SIMULTANEOUS DETERMINATION OF GOLD AND URANIUM IN ORES BY RADIOACTIVATION ANALYSIS

Alcidio Abrão

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INTRODUCTION

The determination of gold and uranium by radioactivation analysis has been made in separated materials. These two elements are frequently associated in ores (1,2,3),in the refined products of uranium (3) and in uranium alloys (3). A method which would allow a simultaneous analysis of both elements in a simple operation would be opportune, and this method has been developed, in the present work, by associating the activation analysis and ion exchange techniques.

Mahlman and Leddicotte (4) have determined U-238 by radioactivation, and the Np-239 formed on the U-238 (n,gamma) reaction was coprecipitated with lanthanum fluoride. On the other hand, Au-198 activated by (n,gamma) reaction in the analysis of ores has been isolated from the ore, after solublization; the method was solvent extraction after the addition of gold carrier, and determining the gold in the metallic form (5,6).This method is troublesome, needs addition of gold carrier and requires complete elimination of the nitrate ion, otherwise the reduction of gold to metal will not be quantitative.

Gold in submicrogram or macrogram level can be adsorbed on activated carbon (7,8). Schweitzer and Bishop (8) called attention to the fact that this adsorption is almost independent of the pH of the solutions, although the carbon has the tendency to buffer the solution to a pH of 7,5. They claimed an adsorption of 93% for solutions of pH 11 and 97 % for solutions of pH zero. The adsorption is made on batch equilibration and the best time for adsorption is one hour.

The chlorosauric acid and cyanide anionic complexes of gold are well retained on anionic ion exchanger (9,10). If the adsorption of those anionic complexes of gold on the ion exchange is easy and seletive, on the other hand the desorption is difficult, and this had prevented a larger

use of anionic resins for the analytical procedures for gold.

Sussman, Nachod and Wood (9) studied the adsorption of the adsorption of the chloroauric acid on strong anionic ion exchange, but an eluent for the desorption was not indicated.

Lima, Abrão and Pagano (11,12) used the radioactivation technique for analysis of traces of uranium that was fixed on the ion exchangers tanks for purification of the water of the Swimming Pool Reactor of São Paulo.

After elution of the ion exchanger, uranium was extracted by ether, the ether was evaporated and uranium was irradiated with neutrons, the neptunium-239 was detected and determined by the technique of Mahlman and Leddicotte (4). Lima "et al" (11,12) had began to study the determination of gold and uranium in ores, by activation analysis; they tried to determine both elements but they called attention to the fact that the method was precarious and the precision was poor when counting the irradiated ore, without previous chemical processing. Owing to the previous considerations the present author developed the method presented in this paper in which the analysis of materials containing both ions, uranium and gold are made.

INSTRUMENTS AND REAGENTS

For gamma scanning it was used a one channel pulse analyser (Inst. Energia Atômica); a Linear Amplifier Technical Measurement Corp., AL-4A; a model 181-A decimal scaler, and a sodium iodide-thallium activate well scintillation crystal, Model XT-100 both from Nuclear Chicago Corp. The standardization of the gamma counting system was made by using Pb-210 (0.047 Mev), Cd-109 (0.087 Mev), Sn-113 (0.393 Mev) and Cs-137(0.662 Mev) sources.

STRONG ANIONIC RESIN

Nalcite SAR (National Aluminate Corp., U.S.A.).The ion

exchanger was conditionated with 1.0 M NaOH, 10 M HCl and 0.1 M HCl.

STANDARD GOLD SOLUTION

Spectrographic pure metallic gold was dissolved with aqua regia and the nitrate ion was completely eliminated by fuming with hydrochloric acid. This standard solution had its acidity ascertained to 0.5 M HCl.

STANDARD URANIUM

A standard of uranium was prepared by calcination of uranyl nitrate, in a platinum crucible, to U_3O_8 which was used for irradiation.

SOURCE MATERIAL FOR ANALYSIS

The ore analysed were samples from the Mina de Canavieiras, Jacobina, Bahia (1), which was formed by SiO_2, iron, sulfur (pyrite), arsenic and gold, uranium and sodium being present as the minor components.

The best method to open small aliquots of the ore is the fusion with sodium hydroxide, leaching with hot water and neutralization with hydrochloric acid. There is coagulation of hydated silica if the solution is left undisturbed for some days, but by increasing the acidity of the mixture the precipitation of silica may occur in a few minutes. In this case it is indispensable to desicicate the mixture by fuming with acid, using classical methods (13). The silica precipitated with hydrochloric acid, on steam batch was washed with acid, then with water and the precipitate had no activity. The operation of silica insolubilization is time consuming and can be avoided without any inconvenience.

An acid attack of the ore was made with an attempt to investigate how the opening of the ore should be conducted. For this, a 0.1 g of the irradiated ore was scanned on a gamma-spectrometer, after allowing the ore to cool for a 24 hours period. The following photopeaks were detected: Np-239 (0.106, 0.230 and 0.323 Mev), Au-198 (0.412 Mev) and Na-24 (1.38 and 2.76 Mev) (figure 1).

Np-239 was formed by decay of U-239,after (n,gamma) reaction on U-238 (4). The four peaks of Np-239 are 0.106, 0.230, 0.276 and 0.323 Mev (14). Beyond the peaks of Np-239 only Au-198 has an important contribuition, because the peaks of Si-31 (0.52 Mev) will not show up after the cooling period.

After scanning the irradiated ore it was attacked with aqua regia, evaporated to almost dryness, leached with 5 M hydrochloric acid and centrifuged; the residue, characteristic of SiO_2, was once more scanned on the gamma scintilometer. It was noticed that only the peaks of neptunium were still present butnot the ones corresponding to Au-198 (fig.2). The conclusion is that the acid attack of the ore makes soluble all gold and a considerable fraction of the neptunium since the scanning of the solution did show that Np-239 was present. For actual analysis an acid attack of the ore was made and the residue was solubilised with a mixture of nitric and hydrofluoric acids.

The disruption of the ore by steps, i.e., first with aqua regia and then solubilization of the residue with a nitric and hydrofluoric acids mixture had to be more efficient and less troublesome than the direct digestion with nitric and hydrofluoric acids mixture.

PROCEDURE

Neutron irradiation

Aliquots from 0.5 to 1.0 gram of the ore were put in polystirene vial and irradiated for two hours in a flux 10^{12} neutrons/sec.cm^2. Standards of gold (as chloroauric acid) and uranium (as U_3O_8) were irradiated at the same time and with identical geometry. After the irradiation a cooling time of 24-72 hours was observed.

Ore digestion

Aliquots of irradiated ore, weighing about 0.3g, were attacked with aqua regia, centrifuged, and the residue washed twice with 5 M hydrochloric acid and then with water. The residue was then dissolved with nitric and hydrofluoric acide mixture, fumed with sulphuric acid and finally leached with water. The solutions were collected together and diluted to 100 milliliters. For analysis aliquots were taken and the acidity was ascertained with hydrochloric acid to 0.5 M.

GOLD DETERMINATION

Small columns of 0.5 cm of diameter by 1.0 cm of height, with one milliliter of anionic resin in chloride form were used. Some analysis were made by adding gold as isotopic carrier at maximum of 1.5mg and others without gold as carrier.

After the resin had been loaded it was washed with 20 milliliters of 0.5 M hidrochloric acid and then with water until absence of hydrogen ion in the washings. The resin with gold was transferred to another polystirene vial that would fit the well in a gamma-scintilometer and the Au-198 activity was counted. Standards containing both gold and uranium were prepared and the same procedure was applied to them and the gold of the standard solution was sorbed on the anionic resins exactly as described above. The efluents and washings of the column were colected together and kept for the determination of neptunium (uranium).

GOLD IDENTIFICATION

The identification of gold was made by gamma - energy scanning and its purity was checked by determining the decay via integral gamma ray counting. Figures 3 and 3A show the gamma scanning of gold standard and gold analysis (ores). The gold ore content was evaluated by the areas

under the peaks (15), by their heights and also by the integral gamma ray counting, compared with the same measurements made with the standards.

Table I presents the results of gold analysis of two ores samples, expressed in microgram of gold per gram of ore.

URANIUM DETERMINATION

The efluents and washings of the anionic resin column were warmed, neutralized with ammonium hydroxide and treated with hydrochloric acid until a little excess. To the solution, hydroxilamine hydrochloride was added until the yellow color of ferric iron had fadded to be sure that the reduction of neptunium was complete. The solution was transferred to a platinum crucible and one milliliter of 20 M hydrofluoric acid and 20 milligrams of lanthanum (nitrate) were added dropwise. After the lanthanum addition the mixture was stirred during 5 minutes and centrifuged in a polystirene vial.

The precipitate was washed twice with one milliliter of a 1M hydrofluoric-nitric acids mixture, centrifuged again and then counted in the gamma scintilometer.

The standard containing both gold and uranium, as mentioned above, after passing through the amionic resin, was submited to an identical treatment.

NEPTUNIUM IDENTIFICATION

The identification of neptunium, as in the case of gold was made by the gamma energy spectrum and the purity was checked by half-life.

The decay of Np-239 was followed by integral gamma activity counting of the precipitate of lanthanum (neptunium) fluoride. As in the determination of gold, the evaluation of neptunium content, consequently U-238, was made by the areas of the peaks, their height, and by the integral gamma activity counting, compared with the corresponding data for the standard. Table I presents the results of uranium analysis in two samples of ore. The results were expressed in percentage of U_3O_8.

DISCUSSION

It is observed that neptunium and gold had been separated from silica with relative facility by attacking the ore with aqua regia. After one digestion all the gold and a considerable fraction of the neptunium were solubilised. Using strong anionic resin for retention of gold the chloroauric acid complex is sorbed even at a very low concentration, without addition of isotopic carrier. Other impurities were eliminated from the resin by washing with hydrochloric acid.

The common methods where gold is separated by solvent extraction (ether or ethyl acetate), then precipitated by reduction to metallic gold, requires 20-40 milligrams of gold carrier. The chloroauric acid is strongly fixed by anionic resin(chloride form) from its solutions with hydrochloric acid concentration ranging from 0.1 to 12 M (10) and the resin may be counted directly. Another advantage on fixing gold in the anionic resin is that these sorption is good even in the presence of nitric acid(10),however, in the common processes of reduction it is imperious to complete the elimination of nitrate ion, otherwise the reduction to metallic gold is not quantitative.

With respect to the ore opening it is better to proceds by steps, i.e., first with aqua regia, then the solubilization of the residue with nitric-hydrofluoric acids mixture. In this way the desagregation of the ore is more efficient and less troublesome than direct digestion with nitric hydrofluoric mixture.

The separation of gold from the activities of the irradiated uranium was checked by using a synthetic mixture containing 26 micrograms of gold and 200 micrograms of irradiated uranium in 20 milliliters of solution and analysing this mixture by the same method as for the ores.

The acidity of this mixture was ascertained to 0.5 M with hydrochloric acid and then passed through an anionic resin column, in chloride form, 0.5 cm of diameter by 2.0 cm of height, with a flow of 2 milliliters/minute. The column was washed with 10 milliliters of 0.5 M hydrochloric acid and then with water until no more hydrogen ion could be detected, in the washings. The resin was transferred to a plastic vial and was scanned with the aid of the gamma scintilometer. Figure 3 shows this scanning, where only the peaks corresponding to Au-198 are present. The column efluents and washings were concentrated simply by evaporation on a hot plate, transferred to a plastic vial and then scanned with the gamma-scintilometer. Figure four shows this scanning where only the Np-239 peaks are present.

Figure 4A was obtained by scanning the efluent of an anionic resin column in chloride form, to which the irradiated uranium standard was passed. Experiments made by using solutions with a lower concentrations of gold and uranium had shown that isotopic carriers of gold and non-isotopic carrier for neptunium (lanthanum) were dispensable when the separation of those elements was made with the aid of an anionic resin. Mahlman and Leddicotte's method could be simplified by omiting the hydroxides precipitation and precipitating the fluorides directly, since it was not necessary the separation of Pu-239 (alfa emiter).

The precision of the methods is the one for radioactivation analysis, i.e., from 1 to 10%, accordingly with the standards deviation presented on Table I.

SUMMARY

Gold and uranium, frequently found together in thesame ore, were qualitative and quantitatively analysed by means of Au-198 and Np-239 nuclides formed by nuclear reactions after irradiation in a neutron flux. Gold was separated from neptunium and fission products with the aid of a strong anionic resin, without the addition of gold isotopic carrier and of non isotopic carrier for neptunium. Beside this advantage, the separation made with the aid of anionic resins is a very easy and simple operation in contrast with the solvent extraction of gold (5,6).

The eficiency of the separations and the purity of isolated radioisotopes were checked by gamma-ray spectrometry and measurement of the half-lives.

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TABLE I

Results of gold and uranium ore determination

Sample A	gold*	uranium U_3O_8 %
nº 1	20,40	0.110
2	21,40	0.110
3	24,40	0.120
4	21,40	0.110
5	24,80	0.110
6	24,70	0.130
Average	22,85 ± 2.00**	0.115 ± 0,008**
Sample B		
nº 1	20,80	0,140
2	17,90	0,130
3	19,20	0,120
4	17,60	0,120
5	17,90	0.120
6	17,30	0,130
7	17,50	0,140
8	19,30	-
Average	18,44 ± 1,21**	0,128 ± 0,009**

* micrograms/gram of ore

** standard deviation

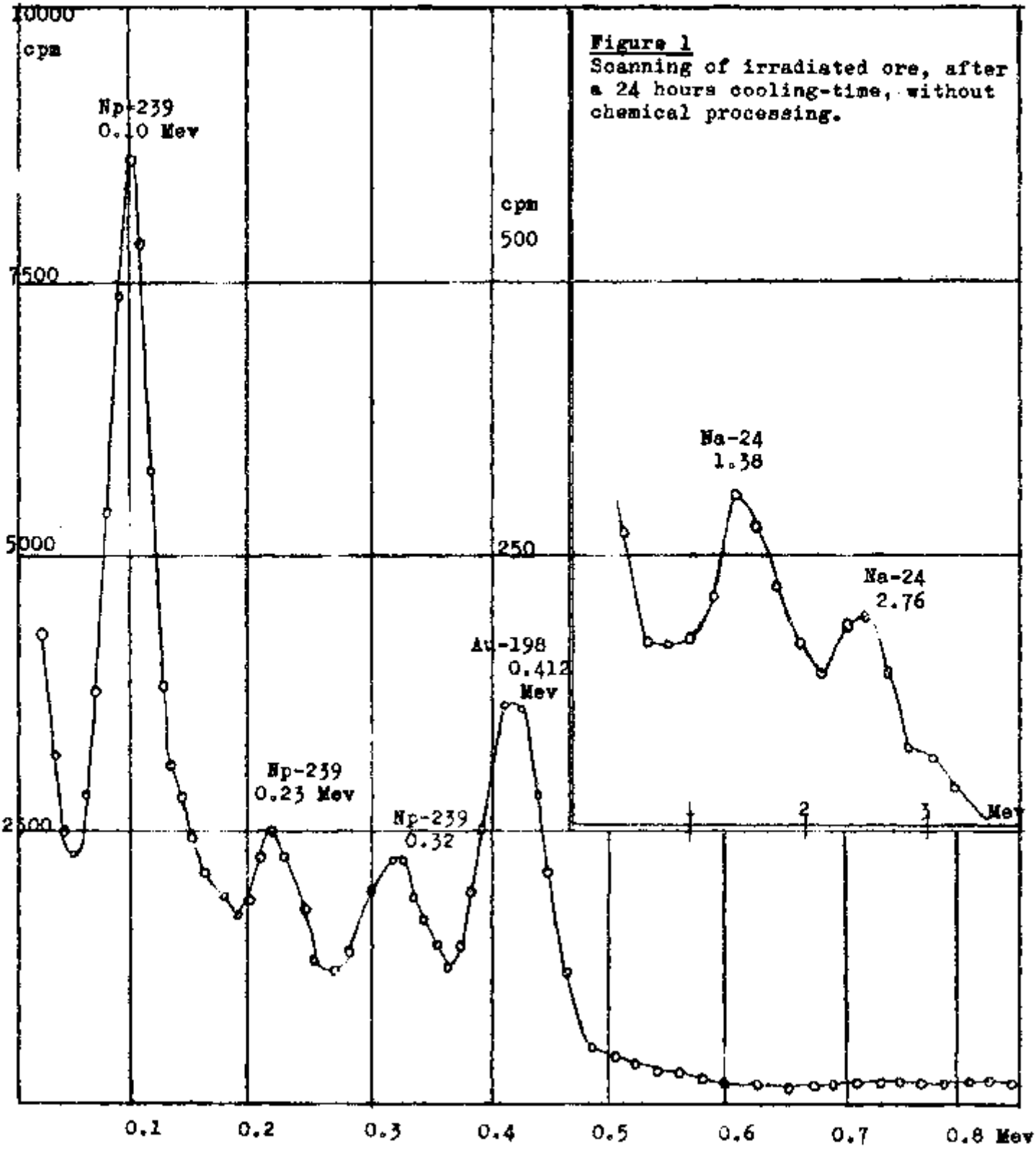

Figure 1
Scanning of irradiated ore, after a 24 hours cooling-time, without chemical processing.

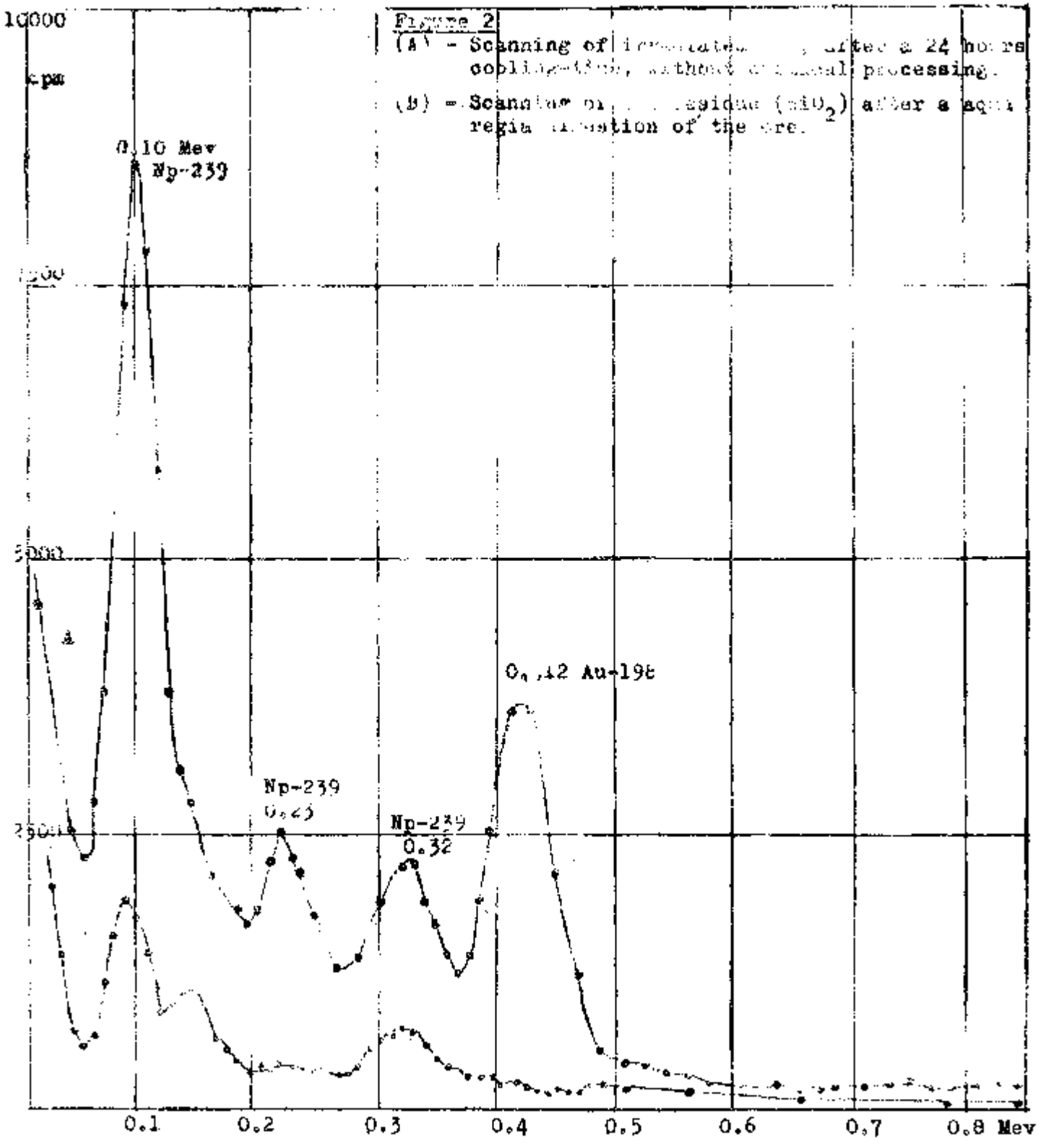

Figure 2

(A) - Scanning of irradiated [illegible] after a 24 hours cooling-off, without chemical processing.

(B) - Scanning of the residue (SiO_2) after a aqua regia dissolution of the ore.

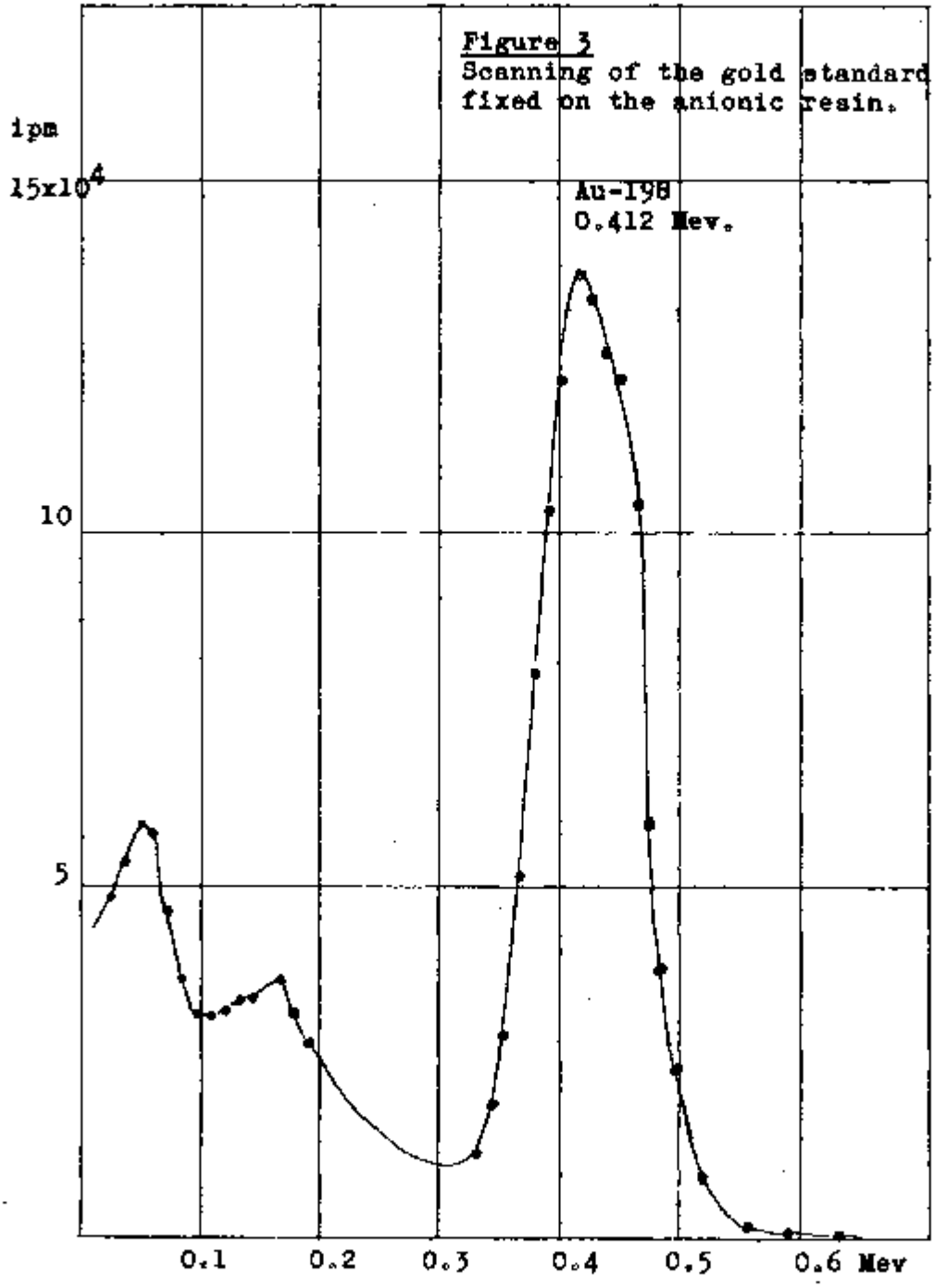
Figure 3
Scanning of the gold standard fixed on the anionic resin.
ipm
15x10⁴
10
5
Au-198
0.412 Mev.
0.1
0.2
0.3
0.4
0.5
0.6 Mev

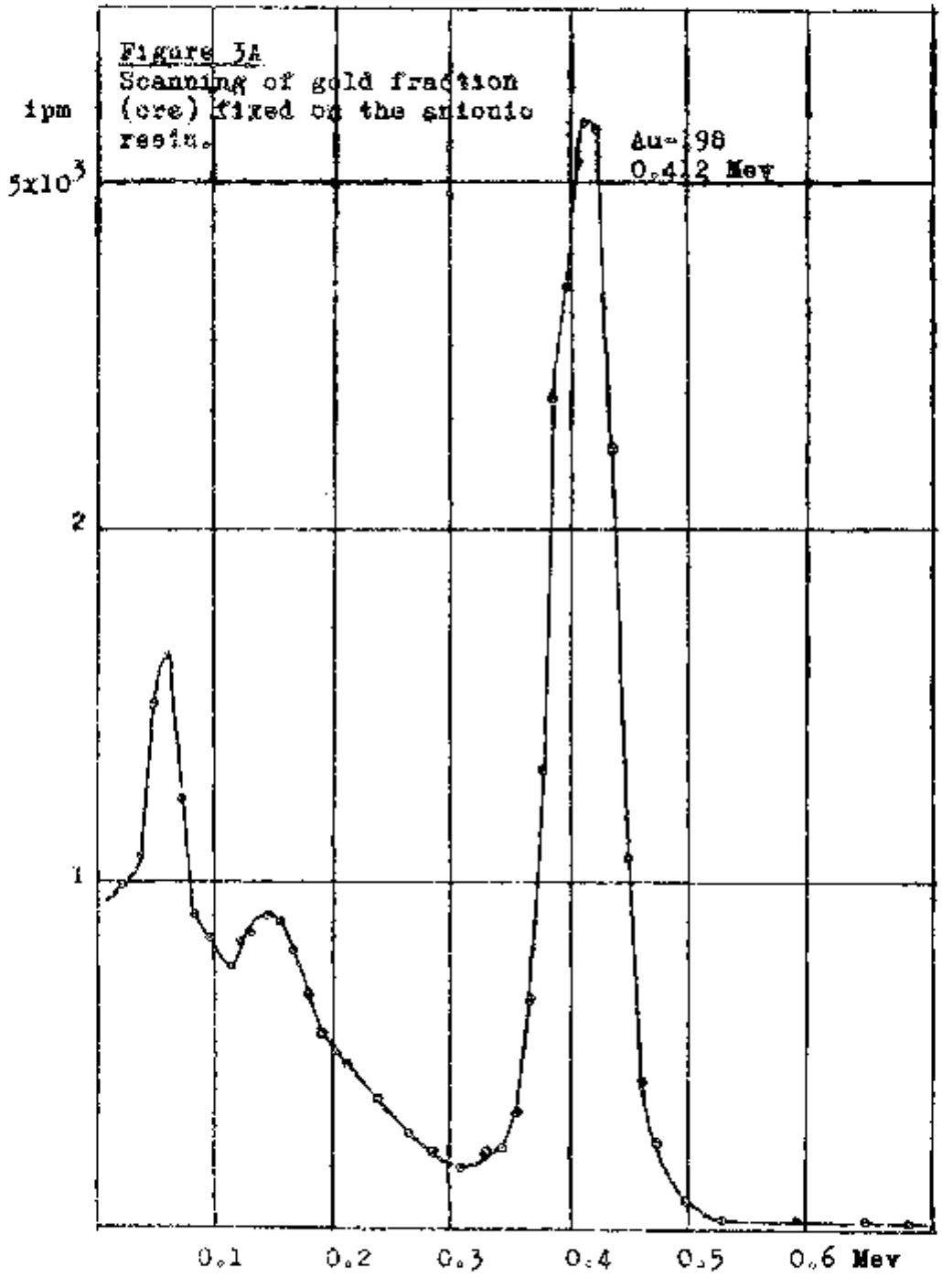
Figure 3A
Scanning of gold fraction (ore) fixed on the anionic resin.
ipm
5x10³
2
1
Au-198
0.412 Mev
0.1
0.2
0.3
0.4
0.5
0.6 Mev

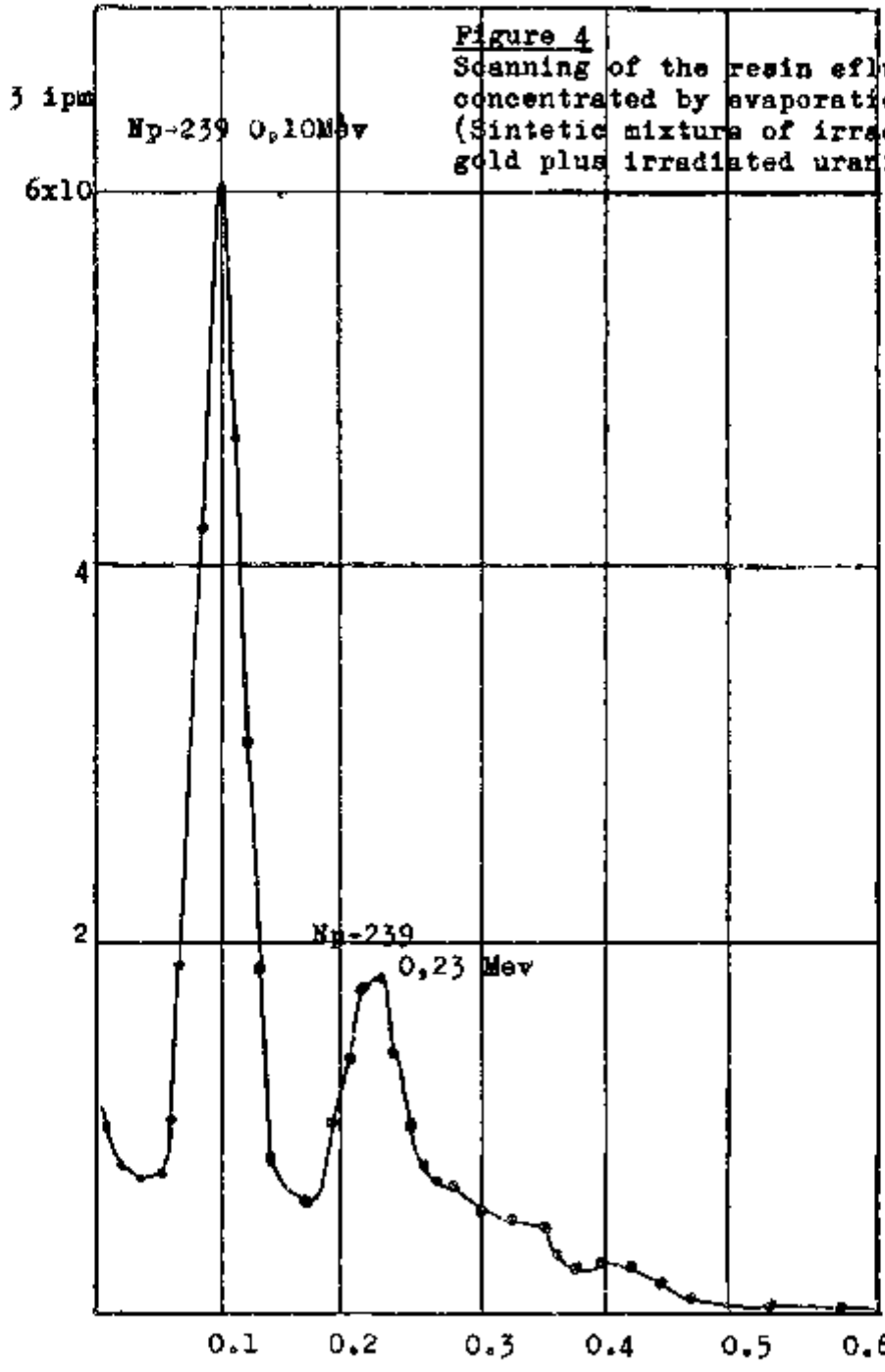

Figure 4
Scanning of the resin efluents, concentrated by evaporation. (Sintetic mixture of irradiated gold plus irradiated uranium).

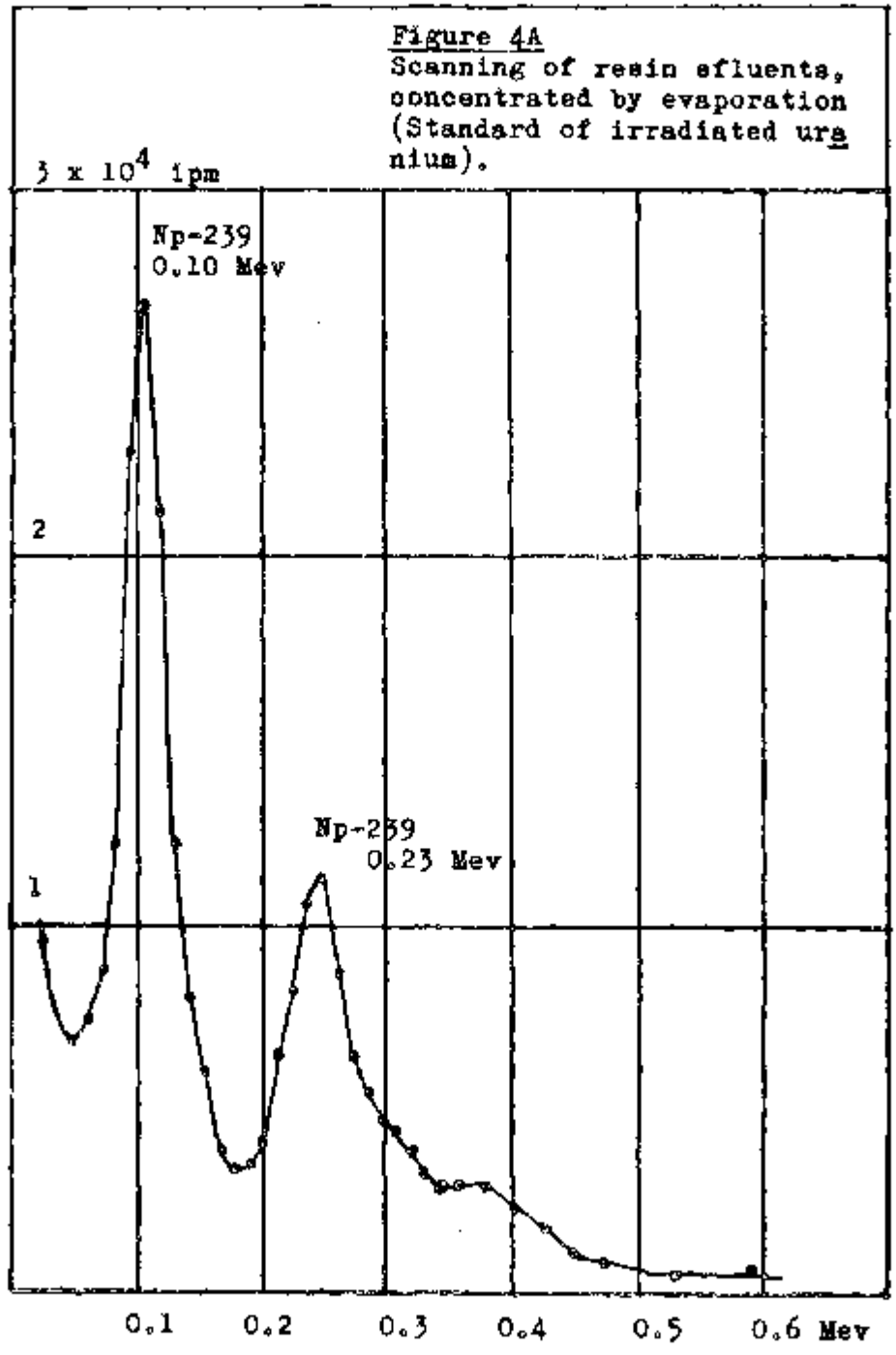

Figure 4A
Scanning of resin effluents, concentrated by evaporation (Standard of irradiated uranium).