

## **ANION EXCHANGE SEPARATION OF SOME LANTHANIDE IONS WITH URANIUM (VI) USING NITRITE COMPLEXING MEDIA**

**ARCHANA BHARADWAJ\* and S.D. BHARADWAJ\*\***

\*Deptt. of Chemistry, Kamla Raja (Autonomous) Girls College, Gwalior (M.P.) INDIA

\*\*Cancer Hospital & Research Institute, Gwalior-9 (M.P.) INDIA

### **ABSTRACT**

Anion exchange separation of some lanthanide metal ions from uranium (VI) has been studied in sodium nitrite and acetone-sodium nitrite media using Dowex- 1X8, in nitrate form of resin. The useful separation performed are La (III)-U (VI), Ce (III)-U (VI) and Sm (III)-U (VI).

**Key words:** Anion exchange separation, Lanthanide ions, Uranium (VI), Nitrite complexing media.

### **INTRODUCTION**

The complex forming acids, mineral acids or their salts have been used since long for cation-exchange studies to bring about metal ion elution according to the stability of the metal ion complex formed. Strelow<sup>1</sup>, Marcus<sup>2</sup>, Samuelson<sup>3</sup> and Korkisch<sup>4</sup> reviewed intensively applications of ion-exchange for separation of metal ions and the utility of such complex forming reagent. Korkisch<sup>5</sup>, and others<sup>1,2</sup> have used complexing media with mixed organic solvents. Bhatnagar and coworkers<sup>6-11</sup> made use of sodium nitrite as a new complexing eluant for number of cation-exchange chromatographic separation. Inorganic complexing agent can be decomposed easily after separation process to convert the separated metal ions into their simple metal salts. With organic complexing agents, stable complexed species are formed and their complete break needs quite drastic treatment. Hence, inorganic complexing agents are more preferred as newer ion-exchange separation procedures. Therefore, we have used simple nitrite complexing media in present anion-exchange separation studies.

### **EXPERIMENTAL**

**Metal ion salt solution:** Rare earth metal ion solutions were prepared from their nitrates in double distilled water to give 0.2 N stock solutions.

**Sodium nitrite:** Pure sodium nitrite (BDH, AnalaR) was used to prepare the complexing media, both in water and aqueous acetone as solvents.

**Organic solvent:** Acetone (BDH, AnalaR) was used in all elution and separation studies.

**Resin column:** Dowex-1X8 was used in its nitrate form and it was packed in an ion-exchange column of corning glass tube provided with a perforated disc at the lower end. A Glass wool plug of about 1cm thickness was used over this disc. Resin was filled in the fully swollen condition by preparing its slurry in double distilled water. A resin column of 10.0 x 1.0 cm was prepared in this way for all elution and separation studies.

**Titrant :** Disodium EDTA solution (0.025N) was prepared from the pure salt to get the titre for most of the rare earth metal ions. Titrations were carried at proper pH<sup>5</sup> using suitable indicators. (bromopyrogallol red.)

**Uranium estimation:** Estimation of U (VI) colorimetrically-Photoelectric colorimeter was used for estimating uranium (VI) using ferrocyanide-sodium sulphate mixture to develop the colour in uranium solution suitably diluted before developing colour.

### Preliminary Elution Study of Uranium (VI)

A resin bed of 10.0 x 1.0 cm was used for preliminary studies with lanthanide ions and uranyl ion. 10.0 mL solution of uranyl nitrate with 1.0 N sodium nitrite complexing agent was poured over the resin column and the flow rate was adjusted to 2 mL per minute. As it started percolating through the resin bed, the effluent was tested intermittently for the presence of uranium (as uranyl ion) in it by potassium ferrocyanide solution. When the elution of uranium ions stopped the column was washed twice with distilled water and then its elution was carried out in the aqueous nitric acid solution (0.05N or 0.1%). Effluent fractions of 10 mL each were collected and estimated colorimetrically after removing nitrite ions completely and adjusting the acidity as per the requirements of the estimation procedure. All uranium was found to be present in first to seventh fraction of 10.0 mL each.

### Preliminary Elution Study for Tripositive Lanthanide Ions

Preliminary studies were performed with La (III) by taking 10.0 mL of 0.1 N solution of lanthanum nitrate complex as influent volume for sorption step. During the sorption step, a flow rate of 2.0 mL per minute was fixed for this ion. The effluent solution was tested intermittently for the presence of lanthanides using a metal indicator bromopyrogallol red. No leakage of ion was detected during this step; thus it confirmed the complete exchange of ion on a 10.0 mL column of Dowex-1X8 in nitrate form. The elution of La (III) and Sm (III) were then carried out with 2.5% (w/v) NaNO<sub>3</sub> in 10% aqueous acetone for La<sup>3+</sup>, 5% (w/v) NaNO<sub>3</sub> in 10% aqueous acetone for Ce<sup>4+</sup>, and 2.5% (w/v) NaNO<sub>3</sub> in 10% aqueous acetone for Sm<sup>3+</sup>.

During these elution studies, 10.0 mL fraction of effluent solutions were collected and estimated for the presence of the concerned ions complexometrically.

### Separation Studies of Uranium (VI) from Tripositive Lanthanide Ions

Separation studies were performed with 10.0 x 1.0 cm resin bed again with a fixed flow rate of 2.0 mL cm<sup>-1</sup> min<sup>-1</sup>. Binary electrolyte mixtures were prepared for separation studies using 10.0 mL of 0.1 N uranyl nitrate solution and 10.0 mL of 0.1 N tripositive lanthanide ions with 1.0 N sodium nitrite (complexing agent) keeping the total influent volume of 20.0 mL. Elution of lanthanides was tried first. All the lanthanides were eluted in first 9 to 10 fractions and all these fractions were estimated after nitrite decomposition titrimetrically using disodium EDTA as titre and bromopyrogallol red as an indicator at pH 5.0.

After complete elution of lanthanides, the elution of uranium (VI) was tried with 0.05% (v/v) nitric acid solution. All uranium was eluted in later 8 to 10 fractions. All these fractions were estimated colorimetrically for uranium (VI) and results reported as meq. of uranium (VI) in each fraction.

**Table 1. Separation of Lanthanides (III) from Uranium (VI)**

Column Characteristics	
Resin-Dowex	- 1 X 8 (NO <sub>3</sub> ), capacity-2.1 meqg <sup>-1</sup>
Column dimension	- 10.0 x 1.0 cm
Influent	- 10 mL of 0.1 N La(NO <sub>3</sub> ) <sub>3</sub> , Ce(NO <sub>3</sub> ) <sub>3</sub> , Sm(NO <sub>3</sub> ) <sub>3</sub> Separately + 10 mL of 0.1 N UO <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>
Complexing agent	1.0 N (1.725 g) NaNO <sub>2</sub> in the influent solution.
Eluant	
(i) Component	(a) 2.5% (w/v) NaNO <sub>3</sub> in 10% aqueous acetone for La <sup>3+</sup> (b) 5% (w/v) NaNO <sub>3</sub> in 10% aqueous acetone for Ce <sup>3+</sup> (c) 2.5% (w/v) NaNO <sub>3</sub> in 10% aqueous acetone for Sm <sup>3+</sup>
(ii) Component	- 0.05% (v/v) aqueous HNO <sub>3</sub> for U <sup>6+</sup>
Flow rate	- 2.0 mL. cm <sup>-1</sup> min <sup>-1</sup>
Fractional Volume	- 10.0 mL each.
Titre	(a) Disodium EDTA (0.025N) for La <sup>3+</sup> (b) Photo-Colorimetric estimation for U <sup>6+</sup>

**Table 2. Eluate Concentration, meq**

Fraction Number	10.0 mL	La (III)	U (VI)	Ce (III)	U (VI)	Sm (III)	U (VI)
1.	0.0785	Nil	0.2875	Nil	0.3750	Nil	
2.	0.1375	Nil	0.2250	Nil	0.2270	Nil	
3.	0.1375	Nil	0.2000	Nil	0.1875	Nil	
4.	0.1500	Nil	0.1500	Nil	0.1375	Nil	
5.	0.1250	Nil	0.1125	Nil	0.1125	Nil	
6.	0.1125	Nil	0.0625	Nil	0.0750	Nil	
7.	0.1000	Nil	0.0375	Nil	0.0500	Nil	
8.	0.1000	Nil	0.0250	Nil	0.0375	Nil	
9.	0.0750	Nil	Nil	Nil	0.0375	Nil	
10.	0.0625	Nil	Nil	0.0210	Nil	Nil	
11.	0.0375	Nil	Nil	0.0394	Nil	Nil	
12.	Nil	Nil	Nil	0.1910	Nil	0.2630	
13.	Nil	Nil	Nil	0.1160	Nil	0.2270	
14.	Nil	0.0140	Nil	0.0990	Nil	0.1670	
15.	Nil	0.0320	Nil	0.0069	Nil	0.1040	
16.	Nil	0.3300	Nil	0.0025	Nil	0.0770	
17.	Nil	0.2900	Nil	0.0010	Nil	0.0650	
18.	Nil	0.0160	Nil	0.0010	Nil	0.0260	
19.	Nil	0.0050	Nil	Nil	Nil	0.0260	
20.	Nil	0.0040	Nil	Nil	Nil	0.0160	
21.	Nil	0.0040	Nil	Nil	Nil	0.0160	
22.	Nil	Nil	Nil	Nil	Nil	Nil	

## RESULTS AND DISCUSSION

Results of the separation studies have been provided first as comparative  $K_D$  values to calculate and report separation factors.

The results of separation studies performed with different tripositive combination of metal ions have been reported in the Table 1 and 2. These tables give fraction wise metal ion concentrations in milliequivalents and the data have been used to plot elution curves for these separations. (Figure 1, 2 and 3).

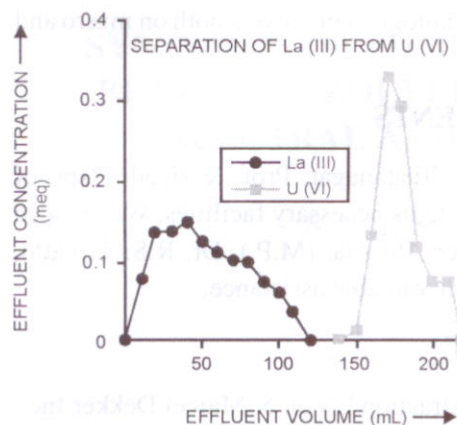


Figure 1

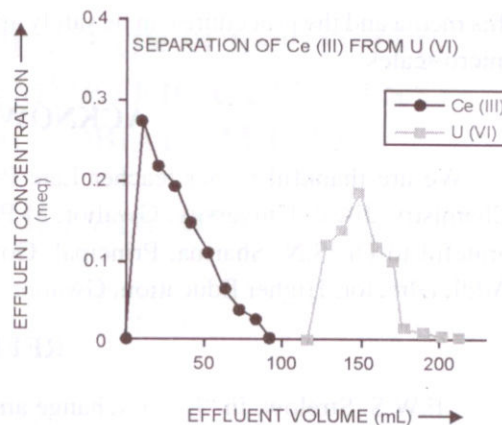


Figure 2

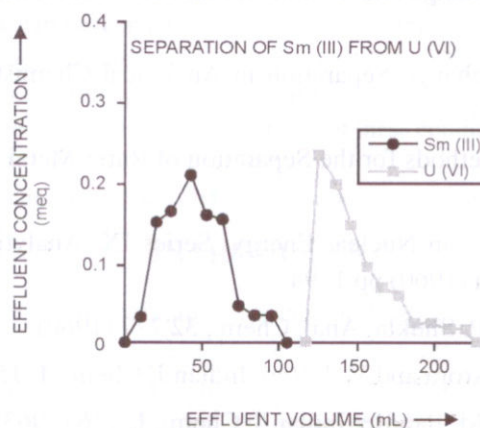


Figure 3

Ion-exchange chromatography is probably the only important analytical method which can separate and concentrate any combination of elements. It is a powerful tool for the separation of trace elements and also closely related group of elements like rare earths and transuranics.

Separation of uranium (VI) from tripositive rare earth metal ions was a clear cut proposition and all separations reported in this part of the work i.e. for U-La, U-Ce, and U-Sm, were quantitative also. The rare earth metal ions were eluted first with 2.5% NaNO<sub>3</sub> in 10% aqueous acetone while uranium was eluted by an aqueous nitric acid (0.05%) solution as the second component. Thus, the results reported in this part of the work indicate the utility of complex nitrite media for anion exchange separation studies of metal ions from inner transition series. Many useful separations have been carried out from U (VI), which were not possible with cation exchange studies. Uranium (VI) separation from rare earth metal ions has been very efficient in

this media and the procedure can be safely applied to technological processes both on macro and micro scales.

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