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Separation of Carrier-Free ^{99m}Tc from ^{99}Mo and ^{144}Pr from ^{144}Ce over a Column of Zirconium Arsenate

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Abstract

Carrier-free ^{99m}Tc and ^{144}Pr activities were separated from ^{99}Mo and ^{144}Ce, respectively, by using simple chemical procedures and a column of zirconium arsenate. A crystalline variety of zirconium arsenate was prepared by mixing a proportionate quantity of sodium arsenate solution in water with a solution of zirconium oxychloride in 2*N* HCl at 70°C. The ratio of zirconium:arsenate was 1:2. γ-Ray spectra of the separated ^{99m}Tc, and β-decay studies of ^{144}Pr showed that both were of high radionuclidic purity. The overall separation processes were simple, clean, and in each case required less than half an hour, with quantitative yield. After separation, the daughter activities were allowed to form in the column, so that it was possible to obtain these freshly formed species by eluting the column with suitable reagents.

INTRODUCTION

Zirconium arsenate belongs to the group of acidic salts of quadrivalent metals, the most extensively studied group of synthetic ion exchangers. The crystalline zirconium arsenate $Zr(HAsO_4)_2 \cdot H_2O$ has been shown (*1*) to be isomorphous with α-zirconium phosphate. The parameters of monoclinic crystals of both the salts are quite similar, and the average As—O and Zr—O distances are close to those in the α-zirconium phosphate. Though problems on ion-exchange separations have not been performed extensively with zirconium arsenate, it was suitably used (*2*) for concentrating cesium from a mixture of alkali metals and some other multivalent cations. It was expected that it should also be thermally stable, withstand intense radiation, show appreciable ion-exchange capacity, and become selective toward certain chemical separations. A study has therefore been undertaken with a view to

broaden the idea as to its ion-exchange efficiency with respect to the separation of carrier free ^{99m}Tc from ^{99}Mo, and ^{144}Pr from ^{144}Ce.

^{99m}Tc ($t_{1/2}$ = 5.9 h) has been found to be most useful for tracer work since its discovery by Seaborg and Segre (*3*). This isotope has the advantage of having a very simple decay scheme. For all practical purposes it emits mostly a gamma ray of 140 keV energy, enough to penetrate the human body easily yet soft enough to be readily adsorbed by heavy elements like lead. With relatively high efficiency of detection it is a nearly ideal radionuclide for use in scanning.

Coprecipitation of Tc with tetraphenylarsoniumperrhenate was the method usually applied (*4*) for its separation from Mo in the earlier days. Besides methods like solvent extraction and volatilizations, use of columns of alumina (*5–7*), hydrous zirconia (*8*), activated charcoal (*9*), and ammonium molybdophosphate impregnated with ^{99}Mo have been reported (*10*). Coprecipitation of ^{99}Mo with $CaMoO_4$ has been claimed (*11*) to give 99.7% separation of ^{99m}Tc. Nevertheless, newer methods of separation were being tried to find simpler and quicker ways with a high percentage of radionuclidic purity and yield.

Carrier-free ^{144}Pr was also separated from ^{144}Ce by various methods including the use of inorganic materials such as MnO_2 (*12*), di-(2-ethylhexyl) phosphoric acid supported on Hostaflon C_2 (*13*), alumina (*14*), and zirconium phosphate (*15*).

The present investigation dealt with these two separations by adopting very simple chemical procedures in a column of zirconium arsenate. The procedure, as a whole, is viewed in the light of the results obtained so far in similar studies with zirconium phosphate and compared.

EXPERIMENTAL

^{99}Mo (as $NaMoO_4$) in equilibrium with ^{99m}Tc, and ^{144}Ce (as $CeCl_3$) with ^{144}Pr, was supplied by BARC, Trombay, India. Zirconium oxychloride was of Riedal quality, and sodium arsenate was of GRE Merck variety. All other reagents were of analytical grade.

As the ion-exchange efficiency of an inorganic ion exchanger material largely depends on the mode of chemical reaction, aging, washing, drying, etc., sufficient care was taken to provide for the efficient mixing of reagents, gel formation, and obtaining a stable and granular form of crystal suitable for use in a column.

Preparation of Zirconium Arsenate

Zirconium arsenate, both anhydrous as well as with various degrees of hydration, has been obtained by many workers (*1*). It was claimed (*1*) that

when mixtures of arsenic acid and zirconyl nitrate in concentrated nitric acid were refluxed, the crystalline monohydrogen arsenate, similar to the H^+ form of zirconium phosphate, was obtained. However, a simpler procedure was found, examined, and adopted as follows.

A freshly prepared hot solution of 25 g $ZrOCl_2 \cdot 8H_2O$ in 100 mL 2 *N* HCl was added dropwise to a solution of sodium arsenate (48.4 g) in 250 mL water with occasional stirring while the temperature was maintained at 70°C until precipitation was complete. This was diluted to 2 L, allowed to stand overnight, and washed with hot water to remove chloride. The precipitate was filtered, dried at 80°C to obtain hard solids, and then further dried at 130°C for 48 h. The solid was found to be chemically stable in cold dilute and concentrated acids such as HNO_3 and HCl. Treatment with hot concentrated acids, however, caused some slight dissolutions.

A weighed quantity of the solid thus obtained was fused with NaOH and analyzed for its zirconium (as pyrophosphate) and arsenate (as magnesium ammonium arsenate). The ratio zirconium:arsenate was found to be 1:2.

A glass column (10 × 0.6 cm) was packed with the zirconium arsenate crystals as prepared above. It was connected to a receiver at the bottom, and a water suction pump unit was used to control the flow rate of eluent at 15–16 drops/min.

^{99}Mo–^{99m}Tc System

A 10-mL solution containing 30,000 counts/min of ^{99}Mo in equilibrium with ^{99m}Tc was warmed. A solution of 1% lead nitrate was added dropwise, with vigorous stirring, up to the point of the start of precipitation. The solution was faintly alkaline, and no precipitate or suspension was visible. This was again warmed and fed into the column of zirconium arsenate. The flow rate of the eluent was 15 drops/min. After elution, 10 mL of warm water was added. A 10-mL aliquot was then taken from the collected washings and counted for β-activity with a Philips-type liquid G.M. counter (mica window, thickness 2.5–3.5 mg/cm^2, diam. 27.8 mm) which showed no β-activity from ^{99}Mo.

To determine whether the ^{99m}Tc activity was present in this fraction of solution, ~50 mg of Mo-carrier (as ammonium molybdate) was added and a slight excess of lead nitrate solution (~1%) was added, precipitating $PbMoO_4$. The precipitate was washed with water, then acetone, and centrifuged. It was dried, mounted in an aluminum tray, and the γ-spectrum (Fig. 1a) was obtained.

An ORTEC Ge(Li) detecter having approximately 2 cm^3 active volume and a Nuclear Data 512-Channel analyzer were used to assay the γ-rays of the ^{99}Mo and ^{99m}Tc. The system resolution was 3.5 keV for the 122 keV γ-

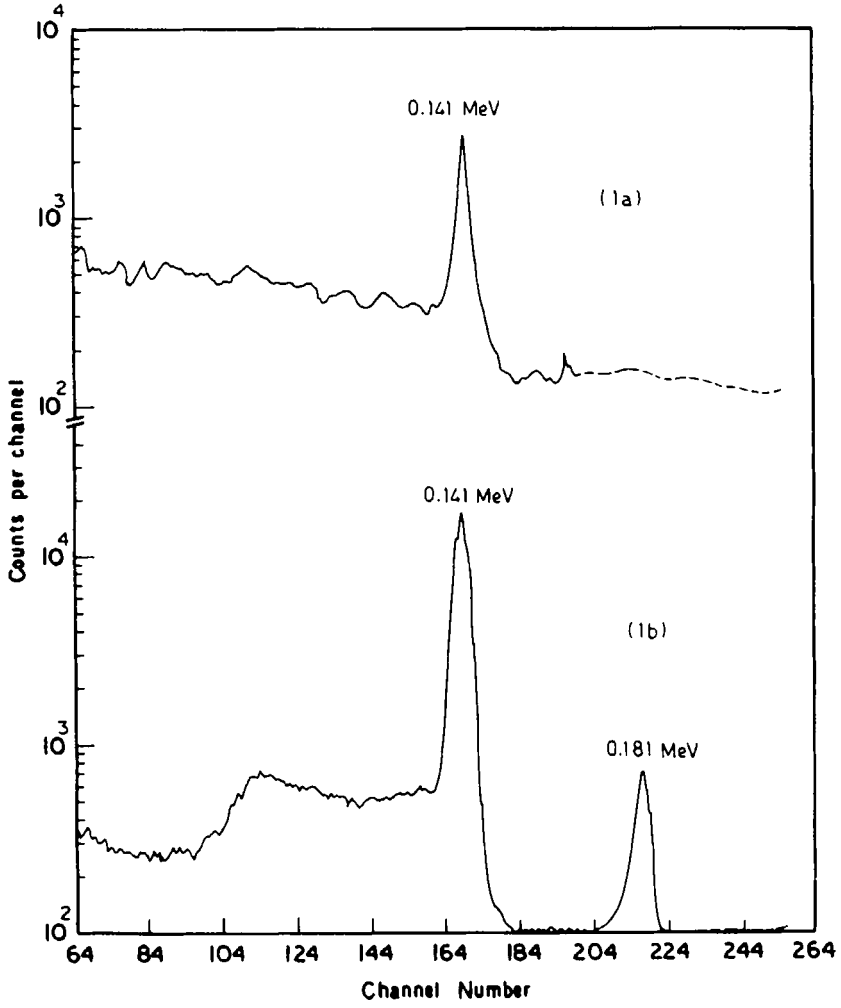

FIG. 1. Gamma spectrum obtained with a Ge(Li) detector of (a) ^{99m}Tc separated from the ^{99}Mo, and (b) the equilibrium mixture of ^{99}Mo and ^{99m}Tc before separation. The energies marked are in MeV.

ray of ^{57}Co. The relative photopeak efficiency of the detector over the energy range of γ-rays investigated was obtained using the known relative γ-ray intensities of ^{57}Co, ^{60}Co, ^{133}Ba, and ^{207}Bi.

A point source was also prepared using the original solution containing ^{99}Mo in equilibrium with ^{99m}Tc. A γ-spectrum was obtained (Fig. 1b) for comparison. Both ^{99}Mo and ^{99m}Tc have the prominent photopeak of 0.141

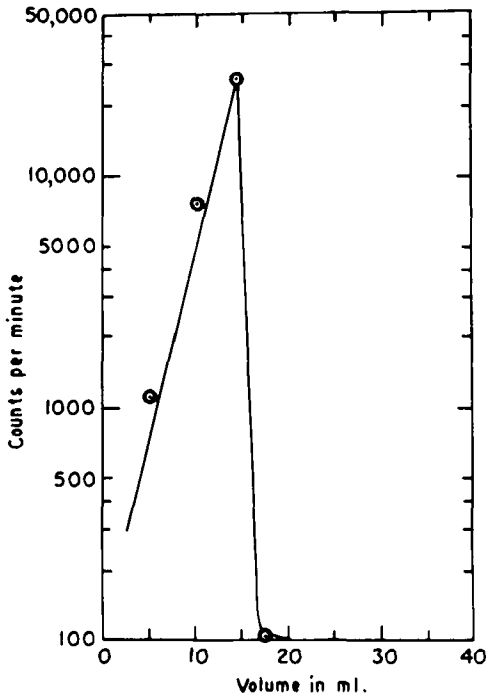

FIG. 2. Elution curve for ^{99}Mo.

keV γ-ray, among others. It should be noted that addition of only 10 mL of warm water eluted all ^{99m}Tc activity from the column and that any further addition of warm water did not increase the quantity of ^{99m}Tc in the eluent.

The ^{99}Mo activity retained in the column over a period of time could be removed by washing with portions of hot (1:1) H_2SO_4. An elution curve was obtained (Fig. 2) which showed that only 15 mL of (1:1) H_2SO_4 was required for the complete recovery of the ^{99}Mo activity.

An attempt was then made to determine whether freshly formed ^{99m}Tc could be removed from the ^{99}Mo retained in the zirconium arsenate column after removal of the ^{99m}Tc present initially in equilibrium with ^{99}Mo. ^{99m}Tc was allowed to form from the ^{99}Mo retained in the column for about 4 d, and the column was slowly washed (flow rate 17 drops/min) with 0.5 *M* HNO_3. The collected washing (~40 mL) was found to contain no ^{99}Mo activity. This was next processed to form $PbMoO_4$ by adding Mo carrier as before, and the γ-spectrum was obtained. The spectrum obtained was very similar to that obtained earlier (Fig. 1a).

^{144}Ce–^{144}Pr System

A solution of ^{144}Ce in equilibrium with ^{144}Pr containing ~10,000 counts/min was evaporated with nitric acid to remove chloride and then with water to remove nitrate as much as possible. After repeating this several times, the solids were dissolved in 5 mL water. To this 0.5 g boric acid, 5 mL conc HNO_3 and 5 mL 10% $NaBrO_3$ solution were added after warming on a steam bath for 15 min and cooling; 15 mL KIO_4 solution (200 mg of KIO_4 in boiling 1:3 HNO_3) was then added. This was again warmed on a steam bath for 10 min and fed into a fresh column of zirconium arsenate.

The solution flowed down at the rate of 16 drops/min after which 20 mL of 0.1% solution of KIO_4 was added to the column. A 10-mL aliquot from the collected washings was taken and counted by the β-counter in the way already described. Results in Fig. 3 show that this solution contained only

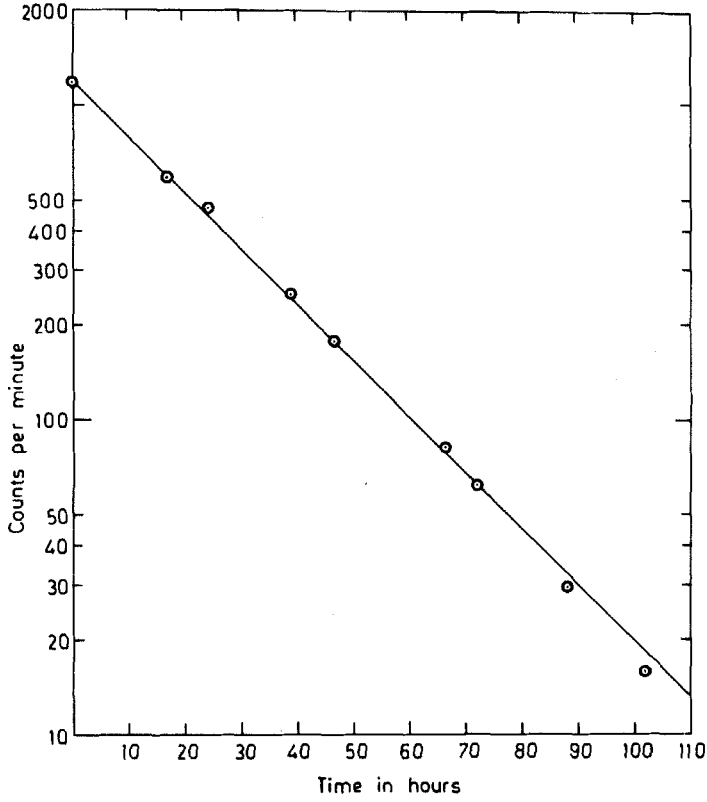

FIG. 3. Decay curve of ^{144}Pr separated from ^{144}Ce.

^{144}Pr activity and no ^{144}Ce. An elution curve was also obtained at this stage for carrying down the maximum amount of ^{144}Pr which showed that only 35 mL of the 0.1% KIO_4 was required for the purpose (Fig. 4).

An attempt to elute the ^{144}Pr which was produced from the ^{144}Ce retained in the column after the initial separation of ^{144}Pr was also made by washing the column slowly with 0.1% KIO_4 solution slightly acidified with HIO_4. The process was found to be slower and required 50 mL of eluent to remove an appreciable amount of ^{144}Pr.

DISCUSSION

The data in Fig. 1(a) indicate that ^{99m}Tc (0.141 MeV) separated from parent ^{99}Mo was of high radionuclidic purity. Since ^{99}Mo also has a 0.141 MeV γ-ray photopeak independent of ^{99m}Tc, the contribution of ^{99}Mo in the whole area of the mixed photopeak at equilibrium had to be distinguished. Figure 1(b) showed the presence of both of ^{99}Mo and ^{99m}Tc placed together for comparison. Since ^{99m}Tc does not emit any suitable β-radiation, the solution collected was processed with carrier molybdenum and all ^{99m}Tc activity was taken up as was evidenced in the γ-spectrum (Fig. 1a).

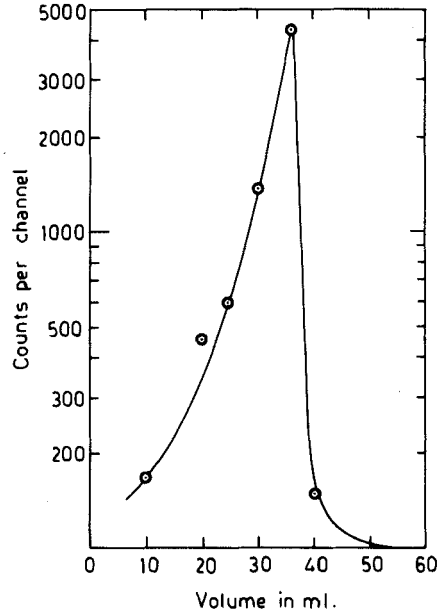

FIG. 4. Elution curve of ^{144}Pr during separation from ^{144}Ce.

It has already been stated that the equilibrium mixture of the two activities after treatment with lead nitrate was fed in the zirconium arsenate column followed by only 10 mL of warm water. Addition of more water did not elute any more activity, and the removal of ^{99m}Tc activity was found to be complete. It was decided not to obtain any elution curve at this stage, as only 10 mL of water was required to elute all the ^{99m}Tc.

^{99}Mo was retained in the column, most likely as insoluble lead molybdate. The zirconium arsenate was thus found to possess good capacity for the preferential adsorption of molybdenum in tracer concentration. The exchanger suggested by earlier workers (*15*) would be expected to be isomorphous with zirconium monohydrogen phosphate, and the structure would be a layered one. Each layer consists of sheets of Zr atoms held together by arsenate ion bridges. The mechanism in retaining the molybdenum activity, which involves either an adsorption process or ion-exchange, requires detailed study with respect to the affinity of exchange material with higher concentrations of cations.

It is interesting to note that ^{99m}Tc could be produced by decay of the ^{99}Mo adsorbed in the zirconium arsenate, and subsequently be removed by eluting with 0.5 *M* HNO_3, though for the purpose of separating ^{99m}Tc from ^{99}Mo an alumina column was proven (*5, 6*) to be simpler, less complicated, and is more popular.

The elution of ^{99}Mo retained after separation of ^{99m}Tc required only 15 mL of 1:1 H_2SO_4 solution. The method as a whole did not produce any interference, and the resulting solution contained no suspended particles.

In the case of the (4+) ^{144}Ce–^{144}Pr system the experimental procedure followed was also very simple, somewhat similar to a method for separating thorium from rare earths (*16*). It is probable that tracer amounts of ceric ion formed from reaction with periodate similar to its macro form adsorbed in the exchanger column, and the ^{144}Pr was removed unreacted. The oxidation of cerous to ceric at the begining was found to be very important, because without it separation was not possible. Simple oxidation alone could not effect the separation successfully, so the periodate step was undertaken. The β-decay curve in Fig. 3 showed that the separated ^{144}Pr activity was of high radionuclidic purity. The method of separation adopted here for carrier-free ^{144}Pr from ^{144}Ce was thus found to be very simple.

The experiments carried out therefore indicated that good separation of cations was possible with the zirconium arsenate column. Properties such as capacity, affinity for different cations, chemical stability toward different reagents, as well as thermal stability have not been studied. Therefore, it appears to be difficult at the moment to suggest the type of mechanism involved in the processes studied. It can, however, be expected that at least

certain similar chemical separations can be achieved with zirconium arsenate prepared in suitable form.

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