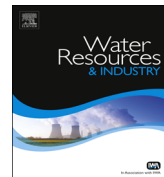




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## Recovery of uranium, thorium and zirconium from allanite by extraction chromatography using impregnated chromosorb

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### ABSTRACT

Chromosorb 102 impregnated with Cyanex 923 was used as a stationary phase in the extraction chromatographic separation of lanthanides, U(VI), Th(IV) and Zr(IV). Batch studies were carried out to investigate the uptake behaviour of these metal ions, along with few other metal ions. The effect of different parameters like equilibration time, concentration of acid, metal ions and extractant has been studied. The distribution data has been used to develop suitable eluting agents. The sorbing and desorbing capacity of the column for U(VI), Th(IV) and Zr(IV) was determined. Results indicate an insignificant change in the efficiency of the column up to 10 such cycles. The practical utility of the column has been demonstrated by the recovery of around 95% of U(VI), Th(IV) and Zr(IV) from allanite sample with a purity of around  $97\% \pm 2\%$ .

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## 1. Introduction

Separation science plays an important role in the development of recovery and purification processes. A variety of separation methods such as solvent extraction, ion exchange, adsorption and

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various forms of chromatography have been explored for the separation and recovery of metal ions. Extraction chromatography, in contrast, has received limited attention. It is a form of liquid–liquid chromatography in which the stationary phase is either an extractant or a solution of extractant supported on an inert support [1]. The technique thus combines the selectivity of solvent extraction with the multistage character of a chromatographic process accompanied by ease of handling. The technique offers tremendous potential for the separation of intricately similar metal ions. The liquid–liquid extraction data provides a database for developing an extraction chromatographic procedure.

U(VI), Th(IV) and Zr(IV) are the vital elements for nuclear energy and the demand for these elements has increased enormously. With the advancement of science and technology lanthanides have found utility in the fields like rechargeable batteries, advanced ceramics, fiber optics, permanent magnets and superconductors. In nature, uranium, thorium and zirconium are invariably associated with lanthanides and their mutual separation is of vital significance. Most of the natural sources of these elements are lean and elegant separation schemes are required to meet the stringent demands of purity and recovery. A number of alkyl phosphorus compounds such as tributyl phosphate [2], di-2-ethylhexyl phosphoric acid [3] and trioctyl phosphine oxide [4,5] have been explored as extractants for these elements. But only in a few reports have the partition data been explored. The alkylphosphine extractants marketed under the trade name of ‘Cyanex’ have gained prominence as extractants for these elements due to their poor aqueous solubility, good hydrolytic stability and selectivity. These inherent advantages make these extractants attractive alternatives for use as stationary phase in extraction chromatography for the separation of metal ions [6–8]. Literature suggests that several attempts have been made to explore Cyanex extractants for these elements [9–12]. The selectivity of Cyanex 923 for the extraction of U(VI), Th(IV), Zr(IV) and lanthanides has already been investigated by the authors [13–15]. The potential of this extractant as impregnant for the said metal ions still remains to be fully explored. In view of this it was planned to explore this extractant for the separation and recovery of U, Th, Zr and lanthanides from a complex matrix by extraction chromatography.

The present paper deals with the uptake of U(VI), Th(IV), Zr(IV) and lanthanides on Cyanex 923 impregnated Chromosorb 102. The effect of shaking time and concentration of acid, metal ion and extractant on the uptake of metal ions has been investigated. The stoichiometries of the extracted species have been proposed. The uptake behaviour of lanthanides [La(III), Yb(III)], Y(III), Fe(III), Al(III), Mn(II), V(IV) and Ti(IV) has also been investigated. Based on the sorption data a separation scheme has been designed. The developed procedure has been applied to allanite for the separation and recovery of U(VI), Th(IV), Zr(IV) and lanthanide fractions. Allanite is an ore with a relatively high content of rare earths and yttrium with small amounts of thorium, uranium and zirconium.

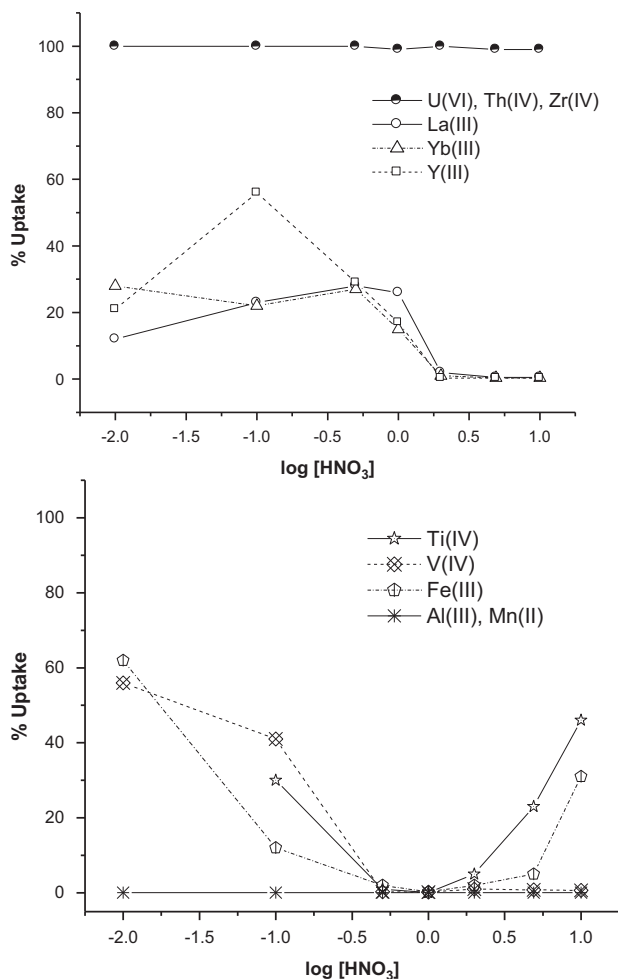
## 2. Experimental section

### 2.1. General details

All the chemicals and solvents were of analytical-reagent grade from E. Merck (Germany)/Aldrich (USA)/Fluka (Germany) and were used as purchased. The stock solutions of metal ions were prepared in double distilled water after dissolving their suitable salts containing a minimum amount of the corresponding mineral acid. Cyanex 923 (Avg. Mol. Wt. 348, 93% purity) was received from Cytec Canada Inc (Canada). It was used without further purification. Chromosorb 102 (particle size of 80/100 mesh) was procured from John’s Manville, USA. A sample of allanite from Rajasthan (India) was used for the recovery of lanthanides, U, Th and Zr.

The quantification of metals in the aqueous solutions was done using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Calibration of this instrument was carried out by sequential peak measurement of the corresponding emission signal and background. The calibration standards used for the determination of various metal ions ranged from 1 to 100  $\mu\text{g L}^{-1}$ .

Chromosorb 102 was impregnated with varying amounts of Cyanex 923 [0.174–8.7 g] per g of the inert support by making slurry of the former in toluene solution of the latter. The toluene was then evaporated by warming up with gentle stirring.



**Fig. 1.** Effect of nitric acid concentration on the uptake of different metal ions on the Cyanex 923 impregnated Chromosorb 102 (IC). Conditions: [Metal ion] =  $1.0 \times 10^{-4} \text{ mol L}^{-1}$ ; [IC] = 1.74 g Cyanex 923 per g chromosorb.

## 2.2. Batch studies

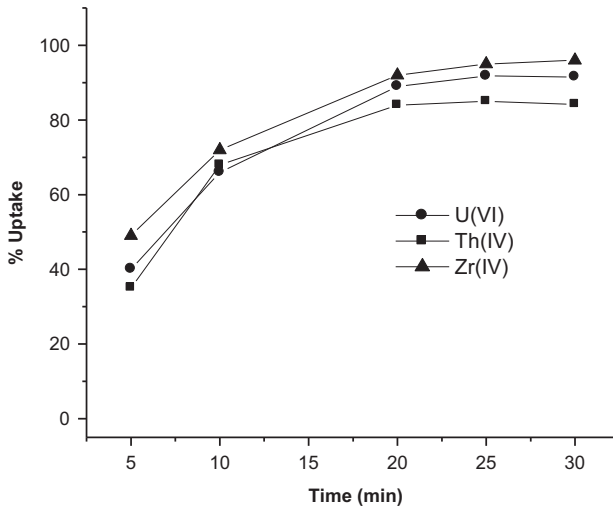
To investigate the effect of different parameters on the uptake of U(VI), Th(IV), Zr(IV) and lanthanides batch studies were carried out. The distribution behaviour of the various metal ions at different acidities was determined by adding about 0.1 g of the impregnated chromosorb (IC) in 10 mL solution of the metal ion ( $1.0 \times 10^{-4} \text{ mol L}^{-1}$ ) in varying concentrations of  $\text{HNO}_3$  ( $1.0 \times 10^{-2}$ – $10.0 \text{ mol L}^{-1}$ ). The mixture was equilibrated in a mechanical shaker at  $25 \pm 1^\circ \text{C}$ . The concentrations of the metal ions in the aqueous phase before and after equilibration were determined. The per cent uptake of the metal ion by impregnated support was calculated as,

$$\% \text{Uptake} = [(A_i - A_f) / A_i] \times 100$$

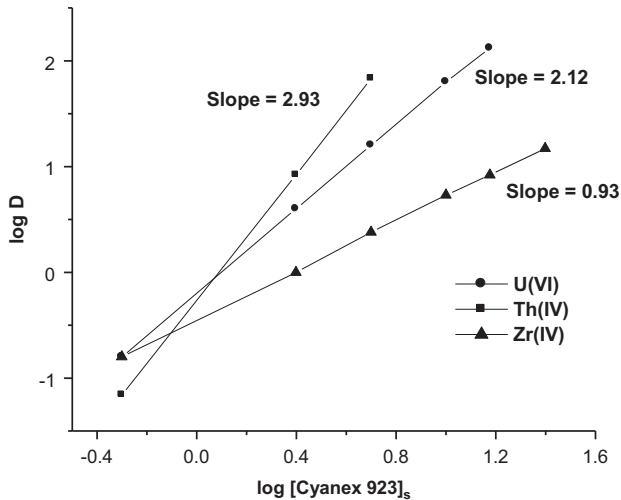
and the distribution ratio ( $D$ ) values were calculated as follows:

$$D = [(A_i - A_f) / A_f] \times [V / M] \text{ mL g}^{-1}$$

where,  $A_i$  and  $A_f$  are the initial and final concentrations of the respective metal ion in solution.  $V$  is the



**Fig. 2.** Effect of equilibration time on the uptake of metal ions on the Cyanex 923 impregnated Chromosorb 102 (IC). Conditions: [Metal ion] =  $1.0 \times 10^{-4}$  mol L $^{-1}$ ; [HNO $_3$ ] = 5.0 mol L $^{-1}$ ; [IC] = 1.74 g Cyanex 923 per g chromosorb.

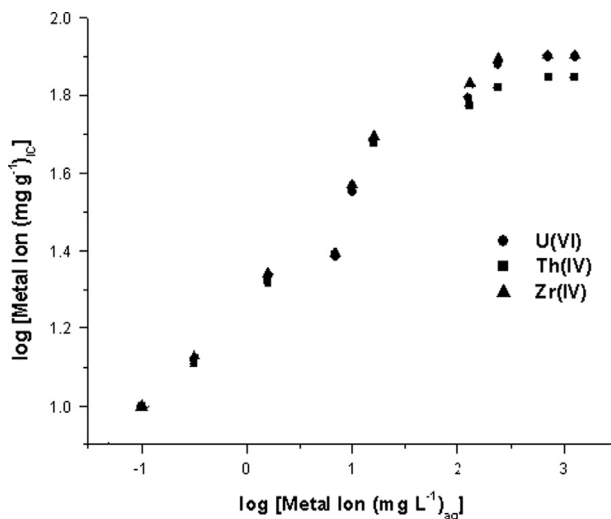


**Fig. 3.** Effect of concentration of Cyanex 923 on the impregnated Chromosorb 102 (IC) for the uptake of U(VI), Th(IV) and Zr(IV). Conditions: [Metal ion] =  $1.0 \times 10^{-4}$  mol L $^{-1}$ ; [HNO $_3$ ] = 5.0 mol L $^{-1}$ .

volume of solution taken in a particular experiment and  $M$  is the amount of the impregnated inert support. In all the experiments the solution was centrifuged and a suitable aliquot of the solution was assayed.

### 2.3. Column studies

For column studies, 1 g of the impregnated chromosorb was left overnight in contact with 5 mol L $^{-1}$  HNO $_3$  and then transferred to a glass column (i.d. = 1 cm) having a fritted disk. The bed height of the impregnated chromosorb in the column was 2 cm. For separations, the column was loaded with 10 mL allanite as feed solution. Elution was started after 25 min at a flow rate of 0.2 mL min $^{-1}$ . The retained metal ions were eluted with 5 volumes of 2.0 mol L $^{-1}$  HCl, 5 volumes of 0.5 mol L $^{-1}$  H $_2$ SO $_4$  and 2 volumes of



**Fig. 4.** Adsorption Isotherm for U(VI), Th(IV) and Zr(IV) on Chromosorb 102 impregnated with Cyanex 923 (IC). Conditions:  $[\text{HNO}_3]=5.0 \text{ mol L}^{-1}$ ;  $[\text{IC}]=5.22 \text{ g Cyanex 923 per g chromosorb}$ .

$0.1 \text{ mol L}^{-1}$  oxalic acid. After each use, the impregnated chromosorb was washed with large volumes of water and then preconditioned with the required concentration of the acid and used again.

#### 2.4. Dissolution of ore

The sample of allanite was brought into the solution by following a method cited elsewhere [16]. The brief details are given below.

About 5 g of the powdered sample was digested with 100 mL mixture of concentrated HF,  $\text{HNO}_3$  and  $\text{HClO}_4$  (3:1.5:0.5) in a teflon vessel for 24 h at  $80^\circ\text{C}$ . The paste obtained was dissolved in 50 mL of concentrated  $\text{HNO}_3$ . This solution was again brought to near dryness by heating for 2–3 h. The step was repeated and the paste was finally dissolved in 50 mL of  $5.0 \text{ mol L}^{-1} \text{ HNO}_3$ .

### 3. Results and discussion

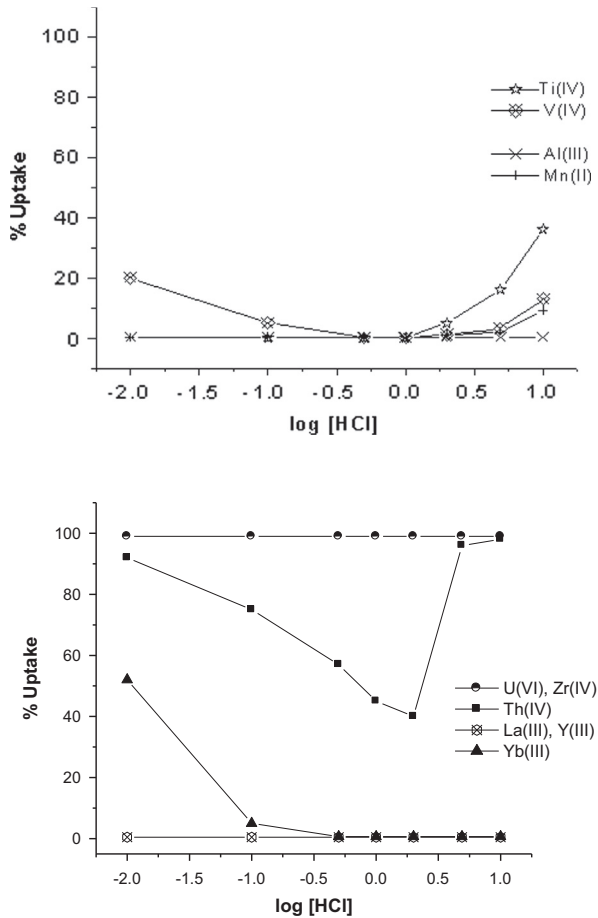
#### 3.1. Uptake behaviour

The uptake behaviour of U(VI), Th(IV), Zr(IV), V(IV), Ti(IV), Y(III), La(III), Yb(III), Fe(III), Al(III) and Mn(II) was studied from  $1.0 \times 10^{-2}$  to  $10.0 \text{ mol L}^{-1} \text{ HNO}_3$  acid using impregnated chromosorb. As illustrated in Fig. 1, U(VI), Th(IV) and Zr(IV) show quantitative uptake in the investigated range of  $\text{HNO}_3$  molarity. Lanthanides [La(III), Yb(III)] and Y(III) show a peak in their uptake at around  $0.5 \text{ mol L}^{-1}$  and  $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ , respectively. Uptake of Fe(III) and Ti(IV) decreases to a negligible value around  $0.5 \text{ mol L}^{-1} \text{ HNO}_3$  and again increases with an increasing acidity. Uptake of V(IV) shows a continuous decrease with the increasing acidity and is negligible beyond  $1.0 \text{ mol L}^{-1} \text{ HNO}_3$ . The uptake of Al(III) and Mn(II) remains negligible in the entire investigated range of acid molarity.

Results of the uptake behaviour reveal that under the investigated experimental conditions only U(VI), Th(IV) and Zr(IV) are quantitatively sorbed on the impregnated inert support. Therefore, the effect of different experimental variables on the uptake of U(VI), Th(IV) and Zr(IV) were investigated.

#### 3.2. Effect of equilibration time

The time required for the uptake of U(VI), Th(IV) and Zr(IV) was determined by shaking a known amount of IC with a known volume of the respective metal ion solution ( $1.0 \times 10^{-4} \text{ mol L}^{-1}$ ) for

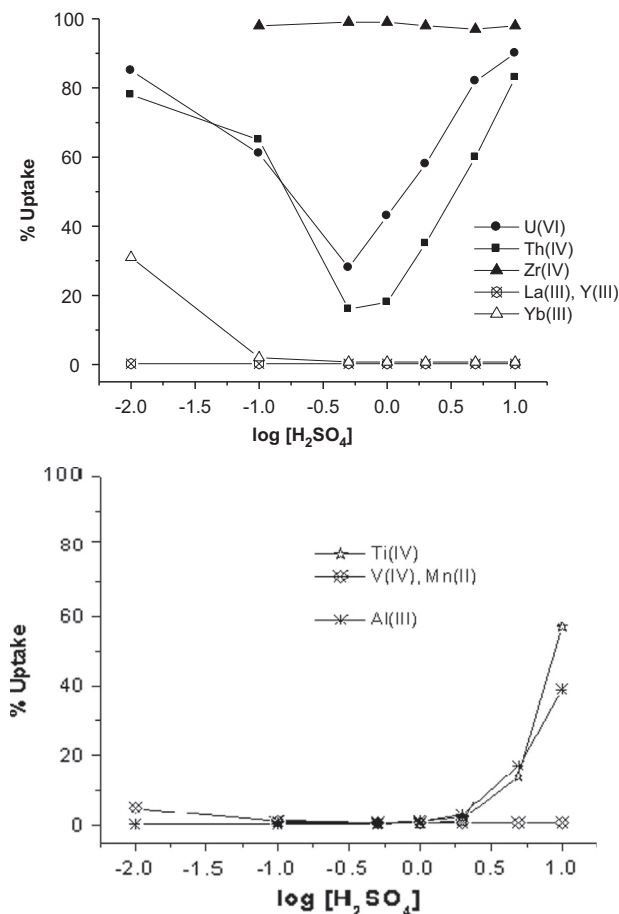


**Fig. 5.** Effect of hydrochloric acid on the uptake of different metal ions on the Cyanex 923 impregnated Chromosorb 102 (IC). Conditions: [Metal ion]= $1.0 \times 10^{-4}$  mol L<sup>-1</sup>; [IC]=1.74 g Cyanex 923 per g chromosorb.

different time intervals (5–30 min). Plots drawn between percentage uptake and time (Fig. 2) indicate that a minimum of 20 min is required for the maximum uptake of the metal ion. Shaking time of 25 min was applied for all further studies.

### 3.3. Effect of Cyanex 923 concentration

To study the effect of concentration of extractant on the uptake of metal ions, batch studies were carried out for the uptake of U(VI), Th(IV) and Zr(IV) from 5.0 mol L<sup>-1</sup> HNO<sub>3</sub> on chromosorb loaded with different amounts of Cyanex 923 (0.174–8.7 g sorbed per g of the inert support). Results indicate an increase in the uptake of U(VI)/Th(IV)/Zr(IV) with the increase in the concentration of the extractant coated on the inert support (Fig. 3). Plot of  $\log[\text{Cyanex } 923]_s$  versus  $\log D$  {where  $[\text{Cyanex } 923]_s$  = weight of Cyanex 923 per kg of impregnated support/molecular weight of the Cyanex 923} gave straight lines with slope values around 1, 2 and 3 for Zr(IV), U(VI) and Th(IV), respectively. Thus, the stoichiometry of Metal:Extractant in the extracted species is found to be 1:1 for Zr(IV), 1:2 for U(VI) and 1:3 for Th(IV). A similar stoichiometry for the extracted species has been proposed by the authors on the basis of liquid–liquid extraction data [14–16].



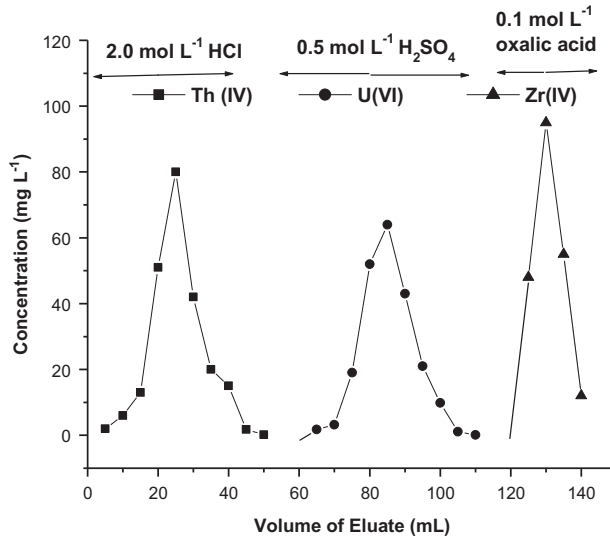
**Fig. 6.** Effect of sulphuric acid on the uptake of different metal ions on the Cyanex 923 impregnated Chromosorb 102 (IC). Conditions:  $[Metal\ ion]=1.0 \times 10^{-4}$  mol L $^{-1}$ ;  $[IC]=1.74$  g Cyanex 923 per g chromosorb.

### 3.4. Adsorption isotherm

The results of the batch experiments carried out to investigate the partition of U(VI), Th(IV) and Zr(IV) on IC from 5.0 mol L $^{-1}$  HNO $_3$  are shown in Fig. 4. The uptake of the said metal ions increases linearly with the increasing metal ion concentration before attaining saturation. The results indicate that Cyanex 923 can hold U(VI), Th(IV) and Zr(IV) up to 1/46th, 1/51th and 1/18th of its molar concentration, respectively. Based on the results of the sorption studies, the capacity of the impregnated chromosorb for U, Th and Zr was found to be 2.84, 3.18 and 8.55 mmol g $^{-1}$  of IC, respectively.

### 3.5. Elution studies

Uptake studies carried out for the said metal ions from HCl (Fig. 5) and H $_2$ SO $_4$  (Fig. 6) media using impregnated chromosorb indicate that 2.0 mol L $^{-1}$  HCl, 0.5 mol L $^{-1}$  H $_2$ SO $_4$  can be used as eluting agents for Th(IV) and U(VI), respectively. Elution studies further revealed that 0.1 mol L $^{-1}$  oxalic acid effectively elutes U(VI), Th(IV), Zr(IV), Ti(IV), V(IV) and Y(III). Therefore, in all further studies 5 volumes of 2.0 mol L $^{-1}$  HCl/0.5 mol L $^{-1}$  H $_2$ SO $_4$  were used for the elution of Th(IV)/U(VI) and 2 volumes of 0.1 mol L $^{-1}$  oxalic acid for Zr(IV). Elution studies were performed for U, Th and Zr on the



**Fig. 7.** Elution curves for U(VI), Th(IV) and Zr(IV) from synthetic mixture on the Cyanex 923 impregnated Chromosorb 102 (IC). Conditions: feed solution: [Metal ion]=100 mg L<sup>-1</sup>; [HNO<sub>3</sub>]=5.0 mol L<sup>-1</sup>; flow rate=0.2 mL min<sup>-1</sup>; [IC]=5.22 g Cyanex 923 per g chromosorb.

**Table 1**

Variation in the sorption/desorption of U(VI), Th(IV) and Zr(IV) in successive cycles.

Cycles	U(VI)		Th(IV)		Zr(IV)	
	Uptake %	Recovery %	Uptake %	Recovery %	Uptake %	Recovery %
1	99.9 ± 0.5	96.8 ± 2.0	99.9 ± 1.0	95.6 ± 0.5	99.5 ± 1.0	99.4 ± 0.5
2	99.8 ± 0.5	98.5 ± 1.5	99.8 ± 1.2	99.1 ± 0.5	98.7 ± 0.5	98.5 ± 0.6
3	99.9 ± 1.4	98.9 ± 1.5	99.9 ± 1.0	99.4 ± 1.0	99.2 ± 1.0	98.3 ± 0.5
4	99.5 ± 1.0	98.4 ± 1.2	99.5 ± 0.5	96.9 ± 2.0	99.5 ± 1.1	99.5 ± 1.5
5	99.9 ± 0.5	95.6 ± 2.1	98.5 ± 1.5	98.7 ± 1.5	99.4 ± 1.2	98.3 ± 1.0
6	97.9 ± 1.4	95.9 ± 2.0	98.5 ± 1.2	97.9 ± 1.0	98.9 ± 0.5	98.3 ± 1.3
7	98.7 ± 2.0	95.4 ± 1.8	97.3 ± 2.0	96.8 ± 1.5	98.5 ± 0.8	98.8 ± 1.6
8	99.4 ± 0.5	96.8 ± 2.0	98.4 ± 1.3	95.8 ± 1.8	98.9 ± 1.0	97.7 ± 0.6
9	99.6 ± 0.5	98.9 ± 1.6	99.3 ± 1.0	96.4 ± 1.3	99.2 ± 0.5	97.5 ± 0.7
10	99.3 ± 0.5	98.9 ± 1.2	99.5 ± 1.3	99.5 ± 1.4	99.5 ± 0.8	96.8 ± 1.8

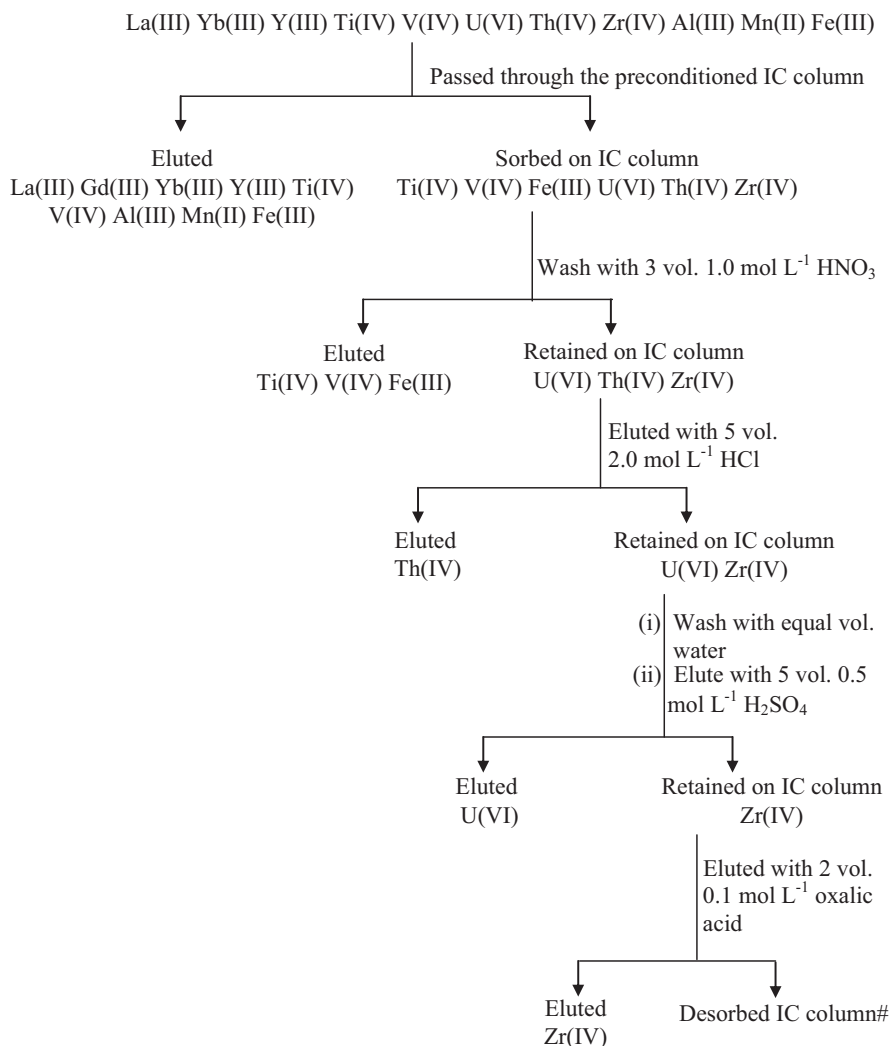
Conditions: feed solution: [Metal ion]=100 mg L<sup>-1</sup>; [HNO<sub>3</sub>]=5.0 mol L<sup>-1</sup>; flow rate=0.2 mL min<sup>-1</sup>; [IC]=5.22 g Cyanex 923 per g chromosorb.

column bed of impregnated chromosorb containing 5.22 g Cyanex 923 per g inert support preconditioned with 5.0 mol L<sup>-1</sup> HNO<sub>3</sub>. A synthetic mixture containing 100 mg L<sup>-1</sup> of each U(VI), Th(IV) and Zr(IV) in 5.0 mol L<sup>-1</sup> HNO<sub>3</sub> was passed through the column at a flow rate of 0.2 mL min<sup>-1</sup>. Elution of the retained metal ions was carried out with suitable eluting agents (Fig. 7).

### 3.6. Regeneration of the column

Experiments were conducted to check the regeneration capacity of the column packed with impregnated chromosorb for the repeated use by sorbing U(VI), Th(IV) or Zr(IV) from 5.0 mol L<sup>-1</sup> HNO<sub>3</sub>. The loaded Th(IV), U(VI) and Zr(IV) were eluted by passing 5 volumes of 2.0 mol L<sup>-1</sup> HCl/ 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 2 volumes of 0.1 mol L<sup>-1</sup> oxalic acid solution, respectively. Finally, the column was washed with water till the washings were neutral. Thereafter, it was preconditioned with





**Fig. 8.** Separation of lanthanides and associated elements from a synthetic mixture. # The column can be reused after washing with water and conditioning.

5.0 mol L<sup>-1</sup> HNO<sub>3</sub> for subsequent use. The sorption/elution efficiency was checked for 10 cycles. The results revealed a practically insignificant change in the efficiency of the column. The results of successive sorption–elution cycles for U(VI), Th(IV) and Zr(IV) are illustrated in [Table 1](#).

### 3.7. Recovery of lanthanides and other associated elements from allanite

Based on the uptake behaviour of different metal ions on Cyanex 923 impregnated chromosorb, a scheme has been designed to recover U, Th, Zr and lanthanide fractions from allanite where all these metals exist simultaneously ([Fig. 8](#)).

The column bed of impregnated chromosorb containing 5.22 g Cyanex 923 per g inert support was preconditioned with 5.0 mol L<sup>-1</sup> HNO<sub>3</sub>, then was loaded with 10 mL of allanite solution and the elution was started after 25 min. U, Th and Zr were retained by the column, whereas, lanthanides and

**Table 2**

Composition of fractions obtained from allanite using column packed with Cyanex 923 Impregnated Chromosorb 102 (IC).

Metal ion	Amount in feed solution ( $\mu\text{g}$ )	Amount in solution after sorption ( $\mu\text{g}$ )	Amount eluted with 5 volumes of $2.0 \text{ mol L}^{-1}$ HCl ( $\mu\text{g}$ )	Amount eluted with 5 volumes of $0.5 \text{ mol L}^{-1}$ $\text{H}_2\text{SO}_4$ ( $\mu\text{g}$ )	Amount eluted with $0.1 \text{ mol L}^{-1}$ oxalic acid ( $\mu\text{g}$ )	Recovery %	Purity %
La(III)	12,500	12,400	55	0.5	< 0.1	$\sim 96 \pm 1.5$	$\sim 98 \pm 1.0$
Yb(III)	22.8	21.5	< 0.1	< 0.1	< 0.1	$\sim 95 \pm 1.5$	$\sim 99 \pm 2.0$
Y(III)	351	348	< 0.1	< 0.1	< 0.1	$\sim 97 \pm 1.5$	$\sim 99 \pm 2.0$
U(VI)	745	< 0.1	1	718	< 0.1		
Th(IV)	4500	< 0.1	4278	2	< 0.1		
Zr(IV)	22.5	< 0.1	< 0.1	< 0.1	2.18		
V(IV)	47.6	45.2	< 0.1	< 0.1	< 0.1		
Ti(IV)	1220	1101	< 0.1	< 0.1	< 0.1		
Mn(II)	1200	1150.1	< 0.1	< 0.1	< 0.1		

Conditions: feed solution = 10 mL allanite; flow rate =  $0.2 \text{ mL min}^{-1}$ ; [IC] = 5.22 g Cyanex 923 per g chromosorb; bed height = 2 cm; bed density =  $0.67 \text{ g mL}^{-1}$ ; free column volume = 1.57 mL; volume of mobile phase = 0.079 mL; volume of stationary phase = 1.49 mL.

associated elements pass through the column. Th, U and Zr were subsequently recovered from the column using 5 volumes of  $2 \text{ mol L}^{-1}$  HCl, 5 volumes of  $0.5 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$  and 2 volumes of  $0.1 \text{ mol L}^{-1}$  oxalic acid solutions, respectively. The percentage recovery and purity of these fractions are given in Table 2.

#### 4. Conclusions

The results presented herein clearly indicate the potential of Cyanex 923 loaded columns for the separation and recovery of U(VI), Th(IV) and Zr(IV) from lanthanides and other associated elements. The low aqueous miscibility of the extractant imparts a good regeneration power to the column. Experiments conducted up to 10 cycles show practically insignificant change in the efficiency of the column. Sharp elution curves are obtained with simple eluting agents. The preparation of impregnated chromosorb column is convenient because no silanization step is required as in the case of silica gel columns. Recovery of U(VI), Th(IV) and Zr(IV) from synthetic mixture as well as natural matrix was more than 95% with a purity of around 97%. Furthermore, at the proposed separation conditions the column shows selectivity towards U, Th and Zr. This avoids unnecessary loading of the column with other metal ions present in the sample.

#### Conflict of interest

There is no conflict of interest.

#### Acknowledgements

Thanks are due to Cytec Inc., Canada for providing Cyanex 923 sample as gift and to John's Manville, USA for providing the gift sample of Chromosorb 102. Financial support of the Council of Scientific and Industrial Research (CSIR), India and the Ministry of Human Resource Development (MHRD), India are gratefully acknowledged.

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