# Adsorption Behaviour of <sup>134</sup>Cs and <sup>22</sup>Na Ions on Tin and Titanium Ferrocyanides

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**Abstract.** Tin and titanium ferrocyanides were studied as adsorbents for alkali metal ions, viz.,  $^{134}$ Cs and  $^{22}$ Na, which represent radioactive wastes. The ferrocyanides were prepared in granular form. The tin version contained 11.2% water, while the titanium version contained 17.7% water. The exchange capacities for Cs<sup>+</sup> and Na<sup>+</sup> in the hydrated tin version were about 1.5 and 0.7 meq/g, respectively, while those in the titanium version were 2.2 and 1.2 meq/g, respectively. Drying at 250°C decimated those capacities. The diffusional time constant of Cs<sup>+</sup> at 25°C, determined via Fick's second law, was of order of magnitude  $1 \times 10^{-3}$  s<sup>-1</sup>, though there were minor differences due to particle size and the form of ferrocyanide. Similarly, the effective diffusivity was of order of magnitude  $1 \times 10^{-8}$  cm<sup>2</sup>/s. The titanium version responded slightly faster than the tin version. Likewise, equilibrium measurements in mixtures with sodium nitrate, potassium nitrate, or uranium oxide, showed that the titanium version exhibited significantly greater selectivity for Cs<sup>+</sup> than did the tin version. Unfortunately, tests of complete elution of the Cs<sup>+</sup> from the ferrocyanides were mostly disappointing. Work continues on that subject.

Keywords: ion exchange, equilibrium, kinetics, radioactive waste treatment

#### 1. Introduction

Tin and titanium hexacyanoferrate(II) have been prepared as inorganic ion exchangers having a Sn/Fe or Ti/Fe ratios of 1:1, with a composition of K<sub>0.3</sub>Sn<sub>1.3</sub>  $Fe(CN)_6 \cdot 2.6H_2O$  and  $K_{0.4}Ti_{1.2}Fe(CN)_6 \cdot 3.4H_2O$ , respectively. The prepared materials are suitable for use in a large scale ion exchange column. The sorption behaviour of <sup>134</sup>Cs and <sup>22</sup>Na ions by the prepared materials under different conditions of particle sizes, drying temperatures and different concentrations of ions have been investigated. The results indicated that titanium ferrocyanide has more useful properties and ion exchange capacity than tin ferrocyanide. Feasible separation of cesium in the presence of some competing ions (UO<sub>2</sub><sup>2+</sup>, KNO<sub>3</sub> and NaNO<sub>3</sub>) have been reported. Values of diffusion coefficient (D<sub>i</sub>) of Cs<sup>+</sup> ions on both tin and titanium ferrocyanides have been calculated at differ-

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ent particle diameters. Adsorption data of cesium on titanium ferrocyanide are quite fit with the Freundlich adsorption isotherm. Values of breakthrough capacity and chromatographic separation of cesium-134 ions on both tin and titanium ferrocyanides have been recorded. Some progress was achieved for elution of adsorbed cesium on tin and titanium ferrocyanides. In the area of cesium removal tin and titanium ferrocyanide were evaluated and compared with other adsorbents reported in literature.

Inorganic ion exchangers have received increased attention recently because of their radiation stability and high selectivity for alkali metal ions. Among the inorganic materials exhibiting selective adsorption properties, the ferro- and ferricyanides of the transition metals have been extensively investigated, owing to their property of forming insoluble precipitates with different cations (Valentini et al., 1972; Huys and Baetsle, 1964). The main purpose of most investigations involving hexacyanoferrates have been their use in the

selective separation of cesium from radioactive waste solutions and to lesser extent from environmental samples such as milk, urine, and sea waters (Boni, 1966; Petrov and Levine, 1967). A large number of transition metal hexacyanoferrates are insoluble solids. Many authors have recognized the ion exchange properties of ferrocyanides and most of these exchangers are easily prepared in a granular form suitable for use in a packed column (Hooper et al., 1984). Lieser and Bastian (1967) demonstrated that ferro- and ferricyanides of transition metals precipitated cesium from acidic or slightly alkaline solutions (Lieser and Bastian, 1967). Tananoev (1958) measured the solubilities of complex ferrocyanides of the type  $X_2[YFe(CN)_6] nH_2O$ , where X = an alkali metal and Y = a transition metal. They reported that the solubilities could be arranged in the following sequence, when only the alkali ions were varied (Tananoev, 1958)

$$Tl \ll Cs < Rb < K$$

Gill and Tandon (1973), reported the synthesis and ion exchange properties of zirconium and stannic hexacyanoferrates(II). The distribution coefficients for 21 cations were determined (Gill and Tandon, 1973). The separation of cesium ions from sea water by ferrocyanide compounds was recorded by Sakura and Wadachi (1971). They studied the decontamination of cesium in the presence of salts (Sakura and Wadachi, 1971). Vol'khin et al. (1976) and Shul'ga et al. (1971) used ferrocyanide compounds to separate cesium salts from rubidium salts. The same authors studied the adsorption properties of some alkali elements on transition metal ferrocyanides in presence of organic salts (Shul'ga et al., 1972). Barton et al. (1958) prepared titanium ferrocyanide and reported the following selectivity series for monovalent and divalent metal ions;

$$Cs^{+} > Rb^{+} > K^{+} > NH_{4}^{+} > Li^{+}$$

and

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Be^{2+}.$$

Bastian and Lieser (1967) studied the effect of pH on the  $k_d$  values for alkali and alkaline earth metals and found that  $k_d$  falls with decreasing pH, except for Cs<sup>+</sup> which has a maximum at pH 1.

This paper describes results from research on the adsorption of cesium and sodium ions on tin and titanium hexacyanoferrates(II). Tin and titanium ferrocyanides were chosen for this investigation on account of the

fairly high sorption of cesium, which in turn may be easily released under suitable conditions. Sorption and elution procedures for cesium using a column technique have been reported.

# 2. Experimental

All chemicals used were of analytical grade purity and used without further purification.

# 2.1. Preparation of Tin and Titanium Ferrocyanides

Tin and titanium hexacyanoferrate(II) were prepared in a granular form as reported earlier (Kourim et al., 1964; Qureshi et al., 1971, 1972; Loewnchuss, 1982), by adding 300 ml of 0.1 mol dm<sup>-3</sup> tin tetrachloride or titanium tetrachloride to 300 ml of 0.1 mol dm<sup>-3</sup> potassium ferrocyanide to give volume ratio 1:1 (for Sn/Fe and Ti/Fe) with constant stirring in thermostatted shaker water bath at room temperature. The proposed reactions for both tin and titanium hexacyanoferrate(II) may be written as follows:

$$K_4Fe(CN)_6 + XCl_4 \rightleftharpoons XFe(CN)_6 + 4KCl.$$

where  $X = \operatorname{Sn}$  or Ti

The mixture was left standing overnight at  $80^{\circ}\text{C}$  ( $\pm 1^{\circ}\text{C}$ ). After standing overnight, the precipitate was filtered and dried at  $60^{\circ}\text{C}$  ( $\pm 1^{\circ}\text{C}$ ) and then washed several times with bidistilled water until the filtrate became free of chloride ions and finally oven dried at  $100^{\circ}\text{C}$  ( $\pm 1^{\circ}\text{C}$ ). The resulting granules were crushed, sieved and dry screened and stored at room temperature

The elemental composition of the prepared tin and titanium hexacyanoferrate(II) (tin, titanium, iron and potassium) were determined by Total Reflection X-ray Fluorescence (Italics Structure product from Italy) using gallium as internal standard. Water contents of the prepared materials were determined by thermogravimetric analysis (TG) by heating samples to 250°C (±1°C) at a heating rate 10°C/min using DTG-40 Shimadzu Kyoto Japan, and by calculating the % weight loss.

The chemical stability of the prepared ferrocyanide samples was determined in water, nitric and hydrochloric acids at different concentrations (0.01 M, 0.1 M, 0.5 M, 1.0 M and 2.0 M) by shaking 500 mg of exchanger with 50 ml of solvent at the desired concentrations in a thermostatted shaker water bath adjusted at

room temperature ( $25 \pm 1^{\circ}$ C) for 48 hour. After equilibration the filtrate was analyzed for each element using Total Reflection X-ray Fluorescence.

### 2.2. Ion Exchange Experiments

The ion exchange capacities for <sup>134</sup>Cs and <sup>22</sup>Na ions on both tin and titanium ferrocyanides were determined by batch and column techniques. In the batch experiments, the capacity was determined by repeated batch equilibration of 0.03 g and 3 ml of desired solution until equilibrium was achieved (solution volume to exchanger weight was 100 ml/g). Different grain sizes of the exchanger were used. After equilibration the phases were separated and analyzed by measuring the radioactivity of <sup>134</sup>Cs and <sup>22</sup>Na in the solution before and after equilibration.

The distribution coefficients of tin and titanium ferrocyanides were determined by adding 0.03 g of exchanger with 3 ml of the desired concentration ( $10^{-4}$  M) at natural pH in thermostatted shaker water bath at 25°C ( $\pm 1$ °C). After equilibration both of the filtrate and exchanger were analyzed radiometrically. The values of distribution coefficient ( $k_d$ ) were calculated by using the following relation:

$$k_d = \frac{A_o - A_f}{A_f} \cdot V/m \text{ ml/g}$$

where  $A_o$  and  $A_f$  is the initial and final counting rates of the considered element in solution, respectively, V is the volume of solution (ml) and m is the mass of the exchanger (g).

The sorption isotherm for Cs<sup>+</sup> ions on titanium ferrocyanide was determined over the concentration range  $10^{-4}$ – $10^{-2}$  mol dm<sup>-3</sup>, at 0.1 mol dm<sup>-3</sup> HNO<sub>3</sub>, and a constant V/m ratio of one hundred, at  $25 \pm 1^{\circ}$ C.

Column experiments were performed by passing  $5 \times 10^{-2}$  mol dm<sup>-3</sup> CsCl solution (pH = 5.54) through 0.75 g of tin and titanium hexacyanoferrate(II) having a mesh size of 0.1–0.215 mm. The diameter of the column was 5 mm and the flow rate 1 ml per 4 minute. Breakthrough curves were determined by collecting fractions of the effluents and measuring their <sup>134</sup>Cs radioactivity. Elution of Cs<sup>+</sup> ions was conducted on the same column.

## 2.3. Radiometric Assay

The specific radioactive nuclides of  $^{134}$ Cs and  $^{22}$ Na ions used in this study were assayed by measuring their  $\gamma$ -

rays in both solid and solution phases using NaI(Tl) scintillation detector connected to a Scalar of the type SR7 obtained from Nuclear Enterprises, USA. The experiments showed that the standard deviation was less than  $\pm 6\%$  at all conditions studied.

## 3. Results and Discussion

Hexacyanoferrates(II) are generally prepared by mixing a solution of a transition metal salt, with a solution containing hexacyanoferrate(II) ions usually  $Na^+$ ,  $K^+$  or  $NH_4^+$  ions and or ferrocyanic acid (Hooper et al., 1984). In this paper, tin and titanium ferrocyanides were prepared by mixing  $XCl_4$  (X = Ti or Sn) and potassium hexacyanoferrate(II).

The chemical stability of the prepared tin and titanium ferrocyanides was determined as mentioned in Section 2.1. Tin and titanium ferrocyanides are stable in water, and in slightly acidic solutions up to 0.5 M acid. At higher concentrations of acid (more than 1 M) the solubility of the prepared materials increased due to oxidation of ferrocyanide to ferricyanide; which is more water soluble than ferrocyanide. Similar trends were observed by Lieser et al. (1967).

Analyses of tin and titanium ferrocyanides for potassium, tin, titanium, and iron by total reflection X-ray fluorescence are summarized and given in Table 1. Analysis of the data presented in Table 1 reveals that, tin- to- iron or titanium- to- iron ratios were nearly 1:1. The water contents determined by thermogravimetric analysis were about 11.16% for tin ferrocyanide and 17.67% for titanium ferrocyanide which was corresponding to 2.6 moles of  $H_2O$  per mole of iron in titanium ferrocyanide. The formulae of the products, after calculating the ratio of atoms are  $K_{0.3}Sn_{1.3}Fe(CN)_6 \cdot 2.6H_2O$  and  $K_{0.4}Ti_{1.2}Fe(CN)_6 \cdot 3.4H_2O$  as proposed in Table 1.

The rate and equilibrium uptake of  $^{134}$ Cs ions (as a sake of brevity) on tin and titanium hexacyanoferrate(II) at different particle diameters were investigated at  $25^{\circ}$ C ( $\pm 1^{\circ}$ C) and the results are shown in Fig. 1 as a relation between Bt (mathematical function) and F (F = fractional attainment of equilibrium) Vs time (minute) (where F = uptake at time t/uptake at equilibrium). From the data presented in Fig. 1, it is clear that the rate of exchange of  $Cs^+$  ions on titanium ferrocyanide is higher than that on tin ferrocyanide and also the rate of exchange of  $Cs^+$  ions increased as the particle diameter of exchangers decreased. The increase

Table 1. Preparation, characterization and chemical analysis of tin and titanium ferrocyanides.

	Additives											
	X		R		Ratio		TXRF analysis		Water content			
Exchanger	M	V	M	V	X/R	Colour	K	у	Fe	%	mole	Formula
Tin ferrocyanide	0.1	300	0.1	300	1	Black	K <sub>0.3</sub>	Sn <sub>1.3</sub>	Fe	11.16	2.6	SnO·H <sub>4</sub> Fe(CN) <sub>6</sub> ·2H <sub>2</sub> O (Qureshi et al., 1972) SnFe(CN) <sub>6</sub> ·4H <sub>2</sub> O (Ayers and Waggoner, 1972) $K_{0.3}Sn_{1.3}Fe(CN)_62.6H_2O^*$
Titanium ferrocyanide	0.1	300	0.1	300	1	Black	K <sub>0.4</sub>	Ti <sub>1.2</sub>	Fe	17.67	3.4	$\begin{split} &\text{TiO}_2(\text{OH}) \cdot \text{HFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O} \text{ (Qureshi et al., 1972)} \\ &\text{TiFe}(\text{CN})_6 \cdot 2\text{H}_2\text{O} \text{ (Lieser et al., 1967)} \\ &K_{0.4}\text{Ti}_{1.2}\text{Fe}(\text{CN})_63.4\text{H}_2\text{O}^* \end{split}$

where  $X = SnCl_4$  or  $TiCl_4$ ;  $R = K_4Fe(CN)_6$ ; V = Volume, ml.; M = Concentration; y = Sn or Ti; \* refer to the calculated formula for prepared materials.

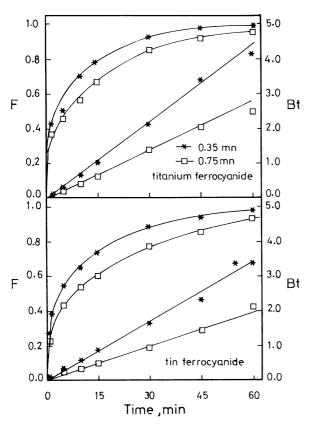


Figure 1. F and Bt against time (t) for exchange of  $^{134}\text{Cs}$  ions on tin and titanium ferrocyanides at different particle diameters (at  $25 \pm 1$  °C).

of the rate of exchange of Cs<sup>+</sup> ions with decreasing particle diameters of exchanger may be attributed to diffusion resistance in the ferrocyanide particles. From analysis of Fig. 1 we can say that one hour is necessary to attain equilibrium for the exchange of the studied cations on the prepared ferrocyanide materials.

For every observed value of F, corresponding Bt values are obtained, from the following equation

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \exp^{-\frac{n^2 \text{Bt}}{r^2}}.$$

where F is the fractional attainment of equilibrium at time t with radius r of the exchanger particles and Bt values are obtained from the Reichenberg Table (Reichenberg, 1953).

Additional data were obtained from the Bt vs t plots as shown in Fig. 1. From this figure (Fig. 1) the values of diffusion coefficient ( $D_i$ ) of Cs<sup>+</sup> ions on both tin and titanium ferrocyanides were calculated from the following relation:

$$B = \pi^2 D_i / r^2$$

where B is a mathematical function,  $D_i$  is the diffusion coefficient of the sorbed ions and r refers to the radius of the ferrocyanide particles. The values of B (the slope of Bt vs t plots) and diffusion coefficient ( $D_i$ ) of  $Cs^+$  ions on both tin and titanium ferrocyanides are calculated and tabulated in Table 2. Table 2 indicates that the values of self-diffusion coefficient ( $D_i$ ) of  $Cs^+$  ions on titanium ferrocyanide is higher than that on tin

*Table 2.* Values of *B* and effective diffusion coefficient  $(D_i)$  of <sup>134</sup>Cs ions on tin and titanium ferrocyanides at different particle diameters (at  $25 \pm 1^{\circ}$ C).

Particle	TIN FERRO	OCYANIDE	TITANIUM	FERROCYANIDE		
diameter	B	$D_i$	$B_{\cdot}$	$D_i$		
(mm)	$(s^{-1})$	$(cm^2 s^{-1})$	$(s^{-1})$	$(cm^2 s^{-1})$		
0.35	$9.40\times10^{-4}$	$3.03 \times 10^{-8}$	$1.22\times10^{-3}$	$3.9 \times 10^{-8}$		
0.75	$5.56 \times 10^{-4}$	$7.92 \times 10^{-8}$	$7.02 \times 10^{-4}$	$10.01 \times 10^{-8}$		

ferrocyanide. Also the values of diffusion coefficient  $(D_i)$  increase with decreasing the particle diameters of the prepared materials. Comparing the values of self diffusion coefficient  $(D_i)$  reported in Table 2 with similar values reported in literature, we can say that the rate of exchange of  $Cs^+$  ions on the prepared materials approaches those of organic resins as well as some of inorganic exchangers (El-Naggar et al., 1999; Misak and El-Naggar, 1989).

The effect of drying temperatures of tin and titanium ferrocyanides on saturation capacity and distribution coefficients of Na+ and Cs+ ions was investigated at  $25^{\circ}$ C ( $\pm 1^{\circ}$ C) and the results are given in Table 3. Values of separation factors ( $\alpha_{\text{Na}}^{\text{Cs}} = k_d$  of cesium/ $k_d$  of sodium) are calculated at the same conditions and given in Table 3. From Table 3 it is clear that, the capacity of Cs<sup>+</sup> ions is higher than the capacity of Na<sup>+</sup> ions for both exchangers and also the capacity of titanium ferrocyanide is higher than the capacity of tin ferrocyanide for both Na<sup>+</sup> and Cs<sup>+</sup> ions at the same conditions. From Table 3 we can conclude that, tin and titanium ferrocyanides have a high affinity to uptake Cs<sup>+</sup> than Na<sup>+</sup> ions, and this phenomenon is characteristic behaviour for ferrocyanide compounds in general (Hooper et al., 1984). Analysis data presented in Table 3 shows that the capacity of Na<sup>+</sup> and Cs<sup>+</sup> ions decreased with increasing drying temperatures for both exchangers from  $50^{\circ}$ C to  $250^{\circ}$ C ( $\pm 1^{\circ}$ C). The decrease in capacity for both ferrocyanides with increasing the drying temperature may be attributed to loss of water in ferrocyanides with increasing drying temperature, and this is very clear for the samples heated at 250°C ( $\pm 1$ °C), whereas strongly bonded water is removed and the capacity decreases sharply (Loewnchuss, 1982).

From the data of distribution coefficients  $(k_d)$  and separation factors  $(\alpha_{\rm Na}^{\rm Cs})$  of  ${\rm Cs^+}$  and  ${\rm Na^+}$  ions on both tin and titanium ferrocyanides which was reported in Table 3. It could be deduced that both investigated elements ( ${\rm Na^+}$  and  ${\rm Cs^+}$  ions) are highly retained with  $k_d$  values of the order  $10^2$  and  $10^2$ – $10^3$  for tin and titanium ferrocyanides, respectively. Also, from the results of Table 3 we can say that titanium ferrocyanide can be used for recovery of radioactive cesium (Cs-134) due to its high values of distribution coefficient and ion exchange capacity for cesium ions.

Tests of the influence of various quantities of sodium, potassium and uranium ions as competing ions on the distribution coefficients of  $Cs^+$  ( $10^{-4}$  M) ions on tin and titanium ferrocyanides were carried out at different concentrations of competing ions ( $10^{-4}$  M and  $10^{-2}$  M). The results are summarized in Table 4. From Table 4 it is clear that the competing ions slightly affect

Table 4. Distribution coefficients of  $^{134}\mathrm{Cs}$  ions on tin and titanium ferrocyanides at different concentrations of competing ions (NaNO<sub>3</sub>, KNO<sub>3</sub> and UO<sub>2</sub><sup>2+</sup>) at natural pH's (at  $25^{\circ} \pm 1^{\circ}\mathrm{C}$ ).

	Concentration of	Distribution coefficient $k_d$ (ml/g)				
Competing ions	competing ions, (M)	Tin ferrocyanide	Titanium ferrocyanide			
NaNO <sub>3</sub>	$10^{-4}$	293	918			
	$10^{-2}$	225	320			
$KNO_3$	$10^{-4}$	300	605			
	$10^{-2}$	136	226			
$UO_{2}^{2+}$	$10^{-4}$	306	1242			
-	$10^{-2}$	283	816			

Table 3. Values of water contents, distribution coefficients  $(k_d)$ , separation factors  $(\alpha)$  and saturation capacity (meq/g) of tin and titanium ferrocyanides at different drying temperatures at  $25 \pm 1$ °C.

Drying	Wate	er loss	Capacity (meq/g)		$k_d$ (ml/g)		Separation
temperature (°C)	Mole	%	Cs <sup>+</sup>	Na <sup>+</sup>	Cs <sup>+</sup>	Na <sup>+</sup>	factor $\alpha^{\text{Cs}}_{\text{Na}}$
50	-	-	1.54	0.68	316	56	5.6
100	1.5	6.34	1.34	0.63	127	42	3.0
200	2.1	9.01	1.07	0.39	78	31	2.5
250	2.6	11.16	0.10	0.09	_	_	_
50	_	_	2.17	1.21	132	127	10.4
100	1.46	6.58	2.06	1.15	8	85	7.2
200	2.76	14.34	1.18	0.53	614	47	2.46
250	3.40	17.67	0.14	0.13	150	-	-
	50 100 200 250 50 100 200	Drying temperature (°C) Mole  50 - 100 1.5 200 2.1 250 2.6 50 - 100 1.46 200 2.76	temperature (°C) Mole %  50 100 1.5 6.34 200 2.1 9.01 250 2.6 11.16 50 100 1.46 6.58 200 2.76 14.34	Drying temperature (°C)         Mole         %         Cs+           50         -         -         1.54           100         1.5         6.34         1.34           200         2.1         9.01         1.07           250         2.6         11.16         0.10           50         -         -         2.17           100         1.46         6.58         2.06           200         2.76         14.34         1.18	Drying temperature (°C)         Mole         %         Cs+         Na+           50         -         -         1.54         0.68           100         1.5         6.34         1.34         0.63           200         2.1         9.01         1.07         0.39           250         2.6         11.16         0.10         0.09           50         -         -         2.17         1.21           100         1.46         6.58         2.06         1.15           200         2.76         14.34         1.18         0.53	Drying temperature (°C)         Mole         %         Cs+         Na+         Cs+           50         -         -         -         1.54         0.68         316           100         1.5         6.34         1.34         0.63         127           200         2.1         9.01         1.07         0.39         78           250         2.6         11.16         0.10         0.09         -           50         -         -         2.17         1.21         132           100         1.46         6.58         2.06         1.15         8           200         2.76         14.34         1.18         0.53         614	Drying temperature (°C)         Mole         %         Cs+         Na+         Cs+         Na+           50         -         -         -         1.54         0.68         316         56           100         1.5         6.34         1.34         0.63         127         42           200         2.1         9.01         1.07         0.39         78         31           250         2.6         11.16         0.10         0.09         -         -           50         -         -         2.17         1.21         132         127           100         1.46         6.58         2.06         1.15         8         85           200         2.76         14.34         1.18         0.53         614         47

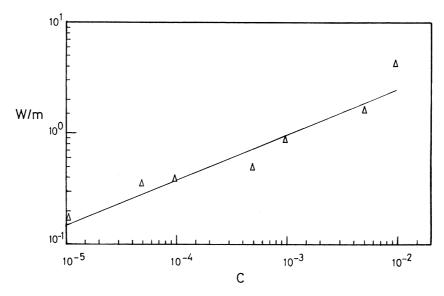


Figure 2. Freundlich adsorption isotherm for the adsorption of  $^{134}$ Cs on titanium ferrocyanide (at  $25 \pm 1^{\circ}$ C).

the distribution coefficient of  $Cs^+$  ions on tin and titanium ferrocyanides at  $10^{-2}$  M of competing ions ( $Na^+$ ,  $K^+$  and  $UO_2^{2+}$ ), but there is nearly no effect of competing ions at  $10^{-4}$  M. The effect of competing ions  $Na^+$ ,  $K^+$  and  $UO_2^{2+}$ ) on the distribution coefficient of  $Cs^+$  ions on both tin and titanium ferrocyanide decrease in the order:

$$UO_{2}^{2+} < Na^{+} < K^{+}$$

From the above sequence and data presented in Table 4, it is clear that uranium has less effect as a competing ions on the distribution coefficient of  $Cs^+$  ions on tin and titanium ferrocyanides than sodium and potassium ions. The lesser effect of uranium may be attributed to its charge and chemical behaviour, which are different than both  $Na^+$  and  $K^+$  ions. Also, ferrocyanides, in general, behave as strong cationic exchangers (Loewnchuss, 1982), and uranium may be anionic at the studied concentrations ( $10^{-4}$  M and  $10^{-2}$  M). Hence at these conditions, uranium slightly affects the sorption of  $Cs^+$  ions on tin and titanium hexacyanoferrate(II) compared with other competing cations ( $Na^+$  and  $K^+$ ).

From the above results, we can conclude that, selective separation of cesium ions in the presence of some competitive ions ( $UO_2^{2+}$ ,  $KNO_3$  and  $NaNO_3$ ) is feasible and can be achieved using tin and titanium hexacyanoferrate(II).

The adsorption of <sup>134</sup>Cs ions on titanium hexacyanoferrate(II) was further analysed by the Freundlich adsorption isotherm using the following equation;

$$\log W/m = K + n \log C$$

The amount adsorbed at equilibrium (W/m) is plotted against equilibrium concentration (C) on a logarithmic scale as shown in Fig. 2. The relationship between log W/m against log C is found to be linear as shown in Fig. 2, which clearly indicates the applicability of the Freundlich adsorption isotherm. The values of Freundlich constants (n and K) in the above equation which measure the intensity and adsorption capacity of titanium ferrocyanide were measured from the slope (n) and intercept (K) of Fig. 2. The values of n and K were found to equal 0.4 and 0.096 M, respectively. The numerical value of n < 1.0 (n = 0.4) suggests the nonapplicability of Henry's law and also indicates that the surface of the titanium ferrocyanide sorbent is heterogeneous (Mishra and Srinivasu, 1993).

On the other hand, Fig. 3 shows breakthrough curves for  $^{134}\mathrm{Cs}$  ions from tin and titanium ferrocyanides using concentration of feed solution  $5\times 10^{-2}$  M CsCl labelled with  $^{134}\mathrm{Cs}$  Fig. 3. The values of the corresponding uptake of meq of  $^{134}\mathrm{Cs}$  ions per gram ferrocyanide were calculated from the following formula

Capacity = 
$$\frac{V_{(50\%)} \times C_{o}}{m}$$
 × valence (meq/g)

where,  $V_{(50\%)}$  is the effluent volume in ml at 50% breakthrough of  $^{134}$ Cs, Co is The initial concentration of

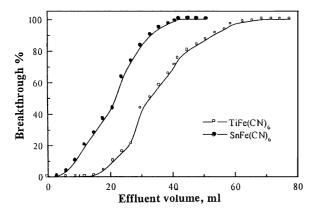


Figure 3. Breakthrough curves for  $^{134}$ Cs from tin and titanium ferrocyanides using feed solutions  $5 \times 10^{-2}$  M CsCl at flow rate 1 ml/4 min, at room temperature.

cesium chloride ( $5 \times 10^{-2}$  M), and m is the weight of exchanger (gram). From the results of the breakthrough curves shown in Fig. 3, the calculated breakthrough capacity of Cs<sup>+</sup> ions was found to be 1.33 and 2.00 meq of cesium per gram of tin and titanium ferrocyanides, respectively. The calculated values of breakthrough capacities are appreciably smaller than the values given in batch experiments presented in Table 3. This may be due to small particle size used in column experiment and also the alsow flow rate used (1 ml/4 min). From above results we can emphasize that removal of cesium with conventional columns filled with hexacyanoferrate complexes is possible using the prepared materials, similar observation was reported (Galiba and Lieser, 1980; Kawamura and Kurotaki, 1969).

Attempts to elute the adsorbed cesium ions on tin and titanium hexacyanoferrate(II) were only) partially successful. No satisfactory procedures for elution and regeneration of ferrocyanide matrix using  $10^{-1}$  M HNO<sub>3</sub> and  $10^{-1}$  M NH<sub>4</sub>Cl was achieved. A solution of  $10^{-1}$  M EDTA removed very little  $^{134}$ Cs ions as shown in Fig. 4 (a) and (b). Figure 4 also shows the elution profile of  $^{134}$ Cs ions from tin and titanium ferrocyanides columns with nearly 20 ml 0.1 M AgNO<sub>3</sub> as a flow rate 1 ml/ min, whereas some progress for elution of  $^{134}$ Cs ions using AgNO<sub>3</sub> as eluent. The elution yield of  $^{134}$ Cs was about 54–65% and 62–74% for tin and titanium ferrocyanides, respectively.

A number of organic and inorganic ion exchangers are being developed and evaluated for cesium removal. The exchangers of interest that are investigated in this work include tin and titanium hexacyanoferrate(II) are compared with other adsorbents such as sodium tetraphenylborate (Doherty et al., 1986; Lee and Kilpatrick, 1984) (TPB) and crystalline silicotitanate (CST) (Lee and Kilpatrick, 1982). In this concern sodium tetraphenylborate was used for removal and precipitation of cesium from high level radioactive waste and shows a high  $k_d$  and capacity for cesium (Doherty et al., 1986; Lee and Kilpatrick, 1984). Lee and Kilpatrick (1982) developed, a tetraphenylboratemica complex that completely precipitates Cs<sup>+</sup> from high Na<sup>+</sup> solutions (Lee and Kilpatrick, 1982). Also, a low price of titanate, sodium and silicon was used with high efficiency for removal and precipitation of cesium from high salt solutions (Brown et al., 1996).

From the above results we can conclude that tin and titanium ferrocyanides are the preferred materials for

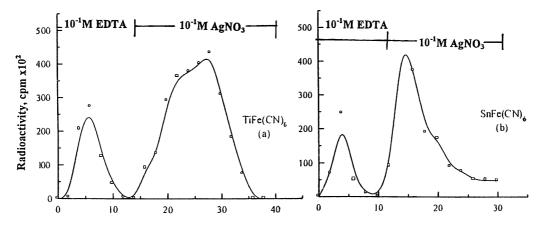


Figure 4. Elution curves of  $^{134}$ Cs with  $10^{-1}$  M EDTA and  $10^{-1}$  M AgNO<sub>3</sub> eluents from tin and titanium ferrocyanides at flow rate 1 ml/min. at room temperature.

the removal of  $Cs^+$  from salt solution with high  $k_d$  and capacity in presence of some competitive ions ( $UO_2^{+2}$ ,  $KNO_3$  and  $NaNO_3$ ) in both batch and column techniques.

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