

of electrophoresis was 2.5 h. Here, as in the acid solution, americium could be separated from the lanthanides present, the difference being that now the elements move to the anode.

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### Quantitative analysis of lithium, potassium and caesium chlorides by paper chromatography and flame spectrophotometry

Paper chromatography of alkali metal ions has been the subject of much research involving work on inorganic<sup>1-26</sup> as well as organic salts<sup>7,12,27-32</sup>. We do not, however, consider that a sufficiently simple method, giving separation of the cations in reasonable quantities (*ca.* 6 mg) for their individual determination, has so far been reported in the literature. We have therefore here examined the paper chromatography of lithium, potassium and caesium chlorides, in order to determine the most suitable experimental conditions for quantitative evaluation of the results. This was attained by using two different eluants and applying first the descending method and then the ascending method on the same chromatogram. The first eluant, consisting of butyl alcohol (I), has the advantage of separating lithium alone, while the second eluant, consisting of a mixture of hydrochloric acid, methanol and butanol (II), permits the separation of caesium from potassium. Lithium must be removed first from the chromatogram, as this cation eluted with (II) would contaminate both Cs<sup>+</sup> and K<sup>+</sup>.

After separation, the cations extracted from the strip are individually determined quantitatively by means of flame spectrophotometry.

In order also to obtain data on the behaviour of sodium and rubidium chlorides, the possibility of separating these two cations by the eluants (I) and (II) was examined. It was observed, however, that Na<sup>+</sup> in the amounts considered here (10-15 mg) shows

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a behaviour analogous to  $\text{Li}^+$ . In fact, it is eluted by butanol and contaminates  $\text{Cs}^+$  and  $\text{K}^+$  when eluted with eluant (II)\*.

$\text{Rb}^+$ , on the contrary, has a behaviour analogous to  $\text{K}^+$  and  $\text{Cs}^+$ . When the chromatogram is eluted with butanol,  $\text{Rb}^+$  remains with potassium and caesium on the starting line, whilst, in the subsequent elution with (II), it lies between  $\text{K}^+$  and  $\text{Cs}^+$ , but very near the former ( $R_F$  0.39). If  $\text{Rb}^+$  is to be separated, for quantitative determination, this is preferably carried out by means of circular chromatography, using Whatman No. 3MM 30 cm diameter paper discs and eluant (II).  $\text{Rb}^+$  separates sharply from  $\text{K}^+$  ( $R_F$  0.49) and from  $\text{Cs}^+$  ( $R_F$  0.72) with an  $R_F$  value of 0.63. In the analysis of synthetic mixtures having the constituents  $\text{K}^+ = 1,000 \mu\text{g}$ ,  $\text{Rb}^+ = 500 \mu\text{g}$ ,  $\text{Cs}^+ = 500 \mu\text{g}$  the original amount of rubidium was recovered entirely by eluting the carefully cut chromatogram with water and examining the solution by flame spectrophotometry at the wave length  $794.8 \text{ m}\mu$ .

### Experimental

For chromatographic separation, strips of Whatman No. 3MM filter paper ( $30 \times 3 \text{ cm}$ ) were used. The mixture of the three chlorides, lithium, potassium and caesium, dissolved in water, was spotted 2 cm from the lower end and along the whole width of the strip. Synthetic mixtures were analysed, the compositions of which, referred to the cation in question, are given in Table I.

TABLE I  
ANALYSIS OF SYNTHETIC MIXTURES OF LITHIUM, POTASSIUM AND CAESIUM CHLORIDES

Present ( $\mu\text{g}$ )			Found ( $\mu\text{g}$ )		
Lithium	Potassium	Caesium	Lithium	Potassium	Caesium
500	5000	100	490	4980	100
500	3000	100	500	2990	100
500	2000	100	500	2000	100
100	2000	50	100	1995	50
50	2000	50	50	1995	50

The strip was developed using the equipment shown in Fig. 1. The upper portion of the chromatographic strip (S) was wrapped around the horizontal glass rod (A) and the remaining portion of the strip was laid in the container (B), which was filled with the eluant. The strip was kept in place by means of a glass rod (C). In this way, the lower end of the chromatogram remains out of the container for 6 to 7 cm. The first development, by the descending method, occurs along this direction. Butyl alcohol was employed as first eluant; potassium and caesium ions stayed at the line of application, while lithium chloride was extracted from the chromatogram and collected directly into the container (D). After evaporation of the butyl alcohol and addition of 5 ml distilled water, lithium was quantitatively estimated by examining the aqueous solution by flame spectrophotometry, at a wave length of  $670.8 \text{ m}\mu^{**}$ .

\* Owing to this behaviour and also because of the considerable amount of  $\text{Na}^+$ , in comparison with the other cations, it can be removed from the mixture under examination, by means of suitable quantitative precipitation as sodium zinc uranyl acetate.

\*\* For these measurements a Beckman D.U. unit was used as flame spectrophotometer. As fuel gas, hydrogen at 5 p.s.i. was used. Atomising and oxidising gas was oxygen at 15 p.s.i.

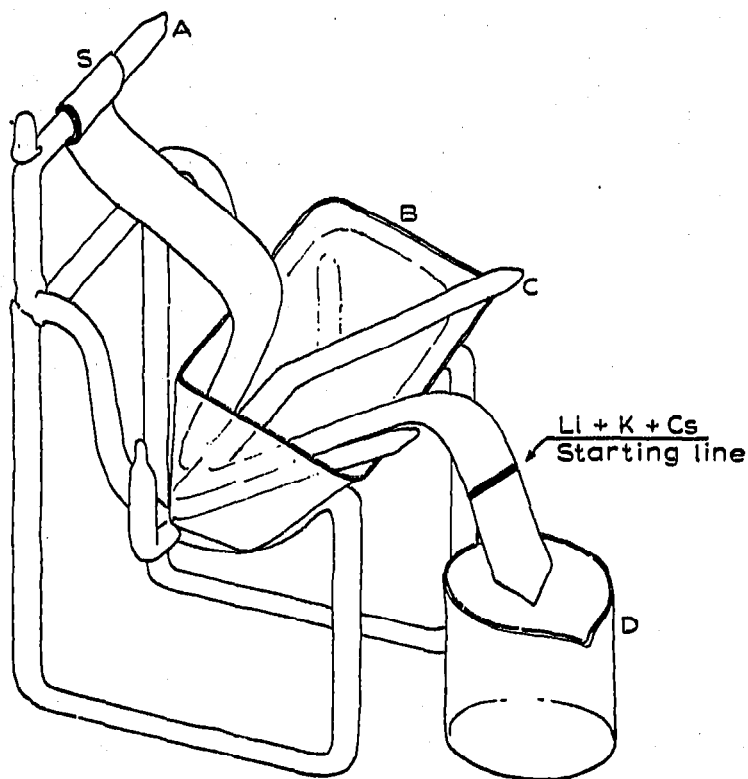


Fig. 1. Separation of  $\text{Li}^+$  in a mixture with  $\text{K}^+$  and  $\text{Cs}^+$  by paper chromatography. Descending method.

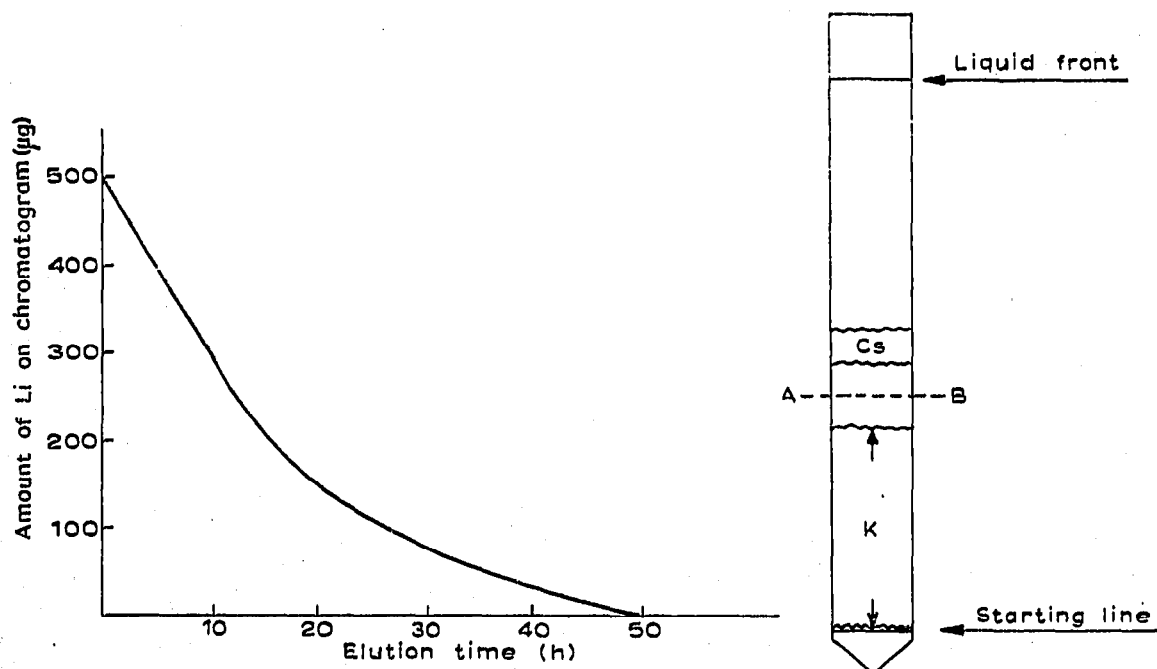


Fig. 2. Amounts of  $\text{Li}^+$  on chromatogram after various elution times.

Fig. 3. Separation of  $\text{K}^+$  and  $\text{Cs}^+$  by paper chromatography. Ascending method.

A typical elution curve is shown in Fig. 2. It represents the amount of lithium remaining on the chromatogram during elution.

After complete drying, the chromatogram was developed in a glass cylinder for 25 cm (8 h) by the ascending method. As eluant the following mixture was employed: 58 ml hydrochloric acid ( $d$  1.19), 36.5 ml methanol and 5.5 ml butanol. Caesium separated as a band about 1 cm high with an average  $R_F$  value of 0.52. Potassium remained below caesium, sharply separated from the latter, with an  $R_F$  value ranging from 0.10 to 0.37. With higher amounts of potassium,  $R_F$  values ranged from 0.00 to 0.37. The chromatogram was now carefully dried and then cut along line AB, as shown in Fig. 3; the two sections of it were eluted with distilled water, and potassium and caesium chlorides were separately collected. Individual determination of cations was performed by flame spectrophotometry, examining the solutions at a wave length of 769.9  $m\mu$  for potassium and 852.1  $m\mu$  for caesium.

Amounts present in synthetic mixtures are compared in Table I with those found by the technique described above.

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