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ANALYSIS AND ISOTOPIC DILUTION. DETERMINATION OF COPPER
IN HIGH PURITY GOLD SAMPLES**

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SUMMARY

Activation analysis of impurities in high neutron cross section matrixes is complicated by problems such as neutron flux depression and very high activity levels induced in the matrix, making difficult the handling and processing of the sample. Isotopic dilution method applied to such a sample would avoid the handling of high activities and neutron shadowing problems. However, isotopic dilution makes necessary the weighing of very small masses to determine specific activity of the substance to be analyzed, after chemical separation. Weighing such small masses is not often easy; activation analysis, instead of gravimetry, may, in some cases, improve results.

INTRODUCTION

Activation analysis problems for some elements in certain special types of matrixes have already been discussed at length by Lima and Silva in another paper in this Meeting¹. Matrixes made up of high thermal neutron absorption cross section, for instance, are rather inconvenient for direct irradiation due to neutron shadowing problems and handling of very active samples after irradiation. Gold is one of those matrixes and in fact the number of activation analysis papers for elements present in gold is very scarce. The bibliography on activation analysis published by the National Bureau of Standard² issued in September of 1968, lists only 17 papers for activation analysis in which silver, mercury and gold were collectively taken as matrixes.

Cattaneo et al³. were able to determine impurities such as cobalt, osmium, silver and iridium in zone-refined gold by letting the irradiated sample to cool for very long periods (about 100 days), and counting the long-lived isotopes of the elements to be analysed, after the activity due to gold isotopes had decayed to negligible value. Main impurities in the samples, before zone refinement, were copper, silver and silicon and of these only the long-lived isotope of silver (¹¹⁰Ag 250 days half life) could be measured by this method.

Yakovlev et al⁴. determined cobalt, copper, tellurium, arsenic and antimony by irradiating the gold samples for 48 hours in a neutron flux of 5×10^{12} n/sec.cm² and chemically processing the samples after irradiation. 0.2 g of gold were irradiated and it is not stated if the samples were processed by remote control or not. To reduce self-shielding effect, which amounted to 8% for a 0.1 g sample as compared to a 1μg sample, the gold sample was exposed to irradiation as metallic powder (0.1 g) spread over an area of 2 cm².

Owing to the same crystallization system as gold (isometric; hexoctahedral $4/m \bar{3} 2/m$; space group Fm $3m^2$) copper (and also silver) is one of the commonest impurities in gold and this makes the determination of trace amounts of copper in gold an important problem. Direct activation analysis for copper in gold is a typical case in which high activity induced in the matrix would require remote handling for processing the sample after irradiation. Also, shadowing problems would be present specially if taking into account that copper may not always be homogeneously distributed in the irradiated samples; use of powdered samples spread over large areas to avoid neutron shadowing, is not advisable due to flux variation along the longest dimension of large samples.

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2.

The inconveniences mentioned for activation analysis of copper, and other elements, in gold matrixes may be avoided if the method of isotopic dilution is applied to such samples. Such a method will still allow a high sensitivity to be attained without having to face the difficulty of working with very active samples requiring, eventually, remote control. Also, errors introduced by neutron shadowing will not be present, obviously.

APPLICATION OF THE METHOD

The method is applied in the following general way: to a known mass of gold sample, a mg of copper, labeled with ^{64}Cu , is added. If A is the total activity of the added copper, its specific activity A' is

$$A' = A/a \quad (1)$$

The gold sample is dissolved with aqua-regia and gold is retained in an anionic exchanger as the chloride complex. Copper will pass through the exchanger without being absorbed and will be collected in the effluent. To the effluent, lead ions are added and lead sulfide is precipitated, entraining copper with it. The activity B of ^{64}Cu in the sulfide is determined and from this the specific activity B' can be calculated, i.e.

$$B' = B/b \quad (2)$$

in which b is the recovered mass of copper in the lead sulfide precipitate. The chemical yield r is $r = B/A$.

In order to determine b , the lead sulfide precipitate is irradiated together with a standard of copper with a mass M_s . If B_1 is the activity of copper in this sample, after irradiation; B_t the remaining activity of the recovered tracer, corrected for a decay time up to the end of irradiation of b ; A_s the activity induced in the copper standard, one has

$$b/M_s = (B_1 - B_t) / A_s \quad (3)$$

In this way b can be calculated and one has all the elements to apply the classical formula for isotopic dilution analysis, i.e.,

$$X = a \left(\frac{A'}{B'} - 1 \right) = a \left(\frac{A}{B} \cdot \frac{b}{a} - 1 \right) \quad (4)$$

in which X is the amount of copper in the gold samples (x) plus the copper introduced with the reagents (x_0). B/A is the chemical yield (r) of copper recovered in the lead sulfide precipitate. In this way (4) gives

$$x + x_0 = \frac{b}{r} - a \quad (5)$$

Substitution of b for the value given in (3) and application of the same reasoning for calculation of x_0 (amount of copper in the blanks or reagents) gives (see ref. 1 for details):

$$x = \left[(B_1 - B_t) / r - (B_{01} - B_{0t}) / r_0 \right] M_s / A_s \quad (6)$$

The same set of operations is carried over, in parallel, using only the reagents in order to get the blank values for B_{01} , B_{0t} and r_0 .

If the half-life of tracer is short, the activity of the tracer is negligible by the time of irradiation of the mass b . In this case B_t and B_{0t} will be equal to zero and formula (6) simplifies to

$$x = (B_1 / r - B_{01} / r_0) M_s / A_s \quad (7)$$

The same formula (7) is also applied when an isotope of the element being analysed, different from the one used as tracer, is used for the determination of \underline{b} . For instance, in the case of analysis for silver, the isotope ^{110m}Ag ($t_{1/2} = 250$ days) may be used as tracer and ^{110}Ag ($t_{1/2} = 24$ seconds) for the determination of \underline{b} by activation analysis.

EXPERIMENTAL

Reagents

Ammonium hydroxide, 25% in NH_3

Sulfuric acid, 95%

Hydrochloric acid, 36.5%

Nitric acid, 65%

Lead acetate solution, 5 mg of lead per ml of solution.

Anionic ion exchanger, Amberlite IR-400; a 20 cm x 0.8 cm column is used and the resin is prepared by passing through it 50 ml of nitric acid 1N, 50 ml of water, 50 ml of ammonium hydroxide 1N, 50 ml of water and 50 ml of hydrochloric acid 1N.

Ferric chloride solution, 10 mg of iron per ml of solution.

Zinc chloride solution, 10 mg of zinc per ml of solution.

Copper nitrate solution, 10 mg of copper per ml of solution.

Hydrochloric acid solution 1:20.

Ammonium sulfide 24%, solution 1:5.

^{64}Cu tracer solution: 1 mg of CuO is irradiated in a thermal neutron flux of about 10^{13} n/sec.cm² for 8 hours. The irradiated CuO is dissolved with a few drops of diluted nitric and hydrochloric acids and diluted with water to obtain a concentration of about 0.03 μg of labelled copper, per milliliter of solution.

Method

Gold samples of about 100 mg are washed with warm diluted nitric acid, water, dried, weighed and placed into 50 ml beakers. 1 ml of lead acetate solution, 2 ml of copper tracer solution, 1 ml of nitric acid and 3 ml of hydrochloric acid are added and gold dissolution is carried out under gentle heating. Next, 20 ml of 1:20 hydrochloric acid is added and the resulting solution is passed through the anion exchanger resin at a rate of about 50 ml per hour. The resin is then washed twice with 10 ml of water each time. The effluent is received in 100 ml beakers and heated. Concentrated ammonium hydroxide is added up to alkaline reaction and then 1 ml of ammonium sulfide solution to precipitate lead sulfide which will carry copper. The precipitate is aged for about 30 minutes and filtered under vacuum using a chimney funnel glass apparatus. The precipitate is next washed three times with 2 ml of water each time. The filter paper with precipitate is dried under infra-red heat and placed in polyethylene envelopes which are sealed and counted in a 400 channel gamma spectrometer (TMC-404-6) coupled to a 3" x 3" well type NaI(Tl) scintillator (Harshaw) giving the activity B_1 . A known amount of tracer is also counted at this time in order to get A_1 and in this way the chemical yield is calculated, $r = B_1/A_1$.

4.

The same set of operations, as described for the gold samples, is applied in parallel as blank operation using only reagents and no gold samples.

The lead sulfide precipitate and copper standard are then irradiated for one hour in a thermal neutron flux of about 10^{12} n/sec.cm² (100 mg gold samples with 2 ppm or more of copper). After irradiation, 20 mg of carrier copper (nitrate) are added to sample and standard which are then treated with 2 ml of concentrated sulfuric acid and enough nitric acid to destroy organic matter from the filter papers. 20 ml of water and 2 ml of hydrochloric acid are added and the resulting solution is passed through a anionic resin, prepared as before, in order to retain any traces of gold. Next 0.5 ml of ferric chloride solution is added and ferric is precipitated as the hydroxide. ³²P formed as consequence of irradiation of sulfur is eliminated in this operation as well as other impurities which are carried down by the iron hydroxide precipitate.

To the filtrate 2 ml of zinc chloride are added and the sulfides are precipitated with ammonium sulfide. The precipitate is filtered and washed with hot 1 : 20 hydrochloric acid. In this way zinc and other sulfides which are soluble in hydrochloric acid are eliminated.

The precipitates and filter paper are transferred to a counting vial and the activities are determined. The peak at 1.02 MeV is used to avoid any interference from traces of ¹⁹⁸Au (0.41 MeV) when counting the annihilation peak of ⁶⁴Cu at 0.51 MeV.

RESULTS

In order to check the method 0.823 g of gold sample 99.99% purity were dissolved in 15 ml of aqua-regia and the volume was made to 50 ml by adding deionized water. From this solution 5 samples of 6 ml each were taken. To each of the 5 samples, increasing amounts of copper were added in such a way as to give samples with 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 ppm of copper. The samples and four blanks were analysed in accordance with the described procedure. Results are presented in Table I.

TABLE I
Results of "Copper Found" as
Compared to "Copper Added"

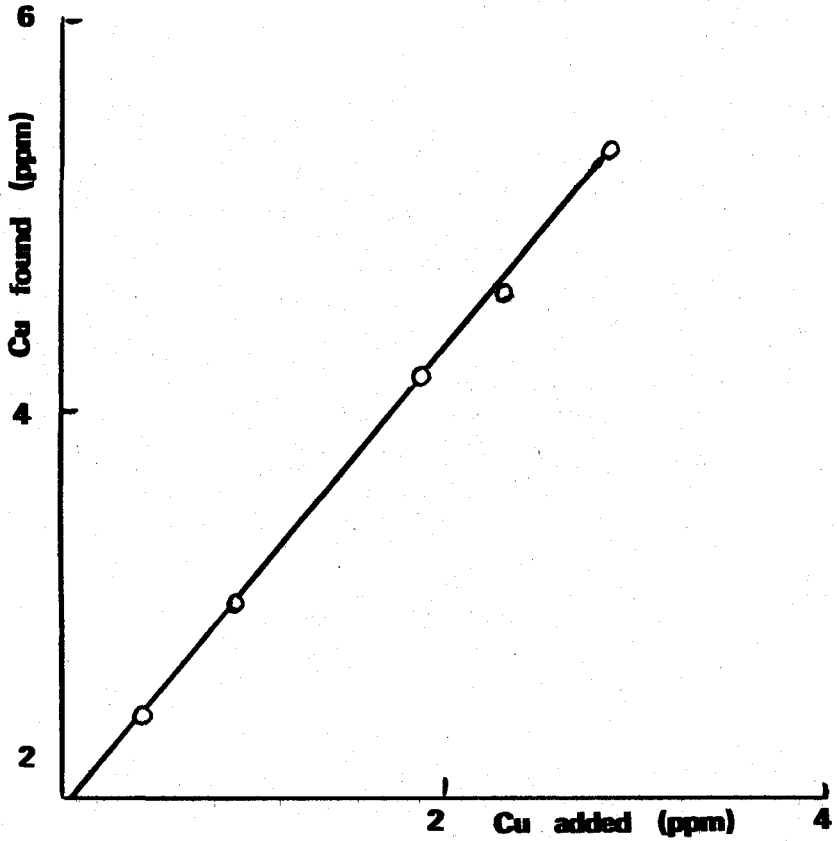
Sample	Cu (ppm)	
	added	found
	x	y
1	0.50	2.51
2	1.00	3.12
3	2.00	4.26
4	2.50	4.73
5	3.00	5.55

The best straight line (figure 1) was adjusted through these points, by the method of least squares, giving

$$y = 1.914 + 1.178 x$$

and from whose intercept the original amount of copper present in the gold sample can be calculated, i.e., 1.91 ppm of copper.

Fig. 1
Check of Linearity of the Method



6.

Accuracy was also checked by preparing five solutions with known amounts of copper and analysing them in triplicate or quadruplicate. Non active gold was added before processing of the solutions. Results are presented in Table II.

TABLE II(*)

Added and Recovered Copper

		Added (ppm)				
		0	0.050	0.100	0.200	0.400
Found (ppm)						
		0.011	0.055	0.097	0.206	0.402
		0.009	0.038	0.118	0.197	0.373
		-0.001	0.072	0.086	0.180	0.388
		-	0.050	-	0.207	-
	Mean \bar{x}	0.006	0.054	0.100	0.198	0.388
	St.dev.s _x (**)	0.007	0.014	0.016	0.013	0.014
St.dev.s _m (***)	0.004	0.007	0.009	0.006	0.008	

(**) Standard deviation of a single value

(***) Standard deviation of mean

(*) - A t test⁷ applied to the results of Table II shows that the differences between "added values" and "found values" (mean) are not significant at the 0.05 probability level.

Precision of the method can be obtained from the results of various replicate analysis of two gold samples, one 99% and other 99.99% purity. Results are presented in Table III and IV.

TABLE III

Results of Analysis for Copper in
Gold Samples 99% Purity

Samples (mg)	Cu (ppm)
45.74	8.7
91.48	12.2
91.48	11.7
182.97	9.2
182.97	8.6

TABLE IV

Results of Analysis for Copper in
Gold Samples 99.99% Purity

Samples (mg)	Cu (ppm)
144.30	2.6
121.40	2.5
81.64	2.5
77.40	1.6
11.21	2.4
37.47	3.6
18.03	3.1

Mean \bar{x} 10.1
St.dev. s_x 1.5
St.dev. s_m 0.7

Mean \bar{x} 2.6
St.dev. s_x 0.6
St.dev. s_m 0.2

In each case blank analysis were also performed applying the method, as described, but using only the reagents and no gold samples. A set of typical results is shown in Table V for two trade marks of reagents.

8.

TABLE V
Blank Analysis for Two
Trade Mark Reagents

Sample	Cu (μ g)	
	Trade Mark I	Trade Mark II
1	0.049	1.12
2	0.074	1.13
3	0.066	1.16
4	0.054	1.28
5	0.044	1.06
6		1.33
Mean \bar{x}	0.057	1.18
St.dev. s_x	0.012	0.10
St.dev. s_m	0.005	0.02

DISCUSSION

Results in Table and Figure 1, in which five gold samples having increasing amounts of copper were analysed, show the linearity of the method in the range from 0.50 to 3.00 ppm. By making a regression of these data⁷ it was possible to calculate the amount of copper originally present in the gold. This range of linearity, in fact, can be extended to larger values, since for gold samples with known contents of copper, of the order of tenths of a percent, there was agreement between "existing copper" and "found copper". In this case a gold sample containing 0.16% of copper was analysed in duplicate giving 0.166% and 0.160%.

Values in Table II show the accuracy of the method with good agreement between actual amount of copper in the samples and the mean indicated by the analysis. A t test⁷ applied to the set of values listed in Table II shows no significant difference between "added values" and "found values".

The gold samples of listed purity as 99% and 99.99% were analysed in various replicates for copper and results were presented in Tables III and IV. Precision or reproducibility of the method can be evaluated by means of the standard deviations for these results.

It was observed a lack of homogeneity of copper distribution when samples were taken from different parts of very long pieces of laminated gold of the same listed purity. Since copper and gold, as mentioned, have the same crystallization system, it should be expected that copper should be uniformly distributed in the gold samples. It is possible that during the lamination process the impurity is introduced in different amounts along the laminated pieces and that this impurity is not removed by the surface cleaning procedure as indicated in the Method.

In each set of analyses blank analyses for the reagents were also carried out. Detailed results for each specific reagent are presented in another paper in this Meeting⁸.

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Résumé

L'analyse par activation neutronique des éléments traces présents dans des matrices à haute section efficace devient difficile à cause de la décroissance du flux neutronique à l'intérieur de l'échantillon et aussi à cause des activités élevées induites dans la matrice.

Pour éviter ces problèmes, en ces matrices on utilise la méthode de dilution isotopique qui exige la détermination de petites masses de matériel recuperé qui peut - être fait par activation, puisque l'élément à analyser a été déjà séparé de la matrice.

Resumo

A análise por ativação neutrônica de elementos traços presentes em matrizes de alta seção de choque torna-se complicada em virtude de problemas de sombreamento de neutrons exigindo, além disso, o manuseio das altas atividades que são induzidas na amostra. O método de diluição isotópica, aplicado a tais matrizes, contorna os problemas mencionados mas exige a determinação de pequenas massas de material recuperado, o que pode ser feito por ativação visto que o elemento a ser analisado já foi separado da matriz.