

## SEPARATIONS BY REVERSED-PHASE COLUMN PARTITION CHROMATOGRAPHY WITH KEL-F SUPPORTING TRI-*n*-OCTYLPHOSPHINE OXIDE

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In recent years reversed-phase partition chromatography has received increasing interest in the field of inorganic chemistry, since it helps to solve problems relating to new analytical procedures or to the preparation of certain specific elements. In this connection, the chemistry of nuclear materials or, in general, nuclear reactor technology has provided the incentive.

Tri-*n*-butyl phosphate (TBP), the well known organic solvent which is widely used in the liquid-liquid extraction of substances such as uranium, plutonium, zirconium, thorium, etc., has been fixed on different types of supports and used as the stationary phase in column chromatography.

FIDELIS AND SIEKIERSKI<sup>1, 2</sup> as well as ESCHRICH<sup>3</sup> used suitably treated kieselguhr powder as a support for TBP, while SMALL<sup>4</sup> used styrene-divinylbenzene powder.

TBP is not the only extractant which gives good results. Di-(2-ethylhexyl) orthophosphoric acid on alumina<sup>5, 6</sup>, on polystyrene-divinylbenzene<sup>6</sup>, or on cellulose powder<sup>7</sup>, and tri-*n*-octylamine<sup>8</sup> (TNOA) or tri-*n*-octylphosphine oxide<sup>9</sup> (TOPO) on cellulose powder, have also been used with success.

Recently, a new organic support has been proposed by HAMLIN and co-workers<sup>10</sup>, who fixed TBP or TNOA on poly-trifluoro-chloro-ethylene (Kel-F) and used this material for the selective retention of uranium and its purification.

Since in our laboratory as mentioned above<sup>9</sup>, the system TOPO-cellulose has given good results in the separation of many elements or for the isolation of traces from undesired major components, it was our aim to combine the selectivity of TOPO with the high capacity of Kel-F and to investigate the chromatographic behaviour of this system.

The experiments and results are reported in the present paper.

### EXPERIMENTAL

#### *Reagents and equipment*

Kel-F moulding powder (chemical composition  $[-CClF-CF_2-]_x$ , low density type, grade 300) was supplied by Minnesota S.p.A. (Milan). It is a halofluorocarbon polymer, which is non-inflammable, exceptionally stable and resistant to temperature as well as chemically highly inert.

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Tri-*n*-octylphosphine oxide (chemical composition  $(C_8H_{17})_3PO$ ; mol. wt. 386.65; m.p.  $54-55^\circ$ ) was supplied by Eastman Organic Chemicals, New York, U.S.A.

All the acids, salts and organic compounds were analytical grade.

The chromatographic columns were 8.6 mm i.d. pyrex tubes fitted with a fritted glass disc at the bottom.

The Kel-F powder was ground in a laboratory hammer-mill and reduced to the required size by means of a series of standard sieves.

#### Preparation of Kel-F/TOPO

The general procedure was as follows: to 5 g of Kel-F powder of the required grain size, a solution containing 4 g of TOPO in 9 ml of cyclohexane was added and the mixture stirred in a small beaker until it was homogeneous. Then 20 ml of 1:1 HCl was added and the mixture stirred again for a few minutes and finally allowed to stand for one hour. After that, the mixture was poured into the column and the voids were eliminated by gently pressing with a glass rod. A 12 cm high bed was obtained which was washed with 200 ml of 1:1 HCl to eliminate the excess of organic solution.

Three slightly different preparations (A, B and C) were made in order to select relatively good operating conditions of the bed.

In preparation A, Kel-F powder of 100-170 mesh grain size was used, in preparation B, the grain size was 35-50 mesh, and in preparation C a slight variation of preparation A was obtained by volatilizing cyclohexane at  $60^\circ$  before adding the 20 ml of 1:1 HCl.

Types A and B were used for the separation Fe-Co-Ni, and the results given in Fig. 1 show that the smaller grain size has a favourable effect on the separation and definition of the peaks.

A comparison between types A and C, reported in Fig. 2, shows that on elution of iron with 0.5 M  $H_2SO_4$  the curve is steeper in the case of type A than in that of

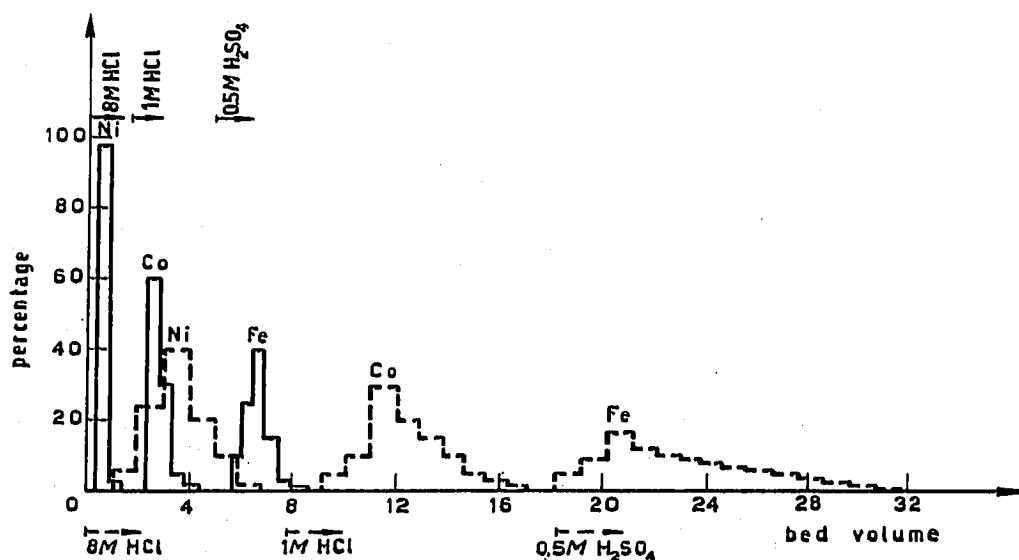


Fig. 1. Effect of grain size of Kel-F on the separation of Ni-Co-Fe. Solid line: 5 g Kel-F 100-170 mesh + 4 g TOPO-cyclohexane (10 ml). Dashed line: 5 g Kel-F 35-50 mesh + 4 g TOPO-cyclohexane (10 ml). Bed volume: 7 cm<sup>3</sup>; feed solution: Fe-Co-Ni, 10 mg each in 0.5 ml of 8 M HCl; flow-rate 0.5 ml/min.

type C. This probably means that TOPO has a higher reactivity when in the presence of the organic solvent than when it is in the solid state even though adsorbed on the surface of the organic support.

These results led us to use the type A preparation for further investigations and the break-through curve reported in Fig. 3 was determined with a  $\text{Fe}^{3+}$  solution. The

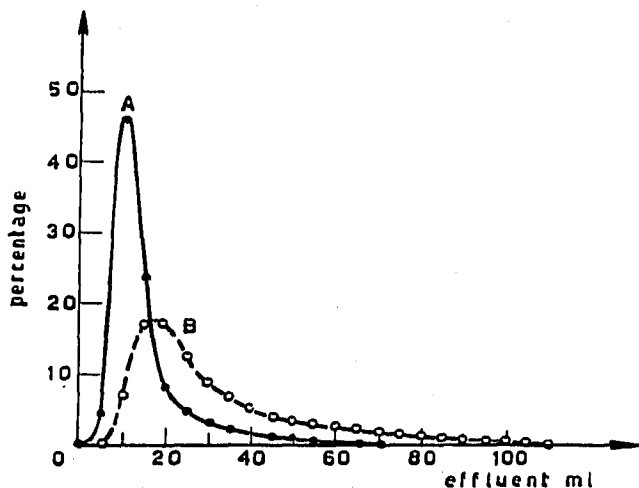


Fig. 2. Elution peak of 10 mg Fe with 0.5 M  $\text{H}_2\text{SO}_4$  at 1 ml/min. Curve A: 100–170 mesh Kel-F; TOPO added in cyclohexane solution without volatilization of the organic solvent. Curve B: the same as curve A, but using a preparation of Kel-F/TOPO from which cyclohexane had been removed by volatilization at 60°.

column was pre-treated with 50 ml of 8 M HCl and then a solution containing 1 mg/ml of iron in 8 M HCl was percolated through the column at 1 ml/min. Iron was well retained by the bed, and its retention within the column could be followed by the slow downward movement of the yellow band. Iron broke through after 115 ml, and the bed was saturated with about 130 mg of iron.

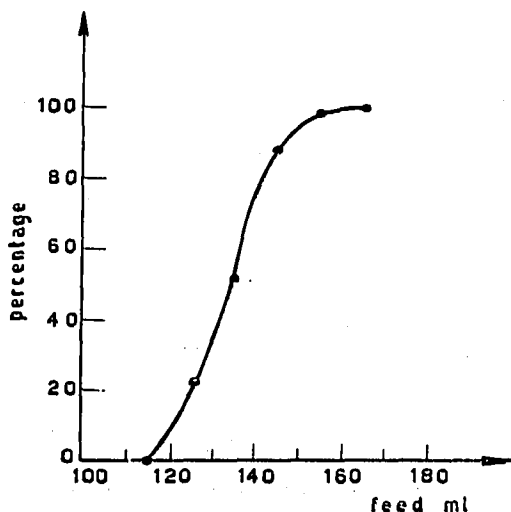


Fig. 3. Break-through curve of iron on a 100–170 mesh Kel-F/TOPO bed (solvent not volatilized). Bed: height 120 mm, volume 7  $\text{cm}^3$ . Feed: 8 M HCl with 1 mg/ml Fe at a rate of 1 ml/min.

## CHEMICAL SEPARATIONS

On the basis of results obtained in experiments carried out some time ago with TOPO-treated cellulose powder<sup>9</sup> or with paper chromatography<sup>11</sup>, the following separations were investigated with Kel-F/TOPO columns. As a general procedure, the hydrochloric solution of the ions to be separated was fed onto the top of the column, and then elution was started with the various solvents at the rates indicated in the legends to the figures.

*Separation of Ni-Co-Fe<sup>3+</sup>-U<sup>6+</sup>*

Nickel is not complexed by hydrochloric acid, and hence it is not retained by the bed. In fact the pale green band of this element moves with the solvent front (8 M HCl), followed by the blue band of cobalt which is only weakly fixed. Iron and uranium (yellow bands) are firmly held on the upper part of the column. As shown in Fig. 4, after the break-through of nickel, cobalt is rapidly eluted with 1 M HCl, whilst iron and uranium are removed with 0.5 M H<sub>2</sub>SO<sub>4</sub> and 4 M H<sub>3</sub>PO<sub>4</sub> respectively.

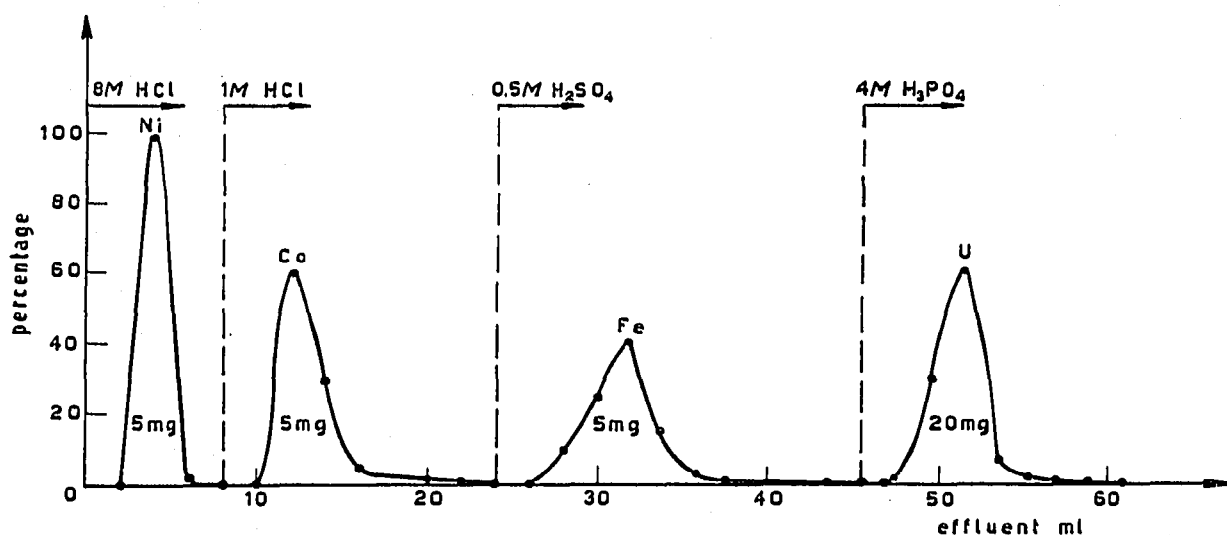


Fig. 4. Separation of Ni-Co-Fe<sup>3+</sup>-U<sup>6+</sup> on a Kel-F/TOPO bed (solvent not volatilized). Bed: height 120 mm, volume 7 cm<sup>3</sup>. Flow-rate 0.5 ml/min. Feed solution volume 0.5 ml.

*Separation of Al-Cu-Fe<sup>3+</sup>-U<sup>6+</sup>*

Aluminium travels with the solvent front (8 M HCl) and copper (yellow band) moves more slowly. In Fig. 5 are shown the elution peaks obtained by using 1 M HCl for copper, 0.5 M H<sub>2</sub>SO<sub>4</sub> for iron and 4 M H<sub>3</sub>PO<sub>4</sub> for uranium.

*Separation of V<sup>4+</sup>-Ti<sup>4+</sup>-U<sup>6+</sup>*

The blue band of vanadium runs along the column with 8 M HCl, whilst titanium and uranium are strongly held. Titanium can be eluted, rather slowly, with 2 M H<sub>2</sub>SO<sub>4</sub>, while for uranium 4 M H<sub>3</sub>PO<sub>4</sub> is used, as usual (Fig. 6).

*Separation of Mn-Cu-U<sup>6+</sup>*

This separation is shown in Fig. 7; manganese is not retained at all in 4 M HCl and forms a pink band which moves with the front. Copper (yellow band) is eluted with 1 M HCl and uranium (yellow band) with 4 M H<sub>3</sub>PO<sub>4</sub>.

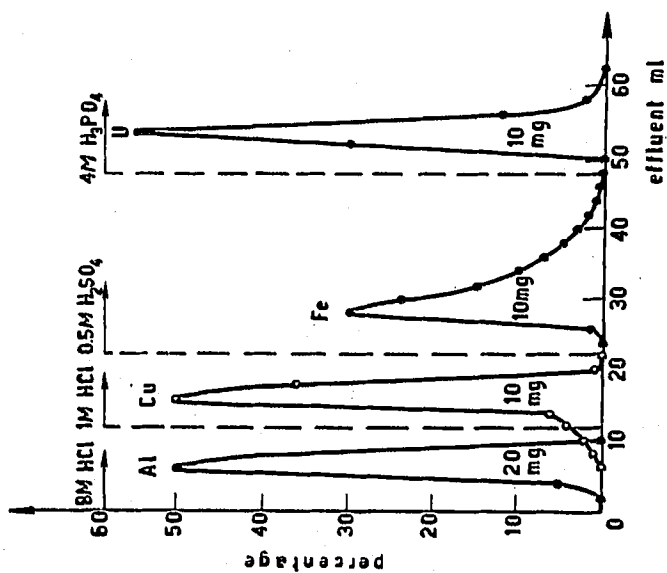


Fig. 5. Separation of Al-Cu-Fe<sup>3+</sup>-U<sup>6+</sup> on a Kel-F/TOPO bed (solvent not volatilized). Bed: height 120 mm, volume 7 cm<sup>3</sup>. Flow-rate 0.5 ml/min. Feed solution volume 2 ml.

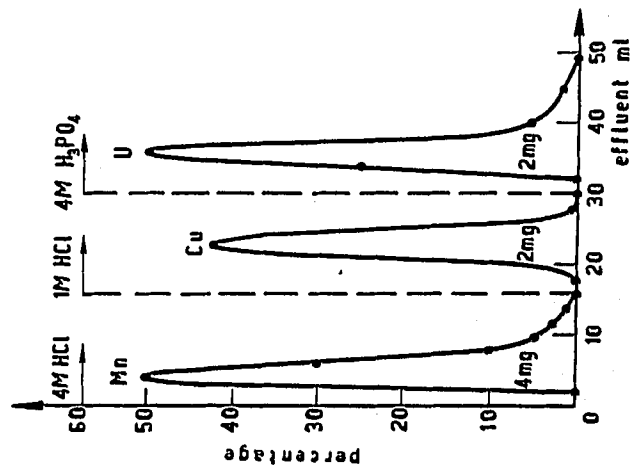


Fig. 7. Separation of Mn-Cu-U<sup>6+</sup> on a Kel-F/TOPO bed (solvent not volatilized). Bed: height 120 mm, volume 7 cm<sup>3</sup>. Flow-rate 1 ml/min.

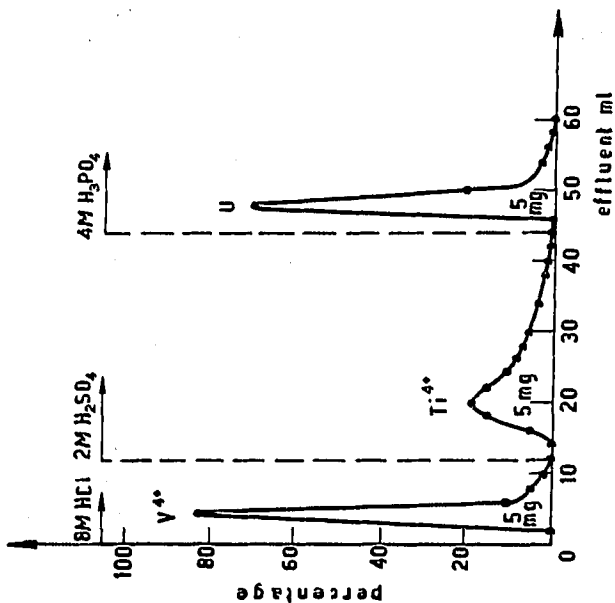


Fig. 6. Separation of V<sup>4+</sup>-Ti<sup>4+</sup>-U<sup>6+</sup> on a Kel-F/TOPO bed (solvent not volatilized). Bed: height 120 mm, volume 7 cm<sup>3</sup>. Flow-rate 1 ml/min. Feed solution volume 1 ml.

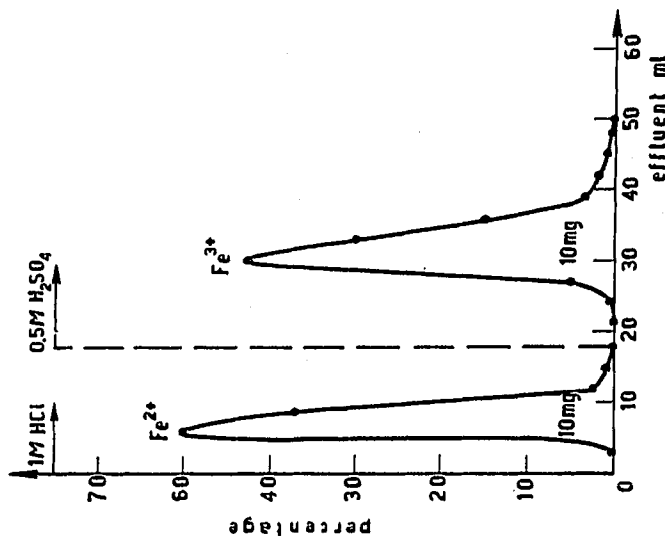


Fig. 8. Separation of Fe<sup>2+</sup>-Fe<sup>3+</sup> on a Kel-F/TOPO bed (solvent not volatilized). Bed: height 120 mm, volume 7 cm<sup>3</sup>. Flow-rate 1 ml/min.

### *Separation of Fe<sup>2+</sup>-Fe<sup>3+</sup>*

Since divalent iron does not form chloride complexes, it can be separated from trivalent iron. In Fig. 8 the elution of Fe<sup>2+</sup> with 1 M HCl and that of Fe<sup>3+</sup> with 0.5 M H<sub>2</sub>SO<sub>4</sub> are shown.

### ISOLATION AND QUANTITATIVE DETERMINATION OF SOME ELEMENTS BY MEANS OF KEL-F/TOPO BEDS

Our previous experiments indicated that the exchange rate and selectivity of Kel-F/TOPO columns are adequate for the isolation of some elements when in the presence of large amounts of other elements. To demonstrate the practical usefulness of the method, some typical cases were investigated and the results obtained are reported in the following sections.

#### *Simultaneous quantitative determination of traces of cobalt and iron in nickel*

A synthetic solution was prepared by dissolving 1 g of nickel containing 0.2 % w/w of cobalt and iron respectively in 25 ml of 8 M HCl. The column used in previous separations, after treatment with 8 M HCl, was fed with the synthetic solution at 2 ml/min.

As mentioned above, nickel was not retained, so that after washing with 20 ml 8 M HCl to remove the last traces of nickel, cobalt was eluted with 10 ml of 1 M HCl at 0.5 ml/min. The cobalt-containing solution was evaporated to dryness and re-dissolved with water. Cobalt was then determined by complexometry, back-titrating with 0.01 M MgSO<sub>4</sub> and using Eriochrome Black T as indicator<sup>12</sup>. The recovery of cobalt was 102 %.

Iron was finally eluted with 30 ml of 0.5 M H<sub>2</sub>SO<sub>4</sub> at 0.5 ml/min; complexometric titration with EDTA and salicylic acid<sup>13</sup> showed a recovery of 100.5 %.

If only iron has to be determined in nickel, a shorter bed (3 cm) can be used; after percolation of the solution at 4 ml/min, iron can be eluted directly with 10 ml of 0.5 M H<sub>2</sub>SO<sub>4</sub>.

If the amounts of cobalt and iron are smaller than those considered above, a spectrophotometric method can of course be used instead of the complexometric titration.

#### *Simultaneous determination of uranium and thorium in dilute solutions containing foreign ions*

Uranium and thorium are very selectively retained by TOPO from a 1 M HNO<sub>3</sub> solution<sup>9,11</sup>; therefore they can easily be separated from alkali metals, alkaline earths, rare earths and from the majority of the chemical elements.

A synthetic solution was prepared consisting of 200 ml of 1 M HNO<sub>3</sub> which contained 40 mg of each of the following ions: Na<sup>+</sup>, Ca<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Al<sup>3+</sup>, Y<sup>3+</sup> and La<sup>3+</sup>.

The solution was fed at 4 ml/min onto a 3 cm high bed of type A Kel-F/TOPO which had been pre-treated with 20 ml of 1 M HNO<sub>3</sub>. After washing the feed container and the bed with 100 ml of 1 M HNO<sub>3</sub> to eliminate any trace of foreign elements, thorium was removed from the bed with 100 ml of 0.5 M HCl. In a 10 ml sample of the solution obtained, thorium was determined by spectrophotometry with thoron, the recovery being 96 %. Uranium was eluted with 25 ml of 1 M H<sub>3</sub>PO<sub>4</sub>, and 5 ml of the solution was checked for uranium with NaOH-H<sub>2</sub>O<sub>2</sub> colorimetry. The recovery was 101.5 %.

*Determination of traces of zirconium in copper*

Zirconium is quantitatively held by Kel-F/TOPO in 1:1 HNO<sub>3</sub>, whilst copper is not retained at all. A synthetic solution was prepared in the following way: 1 g of copper was dissolved in 10 ml of conc. HNO<sub>3</sub>, and then 3 mg of zirconium were added. This solution was reduced to 2 or 3 ml by evaporation and then 20 ml of 1:1 HNO<sub>3</sub> was added.

The liquid obtained was fed onto the bed, which had been pre-treated with 20 ml of 1:1 HNO<sub>3</sub>, at a flow-rate of 1 ml/min. The bed was washed with 20 ml of 1:1 HNO<sub>3</sub> at the same flow-rate and finally zirconium was eluted at 0.5 ml/min with 20 ml of 0.5 M oxalic acid.

After elimination of oxalic acid by heating the solution with perchloric acid, the liquid was evaporated almost to dryness, then 50 ml of distilled water were added, and zirconium was determined by complexometry, back-titrating with 0.01 M FeCl<sub>3</sub> and salicylic acid<sup>12</sup>. The error in this analysis was  $\pm 3\%$ .

When zirconium is present in microgram quantities, colorimetric determination of this element becomes necessary.

*Evaluation of the exchange capacity of a type A Kel-F/TOPO bed, after 15 cycles*

The exchange capacity of a type A Kel-F/TOPO bed which had been used for 15 consecutive cycles was determined again at the end of the last cycle. The usual solution of iron, 1 mg/ml, in 8 M HCl was used. The exchange capacity was found to be about 30 % less than the initial value. In view of the fact that during the numerous cycles the bed comes into contact with hydrochloric, nitric, sulphuric, and phosphoric acid of various concentrations, this result can be considered as quite satisfactory.

## CONCLUSIONS

Kel-F was found to be a suitable inert support for solutions of TOPO-cyclohexane. As was to be expected from the general data on halofluorocarbon polymers, this support is practically unaffected by acids, alkalis and, to a large extent, also by temperature. By virtue of its porosity it is able to retain a considerable amount of the organic extractant which is not appreciably stripped by the aqueous solution used in the chromatographic process.

As confirmed also by preceding work<sup>9, 11</sup>, the great extractive ability of TOPO and its good reaction rate make it suitable for use in a great variety of chemical separations, narrow peaks being obtained. In addition, traces of some elements in dilute solutions and in the presence of foreign ions can be retained by passing the liquid rapidly through short beds of Kel-F/TOPO. The columns can be prepared very quickly and each column can withstand many operative cycles with only a relatively small loss of exchange capacity.

## SUMMARY

The use of chromatographic columns filled with Kel-F (poly-trifluorochloro-ethylene) supporting concentrated solutions of tri-*n*-octylphosphine oxide (TOPO) in cyclohexane has been investigated.

After selecting the best way of preparing the columns examples are given of the following separations: Fe<sup>3+</sup>-Co-Ni-U<sup>6+</sup>, V<sup>4+</sup>-Ti<sup>4+</sup>-U<sup>6+</sup>, Mn-Cu-U<sup>6+</sup>; Al-Cu-Fe<sup>3+</sup>-U<sup>6+</sup> and Fe<sup>2+</sup>-Fe<sup>3+</sup>.

Short columns of Kel-F/TOPO were also used for the isolation and quantitative determination of traces of elements in dilute solutions and in the presence of large amounts of foreign ions. The following examples are discussed: Fe and Co in Ni, U and Th in the presence of 13 foreign ions and Zr in Cu.

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