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## STUDIES ON THORIUM PHOSPHATE ION EXCHANGER

### I. SYNTHESIS, PROPERTIES AND ION-EXCHANGE BEHAVIOUR OF THORIUM PHOSPHATE

ANIL K. DE and KAILAS CHOWDHURY

*Department of Chemistry, Visva-Bharati, Santiniketan, West Bengal (India)*

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#### SUMMARY

Thorium phosphate has been prepared by mixing solutions of 0.1 *M* Th(NO<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O in 1 *M* nitric acid and 1 *M* phosphoric acid. Four different thorium phosphate materials were obtained under various conditions with PO<sub>4</sub>:Th ratios of 1.9, 2.1, 1.69 and 1.9. Preparative procedures, chemical stability, derivative thermogravimetric analysis results and infrared spectra of these materials are reported and discussed.

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#### INTRODUCTION

The importance of synthetic inorganic ion exchangers for the preparation of selective ion-exchange sheets and papers and also for column operation have increased since the publication of a book by Amphlett<sup>1</sup>. Insoluble salts of polybasic metal ions have generally been obtained as amorphous, fibrous, semi-crystalline and crystalline materials. However, little work has been reported on thorium phosphate<sup>2-4</sup>. Alberti and Constantino<sup>4</sup> prepared both amorphous and fibrous thorium phosphate with PO<sub>4</sub>:Th ratios from 1.5 to 2.1. They showed that the composition of thorium phosphate is ThO<sub>2</sub>·P<sub>2</sub>O<sub>5</sub>·4H<sub>2</sub>O, and the ion-exchange capacity for Na<sup>+</sup> was reported to be 3.7 mequiv./g. But detailed studies of thorium phosphate were lacking in the earlier papers. This paper reports systematic studies on thermogravimetric analysis, infrared spectra, chemical stability, pH titration curves and ion-exchange capacity of thorium phosphate. Thorium phosphate sheets can be used in both electrophoretic and chromatographic analyses.

#### EXPERIMENTAL

##### *Reagents*

Th(NO<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O was of reagent-grade quality (E. Merck, Darmstadt, G.F.R.). All other reagents were of AnalaR grade (BDH, Poole, Great Britain).

### Apparatus

pH measurements were made with an ELICO Model LI-10 pH meter. Spectrophotometric measurements were carried out using a Spectromom 202 instrument (Mom, Budapest, Hungary). An Owa Labor Type 707.04 analytical balance was used.

## RESULTS AND DISCUSSION

### Synthesis

The method of preparation of the thorium phosphate ion exchanger was very similar to that of Alberti and Constantino<sup>4</sup>, with slight modifications. A 0.1 M solution of  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  in 1 M nitric acid solution was added at the rate of 2-3 ml/min to 1 M phosphoric acid at  $80 \pm 5^\circ$  over a steam-bath with constant stirring. After digestion of the mixture for several hours, it was cooled to room temperature, filtered and washed with water to pH 3-3.5, and dried over  $\text{P}_4\text{O}_{10}$ . It has been found that when the phosphoric acid concentration is high and the preparation is carried out at room temperature by stirring the mixture for 4-10 h, a gel-type product is obtained. By increasing the digestion time, the  $\text{PO}_4:\text{Th}$  ratio increased and fibrous properties developed, leading to the preparation of stable thorium phosphate sheets. The compositions of the exchangers are given in Table I.

TABLE I  
PREPARATION AND COMPOSITION OF EXCHANGERS

Batch No.	0.1 M $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ in 1 M $\text{HNO}_3$ -1 M $\text{H}_3\text{PO}_4$ (v/v)	Initial pH of the mixture	Digestion time (h)	$\text{PO}_4:\text{Th}$ ratio of the exchanger (by analysis)
1	5:2	0.25	4	1.9
2	5:2	0.25	24	2.1
3	5:1	0.20	4	1.69
4	5:3	0.30	4	1.9

### Composition, chemical and thermal stability

**Composition.** Phosphate was determined volumetrically by the standard ammonium phosphomolybdate method<sup>5</sup>. As phosphate interferes in the determination of thorium as oxalate, thorium was first precipitated as iodate, then dissolved in dilute hydrochloric acid, precipitated as oxalate, ignited and determined as thorium dioxide.

**Chemical stability.** The products are in the form of both amorphous and fibrous, hard white materials, suitable for use as support-free ion-exchange sheets. On heating above  $200^\circ$  the material turns light grey in colour. No change in the form or colour was observed when it was heated in boiling water, dilute mineral acids and dilute alkalis, but when the product was refluxed with 5 M phosphoric acid for 12 h, it changed to semi-transparent beads. When the exchanger was immersed in 1 M nitric acid at room temperature for 24 h, the  $\text{PO}_4:\text{Th}$  ratio decreased from its original value.

The exchanger remained unaffected in concentrated ammonia solution even after 48 h, but the sample dissolved completely in concentrated nitric acid, sulphuric acid, perchloric acid (60%) and hydrochloric acid after 10 h at room temperature

TABLE II  
CHEMICAL STABILITY OF THORIUM PHOSPHATE (BATCH NO. 2)

Serial No.	Solvent	Refluxed for 1 h		Shaken for 4 h	
		Phosphorus dissolved (mg per 50 ml)	Thorium dissolved (mg per 50 ml)	Phosphorus dissolved (mg per 50 ml)	Thorium dissolved (mg per 50 ml)
1	Deionized water	1.13	0.00	1.00	0.00
2	1 M HCl	5.05	0.018	6.5	—
3	4 M HCl	Completely dissolved		—	—
4	0.5 M H <sub>2</sub> SO <sub>4</sub>	25.5	—	39.37	—
5	1 M H <sub>2</sub> SO <sub>4</sub>	Appreciably dissolved		—	—
6	0.5 M HNO <sub>3</sub>	2.31	0.007	2.25	—
7	2 M HNO <sub>3</sub>	Appreciably dissolved		—	—
8	10% HClO <sub>4</sub>	8.87	—	8.25	—
9	60% HClO <sub>4</sub>	Completely dissolved		—	—
10	0.1 M NH <sub>4</sub> OH	—	—	2.5	—
11	4 M NH <sub>4</sub> OH	—	—	2.5	—
12	0.1 M NaOH	3.75	—	2.1	—
13	1 M NaOH	35.5	—	39.5	—

(25°). In concentrated hydrochloric acid, the sample became yellow after a few hours.

Detailed studies on the solubility of the exchanger were carried out after first washing it with hot water so as to remove any thorium or phosphoric acid adhering to the particles. The exchanger (500 mg) was refluxed with 50 ml of the required solution for 1 h (ref. 6). The solution was cooled and then filtered. Phosphorus was determined spectrophotometrically at 830 nm (ref. 7) from the filtrate with ammonium phosphomolybdate and hydrazine sulphate solution. Thorium was also determined spectrophotometrically with Thoron reagent at 545 nm (ref. 8). The solubility of the exchanger was also determined by shaking 500 mg of the sample with 50 ml of the required solution for 4 h. The results are given in Table II.

*Heat treatment.* Thorium phosphate (batch No. 2) was heated at 110, 200, 300 and 500° in a muffle furnace for 2 h. The colour of the sample changed as shown in Table III.

Thorium phosphate (batch No. 2) (517.4-mg sample) was subjected to thermogravimetric analysis at a heating rate 4°/min using a Stanton thermobalance. Thermogravimetric analysis of thorium phosphate (batch No. 3) (940-mg sample) was also carried out at the same heating rate. The results obtained from these analyses were

TABLE III  
HEAT TREATMENT OF THORIUM PHOSPHATE (BATCH NO. 2)

Temperature (°C)	Colour of sample
110	Light grey
200	Light grey
300	Light grey
500	White

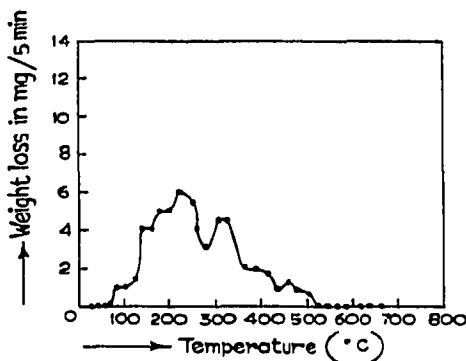


Fig. 1. Derivative thermogravimetric (DTG) analysis for thorium phosphate (batch No. 2).

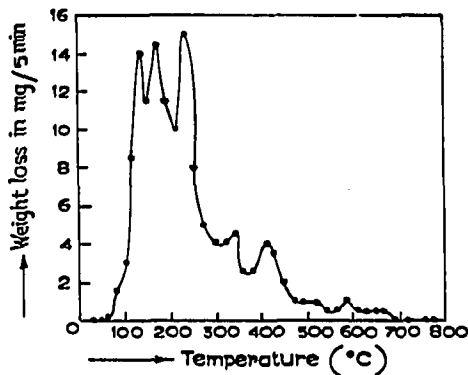


Fig. 2. Derivative thermogravimetric (DTG) analysis for thorium phosphate (batch No. 3).

converted into curves of weight loss in milligrams per 5 min *versus* temperature, which are shown in Figs. 1 and 2.

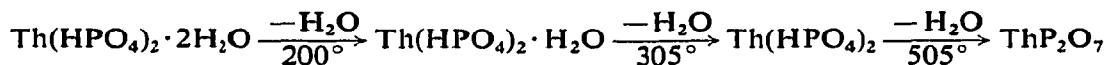
The weight loss of thorium phosphate (batch No. 2) at 505° can be related to water loss, which is constant up to 665°. From the experiment, weight loss at 505° is 12.09%. Assuming that at this temperature the composition of the sample is  $\text{ThP}_2\text{O}_7$  (Th:P = 1:2, by analysis), the number of moles of water lost per formula weight of exchanger was calculated by the method of Alberti *et al.*<sup>9</sup>:

$$\frac{n \times 18}{n \times 18 + \text{ThP}_2\text{O}_7} = \frac{12.09}{100}$$

where  $n$  = total number of moles of water.

From this equation,  $n = 3.1$ , so that the formula of thorium phosphate (batch No. 2) can be suggested as  $\text{ThO}_2 \cdot \text{P}_2\text{O}_5 \cdot 3.1\text{H}_2\text{O}$  or  $\text{Th}(\text{HPO}_4)_2 \cdot 2.1\text{H}_2\text{O}$  (dried over  $\text{P}_4\text{O}_{10}$ ).

The third molecule of water results from the decomposition of  $\text{Th}(\text{HPO}_4)_2$  itself, on heating at 505°:



The sample is stable up to 200°, then one molecule of water is eliminated at 200°, a second molecule at 305° and finally, at 505°, the last molecule of water is eliminated with decomposition.

Similarly, the total number of molecules of water present in batches 1, 3 and 4 are 3.21, 3.5 and 3.65, respectively.

### IR spectra

The IR spectra of three samples of thorium phosphate (batches 1–3) (Figs. 3–5) reveal two well defined peaks at 980–1140  $\text{cm}^{-1}$  (peak at 1090  $\text{cm}^{-1}$ ) and 1640  $\text{cm}^{-1}$ . This can be compared with the IR spectrum of normal thorium phosphate (Fig. 6)

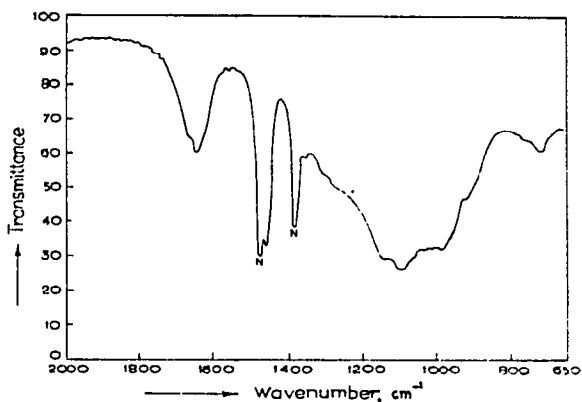


Fig. 3. Infrared spectra of thorium phosphate (batch No. 1).  $\text{PO}_4:\text{Th} = 1.9$ .

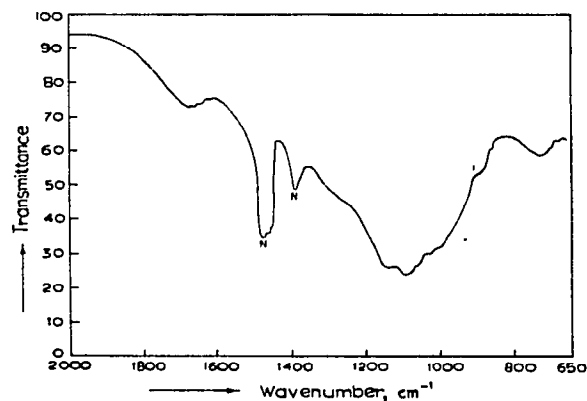


Fig. 4. Infrared spectra of thorium phosphate (batch No. 2).  $\text{PO}_4:\text{Th} = 2.1$ .

prepared from thorium nitrate and trisodium phosphate, which shows a peak at  $1050\text{ cm}^{-1}$  only. The first peak ( $980\text{--}1140\text{ cm}^{-1}$ ) is due to ionic phosphate, which is observed as one sharp peak in normal phosphate but as an assembly of three peaks in the polymer samples. The multiple peaks indicate the formation of polymer, with a shift in the peak from  $1050$  to  $1090\text{ cm}^{-1}$ . The second peak at  $1640\text{ cm}^{-1}$  may be due to interstitial water present in the polymer molecules (Figs. 3–5).

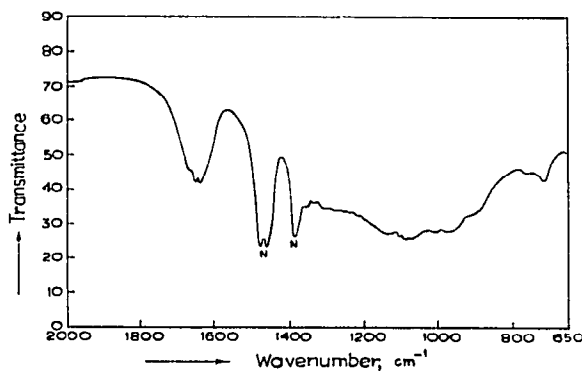


Fig. 5. Infrared spectra of thorium phosphate (batch No. 3).  $\text{PO}_4:\text{Th} = 1.69$ .

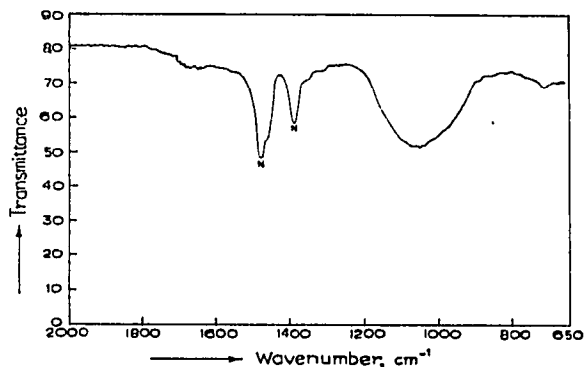


Fig. 6. Infrared spectra of thorium phosphate,  $\text{Th}_3(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ .

### *pH titration curves*

For pH titration, Topp and Pepper's method<sup>10</sup> was employed. A 100-ml volume of solution containing different amounts of MOH ( $M = \text{Li}, \text{Na}$  or  $\text{K}$ ) was added to 500 mg of the exchanger. After intermittent shaking for 2 days at constant temperature ( $30 \pm 2^\circ$ ), the pH was recorded. The experiment was repeated in the presence of salt, keeping the metal ion concentration constant at  $0.1\text{ M}$  using sodium hydroxide and sodium chloride. The results are shown in Figs. 7 and 8.

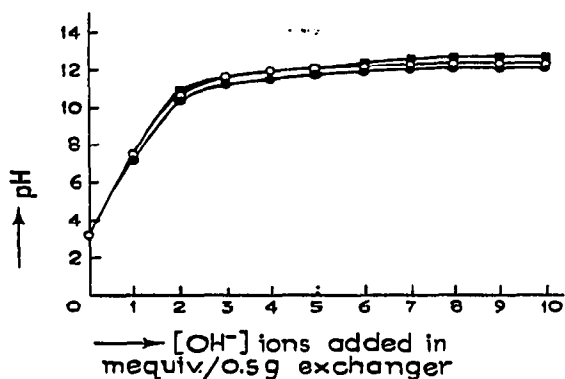


Fig. 7. pH titration curve for thorium phosphate (batch No. 2) in the absence of salt. Titrant: ●, LiOH; ○, NaOH; ■, KOH.

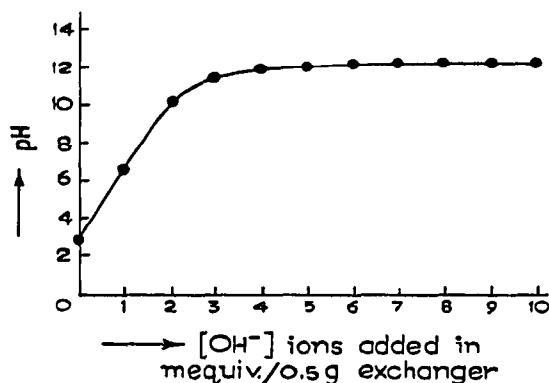
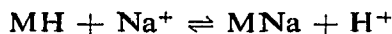


Fig. 8. pH titration curve for thorium phosphate (batch No. 2) with 0.1 M NaOH + NaCl.

As there is only one break in the titration curves (Fig. 7), the exchanger should comprise monofunctional acids. Fig. 7 shows that the titration curves with  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  lie on the same line at low pH values, but at higher pH, the curve for  $\text{Na}^+$  lies between those for  $\text{Li}^+$  and  $\text{K}^+$ . On titration with alkali alone, there is a more rapid increase in pH than in the presence of salt (e.g., sodium chloride). The addition of sodium chloride releases some of the  $\text{H}^+$  from the exchanger and thus lowers the pH. It is hydrolyzed significantly in water. The pH of the supernatant liquid on keeping 500 mg of thorium phosphate in 100 ml of water for 2 days is 3.15, but when the same experiment was carried out in 0.1 M sodium chloride solution the pH was 2.7. It appears that the sodium form is more stable than the hydrogen form under these conditions, and the lower pH in this case is due to the release of  $\text{H}^+$  ions by the exchangers.

#### Determination of exchange capacity

Thorium phosphate polymer is a cation exchanger. The exchange capacity, which is generally taken as a measure of the hydrogen ion liberated by a neutral salt such as sodium chloride, is found to depend upon the concentration and volume of eluent for column operation. The hydrogen ion eluted from the column was determined titrimetrically using methyl orange as indicator. The results with 1 and 2 M sodium chloride solution are shown in Fig. 9. The exchange proceeds rapidly at first, but elution continues for a long time. The reaction can be postulated as



where MH represents the hydrogen form of the exchanger. Initially, the release of hydrogen ions is rapid, as all of the exchanger is in the hydrogen form and the forward reaction is rapid. The hydrogen ions were still liberated even after the passage of 100 ml of sodium chloride solution, but the amount of hydrogen ion eluted with larger volumes of eluent was so small that the exchange capacity was calculated from the amount of hydrogen ion liberated up to this point. The effect of the concentration of

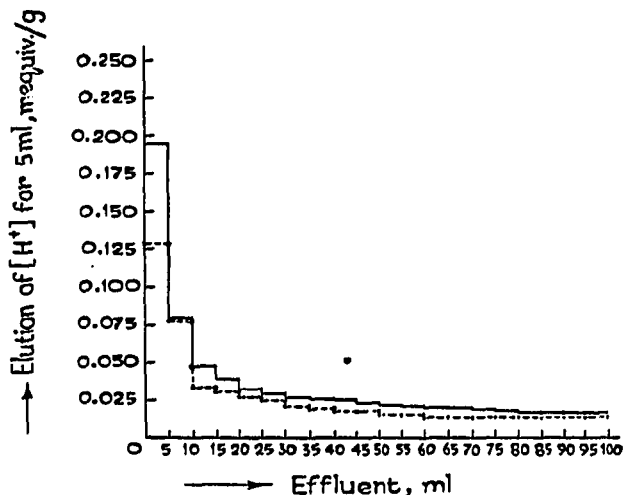


Fig. 9. Elution curve of hydrogen ion of thorium phosphate (batch No. 2). Continuous line, eluent 2 M NaCl; dotted line, eluent 1 M NaCl.

neutral salt solution and the time of equilibrium on the exchange capacity of thorium phosphate (batch No. 2) in batch operation<sup>11</sup> is shown in Figs. 10 and 11.

A constant exchange capacity was obtained for sodium chloride solution of concentration greater than 2 M, and it required almost 12 h for complete equilibrium to be attained. The ion-exchange capacity by batch operation of thorium phosphate polymers was determined as follows. A 100-ml volume of 2 M sodium chloride solution was shaken with 1 g of exchanger for 2 days with intermittent shaking. After complete equilibrium a 50 ml aliquot was taken and titrated with standard alkali solu-

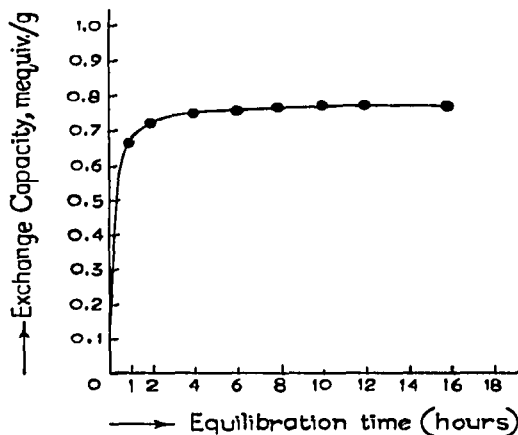
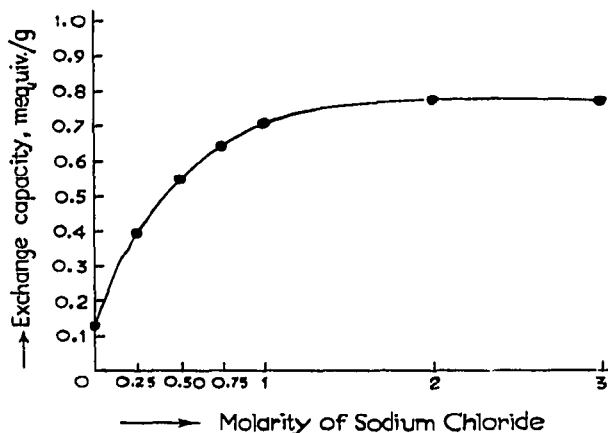


Fig. 10. Exchange capacity of thorium phosphate (batch No. 2) as a function of concentration for Na<sup>+</sup> ions.

Fig. 11. Effect of time of equilibrium on exchange capacity of thorium phosphate (batch No. 2) for Na<sup>+</sup> ions.

TABLE IV

ION-EXCHANGE CAPACITY OF THORIUM PHOSPHATE AT pH 6.0-6.5 FOR UNIVALENT CATIONS

Metal ion	Hydrated ionic radius ( $\text{\AA}$ )	Ion-exchange capacity (mequiv./g)		
		Batch No. 1	Batch No. 2	Batch No. 3
Li <sup>+</sup>	3.4	0.38	0.31	0.41
Na <sup>+</sup>	2.76	0.74	0.77	0.61
K <sup>+</sup>	2.32	1.12	1.15	0.83

tion using methyl orange as indicator. The same procedure was carried out using 2 *M* potassium chloride and 2 *M* lithium chloride solution. The results are given in Table IV.

The total ion-exchange capacity of a weakly acidic cation exchanger must generally be determined under alkaline conditions. The capacity of thorium phosphate polymer in alkaline medium for univalent cation was determined as follows<sup>12</sup>. To 1 g of exchanger in a 250-ml bottle were added 100 ml of standard 0.1 *N* sodium hydroxide solution in 5% sodium chloride solution. The bottle was shaken intermittently for 2 days. After equilibrium, a 25-ml aliquot of the supernatant liquid was titrated to a phenolphthalein end-point with standard oxalic acid. The cation-exchange capacity was calculated as follows:

$$\frac{(100 \times N \text{ NaOH}) - 4 (\text{ml of acid} \times N \text{ acid})}{\text{Sample weight}} = \frac{\text{mequiv. of cation-exchange capacity}}{\text{g of exchanger}}$$

Similarly, the exchange capacities of lithium and potassium were determined by using lithium hydroxide + lithium chloride solution and potassium hydroxide + potassium chloride solution, respectively.

At pH 12, phosphate is released from the exchanger and three OH<sup>-</sup> groups are consumed for each hydrolyzed phosphate group. The corrected ion-exchange capacity values are given in Table V. The ion-exchange capacity of Li<sup>+</sup> is higher than the theoretical value (4.35 mequiv./g), presumably because lithium phosphate is precipitated at pH 12.

The ion-exchange capacities at pH 11.5-12.5 can be compared with those reported by Alberti *et al.*<sup>4</sup>: Li<sup>+</sup> 3.2, Na<sup>+</sup> 3.7 and K<sup>+</sup> 3.1 mequiv./g. In the present

TABLE V

ION-EXCHANGE CAPACITY OF THORIUM PHOSPHATE AT pH 11.5-12.5 FOR UNIVALENT CATIONS

Metal ion	Initial pH	Phosphate losses (mmole/g)	Ion-exchange capacity (corrected, mequiv./g)		
			Batch No. 1	Batch No. 2	Batch No. 3
Li <sup>+</sup>	11.6	0.81	5.15	5.58	6.53
Na <sup>+</sup>	12.3	0.22	4.35	4.50	4.34
K <sup>+</sup>	12.1	0.42	3.5	3.64	3.34



work, the ion-exchange capacities at pH 6.0–6.5 increase in the order  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ , and this order is reversed at pH 11.5–12.5.

It should be pointed out that whereas Alberti *et al.*<sup>4</sup> employed an ion exchanger with a total of four water molecules, our exchanger had a water content from 3.1 to 3.5 molecules. The degree of hydration has an important effect on ion-exchange capacity.

The ion-exchange capacities of bivalent metal ions were also determined by batch operation using corresponding 2 *M* solutions (Table VI).

The ion-exchange capacities at pH 6–6.5 for univalent ions follow the order  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$  and for bivalent ions  $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$ . As the hydrated ionic radius decreases, the ion-exchange capacity increases.

The ion-exchange capacity of thorium phosphate polymer decreases as the temperature increases, as shown in Table VII.

The ion-exchange capacity is 4.5 mequiv./g at 80° and 4.54 mequiv. at 150°, due to the elimination of adsorbed moisture (0.1 mole). Then ion-exchange capacity decreases as the temperature increases; one molecule of water is lost at 305°.

The distribution coefficients of metal ions and their analytical applications on thorium phosphate will be reported in the following paper in this series<sup>13</sup>.

TABLE VI

ION-EXCHANGE CAPACITY OF THORIUM PHOSPHATE (BATCH NO. 2) FOR BIVALENT CATIONS AT pH 6–6.5

<i>Metal ion</i>	<i>Hydrated radius (Å)</i>	<i>Ion-exchange capacity (mequiv./g)</i>
$\text{Mg}^{2+}$	7.00	0.54
$\text{Ca}^{2+}$	6.30	0.89
$\text{Sr}^{2+}$	—	1.3
$\text{Ba}^{2+}$	5.90	1.5

TABLE VII

EFFECT OF TEMPERATURE ON ION-EXCHANGE CAPACITY OF THORIUM PHOSPHATE (BATCH NO. 2) IN ALKALINE MEDIUM (pH 11.5–12.5)

<i>Temperature (°C)</i>	<i>Ion-exchange capacity (Na<sup>+</sup>) (mequiv./g)</i>
30	4.5
80	4.5
150	4.54
200	4.2
400	0.20
500	0.12

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