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Synthesis and Characterization of New Three-Component Ion-Exchange Material: Zirconium(IV) Selenophosphate

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Zirconium(IV) selenophosphate has been prepared by adding a mixture which is 0.05 M in sodium selenite and 0.05 M in orthophosphoric acid to a 0.05 M solution of zirconium(IV) bis(nitrate) oxide in different volume ratios at pH 1. Its ion-exchange capacity, thermal and chemical stability, pH titration curves, and chemical composition were studied. Adsorption of some of the metal ions in different solvent systems has been studied. The effect of particle size on the sorption behavior of metal ions has also been studied. The analytical importance of this material has been demonstrated by achieving the eleven quaternary separations of metal ions. A comparison of ion-exchange properties of this material has also been made with some other ion-exchangers.

The most intensively studied group of synthetic inorganic ion-exchangers are the acidic salts of multivalent metals (especially quadrivalent metals) prepared in combination with the anions of phosphate, arsenate etc. as two-component ion-exchangers.[1–3] Three-component inorganic ion-exchangers which consist of a combination of zirconium phosphate compound with other organic or inorganic salts such as zirconium arsenate, molybdate, tungstate, tellurate, oxalate, silicate etc. have been prepared. Attempts were made to increase the ion-exchange capacity by increasing degree of polymerization of the component materials.[4] However, a higher content of polyphosphate in the exchanger is considered to effect the kinetics of absorption[5] and therefore, the conditions are set within optimum limits.[6] A study of the literature shows the preparation of a large number of three-component ion-exchangers with increased ion-exchange capacity and selectivity of these materials.[7–16] In this manuscript, we describe the preparation and properties of zirconium(IV) selenophosphate. Some analytically important separation of metal ions of quaternary systems have been successfully achieved.

Experimental

Reagents. Zirconium(IV) bis(nitrate) oxide (B.D.H.), sodium selenite (B.D.H.), and orthophosphoric acid (B.D.H.) were used for the synthesis of ion-exchangers. All other chemicals were of analytical grade.

Apparatus. An Elico model Li-10 pH meter was used for pH measurement. A Bausch and Lomb Spectronic 20 colorimeter and a Perkin Elmer 137 spectrophotometer were used for spectrophotometric and IR studies respectively. An electric temperature-controlled shaker (SICO) was used for shaking.

Synthesis. Samples of zirconium(IV) selenophosphate ion-exchangers were synthesized by adding an aqueous solution which is 0.05 M (1 M=1 mol dm^{-3}) in sodium selenite and 0.05 M in orthophosphoric acid to an aqueous solution of zirconium(IV) bis(nitrate) oxide. The desired pH was adjusted by adding dilute HNO_3 or NaOH solution. The gel so formed was allowed to settle down for 24 h, washed several times with demineralized water to remove excess reagents and finally filtered under suction. It was

Table 1. Synthesis and Properties of Zirconium(IV) Selenophosphate

Sample No.	Zirconium(IV) bis(nitrate) oxide	Sodium selenite	Orthophosphoric acid	Mixing ratio	pH	Appearance of precipitate	Appearance of beads after drying at 40 °C	Ion-exchange capacity for K^+ (meq g^{-1}-dry exchanger)
	M	M	M	v/v/v				
ZSP_1	0.05	0.05	0.05	1 : 1 : 1	1.0	White gelatinous	White opaque	1.51
ZSP_2	0.05	0.05	0.05	2 : 1 : 1	1.0	White gelatinous	White opaque	1.07
ZSP_3	0.05	0.05	0.05	1 : 2 : 1	1.0	White gelatinous	White opaque	1.13
ZSP_4	0.05	0.05	0.05	1 : 1 : 2	1.0	White gelatinous	White opaque	1.15
ZSP_5	0.05	0.05	0.05	1 : 1 : 2	<0	White gelatinous	White opaque	0.95
ZP	0.05	—	0.05	1 : 1	1.0	White gelatinous	White opaque	0.64
ZS_1	0.05	0.05	—	1 : 1	1.0	No precipitation		—
ZS_2	0.05	0.05	—	1 : 1	4.0	White gelatinous	White opaque	0.44

then dried at 40 °C for 7 d in an oven. The dried material was then treated with demineralized water, which resulted in cracking of the substance into smaller particles with slight evolution of heat. To convert the sample into H^+ form, the material was kept for 24 h in 1.0 M HNO_3 solution. It was then washed with demineralized water to remove excess acid.

Ion-Exchange Capacity. A half gram of the exchanger in H^+ form was taken into the column with the glass wool support. One molar solutions of different uni- and bivalent metal salts were passed through the column and the H^+ ion liberation capacity was determined as usual.[17] The ion-exchange capacities thus determined were therefore those at neutral pH conditions (pH ≈6.5).

Chemical Stability. A 0.50 gram exchanger material (ZSP_1, Table 1) was equilibrated with 50 ml of the solution or solvent of interest at room temperature and kept for 24 h with occasional shaking. Zirconium and selenium in the solution was determined spectrophotometrically using Alizarin Red-S[18] and 3,3′,4,4′-tetraaminobiphenyl tetrahydrochloride[19] as coloring reagents respectively. The phosphate was determined titrimetrically.[20]

pH-Titration. pH-Titrations for NaCl–NaOH and KCl–KOH systems, (using 0.1 M solution of NaCl and KCl each) of sample ZSP_1 were performed by the method of Topp and Pepper.[21]

Thermal Treatment. Thermogravimetric analysis of sample ZSP_1 in the H^+ form was performed at a heating rate of 10 °C min^{-1}. To examine the effect of drying temperature on the ion-exchange capacity the materials were heated at different temperatures in a muffle furnace for 1 h.

Chemical Composition. For the determination of chemical composition of zirconium(IV) selenophosphate sample ZSP_1, 0.10 g of exchanger was dissolved in hot concentrated sulfuric acid. Then the solution was diluted to 100 ml with water. Zirconium and selenium were determined gravimetrically[22,23] while phosphate was determined titrimeterically.[20] The mole ratio of Zr, Se, and P was found to be 5.06:2.0:4.05.

Infrared Spectrum. Infrared analysis of zirconium(IV) selenophosphate was performed using KBr technique.

Distribution Coefficient. The distribution coefficients of metal ions in various aqueous solutions were determined. A quarter gram of exchanger in H^+ form (30—50, 50—100, 100—150, 150—200 mesh sizes) was treated with 25.0 ml of 2.0×10^{-4} M metal salt solution in 250 ml Erlenmeyer flask. The mixture was then shaken for 6 h at 25±2 °C in a shaker incubator. The amount of metal species left in the solution was then determined by titrating against the standard solution of EDTA. The K_d values were calculated according to the formula.

$$K_d = \frac{\text{mmoles of metal species/gram of exchanger}}{\text{mmoles of metal species/ml of the total volume of the resultant solution.}}$$

Separation of Metal Ions. Quantitative separations of metal ions were achieved on a 0.6 cm diameter (i.d.) glass column using 2.0 g exchanger (50—100 mesh) in H^+ form. A metal ion mixture was poured on the top of the column. The flow rate of the effluent was maintained at 1 ml min^{-1} throughout the elution process.

Results and Discussion

Table 1 describes the preparations of samples of Zr(IV) selenophosphate. It is apparent from the table that the ion-exchange capacity of the mixed salt is greater when compared with other simple salts such as zirconium phosphate and zirconium selenite. The ion-exchange capacities for alkali and alkaline earth metals are shown in Table 2. It is clear from the table that the capacity increases with the decrease of hydrated ionic radii for both the alkali and alkaline earth metals.

The effect of heating on the ion-exchange capacities of Zr(IV) selenophosphate and other ion-exchange materials[5,13,15] at different temperatures has been shown in Fig. 1 and interpreted. A 300, 500, and 600 °C, the decreasing orders of the ion-exchange capacities are [Zr(IV) selenophosphate, Sn(IV) selenoarsenate, Sn(IV) selenite, Cr(III) arsenophosphate, Sn(IV) arsenophosphate], [Sn(IV) selenite, Sn(IV) selenoarsenate, Zr(IV) selenophosphate, Cr(III) arsenophosphate, Sn(IV) arsenophosphate], and [Sn(IV)

Table 2. Ion-Exchange Capacity (meq g^{-1}-dry exchanger) of Zirconium(IV) Selenophosphate Sample ZSP_1 for Various Cations at pH 6.5 and 25 °C

Sample No.	Cation	Hydrated ionic radius/Å	Ion exchange capacity (meq g^{-1}-dry exchanger)
1	Li^+	10	1.11
2	Na^+	7.9	1.23
3	K^+	5.3	1.51
4	Rb^+	—	0.71
5	Mg^{2+}	10.8	1.21
6	Ca^{2+}	9.6	1.31
7	Sr^{2+}	9.4	1.42
8	Ba^{2+}	8.8	1.44

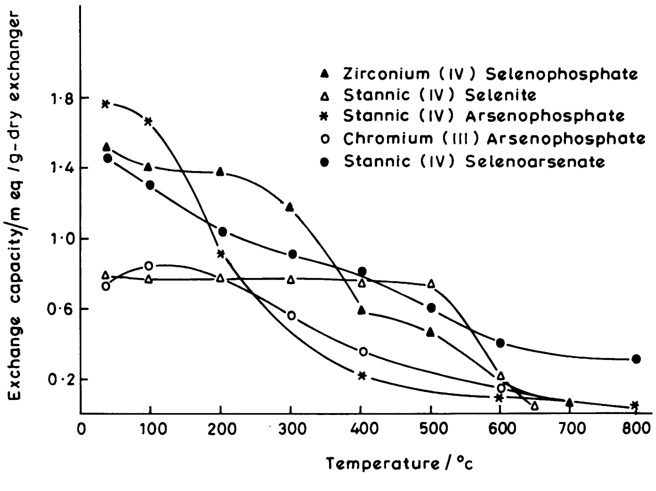


Fig. 1. Plot of exchange capacity vs. drying temperature.

selenoarsenate, Sn(IV) selenite, Zr(IV) selenophosphate, Cr(III) arsenophosphate, Sn(IV) arsenophosphate] respectively. The ion-exchange capacity of Zr(IV) selenophosphate for K^+ was found to be 1.51 meq g^{-1} when the sample was dried at 40 °C. However, a decreasing trend in ion-exchange capacities was observed when the drying temperature was elevated. The ion-exchange capacity became negligible i.e., 0.05 meq g^{-1} at 700 °C.

It is apparent from Table 3 that Zr(IV) selenophosphate is quite stable in water. It is fairly stable in dilute mineral acids such as hydrochloric acid, perchloric acid, nitric acid, and sulfuric acid. The material is also fairly stable in organic acids like formic acid, oxalic acid, acetic acid, citric acid, and tartaric acid and in organic solvents such as ethanol, 1-butanol, DMSO, and dioxane but is highly soluble in 2 M sodium hydroxide.

The titration curves with added salts have been shown in Fig. 2. The curve in the presence of added sodium salt showed a slight difference from that in the presence of potassium salt and the ion-exchange capacities calculated from these curves are 1.20 and 1.50 meq g^{-1} for sodium and potassium salts and those obtained from column operation are 1.23 and 1.51 meq g^{-1} respectively. Further the titration curves showed a monofunctional behavior of the exchanger.

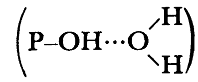
Berardelli and coworkers[24)] have synthesized a single crystalline phase, a layered mixed inorganic ion-exchanger, $Zr(HAsO_4)(HPO_4)\cdot H_2O$, containing two anions. The X-ray diffraction studies and differential thermal analysis of the crystalline product showed a great similarity with those of α-$Zr(HPO_4)_2\cdot H_2O$ and α-$Zr(HAsO_4)_2\cdot H_2O$ and possessed an interlayer spacing of 7.73Å intermediate between those of the last two compounds. It was, therefore, concluded that the mixed crystalline product possessed an α-type layered structure. Taking the example of this product we have tried to explain the increased ion-exchange capacity and tentatively extending this concept on synthesized material, zirconium(IV) selenophosphate (assuming that it possessed an α-type layered structure). Its ion-exchange capacity was reported to be 5.80 meq g^{-1}. In describing the structure of zirconium phosphate in terms of three-dimensional skeleton which composed of Zr, P, and O, Clearfield[25)] suggested that each phosphate group is bonded to three different zirconium atoms through oxygen forming a sheet-like structure. The remaining phosphate oxygen atoms bear the hydrogen atoms. Half of these P–OH groups are believed to form hydrogen bonds with phosphate oxygen atoms in the adjacent layers (P–O–H············O–P) and form a zigzag array of weak interlayers running parallel to the *b*-axis. The other half of the P–OH groups are thought to be hydrogen bonded to the water molecules to form interlayer bonds  $\left(\text{P–OH}\cdots\text{O}\begin{smallmatrix}\text{H}\\ \\ \text{H}\end{smallmatrix}\right)$. These differences in hydrogen bonding give rise to different acidities or ion-exchange sites for the two hydrogen atoms. The ion-exchange capacity has been measured as the amount of the total H^+ ions available from the

Table 3. Chemical Stability of Zirconium(IV) Selenophosphate (sample ZSP_1, 0.5 g) in Solution (50 ml)

No.	Solution or solvent[a)]	Zr released mg/50 ml	Se released mg/50 ml	PO_4^{3-} released mg/50 ml
1	Water	0.00	0.00	0.00
2	1 M HNO_3	0.18	0.15	0.13
3	2.0 M HNO_3	0.54	0.23	0.21
4	1.0 M H_2SO_4	0.41	0.18	0.29
5	2.0 M $HClO_4$	0.54	0.16	0.24
6	1.0 M Acetic acid	0.18	0.12	0.20
7	1.0 M Citric acid	0.11	0.13	0.21
8	1.0 M Tartaric acid	0.12	0.19	0.24
9	1.0 M Oxalic acid	0.11	0.18	0.21
10	1.0 M Formic acid	0.13	0.15	0.22
11	0.1 M NaOH	0.98	0.39	0.54
12	2.0 M NaOH	Complete dissolution		
13	4.0 M NH_4NO_3	0.11	0.21	0.18
14	4.0 M NH_4Cl	0.12	0.17	0.21
15	0.1 M HCl	0.20	0.13	0.23
16	2.0 M HCl	0.28	0.22	0.26
17	2.0 M DMSO	0.11	0.13	0.17
18	2.0 M Dioxane	0.17	0.12	0.19
19	Ethanol	0.13	0.12	0.21
20	1-Butanol	0.12	0.14	0.19

a) No. 2—18, aqueous solution.

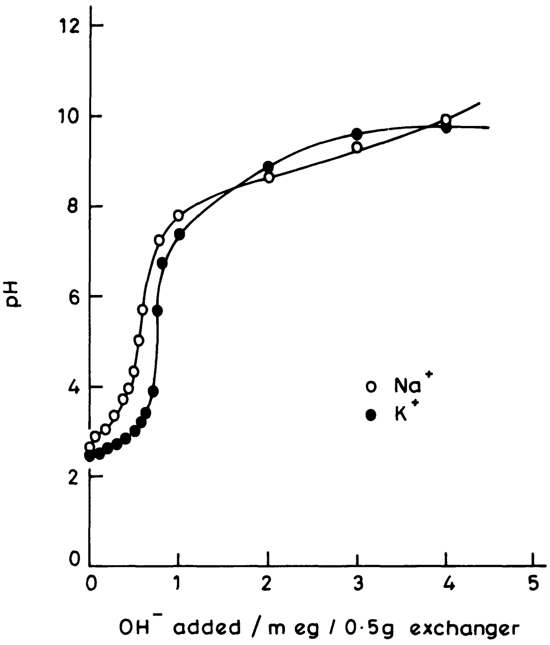


Fig. 2. pH Titration curves of zirconium(IV) selenophosphate.

two different interlayer bonds of P–OH groups. In case of three-component materials e.g., $Zr(HAsO_4)(HPO_4)\cdot H_2O$, X-ray diffraction studies revealed the existance of a mixed exchanger to give solid solutions because of the presence in the lattice layer of atoms (P and As) with analogous chemical characteristics but with different dimensions. Moreover, the substitution of P with As provided strength of their acidic sites when employed as acid catalysts.[24] On the basis of these studies, it can be suggested that in addition to the two different P–OH groups there should also be a third exchange site (in case of three-component materials) formed by mixed interlayer bonds (As–OH·····O–P), whose existance was supported by mixed ion-exchanger to give solid solution. The ion-exchange capacity is therefore a total contribution from all these different exchange sites. new let P–OH and As–OH represent dihydrogenphosphate ($-H_2PO_4$) and dihydrogenarsenate ($-H_2AsO_4$) groups corresponding to the second dissociation constant of the phosphoric and arsenic acid. The magnitude of the dissociation constants of these groups ($H_2PO_4^- \overset{K_2}{\rightleftharpoons} H^+ + HPO_4^{2-}$; $K_2=6.2\times10^{-8}$ and $H_2AsO_4^- \overset{K_2'}{\rightleftharpoons} H^+ + HAsO_4^{2-}$; $K_2'=8.3\times10^{-8}$) are almost of the same order and therefore the hydrogen ions released from these ion-exchange sites should be the sum from the above two groups. The total hydrogen ions released from all three different sources must be greater than the hydrogen ions released from the two ion-exchange sites.

The IR spectrum of Zr(IV) selenophosphate shows the presence of usual characteristic groups such as lattice water, free water and phosphates at corresponding frequencies. On the other hand, the separate identity of $-SeO_3$ group is indicated by a strong band at a frequency of 720 cm^{-1}.[26]

The combined studies of thermogram of Zr(IV) selenophosphate in H^+ form (Fig 3) and its exchange capacity at different temperatures compared with other exchange materials (Fig. 1) reveal some interesting results. At 200 °C about 8.6% of the total capacity is lost due to the loss of water molecules and start of the formation of pyrophosphate groups. The corresponding weight loss of exchanger is about 2.58%. At 560 °C, there is a complete conversion to pyrophosphate with a decrease in capacity equal to 72% of the starting value and the corresponding weight loss is about 4.6%. Further decrease in capacity may be attributed due to the condensation of $-HSeO_3$ group to $(Se_2O_5)H_2O$. After 800 °C the weight becomes constant and the capacity decreases, is 96% of the original value.

On the basis of the exchange capacity, pH titration curve, chemical composition and thermogravimetric analysis, the following formula for Zr(IV) seleno-

Table 4. Distribution Coefficients (ml g^{-1}) of Metal Ions on Zirconium(IV) Selenophosphate (sample ZSP_1, 50—100 mesh) at 25±2 °C

No.	Metal ion	Water	0.001 M HNO_3	0.01 M HNO_3	0.1 M HNO_3	1.0 M NH_4NO_3	0.01 M HNO_3 + 1.0 M NH_4NO_3 (1 : 1)
1	Mg^{2+}	2	2	2	2	8	8
2	Ca^{2+}	52	26	90	375	3700	3700
3	Ba^{2+}	17	11	8	5	2	5
4	Sr^{2+}	22	3	8	3	4800	30
5	Al^{3+}	109	27	9	2	27	35
6	Zn^{2+}	40	20	12	5	425	180
7	Cu^{2+}	15	22	15	2	8	2
8	Co^{2+}	5	10	28	4800	28	22
9	Ni^{2+}	6	6	12	28	20	6
10	Fe^{3+}	4300	780	340	214	144	17
11	Pb^{2+}	780	780	340	17	340	486
12	VO^{2+}	100	77	25	3900	33	23
13	Zr^{4+}	560	1220	560	340	3200	3200
14	Th^{4+}	3400	3400	3400	3400	3400	3400
15	Gd^{3+}	69	61	42	36	27	11
16	Y^{3+}	30	15	20	24	11	7
17	Sm^{3+}	82	93	138	244	12	161
18	Eu^{3+}	45	7	12	40	3	12
19	Er^{3+}	8	8	11	23	3	6
20	Nd^{3+}	37	12	24	3000	12	3
21	Pr^{3+}	7	10	7	8500	1	14
22	Tb^{3+}	16	16	16	22	5	3
23	Yb^{3+}	1	8	1	1	1	8

phosphate is tentatively suggested.

$$[(ZrO)_5(OH)_4(HSeO_3)_2(H_2PO_4)_4]_n\cdot 2nH_2O$$

If it is assumed that the weight loss (2.58%) up to 200 °C is due to the removal of water molecules, then the number of water molecules (n) per molecule of exchanger, calculated from the formula given by Alberti[27] is 2. If two hydrogen ions in the tentative formula above are exchanged at pH 6.5, the ion-exchange capacity calculated from the above formula is 1.55 meq g^{-1} which is in accordance with the experimental value (1.51 meq g^{-1}). The mole ratio of Zr, Se, and P, which is calculated from the above formula is found to be 5.04:2.00:4.01.

It is clear from Table 4 that the K_d values vary with

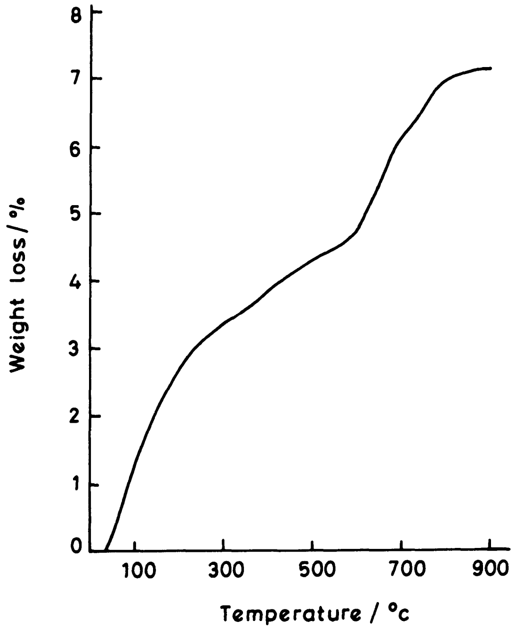


Fig. 3. Thermogram of Zr(IV) selenophosphate in H$^+$ form.

Table 5. Distribution Coefficient (ml g^{-1}) of Metal Ions on Zirconium(IV) Selenophosphate of Different Particle Sizes at 25±2 °C in 0.1 M Acetic Acid

No.	Metal ion	30—50 mesh	50—100 mesh	100—150 mesh	150—200 mesh
1	Mg^{2+}	8	15	29	35
2	Ca^{2+}	5	22	32	70
3	Sr^{2+}	6	13	23	36
4	Ba^{2+}	29	52	65	68
5	Cu^{2+}	2	12	24	142
6	Zn^{2+}	8	16	32	69
7	Hg^{2+}	147	666	820	1050
8	Th^{4+}	25	89	106	164
9	Zr^{4+}	560	560	840	1220
10	Pb^{2+}	14	137	170	175
11	Cd^{2+}	5	38	72	127
12	Al^{3+}	10	80	100	300

Table 6. Separations of Metal Ions Achieved on Zirconium(IV) Selenophosphate Columns

No.	Separation achieved	Amount loaded μg	% of metal ions eluted	Volume of effluent ml	Eluent used
1	Y^{3+}	138	99	40	0.001 M HNO_3
	Al^{3+}	24	100	40	0.01 M HNO_3
	Pb^{2+}	190	96	40	0.05 M HNO_3
	Fe^{3+}	49	98	30	1.0 M HNO_3
2	Yb^{3+}	132	100	30	H_2O
	Gd^{3+}	280	100	50	0.01 M HNO_3
	Pb^{2+}	190	97	40	0.05 M HNO_3
	Th^{4+}	177	92	40	1.0 M HNO_3
3	Cu^{2+}	58	98	30	H_2O
	Al^{3+}	24	100	40	0.01 M HNO_3
	Pb^{2+}	186	98	40	0.05 M HNO_3
	Fe^{3+}	49	98	30	1.0 M HNO_3
4	Eu^{3+}	94	97	50	H_2O
	Gd^{3+}	280	99	50	0.01 M HNO_3
	Pb^{2+}	190	96	40	0.05 M HNO_3
	Th^{4+}	177	93	40	1.0 M HNO_3
5	Pr^{3+}	242	99	40	H_2O
	Gd^{3+}	280	100	50	0.01 M HNO_3
	Pb^{2+}	190	96	40	0.05 M HNO_3
	Th^{4+}	177	92	40	1.0 M HNO_3
6	Er^{3+}	381	99	40	H_2O
	Gd^{3+}	280	99	50	0.01 M HNO_3
	Pb^{2+}	190	97	40	0.05 M HNO_3
	Th^{4+}	177	93	40	1.0 M HNO_3
7	Tb^{3+}	181	100	40	H_2O
	Gd^{3+}	280	99	50	0.01 M HNO_3
	Pb^{2+}	190	97	40	0.05 M HNO_3
	Th^{4+}	177	93	40	1.0 M HNO_3
8	Mg^{2+}	23	96	40	H_2O
	Al^{3+}	24	100	40	0.01 M HNO_3
	Pb^{2+}	190	96	40	0.05 M HNO_3
	Zr^{4+}	64	97	50	1.0 M HNO_3
9	Ca^{2+}	40	98	40	H_2O
	Al^{3+}	24	100	40	0.01 M HNO_3
	Pb^{2+}	190	96	40	0.05 M HNO_3
	Zr^{4+}	64	95	50	1.0 M HNO_3
10	Sr^{2+}	86	98	40	H_2O
	Al^{3+}	24	100	40	0.01 M HNO_3
	Pb^{2+}	190	96	40	0.05 M HNO_3
	Zr^{4+}	64	97	50	1.0 M HNO_3
11	Ba^{2+}	115	98	40	H_2O
	Al^{3+}	24	96	40	0.01 M HNO_3
	Pb^{2+}	190	96	40	0.05 M HNO_3
	Zr^{4+}	64	95	50	1.0 M HNO_3

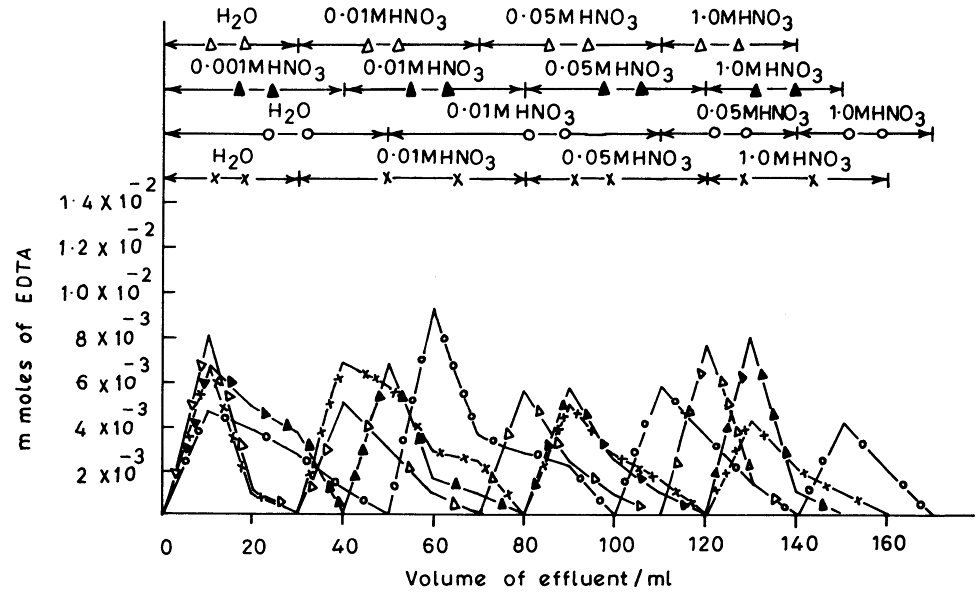


Fig. 4(a) Separation of (—△—) Cu^{2+}–Al^{3+}–Pb^{2+}–Fe^{3+}, (—○—) Eu^{3+}–Gd^{3+}–Pb^{2+}–Th^{4+}, (—▲—) Y^{3+}–Al^{3+}–Pb^{2+}–Fe^{3+}, and (—×—) Yb^{3+}–Gd^{3+}–Pb^{2+}–Th^{4+} on Zirconium(IV) selenophosphate column.

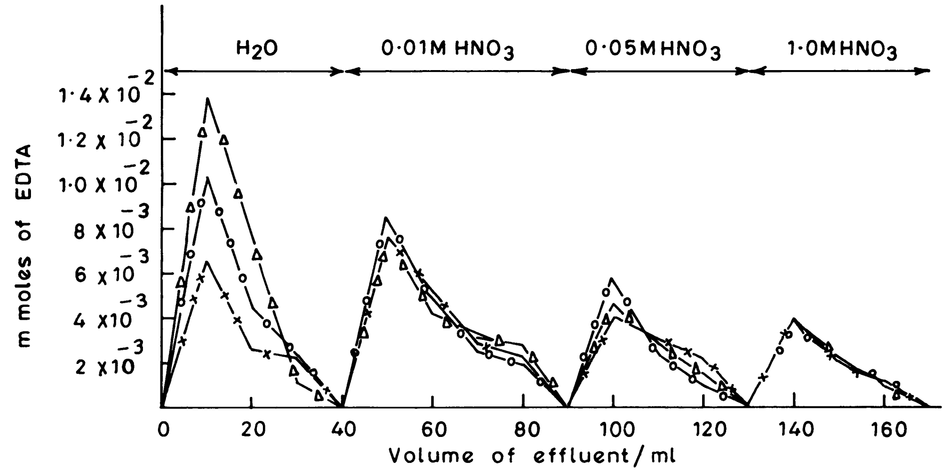


Fig. 4(b) Separation of (—△—) Er^{3+}–Gd^{3+}–Pb^{2+}–Th^{4+}, (—○—) Pr^{3+}–Gd^{3+}–Pb^{2+}–Th^{4+}, and (—×—) Th^{4+}–Gd^{3+}–$Pb^{2+}Th^{4+}$ on zirconium(IV) selenophosphate column.

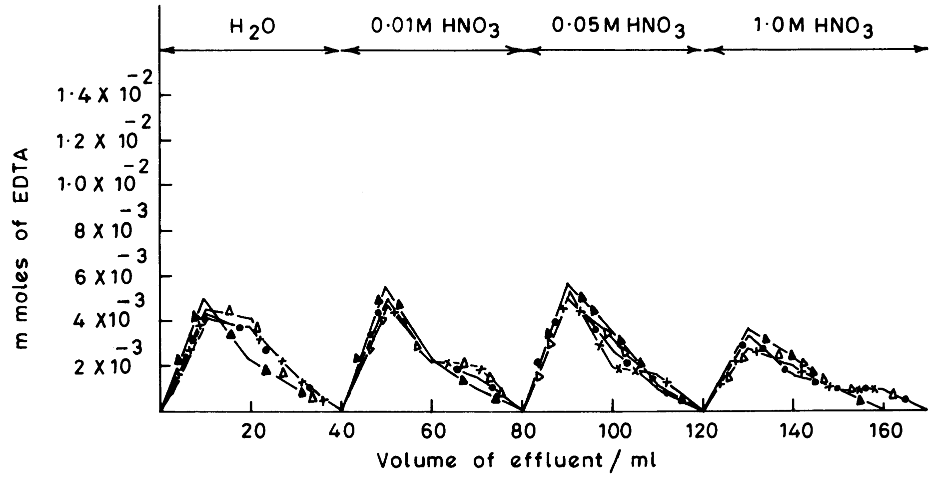


Fig. 4(c) Separation of (—○—) Mg^{2+}–Al^{3+}–Pb^{2+}–Zr^{4+}, (—△—) Ca^{2+}–Al^{3+}–Pb^{2+}–Zr^{4+}, (—▲—) Ba^{2+}–Al^{3+}–Pb^{2+}–Zr^{4+}, and (—×—) Sr^{2+}–Al^{3+}–Pb^{2+}–Zr^{4+} on Zirconium(IV) selenophosphate column.

the composition and the nature of the contacting solution. The K_d value for Th^{4+} is very high showing a high affinity of Zr(IV) selenophosphate to Th^{4+}, whereas the rare earth metals are least strongly adsorbed in almost all the solution systems studied. An increase in the concentration of nitric acid has significant effect on the adsorption of Pb^{2+} and Fe^{3+} but has a little effect on the behavior of rare earth metals. Kd values are increasing as the mesh size of the exchanger increases (Table 5). The sorption studies on Zr(IV) selenophosphate for different metal ions reveal some important separations. As a result, eleven quaternary separations were performed by using small column (30 cm length and 0.6 cm internal diameter) of Zr(IV) selenophosphate. Results are summarized in Table 6. The elution profiles are shown in Fig. 4a—c.

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References

1) C. B. Amphlett, "Inorganic Ion Exchangers," Elsevier, New York (1964).

2) Y. Inoue, *J. Inorg. Nucl. Chem.*, **26**, 2241 (1964).

3) M. Qureshi, R. Kumar, V. Sharma, and T. Khan, *J. Chromatogr.*, **118**, 175 (1976).

4) E. S. Boichinova and T. I. Podgorelova, *Zh. Prikl. Khim. (Leningrad)*, **40**, 1837 (1967).

5) E. S. Boichinova and D. A. Sokolova, *Zh. Prikl. Khim. (Leningrad)*, **38**, 1732, (1965).

6) V. Pekarek and V. Vesley, *Talanta Rev.*, **19**, 224 (1972).

7) K. G. Varshney and Asif A. Khan, *J. Inorg. Nucl. Chem.*, **41**, 241 (1979).

8) M. Qureshi and R. C. Kaushik, *Anal. Chem.*, **49**, 165 (1977).

9) M. Qureshi, R. Kumar, and R. C. Kaushik, *Sep. Sci. Technol.*, **13**, 185 (1978).

10) K. G. Varshney, U. Sharma, and S. Rani, *Indian J. Technol.*, **22**, 99 (1984).

11) K. G. Varshney, R. Pal Singh, and S. Rani, *J. Indian Chem. Soc.*, **61**, 220 (1984).

12) K. G. Varshney and A. Premadas, *J. Liq. Chromatogr.*, **4**, 1245 (1981).

13) P. S. Thind, S. S. Sandhu, and J. P. Rawat, *Chim. Anal. (Warsaw)*, **24**, 65 (1979).

14) S. A. Nabi, R. A. K. Rao, and W. A. Siddiqui, *J. Liq. Chromatogr.*, **6**, 777 (1983).

15) S. A. Nabi, R. A. K. Rao, and A. R. Siddiqui, *Z. Anal. Chem.*, **311**, 505 (1982).

16) K. G. Varshney and A. Premadas, *J. Liq. Chromatogr.*, **4**, 915 (1981).

17) M. Qureshi and S. A. Nabi, *Talanta*, **19**, 1033 (1972).

18) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," D. Van Nostrand, Princeton, New Jersey (1959), Vol. IIA, p. 235.

19) Ref. 18, p. 679.

20) N. H. Furman, "Standard Methods of Chemical Analysis," 6 th ed, D. Van Nostrand, Princeton, New Jersey (1962), Vol. 1, p. 814.

21) N. E. Topp and K. W. Pepper, *J. Chem. Soc.*, **1949**, 3299.

22) Ref. 18, p. 1270.

23) Ref. 18, p. 929.

24) M. L. Berardelli, P. Galli, A. L. Ginestra, M. A. Massucci, and K. G. Varshney, *J. Chem. Soc., Dalton Trans.*, **1985**, 1741.

25) A. Clearfield and J. A. Stynes, *J. Inorg. Nucl. Chem.*, **26**, 128 (1964).

26) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1281 (1952).

27) G. Alberti, E. Torracca, and A. Conte, *J. Inorg. Nucl. Chem.*, **28**, 607 (1966).