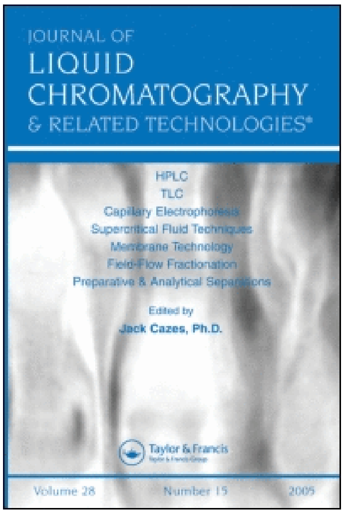

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Varshney, K. G. and Prehadas, A.(1981) 'Silica Based Double Salts as Cation-Exchangers-I Synthesis and Analytical Applications of Cerium (IV) Phosphosilicatte', Journal of Liquid Chromatography & Related Technologies, 4: 7, 1245 — 1259

To link to this Article: DOI: 10.1080/01483918108068809

URL: http://dx.doi.org/10.1080/01483918108068809

JOURNAL OF LIQUID CHROMATOGRAPHY, 4(7), 1245-1259 (1981)

SILICA BASED DOUBLE SALTS AS CATION-EXCHANGERS -I
SYNTHESIS AND ANALYTICAL APPLICATIONS OF CERIUM(IV)PHOSPHOSILICATE.

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ABSTRACT :- This paper deals with the synthesis of cerium(IV) phosphosilicate as a new, reproducible and stable inorganic ion-exchanger. The studies on its composition, chemical and thermal stability, pH-titration, IR, and TGA have been discussed alongwith the distribution behaviour for metal ions. On the basis of distribution studies some ternary and binary separations of metal ions have been achieved which are important both analytically and industrially.

INTRODUCTION

Inorganic materials possessing ion-exchange properties have been of much interest during the last so many years.[1,2,3] Double salts are now receiving more attention due to their peculiar characteristics. Silica based inorganic materials are known to possess enhanced ion-exchange properties and stability. Phosphosilicates of zirconium[4] and titanium[5] are used for the separation of trace amounts of plutonium and in the separation of radioisotopes. However a systematic and detailed study of the phosphosilicates of other tri-andtetra-valent metals has been lacking in the literature. We have therefore concentrated our efforts to prepare and use silica based double salts of tri- and tetra-valent metals as inorganic ion-exchangers. The following pages summarise our such a study on Ce(IV) phosphosilicate (CPS).

EXPERIMENTAL

Reagents and Chemicals :- All the reagents and chemicals used were of AnalaR grade obtained either from BDH (Poole) or E. Merck (Darmstadt). Sodium silicate powder was a Reidel(Germany) product.

Apparatus:- An Elico model LI-10 pH-meter was used for pH-measurements while spectrophotometric studies were performed on a Bausch & Lomb Spectronic-20 colorimeter. IR studies were performed on a Perkin-Elmer 621 Grating infrared spectrophotometer and thermogravimetric analysis was done on a modern TGA balance of FCI (India).

Synthesis of ion-exchange material:- About 80 g. of sodium silicate was heated with 1 liter of demineralised water (DMW) for 10-15 minutes and filtered. The SiO_2 content of this solution, analysed gravimetrically[6], was found to be ~36 g. SiO_2/liter. It was further diluted four times with DMW followed by 250 ml of conc: H_2SO_4 and 1 liter of 0.1M ceric ammonium sulphate. The solution was then made basic (pH~8) by adding liquor ammonia dropwise with continuous stirring. The gel thus obtained was digested for 8 hours at room temperature (~30°C) filtered, washed with DMW and dispersed with continuous stirring, in a 5 liter mixture of 2.5 moles each of phosphoric and nitric acids at ~ 65°C. The resultant gel was filtered by suction, washed with DMW and dried at ~ 65°C. It was immersed in DMW to crack into small granules which were converted into the H^+ form with 1M HNO_3 as usual. The same material was synthesized in different batches for checking the reproducibility.

Composition :- 500 mg. of the exchanger were heated with 20 ml of 10M H_2SO_4 and diluted to 50 ml with DMW. The undissolved SiO_2 was filtered out and estimated gravimetrically[6]. In the filtrate Ce(IV) was determined volumetrically[7] using ferroin as indicator and phosphate[8] was estimated spectrophotometrically after reducing Ce(IV) to Ce(III). The results are summarized in table 1.

Ion-Exchange Capacity (i.e.c):- As the material was a cation-exchanger its exchange capacity was determined by passing a fixed volume (250 ml) of a 1M metal solution on a column of 0.5g sample maintaining the flow rate as ~ 0.5 ml $minute^{-1}$. Table 2 shows the i.e.c of the exchanger for different metals.

TABLE-1. Composition of cerium(IV) phosphosilicate.

S. No.	Amount of Sample taken(mg)	Millimoles of Cerium	Millimoles of Silicon	Millimoles of Phosphorus	Mole ratio
1	500	0.96	2.50	1.95	2:5:4
2	500	0.95	2.47	1.90	2:5:4
3	500	0.97	2.50	1.95	2:5:4

TABLE-2 : Ion-Exchange **Capacity** of Cerium(IV) phosphosilicate dried at 65°C.

Metal ion	i.e.c in meq/dry g.
Li(I)	1.22
Na(I)	1.50
K(I)	1.53
Rb(I)	1.10
Mg(II)	1.10
Ca(II)	1.84
Sr(II)	1.68
Ba(II)	1.68

Chemical and thermal stability :- 250 mg. of the exchanger were placed in 25 ml each of the various mineral acids, bases and salt solutions of different concentrations for 24 hours with intermittent shaking. The supernatant liquid was analysed for the cerium, silicon and phosphorus contents by the standard spectrophotometric methods.[9-11] The results are summarised in table 3.

For thermal stability the exchanger was heated to different temperatures for one hour each and the Na ion-exchange capacity was determined after cooling it to the room temperature. The i.e.c (m:equivalent g^{-1}) of the exchanger after heating at various elevated temperatures are : 1.40 (100°C), 1.21 (200°C), 0.83 (300°C), 0.62 (400°C), 0.43 (500°C), 0.31 (600°C), and 0.10 (800°C).

pH-titrations :- They were carried out by the batch process of Topp and Pepper[12], the results being summarised in Figure -1.

TABLE-3 : Solubility of Cerium(IV) phosphosilicate in different acids, bases and salts solutions.

	Amount of different components present in solution in(mg)		
Solution	Ce	P	Si
1M HNO_3	0.31	0.54	0.32
2M HNO_3	1.60	2.10	1.23
4M HNO_3	3.42	5.60	5.20
8M HNO_3	Partially dissolved.		
1M HCl	1.20	0.71	0.74
2M HCl	3.10	1.51	1.42
4M HCl	7.20	4.12	3.92
8M HCl	Partially dissolved.		
0.5M H_2SO_4	0.80	4.10	3.20
1M H_2SO_4	1.71	5.00	4.60
2M H_2SO_4	Partially dissolved.		
1M $HClO_4$	0.22	0.25	0.20
2M $HClO_4$	0.78	0.35	0.42
4M $HClO_4$	0.96	0.70	0.68
8M $HClO_4$	1.30	0.80	0.78
4M CH_3COOH	0.42	0.70	0.74
4M HCOOH	0.53	1.40	1.38
4M Citric Acid	0.49	-	0.42
2M NH_4NO_3	0.12	0.11	0.18
2M KCl	0.41	0.70	0.48
2M $NaNO_3$	0	0.30	0.20
0.05M NaOH	0	1.57	1.24
0.1M NaOH	0	3.90	2.89
0.05M KOH	0	2.10	1.90
0.1M KOH	0	4.20	3.94
0.1M NH_4OH	0	2.80	2.92

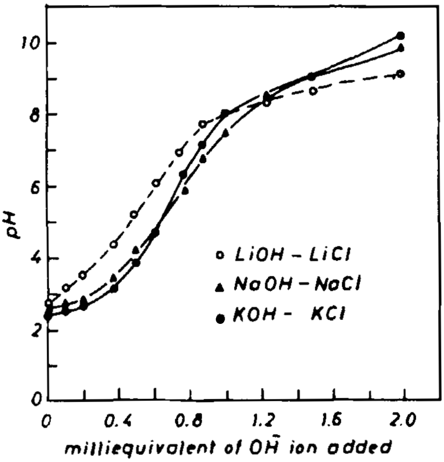

FIGURE -1: pH-titration curves for cerium(IV)phosphosilicate.

IR and TGA Studies:- Figures 2 and 3 summarize the IR and TGA results respectively for the exchanger.

Distribution Studies:- Molar distribution coefficients for 24 metal ions in nine solvent systems were determined by shaking

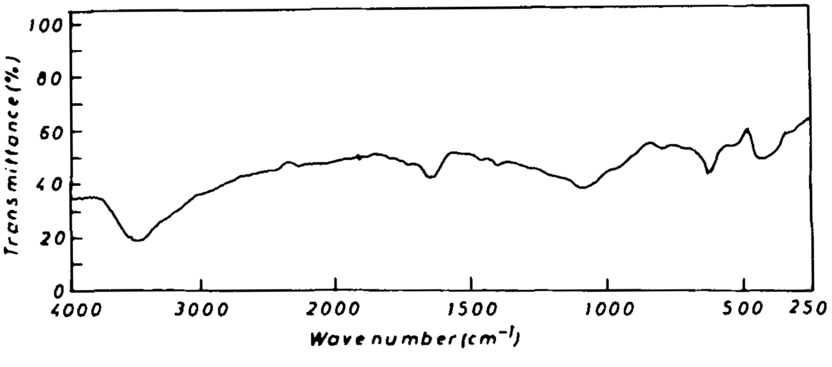

FIGURE -2: IR Spectrum of Cerium(IV)phosphosilicate in H^+ form dried at 65°C.

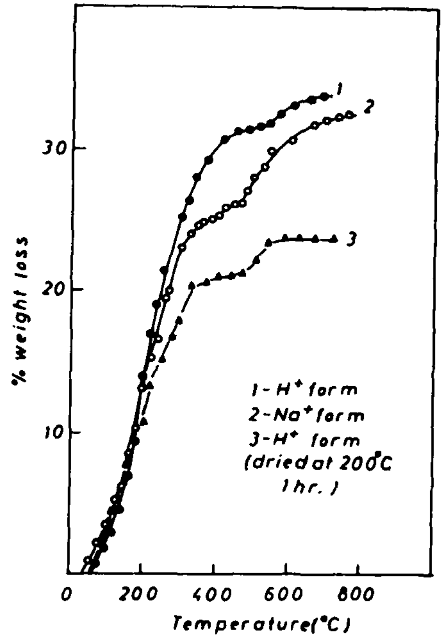

FIGURE -3: TGA Curves of Cerium(IV)phosphosilicate.

250 mg. of the exchanger for 4 hours with 25 ml of the solvent containing the metal not more than 3% of the total i.e.c. All the metal ions, except Ti(IV), UO_2(II) and Ag(I), present in the solution before and after equilibrium, were determined with EDTA[13]. Ti(IV), UO_2(II) and Ag(I) were determined spectrophotometrically[14-16]. The distribution coefficients (Kd in ml/g.) are summarized in table 4.

Separations achieved :- 1g. of the exchanger in H^+ form was packed in a glass tube of i.d ~ 0.6 cm and the mixture of metal ions to be separated was passed through it at a rate ~ 2-3 drops minute^{-1}. The elution was made with a suitable solvent at a flow rate of ~ 0.5 ml minute^{-1} and the effluent was analysed for the metal ion by the

TABLE -4: K_d values of metal ions on cerium(IV) phosphosilicate in different media.

Metal ion	Water	0.01M HNO_3	0.1M HNO_3	0.01M $HClO_4$	0.1M $HClO_4$	0.1M NH_4NO_3	0.1M $NaClO_4$	0.1M HCOOH	0.1M CH_3COOH
Mg(II)	433	6	0	14	0	3	3	60	220
Ca(II)	2900	11	0	50	0	15	9	200	900
Sr(II)	TA	84	0	127	0	47	269	392	1376
Ba(II)	TA	129	45	450	72	129	175	816	TA
Zn(II)	1400	20	0	36	0	9	20	130	650
Cd(II)	3150	20	0	30	0	8	12	132	600
Hg(II)	43	0	0	0	0	6	0	0	14
Pb(II)	TA	360	15	1050	35	1050	666	TA	TA
Cu(II)	TA	64	0	68	0	23	30	228	1975
VO(II)	400	0	0	11	0	0	0	3	11
Mn(II)	1400	11	0	20	0	7	0	58	230
Ni(II)	833	16	0	16	3	0	3	55	180
Co(II)	800	8	0	54	35	59	50	125	350
Ag(I)	1600	32	4	50	4	48	50	725	TA
Fe(III)	1200	766	63	1200	52	225	205	550	1200
Al(III)	1600	56	4	38	0	66	25	38	150
Th(IV)	TA	TA	262	TA	625	TA	TA	TA	TA
Y(III)	TA	3500	0	3500	0	620	1100	20	350
La(III)	TA	2900	110	TA	290	50	275	290	TA
Ho(III)	TA	1400	145	1650	150	50	87	275	500
Gd(III)	1900	1275	120	1900	133	40	328	114	1900
Nd(III)	TA	2600	98	2160	113	80	225	170	TA
Pm(III)	TA	1600	138	TA	125	67	115	115	TA
Sm(III)	TA	2200	120	TA	110	90	140	400	TA

methods used in the distribution studies. The separation limits were determined by varying the amounts of loading. The details are summarised in table 5 and fig.4. To study the effect of drying temperature on the nature of elution, the samples heated to 100°, 200° and 300°C and cooled to room temperature were used

TABLE -5: Separation of metal ions on Cerium(IV) Phosphosilicate Columns.

S.No.	Separation achieved	Amount loaded (µg)	Amount found (µg)	% of error	Limit of separation in µg on 1 g. exchanger	Eluent used	Volume of eluent in (ml)
1	Fe(III)-Cu(II)-Ni(II)	528 Ni	528 Ni	0	110 - 1300	0.01M HNO_3	50
		686 Cu	674 Cu	-1.8	125 - 1375	0.2M HNO_3	60
		502 Fe	491 Fe	-2.2	110 - 890	1.0M HCl + 1M KCl	60
2	Pb(II)-Cd(II)-Hg(II)	1085Hg	1085 Hg	0	200 - 2000	0.005M HNO_3	40
		1011Cd	1011 Cd	0	220 - 1800	0.1M HNO_3	60
		1864 Pb	1823 Pb	-2.2	200 - 4000	1.0M $HClO_4$	60
3	Pb(II)-Ag(I)-Hg(II)	1085 Hg	1085 Hg	0	200 - 2000	0.005M HNO_3	40
		1200 Ag	1180 Ag	-1.7	30 - 1200	0.1M HNO_3	50
		1657 Pb	1613 Pb	-2.7	200 - 4000	1.0M $HClO_4$	60
4	Cu(II) - Hg(II)	1085 Hg	1085 Hg	0	200 - 2000	0.005M HNO_3	40
		699 Cu	674 Cu	-3.6	125 - 1375	0.2M HNO_3	60
5	Pb(II) - Zn(II)	588 Zn	588 Zn	0	130 - 1300	0.1M HNO_3	50
		1657 Pb	1616 Pb	-2.5	200 - 4000	1.0M $HClO_4$	60
6	Pb(II) - UO_2(II)	900 UO_2	890 UO_2	-1.2	50 - 1500	0.1M $HClO_4$	50
		1864 Pb	1815 Pb	-2.6	200 - 4000	1.0M $HClO_4$	60
7	Fe(III)- Mn(II)	495 Mn	495 Mn	0	100 - 1100	0.01M HNO_3	60
		502 Fe	491 Fe	-2.2	110 - 890	1.0M HCl+ 1M KCl	60
8	Fe(III)- Co(II)	528 Co	553 Co	+4.7	120 - 1200	0.01M HNO_3	60
		502 Fe	491 Fe	-2.2	110 - 890	1M HCl+ 1M KCl	60
9	Ba(II) - Mg(II)	218 Mg	228 Mg	+4.5	50 - 250	0.01M HNO_3	60
		1044 Ba	1016 Ba	-2.7	100 - 1100	0.2M HNO_3+1.0M NH_4NO_3	50

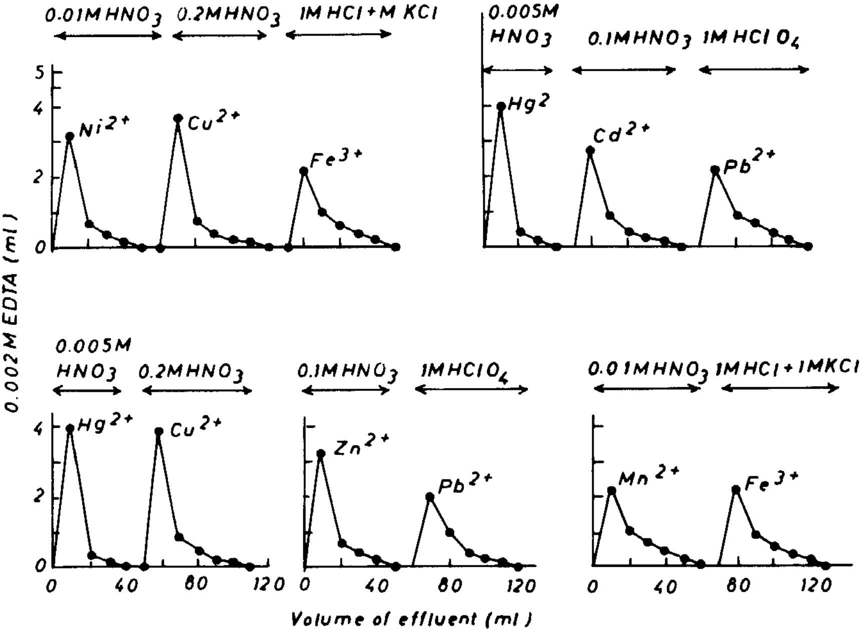

Fig. 4 (a)

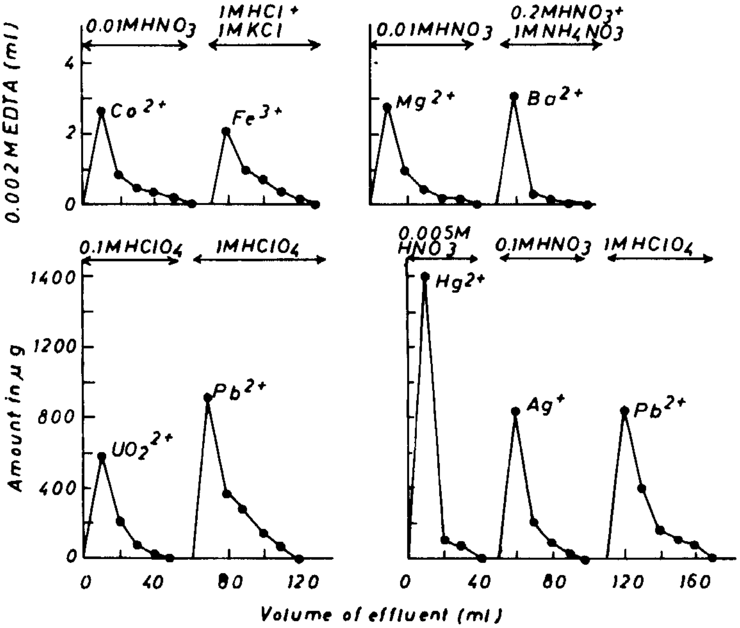

Fig. 4 (b)

FIGURE -4(a)& 4(b) Separation of metal ions on Cerium(IV)phosphosilicate columns.

for the elution of Cu(II) as shown in fig.5. The elution behaviour of the material for Cu(II) ion was also studied at 100°C working temperature by eluting the metal ion with a hot eluant (100°C) through its column surrounded by a steam jacket.

DISCUSSION

The main features of this study are

(i) The synthesis of a reproducible and stable ion-exchange material and

(ii) The separation of metal ions on its column

A continuous stirring of the solution during mixing and the maintanence of an elevated temperature are probably essential for the reproducible bheaviour of the exchanger. These factors are helpful for a uniform phosphotization as is evident from the fact that a sample prepared at room temperature (30°C) and without much stirring did not possess good reproducibility. The material

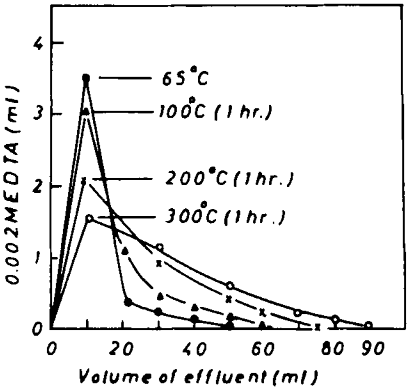

FIGURE -5. Elution of Cu(II) on Cerium(IV)-Phosphosilicate dried at different temperatures.

shows a composition 2:5:4 for Ce; Si and P. Crystalline cerium(IV) phosphate[17] has also been reported to have the composition 1:2 for Ce and P. The IR spectrum (Figure-2) shows peaks at the frequencies ~ 400, ~ 600, ~ 1100, ~1600 and ~ 3600 cm^{-1}. The first peak represent the presence of Ce-O bondings while the second one indicates the Si-O stretching vibrations. The presence of phosphate groups (PO_4^{3-}, HPO_4^{2-} $H_2PO_4^-$) is indicated by the the peak at 1100 cm^{-1} while that of water of crystallisation is shown by the last two peaks.[18]

Figure-3 shows the TGA curves for the exchanger in the H^+ and Na^+ forms. As it is clear from this fugure the exchanger in H^+ form experiences a high weight loss than in the Na^+-form which is obvious because of the presence of a larger number of protons at its exchange sites as compared to the latter. The sample dried at 65°C shows a total weight loss at 400°C as ~ 32% while the one dried at 200°C shows a weight loss at this temperature to be ~ 23% . It is possible that when the sample is heated at 200°C in an air oven for 1 hour the weight loss is due to both the removal of the external water molecules and some condensation. The external water molecules are regained from the atmosphere during cooling to the room temperature. While the loss due to condensation process is not completely regained. This may be the reason for a discrepancy obtained in the weight loss in the samples at 400°C, a temperature where complete condensation might have taken place.

The material is a monofunctional ion-exchanger as indicated by its pH-titration curve (figure-1). The m-equivalent of H^+ replaceable at pH ~ 7 according to this figure are slightly greater than the i.e.c obtained byt the column process. It retains an appreciable i.e.c (0.62 m.equivalent g^{-1}) even after heating at 400°C for 1 hour in contrast to the reported behaviour of ceric phosphate.[19] As the table 3 shows the exchanger is stable chemically in mineral acids upto 4M beyond which it dissolves partially. Sulphuric acid attacks more than the other acids. In alkaline medium it appears to be more stable than the titanium phosphosilicate[5] which reportedly dissolves appreciably in a 0.1M NaOH solution. Cerium(IV) phosphosilicate prepared in these studies therefore seems to be more stable than the other similar salts. The Kd values obtained for the divalents metals decrease in general with the increase in the H^+ ion concentration. In 0.1M HNO_3 and $HClO_4$ solutions the material shows a negligible Kd value for all metal ions except a few such as Pb(II), Fe(III), Ba(II), Th(IV) and lanthanides. The selectivity sequence for alkaline earth metals is as Ba > Sr > Ca > Mg. On this basis Mg(II) has successfully been separated from Ba(II). Other separations achieved are shown in the figure 4 and the details summarized in table-5. In formic and acetic acid media the exchanger shows a higher Kd value probably due to the weak protonation of these acids. The separations achieved are important from the analytical and industrial points of view. They are particularly important for the analysis of alloys such as ferronickel and ferromanganese and the limits of separations resemble closely with the metal concentration in these alloys. As the table-5 suggests the results are precise and lie within the experimental error in all cases. The separations are reproducible and sharp as indicated in figure-4. The rate of elution decreases on a material heated at a high temperature (Figure 5a), a behaviour similar to that of zirconiumphosphate.[20] However a working temperature of 100°C shows an improvement in the elution of Cu^{2+} on CPS. In this behaviour it resembles with the ion-exchange resins.[21]

ACKNOWLEDGEMENT:- The authors are thankful to Prof.M.Qureshi, and Prof. W. Rahman for research facilities. The CSIR (India) is acknowledged for the financial assistance to one of us (P. Das).

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