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Role of Hydrous Titanium Oxide on the Uptake of Several Tracer Cations, and Separation of Carrier-Free ^{125m}Te from ^{125}Sb and ^{132}I from ^{132}Te

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Abstract

Hydrous titanium oxide of good column quality was prepared from a solution of titanic chloride by precipitation with ammonia. The composition of the exchanger was ascertained by TGA to be $TiO_2 \cdot 0.73H_2O$ with an IEC value 0.29 meq/g. Study on the uptake of 21 tracer cations over titania showed high adsorption for many cations. Radiochemical separations of carrier-free ^{125m}Te and ^{132}I from ^{125}Sb and ^{132}Te, respectively, have been carried out on a titania exchanger column by applying very simple chemical procedures. Radionuclidic purity of the separated products ^{125m}Te and ^{132}I were ascertained by γ-ray spectrometry. Overall separation procedures took less than half an hour, and the yields were quantitative.

INTRODUCTION

The use of hydrous titanium oxide in column operations is well known (*1*). It has been utilized for studying the affinity series (*2*) for alkali metal and a few transitional metal cations, determining selectivity of sorption of certain metal ions (*3*), thermodynamic equilibrium constants (*4*, *5*) of Cs^+–H^+ and Na^+–H^+ exchange, kinetic measurements (*1*) on Cu^{2+}–H^+, etc. Because of high chemical and radiation stability as well as good mechanical properties, it has been applied (*6*) for the removal of Pu from highly radioactive solutions and the concentration of uranium (*7*) from seawater. Paper impregnated with hydrous titanium oxide has been utilized (*8*) for the separation of U, Ni, Co, Cu, and Fe(III) cations. Application of crystalline hydrated titania fiber for adsorption of divalent transition metal ions (*9*) and some rare earth metal ions (*10*) has been also described. Sasaki et al. (*11*) reported the ion-exchange and structural behavior of K^+

in respect of titanium dioxide. The number of cation separations performed over a titania column is very small. With a view to obtain more information, it was decided to undertake an investigation on the uptake of various metal cations such as Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Zn^{2+}, Sr^{2+}, Cd^{2+}, Ba^{2+}, Fe^{3+}, Y^{3+}, Ce^{3+}, Sm^{3+}, Tb^{3+}, Yb^{3+}, Zr^{4+}, Te^{4+}, Nb^{5+}, Sb^{5+}, Mo^{6+}, and W^{6+} at tracer concentrations and to utilize this information for the separation of certain tracer cations over this exchanger material.

Tellurium has been reported to be separated from other metal cations by precipitation (*12*); volatility (*13*, *14*); electrolysis (*15*, *16*); solvent extractions (*17*); ion-exchange columns of Dowex-1 (*18*), Dowex-50 (*19*), and Dowex-2 (*20*); paper chromatography (*21*, *22*); and by a few other methods. Separation of carrier-free tellurium radioactivity from antimony and fission products has long been a problem. The method reported by Meinke (*23*) was complicated, contained several steps, and had an unsatisfactory yield. An attempt was therefore made to utilize a titania column for the separation of carrier-free ^{125m}Te from ^{125}Sb by applying a somewhat simple chemical procedure.

The use of a TeO_2 column in an ^{132}I generator for the ^{132}Te–^{132}I system, originally patented by Tucker et al. (*24*), was subsequently replaced by Al_2O_3 where ^{132}I was retained and ^{132}Te passed out unadsorbed. Other methods such as distillation (*25–27*), CCl_4 extraction (*28*, *29*), and ion exchange (*30–32*) have been described. There is still need for a less-complicated chemical procedure for the recovery of carrier-free ^{132}I activity from ^{132}Te.

EXPERIMENTAL

The radioisotopes ^{24}Na, ^{42}K, ^{86}Rb, ^{137}Cs, ^{45}Ca, ^{65}Zn, ^{115}Cd, ^{140}Ba, $^{55+59}Fe$, ^{91}Y, ^{141}Ce, ^{153}Sm, ^{160}Tb, ^{169}Yb, ^{95}Zr, ^{132}Te, ^{95}Nb, ^{125}Sb, ^{99}Mo, and ^{185}W were supplied by B.A.R.C., Bombay, India, and ^{90}Sr was procured from A.E.R.E., Harwell, England. Titanic chloride and the other reagents were of A.R. grade.

Preparation of Hydrous Titanium Oxide

20 g $TiCl_4$ in 100 mL of 4 *N* HCl was treated with ammonia with constant stirring, followed by dropwise addition of ammonia solution until a pH of approximately 7 was attained. A white precipitate appeared which was allowed to settle for 2 h. The precipitate was filtered and washed with water until it was free of chloride. The precipitate was dried in an oven at 70°C for 24 h, powdered, and again washed with water to remove colloidal and suspended particles, and then dried as before. The solid obtained was

of the wet and amorphous type. It was insoluble in cold dilute HCl, H_2SO_4, HNO_3, and of good column quality.

The water content of the solid substance thus obtained was studied by TGA and the thermal stability by DTA with a DT-40 Thermal Analyzer, Shimadzu (Japan) (Fig. 1). The composition of the material was determined to be $TiO_2 \cdot 0.73H_2O$.

The uptake of several cations (radioisotopes) was then studied with 0.5 g exchanger samples, shaken separately with each cation solution (containing ~10,000 cpm) at pH ~ 7 (volume of solution/exchanger = 60 mL/g) at room temperature for 24 h. The solution part was then analyzed for β activity by a Phillips type G.M. liquid β counter (mica

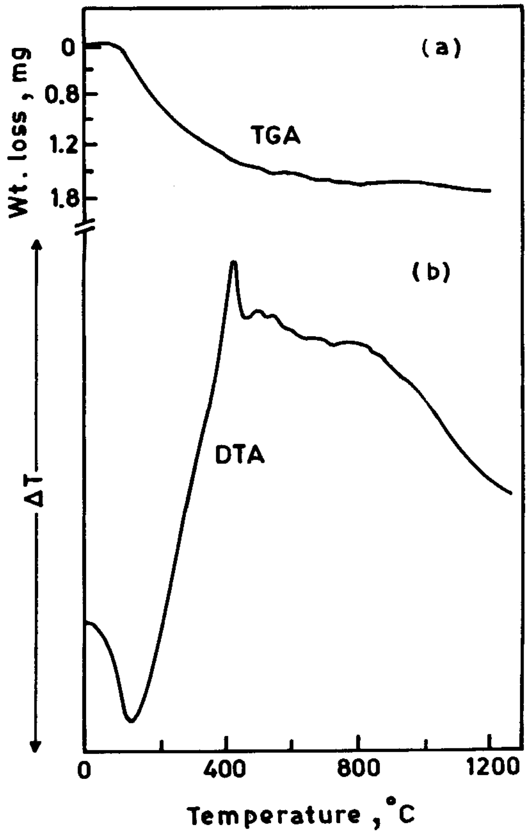

FIG. 1. (a) TGA curve (range 20 mg). (b) DTA curve (range 100 mV) of titania. Temperature rise rate of 20°C/min up to 1200°C.

window 2.5 mg/cm^2, diameter 27.8 mm) and K_D values were calculated in the usual way (*31*).

The ion-exchange capacity of the exchanger was determined by passing 0.1 *M* NaCl solution through the exchanger column and by titrating the eluted acid in the usual way (*31*). The value was found to be 0.29 meq/g.

The pH titration behavior of the exchanger was studied by equilibrating 0.5 g samples in varying proportions of 0.1 *M* NaCl + 0.1 *M* HCl/0.1 *M* NaOH for 24 h at room temperature, and pH was measured in the supernatant liquid by a glass electrode in the ELICO digital pH meter (Fig. 2).

^{125}Sb–^{125m}Te

^{125}Sb in equilibrium with ^{125m}Te (10 mL containing ~15,000 cpm) as chloride in HCl was repeatedly evaporated with water to remove acid as far as possible, cooled, taken in 10 mL water (pH ~ 6.5), and poured into a glass column (10 × 0.5 cm^2) half-packed with titania material. The column was then washed with 50 mL water (at a flow rate of 16 dpm), and the collected eluate was found to contain no β activity, thus indicating that both the ^{125}Sb and ^{125m}Te activities were adsorbed in the column. The column was next washed with 0.04 *N* HNO_3. Aliquots from this washing were separately analyzed for the γ-spectrum in an ORTEC-HPGe detector of 130 active volume, 27% efficiency coupled ND66E, 8K-MCA, and an elution curve was drawn [Fig. 3i, (a)]. It was observed that 70 mL of 0.04 *N* HNO_3 could completely wash out all of the ^{125m}Te activity from the column and analyzed for the γ-spectrum (Fig. 4a). The retained ^{125}Sb was

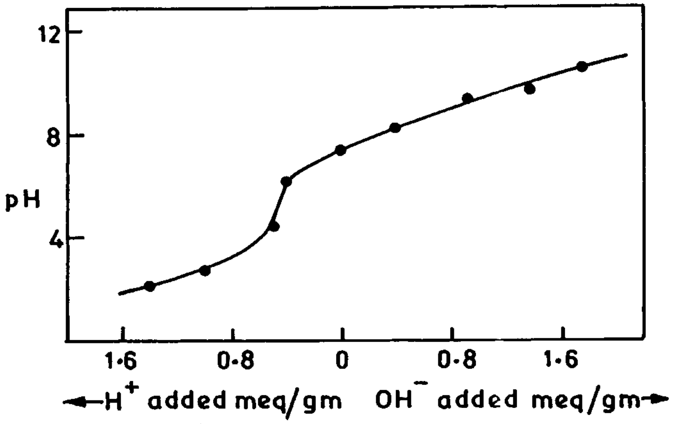

FIG. 2. pH titration curve of titania.

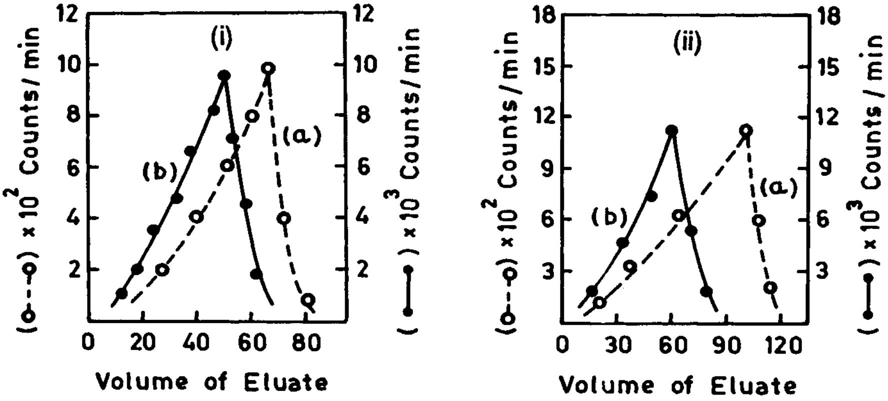

FIG. 3. (i). Elution curves of (a) ^{125m}Te and (b) ^{125}Sb. (ii). Elution curves of (a) ^{132}I and (b) ^{132}Te.

later removed from the column by washing with 50 mL of 1:4 HNO_3 [Fig. 3i(b)] and confirmed by γ-spectrometry. A separate γ-spectrum was also taken with a point source of the original ^{125}Sb–^{125m}Te solution for comparison (Fig. 4b).

^{132}Te–^{132}I

^{132}Te (~12,000 cpm) in equilibrium with ^{132}I (supplied as sodium tellurite in NaOH) in 20 mL water was taken, acidified with dilute HCl, repeatedly evaporated with water until a solution pH of approximately 7 was achieved, taken in 10 mL water and cooled. A 0.05% $Pb(NO_3)_2$ solution was added dropwise until a very faint turbidity appeared. The solution was then poured into a glass column (10 × 0.5 cm^2) and half-packed with exchanger material when both the activities were found to be adsorbed. Elution of either of the activities was attempted with 1 *N* HCl, and it was observed that 100 mL of 1 *N* HCl [Fig. 3ii(a)] could wash out all ^{132}I activity, confirmed by γ spectrometry (Fig. 5a), and the retained ^{132}Te could be removed from the column by washing with 60 mL of 1:6 HCl solution [Fig. 3ii(b)]. A separate γ-spectrum was also taken with a point source of the original ^{132}Te–^{132}I solution for comparison (Fig. 5b).

In a separate experiment after the first stage separation of ^{132}I from the column, fresh ^{132}I activity was allowed to grow for 2 days and an attempt was made to eluate this newly grown ^{132}I by the same procedure. γ-Spectrum analysis of the collected washings showed an identical observation (Fig. 5a), and milking of the ^{132}I activity was appreciable.

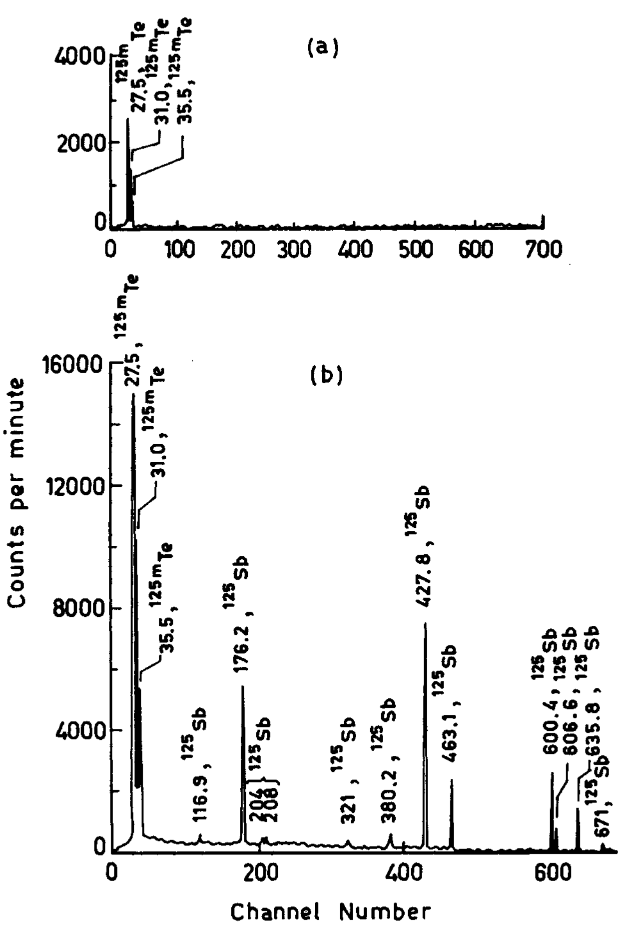

FIG. 4. Gamma spectrum of (a) ^{125m}Te separated from ^{125}Sb. (b) The equilibrium mixture of ^{125}Sb–^{125m}Te before separation.

DISCUSSION

A study of the pH titration curve (Fig. 2) showed that the titania exchanger used had an amphoteric and monofunctional character, and the tracer cation separations under investigation could be best carried out in the pH 6–7 range.

The formula of titania, as ascertained from the TGA-weight loss curve (Fig. 1a) was $TiO_2 \cdot 0.73H_2O$. The DTA curve (Fig. 1b) showed one endothermic peak at ~100°C, one sharp exothermic peak at ~400°C, and a

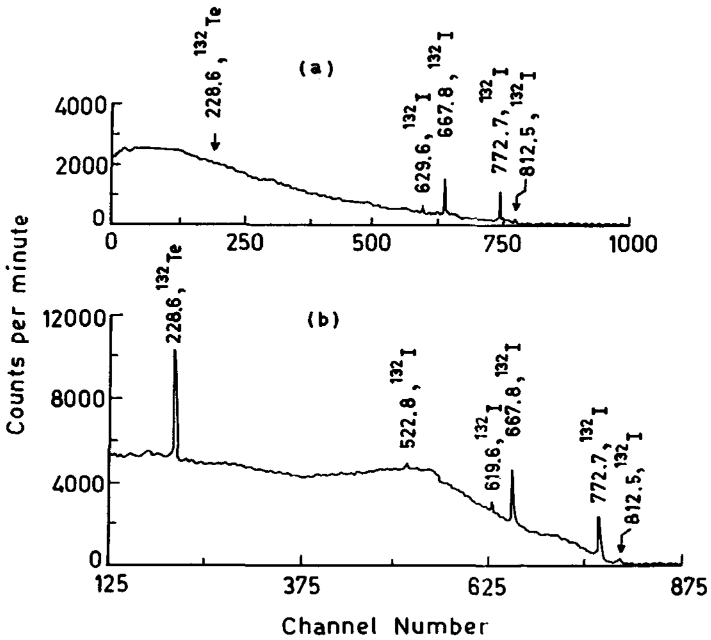

FIG. 5. Gamma spectrum of (a) ^{132}I separated from ^{132}Te. (b) The equilibrium mixture of ^{132}Te–^{132}I before separation.

few insignificant small humps nearby. The endothermic peak appears to be due to the loss of moisture, and the exothermic reaction at ~400°C is related to the modification into the intermediate phase.

The value of the ion-exchange capacity (0.29 meq/g) and the data shown in Table 1 indicate that the titania material used in the investigation could adsorb many tracer cations under similar experimental conditions to those used earlier for SnO_2 (*34*) and ZrO_2 (*35*) materials. The uptake and K_D values for alkali metals follow the order Na < K < Rb < Cs and Cs for very high adsorption; the uptake values of Ca^{2+},Zn^{2+}, Cd^{2+}, Ba^{2+}, Fe^{3+}, Y^{3+}, Ce^{3+}, Sm^{3+}, and Yb^{3+} are very high; and those of Zr^{4+}, Te^{4+}, Nb^{5+}, and Sb^{5+} are fairly high. It was also noted that the uptake values for Sr^{2+}, Tb^{3+}, and W^{6+} are comparatively low, while that of Mo^{6+} is negligible. It is apparent that the titania material used here is a good adsorbent for a number of mono- and multivalent tracer cations. A detailed and similar study with other cations, including determination of the extent of adsorption by way of coprecipitation, may reveal much interesting information on adsorption characteristics in general and the mechanisms.

TABLE 1
Distribution Coefficients of Several Tracer Cations over a Titania Exchanger, Measured Radiochemically

Cations taken		Uptake (%)	K_D (mL/g)
^{24}Na	(as chloride)	4.90	3.09
^{42}K	(as chloride)	12.90	8.88
^{86}Rb	(as chloride)	84.90	337.35
^{137}Cs	(as chloride)	97.19	2075.23
^{45}Ca	(as chloride)	93.46	857.43
^{65}Zn	(as chloride)	94.60	1051.11
^{90}Sr	(as nitrate)	52.75	66.98
^{115}Cd	(as nitrate)	99.30	8511.43
^{140}Ba	(as chloride)	98.45	3810.96
$^{55+59}$Fe	(as chloride)	97.80	2667.27
^{91}Y	(as chloride)	90.28	557.28
^{141}Ce	(as sulfate)	90.75	588.64
^{153}Sm	(as chloride)	91.56	650.90
^{160}Tb	(as chloride)	60.97	93.73
^{169}Yb	(as chloride)	95.49	1270.37
^{95}Zr	(as chloride)	88.16	446.75
^{132}Te	(as tellurite)	88.59	466.19
^{95}Nb	(as chloride)	81.86	270.76
^{125}Sb	(as chloride)	87.63	425.04
^{99}Mo	(as molybdate)	3.79	36.62
^{185}W	(as tungstate)	23.74	18.68

^{123}Sb–^{125m}Te

In Fig. 4(a), ^{125m}Te of high radionuclidic purity is shown to be separated from its parent ^{125}Sb. The separated ^{125m}Te (58d) is mainly in the isomeric state. The γ-spectrum of ^{125m}Te indicates the presence of 35 keV γ-ray. The absence of 176 keV γ-ray and the strong group of γ-rays in the 400–700 keV range for ^{125}Sb in Fig. 4(a) shows that ^{125m}Te has been clearly separated from ^{125}Sb. The γ-spectrum obtained for ^{125}Sb–^{125m}Te (Fig. 4b) containing the γ-peaks for both ^{125}Sb and ^{125m}Te is shown for comparison.

The chemical procedure adopted was very simple and no steps for chemical reaction or complexation with either of Sb or Te was required. Removal of ^{125m}Te from the titania column required only 70 mL 0.04 N HNO_3 [Fig. 3i(a)]. The overall procedure was quick and the yield was quantitative.

^{132}Te–^{132}I

Figure 5(a) shows that the ^{132}I separated from ^{132}Te was of high radionuclidic purity. ^{132}Te was decayed by β emission to produce a strong 228.6

keV γ-ray which finally decayed to ground state ^{132}I. ^{132}I in turn decayed by β emission to various levels of ^{132}Xe, producing strong 667.8 and 772.7 keV γ-rays. The presence of the 228.6 keV γ-peak is enough to indicate ^{132}Te, while the presence of 667.8 and 772.7 keV peaks clearly identifies ^{132}I. The existence of both ^{132}Te and ^{132}I is evident in the γ-spectrum shown in Fig. 5b.

The daughter ^{132}I activity was separated in a very simple manner which required only the formation and adsorption of lead tellurite in the column. ^{132}I could be selectively stripped off by washing with 100 mL 1 *N* HCl [Fig. 3ii(a)]. It has already been pointed out that after the first stage of separation of ^{132}I activity, a further quantity of freshly grown ^{132}I could be taken from the titania column where ^{132}Te had been retained. The milking yield of ^{132}I activity was ~80%, but that yield required delayed washing of the column. The cowing procedure should be carried out more carefully to make the state of affairs comparable to that of the ^{132}I generator of alumina. The desorption mechanism should also be studied in detail.

The separation procedures took less than half an hour, are very simple, and produce a quantitative yield.

It is concluded that when hydrous titanium oxide is suitably prepared, it may act as a versatile adsorbent for many metal cations. It can also be utilized for many interesting chemical separation problems.

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