RADIOCHEMICAL SEPARATION OF THALLIUM FROM THORIUM BY ANION EXCHANGE RESIN
A ^{208}Tl reservoir

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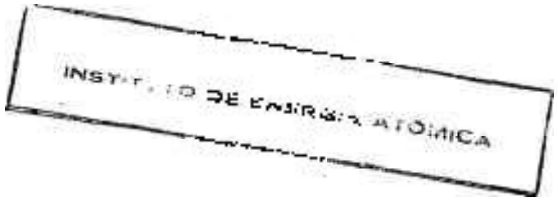

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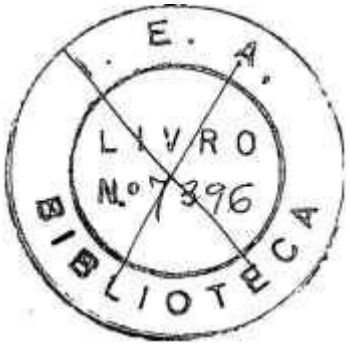

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Êste trabalho apresenta um método símples e rápido para a separação de Tl-208 (3,1 min.) a partir de soluções de tório. O procedimento, o qual faz uso de técnica rápida de separação de radioisótopos, possibilita a separação do Tl-208 em menos de um minuto e se presta para várias demonstrações em cursos de radioquímica, p.ex. determinação de meia vida, relações genéticas entre radioisótopos, equilíbrio transiente, etc.

O método se baseia no fato de ser o cloreto complexo de bismuto fortemente fixado por resina aniônica (forma clorídrica) enquanto o tálio é eluído com ácido clorídrico diluido.

O procedimento dispensa o uso de carregadores de bismuto e de tálio e usa uma coluna contendo apenas um mililitro de resina, na qual é percolada uma solução de cloreto de tório (100 g/l). A coluna é lavada com ácido clorídrico para eliminar o tório e o tálio é eluido no momento desejado com HCl 1M. A coluna-reservatório de Tl-208 possibilita muitas eluições do radioisótopo, decaindo com a meia vida do Bi-212 (60,5 min.).

A meia vida do Tl-208 foi determinada pelo método das contagens acumulativas (integral plot), encontrando-se $T_{\frac{1}{2}} = 3,17 \pm 0,06$ minutos. A pureza radioquímica do Tl-208 é maior que 99,5%.

SOMMAIRE

Ce travail présente une méthode simple et rapide pour séparer le thallium-208 formé de solutions de thorium. Le procédé, qui utilise la technique de séparation rapide de radio-éléments, possibilite la séparation du Tl-208 en moins d'une minute, et sert à faire des demonstrations dans des cours de radiochimie, par exemple, détermination de demi-période, rélations génétiques entre radioéléments, équilibre transitoire, etc.

La méthode tient en compte que le chlorure complexe du bismuth est fortement fixé sur une résine échangeuse d'anions (forme chloridrique) tandis que le thallium est élué avec de l'acide chloridrique dilué. Le procédé n'utilise q'une colonne contenant 1 ml de résine échangeuse d'anions, à travers laquelle on passe une solution de chlo-

La colonne est lavée avec de l'acide chloridrique pour éliminer le thorium; le thallium est élué au moment désiré, avec de l'acide chloridrique 1M.

La colonne réservoir de Tl-208, qui décroît avec la demi-période du Bl-212 (60,5 min) possibilite plusieurs élutions du radioélément.

La demi-période du Tl-208 a été déterminé par la méthode des comptages cumulatifs (integral plot), et on a trouvé une demi-période de 3,17 ± 0,06 minutes. La pureté radiochimique du Tl-208 ainsi obtenu est supérieure a 99,5%.

SUMMARY

The experiment outlined in this paper describes a single procedure for isolating the short half-life thallium-208 (3.1 min.) from common thorium salts. This experiment illustrates a number of important principles and techniques such as the use of the natural radioactive series as a source of suitable and inexpensive radioisotopes, the use of an anionic exchange resin as a speeding up procedure for radiochemical separation, the measurement of short half-lives, genetic relationships, transient equilibrium, etc.

The method described is based upon the principle that the anionic chloride bismuth complex is strongly held by an anionic exchange resin (chloride form), while thallium can be eluted from the resin with dilute hydrochloric acid.

The method makes no use of bismuth and thallium carriers.

The thorium chloride solution (100 g/l Th) is percolated through a small column containing only one ml of resin. After washing the thorium with HCl the Tl-208 is eluted at the desired moment with 1.0M HCl. This reservoir allows many elutions of Tl-208 and decays with the half-life of the parent Bi-212 (60.5 min).

The half-life of Tl-208 was determined by the "integral plot" method. The average value encountered was 3.17±0.06 min. The Tl-208 has a radiochemical purity greater than 99.5%.

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Radiochemical Separation of Thallium from Thorium by Anion Exchange Resin

A ^{208}Tl reservoir

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The experiment outlined in this paper describes a single procedure for isolating the short half life thallium-208 (3.1 min) from common thorium salts. This experiment illustrates a number of important principles and useful techniques such as the use of the natural radioactive series as a source of suitable and inexpensive radioisotopes, the use of an anionic exchange resin as a speeding up procedure for radiochemical separation, the measurement of short half lives and the preparation of a radioisotope reservoir, from which the 3.1-min ^{208}Tl can be eluted many times successively.

A classical procedure (*1*) suggests that ^{208}Tl may be obtained by collecting the recoil atoms of ThC″ (^{208}Tl) resulting from the alpha-ray transformation of ThC (^{212}Bi), on a negatively charged plate. It seems that no rapid method for isolating ^{208}Tl has been reported in the literature.

The method now described is a one-step procedure; the separation of radiothallium is simple, clean and rapid, taking less than 1 min to carry out.

The procedure is based upon the principle that the anionic chloride bismuth complex is strongly held by an anionic exchange resin (chloride form), while thallium can be eluted from the resin with dilute hydrochloric acid. Kraus, Nelson, and Smith (*8*) have shown that Tl(III) in HCl solution is held strongly by an anionic exchange resin while Tl(I) is only weakly held. Presumably, therefore, in the method here described, the eluted Tl is in the (I) form. The column (1 ml of resin) can be "milked" each 5–10 min and supply ^{208}Tl for many experiments during a day. The growth of thallium into column is rapid and the transient equilibrium

$$^{212}Bi\ (60.5\ min) \xrightarrow{\beta} {}^{212}Po\ (0.3\ \mu sec) \xrightarrow{\alpha} {}^{208}Pb\ (stable)$$
$$\qquad\qquad\qquad\quad \rightarrow {}^{208}Tl\ (3.1\ min) \xrightarrow{\alpha}$$

is reached quickly. It is not necessary to use carriers of bismuth or thallium. The column acts as a reservoir for ^{208}Tl extraction and the capacity of the reservoir decays with the 60.5-min half life of ^{212}Bi.

A few experiments have been described using radioisotopes of shorter than 10-min half life. Jones (*2*) suggested the use of ^{207m}Pb (0.8 sec) for this kind of experiment. This short-life isotope was artificially prepared by the reaction ^{207}Pb (p,n) ^{207}Bi in a cyclotron. ^{207m}Pb is the decay product according the scheme:

$$^{207}Bi \xrightarrow[8\ yr]{e.c.} {}^{207m}Pb \xrightarrow[0.8\ sec]{gamma} {}^{207}Pb\ (stable)$$

The ^{207}Bi was strongly held by an anion exchange resin and its lead daughter was continuously eluted with hydrochloric acid. This milking elution allows the repetition of the half-life determination as many times as desired. The papers of Booth (*3*) and Braunstein and Young (*4*) present the isolation of ^{234}Pa (1.14 min) from thorium and its use for the half-life determination.

One milliliter of strong anion exchange resin (Nalcite SAR, 30–50 mesh) was poured into the stem of a small glass funnel containing a plug of glass wool to support the resin thus forming a column of 5-mm diameter. The resin was conditioned by washing with 10 ml of 1.0 *M* HCl.

A thorium chloride solution (100 ml, 10 g of Th) was delivered dropwise from a separatory funnel to the column at a rate of about 3 ml per min. The resin was washed with 10 ml of 1 *M* HCl, 10 ml of 0.01 *M* HCl, and 5 ml of 1% fresh alcoholic solution of dimercaptothiodiazol (2,5-dimercapto-1,3,4-thiodiazol or bismuthiol) slightly acidified with HCl and finally with 5 ml of 1.0 *M* HCl. The radioactive resin was transferred with dilute HCl to another column containing 0.5 ml of "free" anionic resin conditioned with 5 ml of 1.0 *M* HCl, 5 ml of 0.01 *M* HCl, and 2 ml of 1% alcoholic bismuthiol. After waiting for 5–10 min, time sufficient for reaching the transient equilibrium, the resin was eluted with 3 ml of 1.0 *M* HCl into a plastic vial and the vial inserted quickly into the counter.

The total gamma activity was determined with a single channel pulse analyzer (Inst. Energia Atômica), a Linear Amplificator "Technical Measurement Corp." 4L-4A, connected to a scaler type 181-A, and a sodium iodide-thallium activated scintillation crystal, model XT-100 (both from Nuclear Chicago Corp.). The total gamma activity was counted during 1 min each 2 min and the half life of ^{208}Tl was determined graphically on a semilog paper after correction for the background count (Fig. 1, curve 2); the disintegration rate was assumed to be the activity at the midpoint of the time of observation (*5*). A more precise half life determination was made by the "integral plot" method (*6*), the accumulated counts being registered at exactly 30-sec intervals for a period of 20 min and at 60-sec intervals for an additional 20 min (Fig. 1, curve 1). The accumulated count values were corrected only for the background contribution and the $C_\infty - C_T$ was plotted against time. The points followed a straight line up to 7 periods and the half life thus found is in agreement with the theoretical values given in the literature. The half life was calculated from the relation

$$t_{1/2} = \frac{0.693\,t}{\ln(C_\infty - Ct)}$$

where C_∞ is the total number of counts at infinite time and C_T is the total number of counts accumulated at the time t. The average value of $t_{1/2}$ calculated from 47 data points was 3.17 ± 0.06 σ (σ = standard deviation from average).

If desired, the half-life measurement could be done using a Geiger tube connected to a scaler. It is possible to retain the eluted ^{208}Tl activity in a strong cation exchange resin (H-form, 0.5 ml) or deposit it in some granules of metallic zinc (30 mesh); the resin or zinc is spread in a thin layer on a counting planchet and counted.

Discussion

Nelson and Kraus (*7*) studied the distribution coefficients of lead and bismuth in hydrochloric acid solutions and strong anion exchange resin, concluding adsorbed by the resin while the lead was not significantly adsorbed.

After the percolation of thorium chloride solution and washing with 1.0 *M* HCl, a simple elution of the small column with 1.0 *M* HCl furnishes a ^{208}Tl activity and typical composite decay curve (Fig. 1, curve 3). The ^{208}Tl is slightly contaminated with some activity ascribed to the parent ^{212}Bi and ^{212}Pb. Subtraction of curve B from curve A yields curve C, whose 3.1-min half life identifies it as the decay of ^{208}Tl. The tail of the curve is due principally to ^{212}Bi and some ^{212}Pb.

A cleaner decay curve of ^{208}Tl can be obtained by strongly holding the bismuth and lead activities in the resin. This can be achieved by "developing" the resin with an alcoholic dimercaptothiodiazol solution, after which the resin is washed with 1.0 *M* HCl to

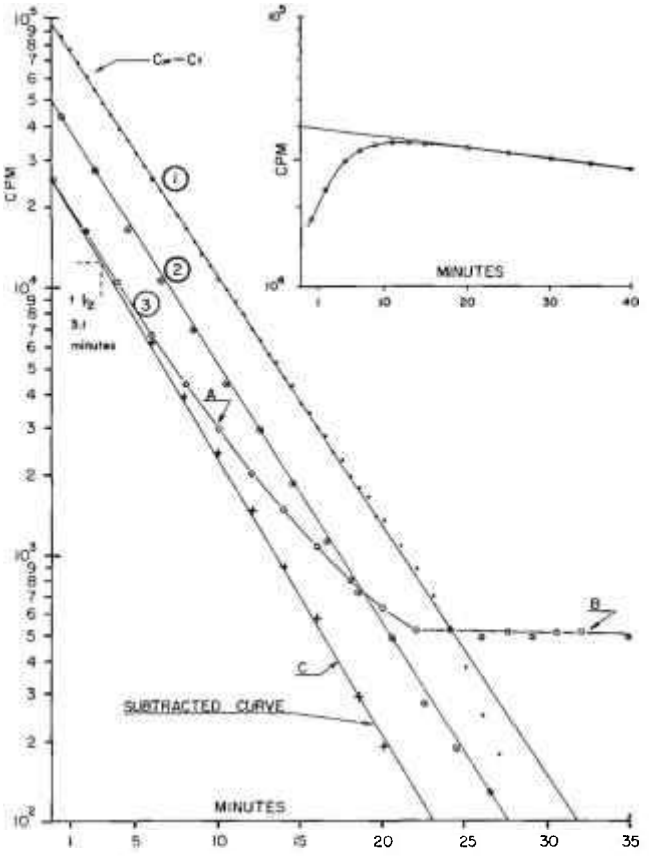

Figure 1.

remove the total thorium. Dimercaptothiodiazol is a specific reagent for lead and bismuth and precipitates both cations (when in macrochemical concentrations) from their acid solution. The use of this reagent to wash the anionic resin containing the carrier-free activity of ^{212}Bi (and some ^{212}Pb) proved successful; the ^{208}Tl is eluted with 1.0 *M* HCl practically without lead and bismuth contamination (Fig. 1, curves 1 and 2). Now the ^{208}Tl fraction is obtained with a purity greater than 99.5% (the points following a straight line over 7–8 half lives) as compared with the 95% ^{208}Tl purity when the column was not "developed"

will remain; but this amounts to less than 0.5% of the original.

Additional experiments involving the growth of ^{208}Tl into the resin also may be performed by counting the resin after washing with dilute HCl. Figure 1 shows a typical growing curve where the transient equilibrium was attained. Following the decay of the resin activity it can be shown that ^{212}Bi is the predominant activity, with little contamination of parent ^{212}Pb.

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