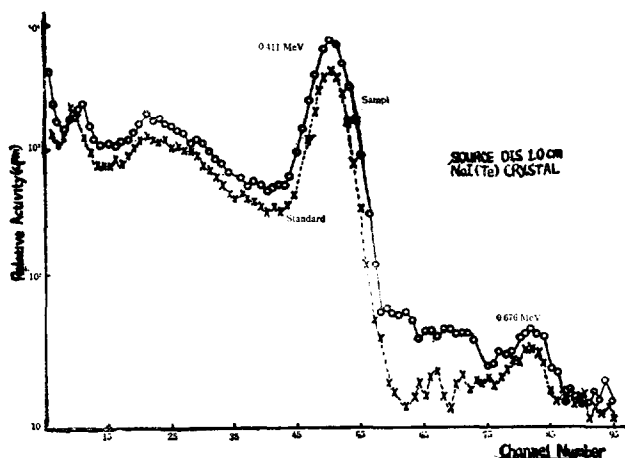
Some characteristic gamma-spectra are given in Fig. 3.

Fig. 3 Gamma-ray spectrum of Au^{198}

The gamma energy for Au^{198} was 411 KeV, as might be expected from its decay scheme. Background and interfering Compton radiations from other activities remaining in the sample were eliminated by extrapolatin of the base line from both sides of the photopeak. For this purpose, the printed-out digital data were used in combination with the following relation. (Fig. 4)

$$Rph = Rt - \left(\frac{X+Y}{2}\right)n$$

where Rph=number of counts under the netto photopeak area.

 Rt=total number of counts, obtained by summing the printed-out data in n channels.

 X=counts in channel b

 Y=counts in channel a

 n=number of channels=b−a+1

4. Results

The results of qualitative and quantitative gold determinations are summarised in Table III and IV.

Table III Qualitative analysis of Gold

Sample No,	Pneumatic system	Rotary specimen rack
1	Detectable	Detectable
2	Undetectable	Undetectable
3	//	//
4	//	//
5	//	//
6	//	//
7	//	//
8	//	//
9	//	//
10	Detectable	Detectable
11	Undetectable	Undetectable
12	Detectable*	Detectable*

*-Scrapings of the cupel upper surface layer.

5. Summary and Discussion

The assay process adopted in this test is a typical procedure for ordinary sulfide ore. The gold ore sample assayed along this procedure is also a common sulfide ore with no significant amount

Table IV Quantitative analysis of Gold

Sample No.	Sample Wt. $(10^{-3}g)$	Chemical Recovery(%)	Wt. of Au found in sample $(10^{-5}g)$	ppm	Mean Value (ppm)
1.	200.63	93.00	5.92	29.60	
	218.71	93.60	6.58	30.10	
	306.10	89.30	9.35	30.30	30.00±0.30
	364.00	92.70	11.30	31.00	
	591.00	92.30	17.20	29.10	
10.	*231.90	81.00	3.95	17.10	
	239.70	82.30	3.84	16.10	16.35±0.34
	268.70	83.60	4.38	16.30	
	270.80	82.50	4.32	15.90	
12.	**231.60	85.60	5.17	22.30	
	260.25	84.50	5.43	20.90	21.20±0.75
	243.40	86.00	5.23	21.50	
	305.50	83.20	0.0124	0.0398	
	382.10	84.50	0.0152	0.0432	0.0412±0.0017
	602.15	82.90	0.0260	0.0407	

of particular elements such as bismuth, arsenic, antimony, and tellurium etc., which are known as the trouble making constituents in ordinary assay process.

From 12 samples taken from strategic points of an assay gold process, judging from the results of this activation analysis, no loss or gain of gold is observed in this case, except the negligible
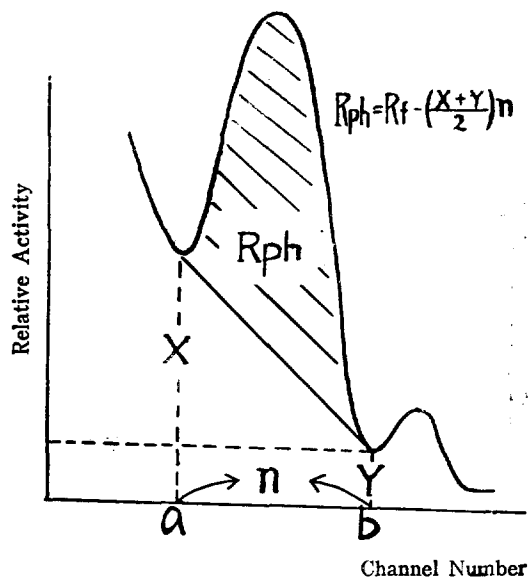

Fig. 4 Photopeak area determination.

amount on the very limrtted area where the cupel surface (sample No. 12) from which gold head was detached. The lead button (sample No. 10) should contain practically all the gold in 15 g of the original ore (sample No. 1) containing 28 ppm which was analysed by pyro-assay method.

The gold contents are considerably different between the results by activation analysis and by pyro-assay method within the deviation of 2.0± 0.3 ppm.

Also the calculated result shows that the gold content in the lead button (sample No. 10)which is supposed to contain all the gold from the original sample is considerably same as that in the original ore analysed by activation analysis, as shown in Table V.

Table V Comparative Au contents between original ore and lead button.

Sample name	Wt. of total sample (g)	ppm of Au in sample	ppm of Au of converting into 15.00g sample
Original Ore	15.00	30.00±0.30	30.00±0.30
Lead button*	27.03	16.35±0.34	29.46±0.54
Lead button**	21.05	21.21±0.75	29.75±1.05

* 27.03g of lead button which contain all gold in 15g of sample.
** 21.05g of lead button which contain all gold in 15g of sample.

The reproducibility of the results of series ana-lyses was good. Radioactivation analysis thus allowed quantitative and precise determination and localization of gold lossed occuring in the given pyro-assay procedure.

Explanation of samples

Sample No. 1...Original gold ore; it's used as a sample in pyroassay procedure.
　// 　2...An unused assay crucible made of clay, which was sampled at random.
　// 　3...Nominally gold free litharge used in fire assay as basic flux and button masking agent.
　// 　4...Nominally gold free quartz powder used in fore assay as acidic flux.

　// 　5...An unused iron nail which would be used as the desulfurizing agent at the fusion stage.
　// 　6...The assay crucible in which gold sample of sulfide are fused with flux.
　// 　7...The iron nail residue which had been charged at the fusion stage.
　// 　8...The slag from a different sample of an oxide ore.
　// 　9...The slag tilted out of the assay crucible from this assay.
　// 　10...The lead button detached from the slag of sample No. 5, in which all the gold in the ore sample supp-osed to be collected.
　// 　11...An unused cupel sampled at random.
　// 　12...The used cupel in which the lead button of the sample No. 7 was cupeled and therefore all the lead was absorbed, remaining the gold and silver on the surface as a bead.

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