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Radiochemical Separation of Thallium(I) Using Cerium(IV) Molybdate as an Ion-Exchanger

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ABSTRACT

A rapid procedure for the adsorption and radiochemical separation of thallium(I) has been developed employing cerium(IV) molybdate as an inorganic ion-exchanger. The adsorption of thallium(I) under various experimental conditions has been determined.

INTRODUCTION

During the last few years interest has grown with regards to the application of synthetic inorganic ion-exchangers for obtaining radiochemically pure elements from neutron irradiated targets (1). Many inorganic ion-exchangers have been synthesized and their use in various radiochemical separations explored (2, 3). The use of hydrated antimony pentoxide for the selective adsorption of sodium ions (4) has increased interest in the use of inorganic ion-exchangers in radiochemistry. A literature survey reveals that cerium(IV) molybdate has not been employed for the separation of Tl(I) from other elements.

The element thallium is present in biological and environmental samples in very low concentrations (5, 6), and so a method of high accuracy and sensitivity is required for its determination and separation. The present communication deals with a study of the development of a rapid and selective radiochemical separation procedure employing cerium(VI) molybdate as an ion-exchanger for the separation of Tl(I) from other elements. Thallium-204 was used as a tracer.

EXPERIMENTAL

Instruments and Reagents

Gamma-emitters were counted at their corresponding photopeaks on a NaI(Tl) well-type detector in conjunction with a single-channel pulse-height analyzer. Thallium-204 and other beta-emitters were counted on an end-window type G.M. counter in conjunction with a decade scaler, timer, and high-voltage unit.

All the chemicals used were of E. Merck or B.D.H. (AnalaR) grade. Thallium-204 and the other isotopes used were available from The Board of Radiation and Isotope Technology, Bhabha Atomic Research Centre, Bombay. A solution of Tl(I) (10 mg/mL) was prepared by dissolving an appropriate amount of thallium sulfate (B.D.H.) in distilled water. Metal-ion solutions of Co(II), Hg(II), Re(VII), Zn(II), Ca(II), Cd(II), Ir(IV), Pb(II), Na(I), K(I), Os(III), Cr(III), In(III), Sc(III), Au(III), Pt(IV), Sn(II), Sb(III), Te(IV), Ru(III), Eu(III), Fe(II), Mn(II), Se(IV), Cs(I), Ag(I), Zr(IV), Ba(II), and Rb(I) (10 mg/mL concentration) were prepared by dissolving their appropriate salts in distilled water containing acid wherever required. The strengths of the solutions were determined by the usual methods (7, 8).

Preparation of Cerium(IV) Molybdate

Cerium(VI) molybdate ion-exchanger was prepared by the procedure given by Shrivastava et al. (9). Ceric sulfate (0.05 M) was mixed with 0.1 M ammonium molybdate at room temperature in a Ce/Mo mixing ratio of 0.5. The pH of the mixture was adjusted to zero. The molybdate solution was added to the ceric solution with constant stirring. The precipitate in contact with the liquid was left overnight at room temperature. It was then filtered, washed with dilute sulfuric acid, then washed with distilled water, and dried. It was converted to the hydrogen form by immersion in ~1 M HNO_3 for 48 hours, and then it was washed with distilled water and dried in air.

Composition of Cerium(IV) Molybdate

One hundred milligrams of cerium(IV) molybdate was dissolved in 4 M HCl. The solution was warmed and diluted to 100 mL. Cerium was estimated as the oxide, and molybdenum was estimated gravimetrically by the oxine method (8). On the basis of chemical analysis, thermal studies, and infrared spectra, a tentative formula of $Ce(OH)_2 \cdot (HMoO_4)_2 \cdot 5H_2O$ was suggested by Shrivastava et al. (9). The values obtained are in agreement with those reported in the literature in Table 1.

TABLE 1
Analysis of Cerium(IV) Molybdate Ion-Exchanger

	Observed	Expected
Cerium(IV)	22.79%	23.91%
Molybdenum(VI)	32.26%	32.74%

RESULTS AND DISCUSSION

Adsorption of Thallium(I)

One hundred milligrams of cerium(IV) molybdate exchanger was taken and 1.0 mg Tl(I) carrier labeled with ^{204}Tl was added to the exchanger for a contact time of 5 minutes. The total volume of the solution was adjusted to 10 mL with distilled water. The reproducibility of the adsorption was tested by evaluating the value five times.

Ion-Exchange Capacity

The ion-exchange capacity was determined by shaking intermittently 500 mg of the exchanger with 10 mg Tl(I) ions at a pH of 6.0. The H^+ ions liberated were estimated by titrating an aliquot with standard NaOH solution. The pH titration of the ion-exchanger was performed by the method of Topp and Pepper (10). The pH titration curve is given in Fig. 1. The value of the exchange capacity was found to be 0.723 milliequivalents/g.

Effect of the Amount of Cerium(IV) Molybdate Exchanger

The adsorption studies were carried out at pH 6.0, as mentioned above, and the amount of the exchanger was varied between 50 and 250 mg. Table 2 reveals that the adsorption of Tl(I) increased from 93% at a 50-mg amount of the exchanger to 96% at a higher amount. Hence, 100 mg of cerium(IV) molybdate ion-exchanger was used in all further adsorption studies.

Effect of pH and Time of Contact

The adsorption values at different pH levels revealed that maximum adsorption occurred at pH 6.0, as shown in Table 3. From Table 4 it can be seen that when the contact time was varied between 1.0 and 10.0 minutes, maximum adsorption was observed at 5.0 minutes. Thallium(I) was found to remain adsorbed on the exchanger for more than 24 hours.

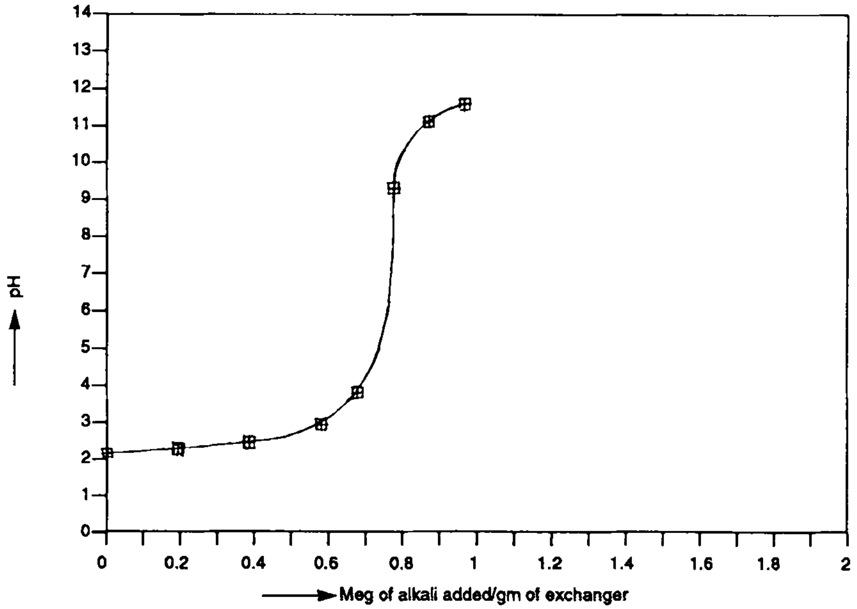

FIG. 1 pH titration curve for cerium(IV) molybdate.

Separation of Thallium(I) from Other Elements

The adsorption of different cations on cerium(IV) molybdate under the experimental conditions mentioned above was studied. One milligram of the metal ion along with its tracer was mixed with 1.0 mg Tl(I) to a total volume of the mixture of 10 mL by the addition of distilled water. The pH

TABLE 2
Effect of the Amount of Cerium(IV) Molybdate Ion-Exchanger on the Adsorption of 1.0 mg Tl(I) in the Batch Process (time of contact, 5 minutes; pH, 6; total volume of the solution, 10 mL)

Amount of exchanger (mg)	Adsorption (%)
50	93.18
100	96.64
150	96.70
200	96.86
250	96.46

TABLE 3

Effect of pH on the Adsorption of 1.0 mg of Tl(I) on Cerium(IV) Molybdate Ion-Exchanger (amount of exchanger, 100 mg; total volume of solution, 10 mL; time of contact, 5 minutes)

pH value used	Adsorption (%)
1.0	77.38
2.0	81.51
3.0	84.21
4.0	90.46
5.0	95.50
5.5	95.78
6.0	96.81
6.5	96.73
7.0	96.55
8.0	92.04

of the solution was adjusted to 6. One hundred milligrams of cerium(IV) molybdate was added. The mixture was stirred for 5 minutes and centrifuged. The percentage adsorption of the metal ion was calculated by measuring the radioactivity (tracer technique). As shown in Table 5, the adsorption process was studied with and without carriers. As expected, the percentage adsorption of the other elements was greater without a carrier than with a carrier. Tin(IV), Sb(V), Cr(III), Ru(III), Zr(IV), Eu(III), Fe(III), and In(III) formed a hydroxide precipitate because the pH of the solution was 6.0. Tungsten(VI) and P(V) interacted with the ion-exchan-

TABLE 4

Effect of Time of Contact on the Adsorption of 1.0 mg of Tl(I) on Cerium(VI) Molybdate Ion-Exchanger (amount of exchanger, 100 mg; total volume of solution, 10 mL; pH, 6)

Time of contact (min)	Adsorption (%)
2.0	89.16
3.0	89.25
4.0	90.86
5.0	97.29
6.0	96.38
7.0	96.64
10.0	96.06

TABLE 5
Percentage Adsorption of Other Elements on Cerium(IV) Molybdate (amount of exchanger, 100 mg; total volume of solution, 10 mL)

Adsorption (%)	Elements	
	Without carrier	With carrier (1 mg)
<1	Hg^{2+}, Re^{7+}	Co^{2+}, Zn^{2+}, Hg^{2+}, Ca^{2+}, Cd^{2+}, Sc^{3+}, Ir^{4+}, Re^{7+}, Sn^{2+}, Cr^{6+}, Au^{3+},[b] Fe^{2+}
1–10	Co^{2+}, Zn^{2+}, Ca^{2+}, Cd^{2+}, Ir^{4+}, Pd^{2+}, Na^{+}, Os^{3+}, Cr^{3+}, In^{3+}	Pd^{2+}, Na^{+}, Os^{3+}, Au^{3+}, K^{+}, Mn^{2+}, As^{3+}, Pt^{4+},[b] Sb^{3+},[a] Sb^{5+},[b] Te^{4+},[a] As^{5+}, Ag^{+},[a] Ru^{3+}, Zr^{4+}, Eu^{3+},[b] Fe^{3+},[b] P^{5+}, In^{3+}[b]
10–50	Sc^{3+}, Au^{3+}, Pt^{4+}, Sn^{2+}, Sn^{4+}, Sb^{3+}, Sb^{5+}, Cr^{6+}, Te^{4+}, Ru^{3+}, Eu^{3+}, Fe^{3+}, Fe^{2+}, Mn^{2+}	As^{5+}, Te^{4+}, Fe^{2+}, Rb^{+}, Cu^{2+}, La^{3+}
>50	K^{+}, Se^{4+}, Cs^{+}, Ag^{+}, As^{3+}, As^{5+}, Zr^{4+}, Ba^{2+}, Rb^{+}, Cu^{2+}, La^{3+}	Sb^{3+}, Cs^{+}, Ag^{+}, Ba^{2+}, Se^{4+}

[a] Removed by washing the ion-exchanger.

[b] Forms precipitate.

ger. The hydroxides were centrifuged and removed prior to the adsorption of thallium ions on the ion-exchanger. The adsorption of ferrous ions was improved by washing the exchanger with EDTA, and that of Au(III) was improved to less than 0.8% by washing the exchanger with 50 mg thiourea. Potassium ions were adsorbed to less than 4.02% by washing the exchanger with hot water. Adsorption of Sb(III) was decreased to less than 2.7% by employing 20 mg iodate. Similarly, the adsorbed Ag(I) ions were decreased by washing the ion-exchanger with 50 mg thiosulfate. The adsorption of As(V) was decreased with one wash containing 20 mg S^{2-} ions, and that of Te(IV) was decreased by precipitating it with SO_2 water prior to adsorption. The coadsorption of Cu(II) and La(III) was prevented by washing the exchanger with dilute NH_3 and 20 mg F^- ions, respectively.

CONCLUSIONS

From the above discussion it is apparent that the separation procedure is quick and sufficiently selective for separating thallium(I) from a large number of activities induced on thermal neutron irradiation of complex matrices.

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