CRYSTALLINE INSOLUBLE SALTS OF POLYBASIC METALS

IV. CHROMATOGRAPHY OF INORGANIC IONS ON (SUPPORT-FREE) CERIUM(IV) PHOSPHATE SHEETS*

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A crystalline form of cerium(IV) phosphate exhibiting a fibrous structure and a high ion exchange capacity has recently been obtained in this laboratory[1].

The fibrous structure permits the preparation of sheets similar to cellulose paper[2]. Such sheets could not be prepared with other inorganic exchangers up to date.

These support-free inorganic ion exchange sheets (CeP paper) have a number of features such as porosity, good mechanical and chemical stability, high ion exchange capacity and selectivity, which make them very attractive for chromatographic or electrophoretic studies of inorganic ions.

This paper reports some results obtained by ascending chromatography using as eluent $HClO_4$ solutions at various concentrations.

EXPERIMENTAL

Reagents and analytical procedures

Erba RP products were used without further purification. $Ce(SO_4)_2 \cdot 4H_2O$ was a Merck "pro analysi" product. The solutions of metal ions were prepared by dissolving the perchlorates in the eluent or by dissolving hydroxides in $HClO_4$. A measured volume of solution containing about $2 \cdot 10^{-4}$ mequiv. of metal ion was spotted 2 cm from the lower end of the strip. Tl, Ag, Ni, Fe, Pb were detected as sulphides; Cs, Rb, Na and Sr were detected radiometrically using ^{134}Cs, ^{86}Rb, ^{22}Na and ^{89}Sr as tracers. Li and K ions were located by flame photometery after cutting the strips in portions (1 cm length) and eluting with a measured volume of 4 N HCl. UO_2(II) was detected by fluorescence[3], dipping portions of the strip (1 cm length) in 4 M H_3PO_4 and then examining the solutions under U.V. lamp (yellow-green fluorescence).

Eu was detected by fluorescence in 0.6 M sodium tungstate solution at pH 9 according to the procedure reported in a previous paper[4]. Since the red fluorescence tends to disappear on CeP paper, detection must be effected as soon as possible employing a short wave U.V. lamp. Other ions were detected by normal spot test reactions.

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Preparation of cerium(IV) phosphate sheets

The fibrous cerium(IV) phosphate (CeP) was prepared as described in a previous paper[1] by adding dropwise 115 ml of 0.05 *M* $Ce(SO_4)_2 \cdot 4H_2O$ solution in 1 *M* H_2SO_4 to 115 m of a well-stirred solution of 6 *M* H_3PO_4 and stirring the slurry for 4–5 h. During preparation and digestion the temperature was kept constant at 90° ± 4°.

The fibrous CeP so obtained was washed free of sulphate ions then suspended in about 250 ml of distilled water. This suspension was poured into a large Buchner funnel (⌀ 19 cm), at the bottom of which was a disc of filter paper. CeP was left to deposit on the bottom (eventually by vibrating the funnel, to obtain a more homogeneous layer) and the water was filtered off by slight suction. The CeP layer was then washed three times with about 100 ml of distilled water and finally air dried. The CeP layer was removed from the filter paper as a flexible disc about 0.5 mm thick (8–9 mg/cm²) whose physical aspect was very similar to cellulose filter paper. The disc was then cut into strips (3.5 × 15 cm) for chromatographic experiments. The remnants were mixed with Whatman No. 1 cellulose paper (1:1 in weight), then pulped in water. This slurry was employed to obtain cellulose-CeP papers with a procedure similar to that described above.

RESULTS AND DISCUSSION

The following chemical and physical characteristics of CeP paper must be kept in mind when used for chromatographic applications:

(a) Appreciable amounts of phosphate are lost by hydrolysis at pH values higher than 10.

(b) CeP paper can be solubilized by some strong complexing agents of Ce(IV) such as concentrated H_2SO_4.

(c) Ce(IV) phosphate can be reduced to Ce(III) phosphate by strong reducing agents.

Thus alkaline solutions or eluents containing complexing or reducing agents must be avoided. For these reasons $HClO_4$ has been employed as eluent.

Tables I and II show the chromatographic behaviour of some inorganic ions on pure CeP paper and on cellulose-CeP paper respectively when eluted with $HClO_4$ at various concentrations. Table I also shows R_F values on Whatman No. 1 paper. These latter values were determined only to ascertain whether precipitation occurs under the experimental conditions employed.

By comparing the R_F values of Tables I and II it can be noted that on cellulose-CeP paper R_F values are generally higher than on pure CeP paper. This was expected since the ion exchange capacity of the cellulose-CeP paper is 50 % of that of pure CeP paper.

On the other hand, the rate of the chromatographic process is slower on pure CeP paper; *e.g.* the time required for a chromatographic development of 12 cm is 4 h on pure CeP paper and 2 h on cellulose-CeP paper. Thus cellulose-CeP paper can be employed if fast separations are required. However, in some cases long tails are obtained. This can be understood taking into account that when the rate of the ion exchange process is slow with regard to the rate of the chromatographic development a state of equilibrium cannot be reached; since the rate of the ion exchange process decreases with increasing size of the ions, tails are observed expecially for larger ions.

TABLE I

R_F VALUES OF INORGANIC CATIONS ON WHATMAN NO. 1 AND CeP PAPERS
Eluent: $HClO_4$ at various concentrations.

Ion	*R_F values*					
	Whatman No. 1 paper		*CeP paper*			
	0.1 M $HClO_4$	*4 M $HClO_4$*	*0.1 M $HClO_4$*	*1 M $HClO_4$*	*2 M $HClO_4$*	*4 M $HClO_4$*
Li(I)	0.95	—	0.8	0.9	0.95	0.95
Na(I)	0.95	—	0.15	0.5	0.7	0.95
K*(I)	0.9	0.95	0.0	0.1	0.1	0.0
Rb(I)	0.9	0.95	0.0	0.05	0.1	long tail
Cs(I)	0.9	0.95	0.0	0.1**	0.2**	long tail
Ag(I)	0.9	0.95	0.0	0.15	0.2	0.4
Tl(I)	0.8	0.90	0.0	0.0	0.1	0.3
Fe(II)	0.95	0.95	0.0	0.2**	0.3**	0.5**
Co(II)	0.95	0.95	0.85	—	—	0.95
Ni(II)	0.95	0.95	0.95	—	—	0.95
Cu(II)	0.9	0.95	0.9	—	—	0.95
Zn(II)	0.9	0.95	0.8	—	—	0.95
Sr(II)	0.9	0.95	0.5	0.9	—	0.95
Pb(II)	0.9	0.95	0.0	0.1	0.2	0.9
Eu(III)	0.9	0.95	0.2**	0.85	—	0.95
Bi(III)	0.8**	0.95	0.0	0.0	0.2**	0.6
Zr(IV)	long tail	—	0.0	0.0	0.1**	0.1**
Th(IV)	0.9	—	0.0	0.05	0.3**	—
UO_2(II)	0.9	0.95	0.2**	long tail	—	long tail

* Spotted as KCl.
** Elongated spot.

TABLE II

R_F VALUES OF INORGANIC CATIONS ON CELLULOSE-CeP PAPER
Eluent: $HClO_4$ at various concentrations.

Ion	*R_F values*			
	0.1 M $HClO_4$	*1 M $HClO_4$*	*2 M $HClO_4$*	*4 M $HClO_4$*
Na(I)	0.7	0.75	0.9	0.95
K*(I)	0.05	0.1	0.25	0.4**
Rb(I)	0.05	0.1	0.1	0.25**
Cs(I)	0.0	0.2**	0.3**	0.5**
Ag(I)	0.15	0.2	0.3	0.4
Tl(I)	0.05	0.1	0.2	0.3
Eu(III)	0.15**	—	—	—
Zr(IV)	0.0	0.0	0.0	0.05
Th(IV)	0.1**	0.15**	—	—

* Spotted as KCl.
** Elongated spot.

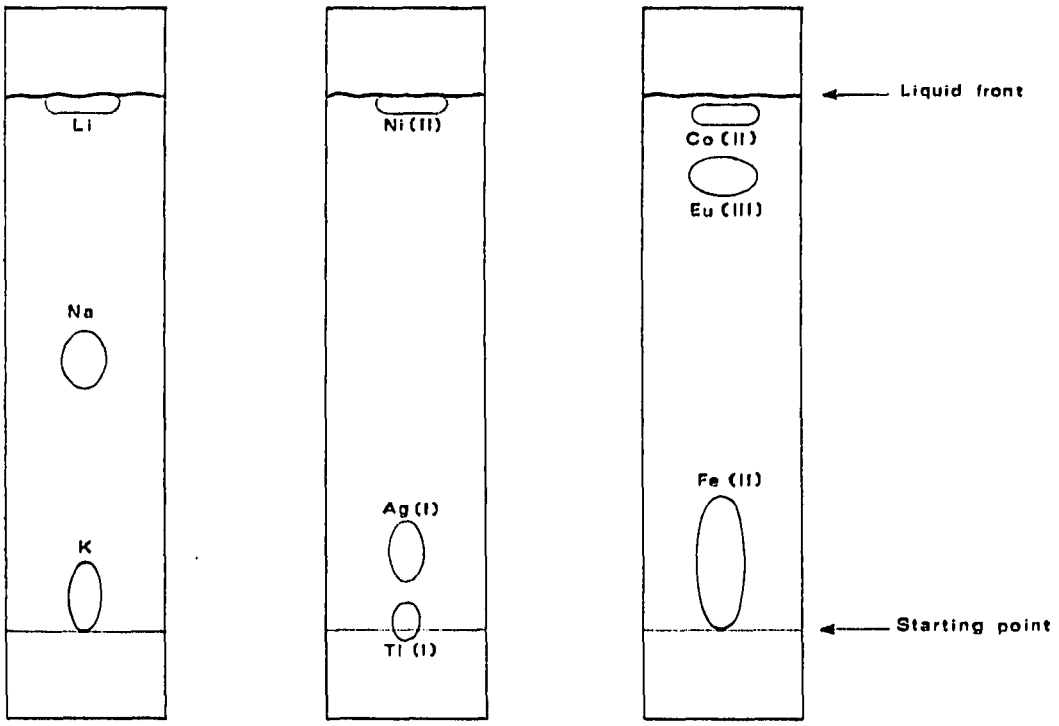

Fig. 1. Representative separations on CeP paper using 1 M $HClO_4$ as eluent.

Thus in cellulose-CeP paper the longer tails are due to the higher rate of the chromatographic process. Long tails observed for Zr(IV), UO_2(II) and Th(IV) in both papers are probably due to slow formation of an insoluble phosphate.

The high selectivity of CeP paper for K(I), Cs(I), Rb(I) Ag(I), Tl(I), Fe(II) and Pb(II) must be emphasised. The considerable differences in some R_F values indicate that it is possible to carry out several separations of inorganic ions. In Fig. 1 a few representative separations are shown. The relative order on CeP paper is somewhat different from that found on zirconium phosphate[5] or ammonium molybdophosphate[6] impregnated papers.

Furthermore, owing to the good stability of CeP at temperatures up to 200°[1], CeP papers could also be used for chromatographic studies in some fused salt systems.

Thus CeP paper is a new ion exchange paper that further increases the possibilities of chromatographic separations of inorganic ions.

SUMMARY

Fibrous cerium(IV) phosphate, a new synthetic inorganic ion exchanger exhibiting a high ion exchange capacity, has been employed to prepare completely inorganic ion exchange papers.

The chromatographic behaviour of several inorganic ions on pure cerium(IV) phosphate papers and on cellulose-cerium(IV) phosphate papers has been examined and discussed. $HClO_4$ at various concentrations was employed as eluent. Considerable differences in the R_F values of various ions have been found and some interesting separations are reported.

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