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CHEMICAL SEPARATION OF THALLIUM FROM MERCURY BY EXTRACTION CHROMATOGRAPHY

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Thallium-201 was obtained by irradiating natural mercury with protons from IPEN's CV-28 Cyclotron. The chemical separation process chosen to separate thallium from mercury was an extraction chromatography technique. It consists on the passage of aqueous solutions (mobile phase), containing the elements that will be separated, through a glass column packed with an inert powder (support) saturated with the extractant (stationary phase).

The radiopharmaceutical thallium-201 chloride ($^{201}TlCl$) is used in nuclear medicine to identify myocardial ischemia or myocardial infarct. It shows adequate nuclear properties for myocardium images. Thallium-201 was obtained by irradiating natural mercury with protons from IPEN's CV-28 Cyclotron. The chemical separation process chosen to separate thallium from mercury was an extrac-

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tion chromatography technique. It consists in the passage of aqueous solutions (mobile phase), containing the elements that will be separated, through a glass column packed with an inert powder (support) saturated with the extractant (stationary phase). The $^{203}Hg^{2+}$, $^{201}Tl^{+}$ and $^{201}Tl^{3+}$ solutions were prepared in 4 to 8N nitric medium and in 0.5 to 4N hydrochloric medium. These solutions were percolated through the columns containing Voltalef 300 LD powder (polytrifluorochloroethylene) impregnated with TBP (tri-n-butylphosphate)/cyclohexane. The $^{201}Tl^{3+}$ was almost totally retained when percolated in hydrochloric solution, and $^{203}Hg^{2+}$ passed to the effluent. Afther that thallium was eluted from the column in two ways: first, with solutions of hydrazine dihydrochloride of different concentrations heated at a temperature between 35 and 40 ^{o}C and second, with distilled water after Tl^{3+} reduction to Tl^{+} with a solution of 10% hydrazine dihydrochloride prepared with 2N NaOH at 35 to 40 ^{o}C. The elution yields were about 94% in both cases.

INTRODUCTION

Thallium was separated from mercury utilizing the extraction chromatography technique. It is a rapid and selective separation method, where the complexing agent is deposited on a carrier material such as fine-grained powder and the aqueous solution is percolated rapidly through this material. The Voltalef powder was impregnated with the organophosphorus compound TBP/cyclohexane. Columns of optimized length and diameter were made. The function of this compound was to separate Tl from Hg in a nitric or hydrochloric acid solution of suitable concentration. This method combines the main advantage

of solvent extraction, its high selectivity, with those of column techniques, their easy use and technical simplicity.

EXPERIMENTAL

Preliminary essays

Columns of glass with a height of 20 cm and internal diameter of 1 cm were packed with 2.0 g of Voltalef powder. The relation 2:1:1 between Voltalef powder:TBP:cyclohexane, according with Denig[1], was maintained for the support preparation. About 20 g of Voltalef powder was previously imbibed with 10 ml TBP/10 ml cyclohexane and dried at temperature between 30 and 35 °C for 24 h. Solutions containing, $^{203}Hg^{2+}$, $^{201}Tl^{+}$ and $^{201}Tl^{3+}$ were prepared in 4 to 8N nitric medium and in 0.5 to 4N hydrochloric acid medium, according to the results obtained by Weinreich[4].

The Hg was completely eluted from the column by washing with 200 ml of 2N HCl.

The Tl^{3+} was eluted from the column after its reduction to Tl^{+} with 25 ml of hot solution of 10% hydrazine dihydrochloride prepared with 2N NaOH.

Test of elution

The following solutions were tested for the elution of Tl:

1. Heated (30 to 35 °C; 35 to 40 °C; 40 to 45 °C and 45 to 50 °C) and
2. Non-heated (25 to 30 °C) solutions (25 ml) of 10% hydrazine dihydrochloride (A) and solutions (25 ml) of 10% hydroxylamine hydrochloride (B), both prepared with 2N NaOH.

3. Heated (35 to 40 ^{o}C) solutions (25 ml) of 5% hydrazine dihydrochloride prepared with 2N and 1N NaOH.
4. Heated (35 to 40 ^{o}C) solutions (25 ml) of 2% hydrazine dihydrochloride prepared with 0.5N NaOH, and
5. Water (30 ml) after reduction of Tl with 5 ml of heated (35 to 40 ^{o}C) solutions of 10% hydrazine dihydrochloride/2N NaOH.

These experiments started with ^{201}TlCl tracer solutions from the Atomic Energy Commission of Canada, kindly given to the Nuclear Medicine Center of São Paulo's University and with ^{203}HgCl tracer solutions obtained by irradiating HgO in the IEA-R1 Reator installed at IPEN-CNEN/SP. Later ^{201}Tl and ^{203}Hg were obtained in the CV-28 cyclotron installed at IPEN-CNEN/SP.

RESULTS AND DISCUSSION

Each result presented in the Tables and Figures is the average value obtained with the use of two columns, and each experiment was performed three times.

Tables 1 and 2 give the retention of $^{203}Hg^{2+}$, $^{201}Tl^{+}$ and $^{201}Tl^{3+}$, respectively, in the column when nitric and hydrochloric acid solutions were used. The results show that in nitric medium the retention of Hg^{2+}, Tl^{+} and Tl^{3+} is very low (1.3%; 1.6% and 2.3%) and that in hydrochloric medium the retention of Hg^{2+} is 2.0%, that of Tl^{+} 1.7%, while the retention of Tl^{3+} is 99%.

Figure 1 shows the elution curve of thallium. Apparently, about 20 ml of eluent was necessary to remove the Tl from the column, and the greater activity of the radioisotope was reached with 5 ml of hot solution of 10% hydrazine dihydrochloride/2N NaOH.

TABLE 1

Retention percentage of Hg^{2+}, Tl^{+}, Tl^{3+} in nitric acid solution with a column containing 2.0 g Voltalef powder imbibed with TBP/cyclohexane

Normality (N)	Retention (%)		
HNO_3	Hg^{2+}	Tl^{+}	Tl^{3+}
8	1.0	2.5	2.5
7	1.0	2.5	3.0
6	1.0	1.0	2.5
5	2.0	1.0	1.0
4	1.5	1.0	2.5

TABLE 2

Retention percentage of Hg^{2+}, Tl^{+} and Tl^{3+} in hydrochloric acid solution with a column containing 2.0 g Voltalef powder imbibed with TBP/cyclohexane

Normality (N)	Retention (%)		
HCl	Hg^{2+}	Tl^{+}	Tl^{3+}
4	2.0	2.0	99.0
3	2.0	2.0	99.0
2	1.5	2.0	99.5
1	2.0	1.5	99.0
0.5	2.5	1.0	98.5

Figure 2 presents the elution percentages of thallium using the solution of hydrazine dihydrochloride (A): 10% $N_2H_4 \cdot 2HCl$/2N NaOH, in different intervals of temperature. In Figure 3 the eluent for thallium was the solution of hydroxylamine hydrochloride (B): 10%

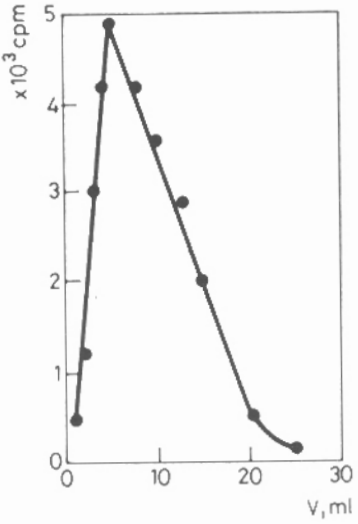

Fig. 1. Elution curve for ^{201}Tl from a 20 cm x 1 cm column at 2N HCl concentration. Eluent: hot 10% $N_2H_4 \cdot 2HCl$ solution in 2N NaOH; Flow rate: 2.0 ml min^{-1}

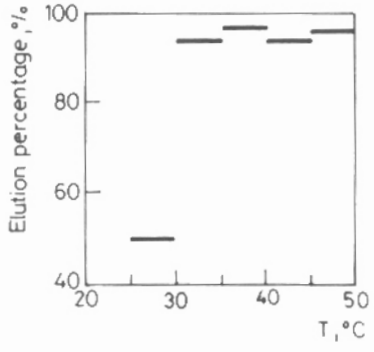

Fig. 2. ^{201}Tl elution percentage utilizing solutions of 10% hydrazine dihydrochloride in 2N NaOH in different temperature intervals.
A) 10% $N_2H_4 \cdot 2HCl$/2N NaOH

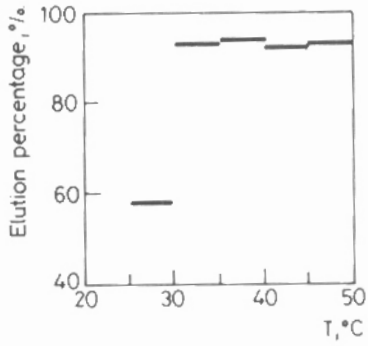

Fig. 3. ^{201}Tl elution percentage utilizing solutions of 10% hydroxylamine hydrochloride in 2N NaOH in different temperature intervals.
B) 10% $NH_2OH \cdot HCl$/2N NaOH

$NH_2OH \cdot HCl$/2N NaOH. The reducing solutions used for tal-thallium elution from the chromatographic columns showed the same behavior. About 94% to 97% of Tl was eluted when heated solutions were used and only 50% and 58% of Tl was eluted, respectively, when the solutions A and B were not heated.

Tables 3 and 4 give the elution percentage of thallium, respectively, utilizing solutions of different concentrations of the reducing agent (hydrazine dihydrochloride) and using distilled water after Tl^{3+} reduction to Tl^{+} with solutions of 10% hydrazine dihydrochloride prepared with 2N NaOH. The thallium elution percentage was about 94% with 5% hydrazine dihydrochloride prepared with 2N NaOH and 1N NaOH, and utilizing water after hydrazine reduction of thallium. The purpose of these experiments was to simplify the procedure for the transformation of the eluted hydrazine solution containing thallium-201 to thallium-201 chloride[3].

TABLE 3

^{201}Tl elution percentage with solutions of different reducing agent concentrations

Reducing agent	^{201}Tl elution, %
$N_2H_4 \cdot 2HCl$ 5%/NaOH 2 N	95.0
$N_2H_4 \cdot 2HCl$ 5%/NaOH 2 N	95.0
$N_2H_4 \cdot 2HCl$ 5%/NaOH 2 N	94.0
$N_2H_4 \cdot 2HCl$ 5%/NaOH 1 N	95.0
$N_2H_4 \cdot 2HCl$ 5%/NaOH 1 N	94.0
$N_2H_4 \cdot 2HCl$ 5%/NaOH 1 N	94.0
$N_2H_4 \cdot 2HCl$ 2%/NaOH 0.5 N	91.5
$N_2H_4 \cdot 2HCl$ 2%/NaOH 0.5 N	93.0
$N_2H_4 \cdot 2HCl$ 2%/NaOH 0.5 N	92.5

TABLE 4

^{201}Tl elution percentage with distilled water after Tl^{3+} to Tl^{+} reduction with hydrazine dihydrochloride solution

Reducing agent and water	^{201}Tl elution, %
$N_2H_4 \cdot 2HCl$ 10%/NaOH 2 N H_2O	94.0
$N_2H_4 \cdot 2HCl$ 10%/NaOH 2 N H_2O	94.0
$N_2H_4 \cdot 2HCl$ 10%/NaOH 2 N H_2O	93.5

CONCLUSION

Due to the fact that TBP stationary phases behave in good accordance with liquid-liquid extraction data, and according to the distribution coefficients of trace elements between 100% TBP and aqueous hydrochloric acid[2], good results were expected for the Tl/Hg separation process when utilizing the extraction chromatography technique with TBP. So, Tl was separated from Hg when perchlorated, in 2N hydrochloric solutions, through a glass column (20 cm x 1 cm) packed with 2.0 g of Voltalef powder impregnated with TBP/cyclohexane, in the proportion of 2:1:1 (powder:TBP:cyclohexane). $^{203}Hg^{2+}$ passed to the effluent and $^{201}Tl^{3+}$ was retained (99%). $^{201}Tl^{3+}$ was eluted from the column after its reduction to $^{201}Tl^{+}$ with the reducing agent (5% hydrazine dihydrochloride solutions prepared with NaOH 1N, heated at 35 to 40 ^{o}C) or it was eluted from the column with distilled water after its reduction ($^{201}Tl^{3+}$ to $^{201}Tl^{+}$) with solutions of 10% hydrazine dihydrochloride/2N NaOH heated to 35 to 40 ^{o}C. The thallium elution yields were about 94% in both cases, with easy transformation of the eluted solution into thallium-201 chloride.

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