

## Separation of lithium from other alkali metal ions by reversed phase chromatography\*

Alkali metal ions do not readily form neutral chelate complexes which can be extracted by water immiscible organic solvents. GUTER AND HAMMOND<sup>1</sup> have extracted lithium with a diethyl ether solution of dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione); however, a 50:1 volume ratio of organic to aqueous phase was needed to obtain a quantitative extraction. Sodium ions also interfered with the quantitative recovery of lithium. JENSEN<sup>2</sup> has discussed the extraction of alkali metal ions with bis-(2-hydroxyl-1-naphthyl)-methane. No quantitative separations of the elements were attempted. O'LAUGHLIN AND BANKS<sup>3</sup> have separated lithium from other alkali metals by reversed phase chromatography on a Kel-F column impregnated with bis-(di-*n*-hexylphosphinyl)-methane.

Many lithium salts are soluble in water immiscible solvents and methods have been devised to separate lithium by the preferential solubility of lithium salts in these solvents<sup>4-7</sup>. However, when these solutions are equilibrated with water the lithium concentrates in the aqueous phase.

FERNELIUS AND VAN UITERT<sup>8</sup> have measured the stability constants for dibenzoylmethane (1,3-diphenyl-1,3-propanedione) complexes of the alkali metal ions in 75 % dioxane-25 % water. The log of the equilibrium constants followed the sequence:  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ . The value for  $\text{Li}^+$  was 5.95. JACKSON AND PETERSON<sup>9</sup> found that lithium dibenzoylmethane at pH 10 was extracted by 50 % tributylphosphate-50 % kerosene.

The use of tributylphosphate (TBP) and other neutral phosphorus compounds such as trioctylphosphine oxide (TOPO) to displace water molecules in the primary solvation sphere of certain cations and cation complexes has induced the extractability of these complexes in several cases<sup>10</sup>. Although the hydrated lithium ion has a more stable structure than water itself<sup>11</sup>, and prefers to remain as that species in aqueous solution, we have found in this work that the synergistic effect of combining a chelate compound, dibenzoylmethane, with a solvating ligand more basic than water, TBP or TOPO, has produced a lithium species which can be extracted from aqueous solution into an immiscible organic solvent. Under proper conditions, these reagents will selectively extract lithium from the other alkali metal ions.

The quantitative separation of lithium from other alkali metal ions by this extraction procedure has been facilitated by a chromatographic column. Reversed phase chromatography on inert supports impregnated with liquid ion exchangers or organic extracting agents has become an important new development in separation procedures<sup>12</sup>. In the work described in this paper, a column of polytetrafluoroethylene supported the organic solution of the extracting reagents as the stationary phase. Sharp separations were made between lithium and other alkali metal ions using this column.

### Experimental

Dibenzoylmethane (DBM) and trioctylphosphine oxide (TOPO) (white-label Eastman Organic Chemicals) were used without further purification. Tributylphosphate (TBP) was supplied by F. H. Ross and Co. Practical grade dodecane from J. T.

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Baker Chemical Co. was used as the solvent. The stationary phase solutions were 0.10 *M* DBM–0.10 *M* TOPO in dodecane, and 0.18 *M* DBM in 50 % vol. TBP–50 % dodecane. The eluents were 3.2 *N* NH<sub>4</sub>OH, 1.6 *N* NH<sub>4</sub>OH, 0.1 *N* KOH and 0.6 *N* HCl. Prior to use, these eluents were saturated with the appropriate organic solution. The alkali metal salts were reagent grade. <sup>22</sup>Na and <sup>134</sup>Cs were used as tracers.

The glass column, 1 cm I.D. × 15 cm long with a glass frit and stopcock on the bottom and an eluent reservoir on top, was packed with the organic phase support. Polytetrafluoroethylene (~ 30–60 mesh Haloport F, F & M Scientific) was thoroughly mixed with a dodecane solution of the extracting reagents (2 g support/1 ml solution). This mixture was slurried with the eluent solution and poured into the column in small portions. The support was lightly tamped with a glass rod after each portion was added until the column was filled. (Heavy tamping will plug the column.) The capacity of the bed was 0.034 mmoles DBM–TOPO per c.c. of bed volume.

Ten to 100 μmoles of the non-radioactive alkali metal ions in 3.2 *N* NH<sub>4</sub>OH and tracer quantities of radioisotopes were placed as a band on top of the column; the band was then eluted with the basic eluting solution. After the heavier alkali metal ions were separated, lithium was removed by elution with 0.6 *N* HCl. The flow rate was ~ 0.2 cm min<sup>-1</sup>. The samples (0.6 ml) were collected on an automatic fraction collector. They were then analyzed by flame spectrophotometry or by radioactive counting.

Liquid–liquid batch extraction coefficients were determined for alkali metal ions. An aqueous solution, 3 *N* NH<sub>4</sub>OH, containing 50 μmoles each of the alkali metals Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> was contacted with an equal volume of an organic solution containing 0.10 *M* DBM–0.10 *M* TOPO in dodecane. The mixture was shaken mechanically for ten minutes to equilibrate the solutions. The mixture was centrifuged and the phases separated. The alkali metal ions were stripped from the organic phase by shaking the organic phase with an equal volume of 0.6 *N* HCl for ten minutes. The organic, aqueous, and acid stripping solutions were analyzed for alkali metal ions.

### *Results and discussion*

A typical separation of lithium from sodium, potassium, rubidium, and cesium is given in Fig. 1. The organic phase used on the polytetrafluoroethylene column for this experiment was 0.10 *M* TOPO–0.10 *M* DBM in dodecane. The eluent for the first twenty-five samples was 3.2 *N* NH<sub>4</sub>OH; the heavier alkali metal ions were completely removed during this interval. Lithium was quantitatively retained on the column, and it was necessary to break the lithium complex with acid before it could be removed.

Various alkali metal ions were individually separated from lithium in similar experiments. The experimental conditions were changed slightly; however, the results were essentially the same. Sodium and lithium were separated on a polytetrafluoroethylene column which had an organic phase of 0.18 *M* DBM in a 1:1 mixture of TBP–dodecane. Na was eluted with 0.1 *M* KOH; 0.6 *N* HCl was used to elute Li. The elution curves are illustrated in Fig. 2. Cs and Li were separated in a similar system. Cs was eluted with 3.2 *N* NH<sub>4</sub>OH; 0.6 *N* HCl was again used to remove Li. Separations of Li–Na, Li–K, and Li–Cs pairs were made on both TBP–DBM and TOPO–DBM columns with equally good results. Varying the flow rate from 0.06 cm min<sup>-1</sup> to 1.8 cm min<sup>-1</sup> did not affect the separation; however, the elution curves had

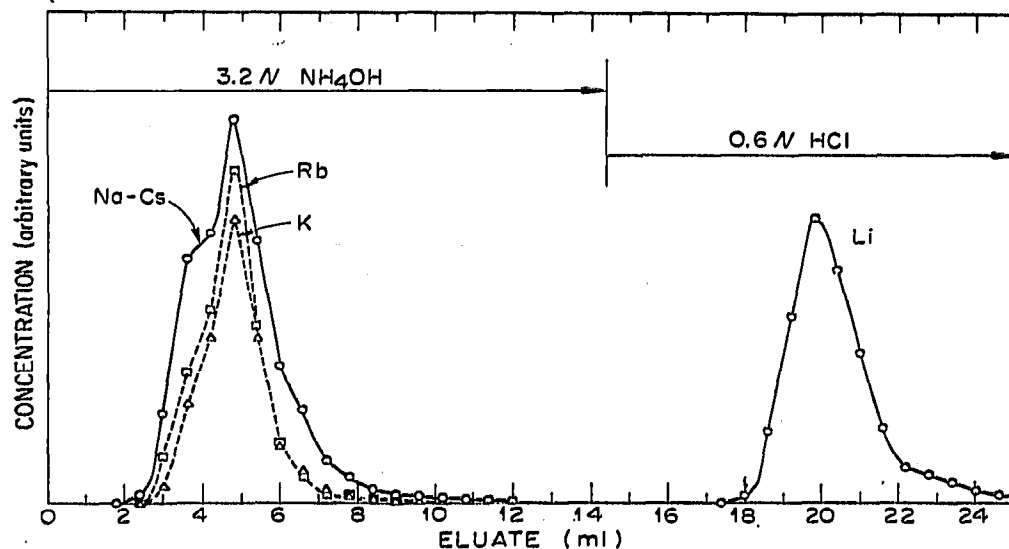


Fig. 1. Separation of lithium from other alkali metals with DBM-TOPO on Haloport F.

a slightly longer tail at the faster flow rates. The minimum column length was not determined; undoubtedly, much shorter columns could have been used for these separations.

In Figs. 1 and 2, the sodium elution curves did not peak at the same elution volume for  $\text{NH}_4\text{OH}$  and  $\text{KOH}$  eluents although the columns were the same. This indicates that there was slight Na-DBM-TOPO complexing in  $\text{KOH}$  solutions but not in  $\text{NH}_4\text{OH}$  solutions.

To establish the synergistic effect, experiments were made in which 0.10  $M$  TOPO in dodecane with no DBM was equilibrated with 0.01  $M$   $\text{Li}^+$  in 3  $N$   $\text{NH}_4\text{OH}$ , and 0.10  $M$  DBM in dodecane with no TOPO was equilibrated with 0.01  $M$   $\text{Li}^+$  in 3  $N$   $\text{NH}_4\text{OH}$ . The extraction coefficient (grams  $M^+$  per liter organic phase/grams  $M^+$  per liter aqueous phase) for Li with no DBM was 0.0036 and with no TOPO 0.0034.

The batch extraction coefficients for the alkali metal ions in 3  $N$   $\text{NH}_4\text{OH}$  extracted with 0.10  $M$  DBM-0.10  $M$  TOPO in dodecane were: Li = 108, Na = 0.188, K = 0.0106, Rb = 0.0100, and Cs = 0.0087. The separation factors calculated from

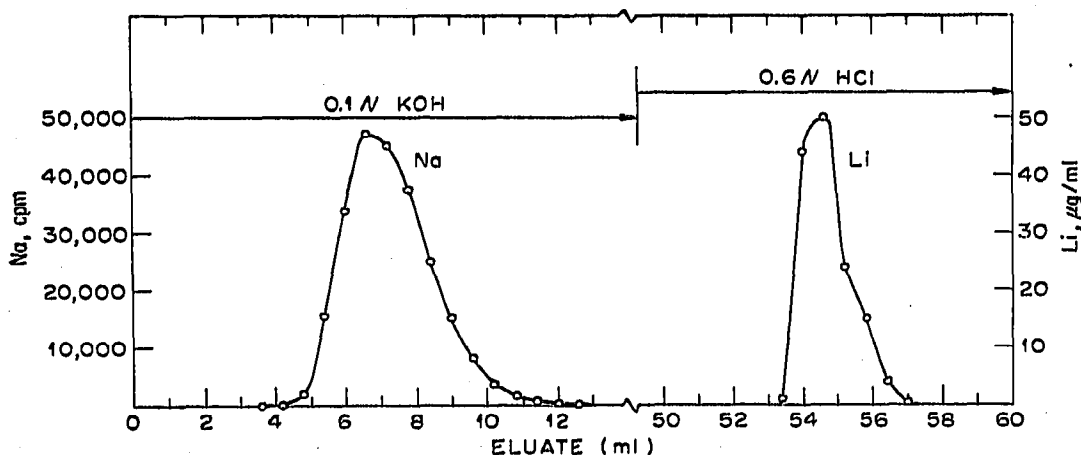


Fig. 2. Separation of lithium from sodium with DBM-TBP on Haloport F.

these data were  $\text{Li/Na} = 570$ ,  $\text{Li/K} = 10,200$ ,  $\text{Li/Rb} = 10,800$ ,  $\text{Li/Cs} = 12,400$ , and  $\text{Na/K} = 18$ . Further studies of the application of these results to two-phase counter-current solvent extraction systems are now in progress.

From these experiments it can be concluded that DBM-TOPO and DBM-TBP form strong lithium complexes in basic solution which are extractable by dodecane, while the other alkali metal ions are not complexed or are very weakly complexed by these reagents. Because of these properties, a quantitative separation of lithium can be easily made by reserved phase chromatography.

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