

CHROM. 5075

INFLUENCE OF TEMPERATURE ON THE ION-EXCHANGE  
PROPERTIES OF STANNIC ARSENATESEPARATION OF  $Pb^{2+}$ ,  $UO_2^{2+}$  AND  $Cr^{3+}$  FROM NUMEROUS METAL IONS

MOHSIN QURESHI, H. S. RATHORE AND RAJENDRA KUMAR  
*Chemical Laboratories, Aligarh Muslim University, Aligarh, U.P. (India)*  
(Received September 21st, 1970)

---

**SUMMARY**

The amorphous precipitates (stannic arsenate) obtained by mixing the 0.1 *M* aqueous solutions of stannic chloride and sodium arsenate in the volume ratio of 1:1 have been dried at different temperatures (40–600°). The ion-exchange properties, the solubility and the IR studies of the dried samples have been investigated. The sorption studies on the sample dried at 40° have been made in detail by raising the temperature (from 20 to 95°) of the equilibrating solution and its columns have been used for the separation of  $Pb^{2+}$ ,  $UO_2^{2+}$  and  $Cr^{3+}$  from numerous metal ions.

---

**INTRODUCTION**

Stannic arsenate<sup>1,2</sup> has promising cation-exchange properties, an outstanding thermal stability, high uptake of certain ions and good resistance against water and dilute acids. However, it is necessary to study its ion-exchange properties at higher temperatures so that its usefulness at these temperatures may be elucidated. Unfortunately very few studies have been made of the effect of temperature on the ion-exchange equilibrium<sup>3</sup>. We therefore summarise in this report the adsorption studies on five samples dried at different temperatures and on one sample using the equilibrating solution at higher temperatures.

**EXPERIMENTAL***Materials*

Stannic chloride crystals (B & A) and sodium arsenate heptahydrate (Poland) were used. All other reagents were of analytical grade.

*Apparatus*

An electric temperature-controlled SICO shaker, Philips X-ray unit and Bausch and Lomb spectronic 20 colorimeter were used for shaking, X-ray studies and spectro-

photometric measurements, respectively. A Perkin-Elmer Model 137 spectrophotometer was used for IR studies.

#### *Method of preparation*

Stannic arsenate was prepared by mixing the aqueous solutions of 0.10 *M* stannic chloride and sodium arsenate (1:1) at room temperature. In order to study the effect of drying temperatures, the precipitate so obtained was dried at different temperatures as given in Table I. The dried products were broken in demineralised water, converted to the hydrogen form as usual and then finally dried at 40°. For sorption studies, 50–150 mesh exchanger particles were used. Determination of chemical composition, solubility and ion-exchange capacity of stannic arsenate was made as reported previously<sup>1,2</sup>.

#### *Distribution coefficient*

The  $K_D$  values for metal ions were determined as reported earlier<sup>2</sup>. In this case the total volume of equilibrating solution was 50 ml instead of 100 ml. Uranyl ions were determined spectrophotometrically with hydrogen peroxide<sup>4</sup> and other ions by titration with 0.002 *M* EDTA solution. The  $K_D$  values at different temperatures were ascertained by shaking at that temperature till equilibrium was achieved. In some cases the system was removed from the shaker and then allowed to attain room temperature before the final cation concentration was obtained. In other cases, the equilibrating solution was separated from the solid exchanger by decantation at the same temperature at which the study was performed, and then the final cation concentration was found in the separated liquid. The  $K_D$  values obtained by these two methods are recorded in Table III under  $Q$  and  $Q^*$ , respectively. In both these cases the loading was 6% of the cation-exchange capacity owing to the high uptake of cations by stannic arsenate and to facilitate comparison of changes in  $K_D$  values.

#### *Preparation of the column*

For separation studies 1.50 g of the exchanger in the hydrogen form were placed in a 30 × 0.39 cm (I.D.) glass column with glass wool support. The column was washed with demineralised water till the washing was neutral. Loading the cations in the column was done as usual<sup>2</sup>.

#### *Measurement of IR absorption spectra*

IR spectra of the samples of stannic arsenate in the hydrogen form dried at 40, 200 and 400° were measured with a standard KBr disk technique.

## RESULTS

#### *Properties*

Almost all the properties of sample 1 are the same as reported in our earlier papers<sup>1,2</sup> on other samples of stannic arsenate. No appreciable decomposition, hydrolysis or change in appearance of exchanger particles was observed during the operations at elevated temperatures.

The ion-exchange capacity for  $K^+$  of all the samples is found as given in Table I.

TABLE I

PROPERTIES OF STANNIC ARSENATE

Sample No.	Drying temperature		Colour	Ion-exchange capacity (mequiv./g)
	Initial (°C)	Final (°C)		
1	40	40	White	1.30
2	100	40	White	1.44
3	200	40	Dirty white	1.25
4	400	40	Bluish black	0.95
5	600	40	Bright bluish black	0.52

Sample 1 has a Sn-As ratio of 1:1. Its solubility in some common solvents is given in Table II.

TABLE II

SOLUBILITY OF STANNIC ARSENATE IN g/l  $\times 10^{-3}$  AT  $33 \pm 1^\circ$ 

Sample No.	Water		4 M HNO <sub>3</sub>		4 M HCl	
	Sn	As	Sn	As	Sn	As
1	1.30	55.00	52.00	62.00	Dissolves completely	
2	2.80	50.00	53.00	68.75	Dissolves completely	
3	2.90	50.00	61.00	68.75	500.00	625.00
4	2.30	57.50	56.00	93.75	Dissolves completely	
5	2.30	60.00	50.00	106.20	Dissolves completely	

The hydrogen form of the dry exchanger is shown to be amorphous by the powder method of X-ray analysis. The results of the sorption studies are summarised in Tables III-V and in Fig. 2.

### Separations

*Separation of Pb<sup>2+</sup> from Zn<sup>2+</sup> and Mn<sup>2+</sup>.* Since the  $K_D$  value for lead is appreciably higher than for other cations it can be separated from Zn<sup>2+</sup> and Mn<sup>2+</sup>; Zn<sup>2+</sup> and Mn<sup>2+</sup> are eluted by 1 M NH<sub>4</sub>NO<sub>3</sub> quantitatively and Pb<sup>2+</sup> with 1 M NH<sub>4</sub>NO<sub>3</sub> in 0.5 M HNO<sub>3</sub>. The results are given in Table VI.

*Separation of UO<sub>2</sub><sup>2+</sup> from numerous metal ions.* Uranyl is adsorbed on the top of the column in the form of a yellow band. Dispersion of the yellow band is not observed on elution with water, 1 M NH<sub>4</sub>NO<sub>3</sub> or 1 M NH<sub>4</sub>NO<sub>3</sub> in 0.02 M HNO<sub>3</sub>. However, metal ions other than uranyl can be eluted completely from the column using the above eluants (Table VII).

*Separation of Cr<sup>3+</sup> from numerous metal ions.* On applying Cr<sup>3+</sup> solution to the stannic arsenate column, a blue band forms on the top which is difficult to elute. The blue band persists and cannot be eluted with NaNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>, NaCl, NH<sub>4</sub>Cl, and NH<sub>4</sub>CNS solutions; dil. HCl, dil. HCl and NH<sub>4</sub>Cl mixture, dil. HNO<sub>3</sub>, dil. HNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> mixture, dil. H<sub>2</sub>SO<sub>4</sub>, dil. H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> mixture. Fe<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup> and Mg<sup>2+</sup> are eluted quantitatively with 1 M NH<sub>4</sub>NO<sub>3</sub> solution.

TABLE III

DISTRIBUTION COEFFICIENT OF METAL IONS UNDER A RANGE OF ELEVATED TEMPERATURES

Cations	$K_D$ values <sup>a</sup> (ml/g at pH 2) at different temperatures (°C)						
	20°	40°	60°	80°	Q*	95°	Q*
	Q	Q	Q	Q	Q*	Q	Q*
Mg <sup>2+</sup>	22.18	20.00	31.30	29.23	34.40	28.40	34.40
Ca <sup>2+</sup>	45.00	40.00	43.00	45.00	51.00	48.10	48.10
Sr <sup>2+</sup>	54.28	50.00	50.00	54.29	58.80	63.10	54.30
Ba <sup>2+</sup>	165.10	147.25	136.50	126.66	136.50	126.66	147.30
Zn <sup>2+</sup>	80.50	80.50	90.85	102.42	180.50	108.70	178.30
Cd <sup>2+</sup>	168.33	180.00	192.72	206.67	330.00	239.00	329.20
Fe <sup>3+</sup>	T.A. <sup>b</sup>	T.A.	T.A.	T.A.	T.A.	T.A.	T.A.
Ni <sup>2+</sup>	33.48	51.30	54.66	64.00	88.10	69.75	88.10
Co <sup>2+</sup>	58.04	75.10	102.50	102.50	116.00	102.50	116.00
Al <sup>3+</sup>	235.00	783.00	793.00	1240.00	1240.00	1240.00	2580.00
Ga <sup>3+</sup>	280.00	122.00	2540.00	2540.00	2540.00	2540.00	2540.00
In <sup>3+</sup>	810.00	T.A.	T.A.	T.A.	T.A.	T.A.	T.A.
Pb <sup>2+</sup>	T.A.	T.A.	T.A.	T.A.	T.A.	T.A.	T.A.
Mn <sup>2+</sup>	71.00	90.00	92.00	101.18	144.50	107.30	137.58
Cu <sup>2+</sup>	220.00	273.50	320.00	380.00	740.00	473.00	740.00
Cr <sup>3+</sup>	T.A.	T.A.	T.A.	T.A.	T.A.	T.A.	T.A.

<sup>a</sup>  $K_D$  in column Q: without quenching the ion-exchange reaction;  $K_D$  in column Q\*: on quenching the ion-exchange reaction.

<sup>b</sup> T.A. = Total adsorbed.

TABLE IV

VARIATIONS OF  $K_D$  VALUES WITH TEMPERATURE FOR TRANSITION METAL IONS

Cations	$dK_D/dt \times 10^{-2}$			
	20°	40°	60°	75°
Zn <sup>2+</sup>	00.00	51.80	54.60	37.60
Cd <sup>2+</sup>	58.40	60.97	63.90	94.20
Ni <sup>2+</sup>	87.30	52.05	50.27	47.88
Co <sup>2+</sup>	85.30	112.50	74.10	59.28
Mn <sup>2+</sup>	95.00	50.30	51.63	48.40
Cu <sup>2+</sup>	267.50	250.00	266.00	337.30

*IR spectra.* The results of IR spectra are shown in Fig. 1. The spectra show four absorption bands: the first between 3700 and 2600  $\text{cm}^{-1}$  with a maximum at 3500  $\text{cm}^{-1}$ , the second between 1800 and 1500  $\text{cm}^{-1}$  with maximum at 1625, the third between 1150 and 750  $\text{cm}^{-1}$  with maximum at 840  $\text{cm}^{-1}$  and the fourth between 650 and 400  $\text{cm}^{-1}$  with maximum at 490  $\text{cm}^{-1}$ . The first band is characteristic of interstitial water (or free water) and hydroxyl groups, the second of interstitial water, the third of  $\text{HAsO}_4^{2-}$  groups and the fourth of the Sn-O bond.

## DISCUSSION

The results show that stannic arsenate is specific for the separation of  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{2+}$  and  $\text{UO}_2^{2+}$  from numerous metal ions. Quantitative separations are thus

TABLE V

DISTRIBUTION COEFFICIENTS OF METAL IONS ON STANNIC ARSENATE SAMPLES DRIED AT DIFFERENT TEMPERATURES AT  $33 \pm 1^\circ$ 

Cations	$K_D$ values (ml/g at pH 2) (Sample No.)				
	1	2	3	4	5
UO <sub>2</sub> <sup>2+</sup>	900.00	900.00	566.66	900.00	900.00
Mg <sup>2+</sup>	98.46	75.20	17.30	43.50	51.80
Ca <sup>2+</sup>	138.10	94.90	31.20	74.70	74.70
Sr <sup>2+</sup>	152.20	136.90	34.66	123.00	102.00
Ba <sup>2+</sup>	240.00	213.8	94.34	191.50	176.00
Zn <sup>2+</sup>	317.00	284.90	92.30	263.10	263.10
Cd <sup>2+</sup>	861.30	716.30	122.20	380.00	380.00
Hg <sup>2+</sup>	52.90	47.60	7.00	7.00	9.64
Fe <sup>3+</sup>	T.A. <sup>a</sup>	T.A.	T.A.	T.A.	T.A.
Ni <sup>2+</sup>	149.40	162.10	34.36	118.40	101.50
Co <sup>2+</sup>	202.50	227.50	51.36	168.40	168.40
Al <sup>3+</sup>	1 900.00	4 900.00	1 900.00	1 900.00	1 900.00
Ga <sup>3+</sup>	4 900.00	4 900.00	4 900.00	4 900.00	4 900.00
In <sup>3+</sup>	13 600.00	13 600.00	5 380.00	5 380.00	5 380.00
Pb <sup>2+</sup>	T.A.	T.A.	T.A.	T.A.	T.A.
Mn <sup>2+</sup>	288.00	265.80	60.90	169.80	156.10
Cu <sup>2+</sup>	760.00	746.60	416.00	1 190.00	916.00
Cr <sup>3+</sup>	T.A.	T.A.	T.A.	T.A.	T.A.

<sup>a</sup>T.A. = Total adsorbed

TABLE VI

SEPARATION OF Pb<sup>2+</sup> FROM Zn<sup>2+</sup> AND Mn<sup>2+</sup> ON STANNIC ARSENATE (SAMPLE NO.2) COLUMNS

Sample No.	Mixture separated	Eluants	Volume of effluent (ml)	Taken (mg)	Found (mg)
1	Zn <sup>2+</sup>	1 M NH <sub>4</sub> NO <sub>3</sub>	60	2.03	2.03
	Pb <sup>2+</sup>	1 M NH <sub>4</sub> NO <sub>3</sub> in 0.5 M HNO <sub>3</sub>	40	3.110	3.110
2	Mn <sup>2+</sup>	1 M NH <sub>4</sub> NO <sub>3</sub>	60	0.8237	0.8190
	Pb <sup>2+</sup>	1 M NH <sub>4</sub> NO <sub>3</sub> in 0.5 M HNO <sub>3</sub>	40	3.110	3.110

possible of Pb<sup>2+</sup> from Fe<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Mn<sup>2+</sup> (Table VI) and of UO<sub>2</sub><sup>2+</sup> from Mg<sup>2+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup> and Sr<sup>2+</sup>. The irreversible adsorption of Cr<sup>3+</sup> suggests the formation of a chromium arsenate.

Table III shows that the  $K_D$  values after cooling the system to room temperature are lower than those determined by quenching the ion-exchange reaction at the temperature under study. This shows the reversibility of the ion-exchange reaction with respect to temperature. There is no appreciable change in the  $K_D$  values of the alkaline earth and trivalent metal ions on raising the temperatures of equilibrating solution from 20–95°. However the increase in  $K_D$  values of divalent transition metal ions such as Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup> and Cu<sup>2+</sup> is significant at elevated temperatures. Since the enthalpy change in the ion-exchange reaction is small, it appears that the

TABLE VII

SEPARATION OF URANYL FROM  $Mn^{2+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Sr^{2+}$ ,  $Cu^{2+}$  AND  $Fe^{2+}$  ON STANNIC ARSENATE (SAMPLE NO. 2) COLUMNS

Sample No.	Mixture separated	Eluants	Volume of effluent (ml)	Taken (mg)	Found (mg)
1	$Mn^{2+}$	1 M $NH_4NO_3$	60	0.8237	0.8190
	$UO_2^{2+}$	0.50 M $HNO_3$	60	3.857	3.753
2	$Ca^{2+}$	1 M $NH_4NO_3$	60	0.6010	0.5873
	$UO_2^{2+}$	0.50 M $HNO_3$	60	3.857	3.753
3	$Mg^{2+}$	1 M $NH_4NO_3$	60	0.3646	0.3711
	$UO_2^{2+}$	0.50 M $HNO_3$	60	3.857	3.904
4	$Sr^{2+}$	1 M $NH_4NO_3$ in 0.02 M $HNO_3$	60	1.322	1.322
	$UO_2^{2+}$	0.50 M $HNO_3$	60	3.857	3.805
5	$Cu^{2+}$	1 M $NH_4NO_3$ in 0.02 M $HNO_3$	60	0.9533	0.9696
	$UO_2^{2+}$	0.50 M $HNO_3$	60	3.857	3.857
6	$Fe^{2+}$	1 M $NH_4NO_3$	60	1.325	1.307
	$UO_2^{2+}$	0.50 M $HNO_3$	60	3.857	3.904

reaction following ion-exchange in these cases involves considerable enthalpy change<sup>5</sup>. Therefore the change in  $K_D$  values with respect to temperature has been calculated for the 6 metal ions mentioned (Table IV). The plots of  $dK_D/dt$  versus  $dt$  (Fig. 2) show a gradual increase in the adsorption of  $Cu^{2+}$  and  $Cd^{2+}$  with an increase in temperature, while the adsorption of  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Mn^{2+}$  and  $Zn^{2+}$  first increases and then finally decreases on increasing the temperature of the system.

The explanation of these changes seems to be quite complicated due to continuous changes in hydrated radii of ions, the structure of exchanger, dielectric constant and the pH of the equilibrating solution with variations in temperature (20–95°). A few points may, however, be stressed<sup>3</sup>. In almost all cases  $Q_t/Q_{95^\circ} < 1$  except for  $Mg^{2+}$  and  $Ba^{2+}$ . These exceptions may be due to specific interactions<sup>3</sup>. The data recorded in Table V show that the  $K_D$  values of metal ions on stannic arsenate decrease<sup>6</sup>

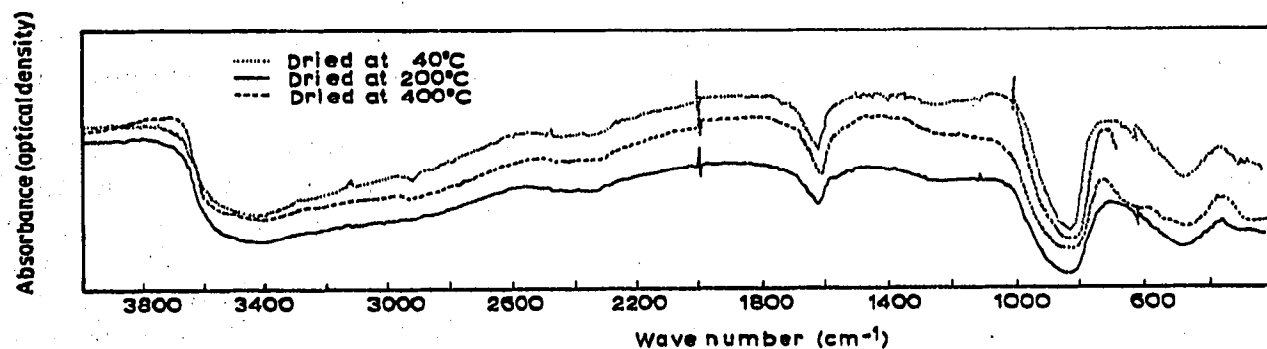


Fig. 1. Infrared absorption spectra of stannic arsenate dried at different temperatures by KBr disk method.

as the drying temperature increases. However, the  $K_D$  values of sample 3 dried at  $200^\circ$  are smaller than of other samples because stannic arsenate loses interstitial water molecules up to  $300^\circ$ , and after this temperature condensation starts. Removal of interstitial water molecules increases the degree of crosslinking while the condensation decreases the concentration of exchangeable hydrogen ions in the sorbent phase and therefore causes a lower sorption of cations. Furthermore the degree of crosslinking in sample 3 (dried at  $200^\circ$ ) is maximal, therefore the lower values of distribution coefficients are obtained on the sample mentioned.

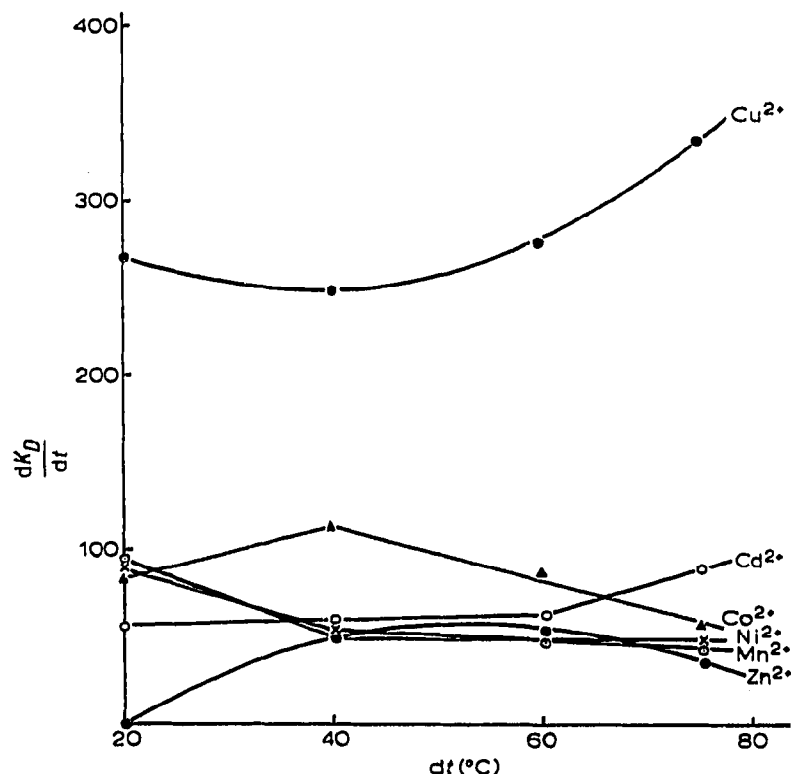


Fig. 2. Change in  $K_D$  value with respect to temperature of divalent transition metal ions.

All the colour changes in stannic arsenate at higher temperatures are due to the formation of tin and arsenic oxides. Since similar colour changes are observed when a mixture of stannic chloride and sodium arsenate was heated at higher temperatures ( $400$ – $800^\circ$ ). However, there is no change in colour when sodium stannate and sodium arsenate were heated separately, while a remarkable change in colour (bluish black) was visualised when stannic hydroxide was heated at temperatures mentioned above.

A comparison of IR spectra of stannic arsenate dried at different temperatures as well as compared to the IR spectra of zirconium phosphate<sup>7</sup> and antimonite acid<sup>8</sup> shows that all the three samples contain interstitial water molecules, replaceable hydrogen ions in the form of  $\text{OH}^-$  group, As–O and Sn–O bonds. Therefore on the basis of IR analysis and the properties observed, a general formula for this product may be postulated as  $\text{SnO}(\text{AsO}_3\text{OH}) \cdot n\text{H}_2\text{O}$ . The above conclusions do not contradict the results of thermogravimetric and X-ray analysis reported in our earlier paper<sup>1</sup>. The good performance of stannic arsenate at elevated temperatures and its thermal

stability makes it promising for the ion-exchange work at higher temperatures such as purification of high-pressure cooling water of pressurised water-cooled reactors.

#### ACKNOWLEDGEMENT

We thank Dr. S. M. F. RAHMAN, Dr. B. RAMA RAO (R. R. L. Hyderabad), Prof. M. V. GEORGE (I. I. T. Kanpur) for research, X-ray and IR facilities. One of us (H.S.R.) thanks C.S.I.R. (India) for financial assistance.

#### REFERENCES

- 1 M. QURESHI, R. KUMAR AND H. S. RATHORE, *J. Chem. Soc. (A)*, 2 (1970) 272.
- 2 M. QURESHI, H. S. RATHORE AND R. KUMAR, *J. Chem. Soc. (A)*, 11 (1970) 1986.
- 3 F. HELFFERICH, *Ion Exchange*, McGraw-Hill, London, 1962, p. 133.
- 4 E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, Interscience Publishers, New York, 1959, p. 915.
- 5 K. A. KRAUS, R. J. RARIDON AND D. L. HOLCOMB, *J. Phys. Chem.*, 63 (1953) 1901.
- 6 C. B. AMPHLETT, *Inorganic Ion Exchangers*, Elsevier, New York, 1964, p. 109.
- 7 V. VESELY AND V. PEKAREK, *J. Inorg. Nucl. Chem.*, 25 (1963) 697.
- 8 M. ABE AND T. ITO, *Bulletin Chem. Soc. Japan*, No. 10, 41 (1968) 2366.

*J. Chromatog.*, 54 (1971) 269-276