# Short Communications

## Chromatography on paper impregnated with zirconium phosphate

During the last few years numerous authors have carried out chromatographic separations of various ions by using paper of which the natural exchange capacity had been increased by introducing suitable functional groups into the cellulose molecule[1–6], and also by using paper impregnated with ion-exchange resins[7–11]. In the latter case, the possible separations depend above all on the type of resin used and not on the type of paper employed.

The advantages of paper containing ion-exchange groups as compared with the usual chromatographic papers or ion-exchange columns, were mentioned by TUCKERMAN[4], LEDERER[8] and HALE[11].

In this paper a separation method on filter paper impregnated with synthetic inorganic ion exchangers is described.

Zirconium phosphate (ZP) was chosen as inorganic ion exchanger, because its ion-exchange capacity can be compared with that of ion-exchange resins, and because it might show a different selectivity for different ions[12–13].

Several attempts were made to prepare strips by dipping them into a freshly prepared suspension, as used by LEDERER[7,8] for the preparation of paper impregnated with ion-exchange resins, but so far without success. We were, however, able to precipitate ZP directly onto the paper fibres.

*Preparation of the ion-exchange paper*

Strips (6 × 40 cm) of Whatman No. 1 filter paper were drawn as uniformly as possible through a 30 % solution of $ZrOCl_2$ in 4 *N* HCl. After this impregnation the strips were quickly placed, for 5 min, on pieces of filter paper, which immediately absorb the excess liquid. The impregnated paper was then dried at room temperature by placing it on another sheet of filter paper. The dry strips were then dipped for 2 min into a 60 % solution of $H_3PO_4$ in 4 *N* HCl, and dried at room temperature. After 6 h the excess $H_3PO_4$ was removed from the strips by washing them first in 2 *N* HCl for 10 min and then twice in $H_2O$.

In order to increase the ZP exchange capacity[14], an additional treatment with the same 60 % solution of $H_3PO_4$ in 4 *N* HCl was carried out and afterwards the strips were put into an oven at 50° for 75 min.

As described above, the strips were subsequently washed with 2 *N* HCl, $H_2O$ and left to dry in the air.

It is important to note that special chromatographic paper is not required for the preparation of these strips. Ordinary filter paper can be used because the $R_F$ value depends essentially on the type of ion exchange employed. In any case all that is required to obtain the same results is to employ the same type of paper and above all to standardize the preparation of the sheets as far as possible, so that the same quantity of ions per unit area is obtained.

*Experimental*

The solutions of metal ions were prepared by dissolving the chlorides.

The chromatogram (Whatman No. 1 filter paper impregnated with 3.5 mg/cm$^2$ of ZP) was 40 cm long and the starting point was situated at 3.5 cm from one end. The strip was developed by the ascending method, with HCl of various concentrations, for 4–8 hours. In Table I the $R_F$ values obtained are given. The values reported show that it is possible to carry out several separations by employing this eluent.

On studying the behaviour of alkaline earths and alkali metals it was found that the same order of adsorption is obtained on ZP-impregnated paper as on ZP columns.

TABLE I

$R_F$ VALUES IN HCl OF VARIOUS CONCENTRATIONS

| Element* | $R_F$ | | |
|---|---|---|---|
| | 0.1 N HCl | 0.5 N HCl | 1 N HCl |
| Hg(II) | 0.67 | — | — |
| Cd(II) | 0.60 | — | — |
| Cu(II) | 0.59 | — | — |
| Bi(III) | — | — | 0.90 |
| Fe(III) | 0 | 0 | 0.04 |
| Al(III) | 0.13 | 0.40 | 0.90 |
| **Cr(III) | 0.75 | 0.80 | — |
| Mn(II) | 0.60 | 0.80 | — |
| Ce(III) | 0.19 | — | — |
| La(III) | 0.31 | 0.73 | 0.80 |
| Ti(IV) | 0 | 0 | 0 |
| $UO_2$(VI) | 0 | — | — |
| Th(IV) | 0 | 0 | 0 |
| Co(II) | 0.67 | — | — |
| Ni(II) | 0.61 | 0.80 | 0.85 |
| **Zn(II) | 0.69 | — | — |
| **Ca(II) | 0.81 | — | — |
| **Sr(II) | 0.81 | — | — |
| Ba(II) | 0.60 | — | — |
| ***Ra(II) | 0.44 | — | — |
| Mg(II) | 0.76 | — | — |
| Li(I) | 0.82 | — | — |
| Na(I) | 0.68 | 0.77 | 0.83 |
| K(I) | 0.53 | — | — |
| Rb(I) | 0.12 | — | — |
| **Cs(I) | 0 | 0 | — |

* The spots were detected by spraying the strips with suitable reagents.
** Starred elements were also detected by radiochemical methods.
*** Only radiochemical methods were employed for radium.

To achieve further separations, which were not possible with HCl, mixtures of $NH_4Cl$–HCl, NaCl–HCl and KCl–HCl at various concentrations and ratios were used.

In Fig. 1 a few representative separations are shown.

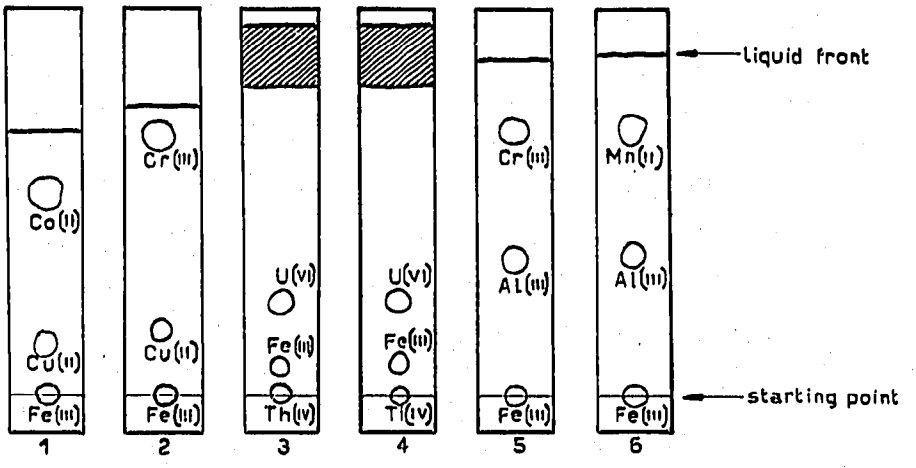


Fig. 1. Representative separations on ZP-paper using: (1) and (2) 0.035 *N* HCl and 0.045 *M* NaCl (1:1); (3) and (4) 2 *N* HCl and 4 *M* $NH_4Cl$ (1:1); (5) and (6) 0.5 *N* HCl. The shaded area represents the localization of several cations, amongst which were La, Ce, Ni, Co, Cr and Al.

The results obtained indicate that ZP-impregnated paper may thus be successfully employed for the chromatographic separation of numerous cations.

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*Istituto di Chimica Generale ed Inorganica, Laboratorio Chimico della Divisione Geomineraria del C.N.R.N., Rome (Italy)*

G. ALBERTI
G. GRASSINI

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