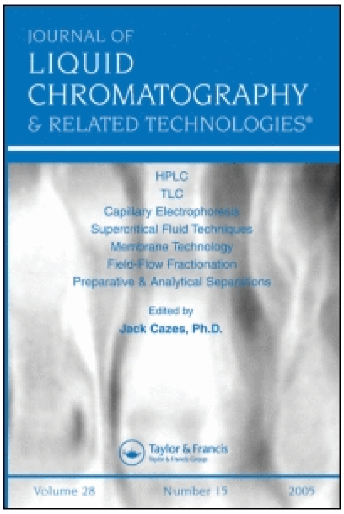

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Separation of Anions and Cations on Thorium Tellurite-A New Amphoteric Ion Exchanger

J. P. Rawat[a]; M. Iqbal[a]; H. M. A. Abdul Aziz[a]
[a] Analytical Laboratories, Department of Chemistry, Aligarh Muslim University, ALIGARH, INDIA

To cite this Article Rawat, J. P. , Iqbal, M. and Aziz, H. M. A. Abdul(1984) 'Separation of Anions and Cations on Thorium Tellurite-A New Amphoteric Ion Exchanger', Journal of Liquid Chromatography & Related Technologies, 7: 8, 1691 — 1706

To link to this Article: DOI: 10.1080/01483918408074077

URL: http://dx.doi.org/10.1080/01483918408074077

JOURNAL OF LIQUID CHROMATOGRAPHY, 7(8), 1691-1706 (1984)

SEPARATION OF ANIONS AND CATIONS ON THORIUM TELLURITE - A NEW AMPHOTERIC ION EXCHANGER

J.P.Rawat, M.Iqbal and H.M.A.Abdul Aziz,

Analytical Laboratories,
Department of Chemistry,
Aligarh Muslim University,
ALIGARH-202001 (INDIA).

ABSTRACT

A new amphoteric ion exchanger, thorium tellurite has been synthesized. Its chemical stability, composition determination and potentiometric titration have been performed. K_d values for various anions and cations have been determined. The material was found useful for separation of NO_3^- from NO_2^-; MoO_4^{2-} from PO_4^{3-}, VO_3^- from MeO_4^{2-}, SO_4^{2-} from $S_2O_3^{2-}$ and BrO_3^- from Br^- and also of Cu(II) from Hg(II), Cu(II) from Ni(II), Pb(II) from Cd(II) and UO_2(I) from Hg(II).

INTRODUCTION

Separation of anions have been of much interest to various workers (1-2). But that have largely been accomplished on organic anion exchangers. Some of the synthetic inorganic ion exchangers are also known to behave both as cation as well as anion exchangers. Such an amphoteric behaviour has been found to be limited mainly to the hydroxides of Sn(IV) (3), Zr(IV) (4), Al(III) (5) and few others (6-7). Their behaviour is usually a function of pH.

In our present studies we have prepared a new inorganic ion exchanger, thorium tellurite, which works as a cation exchanger in the alkaline medium and as an anion exchanger in the acidic

0148-3919/84/0708-1691$3.50/0

medium. Its applications towards separation of BrO_3^- from Br^-, NO_2^- from NO_3^- from the reaction products mark their analytical utility. Such exchangers should be of much use where a single mixed beds of cation and anions exchangers are used.

MATERIALS AND METHODS

Reagents: Thorium nitrate (B.D.H.) and sodium tellurite (B.D.H.) were used for precipitation of the exchanger. The other chemicals employed for separation studies were of analar grade.

Apparatus: A Metzer spectra 75 and an Elico pH meter Li-10 were employed for spectrophotometric and pH measurements. The shaking of the samples were done on a SICO shaking machine.

Synthesis: For precipitation of thorium tellurite, a 0.1M solution of thorium nitrate and a 0.1M solution of sodium tellurite were mixed in the volume shown in Table 1. The white precipitate so obtained was kept at room temperature for 48 h to ensure complete precipitation. The precipitate was then filtered, washed and dried in an oven at 40°C. It took nearly a week for the product to dry completely. On treatment with deionized water, the dried sample broke into small pieces. It was again dried at 40°C. The exchanger was then converted into desired form. For conversion into a particular anionic form an acidic solution of the anion should be taken. When desired to be taken in a cationic form, a basic cation solution, e.g. $Ca(OH)_2$ for Ca^{2+} form should be employed.

Anion exchange capacity: The anion exchange capacity was determined by column operation. One gram thorium tellurite in desired anionic form was taken on a glass wool support of a column and 1M solution of various anions were passed through it at a flow rate of 0.5 ml min^{-1}. The eluted anions were then determined in the effluents. To determine the anion exchange capacity for sulphate, the exchanger was taken in the sulphate form. The eluted sulphate ions were determined by

TABLE - 1

Conditions of preparation and properties of thorium tellurite

Sample	Conditions of synthesis				Properties	
	Molarity of		Mixing volume ratio	pH	Ion-exchange capacity (m.eq. g^{-1})	Nature of precipitation
	Thorium nitrate	Sodium tellurite				
S I	0.1	0.1	1:1	0	0.82	Thick
S II	0.1	0.1	1:2	1	1.40	Thick
S III	0.1	0.1	1:3	2	0.44	Mild
S IV	0.1	0.1	3:1	3	0.26	No precipitation
S V	0.1	0.1	2:1	1	0.60	Thick

precipitation with barium chloride and back titrating the excess of barium ions with 0.1 EDTA. For other anions the exchanger was taken in the chloride form and the eluted chloride ions were determined by Mohr's method (8).

Cation sorption capacity: One gram of thorium tellurite was taken in a glass column and 10 ml fractions of cationic solution containing predetermined amount of the cations, Cu(II), Fe(III), Ni(II), Co(II), Cd(II) and Mg(II) were passed through the column at a flow rate 0.5 ml min^{-1}. The amount of cation in the collected effluent was determined for each fraction. The process was kept continued till the amount of cation in the influent and the effluent remained the same. The amount sorbed was then calculated by substracting the amount of cation found in the effluent from the amount initially taken in each fraction.

Effect of drying temperature on anion exchange capacity: Thorium tellurite sample was heated at different temperatures in a muffle furnace for 2 hrs. The anion exchange capacity of each of the dried sample was then determined by column operation.

Chemical composition: 200 mg portion of the ion exchanger was dissolved in 30 ml of hot concentrated hydrochloric acid. The solution was then cooled to room temperature and diluted to 250 ml with deionized water. 100 ml of this solution was taken and T_e was precipitated with hydrazine hydrochloride-sulphur dioxide mixture (9). In another 100 ml portion Th(IV) was determined volumetrically with EDTA solution.

Chemical stability: A 0.5 g of the exchanger was shaken in a conical flask for four hours in the solution in which its dissolution was to be checked. The supernate was decanted and its thorium(IV) content was determined titrimetrically with EDTA. Tellurium was determined spectrophotometrically with thiourea (10).

Ion exchange potentiometric titration: Thorium tellurite being amphoteric in nature, the pH titrations were performed in both alkali and acid solutions with their respective salts following Topp and Pepper method (11). To study the cation exchange behaviour, 0.1M solution of alkali (NaOH, KOH and LiOH) and 0.1M solution of their respective salts were shaken with 0.5 g of the exchanger. The mixing ratio of the two solutions were taken in such a way that total volume remained 50 ml in all the cases. After being shaken for four hours the pH of the reaction mixture was measured. Similar experiments were performed taking HCl, H_2SO_4 and HNO_3 with their respective salts for determining the anion exchange behaviour on thorium tellurite.

K_d values: Distribution coefficient values for various anions and cations were determined by batch process. A known amount of cation or anion solution was shaken for six hours at room temperature with 0.5 g of the exchanger in a conical flask containing the solutions in which its distribution studies were desired to be made. The total volume of the equilibrating mixture was maintained at 50 ml. The liquid was drained off and its cation/anions content was determined. The K_d values were then determined by the formula

$$K_d = \frac{\text{Amount of cation/anion in the solution phase}}{\text{Amount of cation/anion in the exchanger phase}}$$

Separation: The separation of anions/cations with appreciable differences in their K_d values were tried., 2 g of thorium tellurite was taken in the glass wool support of the columns having a height 30 cm and diameter 0.69 cm . The column was washed thoroughly with deionized water and a mixture containing known amounts of anions or cations to be separated was passed through the exchanger bed at a very slow rate. Repeated recyclization of the mixture was done to allow adequate adsorption of the anions/cations. The elution was then done by the solutions in which the K_d values were lowest. In the eluted fraction the qualitative tests for both the components were performed.

RESULTS AND DISCUSSION

The exchanger, thorium tellurite is best prepared when its acid concentration was maintained at pH 1 as shown in Table. The exchanger so prepared not only gave a good yield but also better chemical stability and, therefore, sample II was taken for the detailed studies.

The results of the ion exchange capacity of thorium tellurite are shown in Tables 2-3. The anion exchange capacity varies from 0.8 $m.eq.g^{-1}$ to 1.4 $m.eq.g^{-1}$. The material possesses a high affinity for OH^- as is evident from the fact that releasing capacity for OH^- is only 0.60 $m.eq.g^{-1}$ while that for its uptake is 1.4 $m.eq.g^{-1}$. This shows that thorium tellurite acts as a weak base in OH^- form.

Although the exchanger, thorium tellurite lacked a H^+ liberation capacity it shows strong uptake for certain metal ions. Table 2 also shows the results of the sorption capacity for some of the bi and trivalent metal ions. The sorption capacity varies from 0.68 to 0.84 m.moles g^{-1}. Strong adherence of some of the metal ions to the exchanger frame work makes it an extremely useful material for

TABLE - 2

Anion exchange and cation sorption capacity for various anions

Sl. No.	Anions	Exchange capacity, m.eq.g^{-1}	Cations	Sorption capacity m.moles g^{-1}
1.	Cl^-	1.40	Cu^{2+}	0.84
2.	NO_3^-	1.00	Ni^{2+}	0.80
3.	SO_4^{2-}	1.24	Fe^{3+}	0.68
4.	PO_4^{3-}	0.80	Co^{2+}	0.74
5.	Br^-	1.22	Mg^{2+}	0.80
6.	OH^-	1.40 (OH^- uptake) 0.60 (OH^- liberation)		

TABLE - 3

Dissolution of thorium tellurite

Solvent	Amount, mg	
	Th	Te
Deionized water	0.0	0.00
HNO_3 (1M)	0.0	0.05
HNO_3 (2M)	14.2	22.62
NH_4OH (2M)	0.0	0.0
NH_4OH (4M)	1.21	1.82
HCl (1M)	0.03	0.06
HCl (2M)	12.80	21.20
CH_3OH	0.0	0.0
NaOH (1M)	8.0	10.1
NaOH (2M)	24.0	22.2
Acetone	0.0	0.0

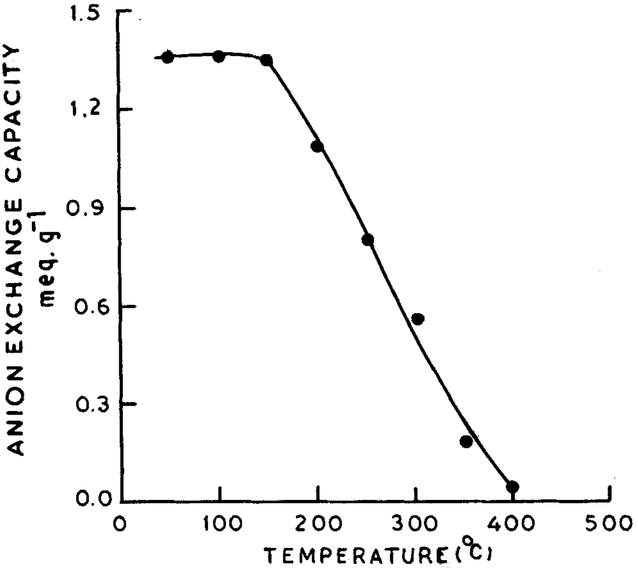

Fig. 1 - ANION EXCHANGE CAPACITY AT DIFFERENT TEMPERATURES

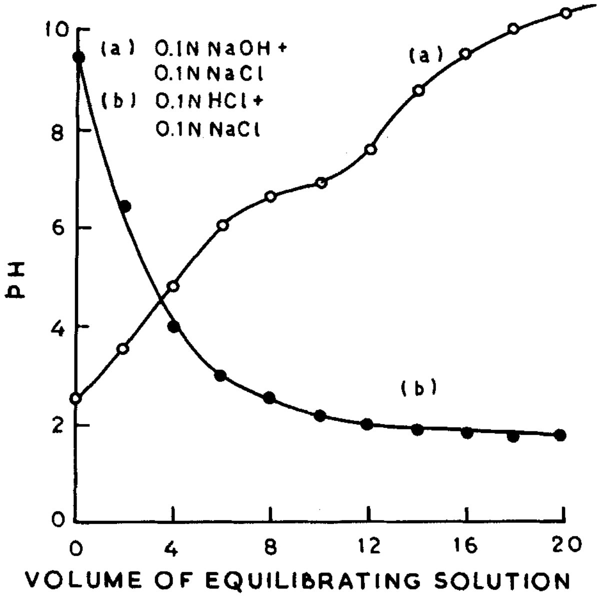

Fig. 2 - POTENTIOMETRIC TITRATIONS ON THORIUM TELLURITE

TABLE - 4

Distribution coefficient values of some anions

Anions	Method of determination	K_d ml g^{-1}				
		Deionized water	0.001M NH_4OH	0.01M NH_4OH	0.1M NH_4OH	0.1M HCl
NO_3^-	Spectr.	T.A.	2000	940	28	T.A.
NO_2^-	Spectr.	400	165	38	06	380
Cl^-	Titr.	2400	1992	728	102	2400
Br^-	Titr.	2800	2120	948	86	2394
I^-	Titr.	3100	2052	1012	495	2843
SO_3^{2-}	Titr.	1680	436	230	112	1290
SO_4^{2-}	Titr.	1440	1020	156	60	1320
AsO_3^{2-}	Iod.Titr.	2049	1150	609	349	1922
AsO_2^-	Spectr.	2296	1164	522	310	1984
IO_3^-	Iod.Titr.	1100	842	491	226	988
BrO_3^-	Iod.Titr.	156	26	06	00	180
SrO_3^{2-}	Iod.Titr.	85	10	00	00	78
SCN^-	Spectr.	720	529	321	206	688
CrO_4^{2-}	Titr.	T.A.	2811	852	224	T.A.
WO_4^{2-}	Spectr.	585	446	319	216	476
MoO_4^{2-}	Spectr.	T.A.	3242	1086	156	T.A.
VO_3^-	Spectr.	442	82	15	00	591
$Fe(CN)_6^{3-}$	Spectr.	714	512	328	164	740
PO_4^{3-}	Spectr.	340	116	42	00	290

the ligand exchange studies in ammonium hydroxide medium - one of the most widely used eluent for LEC studies.

The results of the effect of drying temperature on the ion exchange capacity of thorium tellurite is shown in Fig. 1. It reveals that the exchanger shows no deterioration in its exchange

TABLE - 5

Distribution coefficient values of some cations

Metal ions	K_d ml g^{-1}						
	Deionized water	0.001M HNO_3	0.01M HNO_3	0.1M HNO_3	0.01M NH_4OH	0.1M NH_4OH	0.01M $NaNO_3$
Cu(II)	800	468	335	93	90000	T.A.	600
Fe(III)	T.A.	340	78	4	T.A.	T.A.	T.A.
Ni(II)	21	18	13	2	59	637	782
Co(II)	435	313	268	103	4800	5688	532
Pb(II)	863	30	28	20	8421	9200	8000
Cd(II)	319	22	6	00	27	419	302
Hg(II)	165	105	63	45	185	1440	196
Ag(I)	761	252	182	74	1292	2281	820
Sr(II)	250	92	64	38	143	290	211
UO_2(I)	648	342	221	89	7952	8836	630
Mg(II)	260	150	00	00	280	300	460
Ba(II)	110	103	40	2	400	630	108
Ca(II)	342	220	119	82	480	596	390

behaviour upto 150°C, but the anion exchange capacity decreased appreciably when the drying was done above this temperature.

The results of dissolution of thorium tellurite in different concentrations of acids, base and neutral solutions are shown in Table III. It can be seen that the material is stable in aqueous ammonia upto 4M, HCl and HNO_3 upto 1M. Concentration of neutral solutions and non-aqueous solvents have no effect on the stability of the exchanger. Higher concentrations of strong acids and strong bases, however, cause appreciable dissolution of its constituents.

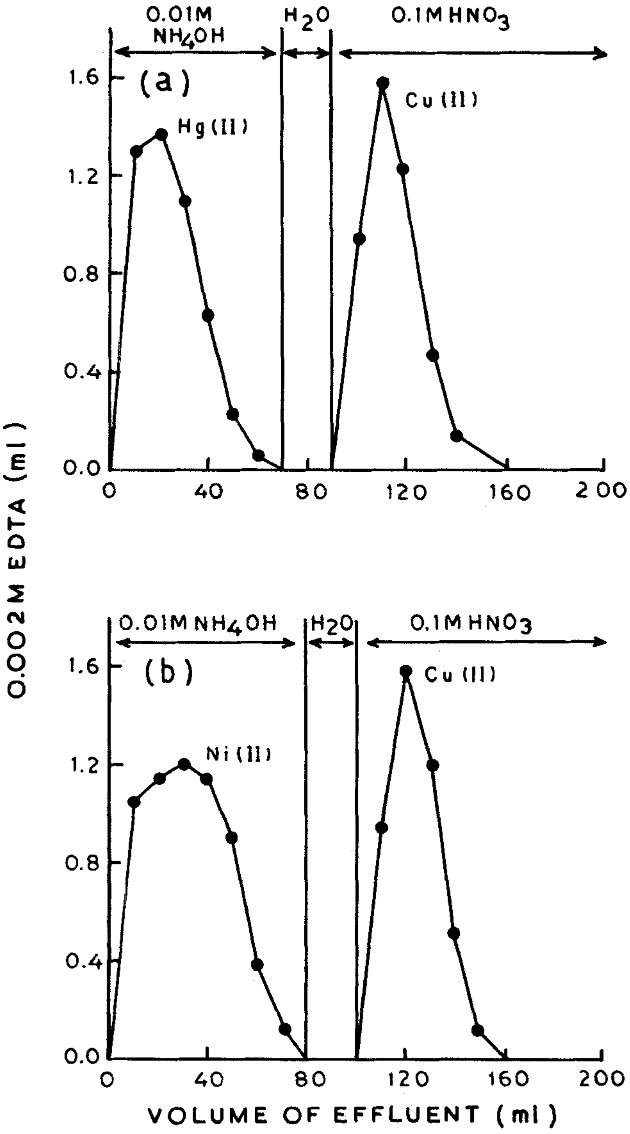

Fig. 3

A - SEPARATION OF Hg (II) FROM Cu (II)

B - SEPARATION OF Ni (II) FROM Cu (II)

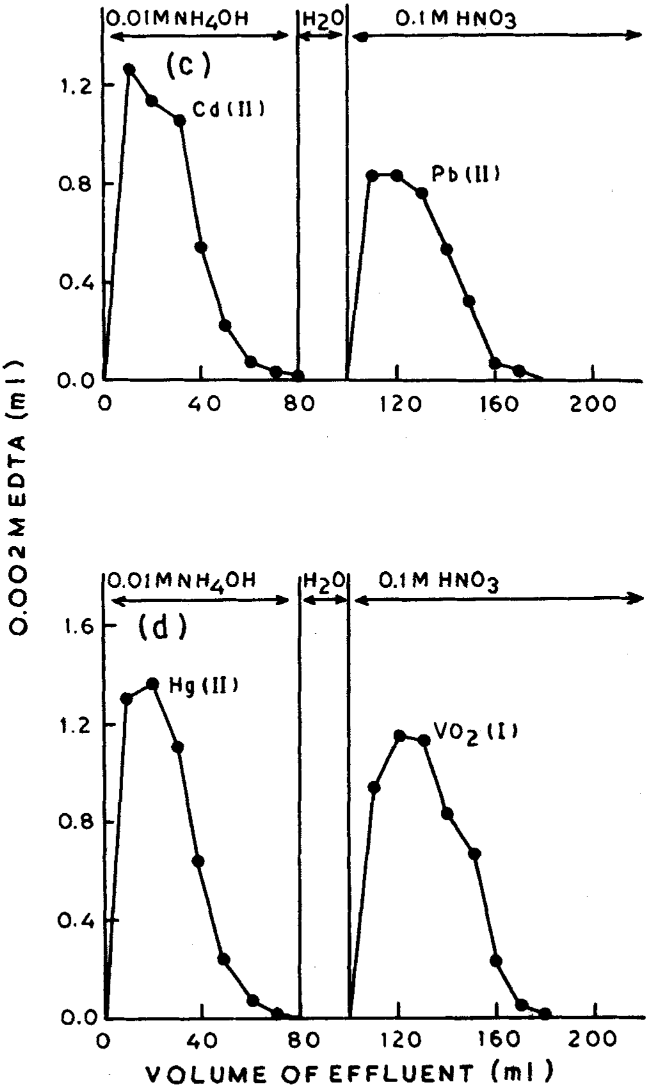

Fig. 3

C - SEPARATION OF Cd (II) FROM Pb (II)

D - SEPARATION OF Hg (II) FROM UO_2 (I)

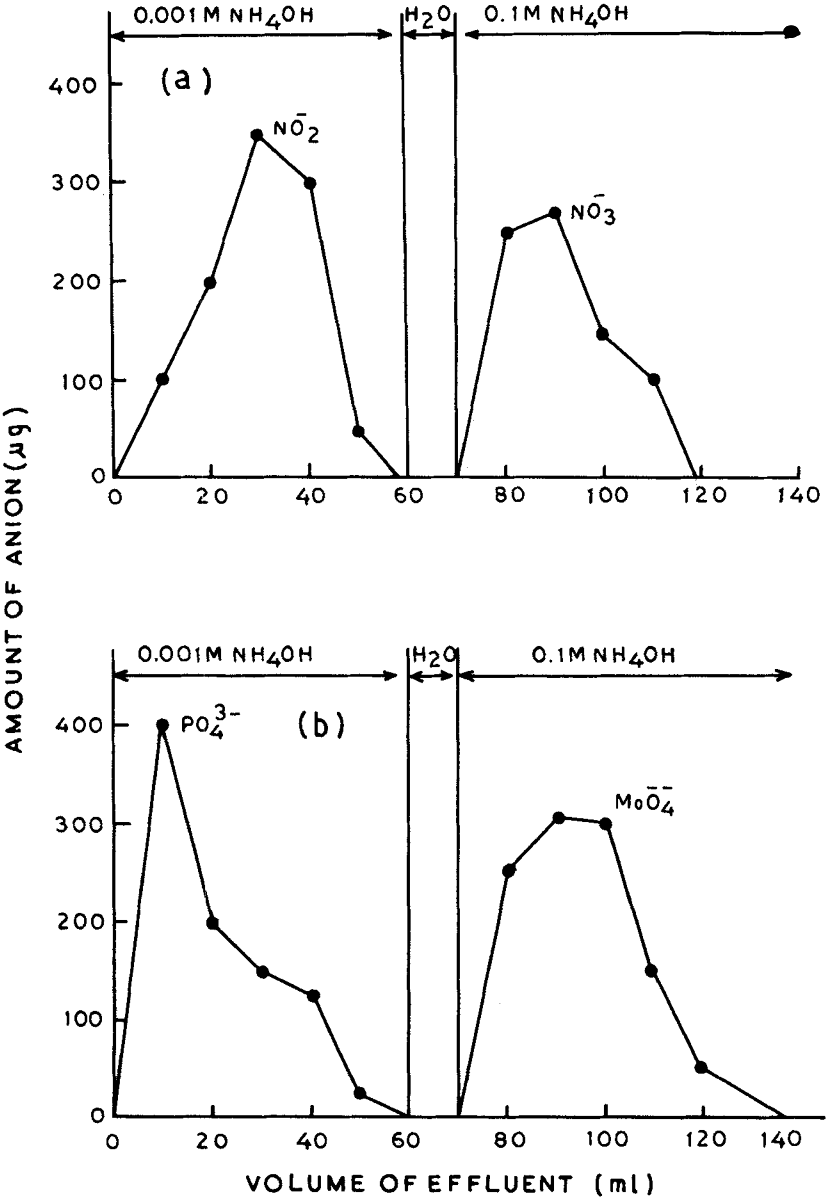

Fig. 4

A - SEPARATION OF NO_2^- FROM NO_3^-

B - SEPARATION OF PO_4^{3-} FROM MoO_4^{2-}

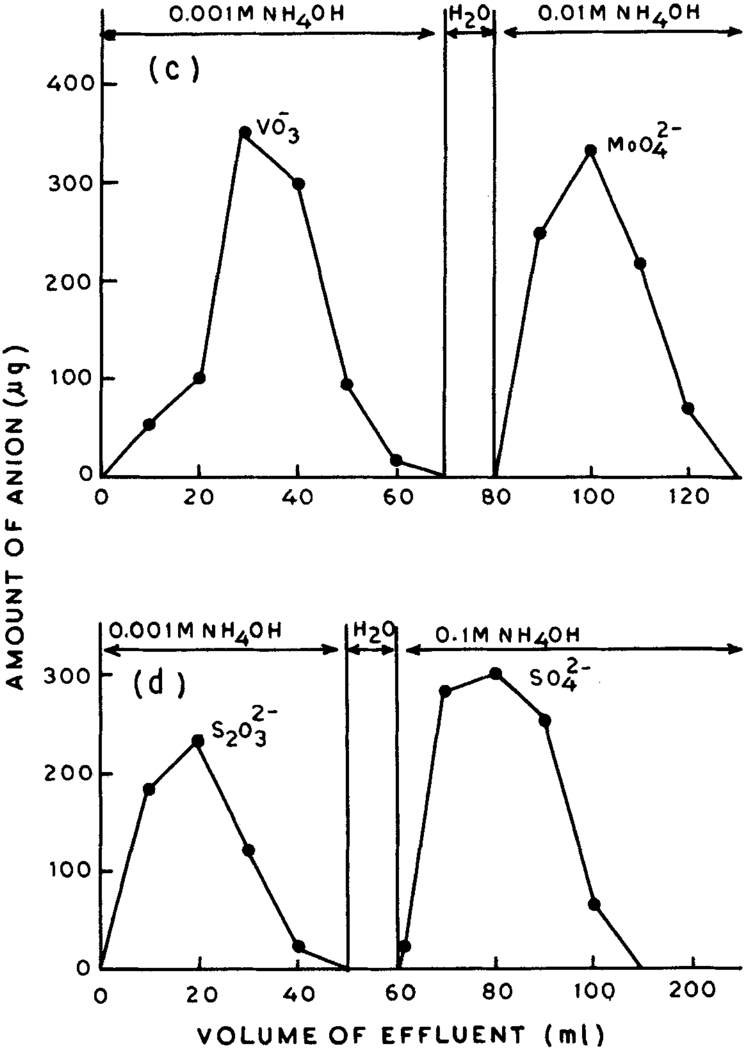

Fig. 4

C - SEPARATION OF VO_3^- FROM MoO_4^{2-}

D - SEPARATION OF $S_2O_3^{2-}$ FROM SO_4^{2-}

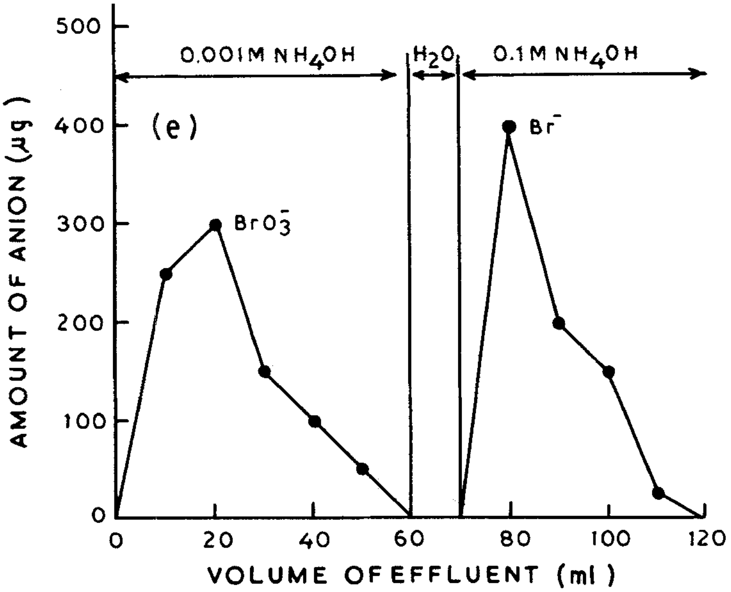

Fig. 4

E - SEPRATION OF BrO_3^- FROM Br^-

The results of the chemical composition of the exchanger showed that thorium and tellurium are present in the ratio Th.Te as 1:2. Shown in Fig. 2 are the pH titration curves for anion as well as cation exchange behaviour on thorium tellurite. A clear bifunctional cation exchange behaviour is observed in NaOH medium while its behaviour as an anion exchanger is not clear in the acidic medium.

The results of the distribution studies for various anions and cations are presented in Tables 4 and 5. It can be seen from these tables that K_d values for both anions as well as cations decrease with increase in the concentration of the equilibrating solution. K_d values were the highest in water medium. It can also be seen that almost all the anions exhibit greater adsorption in 0.1N HCl. This shows that unlike most of the other known inorganic ion exchangers, thorium tellurite, shows anion exchange behaviour in acidic medium.

The lower K_d values of various anions in aqueous ammonia is due probably to the greater preference of the exchanger for OH^- ions than for all other anions. Thorium tellurite serves as a cation exchanger in the basic medium and hence the cationic uptake in 0.01N NaOH was higher than that in water medium. With increasing concentration of acid the desorption of metal ions increased.

On the basis of large differences in K_d values various separations of anions and cations have been tried. Separation of Cu(II) from Hg(II), Cu(II) from Ni(II), Pb(II) from Cd(II) and UO_2(I) from Hg(II) have been successfully achieved and the order of elution and eluents used are shown in Figs. 3a-d. The successful separations of anions are NO_3^- from NO_2^-; MoO_4^{2-} from PO_4^{3-}; VO_3^- from MoO_4^{2-}, SO_4^{2-} from SrO_3^{2-} and BrO_3^- from Br^-. The order of separations are presented in Figs. 4a-e.

ACKNOWLEDGEMENT

Authors are thankful to Prof. W.Rahman, Chairman, Department of Chemistry, Aligarh Muslim University, Aligarh for providing research facilities. One of us (M.I.) is thankful to CSIR (New Delhi) for financial assistance.

REFERENCES

1. Pollard,F.H., Nickless,G. and Rothwell,M.T., J.Chromatog., 10, 212 (1963).
2. Brown,L.C., Begum,G.M. and Boyd,G.E., J.Amer.Chem.Soc., 91(9), 2250 (1969).
3. Kraus,K.A., Phillips,H.O., Carlson,T.A. and Johnson,J.S., Proc.2nd. Int.Conf.Peaceful Uses of Atomic energy, Geneva, 28, 3 (1958).
4. Britz,B. and Nancollas,G.H., J.Inorg.Nucl.Chem., 31, 3861 (1969).
5. Abe,M. and Ito,T., Nippon Kagaku Zasshi, 86, 817 (1965).
6. Venkataramani,B. and Venkateshwarlu,K.S., J.Inorg.Nucl.Chem., 42, 909 (1980).
7. Rawat,J.P. and Iqbal,M., Annali Di Chimica, 69, 241 (1979).

8. Neuss,R. and Naiman,B., "Quantitative Analysis", 3rd Edn, McGraw Hill, New York, p. 70 (1962).

9. Furman,N.H., Standard methods of Chemical Analysis, Vol. I, VI Edn. D.Van Nostrand Co.Inc., Princeton, New Jersey, 932 (1962).

10. Snell,F.D., Snell,C.T. and Snell,C.A., Colorimetric methods of analysis, Vol. IIA, D.Van Nostrand Co.Inc., Princeton,N.J., p. 683 (1959).

11. Topp,N.E. and Pepper,K.W., J.Chem.Soc., 3299 (1949).