699. *Separations by Partition Chromatography on Paper.* (i) *Strontium from Barium, Calcium, and Magnesium.* (ii) *Potassium, Rubidium, and Cæsium.* (iii) *Sodium and Lithium.*

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A mixture of concentrated hydrochloric acid and *n*-butanol (95 : 5 by vol.), saturated with *n*-butyl chloride, has been used to separate strontium chloride from barium, calcium, and magnesium chlorides. Sodium rhodizonate has served for the detection and estimation of 2·5—500 µg. of strontium. 500 Micrograms of barium, calcium, magnesium, or any alkali metal did not interfere with the detection of 2·5 µg.

Potassium, rubidium, and cæsium chlorides (total weight of cations $\not>$1 mg.) have been separated by means of a mixture of concentrated hydrochloric acid, methanol, *n*-butanol, and *iso*butyl methyl ketone (55 : 35 : 5 : 5). For the detection and estimation of 5—1000 µg. of the three cations, the lead cobalt alkali hexanitrites have been formed. One mg. of sodium, lithium, calcium, strontium, barium, or magnesium did not influence the detection of the minimum amounts.

For the separation of sodium and lithium chlorides a mixture of methanol and *n*-butanol (4 : 1) has been used. In solutions containing a maximum of 500 µg. of any combination of the two cations, 2·5—500 µg. amounts of both have been detected and estimated in ultra-violet light as the fluorescent alkali zinc uranyl acetates; 500 µg. of potassium, rubidium, cæsium, calcium, barium, strontium, or magnesium did not influence the results.

In systematic qualitative analysis, in which the alkaline-earth metals and magnesium are commonly separated as a group, the certain detection of strontium in association with a large excess of barium is troublesome, since both metals react similarly with so many reagents. As a rule, barium is first removed by precipitation as chromate and the filtrate is examined for strontium. Unless great care is taken in effecting the precipitation a small amount of strontium may be completely retained by the barium chromate, or a small amount of barium may escape precipitation and subsequently be reported as strontium.

The systematic detection of the alkali metals, in the absence of all other cations, usually involves their separation into two sub-groups containing, respectively, potassium, rubidium, and cæsium, and sodium and lithium. Sodium and lithium chlorides can then be separated from each other by means of an organic solvent, *e.g.*, amyl alcohol, acetone, or pyridine. The separation of potassium, rubidium, and cæsium is by no means easy, the detection of a small amount of either of the first two in the presence of an excess of the others being particularly difficult.

Within the last few years some striking separations by partition chromatography on strips of filter-paper have been effected of metal ions whose detection in the presence of each other by orthodox chemical methods has been difficult. Some such new means were accordingly sought for facilitating especially the detection of a small amount of strontium in the presence of much barium, and the separation of the alkali metals from one another.

Separation of Strontium from Barium.—For the separation of calcium, strontium, and barium chlorides, which were said to be difficult to separate, Burstall, Davies, Linstead, and Wells (*J.*, 1950, 516) recommended pyridine containing 20% of water and 1% of potassium thiocyanate. We have failed to obtain good separations of barium and strontium by this method, barium invariably travelling down the paper like strontium. We paid particular attention to solvents that had been employed for ordinary chemical separations of barium and strontium salts, and first obtained successful indications when a mixture of butanol and concentrated hydrochloric acid (cf. Kallmann, *Anal. Chem.*, 1948, **20**, 449) was applied to the chlorides of barium and strontium. As a result of numerous experiments in which the proportions of these two components were varied, and freshly prepared and old mixtures were used, it was concluded that the best solvent was a mixture of *n*-butanol and concentrated hydrochloric acid (5 : 95 v/v), saturated with *n*-butyl chloride. With all the mixtures tried, barium was held near the original spot of deposition of the test solution whereas strontium, calcium, and magnesium travelled down the paper, magnesium moving the greatest, and strontium the least distance. The proportion of acid in the mixture influenced the relative rates of travel of strontium, calcium, and magnesium, and the mixture selected gave the best separation of all three. The presence of *n*-butyl chloride almost entirely prevented slight "tailing" of barium and thus gave a cleaner-cut separation of barium and strontium, favouring the detection of small amounts of the latter in the presence of a large excess of the former.

For the detection of strontium, sodium rhodizonate could be used after the paper had been freed as far as possible from acid. The colour obtained with strontium, which could not be confused with that due to barium, ranged from orange with small amounts, through orange-red to purple-red for large amounts. Small amounts of barium gave bright pink patches, and large amounts, brilliant carmine. On strips of paper 1·5 cm. wide, 2·5 μg. of strontium were easily found and could be separated from 500 μg. of barium in experiments of 3½—4 hours' duration in which the solvent reached a line 20 cm. below the original spot of deposition of the test solution. The presence of 500 μg. of calcium or magnesium, or any alkali metal did not obviously influence the position of the band due to strontium, or prevent the detection of 2·5 μg. of the element.

Bands due to magnesium in quantities up to 500 μg. ended a short distance above the solvent front and were completely separated from those due to strontium. Bands due to calcium lay between those of strontium and magnesium, and the separation of small and moderate amounts of the three elements was considered to be complete. 500 Micrograms of calcium were separated from 2·5 μg. of strontium. There was probably a tendency for slight overlap of calcium and magnesium and of calcium and strontium to occur when, say, 250 μg. of each were present. This was of no significance for the detection and estimation of strontium, since the rhodizonate test for the latter did not require the complete removal of calcium. The positions of the bands due to 500 μg. amounts of the alkali metals were approximately as follows: That due to sodium extended from just below the starting line to a point more than half-way down the paper. That for lithium was separated by a short distance from that for sodium and reached probably to the solvent front. The bands due to potassium, rubidium, and cæsium were located mainly in the bottom half of the paper, cæsium probably reaching to the solvent front and being partly separated from rubidium, which was likewise partly separated from potassium.

Reasonable estimations of the amounts of strontium separated from mixtures could be made. Chromatograms prepared from quantities of strontium ranging from 2·5 to 500 μg. showed a useful gradation in colour intensity and area of the developed band on which estimations could be based. In experiments in which the solvent travelled 20 cm. beyond the starting line the positions of the bands with respect to the latter were as follows:

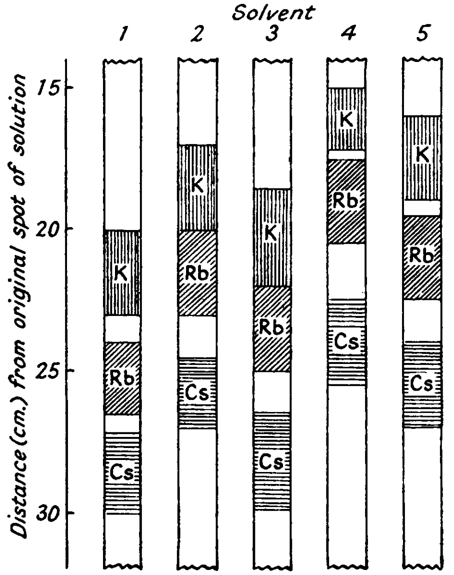
Amount of Sr (μg.)	2·5	5	10	25	50	100	250	500
Upper limit of band (cm.)	8·5	9·1	9·2	8·6	8·3	7·2	4·5	4·5
Lower limit of band (cm.)	11·0	12·3	12·7	13·0	13·6	13·4	13·4	14·0

Separation of Potassium, Rubidium, and Cæsium.—In ordinary chemical extraction work on the separation of the chlorides of potassium, rubidium, and cæsium, mixtures of ethanol and hydrochloric acid have been employed. Hillyer (*Ind. Eng. Chem., Anal.*, **1937**, 9, 236), for instance, recommended a mixture of concentrated hydrochloric acid and ethanol (1 : 2) for the separation of much rubidium chloride and cæsium chloride from a little potassium chloride. In all our preliminary work on neutral chloride solutions of the alkali metals in which partial separations were indicated, the solvents contained concentrated hydrochloric acid or hydrobromic acid together with an alcohol, a ketone, or tetrahydropyran, or mixtures of these. The destructive effect of hydrobromic acid on the dried paper rendered its use impracticable. Promising separations were given with solvents containing, in the main, methanol and concentrated hydrochloric acid. The results for 5 experiments in which solvent mixtures containing these as chief components were allowed to travel 50 cm. from the original spot of deposition of the test solution are shown pictorially in the figure. The composition of solvent No. 5 was chosen so as to incorporate the good features of solvents Nos. 1 and 4, which gave the best separations, respectively, between potassium and rubidium, and between rubidium and cæsium.

For the detection of the three elements the formation of complex hexanitrites containing lead and cobalt was found to be best, although their tinctorial power was not outstanding. All attempts to improve upon this aspect by employing salts other than those of lead and cobalt met with no success. On strips of paper 4 cm. wide, 5 μg. of potassium gave an easily detectable yellow stain, but 5 μg. of rubidium or cæsium gave a very pale yellow stain. Large amounts of potassium, rubidium, and cæsium gave orange-yellow, brownish-black, and orange-brown colours, respectively.

With solvent No. 5 it was possible, in experiments made at room temperature and lasting about 17 hours, to effect complete separation of potassium, rubidium, and cæsium in mixtures containing a minimum of 5 µg. of any of these elements and a maximum of 1 mg. of the combined elements. In one experiment on the separation of 5 µg. of rubidium from 500 µg. of each of potassium and cæsium the positions of the bands with respect to the starting line were: K, 19·6—28·9 cm.; Rb, 29·5—31·5 cm.; Cs, 32·8—36·5 cm. A separation of 10 µg. of potassium from 1 mg. of rubidium similarly gave: K, 24·4—27·1 cm.; Rb, 27·8—32·7 cm.

In all the separations obtained with the same solvent, the relative positions on the strips, with respect to each other, of the bands associated with small amounts of potassium, rubidium, and cæsium, were reasonably constant, but, with respect to the solvent front, the bands might occasionally show an upward or downward displacement of a few cm. (R_F values not constant). If, therefore, a chromatogram showed a single band, one could, by merely calculating the R_F value, confuse potassium with rubidium or rubidium with cæsium. Similarly, if there were two bands near each other, potassium and rubidium could be confused with rubidium and cæsium. Two bands fairly far apart could only be attributed to potassium and cæsium. In examining a solution for potassium, rubidium, and cæsium the simplest way to ensure a correct interpretation is to take two portions and add to one a little cæsium chloride before preparing the chromatograms. The ratios of the R_F values of potassium and rubidium to that of cæsium, which is commonly about 0·7, are approximately 0·8 and 0·9.



K = 100 µg.; Rb = 100 µg.; Cs = 50 µg.

Composition of solvents (parts by volume).

Solvent.	1.	2.	3.	4.	5.
Conc. HCl (*d* 1·18)	55	50	50	50	55
Methanol	40	40	40	40	35
n-Butanol	5	—	—	—	5
Tetrahydropyran	—	10	—	—	—
Methyl propyl ketone	—	—	10	—	—
*iso*Butyl methyl ketone	—	—	—	10	5

The effect of some other metals on the detection of potassium, rubidium, and cæsium was investigated. One mg. of sodium, lithium, barium, calcium, strontium, or magnesium as chloride had no influence on the detection of 5 µg. of potassium, rubidium, or cæsium, or on the position of the bands, in experiments in which the solvent advanced 50 cm. beyond the original spot of deposition of the test solution. The band due to sodium stretched from the starting point to the 7 cm. mark, that of lithium occupied the same position as cæsium but tended to spread down the paper, barium was held mainly at the starting point but trailed somewhat to the 10 cm. mark, and the band due to strontium stretched from the starting point to the 20 cm. mark. Calcium and magnesium were found between 18 and 32 cm. and between 28 and 40 cm., respectively. Ammonium formed a complex hexanitrite like potassium, rubidium, and cæsium, 1 mg. giving a yellow-brown band almost coincident with that due to cæsium. It was important to exclude ammonia vapour at all stages in the preparation of the chromatograms.

The amounts of potassium, rubidium, and cæsium separated from mixtures could be estimated with reference to sets of chromatograms prepared for amounts of the various elements ranging from 5 to 1000 µg. Whereas the band for potassium markedly lengthened, especially in an upward direction, as the amount of the element increased, the bands for rubidium and cæsium remained compact, as the following table shows :

Element, µg.		5	10	25	50	100	250	500	1000
Length of bands (cm.)	K	2·9	3·5	4·0	4·2	4·7	6·2	10·6	15·4
	Rb	2·5	2·8	2·6	2·7	3·0	4·1	5·1	5·4
	Cs	2·7	3·0	3·6	3·8	4·0	4·2	4·9	6·3

Estimations of potassium were related partly to intensity of colour but mainly to band length or area. Intensity of colour was of more importance in estimating rubidium and cæsium.

Separation of Sodium and Lithium.—Burstall *et al.* (*loc. cit.*) used methanol for the separation of 100 µg. amounts of sodium, lithium, and potassium present as neutral chlorides. Although we obtained separations of sodium and lithium chlorides with the solvent mixture used for potassium, rubidium, and cæsium, the bands were not altogether satisfactory. As a result of experiments with mixtures of alcohols it was found that methanol mixed with 25% of *n*-butanol gave better separations than methanol alone, especially when the proportions of sodium and lithium were widely varied. On strips of paper 1·5 cm. wide, down which the solvent was allowed to travel 20 cm. beyond the position of the test solution initially, it was found possible to separate 2·5 µg. of sodium from 500 µg. of lithium and *vice versâ*. A satisfactory means of detecting the elements was not easily found. Ultimately, we used a solution of zinc uranyl acetate which has been used recently by Pollard, McOmie, and Stevens (*J.*, 1951, 771) for the detection of sodium. With both sodium and lithium it gave bands that fluoresced brightly in ultra-violet light, the limit of detection of the elements being about 1 µg.

For the estimation of sodium and lithium on the strips, chromatograms were prepared for amounts of sodium and lithium ranging from 2·5 to 500 µg. The positions of the bands were found to lie within the following distances from the starting line, in experiments in which the solvent travelled 20 cm. beyond that point :

	Position of bands (cm.).	
Element, µg.	Sodium.	Lithium.
2·5	5·9—7·6	16·0—17·2
5	5·5—7·7	15·5—17·4
10	4·5—8·5	14·5—17·4
25	5·8—9·2	13·5—17·5
50	4·2— 8·6	13·2—17·2
100	3·3—10·0	12·3—17·3
250	2·1— 9·5	11·0—17·3
500	1·7— 9·9	9·2—17·7

The area of the fluorescent patch was used as the basis for estimations of quantity.

The influence on the detection of 2·5 µg. of sodium or lithium of 500 µg. of each of the other alkali metals, alkaline-earth metals, and magnesium, as chlorides, was found to be inappreciable. The positions occupied by the various elements on strips down which the solvent had travelled 20 cm. from the starting line were as follows : The bulk of potassium, rubidium, and cæsium remained on the original spot of deposition but some trailed down for about 4·5 cm. The bands due to barium, strontium, calcium, and magnesium lay between 1 and 8 cm., 1 and 13 cm., 4 and 14 cm., and 13 and 17 cm., respectively.

EXPERIMENTAL.

The chromatographic apparatus used for 2—4 hour experiments was similar to that employed by Burstall *et al.* (*loc. cit.*), except that the glass gas-jars which had a ground flange were inverted over sheets of plane glass, and the glass boats (5 ml. capacity) were sealed to short pillars of glass that were inserted into hollow, upright stems sealed on to glass tripods. Boats could thus be interchanged and their heights adjusted to suit the various gas-jars. For the long experiments the apparatus consisted of a glass cylinder (internal diameter 19 cm.) with ground flanges at top and bottom, which rested on a ground-glass plate and was surmounted by a bell-jar so as to give a total height of 70 cm. Within was a glass boat (length 12 cm., capacity 60 ml.) provided with the usual glass supports for the paper. To the boat were sealed 4 short limbs that could be inserted into upright glass tubes fitted into rubber bungs to provide a firm support. From the boat four paper strips could be hung. No special arrangements were made for maintaining constancy of temperature, which was usually between 12° and 15°; even during the long experiments the maximum range was less than 5° and no sharp changes occurred.

All the experiments were made on strips of Whatman No. 1 filter-paper cut 1·5 cm. wide and 30 cm. long for short runs, and 4 cm. wide and 67 cm. long for long runs. Pencil lines were ruled 2·5 and 7·5 cm. from the ends of short strips, and 7 and 10 cm. from those of long strips. Neutral solutions of metallic chlorides were used throughout, small amounts being placed, as indicated later, just below the first lines.

The boats and, unless otherwise stated, beakers at the foot of the chromatographic apparatus were charged with freshly prepared solvent mixture about 1 hour before the insertion of paper strips, which were so placed that the upper ends dipped into the boat and the parts between the two marks hung vertically.

The solvents used were fractionated *n*-butanol, methanol (obtained from James Burrough, Ltd., London, and redistilled), AnalaR hydrochloric acid (*d* 1·18), and *n*-butyl chloride and *iso*butyl methyl ketone (both from British Drug Houses) which were used as received.

For spraying, the strips were held taut and a simple atomiser actuated by a current of compressed air was employed.

Procedure for Strontium.—The solvent mixture was hydrochloric acid and *n*-butanol (95 : 5 by vol.), saturated at room temperature with *n*-butyl chloride. Experiments were made on short strips of paper with 0·01 ml. of test solution containing a maximum of 500 μg. of cations, added a little at a time from a capillary pipette so that the diameter of the spot was $\not>$1 cm. The prepared strip was left on an improvised glass hot-plate (40°) for 5 minutes in order to ensure thorough drying which was essential for satisfactory separations, and then placed within the gas-jar. The solvent was allowed to travel down the paper to the second mark (time 3½—4 hours), then the strip was removed, hung upside down a short distance from a steam radiator (35—40°), and left until dry (30 minutes) and reasonably free from acid. Further treatment with ammonia vapour was required before stable colours could be obtained with sodium rhodizonate. For this purpose the strips were hung for 10 minutes on a frame within a bell-jar under which was a dish of concentrated ammonia.

Finally, the strip was sprayed with a saturated aqueous solution of sodium rhodizonate mixed with 25% of methanol, held above the hot-plate for a minute in order to dry up the bulk of the liquid, and then left in the air to dry completely. The colour did not deteriorate on standing and could be compared at leisure with a previously prepared set of standards.

Detection and Estimation of Calcium and Magnesium.—The presence of calcium and magnesium on the strips was readily shown by spraying them with a solution of 8-hydroxyquinoline (5% in a mixture of methanol, chloroform, and water, 85 : 10 : 5) before the application of sodium rhodizonate, and then exposing them to ammonia vapour for a minute before placing them in ultra-violet light. Greenish-yellow fluorescent bands were observed, 5 μg. of each metal being detectable. The lengths of the bands increased with increasing amounts of the elements, and sets of standards were prepared. Unfortunately, they deteriorated rapidly on standing. If this difficulty were overcome there is little doubt that calcium, magnesium, and strontium could be detected and estimated on the same strip, because the subsequent detection and estimation of strontium by means of sodium rhodizonate were unaffected by the prior spraying with 8-hydroxyquinoline.

Procedure for Potassium, Rubidium, and Cæsium.—The solvent mixture, hydrochloric acid, methanol, *n*-butanol, and *iso*butyl methyl ketone (55 : 35 : 5 : 5 by vol.), was placed only in the boat. The dish at the foot of the chromatographic outfit was charged with concentrated hydrochloric acid, which prevented the bands associated with much potassium trailing back to the starting point. 0·02 Ml. of test solution was very carefully placed as a narrow band on a long paper strip by drawing the fine tip of the pipette quickly across the paper from a point 5 mm. in from one edge to within 5 mm. of the other edge. The strip was hung in air for 15 minutes, intensive drying over a hot-plate not being permissible because it subsequently caused unsatisfactory movement of potassium. The strip was placed as usual in the chromatographic apparatus and left until the solvent had travelled 50 cm. from the starting line (about 17 hours). After removal from the apparatus, the strip was hung upside down near a steam radiator until as free as possible from acid and then held horizontally for spraying.

Detection of the Bands.—The production of complex hexanitrites was very satisfactory. While this work was in progress Beerstecher (*Analyt. Chem.*, 1950, **22**, 1200) recommended the use of a reagent prepared from lead and cobalt nitrates and sodium nitrite. Our final reagent was of the same composition as that mentioned by Behrens-Kley (" Mikrochemische Analyse," Voss, Leipzig, 1921, p. 28), except that copper acetate was replaced by cobalt acetate. It was prepared by dissolving hydrated cobalt acetate (11·4 g.), hydrated lead acetate (16·2 g.), sodium nitrite (20 g.), and glacial acetic acid (2 ml.) in water (150 ml.). The acetate buffered the small amount of hydrochloric acid retained by the paper. For spraying purposes the centrifuged solution was mixed with 25% of methanol. A light initial spray usually served to show the number of bands, but spraying had to be continued until colour development was a maximum. It was, however, important not to spray until the strips were wet. Since the reagent solution was yellow, an excess gave a yellow background to the bands and tended to obscure faint bands. By suspending the sprayed strips in a cylinder of cold water and moving them gently up and down for not more than 5 minutes we effectively removed this background, but slight solution of the complex nitrite of cæsium occurred so that the detection of 5 μg. was less certain. The bands due to potassium and rubidium were unaffected. The washed strips were afterwards hung in front of a radiator to dry, and the positions of the bands noted. The colours were stable.

Procedure for Sodium and Lithium.—The solvent mixture contained methanol and *n*-butanol (4 : 1 by vol.). 0·01 Ml. of test solution was placed in a thin line across a 1·5-cm. strip, but without reaching to the edges. The strip was left to dry in air, then placed in the chromatographic apparatus, and the solvent allowed to travel 20 cm. beyond the starting line (time about 100 minutes). On removal from the gas-jar the strip was left to dry in air and then sprayed from the bottom up with zinc uranyl acetate solution (Barber and Kolthoff, *J. Amer. Chem. Soc.*, 1928, **50**, 1625) to which 25% of methanol had been added. The air-dried sprayed strip was examined under ultra-violet light and compared, if desired, with standards. Sodium and lithium were still detectable on strips that had been kept for 3 months.

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