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Synthesis, Dehydration Studies, and Cation-Exchange Behavior of a New Phase of Niobium(V) Phosphate

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Twenty-three samples of niobium(V) phosphate have been synthesized under different conditions using niobium sulfate and phosphoric acid solutions. The amorphous sample having the ion-exchange capacity of 1.06 mEq g^{-1} and niobium to phosphorus mole ratio of 0.670 was studied in detail for its cation-exchange behavior. Molar distribution coefficients for 25 cations have been studied on this gel at pH 1,2,3, and 5.5. Four quantitative separations of Mg^{2+}-Ca^{2+}, Mg^{2+}-Ba^{2+}, Zn^{2+}-Cd^{2+}, and Bi^{3+}-Zn^{2+} have successfully been achieved on it. The properties of this sample have been compared with those of niobium arsenate, niobium antimonate, and niobium molybdate. A tentative structural formula is proposed for this sample of niobium phosphate on the basis of chemical composition, cation-exchange capacity, pH-titration, IR spectra, T.G.A., water absorption, and heat treatment data.

Synthetic inorganic ion exchangers have been systematically studied during the last ten years owing to their resistance to heat and radiation. However, their analytical applications to the recovery of precious metals from radioactive wastes and to other chromatographic separations are of current interest. The inorganic ion exchangers based on zirconium have been most thoroughly studied followed by those based on tin, titanium and thorium. Very few studies have been reported on niobium(V) based inorganic ion exchanger.

Sukharev et al.[1—5] synthesized niobium phosphate and observed the effect of the presence of trivalent cation (Ce^{3+}, Fe^{3+}, or Cr^{3+}) upon its composition and sorptional behavior. The distribution coefficients were found higher for the precipitate prepared in the presence of trivalent ions. The phase synthesized at pH≤4 showed higher exchange capacity, improved kinetic parameters and ionic diffusion coefficients close to those in organic resin ($\simeq 10^{-8}$ cm s^{-1}). They also found that the amorphous niobium phosphate phases show a preferential uptake for $H_2[Fe(PO_4)_2]^-$ and $H_5[Fe(PO_4)_3]^-$. Shtin et al.[6,7] investigated the complexation of Nb(V) with phosphoric acid and the solubility of complexes of niobium phosphates $[Nb(OH)_3H_{4+z}(PO_4)_3$ where z=2—5] as a function of H_3PO_4 concentrations within the ionic strength 2—20. They also studied the proton exchange in the coordination sphere of $Nb^{IV}(O_2^-)(OH^-)$ radical complexes. Posplev et al.[8,9] observed the effect of concentration of H_3PO_4 acid during synthesis on the properties of granular niobium phosphate $[NbO(OH)_3]_k[NbO(OH)_2]_l[HPO_4]_n[H_2O]_x$ and the effect of synthesis conditions on the composition and its properties. Chernokov et al.[10] prepared crystalline niobium phosphate having formula $NbO(PO_4)\cdot 2H_3PO_4\cdot 5H_2O$.

It is clear from what has been said above that considerable work has been done on the different phases of niobium(V) phosphate but no single phase has yet been exhaustively studied for its ion exchange behavior. Some aspects of these materials need elucidation and therefore we reinvestigated niobium phosphate in continuation of our systematic studies on niobium compounds such as niobium arsenate,[11—13] niobium antimonate,[14,15] and niobium molybdate.[16] The present manuscript describes our findings on a new phase of niobium phosphate.

Experimental

Reagents. Niobium pentaoxide was obtained from BDH (Poole, England). All other reagents of analytical reagent grade were used.

13.291 g Nb_2O_5 was heated with 400 ml of concd. H_2SO_4 containing 135 g $(NH_4)_2SO_4$ until a clear solution was obtained. After cooling the solution, 200 ml concd. H_2SO_4 was added to it and the whole mass was diluted to 1 liter with demineralized water (DMW) to give a 0.1 M solution (1 mol dm^{-3}) in niobium.

Apparatus. The following instruments were used. Elico pH-meter, Bausch and Lomb spectronic-710 colorimeter, DR-EL/4 (HATCH) spectrophotometer, IR Perkin Elmer Unit and Rich Seifort Iso Debyeflex 2002 X-ray diffractometer.

Synthesis. Numerous samples of niobium phosphate were synthesized by mixing acidic solution of 0.1 M niobium (sulfate) with phosphoric acid (Table 1). The concentration of H_3PO_4, mixing ratio, pH of precipitation, total refluxing time and the medium of reflux were the varying parameters. The precipitate so obtained was kept for 24 h with mother liquor to attain equilibrium. In each case the precipitate was separated from the mother liquor by decantation and washed with DMW until the wash solution had a pH of 6 and free from sulfate ions. The precipitate was dried at 40 °C and sieved to get the granules of 50—100 mesh size. The ion-exchange capacities were also determined by the column process for Na^+ ion. Sample 21 (NbP3) having the ion-exchange capacity (I.E.C.) of 1.06 mEq g^{-1} was chosen for detailed study.

Composition. 0.2 g NbP3 was dissolved in an acidic solution which was 10% in H_2SO_4 and 5% in HF. Niobium was determined as Nb_2O_5. It was precipitated with a 10% solution of cupferron[17] as niobium cupferronate. The white precipitate of niobium cupferronate was collected on ashless filter paper with repeated washings with 1% solution of cupferron. The precipitate with filter paper was first dried in

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Table 1. Synthesis and Ion Exchange Capacities of Niobium Phosphate Samples

S.No.	Sample No.	Refluxing		Time/h	Color of final precipitates	I.E.C./mEq g^{-1}
		State of precipitate	Medium			
1	NbPl	Solid	Nil	Nil	Shiny granules	0.94
2	NbP2	Wet	1M H_3PO_4	10	White	1.74
3	NbP3	Solid	1M H_3PO_4	10	Shiny granules	1.06
4	NbP4	Solid	1M H_3PO_4	24	White	1.20
5	NbP5	Solid	1M H_3PO_4	48	White	0.74

Note: Samples were prepared by mixing 0.1M solutions of niobium (sulphate) and phosphoric acid in the ratio of 1:4. The pH was adjusted to 1.1 by liquid ammonia.

Table 2. Solubility of Niobium(V) Phosphate in Different Solvents and Its Comparison to That of Arsenate, Antimonate, and Molybdate of Niobium

S.No.	Solvent	Niobium phosphate (NbP3)		Niobium arsenate[a)] (Sample 2)		Niobium antimonate[b)] (Sample AT 3)		Niobium molybdate[c)]	
		Nb(mg L^{-1})	P(mg L^{-1})	Nb(mg L^{-1})	As(mg L^{-1})	Nb(mg L^{-1})	Sb(mg L^{-1})	Nb(mg L^{-1})	Mo(mg L^{-1})
1	4M H_2SO_4	1051.5	26.2	120.0	156.2	0.0	2.0	—	—
2	4M HNO_3	0.0	1.2	1.5	47.5	0.0	0.0	132.0	418.0
3	4M HCl	0.0	1.8	2.5	81.2	2.0	255.0	321.0	510.0[d)]
4	1M Tartaric Acid	343.7	1.8	475.0	7.5	—	—	—	—
5	1M Acetic Acid	0.0	65.0	1.0	31.2	—	—	—	—
6	4M Ammonia	180.0	91.7	880.0	647.5[e)]	352.0	659.0[e)]	—	—
7	0.1M KOH	2000.0	675.0	—	—	460.0	560.0	Dissolved completely	
8	1M NaCl	0.0	62.5	—	—	—	—	—	—
9	1M NH_4NO_3	0.0	43.7	0.0	5.5	0.0	49.5	2.8	23.5
10	DMW[f)]	0.0	10.4	0.0	11.5	0.0	4.2	3.6	20.1

a) From Ref. 12. b) From Ref. 14. c) From Ref. 16. d) In 2M HCl. e) In 1M Ammonia. f) Demineralized water.

Table 3. Ion-Exchange Capacities of NbP3 and NbP5 for Various Cations

S.No.	Cation	Salt used	pH of the eluent	Concn of salt	I.E.C./mEq g^{-1} (column process)	
					NbP3	NbP5
1	Li^+	LiCl	5.4	0.5 M	0.70	0.46
2	Na^+	NaCl	5.2	1.0 M	1.06	0.74
3	K^+	KCl	5.5	1.0 M	1.18	—
4	Mg^{2+}	$Mg(NO_3)_2$	5.7	0.5 M	0.96	—
5	Sr^{2+}	$SrCl_2$	5.8	0.5 M	1.00	—
6	Ba^{2+}	$BaCl_2$	5.5	0.5 M	1.56	1.34

the IR radiations and then heated in a silica crucible up to 1000 °C to convert it into Nb_2O_5. Phosphorus was obtained as ammonium magnesium phosphate by double precipitation from the former filtrate. The precipitate was heated up to 1000 °C in a silica crucible and determined as magnesium pyrophosphate[18)] gravimetrically.

Chemical Stability. 0.2 g of NbP3 sample was shaken by batch process with different solvents for 24 h. The undissolved material was filtered off. The solutions were then analysed spectrophotometrically for the presence of niobium and phosphorus. Niobium was determined with KSCN[19)] and phosphorus with ammonium molybdate–tin(II) chloride reagent.[20)] The results are given in Table 2.

Ion Exchange Capacity. The I.E.C.'s of the samples of niobium phosphate were determined by column operation[21)] using a column of 0.5 cm. (i.d.). The H^+ ions were eluted by percolating the required cationic solution through the column of the exchanger. The feed was passed until its pH became equal to that of the effluent collected. The hydrogen ions so eluted were titrated against standardized 0.1 M NaOH (Tables 1 and 3).

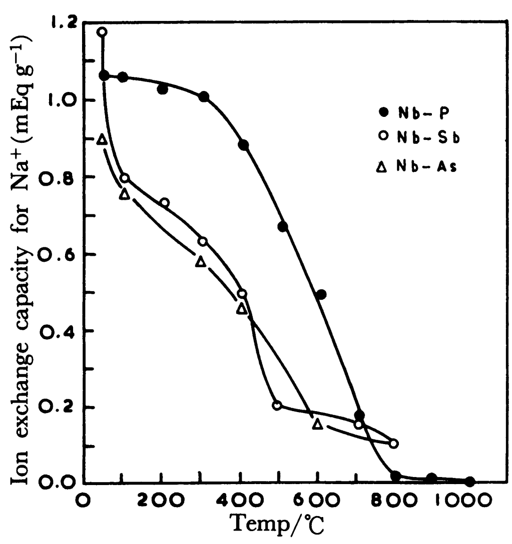


Fig. 1. Effect of temperature on ion-exchange capacities of various inorganic ion-exchangers.

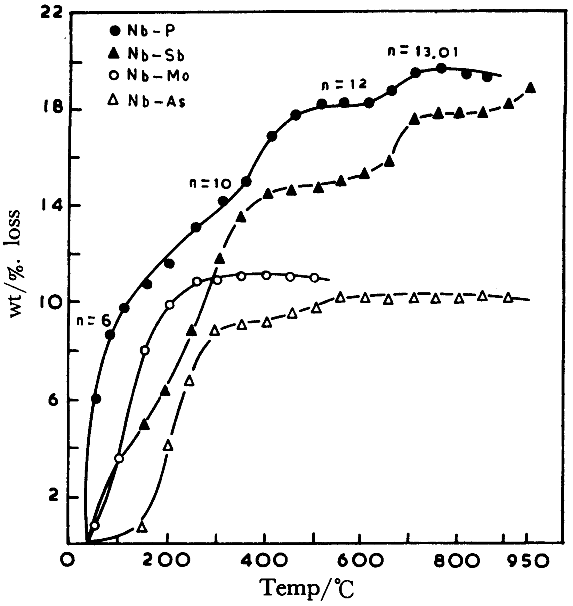


Fig. 2. T.G.A. curves of various inorganic ion-exchangers.

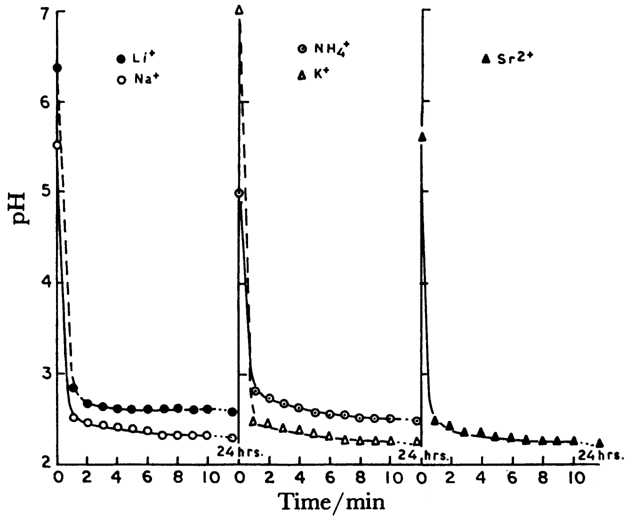


Fig. 3. Plots of pH as a function of time.

Concentration Effect. 0.5 g samples of NbP3 in the H^+ form were equilibrated with 50 ml NaCl solution of different concentrations with intermittent shaking for 24 h in the stoppered conical flasks. The solid material was separated by decantation with repeated washings. The released hydrogen ions were titrated with standard NaOH solution.

Heat Treatment. To check the effect of temperature on the I.E.C. about 2 g of exchanger in the H^+ form was taken in different silica crucibles and each was heated in an automatic temperature controlled muffle furnace at different temperatures until the equilibrium reached. The I.E.C.'s of heated samples were determined with 1M NaCl without reconverting them to the H^+ form and plotted as a function of temperature in Fig. 1.

Thermogravimetric Analysis (T.G.A.). The thermogravimetric analysis was done by taking 0.5 g of the material in the H^+ form. It was heated at a rate of 10 °C min^{-1} from 40 to 1000 °C (accuracy ±5%) in an atmosphere of air and the weight loss as a function of temperature was recorded and shown in Fig. 2.

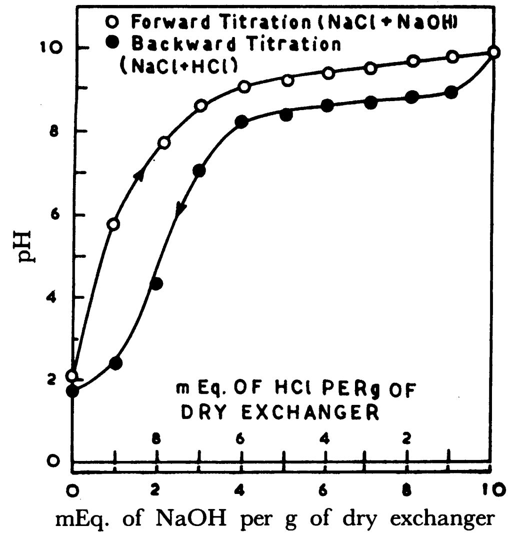


Fig. 4. pH titration curves for Na^+ on NbP_3.

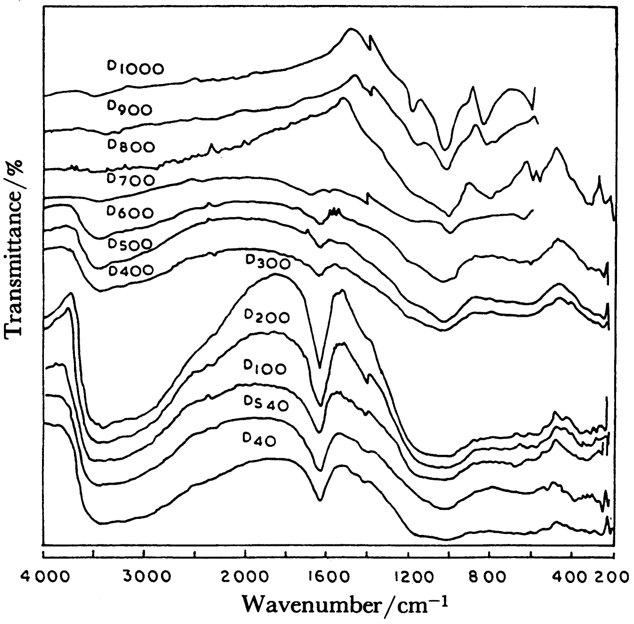


Fig. 5. IR spectra of niobium phosphate heated at various temperatures.
Abbreviations: D-sample 21 in H^+ form.
D_S-sample 21 in Na^+ form.
Subscripts 40—1000: Temperatures in °C.

Water Absorption. 0.5 g of the sample in the H^+ form was heated at 100 and 200 °C. The same sample in the Na^+ form was heated at 220 °C for 1 h. The heated samples were stored in an air tight desiccator over a saturated solution of ammonium nitrate. The absorption of water was recorded at different time intervals.

Rate of Ion Exchange. The rate of ion exchange was measured by taking 50 ml of 1 M solution of the cation. The pH of the solution was measured and then 0.5 g of the exchanger in the H^+ form was added. The solution was shaken at short intervals and pH was recorded. The pH vs. time (in minutes) was plotted and shown in Fig. 3.

pH-Titration. The pH-titrations were performed by the method of Topp and Pepper.[22] 0.1 g samples of dry exchanger in the H^+ form were shaken with 10 ml portions of 0.1 M (NaCl+NaOH) cationic solution in different conical flasks at 25±0.5 °C. The ratio of NaCl/NaOH was varied from 0.1 M/0.01 M to 0.01 M/0.1 M in the equilibrating solution of the flasks. After 24 h the pH of the supernatant solution of each flask was recorded and plotted against the mEq of OH^- added per g of dry exchanger. For reverse titration, the Na^+ form of the exchanger was treated in a similar fashion with 0.1 M (NaCl+HCl) solution (Fig. 4).

X-Ray Diffractogram. Powder X-ray diffraction technique was used to take the diffractogram of the powdered sample using nickel filtered Cu $K\alpha$-radiation (λ=1.5404 Å).

IR Study. IR spectra of the material heated at various temperatures (i.e., from 40 to 1000 °C) were recorded with the standard KBr disc technique. The spectrum of the material in the Na^+ form dried at 40 °C was also recorded. The spectra are shown in Fig. 5.

Distribution Coefficients (K_d Values). K_d values of 25 cations on the exchanger sample were determined in DMW, 0.001, 0.01, and 0.1 M HNO_3 solutions (Tables 4a, 4b, 4c). The cations present in the solution were titrated with 10^{-3} M EDTA solution using the specific metal indicator. The distribution coefficient (K_d) was calculated as:

$$K_d(\text{ml g}^{-1}) = \frac{\text{Moles of metal ion per g of solid}}{\text{Moles of metal ion per ml of solution}}.$$

Separation Studies. The mixture of the metal ions were loaded on the exchanger and then the ions were eluted by suitable eluents. The flow rate of the effluent was maintained at 0.5 ml min^{-1} throughout the process. The released cations were estimated with standard 0.001 M EDTA solution (Table 5).

Results and Discussion

During these studies more than 20 samples of niobium phosphate have been synthesized under various conditions (results omitted to save space). Most of the samples were suitable for column operations and showed ion-exchange capacities varying from 0.16 to 1.2 mEq g^{-1} for the Na^+ ion. Only five of the samples (Table 1) were synthesized thrice, their ion-exchange capacities and chemical compositions were determined and found reproducible. They are designated as NbP1, NbP2,⋯, NbP5 respectively. The amorphous sample, NbP3 having Nb/P mole ratio of 0.67 and I.E.C. of 1.06 mEq g^{-1} was chosen first for detailed studies (reported in this manuscript). The studies on the rest of the samples is in progress and a part of it is reported elsewhere.[23]

Table 3 shows the ion-exchange capacities of samples 3 and 5 for various cations obtained by column process. The capacity increases as the hydrated radii of the cations decrease. The ion-exchange capacity of NbP3 increases from 0.86 to 1.06 mEq g^{-1} as the concentration of the eluent (NaCl) changes from 0.2 to 1 M and then becomes constant.

It is clear from Fig. 3 that the exchange is initially fast and then it slows down after one minute. Li^+, NH_4^+, and Sr^{2+} do not exchange as efficiently as Na^+ and K^+ ions.

The pH-titration of the material with NaOH in the presence of the added salt reveals its monofunctional behavior as it shows only one inflection point. The

Table 4a. K_d Values in DMW upon Phosphate, Arsenate, Molybdate, and Antimonate of Niobium

S.No.	Cation	Niobium phosphate	Niobium arsenate[a]	Niobium molybdate[b]	Niobium antimonate[c] (approximate)
1	Mg^{2+}	1028	171	26	20
2	Ca^{2+}	1078	298	30	398
3	Ba^{2+}	331	2980	20	398
4	Sr^{2+}	70	553	43	398
5	Fe^{3+}	45	115	—	1585
6	Ni^{2+}	71	1005	—	100
7	Co^{2+}	6437	387	—	—
8	Mn^{2+}	4500	1930	60	—
9	Cd^{2+}	5375	950	44	631
10	Cu^{2+}	4687	1600	>3500	399
11	Zn^{2+}	182	1100	27	100
12	Hg^{2+}	1875	31	0	398
13	Pb^{2+}	121	1850	—	2512
14	Zr^{4+}	2812	109	—	—
15	V^{5+}	295	540	—	340
16	Y^{3+}	734	9460	—	631
17	La^{3+}	1375	—	>3500	631
18	Ce^{3+}	375	—	—	795
19	Pr^{3+}	3312	9460	>3000	—
20	Sm^{3+}	112	9260	—	—
21	Eu^{3+}	75	2110	—	—
22	Gd^{3+}	316	2312	—	200
23	Al^{3+}	500	1930	17	251
24	Th^{4+}	110	—	400	631
25	Bi^{3+}	2575	—	1300	—

a) From Ref. 11. b) From Ref. 16. c) From Ref. 14.

Table 4b. K_d Values in 0.1M HNO_3 upon Phosphate Arsenate, Antimonate, and Hydrated Oxide of Niobium

S.No.	Cation	Niobium phosphate	Niobium arsenate[a)]	Niobium antimonate[b)]	Niobium hydrated oxide[c)]
1	Mg^{2+}	0	7	3	0
2	Ca^{2+}	99	22	18	0
3	Sr^{2+}	6	55	23	5
4	Ba^{2+}	120	85	280	62
5	Fe^{3+}	688	72	286	22
6	Ni^{2+}	4	13	27	12
7	Co^{2+}	3156	15	—	—
8	Mn^{2+}	70	11	—	—
9	Cd^{2+}	166	110	39	0
10	Cu^{2+}	115	65	26	3
11	Zn^{2+}	0	71	38	3
12	Hg^{2+}	366	12	410	370
13	Pb^{2+}	128	557	1066	425
14	Zr^{4+}	2813	193	—	—
15	V^{5+}	184	469	260	—
16	Y^{3+}	—	14	30	11
17	La^{3+}	1150	—	50	2
18	Ce^{3+}	675	—	20	0
19	Pr^{3+}	0	47	—	—
20	Sm^{3+}	11	20	—	—
21	Eu^{3+}	0	79	—	—
22	Gd^{3+}	20	10	34	0
23	Al^{3+}	963	133	160	0
24	Th^{4+}	110	—	95	50
25	Bi^{3+}	2575	—	—	—

a) From Ref. 11. b) From Ref. 14. c) From Ref. 14.

Table 4c. K_d Values upon Niobium Phosphate in HNO_3 at pH 2 and 3

S.No.	Cation	0.01M HNO_3	0.001M HNO_3	S.No.	Cation	0.01M HNO_3	0.001M HNO_3
1	Mg^{2+}	531	739	14	Bi^{3+}	2575	2575
2	Ca^{2+}	469	2281	15	Zr^{4+}	2813	2813
3	Sr^{2+}	77	118	16	V^{5+}	609	—
4	Ba^{2+}	281	156	17	Y^{3+}	174	268
5	Fe^{3+}	24	40	18	La^{3+}	1150	1375
6	Ni^{2+}	29	578	19	Ce^{3+}	675	675
7	Co^{2+}	6438	6437	20	Pr^{3+}	625	639
8	Mn^{2+}	4500	4500	21	Sm^{3+}	134	160
9	Cd^{2+}	5375	5375	22	Eu^{3+}	59	60
10	Cu^{2+}	68	4688	23	Gd^{3+}	25	—
11	Zn^{2+}	182	182	24	Al^{3+}	963	604
12	Hg^{2+}	328	—	25	Th^{4+}	110	110
13	Pb^{2+}	640	121				

Table 5. Separations Achieved on Niobium Phosphate Column

S.No.	Mixture loaded	Cation eluted	Eluent	Total volume of effluent collected	Amount loaded	Amount found	Error
				ml	μg	μg	%
1	Mg^{2+}-Ca^{2+}	Mg^{2+}	0.2M HNO_3	100	216	205	−5.09
		Ca^{2+}	0.2% $H_2C_2O_4$	25	160	168	+5.00
2	Mg^{2+}-Ba^{2+}	Mg^{2+}	0.2M HNO_3	110	216	216	0.00
		Ba^{2+}	0.2% $H_2C_2O_4$	25	448	450	+0.45
3	Zn^{2+}-Cd^{2+}	Zn^{2+}	0.2M HNO_3+0.25% NH_4NO_3	60	293	299	+2.05
		Cd^{2+}	1.0M HNO_3+0.5% NH_4NO_3	60	244	250	+2.46
4	Bi^{3+}-Zn^{2+}	Bi^{3+}	2% Na_2CO_3	30	214	219	+2.34
		Zn^{2+}	0.2M HNO_3+0.25% NH_4NO_3	70	290	294	+1.38

Table 6. Comparison of Theoretical and Observed Structural Data of Niobium Phosphate i.e., NbP3

S.No.	Properties	Observed	Theoretical	Remark
1	Behavior	Monofunctional	Monofunctional	$\overset{*}{H}PO_4^-$ — are exchange sites
2	Useful I.E.C. at 40°C	1.06 mEq g^{-1}	—	
3	I.E.C. by pH-titration	1.68 mEq g^{-1}	1.68 mEq g^{-1}	
4	Total I.E.C.	—	4.96 mEq g^{-1}	
5	Empirical formula	$2Nb_2O_5 \cdot 3P_2O_5(H_2O)_{2.96}10.05H_2O$	$2Nb_2O_5 \cdot 3P_2O_5(H_2O)_3 10H_2O$	
6	Mol. Wt.	1192.18	1192.00	
7	Nb/P ratio	0.67	0.67	

behavior appears to be reversible at lower pH values, i.e., pH 1—2. A hysteresis loop occurs at higher pH values. This may be due to the hydrolysis of niobium and phosphate groups at higher pH values which results in a totally different phase formation. This is in accordance with the chemical stability data that the material gets hydrolyzed in alkaline solution. It gave an ion-exchange capacity of 1.68 mEq g^{-1} for Na$^+$ ion.

The chemical dissolution data (Table 2) show that NbP3 is highly stable in 4 M HNO_3 and 4M HCl. It dissolves frequently in 4 M H_2SO_4, 1 M tartaric acid, 4 M ammonia and in 0.1 M KOH solutions probably due to complex formation. Its stability in 4 M HCl is remarkable as most exchangers which are stable in 4 M HNO_3 are unstable in 4M HCl. The comparison of NbP3 with the arsenate, antimonate, and molybdate of niobium shows that in most solutions NbP3 in only next to niobium antimonate in chemical stability.

In order to obtain some informations regarding the empirical formula and theoretical ion-exchange capacity of NbP3, thermoanalytical investigations were carried out. It is clear from Fig. 1 that the ion-exchange capacity of the various ion exchangers decreases with increase in temperature. It also shows that NbP3 is more thermally stable than niobium arsenate and antimonate as far as its ion-exchange behavior is concerned.

X-Ray diffraction studies of the material dried at 40 °C revealed its amorphous behavior while the material heated above 400 °C showed some signs of crystallinity. Only two weak lines viz. at d=8.01 and d=3.22 Å appeared in these samples. The intensities of these lines increased with increase in temperature.

The comparison of T.G.A. curves of various exchangers in the H$^+$ form (Fig. 2) shows that the curves of niobium molybdate and niobium arsenate are simple and similar up to 500 °C. However, the T.G.A. of NbP3 is more complicated than that of the former compounds. It resembles more the curve for niobium antimonate. The most remarkable aspect of this curve is the highest weight loss than for any of the four compounds. Another interesting feature is the three-step weight loss which shows that there are at least three types of dehydrations occurring in this compound. This unusual behavior is probably due to the great affinity of the phosphate groups for water molecules and also due to large content of hydroxophosphate anionic part.

For niobium phosphate the weight loss is maximum (19.65%) up to 700 °C. Assuming that at this temperature the composition of the sample is $2Nb_2O_5 \cdot 3P_2O_5$ (Nb:P=2:3, by chemical analysis) the number of moles of water lost per formula weight of the exchanger corresponding to the weight loss at different temperatures was calculated by the method of Alberti, et al.[24] and shown in Table 6.

If n is the number of moles of water per mole of "mixed oxide," then

$$\%\ \text{weight loss} = \frac{1800\,n}{958+18\,n}, \tag{1}$$

(where mol. wt. of "mixed oxide" = 958).

From this equation the empirical formula can be obtained as follows:

Suppose

W_H = % weight loss in H$^+$-form of exchager up to 800 °C,

W_{Na} = % weight loss in Na$^+$-form of exchager up to 800 °C,

n_H = number of moles of water corresponding to W_H,

n_{Na} = number of moles of water corresponding to W_{Na},

n_{ex} = number of moles of water from –OH groups responsible for exchange,

n_{ab} = number of moles of water absorbed or the water of crystallization,

then

$$n_{ex} = n_H - n_{Na}, \tag{2}$$

$$n_{ab} = n_H - n_{ex}. \tag{3}$$

Treatment of the experimental data according to Eqs. 1, 2, and 3 gives

$$n_{ex} = 2.96,$$

$$n_{ab} = 10.05.$$

Hence we can assign the following formula to NbP3 sample:

$$2Nb_2O_5 \cdot 3P_2O_5(H_2O)_{2.96}10.05\,H_2O.$$

Hence,

$$\text{the theoretical I.E.C.} = \frac{2.96 \times 2 \times 1000}{1192.18}$$

$$= 4.96\ \mathrm{mEq\,g^{-1}}.$$

The sodium ions are exchanged only up to 1.63 mEq g^{-1} in alkaline medium. It is very low as compared to the theoretical exchange capacity (4.96 mEq g^{-1}) and corresponds to two protons per formula weight of the exchanger. It seems that under our experimental conditions only the surface protons take part in the exchange reaction as the ingoing cations are not able to reach all the exchange sites (six protons) in amorphous niobium(V) phosphate. Hence only a part (two protons) of the H^+ present are exchangeable.[25–31]

The exchanger in the H^+ form when heated to 100 and 200 °C shows a weight loss of 10.2% (n=6.04) and 11.8% (n=7.12), respectively. Upon storing these dried samples in air-tight desiccator over a saturated solution of NH_4NO_3 solution, the former reabsorbs 100% water within 20 h while the latter could absorb only 86.06% water (n=6.01) after 100 h. This shows that the loss of water at 100 °C is completely reversible while at 200 °C only 86% reversibility is obtained. When the same sample in the Na^+ form was heated to 200 °C and stored over a saturated solution of NH_4NO_3, it regained the lost water molecules at a slightly higher rate than that of the H^+ form. It recovered approximately all the weight loss within 100 h. This reveals that the hydrated Na^+ ion lies within the cavity and keeps it slightly expanded thus facilitating the reabsorption of the water molecules into the cavity.

The IR spectra of NbP3 heated at various temperatures are given in Fig. 5. All the spectra refer to the niobium phosphate in the H^+ form. Only D_{s40} refers to that of Na^+ form dried at 40 °C. A comparison of D_{40} and D_{s40} spectra is very interesting. Since the band between 3000 and 3600 cm^{-1} refer to strong hydrogen bonds between-OH groups of water molecules and hydrogen-bearing oxygen of phosphate groups, therefore this band may be attributed to the long hydrogen bond P-O-H····O-H and P-O-H····$O\langle^{H}_{H}$.[32] When the hydrogen ion of the P-OH group is replaced by Na^+, the hydrogen bonding is diminished and the band becomes narrower. A similar effect is observed for the band between 940 and 1180 cm^{-1}. This band can be assigned to the symmetric and antisymmetric vibrations for the phosphate groups.[32] When the hydrogen ion of P-OH is replaced by Na^+, which is more strongly ionized we obtain a much narrower peak in D_{s40} spectra in this region at 1020 cm^{-1}. The effect of heating on the band between 3000 and 3600 cm^{-1} and the peak at 1630 cm^{-1} can be interpreted as follows:

Since the band is due to P-O-H····$O\langle^{H}_{H}$ and the peak due to deformation vibration of H_2O and -OH groups it is possible that in the beginning, i.e., from 40 to 300 °C, the absorbed water molecules are lost and therefore the band and the peak become narrower as one goes from 40 to 300 °C. However, at 400 °C the P-OH groups of the phosphates begin to condense and this condensation is complete up to 800 °C. Therefore, at 800 °C (D_{800}) the band and the peak completely disappear. The effect of heat on the band between 940 and 1180 cm^{-1} is quite different. Since this band is due to P-O vibrations[32] it remains unaffected up to 300 °C with the loss of water molecules. Above 300 °C the band becomes narrower due to condensation of P-OH groups and the increase in the concentration of P-O-P groups. At 800 °C all the P-OH groups condense and hence a very sharp peak is obtained owing to the presence of P-O-P groups at 1020 cm^{-1}. This phase also shows some more peaks at 850, 620, 580, 350, and at 250 cm^{-1} corresponding O-P-O and O-Nb-O interatomic stretching vibrations.[32] In this way we can say that D_{800} is completely a new phase having no hydroxyl group or water of free ionic sites responsible for ion exchange.

Theoretical Interpretation of the Heating Effect. The schematic diagram and Fig. 1 show the amount and the type of water molecules lost with temperature. At 100 °C six water molecules attached to $\overset{*}{H}PO_4$ groups are lost. Up to 200 °C, 1.12 more water molecules are irreversibly removed from the cavity resulting in the cavity shrinkage and a negligible effect on the I.E.C. Up to 350 °C all the rest absorbed (probably coordinated to niobium) water molecules are lost. The condensation of phosphate groups starts above 400 °C and up to 550 °C two water molecules are lost as a result of intermolecular condensation of four phosphate groups.

$$(\overset{*}{H}PO_4^{2-})_2(HPO_4^{2-})_4 \xrightarrow[\approx 550\,^\circ C]{-2H_2O} (\overset{*}{H}PO_4^{2-})_2(P_2O_7^{4-})_2$$

Intermolecular Condensation of Monomers

At 650 °C the dimer formation starts due to intramolecular condensation of the monomers and 0.5 water molecule per formula weight is lost from one of the $\overset{*}{H}PO_4^{2-}$ group and thus the I.E.C. is reduced to half.

$$2[(\overset{*}{H}PO_4^{2-})_2(P_2O_7^{4-})_2] \xrightarrow[\sim 650\,^\circ C]{-H_2O} (\overset{*}{H}PO_4^{2-})_2(P_2O_7^{4-})_5$$

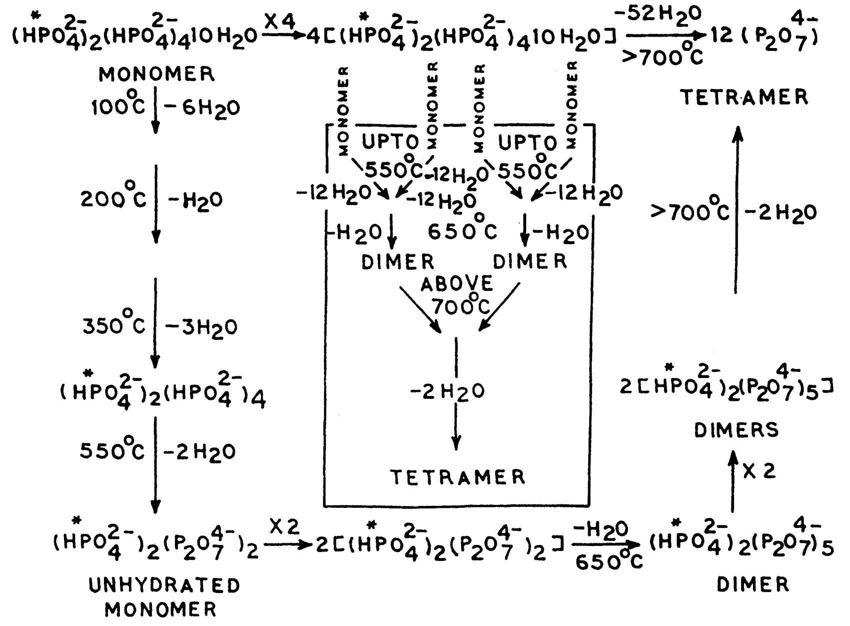
Monomers Dimer

Intramolecular Condensation

Above 700 °C two dimers combine together to give a tetramer. The condensation is complete up to 800 °C and at this stage all the exchange sites are exhausted.

$$2[(\overset{*}{H}PO_4^{2-})_2(P_2O_7^{4-})_5] \xrightarrow[>700\,^\circ C]{-2H_2O} (P_2O_7^{4-})_{12}$$

Dimers Tetramer



Schematic Representation of Heating Effect on Niobium Phosphate

The condensation process in this way agrees with IR, X-ray, T.G.A., and I.E.C. data and the niobium to phosphorus mole ratio remains constant at all the temperatures studied.

The K_d values of 25 metal ions on niobium phosphate (NbP3), niobium arsenate (Nb–As), niobium molybdate (Nb–Mo), and niobium antimonate (Nb–Sb) in DMW are given in Table 4a. All these materials show a high uptake for Cu^{2+}, Bi^{3+}, La^{3+}, Pr^{3+}, Y^{3+}, Sm^{3+}, and Gd^{3+}. Table 4b lists the K_d values on NbP3, Nb–As, Nb–Sb, and Nb_2O_5 which reflects that these exchangers show no absorption of Mg^{2+}, high or preferential uptake of Hg^{2+}, Pb^{2+}, Zr^{4+}, and V^{5+} and moderate preference towards lanthanides in 10^{-1}M HNO_3. Distribution coefficients on NbP3 in 10^{-2}M and 10^{-3}M HNO_3 decrease upon increasing the acid concentration as is evident from Table 4c.

The study of distribution coefficients in nitric acid solutions reveals the appreciable differences among the K_d values of a number of metal ions. The exchanger appears to be selective for Co^{2+} and Zr^{4+} in all the media. It seems that it can be used for the separation and purification of rare earth from various metal contaminants. These studies will require a careful examination of the problem. At present no attempt has been made in this direction, or rather, four quantitative separations of common cations namely, Mg^{2+}–Ca^{2+}, Mg^{2+}–Ba^{2+}, Zn^{2+}–Cd^{2+}, and Bi^{3+}–Zn^{2+} have been tried and successfully achieved on amorphous niobium(V) phosphate column. The results are presented in Table 5 which show that the recoveries of the metal ions lie within the limit of experimental errors.

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References

1) Yu. V. Egorov, Yu. I. Sukharev, and N. N. Pustovalov, *Tovarnyl, Znaki*, **46**, 22 (1969).

2) Yu. I. Sukharev, Yu. V. Egorov, and N. N. Pustovalov, *Zh. Neorg. Khim.*, **16**, 1026 (1971).

3) N. V. Dranitsina, Yu. V. Egorov, N. N. Kalugina, N. N. Pustovalov, and Yu. I. Sukharev, *Neorg. Ionooben. Mater.*, **1**, 97 (1974).

4) Yu. I. Sakharov, O. R. Glukhova, and Yu. V. Egorov, *Tr. Ural'sk Politekhn.*, **226**, 72 (1975).

5) R. M. Belkina, Yu. I. Sukharev, and Yu. V. Egorov, *Zh. Neorg. Khim.*, **21**, 1758 (1976).

6) A. M. Gorelov and A. P. Shtin, Deposited Publication VINITI **22**, 6694 (1973).

7) A. P. Shtin, V. L. Mamoshin, and A. D. Galaktinov, *Kimiya Tvenol. Tela (Sverdlovsk)*, **2**, 41 (1978).

8) A. A. Pospelov, V. N. Krylov, G. I. Deulin, L. M. Slobod-Chikova, and R. B. Dushin, *Iezisy. Dokl. Vses. Nauchno. Tekh. Knof. Tekhol Neorg. Veshchestu Miner Idobr.*, **1**, 141 (1974).

9) G. I. Deulin, N. V. Egorova, V. N. Krylov, V. G. Pitalve, A. A. Pospelov, and L. M. Slobodchikova, *Zh. Prikl. Khim.*, **54**, 1226 (1981).

10) N. G. Chernokov, M. P. Egorov, and V. F. Kutsepin, *Zh. Neorg. Khim.*, **24**, 1782 (1979).

11) M. Qureshi, J. P. Rawat, and A. P. Gupta, *J. Chromatogr.*, **118**, 167 (1976).

12) M. Qureshi, J. P. Rawat, and A. P. Gupta, *Chromatographia*, **11**, 202 (1978).

13) M. Qureshi, J. P. Rawat, and A. P. Gupta, *J. Indian Chem. Soc.*, **LVIII**, 855 (1981).

14) M. Qureshi, A. P. Gupta, T. Khan, and J. P. Gupta, *Chromatogr.*, **144**, 231 (1977).

15) M. Qureshi, A. P. Gupta, D. V. Nowell, and J. P. Gupta, *J. Inorg. Nucl. Chem.*, **40**, 545 (1978).

16) M. Qureshi, A. P. Gupta, J. S. Thakur, and V. P. Singh, *Sepn. Sci. Tech.*, **15**, 1255 (1980).

17) G. E. F. Lundell and J. I. Hoffman, "Outlines of Methods of Chemical Analysis," Wiley, New York (1958), p.

117.
18) N. H. Furman, "Standard Methods of Chemical Analysis," 6th ed, Van Nostrand, New York (1971), p. 812.
19) Alan D. Westland and Jerome Benzaire, *Anal. Chim. Acta,* **66**, 187 (1973).
20) APHA-AWWA-WPCF, "Standard Methods for the Examination of Water and Waste Water," 14th ed, (1975), p. 479.
21) O. Samuelson, Dissertation, Tek. Hogskelan, Stockholm, 1944.
22) N. E. Topp and K. W. Pepper, *J. Chem. Soc.*, **1949**, 3299.
23) Anees Ahmad, "Synthetic Inorganic Ion Exchangers," A Thesis submitted to A. M. U. Aligarh for the degree of Doctor of Philosophy in Chemistry, Aug, 1985.
24) G. Alberti, E. Torracca, and A. Conte, *J. Inorg. Nucl. Chem.*, **28**, 607 (1966).
25) J. S. Gill and S. N. Tandon, *J. Inorg. Nucl. Chem.*, **30**, 3885 (1972).
26) J. S. Gill and S. N. Tandon, *J. Radioanal. Chem.*, **13**, 391 (1973).
27) J. S. Gill and S. N. Tandon, *Talanta,* **19**, 1355 (1972).
28) J. S. Gill and S. N. Tandon, *J. Radioanal. Chem.*, **20**, 5 (1974).
29) J. S. Gill and S. N. Tandon, *Talanta,* **20**, 585 (1973).
30) J. S. Gill and S. N. Tandon, *J. Radioanal. Chem.*, **36**, 345 (1977).
31) J. S. Gill and S. N. Tandon, *J. Radioanal. Chem.*, **49**, 55 (1979).
32) J. A. Marinsky and Y. Marcus, "Ion Exchange and Solvent Extraction Series," Marcel Dekker, Inc., New York (1973), Vol. 5, p. 19.