

CHROM. 4832

## CRYSTALLINE INSOLUBLE ACID SALTS OF TETRAVALENT METALS

XI. SYNTHESIS AND ION-EXCHANGE PROPERTIES OF TIN(IV)  
PHOSPHATE AND TIN(IV) ARSENATE

U. COSTANTINO AND A. GASPERONI

*Laboratorio di Chimica delle Radiazioni e Chimica Nucleare del C.N.E.N. and Istituto di Chimica Generale ed Inorganica dell'Università, Rome (Italy)*

(Received May 25th, 1970)

## SUMMARY

The syntheses of a crystalline tin(IV) phosphate and tin(IV) arsenate are reported. These two new inorganic ion exchangers have been characterised on the basis of their X-ray powder patterns, chemical analysis, chemical stability and thermal dehydration behaviour.

Their ion-exchange properties were investigated with alkali metal ion uptake curves. Tin(IV) phosphate and tin(IV) arsenate have a high ion-exchange capacity for  $\text{Li}^+$  (7.9 and 6.6 mequiv./g, respectively) while they are extensively hydrolysed by the other alkali metal ions.

## INTRODUCTION

The good ion-exchange properties of zirconium phosphate have recently stimulated interest in the preparation of insoluble acid salts of other tetravalent metals such as titanium, cerium(IV), tin(IV) and thorium<sup>1</sup>. In regard to tin(IV) phosphate, various products exhibiting some ion-exchange properties have been obtained by INOUE<sup>2-4</sup> and PIRET *et al.*<sup>5</sup>. All these products are amorphous and very hydrolysable materials and their P:Sn ratio is lower than 2. WINKLER AND THILO<sup>6</sup> have recently obtained a crystalline tin(IV) phosphate with a P:Sn ratio of 2.4. However the ion-exchange properties of this material were only investigated using a titration curve with NaOH, and data on its chemical stability at various pH values and on its affinity for the various cations are not available.

The results obtained in our laboratory on the synthesis of crystalline ion exchangers of the insoluble acid salts of tetravalent metals<sup>7-12</sup> have encouraged us to continue studies in this field and also to investigate the synthesis of crystalline tin(IV) phosphate and arsenate. Among the various products obtained, a crystalline tin(IV) phosphate (P:Sn ratio  $\approx 2$ ) and a crystalline tin(IV) arsenate (As:Sn ratio  $\approx 2$ ) showed good chemical stability and interesting ion-exchange properties. Some details on the synthesis and ion-exchange properties of these new ion-exchange materials are reported and discussed.

## EXPERIMENTAL

*Reagents*

All reagents used were Carlo Erba R.P.  $3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$  was a Merck "pro analyse" product.

*Analytical procedure*

The P:Sn and As:Sn ratios in tin(IV) phosphate and tin(IV) arsenate, respectively, were determined by the following procedure. About 100 mg of sample were dissolved in 10 ml of hot 1 M NaOH. This solution was acidified with 8.5 ml of conc. HCl and then diluted to 100 ml with distilled water. The phosphate or arsenate content was determined colorimetrically in 2 ml of this solution as previously described<sup>7,12</sup>. Tin(IV) was determined in the remaining solution by precipitation with a 6% solution of Kupferron and calcination to  $\text{SnO}_2$ .

The pyrophosphate content in heated tin(IV) phosphate was determined as follows. 100 mg of sample were dissolved in 10 ml of hot 1 M NaOH, and the solution was diluted to 100 ml with distilled water. 2 ml of this solution were directly analysed for the orthophosphate content, while 10 ml of hot conc. HCl were added to 25 ml to hydrolyse the pyrophosphate. The solution was then diluted to 50 ml with distilled water and analysed for orthophosphate. The pyrophosphate content was calculated as described<sup>13</sup>. Titration, hydrolysis, ion uptake and weight loss curves were obtained as previously described<sup>9</sup>. The equilibrium time allowed for titration experiments was 4 days. X-ray photographs of powder patterns were taken using  $\text{CuK}_\alpha$  radiation.

## RESULTS AND DISCUSSION

*Preparation of materials*

Attempts to obtain crystalline materials by refluxing amorphous stannic phosphate (or arsenate) in conc. phosphoric (or arsenic) acid containing 1 M HCl or 3 M  $\text{HNO}_3$  were unsuccessful even after 200 h of refluxing. On the contrary, by refluxing solutions containing tin(IV) chloride, nitric acid and phosphoric (or arsenic) acid in different ratios, microcrystalline products began to precipitate after some hours of refluxing while  $\text{NO}_2$  was evolved during the precipitation.

The crystalline tin(IV) phosphate described in this paper was prepared as follows: To 1 l of 8 M  $\text{H}_3\text{PO}_4$  and 3 M  $\text{HNO}_3$  solution anhydrous tin(IV) chloride was added until the ratio P:Sn was 30. Although the precipitation was complete in 5–7 h, refluxing was continued until no further modification in the X-ray diffraction patterns of this material was observed ( $\sim 100$  h).

The product was then filtered, washed with distilled water until reacting about pH 4, and dried over  $\text{P}_4\text{O}_{10}$  under vacuum to constant weight. Tin(IV) arsenate was prepared by a similar procedure. In this case arsenic acid was 6 M while the As:Sn ratio was 10.

*Composition, thermal and chemical stability of tin(IV) phosphate and arsenate*

Chemical analysis of tin(IV) phosphate and tin(IV) arsenate gave a P:Sn and As:Sn ratio of 2.05 and 1.97, respectively. Weight loss curves for the  $\text{H}^+$  form of

TABLE I

*d*-VALUES (Å) FROM X-RAY POWDER PATTERNS OF CRYSTALLINE TIN(IV) PHOSPHATE IN H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup> AND K<sup>+</sup> FORMS DRIED OVER P<sub>4</sub>O<sub>10</sub>

<i>H</i> <sup>+</sup> form (a)	<i>Li</i> <sup>+</sup> form (b)	<i>Na</i> <sup>+</sup> form (c)	<i>K</i> <sup>+</sup> form (d)
7.76 s	7.76 m	8.13 m	9.13 m
4.21 m	4.39 vw	4.20 m	4.29 vw
3.46 vs	4.22 w	3.72 w	3.90 m
3.16 w	3.46 m	3.51 w	3.43 vw
2.64 w	3.18 vw	2.51 m	3.14 m
2.54 m	2.65 vw	1.86 vw	2.48 m
2.41 vw	2.56 vw	1.64 vw	2.09 vw
2.36 vw	2.41 vw		1.95 vw
2.09 w	2.12 vw		
2.01 w	2.02 vw		
1.95 w	1.53 vw		
1.91 w			
1.80 vw			
1.73 w			
1.62 w			
1.56 m			
1.43 w			

these materials are reported in Fig. 1, while their X-ray powder patterns are listed in Table I(a) and Table II(a).

Since tin(IV) phosphate and arsenate behave in a similar way, this paper is concerned chiefly with tin(IV) phosphate. X-ray diffraction patterns of this material heated to 800° were found to correspond to that reported on A.S.T.M. cards and referred to SnP<sub>2</sub>O<sub>7</sub> (ref. 14). Thus the total weight loss can be related to elimination

TABLE II

*d*-VALUES (Å) FROM X-RAY POWDER PATTERNS OF CRYSTALLINE TIN(IV) ARSENATE IN H<sup>+</sup>, Li<sup>+</sup> AND Na<sup>+</sup> FORMS DRIED OVER P<sub>4</sub>O<sub>10</sub>

<i>H</i> <sup>+</sup> form (a)	<i>Li</i> <sup>+</sup> form (b)	<i>Na</i> <sup>+</sup> form (c)
7.77 m	9.16 w	8.50 m
4.31 m	7.77 m	4.33 m
4.10 vw	4.33 w	3.83 m
3.90 vw	3.68 m	3.59 m
3.51 vs	3.55 w	2.91 vw
3.20 vw	2.75 w	2.75 w
2.67 w	2.65 w	2.66 w
2.53 m	2.54 vw	2.53 w
2.43 w	2.43 vw	2.07 vw
2.18 vw		1.90 vw
2.06 w		
1.99 vw		
1.92 vw		
1.84 vw		
1.76 vw		
1.65 w		
1.60 vw		
1.47 m		
1.44 w		

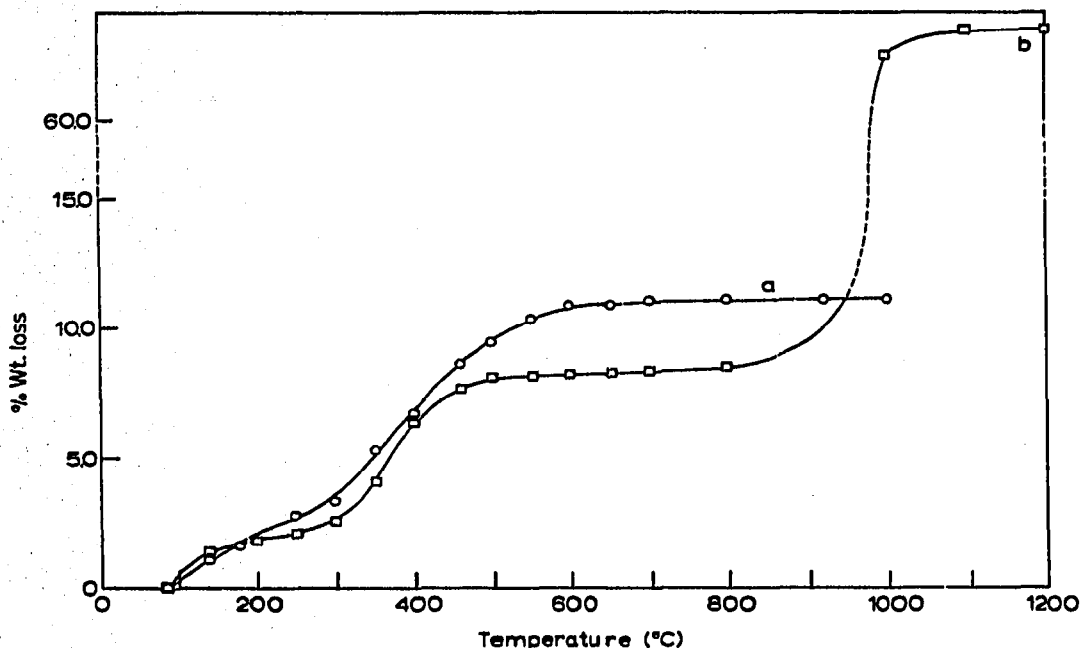
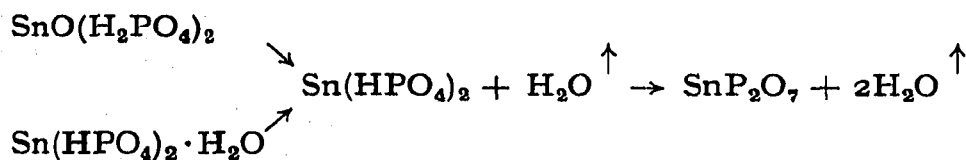


Fig. 1. Per cent weight loss of crystalline tin(IV) phosphate (curve a) and tin(IV) arsenate (curve b) at different temperatures.

of water and, from considerations similar to those reported in previous papers of this series<sup>7,8</sup>, the empirical formula  $\text{SnO}_2 \cdot \text{P}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$  was ascribed to tin(IV) phosphate dried over  $\text{P}_4\text{O}_{10}$  under vacuum\*.

Since one mole of water must be related to the phosphate condensation, the dehydration process can be represented by the following two possibilities:



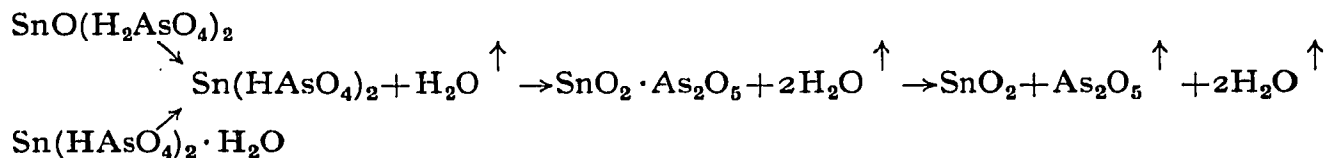
However, contrary to other crystalline exchangers of this series, the weight loss curve does not distinctly show the two dehydration steps, and this fact could be explained by assuming that the two processes overlap.

To corroborate this hypothesis, the pyrophosphate content in a tin(IV) phosphate sample heated to  $350^\circ$ , where the first mole of water is lost, has been determined. It was found that 31% of the phosphate groups was converted to pyrophosphate; this indicates that the condensation begins before the first water molecule is completely lost. Further it was found that tin(IV) phosphate first heated at  $350^\circ$  and then suspended in water for 5 days again takes up only 0.65 moles of water per formula weight. Thus the water not reabsorbed (0.35 moles) is in good agreement with that calculated

\* It is interesting to note that tin(IV) phosphate on standing in a desiccator until constant weight first over a NaCl satd. solution ( $\sim 75\%$  rel. humidity at room temperature) and then over a  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  satd. solution ( $\sim 95\%$  rel. humidity at room temperature) absorbs, respectively, 0.5 and 1.2 moles of water without appreciable modification in its X-ray powder patterns.

using the pyrophosphate content. Unfortunately it was not possible to determine at which temperature the first dehydration process is complete\*. However this temperature being higher than 350°, the water held in the exchanger can be assumed to be constitution water.

In tin(IV) arsenate the sharp weight loss observed between 800° and 1000° must be related to loss of arsenic pentoxide, since the material heated to 1200° was found to correspond to SnO<sub>2</sub>. From considerations similar to those made for tin(IV) phosphate, it was possible to represent the dehydration process by two possibilities:



Chemical stability of tin(IV) phosphate and arsenate was evaluated by equilibrating 100 mg of sample with 50 ml of 8 N and 12 N HCl, 8 N H<sub>2</sub>SO<sub>4</sub>, 8 N HNO<sub>3</sub>, and 8 N HF solutions at room temperature for one week. Phosphate ions (< 0.01 mmoles of phosphate or arsenate per gram of exchanger) were not found in the supernatant liquid. Qualitative tests have shown that the materials are not soluble in concentrated mineral acids also at boiling temperature. These exchangers are not very stable in an alkaline medium and even are soluble in alkaline solutions at concentrations higher than 1 M.

It can be noted that the stannic phosphate prepared according to INOUE<sup>3</sup> is

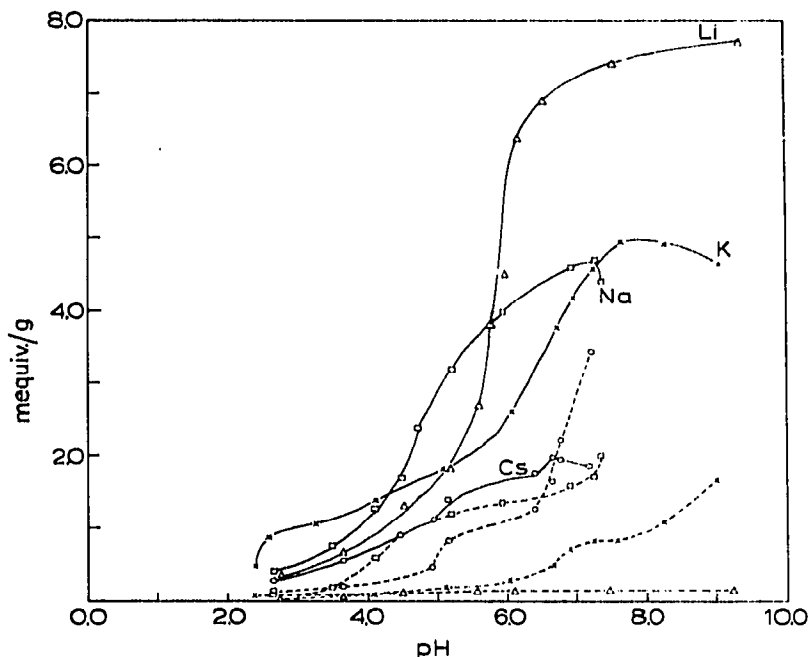


Fig. 2. Ion uptake and hydrolysis curves for crystalline tin(IV) phosphate titrated with 0.1 N (MCl + MOH). Ordinates: solid lines, ion uptake (mequiv./g of tin(IV) phosphate dried over P<sub>4</sub>O<sub>10</sub>); dashed lines, mmoles of phosphate released to solution by 1 g of material.

\* At temperatures higher than 350°, the sample was not completely soluble in hot NaOH, and therefore pyrophosphate could not be determined.

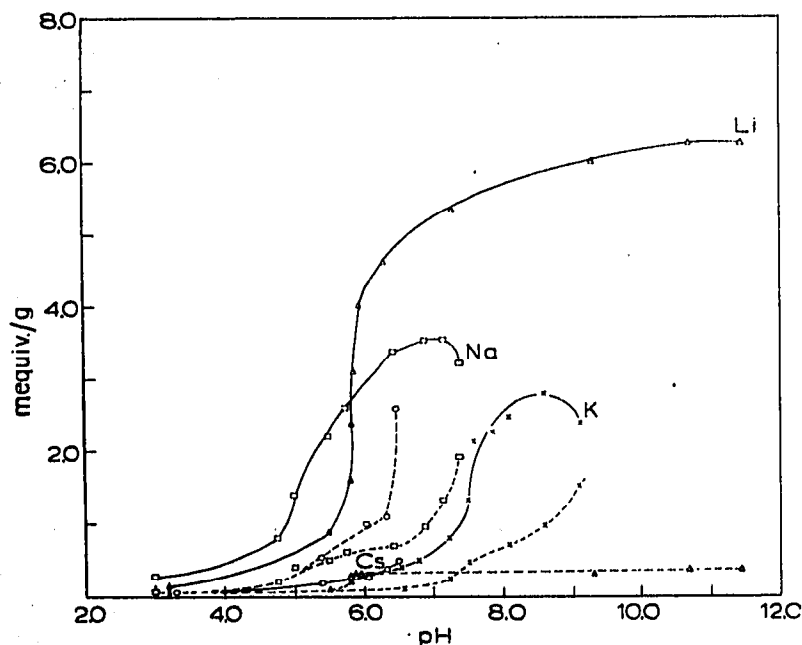


Fig. 3. Ion uptake and hydrolysis curves for crystalline tin(IV) arsenate titrated with 0.1 *N* (MCl + MOH). Ordinates: solid lines, ion uptake (mequiv./g of tin(IV) arsenate dried over  $P_4O_{10}$ ); dashed lines; mmols of phosphate released to solution by 1 g of material.

soluble in 6 *M* HCl and dissolves or peptises in a 0.1 *N* NaOH solution. Thus the crystallisation process increases the chemical stability of the products.

#### *Ion exchange properties*

Uptake curves for  $Li^+$ ,  $Na^+$ ,  $K^+$  and  $Cs^+$  (mequiv./g) and phosphate or arsenate (mmoles/g) released to the external solution as a function of pH are plotted in Figs. 2 and 3 for tin(IV) phosphate and tin(IV) arsenate, respectively.

From these figures the following can be noted. (a) The shape of uptake curves depends on the nature of the exchanging ion and inversions in the selectivity order can be observed. At low salt conversion the selectivity sequence for tin(IV) phosphate is  $K^+ > Na^+ > Li^+ > Cs^+$  but increasing the equilibrium pH the sequence becomes  $Na^+ > K^+ > Li^+ > Cs^+$ , then  $Na^+ > Li^+ > K^+ > Cs^+$  and finally  $Li^+ > Na^+ > K^+ > Cs^+$ . In tin(IV) arsenate we have only the inversion  $Na^+ - Li^+$  while  $K^+$  and  $Cs^+$  are excluded in an acid medium. This behaviour, already observed in other exchangers of this class, can be related to steric effects and is difficult to explain without knowledge of the structure of the materials. In any case, the exclusion effects are more evident in tin arsenate than in tin phosphate, and this fact, probably due to the larger size of arsenate groups, was also found from the comparison of ion-exchange properties of phosphate and arsenate of zirconium, titanium and cerium(IV) (refs. 7-11).

(b) Both exchangers are extensively hydrolysed when titrated with  $Na^+$ ,  $K^+$  and  $Cs^+$  also in neutral or weakly alkaline solutions. Furthermore above a certain pH<sub>max</sub> value the apparent capacity can even decrease, as already found for titanium phosphate<sup>7</sup> and titanium arsenate<sup>11</sup>, and this can be related to the fact that the uptake of ions is less than the amount lost on hydrolysis of the exchanger.

In the case of  $Li^+$  uptake, the exchangers are not appreciably hydrolysed, and

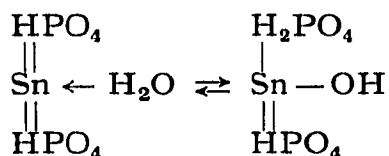
it seems possible to relate the extent of hydrolysis not only to an alkaline medium but also to the mechanical stresses involved in the exchange process with ions of large ionic radius. In this regard, it is interesting to note that exchangers peptise when titrated with KOH and especially with CsOH.

(c) The experimental value of the ion-exchange capacity is markedly influenced by the nature of the exchanging ion. An approximate value of the total ion-exchange capacity can be calculated by adding the alkali metal ions exchanged (mequiv./g) to the phosphate or arsenate released to the external solution (mmoles/g)\*.

For the exchange  $\text{Na}^+ - \text{H}^+$  and  $\text{K}^+ - \text{H}^+$  in tin(IV) phosphate and for the exchange  $\text{Na}^+ - \text{H}^+$  in tin(IV) arsenate this calculation brings a value close to the theoretical capacity calculated assuming two exchangeable hydrogen equivalents per formula weight of the two materials (6.08 mequiv./g and 4.80 mequiv./g, respectively). For  $\text{Cs}^+$  in tin(IV) phosphate and  $\text{K}^+$  and  $\text{Cs}^+$  in tin(IV) arsenate, the value of the exchange capacity is much lower than the theoretical values, showing the screening effects of these materials for ions of large ionic radius. On the other hand, the total ion-exchange capacity for  $\text{Li}^+$  is higher than the theoretical one (7.9 and 6.6 mequiv./g, respectively). This experimental result can be accounted for by assuming the partial precipitation of trilitium phosphate (or arsenate) inside the exchangers or the presence of more than two exchangeable hydrogen equivalents per formula weight of exchanger.

The increase in ion-exchange capacity due to trilitium phosphate (or arsenate) precipitation cannot be excluded but is unlikely. This phenomenon was never observed in other crystalline ion exchangers of this class, such as titanium phosphate<sup>7</sup> and arsenate<sup>11</sup> which are more hydrolysable than tin(IV) phosphate (or arsenate). Moreover the shape of the uptake curves does not show any inflexion, while, in the case of trilitium phosphate (or arsenate) precipitation, a sharp increase in  $\text{Li}^+$  uptake should be observed<sup>9</sup>. Thus the high capacity for  $\text{Li}^+$  could be related to the presence of more than two exchangeable hydrogen ions inside the exchangers.

Taking into account the dehydration process of both exchangers and the fact that tin(IV) phosphate heated to  $350^\circ$  partially reabsorbs its water (see above), it seems possible to account for the high  $\text{Li}^+$  uptake with the existence of the following tautomeric equilibrium, already suggested by MOUNIER AND WINAND<sup>15</sup> for zirconium phosphate.



The existence of this equilibrium seems more probable for tin(IV) phosphate (or arsenate) than for zirconium phosphate, but much more data must be collected to confirm this.

X-ray analyses of tin(IV) phosphate and arsenate at various degrees of salt conversion were also carried out. Except in the case of a  $\text{Li}^+ - \text{H}^+$  exchange, the conversion in the salt form causes a strong degradation in the degree of crystallinity and in the case of  $\text{Cs}^+$  in tin phosphate and  $\text{K}^+$  and  $\text{Cs}^+$  in tin arsenate, the structure is

\* It was assumed that there is only one mequiv. of exchangeable  $\text{H}^+$  per mmole of phosphate or arsenate.

almost completely destroyed. In Table I (*b, c, d*) and Table II (*b, c*) are listed the X-ray powder patterns of the same salt forms of the exchanger, obtained by titration. While X-ray patterns of the  $\text{Li}^+$  forms are not appreciably changed, compared with the  $\text{H}^+$  forms, in the other salt forms the first *d*-value increases, increasing the ionic radius of the exchanging ion. This fact was already found in other crystalline exchangers of this series<sup>7,10</sup>.

#### CONCLUSION

Crystalline tin(IV) phosphate and tin(IV) arsenate compare favourably with amorphous products, but they show low resistance to hydrolysis when titrated with ions having a crystalline radius larger than that of lithium. While in some respect their behaviour is like that of other crystalline ion exchangers of this series, tin(IV) phosphate and arsenate show some peculiar features in the dehydration and  $\text{Li}^+$ - $\text{H}^+$  exchange processes. More data are thus necessary to establish the formulae of these materials and to characterise their ion-exchange properties.

#### ACKNOWLEDGEMENTS

The authors wish to thank Prof. G. ALBERTI for his valuable guidance and for many discussions and helpful suggestions.

This work has been supported by the Istituto di Ricerca sulle Acque of the Consiglio Nazionale delle Ricerche.

#### REFERENCES

- 1 C. B. AMPHLETT, *Inorganic Ion Exchangers*, Elsevier, Amsterdam, 1964.
  - 2 Y. INOUE, *J. Inorg. Nucl. Chem.*, 26 (1964) 2241.
  - 3 Y. INOUE, *Bull. Chem. Soc. Japan*, 36 (1964) 1316.
  - 4 Y. INOUE, *Bull. Chem. Soc. Japan*, 36 (1964) 1324.
  - 5 J. PIRET, J. HENRY, G. BALON AND C. BEAUDET, *Bull. Soc. Chim. France*, (1965) 3590.
  - 6 A. WINKLER AND E. THILO, *Z. Anorg. Allgem. Chem.*, 346 (1965) 92.
  - 7 G. ALBERTI, P. CARDINI GALLI, U. COSTANTINO AND E. TORRACCA, *J. Inorg. Nucl. Chem.*, 29 (1967) 571.
  - 8 G. ALBERTI, U. COSTANTINO, F. DI GREGORIO, P. GALLI AND E. TORRACCA, *J. Inorg. Nucl. Chem.*, 30 (1968) 295.
  - 9 E. TORRACCA, U. COSTANTINO AND M. A. MASSUCCI, *J. Chromatog.*, 30 (1967) 584.
  - 10 G. ALBERTI, U. COSTANTINO, F. DI GREGORIO AND E. TORRACCA, *J. Inorg. Nucl. Chem.*, 31 (1969) 3195.
  - 11 G. ALBERTI AND E. TORRACCA, *J. Inorg. Nucl. Chem.*, 30 (1968) 3075.
  - 12 G. ALBERTI AND M. A. MASSUCCI, *J. Inorg. Nucl. Chem.*, 32 (1970) 1719.
  - 13 G. ALBERTI, A. CONTE AND E. TORRACCA, *J. Inorg. Nucl. Chem.*, 28 (1966) 225.
  - 14 *X-Ray Powder Data File*, Card No. 3-0278, Sets 1-5 (Revised), A.S.T.M. Special Technical Publication 48 J (1960).
  - 15 F. MOUNIER AND L. WINAND, *Bull. Soc. Chim. France*, (1968) 1829.
- J. Chromatog.*, 51 (1970) 289-296