



ACTIVATION ANALYSIS OF GOLD IN ORES SAMPLES

*JOAQUIM G. DA SILVA FILHO, ALCÍDIO ABRÃO
e FAUSTO W. LIMA*

PUBLICAÇÃO I.E.A. N.º 98

Agosto — 1965

INSTITUTO DE ENERGIA ATÔMICA
Caixa Postal 11049 (Pinheiros)
CIDADE UNIVERSITÁRIA "ARMANDO DE SALLES OLIVEIRA"
SÃO PAULO — BRASIL

ACTIVATION ANALYSIS OF GOLD IN ORES SAMPLES

by

Joaquim G. da Silva Fº, Alcídio Abrão and Fausto W. Lima

Radiochemistry Division, Instituto de Energia Atômica
São Paulo, Brazil

Publicação IEA nº 98

Agosto - 1965

Comissão Nacional de Energia Nuclear

Presidente: Prof. Luiz Cintra do Prado

Universidade de São Paulo

Reitor: Prof. Luiz Antonio da Gama e Silva

Instituto de Energia Atômica

Diretor: Prof. Rômulo Ribeiro Pieroni

Conselho Técnico-Científico do IEA

Prof. Helio Lourenço de Oliveira	}	pela USP
Prof. Walter Borzani		
Prof. Rui Ribeiro Franco	}	pela CNEN
Prof. Theodoro H.I. de Arruda Souto		

Divisões Didático-Científicas:

Div. de Física Nuclear: Prof. Marcello D.S. Santos

Div. de Engenharia de Reatores: Prof. Tharcisio D.S. Santos

Div. de Ensino e Formação: Prof. Luiz Cintra do Prado
(licenciado)

Div. de Radioquímica: Prof. Fausto Walter de Lima

Div. de Radiobiologia: Prof. Rômulo Ribeiro Pieroni

Div. de Metalurgia Nuclear: Prof. Tharcisio D.S. Santos

Div. de Engenharia Química: Prof. Kazimiers J. Brill

ACTIVATION ANALYSIS OF GOLD IN ORES SAMPLES

by

Joaquim G. da Silva F^o, Alcídio Abrão and Fausto W. LimaRESUMO

Neste trabalho é relatada a determinação de ouro em minérios por ativação com neutrons. Após várias tentativas de determinação sem processamento químico da amostra irradiada, concluiu-se que o minério apresentava falta de homogeneidade, embora suas partículas fôsem da ordem de alguns micros. A falta de homogeneidade do minério foi confirmada por autoradiografias. Para contornar esta dificuldade as amostras foram processadas quimicamente antes da irradiação. O minério foi atacado por água régia e o ouro foi fixado numa resina aniônica a qual foi irradiada num fluxo de 5×10^{12} neutrons/cm².s. O conteúdo de ouro foi calculado por comparação com padrões de ouro fixado em resina e irradiados ao mesmo tempo e na mesma geometria. As contagens do material irradiado foram feitas em espectrômetro monocanal de raios gama.

Como o ouro apresenta ótimas características nucleares e alta seletividade pelas resinas aniônicas quando na forma de seu complexo cloroáurico ($AuCl_4^-$), o processamento químico anterior à irradiação possibilita o uso de alíquotas maiores de minério (5 a 10 g).

O conteúdo de ouro dos minérios analisados variou de 0,05 a 70 partes por milhão. O rendimento químico do processo é bom, permitindo uma recuperação de ouro acima de 97%.

RÉSUMÉ

Ce travail décrit la détermination quantitative d'or dans des minerais à l'aide de l'analyse par activation. Après différentes tentatives de détermination de l'or sans traitement chimique du matériel irradié, on a conclu que le minerai n'était pas assez homogène, quoique ses composants aient été de l'ordre de quelques microns. Le défaut d'homogénéité des minerais fut confirmé par autoradiographie.

Pour tourner cette difficulté, les échantillons furent traités chimiquement avant l'irradiation. Le minerai fut attaqué par l'eau régale l'or fixé sur une colonne échangeuse d'anions, et celle-ci irradiée dans un flux de 5×10^{12} n/cm².s.

On calcula la quantité d'or par comparaison avec des étalons fixés sur la résine et irradiés en même temps et dans les mêmes conditions des échantillons. Les comptages de l'activité du matériel irradié furent effectués au spectromètre à rayons gamma monocanal.

Comme l'or présente des caractéristiques nucléaires optima et une grande sélectivité vis-à-vis des résines anioniques (AuCl₄-), le traitement chimique avant l'irradiation, permet d'utiliser de plus grandes quantités de minerai (5 à 10g). Par ce procédé on contrebalance le défaut d'homogénéité des échantillons. Le contenu en or des minerais analysés varie de 0,05 à 70 ppm. Le rendement chimique du traitement est très bon, et permet une récupération d'or supérieure à 97%.

SUMMARY

This paper describes the determination of gold in ores by neutron activation. After several attempts for determination of gold by non-destructive technique it was concluded that the ores

analysed were not homogeneous, although the powder was very fine (less than 200 mesh). This lack of homogeneity was verified by radioautography.

In order to overcome this difficulty the samples were chemically processed before irradiation. The ore was digested in aqua regia, the gold retained on an anionic ion exchanger and the resin irradiated in a neutron flux of 5×10^{12} n/cm².sec. The gold content was calculated using gold standards fixed on anionic resins, which were irradiated simultaneously with the samples and in the same geometry and counted with a single channel pulse height analyser.

Since gold has good nuclear characteristics and the anionic AuCl_4^- complex is high and selectively absorbed by anionic resin, 5-10 g. aliquots of ore could be used when neutron irradiation is carried out after the chemical separation. The advantage of using large aliquots is that inhomogeneity of the sample will be of no importance.

The gold content of the ores was in the range 0.05 - 70.0 parts per million. The chemical yield, in terms of gold recovery, was over 97%.

INTRODUCTION

The purpose of this work is to establish a method for the determination of gold in low grade ores by neutron activation technique and to organize an analysis service for this determination in a routine basis.

Existing methods for determination of gold are relatively few compared to the ones for copper, iron, and other metals.

Cupellation is the most widely applied method, but

it requires appreciable mass of gold. In some gravimetric methods gold is reduced to the metal or precipitated with appropriate precipitants, in most cases organic reagents, but milligrams amounts of gold are required.

The colorimetric procedures are among the most sensible methods for the determination of gold. They are subject to various interferences, as for instance that due to nitrogen oxides⁽²⁾ often present, since gold is solubilized by aqua regia.

One of the more recent procedure is the extraction of gold with bromoaurate-triethylphosphine oxide (bromoaurate-TOPO) in chloroform and measurement at 395 mμ; however, this procedure is useful only in the range of 20-100 ug of gold⁽³⁾.

Titrimetric methods are not sensible.

Considering the lack of acceptable analytical methods and low sensitivity of classical procedures, activation analysis for gold (if a neutron source or nuclear reactor is available) is extremely efficient and gives a good contribution in a field of great interest to industry. The sensitivity of this method is so high and specific that surpasses any of the cited ones. As low as 7×10^{-5} ug of gold can be determined by neutron activation analysis⁽⁴⁾ and besides that advantage, the present method is free from the interference of nitric acid and does not require the use of isotopic carrier for gold, what is mandatory in other activation analysis procedures for gold⁽⁵⁾.

Gold is an element having favourable nuclear characteristics to be determined by thermal neutron activation analysis. Its isotopic abundance (Au-197) is 100% and the thermal neutron cross section is high (98 barns). The induced Au-198 radioisotope is a gamma emitter having a well known photopeak at 0.412 Mev that allows the identification and determination of gold very easily.

Applying short irradiation periods (5 to 10 minutes) and observing cooling times of 24 to 48 hours it is possible, in some cases the non-destructive determination of gold in ores.

However, as it will be reported in this paper, more than 50% of the analysed samples, without chemical processing, gave results which were not in agreement when duplicate samples were analysed. This was due to the ores lack of homogeneity, although the samples were very fine (powder of less than 200 mesh).

In a previous paper Abrão⁽¹⁾ described a procedure for the determination of gold in ores applying an ion exchange separation of gold after irradiation.

Since the ores now analysed presented a very pronounced lack of homogeneity, the necessity of using large representative aliquots (5 to 10 g) was imperative. But, on the other hand, the neutron irradiation of large amount of ore presents difficulties, and besides, the induced activity is very high. For this reason chemical separation of gold before irradiation was necessary. Therefore, it is possible to analyse and determine the gold content of large representative aliquots since gold is separated previously.

In general, in activation analysis, samples are processed after irradiation, to avoid contamination by the reagents. However, in the case of ores the contamination of samples by gold provenient from the reagents used in the treatment is not likely to happen since gold is an element not present in P.A. reagents. On the other hand it is relatively simple to check the purity of reagents for gold contamination by running a reagent blank.

METHOD

The ore (5 to 10 g) is diggested with hot aqua regia. The filtrate is made up to the volume and aliquots containing

from 1.0 to 10.0 ug of Au are passed through a small column (1 ml) of anionic resin which retains the gold as its anionic chloroauric complex (AuCl_4^-). The resin is washed with 0.5M HCl and water, successively, then dried and enclosed into a polyethylene bag which is irradiated for 5 to 10 minutes at a 5×10^{12} n/cm².sec. neutron flux. After observing a 24 hours cooling time the resin is transferred to a plastic vial and counted at the 0.412 Mev Au-198 photopeak. The gold is determined by comparison of the areas under the photopeak of sample and standard processed exactly as the analysis.

REAGENTS

1. Hydrochloric acid (conc.)
2. 0.5 M HCl
3. Nitric acid (conc.)
4. Ion exchange resin, anionic, strong type, Amberlite IR-410, 50 mesh, Cl-form. A stock is prepared maintaining the resin under 4M HCl overnight. The resin is transferred to a glass column and washed with demineralized water until complete elimination of interstitial acid in the effluents. The resin is then washed with 5 volumes of 0.5M HCl and stored under 0.5M HCl.
5. Ion exchange column. An aliquot of 1 ml resin is transferred, with 0.5M HCl, to a 0.5 - 0.7 cm.i.d. glass column, provided with a sintered glass plate.
6. Ore samples
The ore samples came from Mina de Canavieiras, Jacobina, Bahia. It is formed mainly by SiO_2 , Fe, S(pyrite), Na and U, Au, Mn as minor constituents. The samples were sent by the "Comissão Nacional de

Energia Nuclear" as a fine powder of less than 200 mesh.

COUNTING EQUIPMENT

A single channel gamma ray analyser, model 1820A, Nuclear Chicago Corp., with a well type NaI (Tl) scintillation crystal was used.

EXPERIMENTAL PART

A. Ore Chemical Treatment

A 5-10 g aliquots of ore samples (duplicate samples) are transferred to 100 ml beaker and digested with 20 ml aqua regia, keeping the beaker covered with a watch glass on a hot plate for 2 hours. The mixture is diluted to approximately 50 ml with water and warmed for half an hour. After decantation the solution is transferred into a 250 ml volumetric flask using a 11 cm/Whatman n° 40 filter paper. The insoluble matter is washed in the original beaker with 0.5M HCl and the washing solution is combined into the volumetric flask. The residue on the filter is transferred to the original beaker and a second acid attack is made with 15 ml of aqua regia, in the same way as the first digestion. The solution is filtered into the volumetric flask using the same filter paper and the insoluble matter is now completely transferred to the filter and washed with 0.5M HCl and then with water. The solution is diluted to the mark with water.

B. Separation of Gold

A 50 ml aliquot of this solution is percolated through the anionic resin from a 125 ml Squibb funnel, with a flow rate of not more than 1 ml/min. After loading, the resin

is washed with 15 ml of 0.5M HCl and next with water until no more HCl is present in the effluents. The resin is dried in the column first by application of vacuum and then in an air oven at 100-110° C.

C. Gold Standard

A gold stock solution is prepared by dissolution of high pure metal in aqua regia. Dilutions are made in order to prepare standards having gold amounts of approximately same magnitude as the samples. The gold standard is retained in the anionic resin in the same way as for the analysis.

D. Neutron Irradiation

The resin is transferred to a small polyethylene bag which is welded by hot air. The sample (duplicate) and gold standard are irradiated for 5-10 minutes in a pneumatic irradiation facility.

E. Counting the Induced Au-198

After observing a 24 hours cooling time the resin is transferred to a plastic vial and the gamma-ray spectrum is recorded. Gold in the sample is determined by comparison of its area under the 0.412 Mev peak with the gold standard area, or by direct comparison of the heights of samples and standard gold peaks. The gold content of sample is calculated by:

$$\frac{A_a}{A_p} = \frac{M_a}{M_p}$$

where: Aa = sample activity
Ap = gold standard activity
Ma = gold mass in the sample
Mp = gold mass in the standard

DISCUSSION

a) Non-destructive gold determination

Having in mind the highly favourable nuclear characteristics for gold a tentative of determining gold in ore samples without chemical treatment was tried. A non-destructive determination would be very useful, rapidity and economy being some of the advantages.

Non-destructive gold determination were made by irradiating about 200 mg of ore enclosed in small polyethylene bag together with a gold standard prepared by evaporation of an aliquot of Au-III chloride in filter paper. Irradiation time varied between 5 and 15 minutes. The same neutron irradiation facility mentioned above was used.

After observing cooling periods of 24 to 48 hours the irradiated samples were transferred to a plastic vial and the gamma-ray spectra recorded. Gold-198 was responsible for almost the whole measured activity; a small contribution due to Mn-56 (2.56 hours and 0.850 Mev) and Na-24 (15 hours and 1.34 Mev) was found which did not interfere in the gold determination via 0.412 Mev Au-198 peak.

Only 14 (33%) samples in 42 showed analytical coherent results between duplicate in the same irradiation. New aliquots of 28 samples that showed incoherent duplicate results were irradiated again. The new results for the duplicate once again were not in agreement; also the results for the same sample obtained in different irradiations occasion were not in agreement.

b) Shadowing and Flux Variation

This lack of reproductibility for the non-destructive gold determination forced us to investigate the existence of irradiation irregularities such as samples shadowing

and neutron flux variation with reference to the sample position. A series of experiments runned irradiating ore samples and gold standard allowed to conclude for the non-existence of flux variation with reference to the samples position and also that there was no sample shadowing capable of explaining the discrepancy for the results of duplicate aliquots.

b-1) Five gold standards in filter paper strips were arranged side by side, as playing cards, inside the same rabbit, the standards occupying a position parallel to the rabbit axis. A second collection of 5 gold standards analogous to the first one, but having the strips perpendicular to the rabbit axis, was irradiated. The activities of all irradiated standards measured by the peaks heights or by the areas under the peaks were in good agreement, that is, with an acceptable error range of 1 to 2%.

b-2) Two gold standards P_1 , P_2 were irradiated simultaneously with two 200 mg ore aliquots A_1 , A_2 , observing the order $P_1 A_1 P_2 A_2$ for the ensemble. The measured activities for the standards were found to be practically the same while the activities for the aliquots were very different.

b-3) A series of analysis were runned utilizing two ore samples whose results obtained by non-destructive neutron irradiation analysis showed deviation of more than 1000 %. For sample A, 13 analysis and for sample B, 9 analysis were carried out and the results, showing very high discrepancies, are presented in Table I. Sample A, for instance, exhibited low (0.04) and high (19.95) extreme results.

The series of experiences b-1, b-2 and b-3 permitted to conclude for the non-existence of sample shadowing and

also that the samples position inside the irradiation rabbit do not interfere with results.

TABLE I

Non-destructive gold analysis

Micrograms of gold per gram of ore		
Analysis n°	Sample A	Sample B
1	0.04	3,30
2	0.04	13,27
3	0.04	5,09
4	0,4	15,26
5	19,95	3,11
6	1,90	3,11
7	2,13	3,57
8	1,21	8,02
9	6,51	3,12
10	1,14	-
11	2,25	-
12	1,34	-
13	0,59	-

c) Ore inhomogeneity

Since the self shadowing of samples and position inside the irradiation rabbit did not explain the discrepancy of gold results, lack of homogeneity of samples was thought to be the cause for this discrepancy.

Apparently, lack of homogeneity could not exist since the samples were a very fine powder; besides that, several analysis of the same sample were carried out after grinding the ore again in an agate mortar and irradiating 100 to 200 mg aliquots. In order to use more representative aliquots, 500 to 600 mg samples of the same pulverized batch were irradiated, and the results, although a little better, were not satisfactory, showing the existence of such inhomogeneity.

On irradiated aliquot of sample A (Table I) was examined under the microscope and large grains or agglomerates were not observed. This same aliquot was spread down on a microscope slide and divided in four portions. The gamma activity of each portion was measured and it was found that one portion contained more than 90% of the total activity of the whole sample. This experiment shows, for certain, that the discrepancy in the results of the same sample is due to the inhomogeneity in the pulverized ore. The inhomogeneity is such that it is almost impossible to be eliminated by conventional methods of grinding and sampling.

d) Radioautography

The inhomogeneity could be shown, easily, by radioautographic technique. Radioautography of more than forty different irradiated samples was carried out. For this 1 to 2 g ore samples were irradiated in a 5×10^{12} n/cm².sec. neutron flux during 30 minutes. After observing a cooling time varying between 100 and 250 hours (for ores with higher gold content) a radioautography was made with an exposure time of 1 to 16 hours (X-ray plate type 508XP-6, DuPont) depending on the ore gold content.

Two simple techniques were used in the irradiated ore sample preparation for the radioautography exposure:

1. In an agate mortar a suspension of ore with nujol oil or arabic gum was prepared and spread between two glass or plexiglass plates. This technique was abandoned because the difficulty in obtaining a homogeneous distribution of the suspension.
2. A 15 cm x 5 cm glass or plexiglass plate was covered with a double face adhesive ribbon. A fine layer of irradiated ore was spread over the adhesive ribbon and covered with a fine polyethylene sheet (Fig. 1). The X-ray plate was placed over the polyethylene. After developing the plate it was possible to identify the more impressed points and regions without impression or having only a little more dark background. Therefore, it was possible to select the ore portions corresponding to the more blackened parts or parts with little impression. These selected ore portions in the plate were analysed by gamma ray spectrometry. Gamma counting allowed to conclude that the ore portion corresponding to the dark spots in the radioautography contained radiogold, while the ones corresponding to the region without or with very little impression, the gold content (activity) was none or very low. In a general way the radioautography displayed a irregular distribution of dark spots, as a confirmation of the existence of inhomogeneity in the ore grains as well in the particle distribution, although the

ore exhibited an apparent perfect homogeneity. Figures 2 and 3 correspond to radioautography of samples with irregular particles distribution. Figure 4 is the radioautography of one sample considered as homogeneous whose non-destructive gold analysis were in good agreement.

e) Radiochemical Treatment for Gold Separation

Considering the above mentioned facts, attention was given in order to analyse all samples applying a chemical treatment for gold separation before irradiation. The separation of gold before irradiation allowed to use more representative ore aliquots (5 to 10 g).

This chemical treatment was necessary considering that the irradiation of relatively large samples for short irradiation period (5 to 10 minutes) should be done in rabbits, (size 4 cm long, 2 cm diameter) the accomodation of 2 or more samples into the irradiation rabbit being difficult. On the other hand the induced activity in gold and other ore constituents would be considerable. Also, only 2 to 3 grams of irradiated ore could be transferred to the counting vial and this represents a new partition of the irradiated ore sample and consequently new difficulties due to inhomogeneity.

In order to overcome this difficulty the gold separation before irradiation was carried out, as described above. As was mentioned before, this chemical separation is perfectly possible keeping in mind the favourable nuclear characteristics of gold for neutron activation analysis and its selective retention in an anionic ion exchanger when absorbed as the chloroauric complex (AuCl_4^-). The risk of gold contamination by the reagents is small as was verified by processing a reagent blank. On the other hand

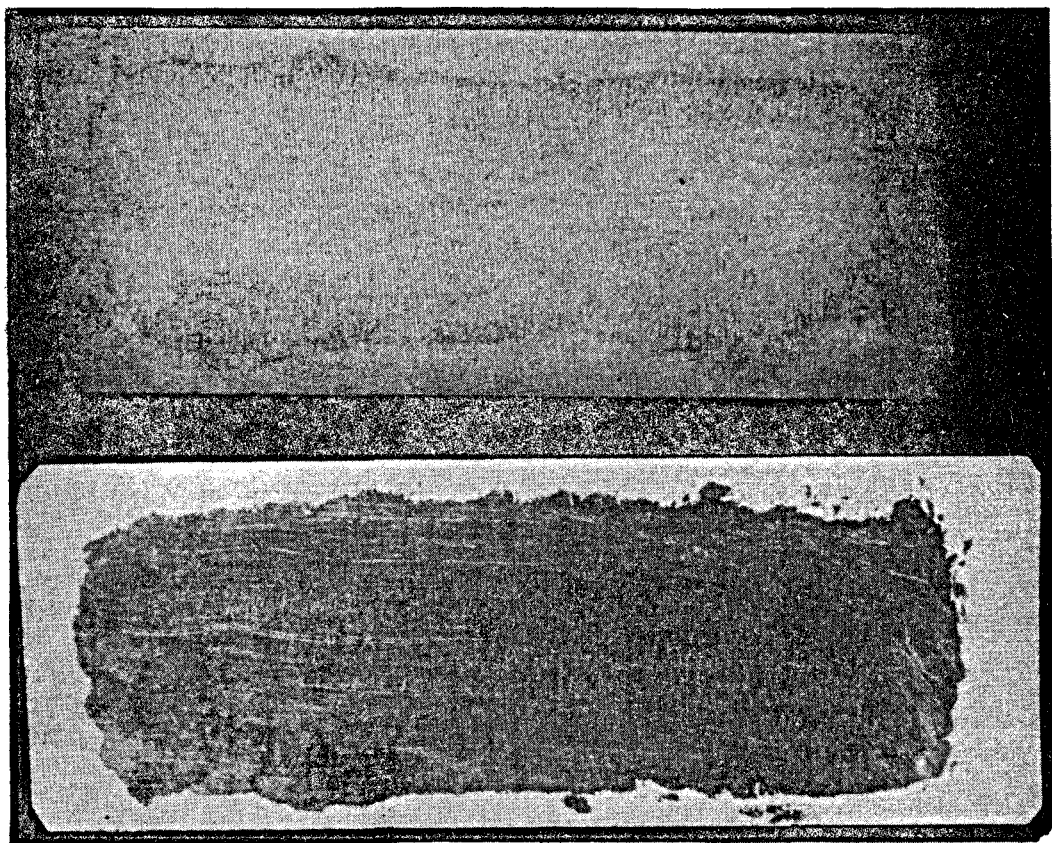


Fig. 1 - Ore sample mounted for radioautography.

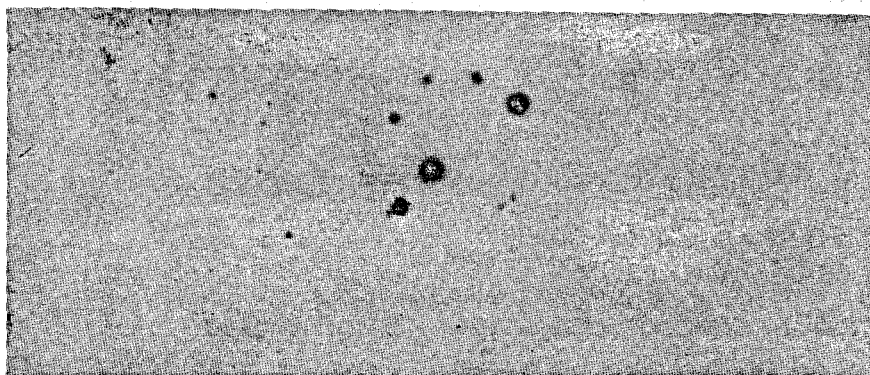


Fig. 2 - Radioautography of an ore sample with lack of homogeneity. Exposure time: 90 min.

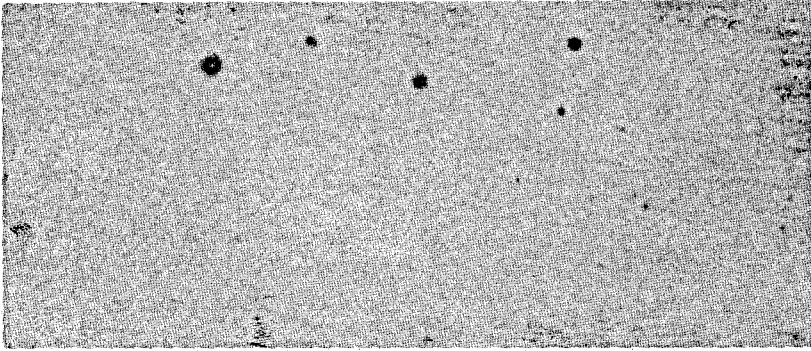


Fig. 3 - Radioautography of an ore sample with pronounced irregular distribution. Exposure time: 90 min.

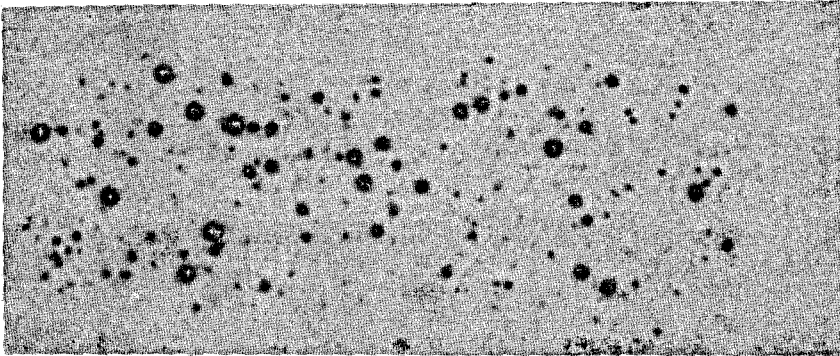


Fig. 4 - Radioautography of an ore sample considered as homogeneous. Exposure time: 90 min.

the gold recovery is high with chemical yield of 97%.

f) Interferences

The procedure suggested in this work can be considered free of interferences, the gold being selective and quantitatively separated⁽¹⁾. Theoretically in the conditions worked out in this method the elements cadmium and zinc could be retained into the anionic resins as its complex chlorides. The presence of both elements in the irradiated ore was not detected. On the other hand with the short irradiation times used and the peaks for radiozinc and radiocadmium do not interfere in the measurement of Au-198 photopeak. The sole radioactive contaminant in the irradiated resin was Cl-38 (37.5 min.) whose interference disappeared with a cooling time of 24 hours or more. No radio-silver, radiopalladium and radioplatinum were found, either.

g) Chemical Yield

One of the great advantages of the activation analysis is that it is not necessary a 100% recovery, though the losses are determined. These losses can be determined in any step of the chemical treatment through the induced radioactivity in the analysed element, thereafter the chemical separation usually is made after the neutron irradiation.

In this paper, as the analysed element was separated before the irradiation, an especial control of all steps in the chemical procedure was imposed. Therefore, the gold losses in the residue (insoluble), in the filter paper, in the resin effluents and in the glassware were verified.

The gold loss in the residue after the ore acid attack was determined by irradiating the residue and a gold standard; it was found a maximum loss of 0.8%. This confirmed the non necessity of complete ore solubilization for the separat-

ion of gold⁽¹⁾. In the same way the loss in the filter paper was determined and an average 0.4% value was found.

The loss in the resin effluent was controlled by using Au-198 tracer. Elemental gold was neutron irradiated, dissolved with aqua regia and dilutions prepared in such a way to have gold mass and activity close to that in the analysis solutions.

Resin effluents from actual samples analysed were used, to which Au-198 tracer was added, using volumes and gold concentration as close as possible to the ones used in the analysis. The solutions prepared as described were percolated through the anionic resin in the same manner as the actual analysis, and to the new effluents gold carrier (0,4 to 10,0 mg) was added and this new solution percolated through a new column, whose activity was measured. With this technique it was possible to measure the loss of gold in the resin effluents, a maximum value of 0.7% being found. It was observed that working in the same conditions the higher losses occurred in the most diluted solutions.

The gold loss in the glassware can be considered as inexistent; due to the high free acidity (pH 0.5 to 0.8) and high salt concentration practically there is no gold adsorption in the glassware.

In short, a total maxima of losses was found to be equal to 2%, that is, a final 97-98% gold recovery could be expected.

RESULTS

Table II shows the results of analysis of the Jacobina ores. The results are in good agreement and the standard deviations are in the expected range for activation analysis, especially if we consider low grade ores and wide range of gold content (0.50 to 70 ppm) in the analysed ores samples.

TABLE II

Analysis of Jacobina ore samples

Sample no	Results ug of gold per g of ore		
	A	B	Average
1	4.25	5.31	4.78
2	5.69	5.01	5.35
3	7.37	7.02	7.19
4	0.10	0.10	0.10
5	0.20	0.23	0.21
6	0.71	0.52	0.61
7	22.15	20.83	21.49
8	3.31	3.71	3.51
9	17.69	17.76	17.72
10	45.03	46.55	45.79
11	1.71	1.59	1.65
12	17.25	18.75	18.00
13	3.31	3.49	3.40
14	13.38	13.23	13.30
15	6.26	6.33	6.29
16	8.00	8.61	8.30
17	36.88	36.93	36.90
18	61.43	59.95	60.68
19	18.31	17.97	18.14
20	9.78	9.21	9.49
21	13.98	13.23	13.60
22	7.63	6.69	7.16
23	63.13	67.36	65.24
24	27.01	24.57	25.79
25	70.23	65.52	67.87

REFERENCES

- (1) Alcídio Abrão - "Simultaneous Determination of Gold and Uranium in Ores by Radioactivation Analysis", Publication I.E.A. n° 7, (1959).
- (2) Edmund M. Wise, Editor, - "Gold: Recovery, Properties and Applications". D. Van Nostrand Company, Inc. New York, 1964.
- (3) Wayne B. Holbrook and James E. Rein - Anal. Chem. 36, 2451 (1964).
- (4) Herbert P. Yule - Anal. Chem. 37, 129 (1965)
- (5) J.F. Emery and G.W. Leddicotte - "The Radiochemistry of Gold". NAS-NS 3036, Oak Ridge National Laboratory (1961).