

## ION EXCHANGE PROCEDURES

## VII. SEPARATION OF ALKALI METAL IONS\*,\*\*

FREDERICK NELSON, DONNA C. MICHELSON, HAROLD O. PHILLIPS AND  
KURT A. KRAUS

*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. (U.S.A.)*

(Received March 12th, 1965)

This paper describes procedures for separating alkali metal ions from each other. The methods are based on published data and some new results on adsorption of these elements by a sulphonated cation exchange resin of the phenol-formaldehyde type and by the inorganic exchanger, hydrous zirconium phosphate.

Separation of alkali metals by cation exchange has been studied extensively with both organic and inorganic exchangers. With inorganic exchangers, *e.g.* hydrous zirconium phosphate, hydrous zirconium tungstate and ammonium phosphomolybdate, separation factors are generally more favorable than with organic resins and some striking alkali metal separations have been achieved with relatively short columns<sup>2-4</sup>. The distribution coefficients of the lightest alkali metals, Li and Na, are usually low with these materials and their separation requires low ionic strength media. Also the selectivity for Cs in acid solutions is usually so high that its elution is difficult. On the other hand, hydrous zirconium antimonate<sup>5</sup> shows a unique order of selectivity for alkali metals. In acid solutions, it has an unusually high selectivity for Na relative to Cs and other alkali metals and appears promising in other respects for alkali metal separations. However, at present the material is not sufficiently available to recommend its use in routine separation schemes.

Of the organic exchangers, sulphonated polystyrene-divinylbenzene (*e.g.* Dowex 50, Amberlite IR 120, etc.) and sulphonated phenol-formaldehyde (*e.g.* Duolite C-3, Zeo-Karb 215, etc.) have been used most frequently for alkali metal separations. Aqueous solvents<sup>6-10</sup> and mixed solvents *e.g.* HCl-water-methanol<sup>11-13</sup>, HCl-water-acetone<sup>14</sup> and HCl-water-methanol-phenol<sup>15</sup> have been employed to separate alkali metals.

From examination of data obtained with inorganic and organic exchangers it first appeared that HCl-water-methanol solutions and organic resins would be the most satisfactory systems for routine separation of the alkali elements but optimum conditions could not be deduced. In addition, it was not apparent if polystyrene or phenol-formaldehyde resins would give the better separation factors. A comparative study of the adsorption of alkali metals by resins of both types thus seemed desirable and adsorption functions in HCl-water-methanol solutions were determined for a

\* Research jointly sponsored by The Office of Saline Water, U.S. Department of the interior, and U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

\*\* For Part VI see Ref. 1.

wide range of acid concentrations and solvent compositions. From these data a procedure was devised for separating the alkali elements, Li through Cs. In this procedure, K and Rb are eluted together unless long columns of resin are employed. An alternate procedure was developed for separating these elements on zirconium phosphate columns.

#### EXPERIMENTAL

Phenol-formaldehyde-sulphonic acid resin (Duolite C-3, 10-50 mesh)\* in the hydrogen-form was ground in a porcelain ball mill and dry-sieved to obtain particles of mesh size 325-400. Resin capacity (sulphonate groups) was 2.77 equiv. per kg dry resin (dried over "Anhydrone" in a vacuum desiccator at 60°). The resin had a bed volume of 3.18 ml per g dry resin in 1 M HCl and a bed capacity of 0.87 equiv. per liter bed.

The polystyrene-divinylbenzene-sulphonic acid resin (Dowex 50-X8, —400 mesh, hydrogen-form) had a capacity of 5.1 equiv. per kg dry resin. Its bed volume in 1 M HCl was 2.55 ml per g dry resin and its bed capacity 2.0 equiv. per liter bed.

The zirconium phosphate studied was "Bio-Rad ZP-1", 100-200 mesh, in the hydrogen-form\*\*. The exchanger was characterized by measuring adsorption of  $\text{NH}_4^+$  from 1 M  $\text{NH}_4\text{Cl}$ -1 M HCl mixtures over a wide range of acidity. Weighed amounts of the material, initially in the hydrogen-form, were equilibrated with the solutions for 30 min. The solution phase was separated and analysed for HCl by titration with standard base or, when the HCl concentration was low, by measurement of pH. At low acidities (pH 4 to 7) uptake of  $\text{NH}_4^+$  was measured by equilibrating the exchanger with 1 M  $\text{NH}_4\text{Cl}$ -1 M  $\text{NH}_3$  mixtures since, with these solutions, low equilibrium acid concentration could be attained more easily. In computing  $\text{NH}_4^+$  uptake, equivalent exchange between  $\text{NH}_4^+$  and hydrogen in the solid was assumed.

Distribution coefficients,  $D_v$ , (amount per liter bed/amount per liter solution) were obtained by the band elution technique when adsorption was low and by batch equilibration when adsorption was high ( $D_v > ca. 20$ ). Metal analyses were carried out radiometrically with the tracers  $^{22}\text{Na}$ ,  $^{42}\text{K}$ ,  $^{86}\text{Rb}$ ,  $^{134}\text{Cs}$  and  $^{223}\text{Fr}$ ; lithium and, in some cases, potassium were determined by flame spectrophotometry. In some column experiments with Li, aliquots containing 0.01 M LiCl were added. The columns were eluted with HCl solutions and peak positions determined by evaporating aliquots of effluent on black spot plates. Lithium concentrations were estimated visually from the amount of residue.

Batch distribution measurements with  $\text{Fr}^+$  were carried out by equilibrating  $^{223}\text{Fr}$  ( $T_{1/2} = 22$  m) solutions with weighed amounts of resin for 10 min. With the fine mesh resin used, this equilibration time was found to be adequate through parallel experiments with  $^{134}\text{Cs}$ . Most column experiments with  $\text{Fr}^+$  were carried out at flow rates of *ca.* 1 cm/min, and with relatively short (1 cm) columns of resin so that measurements could be completed before appreciable decay had occurred.

The  $^{223}\text{Fr}$ , a daughter of  $^{227}\text{Ac}$ , was separated by cation exchange from the parent immediately before use. A typical separation is shown in Fig. 1. The  $^{227}\text{Ac}$  was adsorbed from 1 M HCl on a 0.20 cm<sup>2</sup> × 1 cm column of Dowex 50-X4, —400

\* From Diamond Alkali Co., Redwood City, California.

\*\* From Bio-Rad Laboratories, Richmond, California.

mesh resin. On elution with 1 M HCl, the short-lived decay products (36 m  $^{211}\text{Pb}$  and 2.16 m  $^{211}\text{Bi}$ ) were removed with the first two column volumes (c.v.) of effluent;  $^{223}\text{Fr}$  appeared near 4 to 5 c.v. while  $^{227}\text{Ac}$ ,  $^{223}\text{Ra}$  and  $^{227}\text{Th}$  remained strongly adsorbed. The column could be "milked" again after sufficient time had elapsed for growth of Fr daughter.

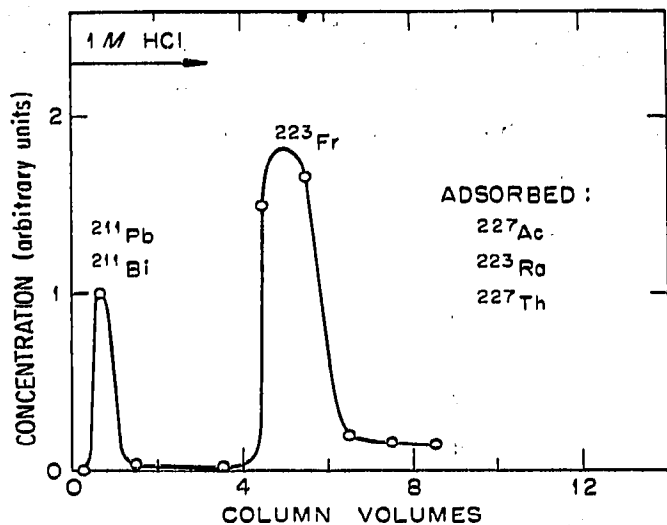


Fig. 1. Separation of  $^{223}\text{Fr}$  from  $^{227}\text{Ac}$  and its decay products (Dowex 50-X4, —400 mesh, 1 cm  $\times$  0.2 cm<sup>2</sup> column, flow rate 1 cm/min, 25°).

## RESULTS AND DISCUSSION

### (1) Adsorption on Dowex 50

Distribution coefficients of alkali metal ions on Dowex 50-X8 in HCl-water solutions are shown in Fig. 2 as log-log plots of  $D_v$  vs.  $M_{\text{HCl}}$ . The slope,  $d \log D_v / d \log M_{\text{HCl}}$  is about  $-1$  at low HCl concentration as expected for "ideal" 1:1 exchange. Departures from unit slope occur at very high HCl concentration, and, as observed

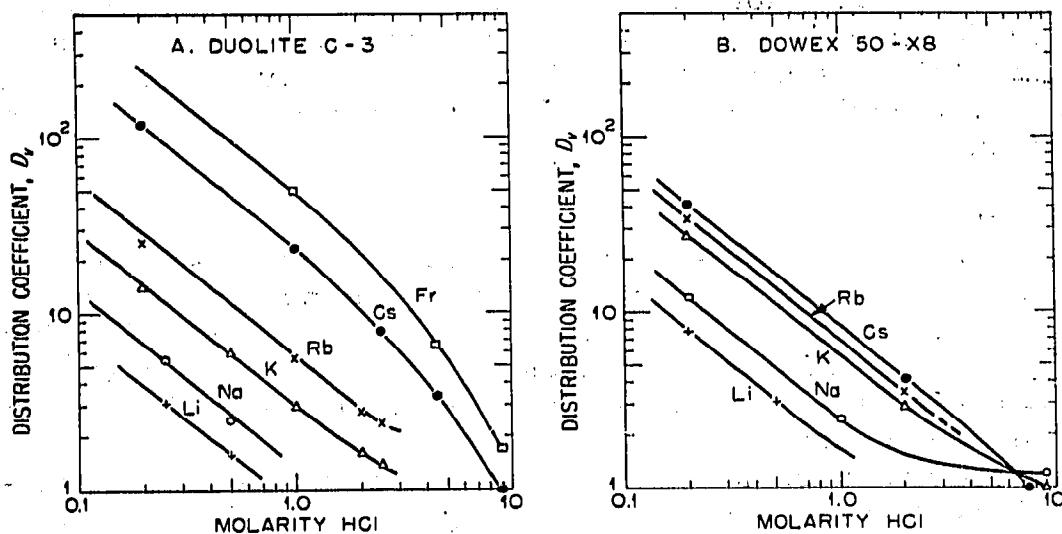


Fig. 2. Adsorption of alkali metals from HCl solutions. (A) Duolite C-3. (B) Dowex 50-X8 (25°).

by others<sup>16,17</sup>, the adsorption order of some alkali metals on Dowex 50 reverses. Over the entire range of HCl concentration, differences in adsorbability of the higher alkali metals (K, Rb and Cs) are small.

Distribution coefficients of alkali metal ions on Dowex 50-X8 in HCl-water methanol mixtures of high methanol content (80 vol. % methanol) are given in Fig. 3, a log-log plot of  $D_v$  vs.  $M_{\text{HCl}}$ . The functions are similar to those for aqueous HCl media but distribution coefficients are larger in 80 % methanol solutions than in aqueous solutions. Differences in adsorbability of K, Rb and Cs are small and inversion of the adsorption order of these elements occurs near 1 M HCl. Ratios of adsorbability of Li and Na are significantly larger in 80 % methanol solution than in aqueous HCl solutions.

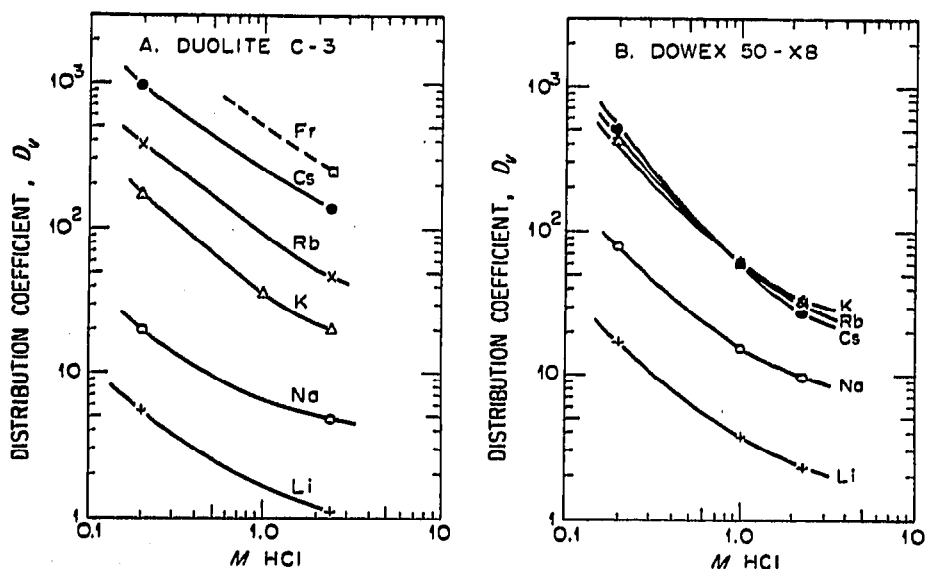


Fig. 3. Adsorption of alkali metals from HCl-H<sub>2</sub>O-CH<sub>3</sub>OH mixtures (80 % CH<sub>3</sub>OH by vol., 25°).

The effect of methanol concentration on the adsorbability of alkali metals on Dowex 50-X8 is shown in Fig. 4, a plot of  $\log D_v$  (at 0.2 M HCl) vs. vol. % methanol (up to 80 %).  $\log D_v$  increases in a non-linear manner with increasing methanol content. Ratios of adsorbabilities of K, Rb and Cs decrease slightly with increasing methanol concentration while the ratios for Li, Na and K increase with increasing methanol concentration.

### (2) Adsorption on Duolite C-3

Adsorbabilities of alkali metal ions on Duolite C-3 in HCl-water solutions are also shown in Fig. 2. While ratios of adsorbabilities of Li, Na and K are about the same for Duolite C-3 and Dowex 50-X8, the ratios for K, Rb, and Cs are considerably larger for Duolite C-3. Thus at 1 M HCl, adsorbability of the alkali metals on Duolite C-3 varies from  $D_v = 0.9$  for Li<sup>+</sup> to  $D_v = 24$  for Cs<sup>+</sup> while for Dowex 50-X8, the corresponding values are  $D_v = 1.6$  and 8.5.

Adsorption functions of alkali metal ions on Duolite C-3 in HCl-water-methanol solutions containing 80 % methanol are shown in Fig. 3. Ratios of adsorbability of Li, Na and K are about the same as those observed for Dowex 50-X8. The ad-

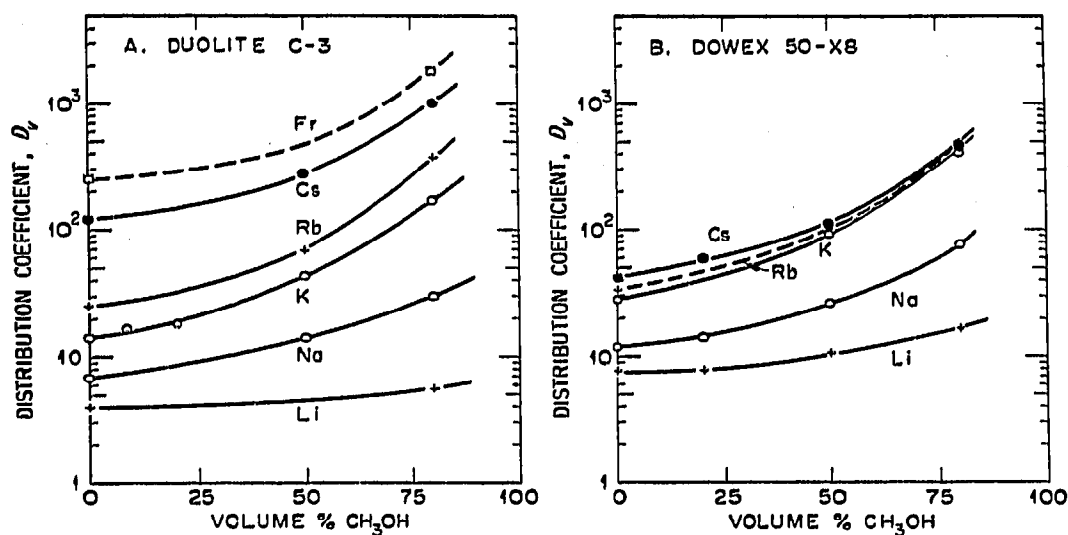


Fig. 4. Adsorption of alkali metals from HCl- $\text{H}_2\text{O}$ - $\text{CH}_3\text{OH}$  mixtures. (A) Duolite C-3. (B) Dowex 50-X8 (0.2 M HCl, 25°).

sorbability ratios of the heavy alkali metals (K, Rb, Cs and, presumably, Fr) are much larger with Duolite C-3 than with Dowex 50-X8.

The effect of methanol concentration on the adsorbability of alkali metals on Duolite C-3 is shown in Fig. 4. As with Dowex 50-X8,  $\log D_v$  increases with methanol content. The ratio  $D_v(\text{Na})/D_v(\text{Li})$  increases with increasing methanol content,  $D_v(\text{Rb})/D_v(\text{K})$  remains about the same and  $D_v(\text{Cs})/D_v(\text{Rb})$  and  $D_v(\text{Fr})/D_v(\text{Cs})$  decrease slightly with increasing methanol content.

### (3) Separations with Dowex 50-X8 and Duolite C-3

(a) *General.* Based on the adsorption data (Figs. 2-4) numerous column separations involving alkali metals may be devised; separation factors,  $\alpha(A/B) = D_v(A)/D_v(B)$ , where A and B are alkali metals, are summarized in Table I for Dowex 50-X8 and Duolite C-3 in aqueous and 80% methanol solutions at  $M_{\text{HCl}} = 1$ .

TABLE I  
SEPARATION FACTORS FOR ALKALI METALS  
(1 M HCl, 25°)

$\alpha$	Duolite C-3		Dowex 50-X8	
	$\text{H}_2\text{O}$	80% methanol	$\text{H}_2\text{O}$	80% methanol
Na/Li	1.8	4.1	1.5	4.2
K/Na	2.3	5.4	2.3	3.9
Rb/K	1.9	2.2	1.2	1.0
Cs/Rb	4.2	2.8	1.2	1.0
Fr/Cs	2.1	2.0		

Separability of  $\text{Li}^+$  from  $\text{Na}^+$  and of  $\text{Na}^+$  from  $\text{K}^+$  and other alkali metals is significantly improved through use of HCl-methanol-water mixtures. For example, with Duolite C-3 in aqueous 1 M HCl,  $\alpha(\text{Na}/\text{Li})$  and  $\alpha(\text{K}/\text{Na})$  are 1.8 and 2.3, respec-

tively, while the corresponding values in 1 *M* HCl–80% methanol solution are 4.1 and 5.4. A similar improvement in separability of these elements in methanol solutions occurs with Dowex 50-X8.

Except for solubility considerations there appears to be no advantage to using HCl solutions of intermediate methanol concentrations as eluting agents. Difficulties from the limited solubilities particularly of the higher alkali metal chlorides at high (*e.g.* 80%) methanol concentration, however, can largely be avoided by first adsorbing the elements from an aqueous solution. Elution may then be carried out with 80% methanol solutions. Apparently the high selectivity of the resin for the heavier alkali metals prevents their precipitation in the column and samples containing appreciable concentrations of alkali metal chlorides (*ca.* 0.1 *M* in each) can be handled without encountering precipitation problems. Some typical separations based on the adsorption functions of Figs. 2 and 3 are shown in Figs. 5 through 8.

(*b*) *Separation of Li<sup>+</sup> from Na<sup>+</sup> and heavy alkali metal ions (Fig. 5).* For the separation of Li<sup>+</sup> and Na<sup>+</sup> and the group of heavy alkali metals a 0.5 ml sample containing 0.01 *M* LiCl, <sup>24</sup>Na, <sup>42</sup>K, <sup>86</sup>Rb and <sup>134</sup>Cs tracers in 0.03 *M* HCl was added to a 0.28 cm<sup>2</sup> × 4 cm column of Dowex 50-X8 (–400 mesh) which had been washed with water.

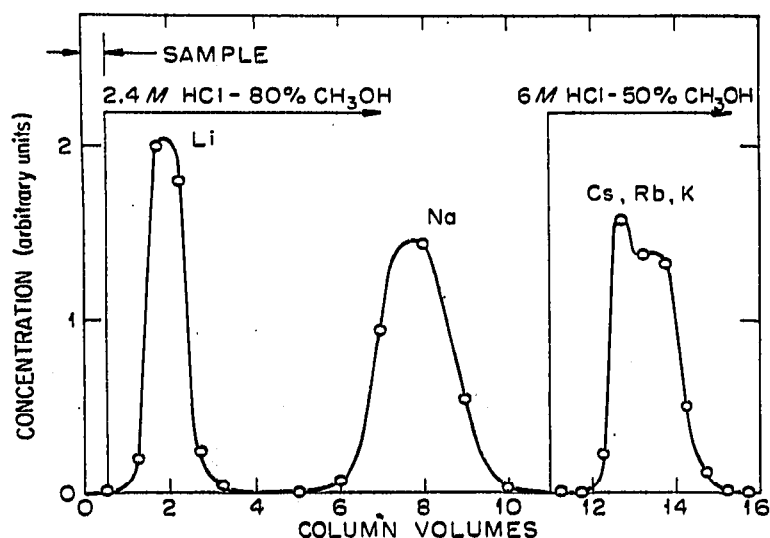


Fig. 5. Separation of Li, Na, Cs–Rb–K by cation exchange (Dowex 50-X8, –400 mesh, 4 cm × 0.28 cm<sup>2</sup> column, 25°).

On elution with 2.4 *M* HCl–80% methanol, Li<sup>+</sup> appeared in a sharp band near 2 column volumes (c.v.) and Na<sup>+</sup>, in a slightly broader band, near 8 c.v. No significant overlap occurred. Cs<sup>+</sup>, Rb<sup>+</sup> and K<sup>+</sup> were removed as a group with 4 c.v. of 6 *M* HCl–50% methanol, though satisfactory removal can also be achieved with aqueous 6 to 12 *M* HCl solutions.

(*c*) *Separation of Rb<sup>+</sup>, Cs<sup>+</sup> and Fr<sup>+</sup> (Fig. 6).* Separation of Cs<sup>+</sup> and Rb<sup>+</sup> at tracer concentrations is of importance in fission product analyses. In aqueous HCl solutions, the separation factor for Cs<sup>+</sup> and Rb<sup>+</sup> on Duolite C-3 is especially favorable,  $\alpha(\text{Cs/Rb}) = 4.2$ , hence separation of these elements is easily achieved with relatively short columns; a typical experiment is shown in Fig. 6A. For this separation a 0.5 ml aliquot containing <sup>86</sup>Rb and <sup>134</sup>Cs tracers in 2.5 *M* HCl was added to a 0.28 cm<sup>2</sup>

$\times 4$  cm column of 325–400 mesh Duolite C-3. On elution with 2.5 *M* HCl,  $^{80}\text{Rb}$  appeared in a sharp band near 3 c.v. of effluent while  $^{134}\text{Cs}$  remained adsorbed;  $^{134}\text{Cs}$  was removed with 9 *M* HCl.

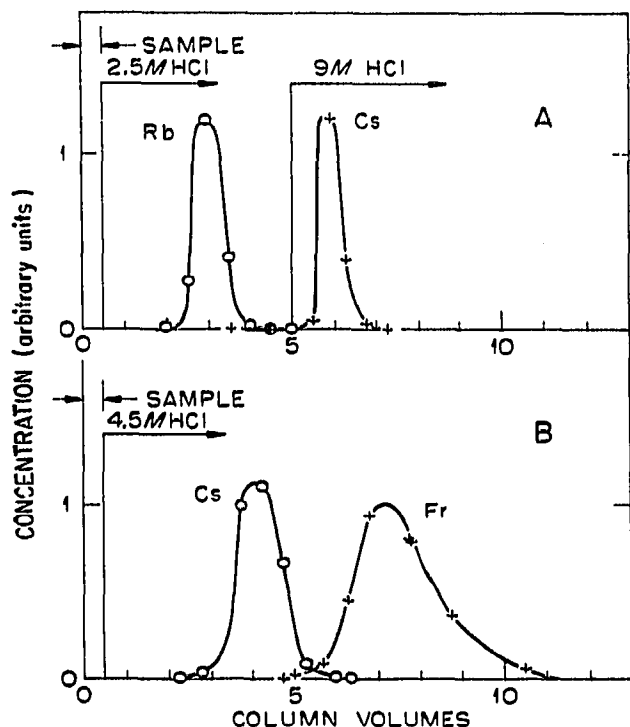


Fig. 6. Separation of Rb-Cs and Cs-Fr by cation exchange (Duolite C-3,  $0.28 \text{ cm}^2 \times 4 \text{ cm}$  column, 400–325 mesh,  $25^\circ$ ).

One might have expected that  $\text{Fr}^+$  and  $\text{Cs}^+$  would also be readily separated with Duolite C-3. However, in aqueous 4–10 *M* HCl solutions, where adsorbability of these elements is relatively low,  $\alpha(\text{Fr}/\text{Cs})$  is only *ca.* 2 and with short columns (*ca.* 4 cm) and elution rates of the order of one cm/min, overlap of the elution bands occurs. A typical column experiment is shown in Fig. 6B. The same column of Duolite C-3 resin used for the Rb-Cs separation (Fig. 6A) was pretreated with 4.5 *M* HCl. A 0.5 ml aliquot containing  $^{134}\text{Cs}$  and  $^{223}\text{Fr}$  in 4.5 *M* HCl was added and elution continued with 4.5 *M* HCl. Cs and Fr appeared in slightly overlapping elution bands at *ca.* 4 and 7 c.v. of effluent, respectively.

(d) *Separation of alkali metals, Li through Cs (Figs. 7, 8).* Separation of the alkali metals, Li through Cs, with Duolite C-3 is illustrated in Figs. 7 and 8. A method employing two columns was used since it was concluded from the adsorption data that complete separation could then be achieved in the least amount of time. Li, Na and Cs are eluted individually from the first column; K and Rb are eluted together and then separated on a second, longer column. For the separations of Fig. 7, a 0.5 ml sample containing the alkali metal chlorides (0.1 *M* each) in water was added to a  $0.28 \text{ cm}^2 \times 4 \text{ cm}$  column of water-washed Duolite C-3. On elution of the column with 2.4 *M* HCl–80% methanol solution, Li appeared in a sharp band near 1.6 c.v. and Na, near 5.5 c.v.; K and Rb were eluted with 1.5 *M* HCl and Cs, with 4 *M* HCl.

The K–Rb fraction was evaporated to near dryness, taken up in 0.5 ml of 1.5 *M*

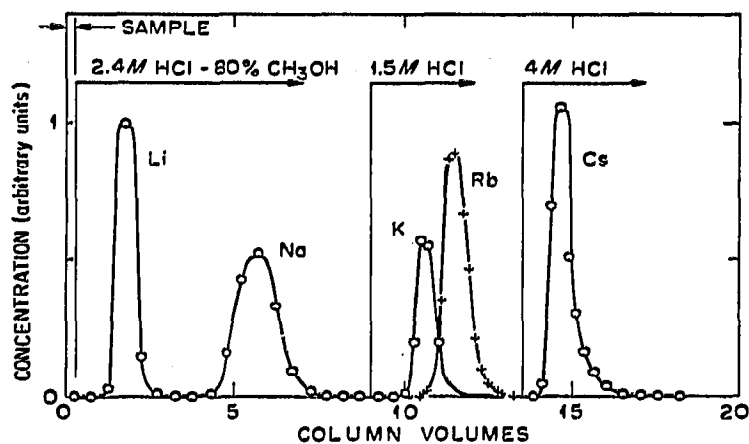


Fig. 7. Separation of alkali metals by cation exchange (Duolite C-3, 325-400 mesh,  $0.28 \text{ cm}^2 \times 4 \text{ cm}$  column,  $25^\circ$ ).

HCl and added to a longer column ( $0.28 \text{ cm}^2 \times 12 \text{ cm}$ ) of the same resin. As shown in Fig. 8, K was removed in a sharp band with  $1.5 \text{ M}$  HCl and Rb with  $6 \text{ M}$  HCl. Although the separation was carried out at a slow flow rate (*ca.*  $0.4 \text{ cm/min}$ ) to reduce overlap of the K and Rb bands, about 1% of the Rb appeared in the K fraction and about 1% of the K was in the Rb fraction.

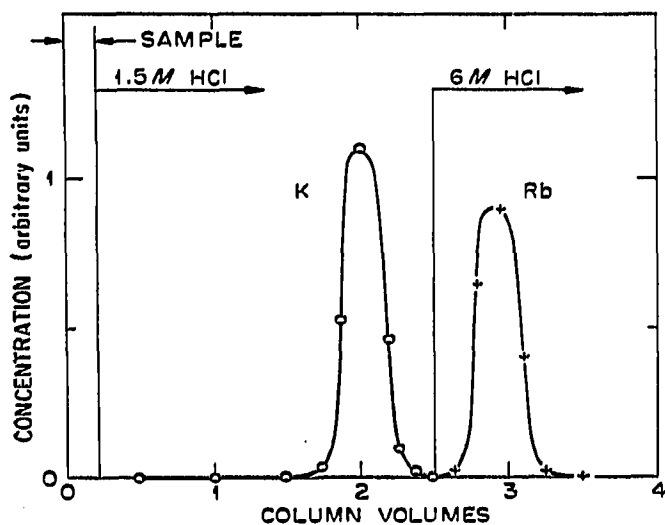


Fig. 8. Separation of K and Rb by cation exchange (Duolite C-3, 325-400 mesh,  $0.28 \text{ cm}^2 \times 12 \text{ cm}$  column,  $25^\circ$ ).

#### (4) Adsorption on zirconium phosphate

(a) *General.* While the separation factors  $\alpha(\text{Na/Li})$ ,  $\alpha(\text{K/Na})$  and  $\alpha(\text{Cs/Rb})$  are satisfactory with organic resins,  $\alpha(\text{Rb/K})$  and  $\alpha(\text{Fr/Cs})$  are only about 2, at best (Table I). Thus quantitative separation of Rb from K and of Fr from Cs require long columns and considerable time. Methods of separating Fr from Cs are rarely needed but methods for separating Rb from K or separating small amounts of Rb from large amounts of K are frequently required. Further studies with K and Rb thus seemed desirable and the adsorbability of these elements on a commercial preparation of the inorganic exchanger, hydrous zirconium phosphate, was examined. Two other commer-



cially available exchangers of this type (zirconium tungstate and ammonium phosphomolybdate) were also examined in a preliminary study; they did not seem to offer sufficient advantages over zirconium phosphate, however, and were therefore not studied further.

Since the introduction of zirconium phosphate as a cation exchanger<sup>2,18</sup>, a large amount of work has been carried out with this material in many laboratories throughout the world. While a review of these studies is beyond the scope of this paper, it is noteworthy that different workers using materials of their own preparation often find significant differences in properties. Thus, capacities sometimes vary widely from one preparation to another as do rates of exchange. Zirconium phosphate precipitates dried at low temperature and used in a powder form appear particularly suitable for column separations<sup>2</sup>. In some gel forms<sup>3,19</sup> the materials have considerably different titration curves and slow rates of exchange so that difficult separations cannot be achieved with short columns without overlap of elution bands. Because of the divergence of properties of materials made in different laboratories, it would seem premature to recommend the use of zirconium phosphate for routine separations; however, since at least one vender supplies a commercial product, evaluation of this material for separations seemed appropriate.

(b) *Adsorption of  $\text{NH}_4^+$  (Fig. 9)*. The properties of zirconium phosphate are somewhat reminiscent of those of weak acid exchangers and uptake of cations other than  $\text{H}^+$  varies widely with the acidity of the solution. For the material we studied,

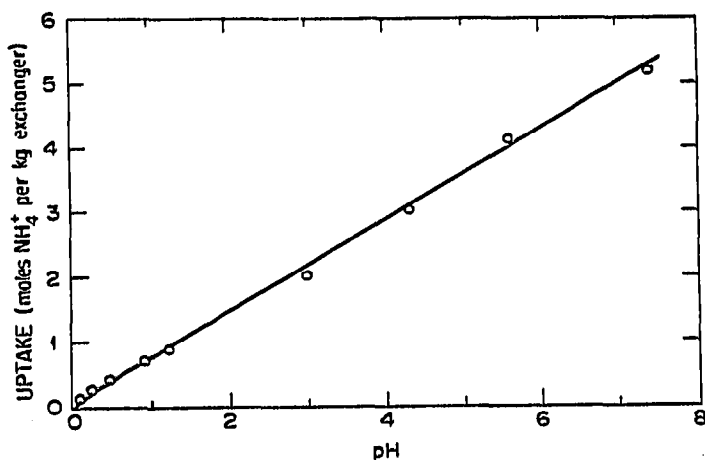


Fig. 9. Uptake of  $\text{NH}_4^+$  by zirconium phosphate in 1 M  $\text{NH}_4\text{Cl}$ -HCl mixtures (Bio-Rad ZP-1, 25°).

Bio Rad ZP-1, the  $\text{NH}_4^+$  concentration of the exchanger in HCl- $\text{NH}_4\text{Cl}$  mixtures of total ionic strength  $\mu = 1$  varied essentially linearly with pH from pure 1 M HCl solutions to 1 M  $\text{NH}_4\text{Cl}$  solutions at pH 7 (see Fig. 9). At pH 4, we find an uptake for  $\text{NH}_4^+$  of 2.9 equiv./kg exchanger which is very much higher than that given by the manufacturer (1.25 equiv./kg exchanger). Our higher value presumably results from a higher  $\text{NH}_4^+$  concentration of the medium used in the measurements. We found a volume capacity of 1.1 equiv./l of bed at pH 4.

Linear variations of uptake with pH have also been observed by others<sup>2,19,20</sup>. Uptake curves with some higher alkali metals have shown a rapid rise at the acid end before becoming substantially linear<sup>20</sup>. With other preparations of zirconium

phosphate, however, inflections similar to weak acid titration curves have been observed<sup>3, 21</sup>.

(c) *Adsorption of  $K^+$ ,  $Rb^+$  and  $Cs^+$  (Fig. 10)*. The ability of zirconium phosphate to adsorb alkali metal ions depends greatly on the degree of neutralization of the exchanger. This is illustrated in Fig. 10 (see also ref. 2) where  $D_v$  of tracer  $K^+$ ,  $Rb^+$  and  $Cs^+$  is plotted on a log-log scale against  $F_{HCl}$ , the fraction HCl in the solution. In the region  $F_{HCl} = 1$  to 0.5,  $D_v$  decreases abruptly with decreasing  $F_{HCl}$ . For  $K^+$  and

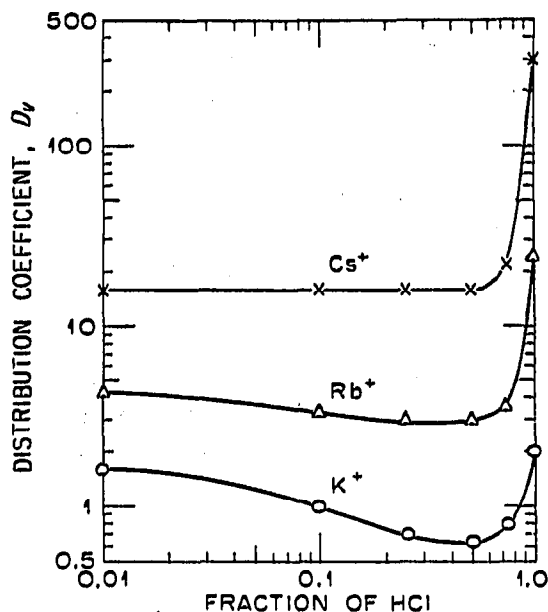


Fig. 10. Adsorption of  $K^+$ ,  $Rb^+$  and  $Cs^+$  from 1 M  $NH_4Cl$ -HCl mixtures (zirconium phosphate, 50°).

$Rb^+$ ,  $D_v$  gradually rises with further decrease of  $F_{HCl}$  while  $D_v$  of  $Cs^+$  becomes essentially constant. Maximum ratios of  $D_v$  occur at high acidity where the exchanger is substantially in the hydrogen-form; in neutral solution where the exchanger is substantially in the  $NH_4^+$ -form, differences in adsorbability are small. Thus,  $\alpha(Rb/K)$  decreases from 12.5 at  $F_{HCl} = 1$  to 4.6 at  $F_{HCl} = 0.5$  where the adsorption functions go through minima. At  $F_{HCl} = 0.01$ ,  $\alpha(Rb/K)$  is about 2. In neutral solutions, group elution of the alkali metals was reported for a different zirconium phosphate preparation<sup>2</sup>.

Because of the rapid decrease of  $D_v$  of  $K^+$  and  $Rb^+$  with loading of the exchanger with  $NH_4^+$  or other cations, separation of K and Rb is difficult when both are at moderately high concentrations. The distribution coefficients which then apply are determined by the salt content of the medium. For example, at  $\mu = 1$  and  $F_{HCl} = 0.8$ , loading by alkali metal is *ca.* 0.1 moles/kg and  $\alpha(Rb/K)$  is only 5. At  $F_{HCl} = 1$ ,  $\alpha(Rb/K)$  is 12.5. However, the larger separation factor should apply for separation of trace quantities of Rb from macro amounts of K. As soon as the macro-potassium has been eluted, the column returns essentially to the hydrogen-form and the distribution coefficients of Rb which are applicable are those at  $F_{HCl} = 1$ .

(d) *Separation of  $K^+$ ,  $Rb^+$  and  $Cs^+$  (Fig. 11)*. Column separations of K, Rb and Cs at tracer concentrations were devised from the adsorption data of Fig. 10 to test

the applicability of this preparation of zirconium phosphate to separations. In a typical case, a  $0.28 \text{ cm}^2 \times 3 \text{ cm}$  column of Bio-Rad ZP-1 (100–200 mesh, hydrogen-form) in a water jacket at  $50^\circ$  was pretreated with *ca.* 2 column volumes of  $2 \text{ M HCl}$  and a  $0.5 \text{ ml}$  sample containing  $^{42}\text{K}$ ,  $^{86}\text{Rb}$  and  $^{134}\text{Cs}$  tracers in  $2 \text{ M HCl}$  was added. On elution with  $2 \text{ M HCl}$ ,  $^{42}\text{K}$  appeared in a sharp band near 2.5 c.v. and was completely eluted after about 5 c.v. Rb was removed with  $0.5 \text{ M HCl}$ – $0.5 \text{ M NH}_4\text{Cl}$ , in which medium its adsorbability is low; the Rb band tailed and about 2% of the Rb remained on the column after treatment with 6.5 c.v. of  $0.5 \text{ M HCl}$ – $0.5 \text{ M NH}_4\text{Cl}$ .

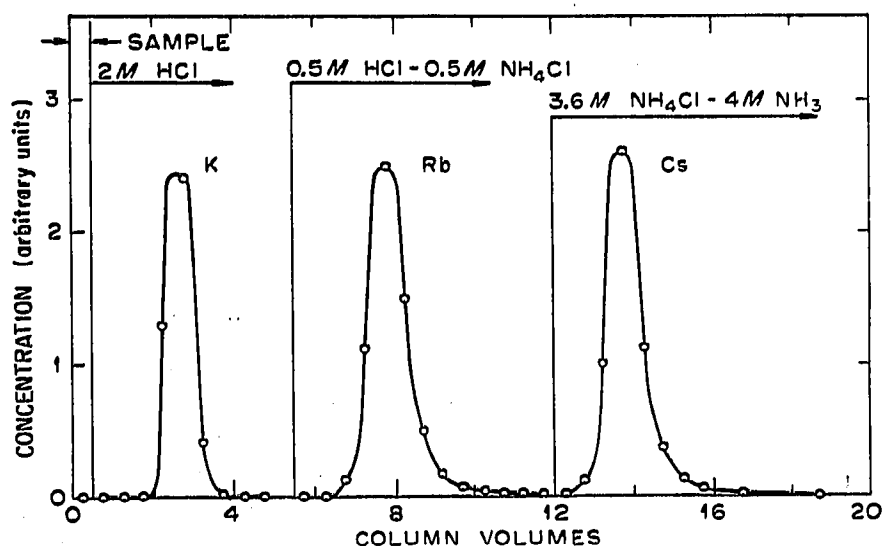


Fig. 11. Separation of  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  (zirconium phosphate,  $3 \text{ cm} \times 0.28 \text{ cm}^2$  column,  $50^\circ$ ).

$\text{Cs}$  was eluted with  $3.6 \text{ M NH}_4\text{Cl}$ – $4 \text{ M NH}_3$  solution in a sharp band which also contained the residual Rb. The Cs band tailed, and even after 7 c.v. of effluent had been collected, about 2% of the Cs remained on the column. Because of tailing of the Rb and Cs bands, quantitative separation and recovery of these elements was not achieved; thus Duolite C-3 (Fig. 6A) appears more suitable than the particular zirconium phosphate tested here for separating Rb and Cs.

(e) *Separation of  $\text{K}^+$  and  $\text{Rb}^+$  (Fig. 12).* In a series of column experiments with  $0.5 \text{ ml}$  samples in which the concentration of  $\text{KCl}$  and  $\text{RbCl}$  ranged from  $0.05 \text{ M}$  to  $0.20 \text{ M}$  each, it was found that satisfactory separations could be achieved if fairly large columns are used, which in effect, serve to increase exchange capacity. A bed volume of zirconium phosphate of approximately  $3 \text{ ml}$  per  $0.05$  mequiv. of alkali metal ( $\text{K} + \text{Rb}$ ) is recommended for separation of the elements in  $2 \text{ M HCl}$ . A typical separation is shown in Fig. 12. A  $0.5 \text{ ml}$  sample containing  $0.04 \text{ M KCl}$ ,  $0.04 \text{ M RbCl}$  and  $2 \text{ M HCl}$  was added to a  $0.75 \text{ cm}^2 \times 4 \text{ cm}$  column of zirconium phosphate and elution continued with  $2 \text{ M HCl}$ . K appeared quantitatively in the first 4 c.v. of effluent essentially completely free of Rb. The Rb was eluted with  $2.0 \text{ M HCl}$ – $2.0 \text{ M NH}_4\text{Cl}$  ( $F_{\text{NH}_4\text{Cl}} = 0.5$ ); three c.v. of this eluent removed  $> 99\%$  of the Rb. Spectroscopic analysis showed that only 0.3% of the K initially present in the sample appeared in the Rb fraction.

Separation of large amounts of K from trace amounts of Rb was investigated with  $0.25 \text{ cm}^2 \times 4 \text{ cm}$  columns of zirconium phosphate at  $50^\circ$ . A convenient acid

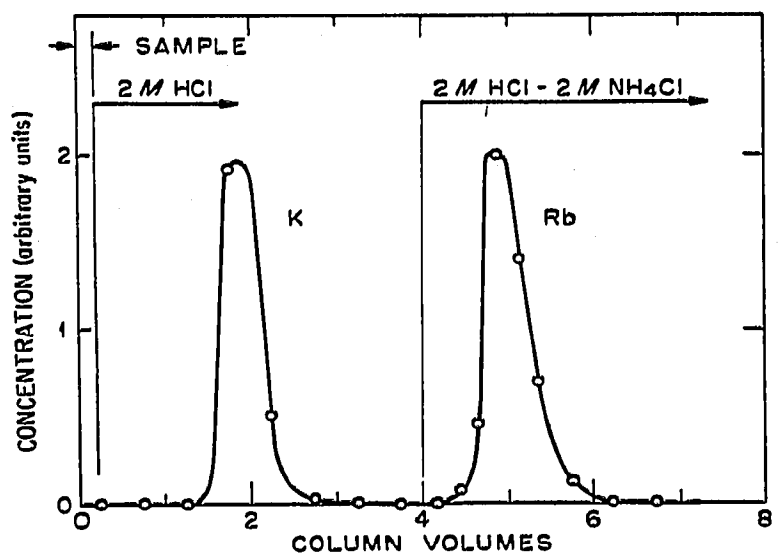


Fig. 12. Separation of K and Rb by cation exchange (zirconium phosphate, 100–200 mesh,  $0.75 \text{ cm}^2 \times 4 \text{ cm}$  column,  $50^\circ$ ).

concentration for achieving separation was found to be *ca.*  $0.25 \text{ M}$  HCl. Break through experiments with  $0.25 \text{ M}$  KCl– $0.25 \text{ M}$  HCl– $10^{-6} \text{ M}$  RbCl, for example, showed that at equilibrium,  $D_v(\text{Rb}) = 5.2$  and  $D_v(\text{K}) = 1.5$ . Under these conditions, the separation factor,  $\alpha(\text{Rb}/\text{K}) = 3.5$ , is sufficiently large to permit separations with reasonably short columns. Efficient separation can be achieved if the KCl concentration in the sample does not exceed *ca.*  $0.25 \text{ M}$  and if the volume of solution processed is not excessive. In a typical separation, 1 ml (1 c.v.) of  $0.25 \text{ M}$  HCl– $0.25 \text{ M}$  KCl– $10^{-6} \text{ M}$  RbCl was added to a 1 ml bed ( $0.25 \text{ cm}^2 \times 4 \text{ cm}$ ) of zirconium phosphate which had been pretreated with  $2 \text{ M}$  HCl. On elution with  $2 \text{ M}$  HCl, the KCl was essentially completely recovered in the first 4 c.v. of effluent. The Rb was eluted with *ca.* 4 c.v. of  $2 \text{ M}$  HCl– $2 \text{ M}$   $\text{NH}_4\text{Cl}$ , as in the previous separation. Analysis of the Rb fraction by flame spectrophotometry showed that it contained only *ca.* 0.05 % of the K originally present in the sample.

## PROCEDURES

Two procedures are described for separating the alkali metals Li to Cs. In both procedures, relatively short (4 cm) columns of Duolite C-3 are used for sequential elution of the alkali metals, except K and Rb which are eluted together. In Procedure I, K and Rb are separated with a longer column of Duolite C-3 while in Procedure II, these elements are separated with a small zirconium phosphate column.

### Procedure I

#### (a) Materials and reagents

*Exchanger.* Duolite C-3, 325–400 mesh, hydrogen-form.

*Apparatus.* Sections of plastic tubing, 0.6 cm in diameter and 10 and 20 cm in length are used to prepare the columns. The tubing is warmed, pulled to a tip at one end and a porous Teflon plug inserted to retain resin. Other apparatus are Teflon evaporating dishes, syringes, test tubes and plastic transfer pipets.

*Solutions.* 2.4 M HCl-80 (vol.) % methanol; 1.5 M HCl; 6 M HCl.

*Columns.*

Column 1: bed volume  $0.28 \text{ cm}^2 \times 4 \text{ cm}$  (1.1 ml).

Flow rate: *ca.* 1 cm/min; 25°.

Effluent volumes - column volumes (c.v.):

Li fraction: 3 c.v. (3.3 ml) 2.4 M HCl-80 % CH<sub>3</sub>OH,

Na fraction: 6 c.v. (6.6 ml) 2.4 M HCl-80 % CH<sub>3</sub>OH,

K-Rb fraction: 4.5 c.v. (5.0 ml) 1.5 M HCl,

Cs fraction: 4 c.v. (4.4 ml) 6 M HCl.

Column 2: bed volume  $0.28 \text{ cm}^2 \times 15 \text{ cm}$  (4.2 ml).

Flow rate: *ca.* 0.5 cm/min; 25°.

Effluent volumes:

K-fraction: 2.5 c.v. (10.5 ml) 1.5 M HCl,

Rb fraction: 1.5 c.v. (2.5 ml) 6 M HCl.

*(b) Sample preparation*

The elements are present as chlorides in HCl solution; the sample is evaporated to dryness. The chloride salts are dissolved in 0.25 ml of water.

*(c) Column operations*

A slurry of Duolite C-3 in water is used to prepare the columns; the first column is pretreated with *ca.* 2 c.v. of distilled water and should have a final bed length of 4 cm. The second column is pretreated with 1.5 M HCl and should have a final bed length of 15 cm.

The sample is added to the first column; after it has passed into the bed, the column is treated with 9 c.v. of 2.4 M HCl-80 % CH<sub>3</sub>OH solution. Flow rate is controlled to about 1 cm/min by air pressure. The first 3 c.v. of effluent contain the Li and the next 6 c.v. the Na. The bed is then eluted with 4.5 c.v. of 1.5 M HCl to remove K and Rb together, and with 4 c.v. of 6 M HCl to remove Cs. The column may be regenerated by washing with distilled water.

The K-Rb fraction is evaporated to near dryness, taken up in 0.5 ml of 2.0 M HCl and added to the second (longer) column; flow rate is held at 0.5 cm/min. K is eluted with 2.5 c.v. of 1.5 M HCl and Rb with 1.5 c.v. of 6 M HCl. The column may be regenerated by treating it with *ca.* 2 c.v. of 1.5 M HCl. The total time required for separating the five alkali elements into separate fractions is about 3 1/2 h, of which 2 h are required for separation of K and Rb. To handle samples of larger initial volume, the bed volumes of the columns may be increased, preferably by increasing the diameter of the columns.

*Procedure II*

This alternate procedure for separating K and Rb with zirconium phosphate permits more rapid separation of K and Rb than is possible with Duolite C-3. If used in conjunction with the first part of the previous procedure, complete separation of the alkali metals, Li to Cs, can be achieved in about 2 1/2 h.

*(a) Materials and reagents*

*Exchanger.* Zirconium phosphate, "Bio-Rad ZP-1" 100-200 mesh, hydrogen-form.

*Apparatus.* Plastic tubing, 1 cm in diameter and 10 cm in length. The tubing is warmed, pulled to a tip at one end and a porous Teflon plug inserted to retain the exchanger. Other apparatus are Teflon evaporating dishes, transfer pipets and test tubes.

*Solutions:* 0.25 M HCl; 2 M HCl; 2 M HCl-2 M NH<sub>4</sub>Cl.

*Column:* Bio-Rad ZP-1, bed volume 0.79 cm<sup>2</sup> × 4 cm (3.2 ml).

*Flow rate:* ca. 0.5 cm/min.

*Temperature:* 50°.

*Effluent volumes - c.v.:*

K-fraction: 4 c.v. (12.4 ml) 2 M HCl,

Rb-fraction: 3 c.v. (5.0 ml) 2 M HCl-2 M NH<sub>4</sub>Cl.

*(b) Sample preparation*

The K and Rb are present as chlorides in HCl solution; the sample is evaporated to near dryness and the residue taken up in 0.5 ml of 2.0 M HCl. If the sample contains macro amounts of K (up to 30 mg) and trace amounts of Rb, the residue should be taken up with 1 ml of 0.25 M HCl.

*(c) Column operation*

A slurry of Bio-Rad ZP-1 in 2 M HCl is used to prepare the column; the column should have a bed length of 4 cm. The column is placed in a water jacket at 50° and pretreated with 2 c.v. of 2 M HCl. Flow rate is adjusted to be 0.5 cm/min. The sample is added and after it has passed into the bed, the column is treated with 4 c.v. of 2 M HCl to elute K; the bed is then eluted with 3 c.v. of 2 M HCl-2 M NH<sub>4</sub>Cl solution to remove Rb. The column may be regenerated by treating it with ca. 6 c.v. of 2 M HCl. The total time required to separate K and Rb into separate fractions is about one hour.

#### ACKNOWLEDGEMENT

The authors are indebted to Dr. E. L. LIND and Mr. D. E. COHN for carrying out some of the preliminary experiments.

#### SUMMARY

A comparative study of the adsorbability of alkali metals, lithium to francium, in HCl-water and HCl-methanol-water solutions has been carried out with sulphonic acid cation exchangers of the polystyrene-divinylbenzene and phenol-formaldehyde types. Separability of potassium, rubidium and cesium has also been studied with a zirconium phosphate cation exchanger. Procedures for separating the alkali elements from each other are described.

#### REFERENCES

- 1 F. NELSON, *J. Chromatog.*, 16 (1964) 538.
- 2 K. A. KRAUS, H. O. PHILLIPS, T. A. CARLSON AND J. S. JOHNSON, *Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva, 1957*, United Nations, 1958, Vol. 28, p. 3.
- 3 C. B. AMPHLETT, *Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva, 1957*, United Nations, 1958, Vol. 28, p. 12.
- 4 J. VAN R. SMIT, J. J. JACOBS AND W. ROBB, *J. Inorg. Nucl. Chem.*, 12 (1959) 104.
- 5 H. O. PHILLIPS AND K. A. KRAUS, *J. Am. Chem. Soc.*, 84 (1962) 2267.

- 6 G. KAYAS, *J. Chim. Phys.*, 47 (1950) 408.
- 7 W. A. BROOKSBANK AND G. W. LEDDICOTTE, *J. Phys. Chem.*, 57 (1953) 819.
- 8 J. B. NIDAY, *Phys. Rev.*, 98 (1955) 42.
- 9 T. T. SUGIHARA, H. I. JAMES, E. J. TROIANELLO AND V. T. BOWEN, *Anal. Chem.*, 31 (1959) 44.
- 10 O. M. LELOVA AND B. K. PREOBRAZHENSKII, *Radiokhimiya*, 2 (1960) 728.
- 11 J. YOSHIMURA AND H. WAKI, *Japan Analyst*, 6 (1957) 362.
- 12 E. MINAMI, M. HONDA AND Y. SASAKI, *Bull. Chem. Soc. Japan*, 31 (1958) 372.
- 13 V. I. GORSHKOV, I. A. KUZNETSOV AND G. M. PANCHENKOV, *Zh. Analit. Khim.*, 14 (1959) 417.
- 14 C. W. DAVIS AND B. D. R. OWEN, *J. Chem. Soc.*, (1956) 167C.
- 15 E. VENTURELLO AND I. MAZZEI, *Ann. Chim. (Rome)*, 53 (1963) 407.
- 16 R. M. DIAMOND, *J. Am. Chem. Soc.*, 77 (1955) 2978.
- 17 G. R. CHOPPIN AND R. H. DINIUS, *Inorg. Chem.*, 1 (1962) 140.
- 18 K. A. KRAUS AND H. O. PHILLIPS, *J. Am. Chem. Soc.*, 78 (1956) 694.
- 19 S. AHRLAND, J. ALBERTSSON, L. JOHANSSON, B. NIHLGÅRD AND L. NILSSON, *Acta Chem. Scand.*, 18 (1964) 707; 18 (1964) 1357.
- 20 S. AHRLAND AND J. ALBERTSSON, *Acta Chem. Scand.*, 18 (1964) 1861.
- 21 A. CLEARFIELD AND J. A. STYNES, *J. Inorg. Nucl. Chem.*, 26 (1964) 117.

*J. Chromatog.*, 20 (1965) 107-121