CHROMATOGRAPHIC SEPARATION OF PROTACTINIUM FROM THORIUM: A PROTACTINIUM-234m AND PROTACTINIUM-234 GENERATOR

ALCÍDIO ABRÃO

PUBLICAÇÃO IEA Nº 214
Julho — 1970

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

CHROMATOGRAPHIC SEPARATION OF PROTACTINIUM FROM THORIUM: A PROTACTINIUM-234m AND PROTACTINIUM-234 GENERATOR*

Alcídio Abrão

Divisão de Engenharia Química
Instituto de Energia Atômica
São Paulo - Brasil

Publicação IEA Nº 214
Julho - 1970

---

*Publicado em "Radiation and Isotope Technology in Latin American Development", Proceedings of The American Nuclear Society Topical Meeting, San Juan, Puerto Rico, May 4-6, 1969. Relatório PRNC 135, pg. 426-430.

Comissão Nacional de Energia Nuclear

Presidente: Prof.Dr. Hervásio Guimarães de Carvalho

Universidade de São Paulo

Reitor: Prof.Dr. Miguel Reale

Instituto de Energia Atômica

Diretor: Prof.Dr. Rômulo Ribeiro Pieroni

Conselho Técnico-Científico do IEA

Prof.Dr. José Moura Gonçalves	pela USP
Prof.Dr. José Augusto Martins	
Prof.Dr. Rui Ribeiro Franco	
Prof.Dr. Theodoreto H.I. de Arruda Souto	pela CNEN

Divisões Didático-Científicas

Divisão de Física Nuclear -
Chefe: Prof.Dr. José Goldenberg

Divisão de Radioquímica -
Chefe: Prof.Dr. Fausto Walter de Lima

Divisão de Radiobiologia -
Chefe: Prof.Dr. Rômulo Ribeiro Pieroni

Divisão de Metalurgia Nuclear -
Chefe: Prof.Dr. Tharcísio D.S. Santos

Divisão de Engenharia Química -
Chefe: Lic. Alcídio Abrão

Divisão de Engenharia Nuclear -
Chefe: Engº Pedro Bento de Camargo

Divisão de Operação e Manutenção de Reatores -
Chefe: Engº Azor Camargo Penteado Filho

Divisão de Física de Reatores -
Chefe: Prof.Dr. Paulo Saraiva de Toledo

Divisão de Ensino e Formação -
Chefe: Prof.Dr. Rui Ribeiro Franco

CHROMATOGRAPHIC SEPARATION OF PROTACTINIUM FROM THORIUM: A PROTACTINIUM-234m AND PROTACTINIUM-234 GENERATOR

Alcídio Abrão

ABSTRACT

The short lived natural radioisotopes protactinium-234m (1.18 min.) and protactinium-234 (6.67 hours), descendants from the thorium-234 (UX1, 24 days) are valuable for radiochemical experiments, as for instance, half-life, and dead-time determination, desintegration and genetic related radioisotopes studies, and as tracer (protactinium-234) as well.

The method here outlined allows a convenient and fast separation of both protactinium-234m and protactinium-234 radioisotopes. The method is extremely simple, requires no special reagents and permit milking of these radioisotopes at any desired moment.

The method is based on the sorption of thorium-234 from a solution containing 0.3M HF on an alumina column, from which the radioprotactinium can be eluted when desired. Thorium-234 is strongly held on the alumina and protactinium-234m and protactinium-234 can be milked many times successively, by simple elution with 0.2 - 0.3M HF. Thorium-234 is directly separated from uranyl nitrate solution (100 g/l U_3O_8) having 0.3M HF, by percolation on an alumina column (2 ml Al_2O_3). After the sorption of thorium-234 the small generator is ready to furnish protactinium-234m that can be milked each 1-5 minutes (for the protactinium-234m ingrowth) with 1-3 ml of 0.2-0.3M HF.

The protactinium-234m and protactinium-234 milked from the alumina generator are radiochemically pure as was checked by their half-lives determination. No contamination due to thorium-234 or any other descendant from the natural uranium series was observed.

The protactinium generator can supply carrier-free protactinium-234m in high activity to be used for the dead-time determination and is a convenient short radionuclide reservoir for training courses and preparation of tracers.

INTRODUCTION

The unique protactinium isotopes occuring in nature are protactinium-231 (32500 years), an uranium-235 descendant, and protactinium-234m (1.2 min.) and protactinium-234 (6.7 hours), both descendants from uranium-238. An artificial important radioisotope it is protactinium-233 (27 days) produced by neutron activation of natural thorium by the nuclear reaction Thorium-232 (n,gama)-thorium-233 and built up by Thorium-233 beta decay. Protactinium-233 is used as tracer and has enormous importance as the uranium-233 precursor, an artificially prepared fissil nuclide.

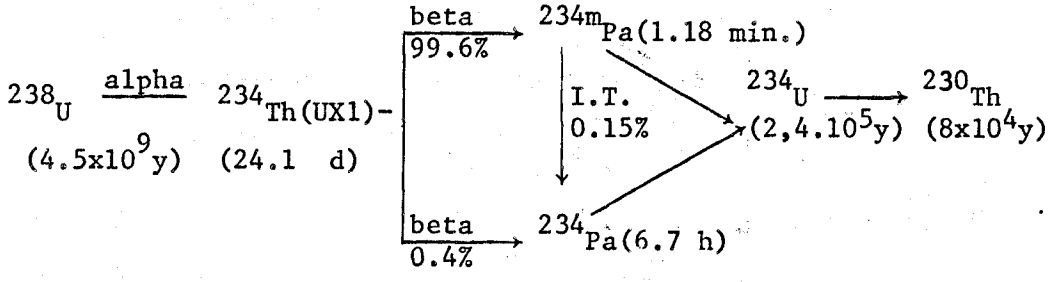
The short-lived natural radioisotopes protactinium-234m (1.2 min.) and protactinium-234 (6.67 hours), descendants from the 24.1 days thorium-234 (UX1) are valuable for radiochemical experiments, as for instance short-half-life and dead-time measurement, desintegration and genetic related radioisotopes studies, as radioactive growth and transient equilibrium, and as tracer (protoactinium-234) as well.

Only a few papers have been published concerning the separation of protactinium-234m, since it requires a very fast procedure. No convenient fast technique has been published for the preparation of protactinium-234m.

The method here outlined describes a convenient and fast separation of both protactinium-234m and protactinium-234 from thorium-234. The method is extremely simple, requires no special reagents and permit these short radioisotopes to be milked repeatedly whenever desired. This milking is accomplished via a small generator where the radiothorium-234 is stored.

PROTACTINIUM-234m AND PROTACTINIUM-234

Both radioisotopes are genetically related to thorium-234 (UX1, 24.1 days):



Protactinium-234m (1.18 min.) as a short radioisotope has great interest for radiochemistry experiments (1-6) and for dead-time determination (6,7). Since it is a reasonable short lived

isotope the methods for its separation and preparation must be simple and fast.

The existing methods described in the literature for the separation of protactinium from thorium use paper chromatography and ion exchange, coprecipitation with zirconium phosphate, cupferron and benzoylphenylhydroxylamine[6], adsorption on MnO_2[8], and solvent extraction techniques. All suggested methods allow only an unique separation from thorium-234, that is, for a second separation it is mandatory to recompose the solution containing the thorium.

A NEW METHOD FOR THE SEPARATION OF PROTACTINIUM FROM THORIUM

The method here proposed offer a contribution to the protactinium chemistry, permiting to prepare a convenient protoactinium-234m and protactinium-234 generator. The separation of protactinium from thorium is extremely simple, does not require specific organic reagents and serve as a protactinium source from which radioprotactinium can be milked repeatedly at any desired moment.

No rapid method for repeatedly separation of short-lived-protactinium has been reported in the literature.

A RADIPROTACTINIUM GENERATOR

Once the thorium-234 was firmly retained on an alumina column (6 mm i.d. having 2 ml Al_2O_3), as yet described[9] and as it is well known that protactinium forms a very stable anionic complex with F^--ion (PaF_7^{--}), it was reasonably understandable that such a behavior could permit the elution of radioprotactinium (234m and 234) from the alumina column by dilute hydrofluoric acid. The author's experiments led to the conclusion that the radioprotoactinium accumulated by the thorium-234 decay it is easely washed

out from the column with dilute HF. It was demonstrated that this small generator can be used as a radioprotactinium source from which these short radioisotopes can be eluted many times repeatedly. A great number of successive protactinium-234m and protoactinium-234 elutions were performed with 0.2M HF without contamination of thorium-234 parent.

Once the thorium-234 is firmly held by the Al_2O_3 column and observing a period of several hours for the longest lived protactinium-234 isotope to be accumulated in, the first volume of elutrient (0.2M HF) remove a protactinium-234 and protoactinium-234 mixture. So, for the preparation of protactinium-234 a period of several hours should be observed for its accumulation into the column, being then eluted along with protactinium-234m with the first 5-10 ml of 0.2M HF. This can be seen on Fig. 1. A 6 mm i.d. column having 2 ml of Al_2O_3 was used, each curve obtained using a 3 ml 0.2M HF as elutrient. Curve A shows the decay of protactinium-234m plus protactinium-234 compositive curve (tail). Following the decay of this tail (Fig. 1, curve C), it led to the conclusion of existence of a 6.7 hours (protactinium-234) radioisotope. In these experiments the samples were gamma counted using 3ml of eluate into a plastic vial. Continuing to elute the same column that has been observing a several hours build-up period for the ingrowth of radioprotactinium and accumulated some protactinium-234, after a 10 to 15 ml of 0.2M elution, the accumulated longest protactinium-234 was washed out. From this moment on the column can be repeatedly eluted after each one to five minutes, the decay curves being a straight line over-8-10 half--lives, since only protactinium-234m it is predominantly present, no sufficient time was observed for the ingrowth of protactinium--234. If desired, the samples can be beta counted using a G.M. tube. In this case a 80 to 100 mg/cm^2 aluminum absorber can be used between the samples and the G.M. tube, only the beta particles of protactinium-234m being counted.

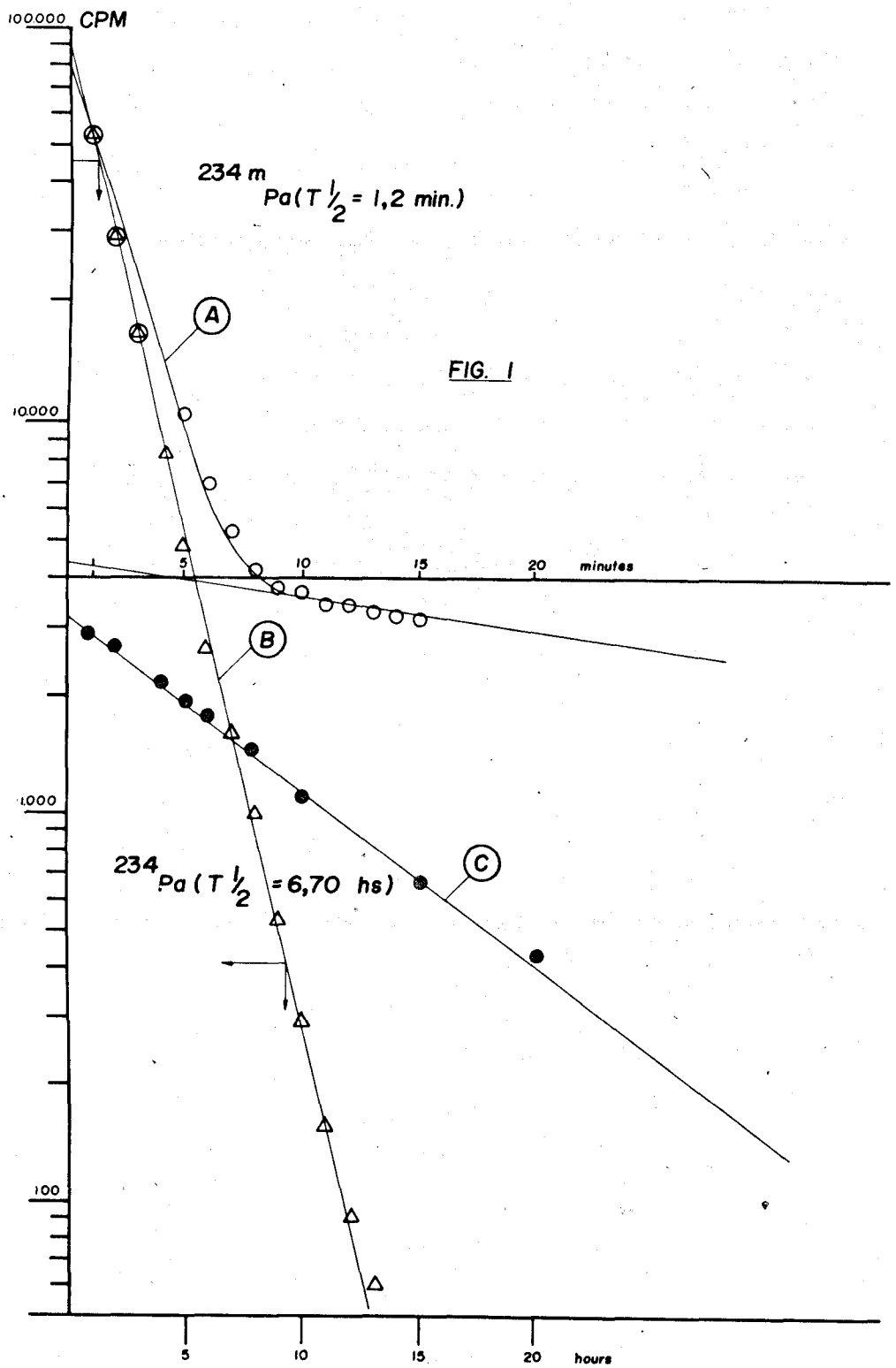

100.000 CPM
234 m
Pa (T 1/2 = 1,2 min.)
A
10.000
1
5
10
15
20
minutes
B
1.000
234 Pa (T 1/2 = 6,70 hs)
C
100
5
10
15
20
hours

FIG. 1

The radioisotopes protactinium-234m and protactinium-234 obtained by the described method are radioactively pure, without contamination of thorium-234 parent, as can be seen by the decay curves (Fig. 1, curve B). Half-lives varying from 1.18 to 1.20 minutes for protactinium-234m and of 6.7 hours for protoactinium-234 were found using only the graphic plot method.

CONCLUSION

The protactinium generator here described allows a clean radiochemical separation of protactinium from thorium, from which the short-lived radioisotopes protactinium-234m and protactinium-234 could be easely prepared. This generator allows to obtain a short-lived carrier-free radioisotope (protactinium-234m) at sufficiently high activity to be used for dead-time counting determination. Protactinium is eluted from the small generator simply by washing the column with 0.2M HF at room temperature.

This generator has been used for classroom demonstration on radiochemistry and nucleonics training, each student eluting and determining the protactinium half-life in a safe and very convenient manner. This protactinium source is being used for half-live, and growth determination of genetically related radioisotopes, with the advantage of being the parent of a reasonable long-lived isotope (thorium-234, 24.1 days).

RESUMO

Os radioisótopos naturais de meias vidas curtas, protactínio-234m (1,18 min.) e protactínio-234 (6,67 h), descendentes do tório-234 (UX_1, 24 dias), são valiosos para experiências radioquímicas, como por exemplo; determinação de meia vida e tempo morto, estudos de desintegração em radioisótopos genèticamente ligados, bem como traçador (protactínio-234).

O método aqui descrito permite uma separação conveniente e rápida de ambos, protactínio-234m e protactínio-234. O método é extremamente simples, não requer reagentes especiais e permite sua obtenção em qualquer momento desejado.

O método é baseado na sorpção de tório-234 de uma solução contendo 0,3M HF sôbre uma pequena coluna de alumina, da qual o radioprotactínio pode ser eluído quando desejado. Tório-234 é firmemente retido na alumina enquanto, protactínio-234m e protactínio-234 podem ser eluidos muitas vêzes sucessivamente, por simples eluição com HF 0,2-0,3M. Tório-234 é separado diretamente de solução de nitrato de uranilo (100 g/l em U_3O_8), contendo 0,3M HF, por percolação na coluna de alumina (2 ml de Al_2O_3). Após a sorpção do tório-234 o pequeno gera-

dor está pronto para fornecer protactínio-234m que pode ser eluido cada 1-5 minutos (para o crescimento do protactínio-234m) com 1 a 3 ml de HF 0,2-0,3M.

O protactínio-234m e protactínio-234 eluídos do gerador (alumina) são radioativamente puros, como foi verificado pela determinação das meias vidas. Não foram observadas contaminações devidas a tório-234 ou qualquer outro descendente da série natural do urânio.

O gerador de protactínio pode fornecer protactínio-234m, livre de carregador em atividade suficientemente alta para ser usado na determinação de tempo morto e é reservatório conveniente de radioisótopos de meias vidas curtas para cursos de treinamento e preparação de traçadores.

RÉSUMÉ

Les radioisotopes naturels qui ont une demi-vie courte, tels que le protactinium--234m (1,18 minutes) et le protactinium-234 (6,67 heures) descendant du thorium-234 (UX_1,24 jours), sont utils pour les expériments radiochimiques, par ex: pour la détermination de la demi-vie et de temps mort, pour les études de désintegration de radioisotopes génétiquement liés, et comme traceur (protactinium-234).

L'auteur décrit une séparation convenable et rapide du protactinium-234m et du protactinium-234. La méthode est simple, n'utilise par des réactifs spécials et permet l'obtention des radioéléments au moment désiré.

Aprés fixation du thorium en solution 0,3M HF, sur une colonne d'alumina, le protactinium-234m et le protactinium-234 sont elués sucessivement avec HF 0,2 - 0,3M.

Le thorium-234 est séparé directement d'une solution de nitrate d'uranyle (100 g/l em U_3O_8) contenant 0,3M HF, par passage dans une colone d'alumina (2 ml de Al_2O_3). Aprés fixation du thorium-234, le petit générateur est prêt pour eluer le protactinium, à chaque 1--5 minutes, (pour la croissance du Pa-234m) avec 1 à 3 ml de HF 0,2 - 0,3M.

La pureté radioactive a été verifié par determination des demi-vie et on n'a pas trouvé contamination par le thorium ou par d'autres descendents de la série naturelle de l'uranium.

Le protactinium-234msans entraineur a une activité suffisante pour la determination de temps mort; le générateur est aussi un reservoir convenable de radioisotopes à demi-vie courte pour l'enseignement et préparation de traceurs.

BIBLIOGRAPHY

(1) R.T. Overman and H.M. Clark Radioisotopes Techniques, Mac Graw-Hill Book Inc., New York, 1960 - p.326.

(2) A.H. Booth, J. Chem. Educ., 28, 144 (1951)

(3) G.R. Choppin, Experimental Nuclear Chemistry, Prentice ... Hall, 1961, p. 151

(4) J. Braunstein and R.H. Young, J. Chem.Educ. 38, 31 (1961)

(5) W. Seelmann-Eggebert, C. Keller and C. Zundel,Radiochemische Demonstrationsversuche, KPK 41, Kernforschungszentrum Karlsrure, 1961, p. 31-38.

(6) O. Cristallini and J. Flegenheimer, "Separación de Pa-234m

(UX2) como práctica de laboratório en la enseñanza de radioquímica. Informe nº 89, Comisión Nacional de Energia Atômica, Buenos Aires, 1963.

(7) G.A. Brinkman, "The dead time of a G.M. Counter Tube", Radiochimica Acta 2, 41-46 (1963)

(8) L.I. Katzin and R.W. Stoughton, J. Inorg. Nucl. Chem., 3 , 229 (1956)

(9) Alcídio Abrão, Chromatographic Separation and Concentration of Thorium and Rare Earths from Uranium using Alumina-Hydrofluoric Acid. Preparation of Carrier-Free Radiothorium and Contribution to the Fission Rare Earths. Radiation and ... Isotope Technology in Latin America Development, American Nuclear Society, San Juan, Puerto Rico - May - 1969 - PRNC-135 pg. 440