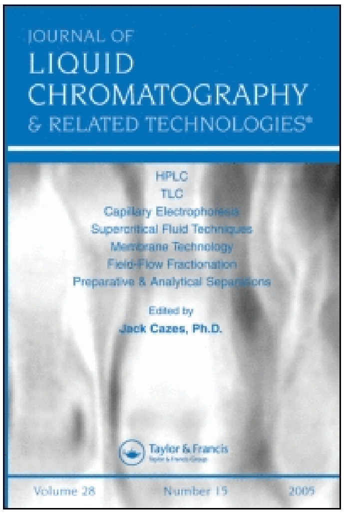

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

SEPARATION OF ANIONS ON THORIUM TRIETHYLAMINE AS A NEW CHELATING AND ANION EXCHANGER

Hasan M. Abdul Aziz[a]
[a] Department of Chemistry, University-Gaza, Gaza, Palestine

To cite this Article Aziz, Hasan M. Abdul(2002) 'SEPARATION OF ANIONS ON THORIUM TRIETHYLAMINE AS A NEW CHELATING AND ANION EXCHANGER', Journal of Liquid Chromatography & Related Technologies, 25: 9, 1387 — 1400

To link to this Article: DOI: 10.1081/JLC-120004754

URL: http://dx.doi.org/10.1081/JLC-120004754

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

J. LIQ. CHROM. & REL. TECHNOL., 25(9), 1387–1400 (2002)

SEPARATION OF ANIONS ON THORIUM TRIETHYLAMINE AS A NEW CHELATING AND ANION EXCHANGER

Hasan M. Abdul Aziz

Department of Chemistry, Al Azhar University-Gaza,
P. O. Box 1277, Gaza-Palestine
E-mail: hasan_aziz@email.com

ABSTRACT

A new inorganic ion exchanger, thorium triethylamine, has been synthesized. The material has been studied for its anion exchange capacity, sorption capacity, K_d values, composition, potentiometric titration, infrared spectrum, and chemical stability. The material was found useful for separation of I^- and Br^- from CrO_4^{2-} and $Cr_2O_7^{2-}$, I^- and Br^- from VO_3^- and PO_4^{3-}, SCN^- and I^- from $Cr_2O_7^{2-}$ and $Fe(CN)_6^{3-}$ and I^- from $S_2O_3^{2-}$.

INTRODUCTION

Separation of anions that have largely been accomplished on organic anion exchangers have been of much interest to various workers.[1,2] The anion exchange resin has limited applications at higher temperatures and in the presence of ionizing radiation. Therefore, to overcome these limitations, efforts were made to develop inorganic ion exchangers. In the continued effort to synthesize a new inorganic anion exchanger with greater selectivity, greater thermal stability, and greater resistance for ionizing radiation, the hydroxides of certain metals were first tried. The hydroxides of III group and IV group metals like Sn(IV), Zr(IV), Al(III), and a few others[3–7] have been found to show anion exchange behaviour only at lower pH values. These materials found limited use at higher pH values. To overcome such limitations, efforts are made to develop some anion exchanger bases on metal hydroxides with an amino group. Some materials of this kind have been tried: Tin(IV)-bis(diethanolamine), titanium-bis(diethanolamine), and aluminium triethanolamine.[8–10]

As strong base exchangers can be prepared by the use of tertiary alkylamines, triethylamine based inorganic anion exchangers are being explored in this work. The chelating ion exchangers have been developed recently and their analytical applications explored.[11] An advantage in introducing amino groups is also observed because of its chelate formation with the metal ions.

In the present work the material thoriom triethylamine has been studied, at the first level, in its application as a new inorganic anion exchanger to develop some analytically important separations of anions, and to propose its utility as a chelating material for uptake of Cu(II). Composition determination and IR studies are made to characterize the exchanger.

EXPERIMENTAL

Synthesis

Research grade chemicals were used in this study without any further purification. Thorium triethylamine was prepared by mixing 0.1 molar solution of thorium nitrate and 0.1 molar solution of triethylamine in the volume ratio of 1 : 4 (Table 1). The precipitate, prepared in this way, was kept standing for 24 hours at a temperature 25°C ± 2. The precipitate was filtered and then washed with deionized water. The precipitate was kept in an oven at 40°C till completely dried. It was then kept in the air for 12 hours and then it was immersed in deionized water. On immersion, the exchanger broke down into smaller particles. It was finally kept in the oven at 40°C for drying. The exchanger granules were then converted into a nitrate form by putting the ion exchange particles in 1 mole dm^{-3} solution of sodium nitrate for 12 hours, intermittently replacing the supernatant liquid with a fresh solution of sodium nitrate, and was finally washed and dried at 40°C.

Anion Exchange Capacity

The anion exchange capacity of thorium triethylamine was determined by the column method. The anion exchanger weighing one gram was poured in a

Table 1. Conditions of Preparation and Properties of Thorium Triethylamine Exchanger

	Condition of Synthesis Molarity of Reagent				Properties	
Sample	Th IV Nitrate (mol dm^{-3})	Triethyl Amine (mol dm^{-3})	Mixing Volume Ratio	Nature of Precipitate	Ion Exchange Capacity ($Cr_2^{2-}{}_7$ (meq g^{-1})	Sorption Capacity [Cu (II)] (meq g^{-1})
S–1	0.10	0.10	1 : 1	No precipitate		
S–2	0.10	0.10	1 : 2	Precipitate appears, dissolves by shaking		
S–3	0.10	0.10	1 : 3	Precipitate appears, dissolves by shaking		
S–4	0.10	0.10	1 : 4	A thick precipitate	3.10	0.41
S–5	0.10	0.10	1 : 5	Precipitate appears, dissolves by shaking		
S–6	0.10	0.10	2 : 1	No precipitate		

glass column measuring 20 cm in length and 0.60 cm diameter with a glass wool support. The capacity was calculated for different anions, namely chloride, bromide, iodide, thiosulfate, chromate, and dichromate by converting the exchanger in the required form with sodium or potassium salts of the required ions. The column was washed with deionized water to remove the excess of anions. The eluent used was 1.0 mole dm^{-3} sodium nitrate solution. The elusion rate was fixed at 0.5 cm^3 min^{-1}. Anion exchange capacities for chloride, bromide, iodide, thiosulfate, chromate, and dichromate were 0.68, 0.61, 0.46, 0.58, 1.85, and 3.10 meq g^{-1}, respectively. For sorption capacity, 1.0 g of the exchanger was taken in the column; 10 cm^2 of 0.1 mole dm^{-3} copper (II) solution was poured over the column at a rate of 0.5 cm^2 min^{-1}. The effluent was then titrated and copper ions were determined. A fresh sample of 10 cm^2 of 0.01 mole dm^{-3} copper (II) nitrate was added over the column, and the effluent again titrated. The readings of EDTA consumed for total effluent, was subtracted from the reading of EDTA consumed for total influent (0.01 mole dm^{-3} copper nitrate). The sorption capacity was then calculated from these readings. For the determination of copper (II) ions, the solution was titrated against 0.01 mole dm^{-3} EDTA solution using buffer of pH 3.6 and 1–(2–pyridlazo) –2–naphthol [PAN]. Sorption capacity for copper (II) was found to be 0.41 meq g^{-1}.

Chemical Composition

One gram of the exchanger was dissolved in 50 cm^3 aquaregia. Heating was avoided in preparing the solution. The volume was made up to 100 cm^3 in a volumetric flask with deionized water. The amount of thorium was determined by titrating against 0.01 M EDTA solution using copper PAN indicator. Triethylamine present in another portion of the sample was determined spectrophotometrically by ninhydrine.[12] The ratio of thorium and triethylamine in the exchanger was found to be 1 : 3.

Chemical Stability

The chemical stability of thorium triethylamine was determined by shaking 0.50 g of exchanger for four hours in the different solutions, in which its stability was to be checked. In the supernatant liquid, the amount of thorium was determined by titrating a known volume of solution against 0.02 molar EDTA solution, while triethylamine was determined spectrophotometrically, by ninhydrine, in another known volume of the sample. The stability of the exchanger in different solvent systems reveal that the exchanger is stable in deionized water, methyl alcohol, ethyl alcohol, and aqueous ammonia (10.0 mole dm^{-3}). However, the exchanger is less stable in concentrated solutions of acids.

Effect of Drying Temperature on Anion Exchange Capacity

Thorium triethylamine was heated in a muffle furnace at different temperatures for four hours. The capacity of the exchanger was determined at 60°C, 100°C, 200°C, 300°C, and 400°C, respectively.

IR Studies

For characterization of the exchanger, IR studies were made. The spectrum was observed using a KBr disc. The results are presented in Figure 1.

Potentiometric Titrations

Potentiometric titrations were performed by the Topp and Pepper method.[13] 0.5 gram of the exchanger was shaken with the solution of 0.01 M HCl and 0.01 M NaCl. The total volume of the reaction mixture was kept at 50 mL in all cases. The pH of the solutions, after equilibration for four hours, was then determined. The results are plotted in Figure 2.

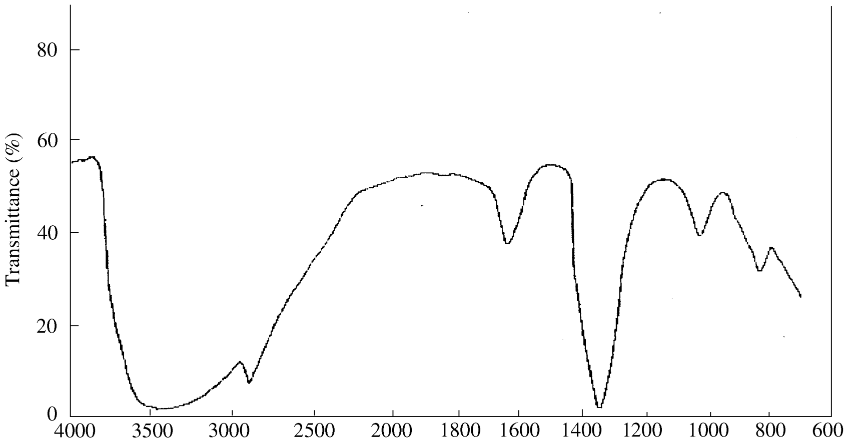

Figure 1. IR Spectrum of thorium triethylamine exchanger.

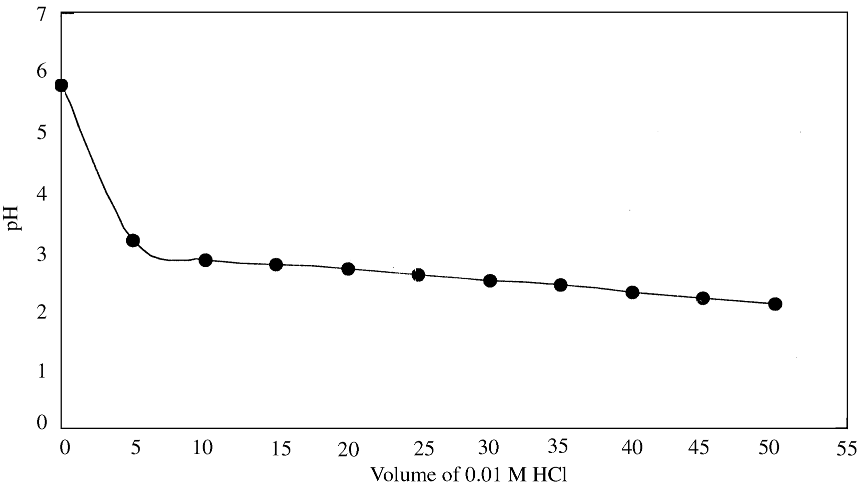

Figure 2. Potentiometric titration curve for thorium triethylamine exchanger.

K_d Values

A batch process determined distribution coefficient values for anions. 1.0 mL of anionic solution was taken in a 50 mL standard flask. The remaining volume of the flask was filled with deionized water or different concentrations of sodium hydroxide, the solutions in which the K_d values were to be studied. The solution was then transferred to a 250 mL Erlenmeyr flask. The exchanger, weighing 0.5 g, was then added to each flask; these flasks were then shaken for 4 hours in a shaker to attain equilibrium. Results of the K_d values in deionized water and different concentrations of sodium hydroxide solution are summarized in Table 2.

Separation

The separations of anions, with appreciable differences in their K_d values, were tried. 2.00 g of anion exchanger (150–200 mesh size) in nitrate form were put into a glass column having a height of 30 cm and diameter 0.60 cm. A mixture of anionic solutions was poured into the column. The solution was allowed to flow down very slowly through the column. These anions were adsorbed at the top of the exchanger bed forming an initial zone. The column was washed with

Table 2. Distribution Coefficient of Some Anions on Thorium Triethylamine Exchanger

	K_d Values				
Anions	H_2O	10^{-4} M NaOH	10^{-3} M NaOH	10^{-2} M NaOH	10^{-1} M NaOH
Chloride	240	168	155	104	34
Bromide	540	540	392	178	18
Iodide	438	438	258	54	13
Thiocyanate	358	293	244	28	04
Dichromate	T.A.	T.A.	T.A.	270	02
Thiosulfate	T.A.	T.A.	T.A.	217	08
Chromate	T.A.	T.A.	T.A.	402	04
Iodate	1340	1100	744	100	00
Ferricyanide	T.A.	T.A.	850	500	00
Sulfite	933	930	786	77	02
Bromate	2062	2062	919	44	00
Persulfate	1042	1042	567	233	00
Arsinite	1933	1930	1425	1120	335
Ferrocyanide	T.A.	T.A.	1205	400	150
Vanadate	T.A.	T.A.	900	305	98
Phosphate	T.A.	T.A.	1500	256	04

T.A. = total adsorption.

deionized water. The anions were then eluted by the appropriate eluting reagent. The amount of anions were then determined by standard methods.

RESULTS AND DISCUSSION

The results summarized in Table 1, show that complete precipitation of thorium triethylamine occurred only when the metal to amine ratio must be kept 1 : 4.

The anion exchange capacity varies from 0.46 to 3.10 for the anions tested. The variation is probably due to the difference in selective uptake of different anions. For halide ions, the order can be given as $Cl^- > Br^- > I^-$. This indicates that the capacity decreases linearly as the ionic size increases, and for some other ionic species the capacity decreases in the order $Cr_2O_7^{2-} > CrO_4^{2-} > S_2O_3^{2-}$. Thus, the exchanger behaves as a chelating, as well as an anion exchanger. On the basis of the above discussions, it is concluded that the exchanger shows anion exchange capacity due to the presence of —N^+— group and chelating properties due to the presence of —N— group.

The sorption capacity of copper (II) was found to be $0.41\,\mathrm{meq\,g^{-1}}$ of thorium triethylamine. When thorium triethylamine in H^+ form was kept in contact with a solution of sodium nitrate, no release of H^+ was observed. When exchanger was kept in Cu (II) solution it turned blue in appearance. Copper (II) ions were strongly attached to thorium triethylamine and cannot be broken by simple complexing agents. However, when EDTA is used as eluted, it showed the release of copper (II) ions. This is because EDTA, being a higher complexing agent than triethylamine, is capable of releasing Cu(II) from the thorium triethylamine phase.

The results of composition studies show that thorium triethylamines are present in the exchanger in the molar ration of 1 : 3.

The results of a heating effect on the capacity of the exchanger show that the capacity decreases with increases in temperature. At higher temperatures, the water molecules and amine molecules are lost from the exchanger, thereby decreasing the capacity. As a result, the capacity at higher temperatures is much lower. Loss in weight per gram of the exchanger at different temperatures shows that at 100°C the weight loss is because of loss in water molecules and amine molecules up to 300°C. Above 300°C there is no appreciable weight loss, since all the amine is lost. These results are in accordance with the results of capacity at different temperatures.

It is quit clear that the exchanger thorium triethylamine is still in possession of the amine group (Figure 1).

The potentiometric titration curve, plotted in Figure 2, reveals that the exchanger behaves as a monofunctional exchanger.

The results of dissolution of the exchanger in different solvent systems, show that the exchanger is quit stable in deionized water, concentrated solution of neutral salts, and basic media.

The distribution on the behaviour of anions, given in Table 2, indicates that the K_d values were high when deionized water was used as a medium. Distribution values were less when a sodium hydroxide solution was used for the studies. Distribution values decreased as the concentration of sodium hydroxide solution was increased. Being a weak anion exchanger, thorium triethylamine has a high affinity for hydroxide ions. Hence, other ions showed less uptake in the presence of hydroxyl ions.

On the basis of large differences in the distribution behaviour of various anions, many separations were tried. Separation of I^- from CrO_4^{2-}, from $Cr_2O_7^{2-}$, from VO_3^-, from $[Fe(CN)_6]^{3-}$, and from $S_2O_3^{2-}$; Br^- from CrO_4^{2-}, from $Cr_2O_7^{2-}$, and from PO_4^{3-}; and SCN^- from $Cr_2O_7^{2-}$were successfully achieved. The quantitative separation of anions on thorium triethylamine exchanger given in Table 3, show a high selectivity towards CrO_4^{2-} and $Cr_2O_7^{2-}$ as predicted by capacity. The order of separations are presented in Figures 3–11.

Table 3. Quantitative Separation of Anions on Thorium Triethylamine Exchanger

No	Mixture	Eluents	Eluate (mL)	Amount Loaded (mg)	Amount Found (mg)	% Error
1.	I^-	0.001 M NaOH	80	2.667	2.540	4.76
	CrO_4^{2-}	0.1 M NaOH	100	11.078	10.904	1.57
2.	Br^-	0.0001 M NaOH	80	2.64	2.48	6.06
	CrO_4^{2-}	0.1 M NaOH	90	11.078	10.846	2.09
3.	I^-	0.0001 M NaOH	80	2.667	2.476	7.16
	$Cr_2O_7^{2-}$	0.1 M NaOH	110	13.068	12.744	2.48
4.	Br^-	0.0001 M NaOH	80	2.64	2.52	4.54
	$Cr_2O_7^{2-}$	0.1 M NaOH	110	13.068	12.852	1.65
5.	I^-	0.0001 M NaOH	100	2.10	2.00	4.76
	VO_3^-	0.1 M NaOH	100	4.27	4.00	6.32
6.	Br^-	0.0001 M NaOH	90	2.64	2.52	4.54
	PO_4^{3-}	0.1 M NaOH	90	4.56	4.20	7.90
7.	SCN^-	0.0001 M NaOH	90	1.595	1.450	9.09
	$Cr_2O_7^{2-}$	0.1 M NaOH	120	13.068	12.744	2.48
8.	I^-	0.0001 M NaOH	80	2.667	2.476	7.16
	$[Fe(CN)_6]^{3-}$	0.1 M NaOH	110	8.586	8.268	3.70
9.	I^-	0.0001 M NaOH	80	2.667	2.540	4.76
	$S_2O_3^{2-}$	0.1 M NaOH	80	3.192	3.08	3.50

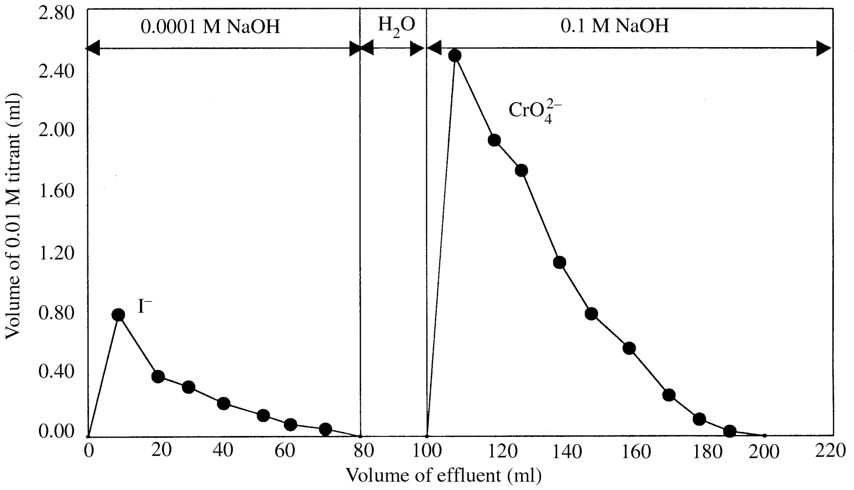

Figure 3. Separation of I^- from $Cr_2O_4^{2-}$.

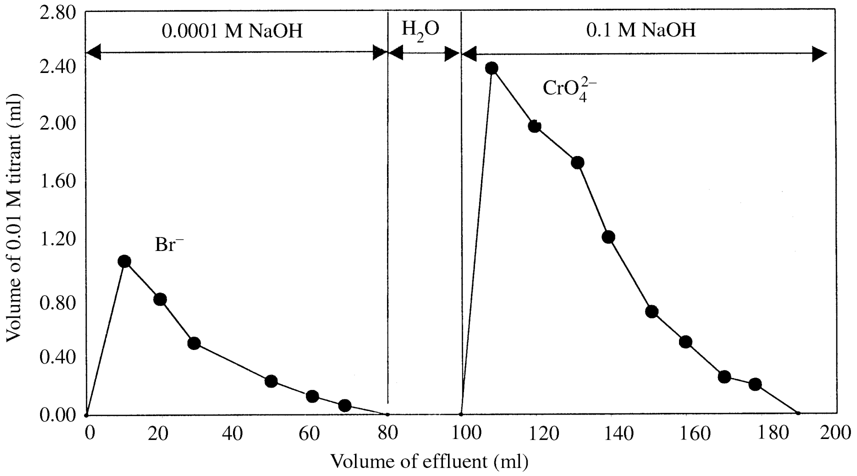

Figure 4. Separation of Br^- from $Cr_2O_4^{2-}$.

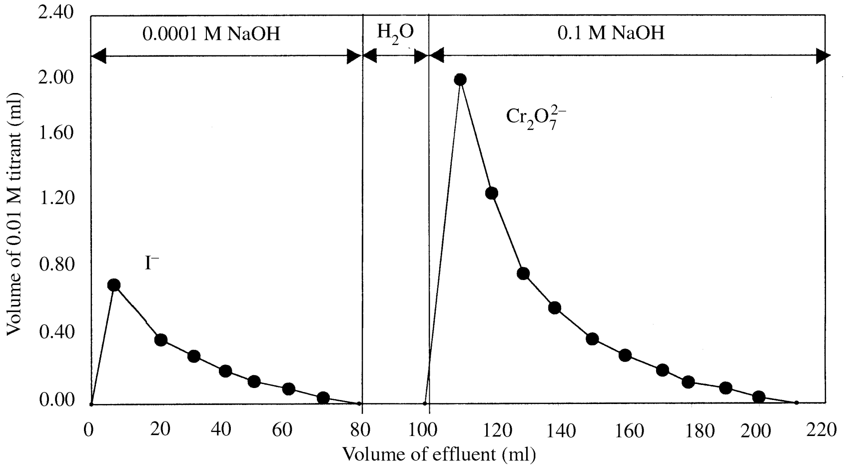

Figure 5. Separation of I^- from $Cr_2O_7^{2-}$.

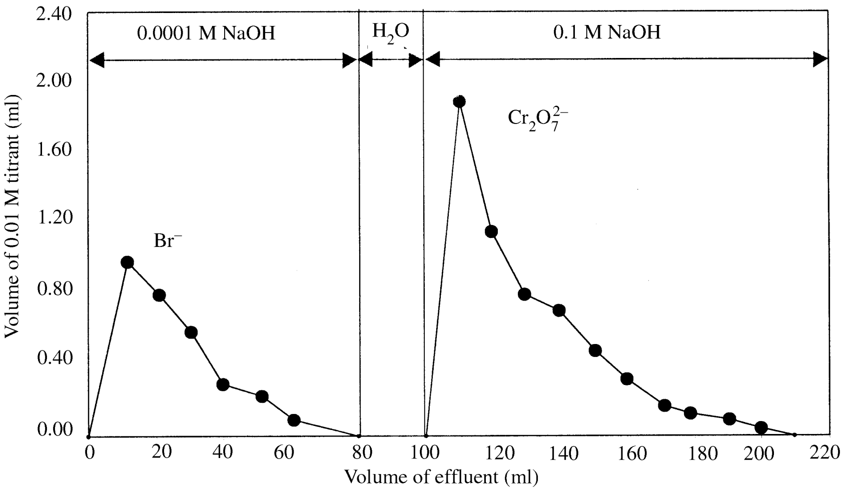

Figure 6. Separation of Br$^-$ from $Cr_2O_7^{2-}$.

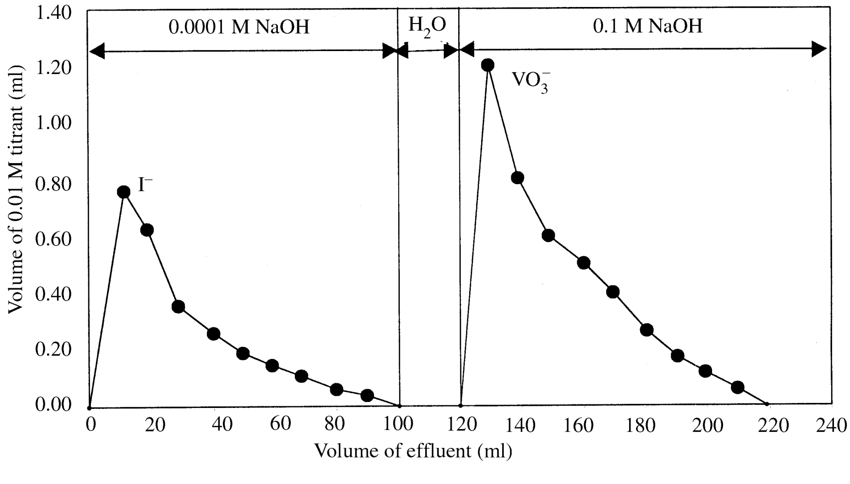

Figure 7. Separation of I$^-$ from VO_3^-.

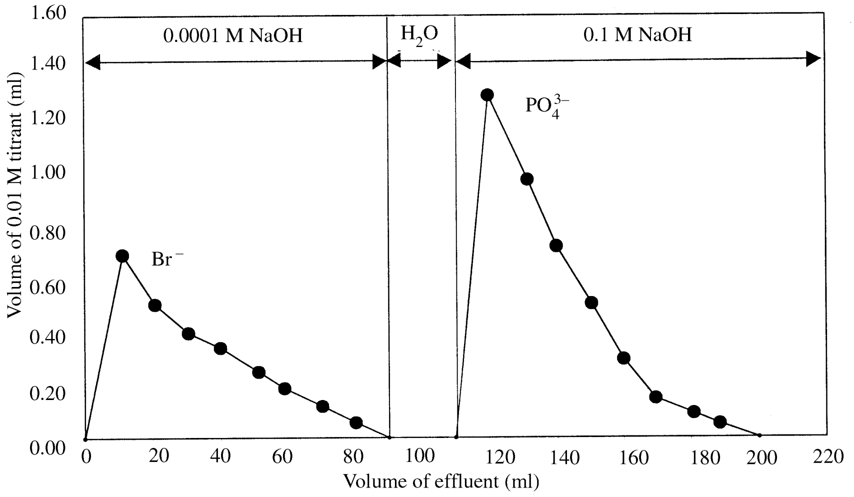

Figure 8. Separation of Br^- from PO_4^{3-}.

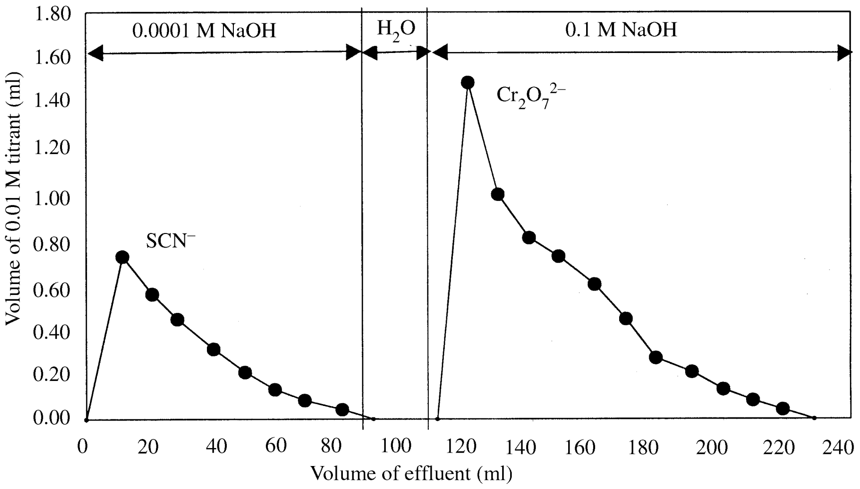

Figure 9. Separation of SCN^- from $Cr_2O_7^{2-}$.

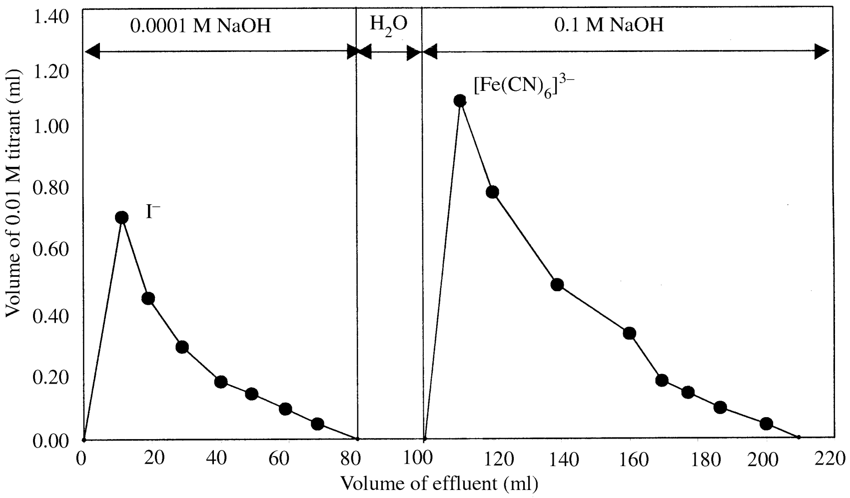

Figure 10. Separation of I^- from $[Fe(CN)_6]^{3-}$.

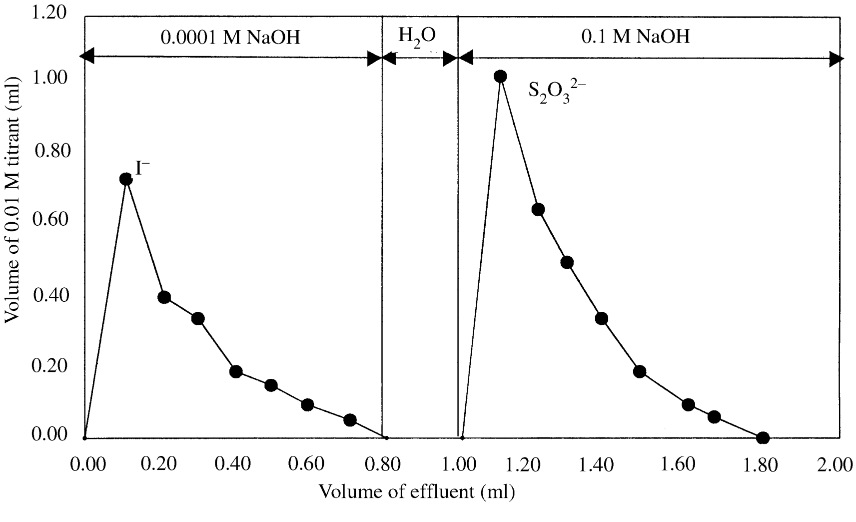

Figure 11. Separation of I^- from $S_2O_3^{2-}$.

ACKNOWLEDGMENT

Prof. J. P. Rawat, AMU-Aligarh, India, is highly acknowledged for his mutual support.

REFERENCES

1. Pollard, F.H.; Nickless, G.; Rothwell, M.T. J. Chromatog. **1963**, *10*, 212.
2. Brown, L.C.; Begum, G.M.; Boyd, G.E. J. Amer. Chem. Soc. **1969**, *91* (9), 2250.
3. Kraus, K.A.; Phillips, H.O.; Carison, T.A.; Johnson, J.S. On *Peaceful Uses of Atomic Energy*, Proceeding of 2nd International Conference, Geneva, March 28, 1958.
4. Britz, B.; Nancollas, G.H. J. Inorg. Nucl. Chem. **1969**, *31*, 3861.
5. Abe, M.; Ito, T. Nippon Kagaku Zasshi **1965**, *86*, 817.
6. Venketaremani, B.; Venketeshwarlu, K.S. J. Inorg. Nucl. Chem. **1980**, *42*, 909.
7. Rawat, J.P.; Iqbal, M. Annali Di Chemica. **1979**, *69*, 241.
8. Rawat, J.P.; Iqbal, M. Ann. Chem. **1981**, 431.
9. Rawat, J.P.; Iqbal, M.; Ali, S. J. Indian Chem. Soc. **1984**, *61*, 185.
10. Rawat, J.P.; Iqbal, M.; Alam, M. Ann. Chem. **1985**, *75*, 87.
11. Rawat, J.P.; Alam, M.; Singh, B.; Aziz, H.M.A. Bull. Chem. Soc. Jpn. **1987**, *60*, 2619.
12. Snell, F.D.; Snell, C.T. *Colorometric Methods of Analysis*, 3rd Ed.; D. Van Nostrand: Princeton, New Jersey, 1954; Vol. 4, 37.
13. Topp, N.E.; Pepper, K.W. J. Chem. Soc. **1949**, 3299.

Received July 5, 2001
Accepted August 1, 2001
Manuscript 5609