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Abstract

In this rapid technique for determining gold at the parts-per-billion concentration level, 1-gram samples are irradiated for 10 hours in a flux of $5x10^{12}$ neutrons per square centimeter per second and are allowed to decay for 10 days. The samples are then carried through classical fire-assay separations in the presence of 20 to 50 milligrams of gold carrier, and the 2.7-day Au^{198} is counted in a gamma-ray spectrometer. Forty samples can be processed in 8 hours, and a detection limit of 0.05 part per billion gold in a 1-gram sample is attainable.

INTRODUCTION

Neutron-activation methods provide exceptional sensitivity for the determination of gold and generally eliminate the problem of reagent blanks. Methods developed by Vincent and Smales (1956), Vincent and Crockett (1960), Shcherbakov and Perezhogin (1964), DeGrazia and Haskin (1964), and Baedeker and Ehmann (1965) and those summarized by Emery and Leddicotte (1961) provide for the irradiation of 0.1 to 0.5 g (gram) of rock sample. After a short cooling period, the gold is radiochemically separated for gamma counting of the 0.413 Mev photopeak for Au^{198} or for beta counting. Generally, the accepted activation-analysis methods involve extensive chemical manipulations to achieve the necessary radiochemical purity.

Washington and Holman (1966) applied activation analysis to the silver bead obtained after the conventional fire-assay procedure. Their detection limit was 10 ppb (parts per billion) gold on a 15-g sample because of the Ag^{110m} activity and the comparatively large reagent blank. Simon and Millard (1968) improved on this method by irradiating the lead button prior to cupellation with silver. Although this method has the advantage of using a 10- to 20-g sample for analysis, it is not applicable to routine analysis because only a few samples can be irradiated simultaneously and the fire-assay flux must be purified before assay to maintain a low blank.

In the method described here, activation analysis was combined with the classical fire assay for the radiochemical separation of gold. The detection limit for gold (defined as 3σ, where σ is the square root of the background) is 0.05 ppb if the sample contains less than 10 ppm (parts per million) silver. Irradiation and decay times were adjusted to provide low radioactivity less than 1 mc (millicurie) for 20 1-g samples). The fire-assay procedure provides for the rapid radiochemical separation of gold with a minimum of operator attention, so that as many as 40 samples can be processed in 8 hours.

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REAGENTS AND APPARATUS

Standard gold-stock solutions: Solution A (1,000 ppm Au)—Dissolve 1.00 g of gold metal in aqua regia and dilute to 1 liter with 2 M HCl. Solution B (10 ppm Au)—dilute 5.00 ml (milliliter) of solution A to 500 ml with 2 M HCl. Solution B is stable for several months. Solution C (0.5 ppm Au)—dilute 5.00 ml of solution B to 100 ml with 2 N HCl. Solution C should be prepared each time monitors are prepared.

Fire-assay flux: Thoroughly mix 1,000 g PbO, 100 g Na_2CO_3, 20 g $Na_2B_4O_7$, and 50 g flour (reducing power ≈10 g Pb per g flour).

Gold carrier: For each sample, place a 20- to 50-mg (milligram) piece of gold metal in a heat-resistant dish, and heat with a torch until the gold fuses into a small bead. Weigh the bead (±0.1-mg accuracy), and place it in a numbered vial.

Counting equipment: A pulse-height-analyzer system, using a four-input mixer-router coupled to four 3- by 3-inch NaI(Tl) well-type crystals, was used to collect four spectra simultaneously.

PROCEDURE

1. Prepare each standard (flux monitor) by placing approximately 0.2 g of gold-free spectrographically pure silica in a small polyethylene vial. Weigh the silica and vial (±0.01-mg accuracy); add two drops of solution C, and weigh again. From the weight of solution and its specific gravity, calculate the amount of gold added (approx 50 ng (nanograms)). Dry overnight and seal the vial with an electric soldering iron.

2. Grind each sample to less than 100 mesh and carefully mix and quarter. Weigh and seal 1 g of each sample in a 2/5-dram polyethylene vial. Irradiate 16 samples plus four monitors for 10 hours in a neutron flux of $5x10^{12}$ neutrons per square centimeter per second. Store samples for 10 days to allow decay of the short-lived isotopes (primarily 15-hour Na^{24} and 2.6-hour Mn^{56}).
3. For each sample, place 80 g of fire-assay flux into a fire-assay crucible and make a depression in the flux to receive the sample.
4. Transfer the irradiated sample to the depression in the flux and mix.
5. Add one bead of gold carrier; cover the mixture with a layer of borax glass and cover the crucible with a scorifying dish.
6. Place the crucible in a fire-assay furnace preheated to 900°-1,000°C and fuse for 1 hour.
7. Pour each melt into a steel mold; cover with a piece of asbestos and allow to cool.
8. Break the slag away from each lead button in a plastic bag to prevent scattering of glass. Each button should weigh 28±8 g.
9. Cupel each lead button at 800°-900°C.
10. Weigh each final gold bead to determine the chemical yield and place in a plastic vial.
11. Collect spectra. After several days, collect another set of spectra to verify the decay of 2.7-day Au^{198}.
12. Standards (monitors) are treated the same as samples.
13. Calculate the area of each 0.413 Mev photopeak for Au^{198} (Covell, 1959) and adjust data to zero decay time.
14. Determine the amount of gold in each sample using the equation:

$$\underline{W}_{\underline{s}}=\underline{W}_{\underline{m}}\frac{\underline{A}_{\underline{s}}\ /\ \underline{Y}_{\underline{s}}}{\underline{A}_{\underline{m}}\ /\ \underline{Y}_{\underline{m}}}$$

where $\underline{W}$ is the weight of gold, $\underline{A}$ is the activity, and $\underline{Y}$ is the carrier yield; the subscripts $\underline{s}$ and $\underline{m}$ refer to sample and monitor, respectively.

RESULTS AND DISCUSSION

Irradiation and decay time

After samples are irradiated for 10 hours and then are permitted to decay for 10 days, the residual radioactivity is generally less than 1 mc. The Au^{198} activity is sufficient to provide 300 to 400 counts per minute per ng of gold in the 0.413 Mev photopeak using Covell's (1959) method for calculating areas.

Fire Assay

Bugbee (1940), Beamish (1966), and Chow and Beamish (1967) have published comprehensive studies of the fire-assay procedures. They found that the fire-assay fusion will recover at least 98 percent of the gold in the samples. From radiotracer experiments Simon and Millard (1968) found that the slag retained from 0.3 to 1.5 percent of the gold and that the silver bead recovered between 97 and 99 percent of the gold. A study was made to determine the fire-assay recovery of gold tracer when gold carrier was added to give a gold bead after cupellation. Better than 98 percent of the gold tracer was recovered in the final gold bead (table 1). As the fusion is virtually quantitative in collecting gold into the lead button, exchange between carrier and active gold during the fusion step is not critical. However, losses may occur during cupellation. The carrier yield will indicate any losses during cupellation, provided that carrier and radioactive gold have exchanged in the molten lead. A brief tracer experiment was made to test for exchange: 1 ml of tracer-gold solution was dried on 1 g SiO_2 in a fusion crucible; flux was added, along with gold carrier in the form of a bead; after fusion, the lead button was cut into two parts and cupelled separately; the final gold beads were weighed and counted. It was found that the specific activity of gold in each portion was identical. Hence, the carrier yield was used to correct for radioactive gold which may have been lost during cupellation. Although yields were usually 97 to 99 percent, an occasional run was as low as 90 percent.

Table 1.—Recovery, in percent, of radioactive gold tracer in the fire assay using gold carrier

Slag	0.1
Crucible	.3
Cupel	1.0
Gold bead	98.6

Interferences

Generally the method is specific for gold, in that the 0.413 Mev photopeak of Au^{198} is used for the calculations. Most silver originally in the sample will be found in the final bead. Ag^{110m} has gamma photopeaks at 0.445, 0.619, 0.665, and 0.884 Mev; the photopeak at 0.445 Mev is very small compared with that at 0.665 Mev. The silver contribution to the gold photopeak is negligible unless the silver in the original sample is greater than 10 ppm. Small amounts of antimony (60-day Sb^{124}) and cerium (33-hour Ce^{144}) may also be found in the gold bead; however, these do not interfere with the 0.413 Mev photopeak of Au^{198}.

DeGrazia and Haskin (1964) reported that the formation of Au^{198} from the fast n,p (neutron, proton) reaction of Hg^{198} is negligible. The formation of Au^{199}, the 3.15-day daughter of 30-minute Pt^{199}, is not an interference, as it has photopeaks at 0.208 and 0.158 Mev which do not interfere with the 0.413 Mev photopeak for Au^{198}.

Precision and accuracy

The neutron flux is monitored by using four standards in each irradiation, placed at different levels in the irradiation bucket. The specific activity of the monitors varies by less than 5 percent from the mean, which can be presumed to be the flux variation.

Table 2.—Eight replicate determinations of gold, in parts per billion, in Hawaiian basalts, G-1, and W-1

	TLW-67-17 Cone Crater, Hawaii	HW-6 Basaltic glass, Hawaii	HK 1955 Kilauea, Hawaii	G-1	W-1
	4.28	1.56	1.03	3.69	4.94
	4.50	1.66	.83	2.65	5.59
	4.08	1.67	.98	2.93	4.62
	4.98	1.63	.93	2.72	3.87
	4.18	1.63	.97	2.43	3.74
	4.38	1.23	.85	2.99	4.00
	4.16	1.38	.81	2.85	4.87
	4.15	1.46	1.00	2.88	5.35
Mean-------------	4.33	1.53	.93	2.89	4.62
Standard deviation------	.27	.16	.08	.37	.69

Table 3.—Comparison of gold values, in parts per billion, obtained by this method with those from other methods

Sample	Rock type	This method	Other methods
W-1	Diabase------	[1]4.62	[2]3.4, [3]3.4, [4]4.9, [4]4.8, [5]8.5, [5]8.4, [6]4.9, [7]4.8, [8]3.6, [9]5.3
G-1	Granite------	[1]2.89	[2]1.9, [3]2.6, [4]2.0, [7]4.6, [5]4.3, [9]11.2
G-2	----do-------	1.1, 1.4, 1.3, 1.1	[2]0.8, [3]0.8, [4]1.1
GSP-1	Granodiorite-	1.5, 1.6, 1.4, 1.1, 1.3	[2]1.1, [3]1.2, [4]1.3
PCC-1	Peridotite---	0.63, 0.73	[2]0.6, [3]0.7, [4]0.7
AGV-1	Andesite-----	0.46, 0.42	[2]0.4, [3]0.5, [4]0.6
DTS-1	Dunite-------	0.98, 0.58, 0.45	[2]0.5, [2]1.0, [3]0.7, [4]0.7
BCR-1	Basalt-------	0.50, 0.51, 0.68	[2]0.4, [2]0.7, [3]0.6, [4]0.9
ZAG-3	Granite from Kershaw, N.C--------	2.5	[3]2.4
ZAG-5	----do-------	4.1, 3.7, 3.6	[3]4.0
ZAG-10	----do-------	2.6, 2.7, 3.0	[3]3.0

[1] See table 2.

[2] Millard (unpub. data, 1968), neutron-activation analysis with separation of gold on ion-exchange paper.

[3] Millard, Rowe, and Brown (unpub. data, 1967), neutron-activation analysis with radiochemical separation of gold.

[4] Baedeker (1967), neutron-activation analysis with radiochemical separation of gold.

[5] Vincent and Crockett (1960), neutron-activation analysis with radiochemical separation of gold.

[6] Hamaguchi and others (1961), neutron-activation analysis, method not described.

[7] Shcherbakov and Perezhogin (1964), neutron-activation analysis with radiochemical separation of gold.

[8] Simon and Millard (1968), neutron-activation analysis after fire-assay preconcentration.

[9] Sarma, Sen, and Chowdhury (1965), emission spectrographic analysis on silver fire-assay bead.

U.S. Geological Survey standard rocks, G-1, and W-1, and three samples of Hawaiian basalts, one of which was a basaltic glass, were each analyzed eight times. The results are shown in table 2. From the replicate analysis, the relative error is estimated to be about ± 10 percent of the amount of gold present.

The determination of gold by this method is in good agreement with results determined by accepted methods of activation analysis. Comparison of results for six standard rocks and several other rock samples is shown in table 3.

Sampling

The determination of gold using 1-g samples for analysis introduces the problem of representative sampling. Wilson (1964) and Washington and Holman (1966) showed that gold may not be homogeneously distributed throughout the sample. Chow and Beamish (1967) discussed the problem of activation analysis versus fire assay with regard to sampling difficulties. The heterogeneity of gold distribution in standard rock W-1 is an example for which reported values vary considerably. It is important that the samples be ground to less than 100 mesh and that the portion taken for analysis be carefully quartered to assure a representative sample. Nevertheless, as can be seen from table 2, more consistent results are obtained for samples which are reasonably homogeneous, such as the basalts. It is possible to overcome some of the sampling problems by irradiating two large samples instead of 16 small ones. The only modification necessary would be the amount of fire-assay flux used to fuse the sample.

Application

The method presented in this paper is being applied to studies of the geochemistry of gold. As it is suitable for rapid routine determination of low concentrations of gold, it extends the capability of laboratories to study background levels of gold in many environments. The method is particularly applicable to studies of hand-picked minerals or samples for which only a limited amount of material is available.

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