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AN ION EXCHANGE-EDTA SEPARATION OF LEAD FROM BISMUTH. APPLICATION TO RADIOCHEMISTRY.*

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RESUMO

Propõe-se neste trabalho a separação chumbo-bismuto baseada no princípio de ser o complexo Bi-EDTA (ácido etileno-dinitrilo-tetraacético) muito estável em soluções ácidas , enquanto o chumbo permanece não complexado. Percolando-se a solução contendo chumbo, bismuto e EDTA, a pH 1,8-2,5, numa coluna de resina catiônica (forma hidrogênica), o cátion chumbo é completamente fixado pela resina, passando o bismuto na forma de seu complexo Bi-EDTA.

A separação foi controlada radioquìmicamente por meio dos traçadores de Pb-212 e Bi-212, sendo bem sucedida quando os dois elementos estão na concentração de traços ou quando um ou ambos se acham em macroconcentração. Numa única separação obtém-se ambos os elementos numa pureza ao redor de 99%, mesmo no caso de ambos estarem em concentração submicroquímica.

A pureza da fração bismuto foi verificada pelos espectros de energia gama, constatando-se a existência ou não do fotopico do Pb-212 (0,23 Mev) e acompanhando-se o decaimento radioativo. A contaminação de chumbo na fração bismuto foi também calculada pela comparação das áreas do pico de 0,23 Mev nas duas frações.

A pureza da fração chumbo foi verificada através da curva de crescimento radioativo pela contagem beta, usando-se um absorvedor de alumínio de 352 mg/cm2. Foi também determinado o tempo de equilíbrio, encontrando-se concordante com o teórico (3,76 hs).

O processo é simples, rápido, o que é de importância no caso de isótopos de meias vidas curtas.

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RÉSUMÉ

L'auteur a fait la séparation de plomb-bismuth s'utilisant du fait que le complexe Bi-EDTA (acide éthylene-diamine-tetracétique) est très stable en solutions acides, tandis que le plomb reste non complexé. Quand on passe sur une colonne de résine cationique .. (forme hydrogénique), une solution contenant plomb, bismuth et EDTA à un pH 1,8-2,5, le cation plomb est entièrement fixé sur le résine, tandis que le bismuth est élué sous la forme du complexe Bi-EDTA.

La séparation a été controlée radiochimiquement par des traceurs de Pb-212 et de Bi-212. Cette séparation a été aussi bonne pour des microquantités que pour les macroquantités de ces élements.

Avec une seule séparation on obtient ces deux élements avec une pureté d'environ 99%, même quand ils sont en quantités de traces.

La pureté de la fraction bismuth a été vérifiée au moyen des spectres de rayonnement gama, par la constatation du pic photoélectrique du plomb 212 (0,23 Mev) et par la décroissance radioactive.

La contamination de plomb dans la fraction bismuth a été aussi calculée par la comparaison des aires situées sous les pics photoélectriques de 0,23 Mev dans les deux fractions.

La pureté de la fraction plomb a été vérifiée par la courbe de croissance radioactive, par comptage beta, avec un absorbant d'alluminium de 352 mg/cm2.

Le temps d'equilibre a été aussi déterminé, et le résultat est d'accord avec le temps théorique (3,76 hs).

Le procedé est très simple et rapide, ce qui est très important, surtout quand on a des radioéléments à demi-vies courtes.

SUMMARY

In this paper it is suggested a separation of lead from bismuth based on the principle that the Bi-EDTA (Ethylenedinitrilo tetraacetic acid) complex is very stable in acid solutions while lead is not complexed. By percolating a solution containing lead,

bismuth and EDTA, at pH 1,8-2,5, in a cationic ion exchange column (Nalcite HCR, hydrogen form), the lead ions are completely adsorbed by the resin while bismuth is eluted as Bi-EDTA complex.

This separation was radiochemically controlled using Pb-212 and Bi-212 as tracers, being successful when both elements are in tracer concentration or when one (or both) of them is at macro concentration. In a single-step separation both elements are obtained in a purity about 99% even when both are at tracer concentration.

The purity of the bismuth fraction was checked by gamma-ray spectrometry, looking for the 0,23-m.e.v. photopeak for Pb-212 and by radioactive decay. The contamination of lead in the bismuth fraction was also calculated by comparison of the areas under the 0,23 m.e.v photopeak in both fractions.

The purity of the fractions was verified by the radioactive growing curve by beta counting using an aluminum absorber of 352 mg/cm2. The transient equilibrium time was determined and was found in agreement with the theoretical (3,76 hours).

The procedure is simple and rapid, which is important when the half lives of the isotopes are short.

INTRODUCTION

The separation of lead from bismuth is an important radiochemical problem, since both elements are frequently associated, for instance, in the nuclear processes like Pb-204 (d, 2n) Bi-204 and Pb-206 (d, 2n) Bi-206,[1,2] and in mixtures of natural radiolead and radiobismuth separated from the natural uranium, thorium, and actinium series. Among the many procedures used for the lead-bismuth separation, one of the best known is the classical sodium hydroxide precipitation where lead forms the soluble sodium plumbite while the bismuth is precipitated as hydroxide. The shortcoming of this procedure lies in the fact that the bismuth hydroxide is contaminated by lead and some bismuth is soluble in the excess of sodium hydroxide.[3] Lima and Abrão[3]

separated lead from bismuth using a mixture of both elements complexed by EDTA (ethylenedinitrilotetraacetic acid) by simply disrupting the Bi-EDTA complex with sodium hydroxide while lead remains in solution. This procedure was performed using radiolead and radiobismuth and showed to be superior to the separation advocated by Pribil and Cuta[4] in which calcium ions were added to an ammoniacal Bi-EDTA and Pb-EDTA solution with consequent replacement to bismuth ions by calcium ions and precipitation of bismuth hydroxide, while lead remained in solution. Lima and Abrão[3] showed that the bismuth hydroxide precipitated by the procedure of Pribil and Cuta was appreciably contaminated by lead, in which the 47 keV photo-peak of Pb-210 was detected. Rudenko[5] achieved the separation of lead from bismuth by precipitating bismuth ions with gallic acid and the lead ions with H_2S, while Moore[6] separated lead traces from bismuth by coprecipitating bismuth with copper sulfide in HCl medium.

Duyckaerts and Lejeune[7] separated the carrier-free radioisotopes Pb-212 and Bi-212 by cation ion-exchange chromatography eluting both elements with EDTA at pH 9.

SUGGESTED PROCEDURE

This paper suggests a lead-bismuth separation based upon the principle that the Bi-EDTA complex is very stable in solutions of relatively low pH's, while lead remains uncomplexed. Percolating the solution containing Pb, Bi, and EDTA at pH 1.8-2.5 in a cationic ion-exchange resin (H-form), the lead cations are completely adsorbed by the resin while the bismuth ions are eluted off as the Bi-EDTA complex. The stability constant of Bi-EDTA complex ($\log K = 27.81$)[8] is higher than the Pb-EDTA one ($\log K = 18.04$.[8] and bismuth can be labeled by EDTA at pH 2-3.[9]

EXPERIMENTAL PART

Pb-212 and Bi-212 Tracer Solution. A carrier-free Pb-212 and Bi-212 solution was prepared by the method described by Abrão,[10] which consists of collecting those radioisotopes from thorium-nitrate solution with bismuthol (2,5 - dimercapto - 1,3,4--Thiodiazol). In these experiments where carriers were added (groups A, B, C) the tracer was separated from thorium with 1 ml of lead or bismuth precipitated with 3 ml of 2% aqueous bismuthol solution, warming the solution to 60-80° C and centrifuging the precipitate. The lead or bismuth bismutholate was destroyed with some drops of HNO_3 and $HClO_4$ until dry and then diluted with water.

Ion-Exchange Resin. Three milliliters of cationic-ion exchange (nalcite HCR, 30-50 mesh) were poured into a glass tube 0.8 cm in diameter. The resin was conditioned successively with 20 ml of EDTA 5 g/l, pH 7, 10 ml of water, 10 ml of H_2SO_4 M, and water until there was no more H^+ in the washings.

Lead-Bismuth Separation. The experiments were performed in four groups, depending on the relative amount of lead and bismuth present, adding 1 mg of each element when in macroconcentration:

Group	Lead	Bismuth
A	1 mg	1 mg
B	1 mg	traces
C	traces	1 mg
D	traces	traces

EDTA, stoichiometrically sufficient to complex both metals plus a 100% excess, was added to groups A, B and C; and 2.5 mg were added to group D. In all experiments the loading solution had a volume of 25-30 ml and the column was washed with 15 ml

of 0.1 g/l of EDTA solution at pH 2.0.

To the beaker containing the Pb-212 and Bi-212 tracers add 5 g/l of EDTA solution to complex stoichiometrically lead or bismuth, or both (groups A, B, C), plus an excess of 100%; to group D experiments add 2.5 mg of EDTA. Dilute the solution with water to 20-25 ml and adjust the pH to 1.8-2.5 using NH_4OH or HNO_3. Pass the solution through the column and then wash with 15 ml of 0.1 g of EDTA solution, pH 2. Both loading solution and washings are percolated at a velocity of 1.5-2.0 ml per minute.

To the effluents containing the radiobismuth add 1 mg of Bi carrier (groups B and D), 3 ml of 2% aqueous bismuthol solution and 1 ml of 5 M HNO_3, warm the solution to 60-80°C. Filter the bismuth bismutholate and wash the precipitate with 0.1 M HNO_3 solution. Transfer the precipitate to a plastic vial.

The radiolead is eluted from the resin with 15-20 ml of 5 M HNO_3 and the column is washed with 10 ml of water. The combined solutions are neutralized with NH_4OH and after the addition of 1 mg of lead carrier (groups C and D) add 3 ml of bismuthol and acidify with HNO_3 adding an excess of 1 ml; warm the solution 60-80°C, filter the lead bismutholate, and mount for counting.

Purity. The purity of the bismuth fraction (effluent) was checked by gamma-ray spectrum looking for the 23 keV Pb-212 photo-peak and by following the decay as well. The lead fraction (eluate) was mounted on a planchet, covered with cellophane and its radioactive growth was followed by beta counting (Superscaler Tracerlab) with a Geiger tube of 1.4 mg/cm^2 window using an aluminum absorber of 352 mg/cm^2. The lead fraction purity was calculated by the Lima[11] method determining the percentage of entrained bismuth. Also the transient equilibrium was determined for the lead fraction and found in agreement with the theoretical 3.76 hr. On the other hand, the contamination of lead in the bismuth fraction was determin

ed by the comparison of the areas of the 23 keV photo-peak of Pb-212 on both fractions. To do this, the resin was transferred immediately, after washing, to a plastic vial and its gamma-ray spectrum determined.

Results. The purity of the lead and bismuth fractions was greater than 99%, even in group D experiments where both elements were present at trace level.

REFERENCES

1. SEABORG, G.T. and PERLMAN, L. Rev. Modern Phys. 20, 585 (1948).

2. TEMPLETON, D.H., HOWLAND, J.J. and PERLMAN, L. Phys. Rev. 72, 766 (1947).

3. LIMA, F.W. and ABRÃO, A. Anal. Chem. 32, 492 (1960).

4. PRIBIL, R. and CUTA, J. Collection Czech. Chem. Communs. 16, 391 (1951).

5. RUDENKO, M.P. J. Anal. Chem. USSR. (Eng.trans.) 11, 385, (1956).

6. MOORE, V.J. Analyst. 81, 553 (1956).

7. DUYCKAERTS, G. and LEJEUNE, R. J. Chromatog. 3, 58-62 (1960).

8. CARTWRIGHT, P.F.S. Analyst. 86, 692 (1961).

9. MALAT, Suk and RYBA. Chem. Listy, 48, 203 (1954).

10. ABRÃO, A. Preparation of radiolead and radiobismuth for use as tracers and sources - This Symposium, pg. 281.

11. LIMA, F.W. Anal. Chem. 25, 1924 (1953).

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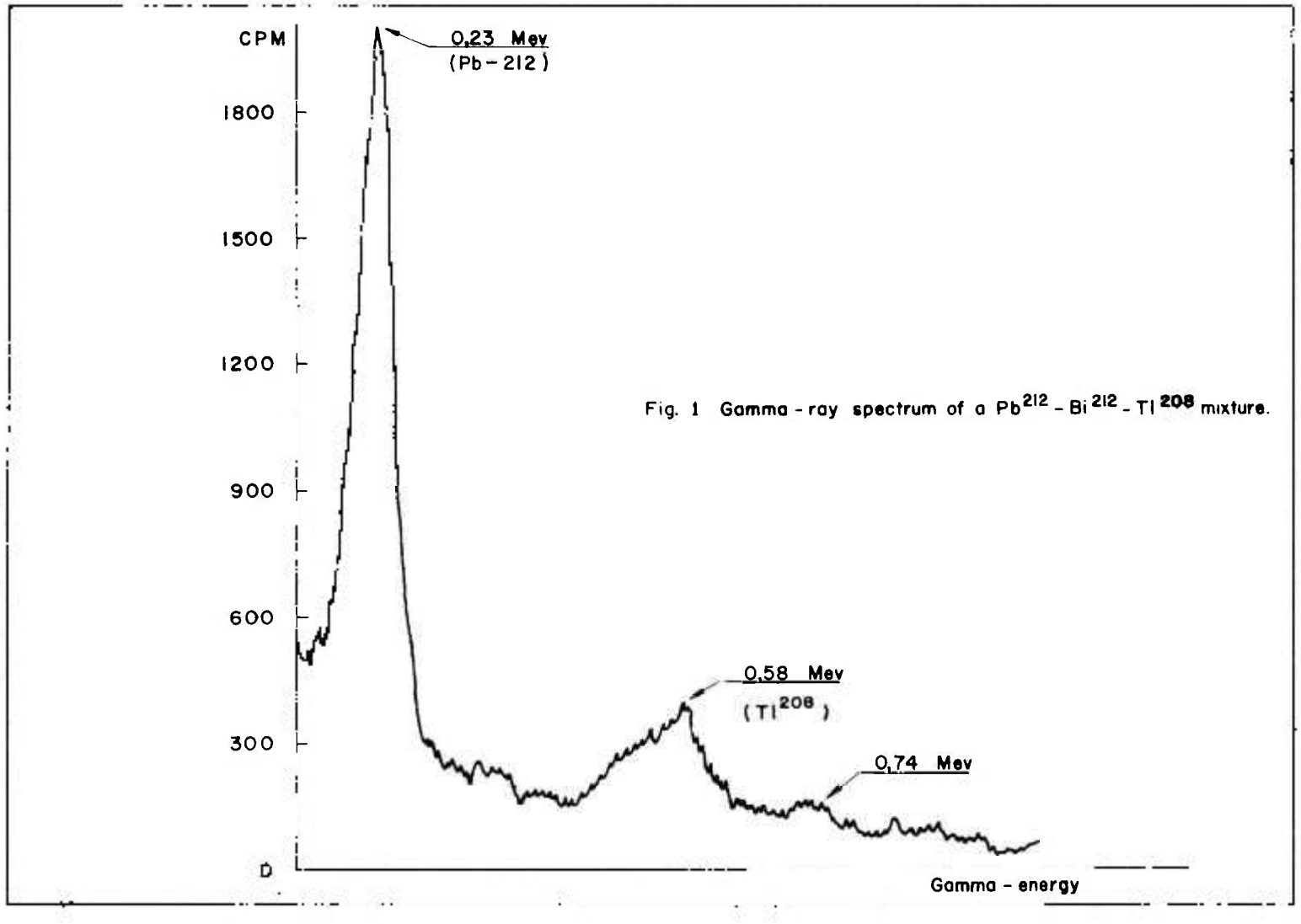

Fig. 1 Gamma - ray spectrum of a $Pb^{212} - Bi^{212} - Tl^{208}$ mixture.

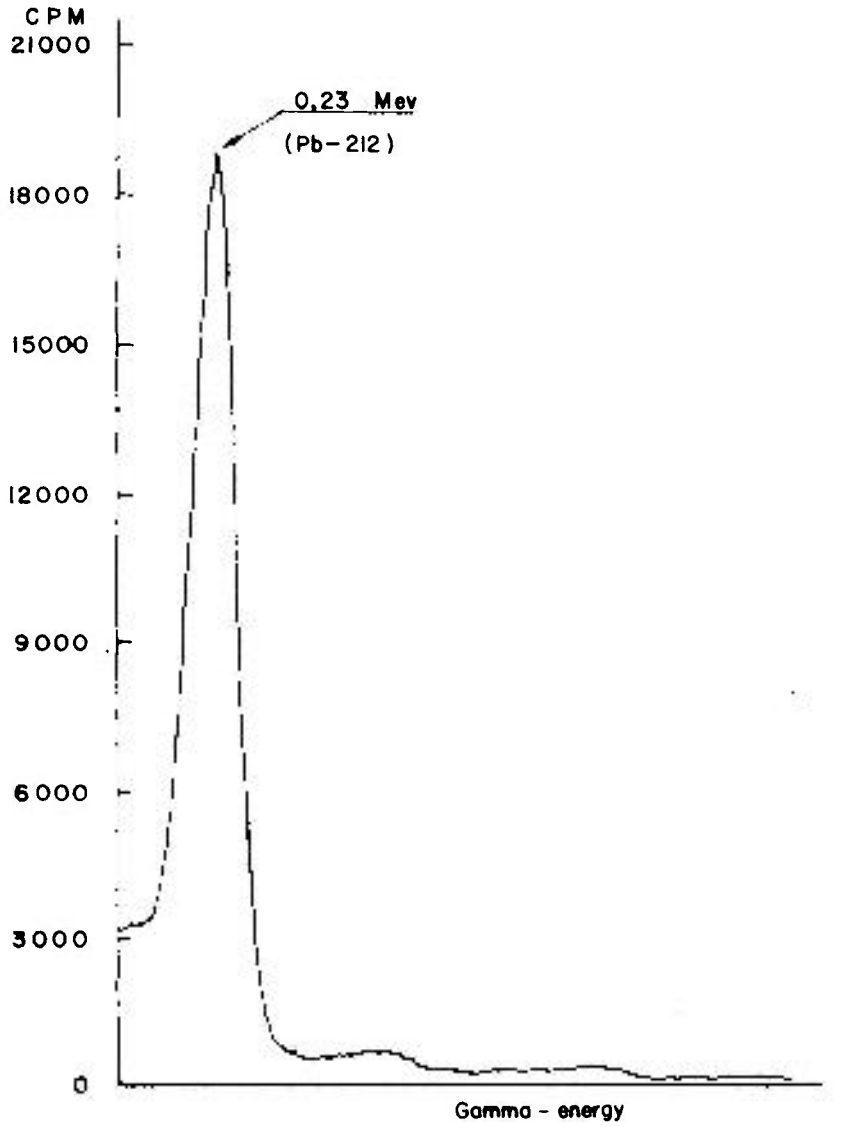

Fig. 2A. Gamma - ray spectrum of the pure Pb^{212} resin fraction.

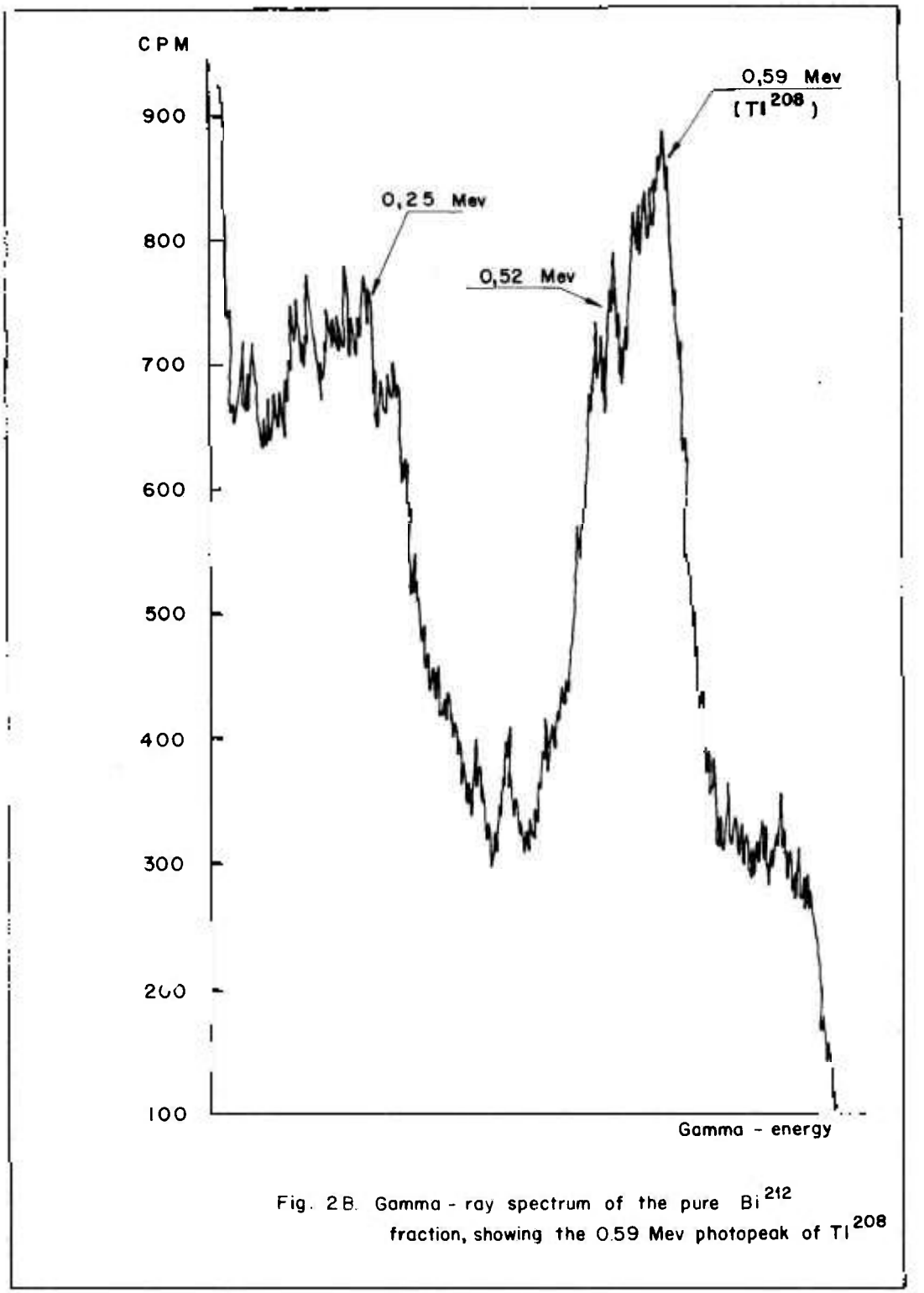

Fig. 2B. Gamma - ray spectrum of the pure Bi^{212} fraction, showing the 0.59 Mev photopeak of Tl^{208}

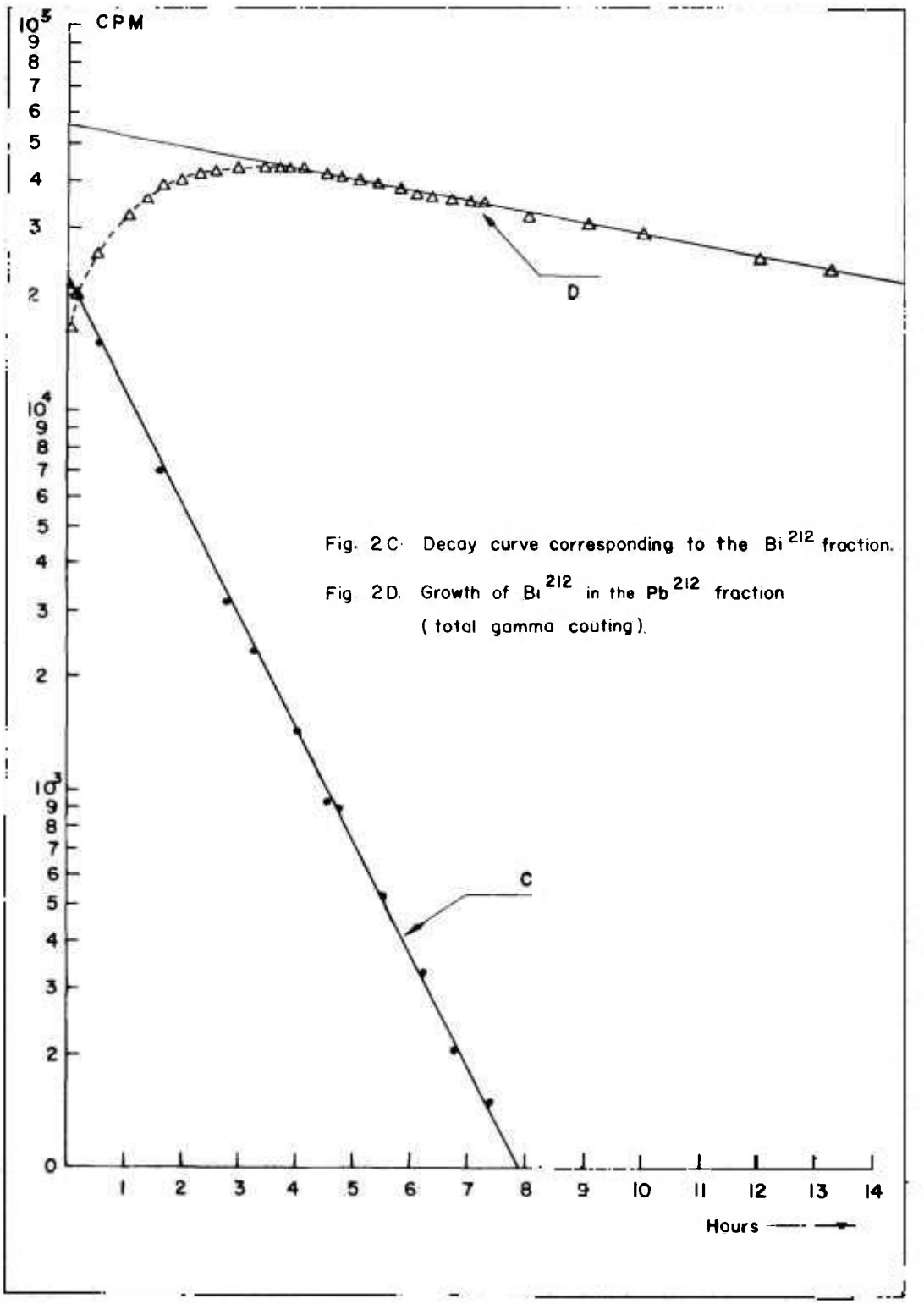

Fig. 2C. Decay curve corresponding to the Bi^{212} fraction.

Fig. 2D. Growth of Bi^{212} in the Pb^{212} fraction (total gamma couting).