

## CHROMATOGRAPHIC BEHAVIOUR OF INORGANIC IONS ON CRYSTALLINE TITANIUM PHOSPHATE OR ZIRCONIUM PHOSPHATE THIN LAYERS

G. ALBERTI, G. GIAMMARI AND G. GRASSINI-STRAZZA

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

(Received December 23rd, 1966)

### INTRODUCTION

Insoluble salts of polybasic acids with tetravalent metals such as phosphates or arsenates of zirconium, titanium and cerium are generally obtained as amorphous or semicrystalline materials which are well known inorganic ion exchangers<sup>1</sup>. Recently a crystalline form of zirconium phosphate<sup>2</sup> (ZP) and a crystalline form of titanium phosphate<sup>3</sup> (TP) have been obtained whose ion exchange properties are very different from those of the corresponding amorphous materials. While all alkali metal ions are easily exchanged on amorphous ZP and TP (the selectivity increasing from Li<sup>+</sup> to Cs<sup>+</sup>) the uptake of Rb<sup>+</sup> and Cs<sup>+</sup> by crystalline ZP and the uptake of K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> on crystalline TP is negligible in acid media<sup>2,3</sup>. On the other hand Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> on crystalline ZP and Li<sup>+</sup> and Na<sup>+</sup> on crystalline TP are easily exchanged with very high ion exchange capacity (about 7 mequiv./g). The large difference in the ion exchange capacity suggested that the crystalline form of ZP and TP could be employed in the separation of alkali metal ions. For this reason the chromatographic behavior of alkali metal ions on crystalline titanium or zirconium phosphate thin layers has been examined. Owing to the lack of information on the exchange properties of these crystalline ion exchangers towards inorganic ions other than alkali metal ions, the chromatographic behavior of alkaline earths and thallium(I) has also been examined and the chromatographic results obtained with crystalline and amorphous materials are compared.

### EXPERIMENTAL

#### *Materials and eluents*

The amorphous ZP was ZP-1 of Bio-Rad Laboratories. Crystalline ZP was prepared from ZP-1 Bio-Rad according to the procedure of CLEARFIELD AND STYNES<sup>2</sup>. Amorphous TP was prepared according to GAL AND GAL<sup>4</sup>. Crystalline TP was prepared by refluxing amorphous TP with 10 M H<sub>3</sub>PO<sub>4</sub> for 50 h<sup>3</sup>. Cellex N-1 cellulose (Bio-Rad) was employed for thin-layer preparations.

Tetramethylammonium acetate or ammonium acetate buffers were prepared by adding conc. acetic acid to 1.1 M tetramethylammonium hydroxide or to 1.1 M ammonium hydroxide respectively, until pH 5 was reached.

*Preparation of thin layers*

For the preparation of cellulose-ion exchanger thin layers a slurry of one part of cellulose, 3.5 parts of water, and the proper amount of ion exchanger (200-400 mesh) was applied to smooth glass plates (60 cm<sup>2</sup>/g cellulose) and air dried. When buffered layers had to be used the layers were sprayed with the eluent and again air dried. The amount of ion exchanger to be mixed with cellulose is related to the mequiv. of ions to be separated, and this will be discussed later.

*Chromatographic procedure*

The solutions of metal ions were prepared by dissolving the nitrates in the eluent.

The lower portion (2 cm) of the thin layer was coated with Whatman 3 MM paper to avoid breakage of the layer. 2-10  $\mu$ l of samples were spotted 3 cm from the lower end of the layer. The plates were allowed to develop by ascending chromatography.

Na<sup>+</sup> and Cs<sup>+</sup> ions were detected radiometrically using <sup>22</sup>Na and <sup>137</sup>Cs as tracers.

Li<sup>+</sup> and K<sup>+</sup> ions were located by flame photometry, after cutting the layers in portions (1 cm in length) and eluting with 0.1 N HCl.

Other ions were detected by suitable spot test reactions.

TABLE I

*R<sub>F</sub>* VALUES OF SOME INORGANIC IONS ON CELLULOSE AND ON INORGANIC ION EXCHANGER THIN LAYERS

Eluent: 0.1 M HClO<sub>4</sub>.

Ion	Thin-layer material				
	Cellex	Amorphous ZP	Crystalline ZP	Amorphous TP	Crystalline TP
Li	1.0	0.9	1.0	0.9	0.9
Na	0.9	0.8	0.9	0.9	0.9
K	0.9	0.3	0.9	0.8	0.9
Cs	0.9	0.2	0.9	0.7	0.8
Tl(I)	0.9	0.2	at L.F. with tail		0.3
Ca	1.0	at L.F. * with tail		0.8**	0.9
Ba	1.0	at L.F. with tail		0.9**	1.0
Sr	1.0	at L.F. with tail		0.9**	1.0

\* L.F. = Liquid front.

\*\* Elongated spot.

## RESULTS AND DISCUSSION

Table I shows the chromatographic behavior of various inorganic ions when eluted with 0.1 M HClO<sub>4</sub> and applied to cellulose thin layers and cellulose thin layers containing amorphous ZP, crystalline ZP, amorphous TP and crystalline TP, respectively. The results show that some uptake of K(I), Cs(I) and Tl(I) ions occurs on thin layers containing amorphous exchangers, whereas all the ions examined behave in nearly the same way on either cellulose, crystalline ZP or crystalline TP. In strongly acid media a negligible ion exchange capacity was found on crystalline ZP and TP for all the ions examined.

Eluent solutions at  $\text{pH} > 3$  were found necessary to exchange the hydrogen ion with other inorganic ions. When such eluents are used the exchanged hydrogen ions may give rise to the formation of an acid zone around the point of application. This acid zone will move with the front of the eluent, not being neutralized during the chromatographic development, even though buffered eluents are used. As a result, a fraction of the ions spotted at the application point migrate with the acid zone.

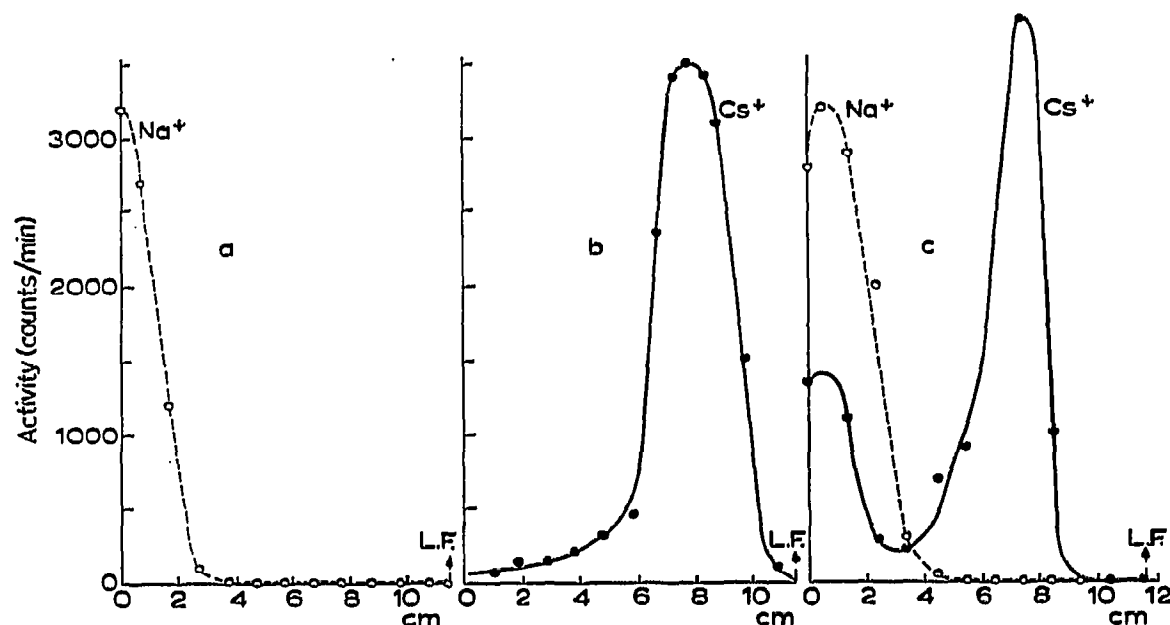


Fig. 1. Chromatographic behavior of  $\text{Na}^+$  (a),  $\text{Cs}^+$  (b) and  $\text{Na}^+$ - $\text{Cs}^+$  mixture (c) on crystalline ZP thin layers ( $4.2 \text{ mg ZP/cm}^2$ ). Amount spotted of each ion:  $7.5 \cdot 10^{-3}$  mequiv. Eluent: tetramethylammonium acetate-acetic acid buffer at  $\text{pH} 5$ . Ordinates: activity in c.p.m.; abscissae: length of the chromatogram in cm; L.F. = liquid front.

In such a case the acid front can be completely neutralized by using a thin layer previously moistened with the eluent and air dried. The chromatographic behavior of the alkali metal ions on crystalline ZP has been examined, using this technique with the tetramethylammonium acetate-acetic acid buffer at  $\text{pH} 5$ . The tetramethylammonium ion was employed since its large ionic size avoids ion exchange by crystalline ZP in  $\text{H}^+$  form at this  $\text{pH}$  value. When eluted with tetramethylammonium acetate-acetic acid buffer at  $\text{pH} 5$ ,  $\text{Li}^+$  and  $\text{Na}^+$  ions are strongly retained at the point of application while  $\text{Cs}^+$  ion, in good agreement with CLEARFIELD's data<sup>2</sup> are not retained. The chromatographic behavior on crystalline ZP of  $\text{Na}^+$  (Fig. 1a) and  $\text{Cs}^+$  (Fig. 1b) would suggest a good separation of these ions. However, when  $\text{Na}^+$  and  $\text{Cs}^+$  ions are both present in a mixture, a large fraction of  $\text{Cs}^+$  is retained together with  $\text{Na}^+$  at the application point (Fig. 1c). This result suggests that while  $\text{Cs}^+$  ion is negligibly retained by crystalline ZP in  $\text{H}^+$  form, it can be retained by the  $\text{Na}^+$  form of the exchanger, probably owing to the characteristic layer-structure of crystalline ZP<sup>5</sup>. Batch experiments carried out in this laboratory<sup>3</sup> showed that it is possible to convert even the crystalline ZP into the  $\text{Cs}^+$  form by percolating  $0.1 \text{ M CsCl}$  over the  $\text{Na}^+$  form of the exchanger. Thus, crystalline ZP seems to be of little use in the separation of alkali metal ions or other inorganic ions.

Attention was then mainly devoted to crystalline TP, since preliminary ex-

periments showed that the amount of  $\text{Cs}^+$  retained by the  $\text{Na}^+$ -form of this exchanger was negligible when compared with the amount retained by crystalline ZP under the same experimental conditions.

TABLE II

$R_F$  VALUES OF SOME INORGANIC IONS ON CELLULOSE AND ON AMORPHOUS TP OR CRYSTALLINE TP THIN LAYERS

Eluent: ammonium acetate-acetic acid buffer at pH 5.

Ion	Thin-layer material		
	Cellulose	Amorphous TP	Crystalline TP
Li	0.8	0.8	0.0
Na	0.8	0.7	0.0
K	0.8	0.6	0.8
Cs	0.7	0.5	0.7
Tl	0.8	0.0	0.4
Ca	0.8	long tail	at L.F.* with tail
Ba	0.8	long tail	at L.F. with tail
Sr	0.8	long tail	at L.F. with tail

\*L.F. = Liquid front.

In our opinion, the ion exchange rate of ions of large size, such as  $\text{K}^+$  or  $\text{Cs}^+$ , is very low on crystalline TP. During the chromatographic development, the relatively short contact-time permits these ions to exchange only at the surface or on the outer layers of the exchanger. Thus, very small amounts of ions of large size can be exchanged by crystalline TP. Nevertheless, when the amounts of the ions to be separated

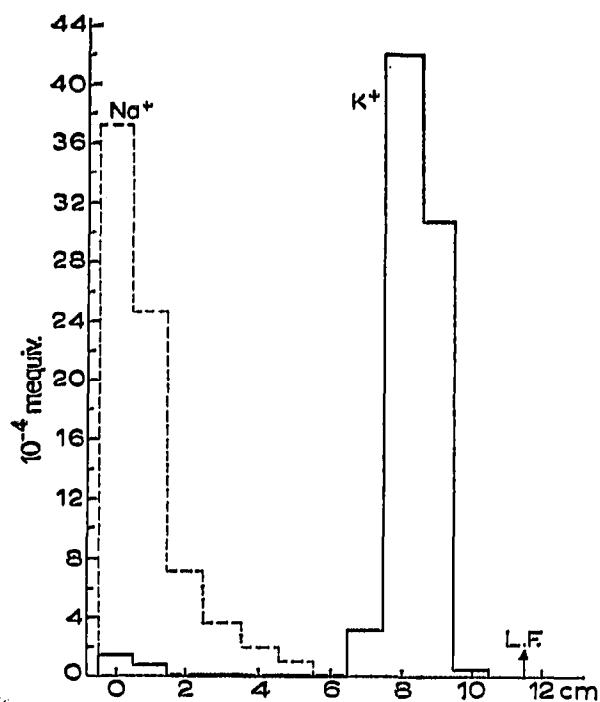


Fig. 2. Separation of  $\text{Na}^+$ - $\text{K}^+$  on crystalline TP thin layer ( $8.3 \text{ mg TP/cm}^2$ ). Amount spotted of each ion:  $7.5 \cdot 10^{-3}$  mequiv. Eluent: ammonium acetate-acetic acid buffer at pH 5. Ordinates:  $10^{-4}$  mequiv.; abscissae: length of the chromatogram in cm; L.F. = liquid front.

are very small (e.g. carrier free solutions), the extent of ion exchange on the crystalline TP may be considerable. For this reason, as already pointed out, the amounts of crystalline TP per  $\text{cm}^2$  of thin layer must be related to the amounts of ions to be separated. In this work it has been found convenient to employ thin layers containing 0.5–1.0 mg of crystalline TP per  $\text{cm}^2$  and per  $\mu\text{equiv.}$  of ion spotted at the application point.

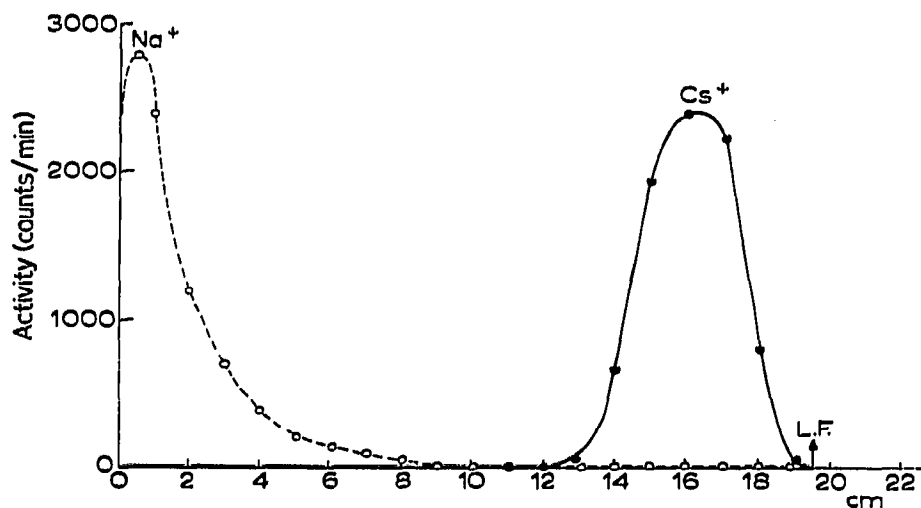


Fig. 3. Separation of  $\text{Na}^+$ – $\text{Cs}^+$  on crystalline TP thin layer ( $8.3 \text{ mg TP/cm}^2$ ). Amount spotted of each ion:  $7.5 \cdot 10^{-3}$  mequiv. Eluent: ammonium phosphate buffer at pH 7. Ordinates: activity in c.p.m.; abscissae: length of the chromatogram in cm; L.F. = liquid front.

Furthermore it has been found that not only  $\text{N}(\text{CH}_3)_4^+$  but even  $\text{NH}_4^+$  ion is poorly exchanged in acid or weak acid media by crystalline TP. It was therefore possible to employ ammonium acetate–acetic acid buffer as eluent. In Table II the chromatographic results obtained with this eluent at pH 5 are reported. In the same table the chromatographic results obtained with amorphous TP are reported by comparison, showing the drastic changes of the ion exchange properties caused by the crystallization process.  $\text{Li}^+$  and  $\text{Na}^+$  ions are in fact retained more by crystalline than by amorphous TP. The opposite behavior shown for  $\text{K}^+$  and  $\text{Cs}^+$  ions is in good agreement with the data reported in a previous paper<sup>3</sup>. The alkaline earth metal ions form somewhat elongated spots due (in our opinion) mainly to the formation of precipitates between these ions and the phosphate ion produced by hydrolysis of the exchanger, rather than to an effective ion exchange process. Beside  $\text{Li}^+$  and  $\text{Na}^+$  ions,  $\text{Tl(I)}$  is the only ion which is partially retained by crystalline TP. Considering the large ionic size of the  $\text{Tl(I)}$  ion, this deserves further investigation. The high selectivity of amorphous TP for  $\text{Tl(I)}$  must also be emphasized.

The chromatographic experiments confirm thus that crystalline TP acts as an ion exchanger with high selectivity for  $\text{Li}^+$  and  $\text{Na}^+$  ions only.

The data of Table II can be used to predict some separations of alkali metal ions. Fig. 2 shows, as an example, the chromatographic separation of  $\text{Na}^+$  and  $\text{K}^+$  ions, using as eluent an ammonium acetate–acetic acid buffer solution at pH 5. A phosphate buffer at pH 7 can be successfully employed in the absence of ions which give insoluble phosphates (Fig. 3). The separation  $\text{Na}$ – $\text{Cs}$  was also performed with tetramethylammonium acetate–acetic acid buffer solution at pH 5 (Fig. 4). The better performance

of crystalline TP, as compared to crystalline ZP, for  $\text{Na}^+$ - $\text{Cs}^+$  separations under the same experimental conditions, can be seen by comparing Fig. 4 and Fig. 1.

It appears that crystalline TP can be successfully employed in the separation of some alkali metal ions. The large difference in the chromatographic behavior of  $\text{Na}^+$  and  $\text{K}^+$  ions, is particularly interesting.

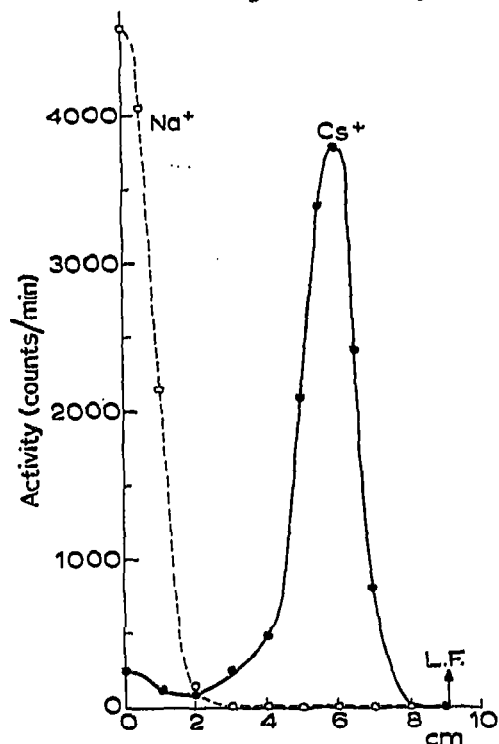


Fig. 4. Separation of  $\text{Na}^+$ - $\text{Cs}^+$  on crystalline TP thin layer ( $8.3 \text{ mg TP/cm}^2$ ). Amount spotted of each ion:  $7.5 \cdot 10^{-3}$  mequiv. Eluent: tetramethylammonium acetate-acetic acid buffer at pH 5. Ordinates: activity in c.p.m.; abscissae: length of the chromatogram in cm; L.F. = liquid front.

#### ACKNOWLEDGEMENT

Thanks are due to the Consiglio Nazionale delle Ricerche for partial financial support.

#### SUMMARY

The chromatographic behaviour of alkali metal ions, alkaline earths and  $\text{Tl(I)}$  on crystalline and amorphous zirconium phosphate and titanium phosphate thin layers has been examined. Large differences in the ion exchange properties of amorphous and crystalline materials were found. Crystalline titanium phosphate has been successfully employed in the separation of some alkali metal ions.

#### REFERENCES

- 1 C. B. AMPHLETT, *Inorganic Ion Exchangers*, Elsevier, Amsterdam, 1964.
- 2 A. CLEARFIELD AND J. A. STYNES, *J. Inorg. Nucl. Chem.*, 26 (1964) 115.
- 3 G. ALBERTI, P. CARDINI-GALLI, V. COSTANTINO AND E. TORRACCA, *J. Inorg. Nucl. Chem.*, 29 (1967) 571.
- 4 J. GAL AND O. GAL, *Proc. Intern. Conf. Peaceful Uses At. Energy 2nd, Geneva*, Vol. 28, United Nations, 1958, p. 24.
- 5 E. MICHEL AND A. WEISS, *Z. Naturforsch.*, 20b (1965) 1307.