INORGANIC CIRCULAR PAPER CHROMATOGRAPHY

IV. Separation of the Alkali Metals

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Abstract

Lithium, sodium and potassium salts present in a mixture have been separated and the individual alkali metals identified, with different solvents using the technique of circular paper chromatography. A mixture of ethyl and methyl alcohols in equal proportions was found to be a better irrigating solvent for clean and sharp separation of the alkali metals than any one of them. Different anions associated with the same alkali metal could not be resolved by this method. Among the several adsorption indicators tried to identify the metallic bands, Phenosafranine mixed with 0.1N silver nitrate solution was found to be the best

The separation and estimation of alkali metals, especially when they are present in traces, has been found to be very difficult by routine methods of analysis. The present authors have separated and identified the individual alkali metals with different solvents using the technique of circular paper chromatography as described earlier [1].

Whatman No. 3 filter discs of about 25 cms. in diameter were used in this investigation. As the filter paper was suspected to contain the alkali earth metals, it was first irrigated with a solution of nitric acid-water (1:250) to eliminate the effect of their presence and dried. The paper was next spotted with the test solution containing an alkali metal, dried and irrigated with the required solvent. After development of the chromatogram with a suitable colouring reagent and comparing it with another, run without prior treatment with nitric acid, it was found that acid treatment was unnecessary as no difference between the two could be observed. Further work was therefore carried out without the preliminary treatment of the filter disc with nitric acid. 0.05 ml. solution which was 0.05 M with respect to the salt was used for spotting the filter discs. Solutions of individual halide salts or their mixtures were used for spotting. The experiments were conducted in air tight chambers at a laboratory temperature of $27^{\circ}C \pm 1^{\circ}C$.

Identification of the Bands

Considerable difficulty is experienced for the location of the alkali metal bands after running the chromatogram [2-9]. Generally, use of adsorption indicators as developing reagents may be satisfactory if a proper indicator is hit upon.

Alcoholic solution of fluorescein and eosin were found to be satisfactory and were employed in the earlier stages in the present investigation. A mixture of equal volumes of 0.1% indicator and 0.1 N silver nitrate solution was sprayed with an atomiser[10] on the chromatograms. But the bands were not clearly visible and therefore the chromatograms were actually dipped in the developing solution in order to get clear and sharp metallic bands. As too much of the developing solution tended to spread the bands a minimum quantity of the solution just necessary to wet the chromatogram had to be taken in an almost plane glass vessel for dipping the chromatogram. A mixture of 2 ml. of eosin and 5 ml. of 0.1 N silver nitrate solution made up to 200 ml. was found to be the best developing reagent.

Several other indicators in acetone solution were also tried to identify the band. Bromo-cresol-purple, bromo-thymol-blue, brom-phenol-blue, safranine, phenosaffranine and di-iodo (R) dimethyl (R) fluorescein were tried. 0.2% of the dye in acetone were mixed with an equal volume of 0.1 N silver nitrate solution and this mixture was used as the developing reagent. Among these, phenosafranine was found to be the best and therefore it was used in all subsequent experiments. This dye could give immediate colouration of the band which could easily be identified without repeated washing of the chromatogram in distilled water. It is well known that phenosaffranine exhibits some exceptional behaviour among the adsorption indicators[11]. The change of the colour to blue occurs from a complex of phenosaffranine and silver nitrate taken over by the silver halide. The exceptional behaviour of the combination of nitrate and silver ions enhances the value of the indicator. Bromides respond better to the development of the colour with the dye more readily than chlorides.

An account of the results obtained in the present investigation using chlorides of lithium, sodium and potassium for spotting and ethyl alcohol of different concentrations for irrigating the chromatograms are presented in Table I.

TABLE I

R_f Values of Cations

Salts used for spotting: 1. Individual chlorides of potassium, sodium and lithium
2. Mixture of chlorides of potassium, sodium and lithium

Percentage used for irrigation	Potassium		Sodium		Lithium	
	Individual	Mixture	Individual	Mixture	Individual	Mixture
Distilled ethyl alcohol (99 %) ..	0.16	0.19	0.32	0.35	0.70	0.70
Ethyl alcohol 92 % ...	0.28	0 28	0.44	0.45	0.72	0.71
Ethyl alcohol 80 %	0.57	0.56	0.67	0.68	0.79	0.79
Ethyl alcohol 70 %	0.71	0 72	0.75	0.75	0.84	0.84
Ethyl alcohol 60 %	0.95	0 95	0.95	0 95	0.95	0 95

It can be readily seen from the results of Table I that R_f values of alkali metal ions decreases with increase in alcohol concentration of the irrigating solvent. An effective separation could be obtained with 99% ethyl alcohol, lithium moving fastest. Potassium has the lowest R_f value Several other irrigating solvents were also tried for irrigating the chromatogram, such as methyl alcohol, mixtures of methyl and ethyl alcohols, N propyl alcohol, N butyl alcohol and acetone. The alkali iodides were spotted in these cases and the following

TABLE II

R_f values of alkali metal ions with different Solvents

Salts used for spotting 1 Individual iodides of potassium, sodium and lithium
2 Mixture of iodides of potassium, sodium and lithium

Irrigating solvent	Potassium		Sodium		Lithium	
	Individual	Mixture	Individual	Mixture	Individual	Mixture
Methyl alcohol 99 %	0.54	0 53	0.71	0.72	0 88	0.88
Methyl alcohol (99 %) ethyl alcohol (99 %) (1 : 1)	0 40	0.39	0.60	0 61	0 84	0.84
N-propyl alcohol 95 % water 5%	0 16	0.15	0.29	0.30	0.55	0 55
Butanol saturated with water	0 29	0 30	0 29	0 30	0 39	0.41
Butanol saturated with 4 N acetic acid . .	0 56	0.57	0.57	0.57	0.57	0 57
Acetone .	0.20	0 17	0.19	0 17	0.29	0.17

TABLE III

R_f values of cations

Solutions spotted (1) Individual halide salts of potassium, sodium and lithium
(2) Mixture of alkali salts having the same anion but different cations

Irrigating solvent	Cations	Chloride		Bromide		Iodide	
		Individual	Mixture	Individual	Mixture	Individual	Mixture
Ethyl alcohol 99 %	Potassium	0 16	0.19	0.20	0 18	0.30	0.24
	Sodium	0 32	0 35	0.38	0 34	0 46	0 40
	Lithium	0 70	0 70	0.69	0 70	0 76	0 73
Methyl alcohol 99 %	Potassium	0.49	0.49	0.49	0 51	0 54	0 53
	Sodium	0 72	0.70	0.64	0.70	0 71	0 72
	Lithium	0 88	0 88	0.84	0 87	0 88	0 88
Butanol saturated with water	Potassium	0 15	0 13	0.19	0.18	0 29	0.30
	Sodium	0.15	0 13	0.20	0 18	0 29	0.30
	Lithium	0.22	0 22	0.27	0 29	0 39	0.41

results were obtained for their R_f value (Table II) A mixture of ethyl and methyl alcohols in equal proportion was found to be a better [illegible] solvent for clear and sharp separation of the alkali metals than any one of them

Propyl alcohol, butyl alcohol and acetone were found to be in no way better than the mixture of ethyl and methyl alcohols. The present result supports the view of Miller and Magee[12] that mixtures of alcohols are better than single components for separation

The present authors have successfully separated[13] certain cations associated with different anions and an attempt was made with the alkali metals to see if the cations corresponding to the different halide-anions could be separated As a preliminary step the individual halide salts of the alkali metals as well as the cationic mixtures were spotted and the R_f values determined using (i) ethyl alcohol 99 %, (ii) methyl alcohol 99 % and (iii) butanol saturated with water as irrigating solvents. The results are given in Table III.

It can readily be seen that there is very little difference between the R_f values of the chloride, bromide and iodide of any of the cations. With the solvents tried it seemed almost impossible to effect an anionic separation The same was confirmed by spotting a mixture having the same cation but different anions using different solents However by using a filter disc of 45 cm. in diameter which takes nearly 9-10 hours for irrigation, only lithium iodide could be separated from the chloride and bromide as the latter two moved through the same distance. Butanol saturated with 4 N acetic acid which was quite efficient in separating other sets of anions[11] did not resolve the halide anions.

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