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ANALYTICAL METHODS USED IN THE STUDIES
ON CONTINUOUS SEPARATION OF IONS BY
COUNTERCURRENT ION EXCHANGE

Technical Report No. 4

By
Nevin K. Hiester
Russell C. Phillips
Shirley B. Radding
Oliver D. Smith

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Stanford Research Institute

Technical Information Service, Oak Ridge, Tennessee

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Approved: L. M. Richards, Chairman, Department of Chemistry
William E. Rand, Director of Research

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April 10, 1953

Technical Report IV

ANALYTICAL METHODS USED IN THE STUDIES
ON CONTINUOUS SEPARATION OF IONS
BY COUNTERCURRENT ION EXCHANGE

I. INTRODUCTION

Ion exchange separations are normally conducted batchwise by saturating and eluting a fixed bed of resin. This process has the usual disadvantages of a cyclic operation, such as variable effluent concentrations, complex operability, and unfavorable ratio of productive time to unproductive time. In an attempt to overcome the shortcomings of the cyclic process, Stanford Research Institute has undertaken an investigation of continuous ion separation means of countercurrent contact between resin and solution.* This research program has had four primary objectives:

1. Theoretical prediction of the behavior of countercurrent systems.
2. Development of equipment for countercurrent operation.
3. Experimental work to verify the theory and provide data for correlation.
4. An economic comparison of countercurrent and fixed bed units.

Early in the development of the theory it became apparent that evaluation of the experimental results would be considerably simplified by studying an ion-resin system in which the relation between the ion concentration on the resin and in the solution was linear. It was

* Previous results of this investigation are contained in earlier technical reports.

therefore decided to study systems in which the ion of interest was present in trace amounts in the presence of a high concentration of another so-called "gross" ion, since in such systems the trace ion exhibits a linear equilibrium isotherm.² This decision, however, adds further complications in that the pertinent ion is in a lower concentration range and more difficult to analyze quantitatively. In addition to these considerations, the chosen ion-resin system must not have a complex exchange mechanism, nor can the trace ions be too similar if separation of ions is to be achieved.

These requirements led to the choice of Li^+ and K^+ as the trace ions with H^+ as the gross component. This particular system was selected because: (1) the three ions are of equal valence, thus simplifying the exchange mechanism; (2) Li^+ and K^+ are both available in pure forms, as the chlorides, at reasonable costs; (3) they may be analyzed rapidly, at low concentrations, by flame photometry;* (4) as the second and fourth elements in the alkali metal series, Li^+ and K^+ differ sufficiently to make separation feasible; and (5) H^+ is used because of its ease of analysis. A nuclear-sulfonic polystyrene-base type of resin, Chempro C-20 cation exchanger, was used because of its homogeneity of structure and uniform exchange strength.

Even after the choice of the ions and of the analytical techniques, it was necessary to refine the procedures continually to meet more stringent requirements, since the evaluation of the ion exchange experiments requires accurate methods of analysis to give satisfactory results.

* At the beginning of the project, facilities were not available for working with radioactive tracers, so flame photometry was selected for the analytical procedure.

II OBJECTIVES

The objectives of the analytical program were:

1. The determination of the concentration of the alkali metal ions in solution in the presence of hydrogen ions and other alkali metal ions.
2. The quantitative removal of the alkali metal ions from the resin in a form suitable for solution analysis.
3. The determination of the ultimate exchange capacity of the resin, i.e., the replacement and measurement of all the ions in the resin instead of just the trace ions.

III SUMMARY AND CONCLUSIONS

The use of the flame photometer for the analysis of Li^+ and K^+ in solution necessitated checking of the operating variables that might affect the result. The approximate wave-lengths were specified by the instrument manufacturer, and optimum slit widths, consistent with high sensitivity and low interference, were used, so only the effects of the other ions were studied. These other ions (K^+ and HCl in the case of Li^+ , and Li^+ and HCl in the case of K^+) were found to affect the readings, with the greater effects occurring at the higher concentrations of the interfering ions. In order to minimize these effects, the final procedure adopted used standards which contained both Li^+ and K^+ , at various concentrations and in varying proportions, in the presence of 1.0 N HCl , and which thus closely approximated the unknown solutions being analyzed.

Two procedures were tested for the removal of Li^+ and K^+ ions from resins: (1) elution with an excess of hydrogen ions, (2) destruction of the resin to a mineral residue by either thermal or wet chemical oxidation. Elution with varying quantities and concentrations of H^+ indicated that essentially complete removal of these trace ions from 10 g of resin could be achieved with 125 ml of 2.0 N HCl . By comparison, the destructive methods were less satisfactory, apparently because of volatilization of potassium and lithium salts and spattering. Extra background interference in the flame also occurred because it was impossible to free completely the potassium and lithium chlorides from the other compounds originally present, such as sulfate, decomposition products of the resin, etc. The elution method, which is relatively

easy and rapid, was adopted as the final procedure.

Two fundamentally different methods for determining the ultimate or total exchange capacity of the resin were evaluated. In one, an aliquot of resin, in the hydrogen form, was completely converted to a metal ion form such as Na^+ or Ca^{++} by contact with a very large excess of the metal salt solution, and the displaced hydrogen ion titrated. In the other method the hydrogen resin was incrementally titrated with OH^- to the pH breakpoint. The two methods gave essentially the same results, 5.11 meq/g for the resin concerned, but the Ca^{++} elution method was chosen as the standard procedure because of its ease, rapidity, and reproducibility of results (± 0.03 as compared to ± 0.07 or ± 0.11 for Na^+ elution or titration procedures.)

The final analytical methods adopted for these three determinations are reproduced in detail in the Appendix.

IV EXPERIMENTAL PROCEDURE AND RESULTS

A. General

The procedure for the analysis of solutions was studied first, since since it was necessary to use it to evaluate the results of the resin elution procedure. The ultimate capacity studies were postponed until last, because they were an extension of the resin elution methods.

In general, the experimental work involved comparison of the accuracy of different procedures, each involving a pertinent variable of the analytical technique. For instance, in the analysis of solutions, one of the variables was the concentration of interfering ions, while in the elution of resins, the amount of elutant was important. In the case of solutions, known concentrations were prepared and were used as standards. However, with the resin elution procedures, the amount of alkali metal ion initially present in the resin was not known, and so the procedures that showed the greatest removal of ion from the resin were considered more satisfactory.

B. Methods for the Determination of K^+ and Li^+ in Solution

General The flame photometer was chosen for the analysis of the Li^+ and K^+ because it offered the highest potential accuracy (and speed) available for analysis of the alkali metal ions in the concentration range of interest.^{1, 3, 4} A Beckman DU spectrophotometer with an acetylene-oxygen flame attachment was used throughout the program.

The four primary variables that might affect the analytical results were the wave lengths and slit widths used for the two ions and the concentrations of the other alkali metal ion and the hydrochloric acid. As suggested by the instrument manufacturer, the wave lengths of the principal lines (on this instrument, 771 m μ for the potassium and 673 m μ for the lithium) were used throughout. In all of the tests involving the other variables, Li⁺ or K⁺ solutions containing 1.0 N HCl were used as the standard. These were prepared, at 0.01, 0.05, 0.1, and 0.5 N, by weighing out the salt and then checking the standardization gravimetrically through precipitation of the Cl⁻ with silver nitrate solution. At least five dilutions of each of the above primary standards were then made up by using concentrated HCl in such a manner that the final solutions were 1 N with respect to hydrogen ion.

In general, the calibration procedure consisted of first adjusting the instrument to the chosen settings of wave length and slit width for the ion concerned. The primary standard was then aspirated into the flame and the photometer set to a reading corresponding to 100% transmission. The relative transmissions of the diluted solutions were then determined and plotted against the actual concentration of the ion of interest. This plot was then considered the calibration curve for the primary standard concerned.

Effect of Slit Width The effect of slit width could not be checked directly since it was first necessary to find the proper slit width to be used with each of the primary standards mentioned above. At too low a slit width the sensitivity becomes poor because so little of the flame intensity reaches the instrument, and when the slit width is too large, the interference from other ions becomes greater; thus, the proper slit width must be based on an optimum balance of these two factors. The optimum values obtained for this instrument were:

Actual Normality of Li ⁺ and K ⁺ in 1.0 N HCl	Optimum Slit Width	
	Li ⁺	K ⁺
0.01	0.15 mm	0.06 mm
0.05	0.15	0.06
0.1	0.08	0.04
0.5	0.05	0.02

As might be expected, the optimum slit width depended on the strength of the flame line and thus on both the ion and its approximate ionic concentration.

The actual effect of slit width can best be shown by re-checking one of the primary standards, and its dilutions, on the flame photometer with the slit width set higher than optimum. For comparison purposes the instrument was set at 100% transmission with the primary standard and at the optimum slit width. The slit width was then increased and the per cent transmission of all of the samples was determined. These values were then used to read the indicated concentrations from the normal calibration curve obtained for the primary standard at the optimum slit width. The results indicated by the new readings were:

Actual Normality of Li ⁺ and K ⁺ in 1.0 N HCl	Ratio of Indicated to Actual Normality*	
	Li ⁺ @ 0.2 mm slit width	K ⁺ @ 0.1 mm slit width
0.005	1.01	-
0.010	1.08	1.09
0.020	1.17	1.01
0.030	1.15	1.04
0.040	1.13	0.96
0.050	1.01	0.98

These values again confirm the fact that, at larger slit widths, extraneous interferences ("background") have a greater effect on the results.

At an early date it became apparent that the Li⁺ and K⁺ exhibited mutual interference and that the HCl, always present in the experimental solutions, also interfered with the readings for the metal ions. These effects have also been reported by Parks and Lykken.⁴ The next set of tests were performed to check the magnitude of this latter effect.

Effect of the Presence of HCl A set of standard solutions, at 0.01 N KCl and 0.01 N LiCl, were prepared and standardized as before but were diluted with distilled water rather than acid. These solutions were then used to prepare a special calibration curve for the flame

* The calibration curve is based on the actual normality and slit widths of 0.15 mm for Li⁺ and 0.06 mm for K⁺.

photometer. Regular, acid-containing, standards were then checked on the flame photometer against this calibration curve, using the narrow slit widths given above. The results were as follows:

Actual Normality of K^+ or Li in 1.0 N HCl	Ratio of Indicated Normality to Actual Normality	
	Li^+	K^+
0.002	1.07	1.13
0.004	1.06	1.12
0.006	1.06	1.12
0.008	1.06	1.12

It is apparent that the use of standards in water, rather than in 1.0 N HCl, will give high readings on the experimental samples.

Effect of Mutual Interference of the Alkali Ions The effect of mutual Li^+ — K^+ interference was evaluated by the preparation of standard solutions, in 1.0 N HCl, containing both K^+ and Li^+ , in 1:1, 3:1, and 1:3 ratios, and at various concentration levels. Readings were then obtained against the pure K^+ or Li^+ calibration standards. Some of the Li^+ results were:

Actual Normality of Li^+ in 1.0 N HCl	Ratio of Indicated Normality to Actual Normality		
	3 Li^+ :1 K^+	1 Li^+ :1 K^+	1 Li^+ :3 K^+
0.001		1.00	1.00
0.002		1.03	1.01
0.003	1.02		
0.004		1.05	1.05
0.006	1.02	1.04	1.04
0.008		1.01	1.04
0.010		1.01	1.02
0.012	1.02		
0.018	1.05		
0.024	1.02		
0.030	1.01		
0.10		0.87	
0.20		1.11	
0.30		1.15	
0.40		1.12	

This information indicates that the greater quantities of K^+ , either ratio-wise or concentration-wise, usually cause increased interference in the Li^+ results.

A comparison of these results with those for K^+ indicate that Li^+ causes less interference with the K^+ readings than K^+ with Li^+ . For example, in the case of 1 Li^+ :1 K^+ , the results are as follows:

Actual Normality of Li^+ or K^+ in 1.0 N HCl	Ratio of Indicated Normality to Actual Normality	
	Li^+	K^+
0.001	1.00	1.01
0.002	1.03	1.00
0.004	1.05	1.01
0.006	1.04	1.01
0.008	1.01	0.99

Conclusions. The presence of interference both from the HCl and the other alkali ion emphasizes the need for the use of standards containing both Li^+ and K^+ , in varying concentrations and proportions, and 1.0 N HCl. The final procedure adopted fulfills this requirement. This procedure, SRI Analytical Method No. 26.01 is reproduced in detail in the Appendix.

C. Methods for the Elution of K^+ and Li^+ from the Resin

General In the case of resin analysis the principal problem is the quantitative transfer of potassium and lithium from the resin sample to a solution which can then be analyzed by the standard procedure established above. The removal methods suggested fall into two general categories: (a) elution with an excess of another ion, and (b) oxidation of the resin followed by an acid leach of the residue.

In the elution method an aliquot of the resin sample was transferred to a tube, and the chosen volume of elutant was passed through it at a slow rate. The resin was then washed with distilled water, and the combined effluents were analyzed for the K^+ and Li^+ removed from the resin. The resin aliquot was then oven-dried, so that the concentrations could be expressed on a consistent basis of dry hydrogen-form resin. Since the amount of alkali metal ion originally present on the resin was not known, each set of tests was performed on aliquots of the same resin sample so that the results could be compared.

Effect of Elution Conditions The elution experiments involved the effect of elutant quantity and concentration. The elution columns used to check the treatments each contained 10 g of oven-dried resin. The results obtained were:

<u>Elution Treatment*</u>	<u>Amount Removed, meq/g</u>	
	<u>Li⁺</u>	<u>K⁺</u>
100 ml 1.0 N HCl	0.078	0.094
200 ml 1.0 N "	0.077	0.137
400 ml 1.0 N "	0.078	0.160
100 ml 2.0 N "	0.079	0.158
400 ml 2.0 N "	0.078	0.159
1000 ml 2.0 N CuCl ₂	0.073	0.140

It would appear that either 400 ml of 1.0 N HCl or 100. of 2.0 N would elute both K⁺ and Li⁺ from the resin satisfactorily. The Cu⁺⁺ elutant was not successful; mainly because it caused interference in the flame photometer readings and thus affected the results. A volume of 125 ml of 2.0 N was selected as best for the elution procedure, because the resin could be washed with an equal volume of distilled water and yield just 250 ml of effluent (a standard volumetric flask volume) at an HCl concentration of 1.0 N, the desired level for analysis.

Effect of Dry-Ashing Conditions The second removal method, oxidation of the resin, was accomplished either by thermal destruction (dry-ashing) or by chemical oxidation (wet-ashing).

The resin samples were oven-dried prior to these destructive treatments so that the results could be expressed on a dry basis. In the dry method the resin was carefully pyrolyzed at 1000°C until only a mineral ash remained. After cooling, this ash was then taken up with 1.0 N HCl and the solution analyzed as usual. The wet method consisted of treating the resin with HNO₃ and H₂SO₄, and in some cases HClO₄, at the boiling point until no residue was apparent. The resultant solution was then evaporated to dryness, taken up with 1.0 N HCl, and analyzed as before.

* The elutant was passed through the resin at a superficial velocity of about 5cm/min.

Again, each set of tests was performed on aliquots of the same resin sample so that the results could be compared. The first experiment compared the elution method with dry-ashing in porcelain.

<u>Treatment</u>	<u>Amount Found, meq/g</u>	
	<u>Li⁺</u>	<u>K⁺</u>
Resin eluted with 100 ml of 2.0 N HCl	0.079	0.158
Resin ashed at 1000°C	0.024	0.025
Li ⁺ and K ⁺ solution ashed at 1000°C	None	None

Ashing in porcelain appears to be completely unsatisfactory, probably because the Li⁺ and K⁺ are taken up in the porcelain glass.

The use of platinum crucibles for the dry-ashing was suggested, so the next experiment compared them with the porcelain crucibles used in the previous series. In some cases, solutions containing known quantities of Li⁺ and K⁺ were added to the ashing containers before treatment. In these cases, the results should be high, by the amount added, as compared to the values obtained by elution. The results for the second experiment were:

<u>Treatment</u>	<u>Amount, meq/g</u>			
	<u>Predicted</u>		<u>Found</u>	
	<u>Li⁺</u>	<u>K⁺</u>	<u>Li⁺</u>	<u>K⁺</u>
Resin eluted with 100 ml of 2.0 N HCl			0.079	0.158
Resin ashed in porcelain at 1000°C			0.024	0.025
Resin ashed in platinum at 1000°C			0.083	0.157
Resin plus known solution in platinum at 1000°C	0.202	0.271	0.188	0.256
Known solution ashed in platinum at 1000°C	0.380*	0.338*	0.075*	0.025*

* Concentrations are given in total meq rather than meq/g.

Although the use of platinum crucibles is much more satisfactory than porcelain, poor recoveries of added solutions were obtained. This may be due to volatilization or to background effect on the flame caused by fine particles of incompletely ashed resin.

Effect of Wet-Ashing Conditions The wet-ashing technique was tried next. In these experiments some of the treatments were repeated several times to check the reproducibilities of the results. In all cases the material was treated with HNO_3 and H_2SO_4 , at the boiling point, until the solution was essentially clear. The results are given below:

Sample	Amount, meq/g			
	Predicted		Found	
	Li ⁺	K ⁺	Li ⁺	K ⁺
Resin			0.103	0.168
"			0.090	0.185
"			0.093	0.185
"			0.089	0.175
"			0.093	0.183
Resin plus known solution	0.172	0.231	0.156	0.237
"	0.206	0.271	0.213	0.266
"	0.179	0.237	0.163	0.233
"	0.202	0.255	0.185	0.259
"	0.165	0.226	0.146	0.220
"	0.254	0.295	0.264	0.275
"	0.245	0.351	0.260	0.256
"	0.314	0.343	0.329	0.315
"	0.274	0.311	0.240	0.301
Known Solution*	0.860	0.676	0.710	0.668
"	0.860	0.676	0.710	0.688
Water	None	None	None	None
"	None	None	None	None
Resin eluted with 100 ml of 2.0 N HCl			0.079	0.158

* Concentrations are given in total meq rather than in meq/g.

The wet-ashing method appears to be fairly reproducible but poor recoveries of the added solutions were obtained. Again volatilization or flame background interference due to unreacted resin constituents may be to blame.

A second series of wet-ashing experiments were undertaken next. In this case HClO_4 was used, in addition to HNO_3 and H_2SO_4 . A few elution runs were also included for comparison purposes on the new resin aliquot. As before, the experiments were performed in replicate.

<u>Sample</u>	<u>Amount, meq/g</u>		<u>Found</u>	
	<u>Predicted</u>		<u>Li⁺</u>	<u>K⁺</u>
	<u>Li⁺</u>	<u>K⁺</u>		
Resin			0.055	0.138
"			0.056	0.142
"			0.059	0.140
"			0.058	0.142
"			0.059	0.141
Known Solution	0.500	0.500	0.460	0.485
Resin eluted with 2.0 N HCl			0.066	0.143
"			0.068	0.145

Conclusions Although fairly good agreement is shown in this wet-oxidation method, elution is simpler and faster and was therefore adopted as the final procedure. This technique, SRI Analytical method No. 27.01 is reproduced in detail in the Appendix.

D. Methods for the Determination of the Ultimate Exchange Capacity of the Resin

General An important factor in ion exchange studies is the ultimate capacity, or total exchange capacity, of the ion exchange resin. It is a measure of the number of positions available for exchange in a given quantity of resin.

Two fundamentally different methods for determining ultimate capacity were evaluated. In one, resin in the hydrogen form was converted to a metal ion form by contact with a large excess of metal salt solution. The amount of hydrogen ion displaced from the resin into the

solution was determined by titration, thereby indicating the capacity of the resin.

The alternate method involved the incremental titration of a hydrogen resin slurry with sodium hydroxide solution to obtain a titration curve. The amount of sodium hydroxide solution required to titrate to the point at which the pH changed rapidly, upon the addition of base, was converted to the H^+ present and thus to the ultimate capacity of the resin.

Experimental Procedure In the experiment a quantity of C-20 resin was converted almost completely to the hydrogen form by extensive elution with HCl in a fixed bed. This resin was thoroughly mixed and eluted further with 2 N HCl. Finally it was washed with distilled water until neutral to methyl orange. After further mixing, the resin was divided into eight portions of about 25 ml (10g) for use in the following treatments.

(a) Two aliquots were transferred to small glass columns, and 1 liter of saturated NaCl solution was passed through each. The resin samples then were washed with distilled water. Aliquots of the effluent solutions were titrated with standard sodium hydroxide to the phenolphthalein endpoint to obtain the quantity of H^+ released by the resin. The resin samples were treated with 250 ml 2 N HCl, washed with distilled water, and dried overnight at $105^{\circ}C$ to obtain the ultimate capacity in terms of the dry weight of hydrogen form resin.

(b) Two aliquots were treated as in procedure (a) except that 2 liters of saturated NaCl solution were used.

(c) Two aliquots were similarly treated with 1 liter each of 5% $CaCl_2$ solution.

(d) Two aliquots were then titrated in increments to pH 14 with standard NaOH. The resin was back titrated with standard HCl. The resin samples were washed with distilled water and dried overnight at $105^{\circ}C$.

Results The results of these treatments are given below:

<u>Treatment</u>	<u>Ultimate Capacity, meq/g</u>
1 l saturated NaCl	5.16
" " "	5.18
2 l " "	5.14
" " "	5.08
1 l 5% CaCl ₂	5.14
" " "	5.08
Titration to pH15	5.00
" " "	5.10
Average	5.11

In the NaOH titration procedure, the break in the pH curve occurred between pH 7 and pH 11 as shown in Figure 1. The reverse titration with HCl to pH 2 did not give a satisfactory end point. No definite break was observed, and the apparent end point resulted in an erroneously high capacity.

Conclusions The procedure selected as the standard method was that of using 1 liter of 5% CaCl₂. This method was economical of the analyst's time and in reagents and gave satisfactorily reproducible results. This procedure is given in detail in the Appendix as Analytical Section Method No. 25.01.

NOTEBOOK REFERENCES AND ACKNOWLEDGMENTS

The details of the experimental results are contained in the following Stanford Research Institute notebooks for permanent record: No. 788, 1148, 1170, and 1225.

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Nevin K. Hiester

Nevin K. Hiester
Associate Chemical Engineer

Shirley B. Radding

Shirley B. Radding
Assistant Chemist

Russell C. Phillips

Russell C. Phillips
Associate Chemical Engineer

Oliver D. Smith

Oliver D. Smith
Assistant Chemist

FIG. 1
DETERMINATION OF ULTIMATE CAPACITY BY
INCREMENTAL TITRATION

A-CU337-70

BIBLIOGRAPHY

1. Berry, J. W., D. G. Chappell, and R. B. Barnes, Ind. & Eng. Chem. Anal. Ed., 18, 19 (1946).
2. Boyd, G. E., J. Schubert, and A. W. Adamson, J. Am. Chem. Soc., 69, 2818 (1947).
3. Gilbert, P. T. Jr., R. C. Hawes, and A. O. Beckman, Anal. Chem., 22, 772 (1950).
4. Parks, T. D., H. O. Johnson, L. Lykken, Anal. Chem., 20, 822 (1948).

APPENDIX

- ASM 25.01 Ultimate Capacity of Ion Exchange Resins
- ASM 26.01 Hydrogen, Potassium and Lithium in Solution
Samples from Ion Exchange
- ASM 27.01 Potassium and Lithium on Resin Samples from
Ion Exchange Runs

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

Determination of
ULTIMATE CAPACITY OF ION EXCHANGE RESINS

SCOPE

1. This method is intended for the determination of the total capacity of an ion exchange resin containing sulfonic acid groups.

OUTLINE OF METHOD

2. An aliquot of resin is first converted to the hydrogen ion state and then eluted with calcium chloride solution. The effluent from the elution step is titrated with standard sodium hydroxide solution and the resin reconverted to the hydrogen ion state, dried, and weighed.

APPARATUS

3. An 8-inch Glass Column, fitted with perforated disk and a delivery flask.

REAGENTS

4. (a) Standard Sodium Hydroxide, 0.10 N. Dissolve 4.0 g. sodium hydroxide in water and dilute to exactly one liter with distilled water. Standardize by titrating weighed portions of potassium acid phthalate to the phenolphthalein end point.

(b) Hydrochloric Acid, 1.0 N. Dilute 95 ml of concentrated hydrochloric acid to exactly one liter with distilled water.

(c) Hydrochloric Acid, 4.0 N. Dilute 380 ml. of concentrated hydrochloric acid to exactly one liter with distilled water.

(d) Calcium Chloride, 5%. Dissolve 50 g. of calcium chloride in distilled water and dilute to one liter with distilled water.

PROCEDURE

5. (a) Transfer approximately 25 ml. of resin in the hydrogen ion state to a column and wash with 100 ml. water. Pass one liter of 1.0 N hydrochloric acid slowly through the resin by means of the delivery flask. Wash the resin in the same manner with distilled water until the effluent is neutral to methyl orange. Discard all effluents up to this point.

(b) Pass one liter of 5% calcium chloride solution through the resin as above, collecting the effluent in a one-liter volumetric flask. Collect exactly one liter.

(c) Wash the resin once more with distilled water, discarding the washings. Pass through one liter of 4.0 N hydrochloric acid, discarding the effluent and wash the resin with 250 ml. of distilled water. Transfer the resin to a tared beaker and dry overnight at 105°C, cool in a dessicator and weigh rapidly (Note 1.)

Note 1. The resin will pick up moisture in weighing and therefore speed in weighing is essential.

(d) Mix the calcium chloride effluent and pipette a 25-ml aliquot into a flask and titrate with standard 0.10 N sodium hydroxide to the phenolphthalein end point.

CALCULATIONS

6. Calculate the total meq/g capacity of the resin as follows:

$$\text{meq/g} = \frac{(A) (B) (C)}{(D) (E)}$$

where:

A = titre, in ml of sodium hydroxide used to reach the phenolphthalein end point,

B = normality of sodium hydroxide used,

C = total volume of sample, in ml,

D = volume of aliquot in ml,

E = weight of oven-dried resin, in g

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

Determination of
HYDROGEN, POTASSIUM, AND LITHIUM
IN SOLUTION SAMPLES FROM ION EXCHANGE

SCOPE

1. This method is intended for the determination of potassium, lithium, and hydrogen ions in solutions from ion exchange resins.

OUTLINE OF METHOD

2. The volume of the sample is recorded and the acid content determined on an aliquot. If the hydrogen ion concentration varies from 1 N by more than 5%, hydrochloric acid is added to a second aliquot to make the solution 1.0 N and the new volume recorded. The potassium and lithium ions are determined on the acid-adjusted sample with a flame photometer at predetermined wave lengths using the proper reference solutions. The amounts of potassium and lithium are obtained by reference to the proper calibration curves.

APPARATUS

3. (a) Automatic Titrator. A Beckman Automatic Titrator, set up to titrate acid, is used.

(b) Flame Photometer. A Beckman Flame Spectrophotometer is used with wave lengths of 771 $m\mu$ for potassium and 673 $m\mu$ for lithium.

REAGENTS

4. (a) Standard Sodium Hydroxide, 1.0 N. Dissolve 40 g. sodium hydroxide in water and dilute exactly to one liter with distilled water.

Standardize by titrating weighed portions of potassium acid phthalate to the phenolphthalein end point.

(b) Hydrochloric Acid, 2.0 N. Dilute 190 ml. of concentrated hydrochloric acid to exactly one liter with distilled water.

(c) Standard Potassium Chloride Solution, 0.5 N. Dissolve exactly 37.275 g. of potassium chloride in 1.0 N hydrochloric acid and dilute to exactly one liter with 1.0 N hydrochloric acid.

(d) Standard Potassium Chloride Solutions, 0.1 N, 0.05 N, and 0.01 N. Prepare by accurate dilutions of (c) using 1.0 N hydrochloric acid.

(e) Standard Lithium Chloride Solution, 0.5 N. Dissolve exactly 21.200 g. of lithium chloride in 1.0 N hydrochloric acid and dilute to exactly one liter with 1.0 N hydrochloric acid.

(f) Standard Lithium Chloride Solutions, 0.1 N, 0.05 N, 0.01 N. Prepare by accurate dilutions of (e) using 1.0 N hydrochloric acid.

STANDARDIZATION OF APPARATUS

5. (a) Using a buffered pH 7.0 solution, adjust zero on the Beckman automatic titrator. Set scale at 7.6 for titration of acid (Note 1).

Note 1. This setting may vary for different instruments.

It is the reading which corresponds to the first faint pink color of phenolphthalein in a titration.

(b) Using the standard solutions of potassium and lithium chlorides described in section 4, prepare solutions to give at least five dilutions of each standard using 1.0 N hydrochloric acid to make the dilutions. In a similar manner, using the standard solutions described in section 4, prepare solutions containing equal molar concentrations of lithium and potassium at 0.5 N, 0.1 N, 0.05 N, and 0.01 N levels. From each of these solutions obtain at least five dilutions using 1.0 N hydrochloric acid. Repeat this procedure for molar ratios of lithium and potassium of 1:3, 1:5, 3:1, 5:1.

(c) Prepare the flame photometer for use according to the instructions of the manufacturer, using a wave-length of 771 m μ for potassium and 673 m μ for lithium. Using the 0.5 N K⁺ standard for reference, obtain readings for all samples containing K⁺. Repeat using

0.1 N K^+ , 0.05 N K^+ , and 0.01 N K^+ standards as references, reading all samples containing K^+ in amounts up to and including the concentration of the standard. Repeat for lithium. Plot percent emission vs. meq/ml as for example:

pure potassium - 0.5 N std. reference

0.1 N " "

0.05 N " "

0.01 N " "

Using all readings obtained for samples containing only potassium chloride.

Pure lithium - repeat as for potassium using readings obtained for lithium.

3 K^+ :1 Li^+ - 0.5 N std. reference

0.1 N " "

0.05 N " "

0.01 N " "

Use readings obtained with 3 K^+ : 1 Li^+ solutions read against pure potassium standards.

Repeat for 3 K^+ : 1 Li^+ (Li^+ readings), 3 Li^+ : 1 K^+ (K^+ + Li^+ readings), 5 K^+ : 1 Li^+ (K^+ + Li^+ readings), 1 K^+ : 1 Li^+ (K^+ + Li^+ readings), and 5 Li^+ : 1 K^+ (K^+ + Li^+ readings). (Note 2). In this manner, 40 graphs can be obtained.

Note 2. All graphs will not read from 0-100% emission. For example, for 5 K^+ : 1 Li^+ , using 0.01 N K^+ as reference, readings will probably be obtained only from 50-100% because the ratio limits the range of the Li^+ and therefore the K^+ . The reverse is also true, in that the Li^+ curve, using the 0.5 N Li^+ , will probably only go from 0-50% emission.

(d) A Beckman pH meter set at 0.1 pH is used for adjusting solutions to 1.0 N with concentrated hydrochloric acid. (Note 3.)

Note 3. This setting is not strictly correct for a 1.0 N solution, but it is the smallest

reading obtainable on the scale and is close enough for this adjustment.

PROCEDURE

6. (a) Record volume of sample and measure out 10-ml aliquot into a 250-ml beaker and add 100 ml of distilled water and titrate on the automatic titrator to a pH of 7.6 (Note 1). Record this value.

(b) To a second 10-ml aliquot in a 100-ml beaker, add conc. hydrochloric acid by means of a burette to a pH of 0.1. (Note 3). Record this new volume.

(c) Obtain flame photometer readings for potassium and lithium using the proper reference standards, and read the potassium and lithium values by interpolation of the proper graphs. Use the adjusted solutions for this analysis.

CALCULATIONS

7. (a) Calculate the meq/ml of hydrogen in the sample solution as follows:

$$\text{hydrogen, meq/ml of sample} = \frac{(A)(B)}{(C)}$$

where:

A = titre, in ml of sodium hydroxide used to reach a pH of 7.6,

B = normality of sodium hydroxide used,

C = ml aliquot of sample.

(b) Calculate the meq/ml of potassium and lithium in the sample solution as follows:

1. Read the meq/ml of potassium from the proper "pure potassium" graph.
2. Repeat for lithium.
3. Determine the potassium-lithium ratio, using the smaller quantity as the denominator.
4. Reread the potassium and lithium results from the proper ratio graphs interpolating where necessary.
5. Correct for the adjusted volumes as follows:

$$K^+ \text{ or } Li^+, \text{ meq/ml} = \frac{(\text{apparent meq/ml})(\text{ml adjusted vol.})}{\text{ml aliquot}}$$

Report results as corrected meq/ml of K^+ and Li^+ .

<u>Standard Reference</u>	<u>Slit Width</u>	<u>Selector Switch</u>
0.01 N K^+ in water	0.03	0.1
0.01 N Li^+ in water	0.15	1.0
0.01 N K^+ in 1.0 N H^+	0.06	1.0
0.01 N Li^+ in 1.0 N H^+	0.15	1.0
0.05 N K^+ in " "	0.06	1.0
0.05 N Li^+ " "	0.15	1.0
0.10 N K^+ " "	0.04	1.0
0.10 N Li^+ " "	0.08	1.0
0.50 N K^+ " "	0.02	1.0
0.50 N Li^+ " "	0.05	1.0

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

Determination of
POTASSIUM AND LITHIUM ON RESIN SAMPLES
FROM ION EXCHANGE RUNS

SCOPE

1. This method is intended for the determination of potassium and lithium ions on resin samples from ion exchange runs.

OUTLINE OF METHOD

2. The resin sample is eluted with acid to remove cations and these cations are then determined in the solution by the flame photometer. The resin is carefully dried and weighed to determine the exact amount used.

APPARATUS

3. (a) 8-inch Glass Column, fitted with perforated disk and delivery flask.

(b) Flame Photometer. A Beckman flame spectrophotometer is used with wave lengths of 771 m μ for potassium and 673 m μ for lithium.

REAGENTS

4. (a) Hydrochloric Acid, 2.0 N. 190 ml of concentrated hydrochloric acid is diluted to exactly one liter with distilled water.

(b) Standard Potassium Chloride Solution, 0.5 N. Dissolve exactly 37.275 g. of potassium chloride in 1.0 N hydrochloric acid and dilute to exactly one liter with 1.0 N hydrochloric acid.

(c) Standard Potassium Chloride Solutions, 0.10 N, 0.05 N, 0.01 N. Prepare by accurate dilutions of (b) using 1.0 N hydrochloric acid.

(d) Standard Lithium Chloride Solution, 0.5 N. Dissolve exactly 21.200 g. lithium chloride in 1.0 N hydrochloric acid and dilute to exactly one liter with 1.0 N hydrochloric acid.

(e) Standard Lithium Chloride Solutions, 0.10 N, 0.05 N, 0.01 N. Prepare by accurate dilutions of (d) using 1.0 N hydrochloric acid.

STANDARDIZATION OF APPARATUS

5. (a) Using a buffered pH 7.0 solution, adjust zero on the Beckman automatic titrator. Set scale at 7.6 for titration of acid. (Note 1).

Note 1. This setting may vary for different instruments. It is the reading which corresponds to the first faint pink color of phenolphthalein in a titration.

(b) Using the standard solutions of potassium and lithium chlorides described in section 4, prepare solutions to give at least five dilutions of each standard using 1.0 N hydrochloric acid to make the dilutions. In a similar manner, using the standard solutions described in Section 4, prepare solutions containing equal molar concentrations of lithium and potassium at 0.5 N, 0.1 N, 0.05 N, and 0.01 N levels. From each of these solutions obtain at least five dilutions using 1.0 N hydrochloric acid. Repeat this procedure for molar ratios of lithium and potassium of 1:3, 1:5, 3:1, 5:1.

(c) Prepare the flame photometer for use according to the instructions of the manufacturer, using a wave length of 771 m μ for potassium and 673 m μ for lithium. Using the 0.5 N potassium ion standard for reference, obtain readings for all samples containing potassium ion. Repeat using 0.1 N K⁺, 0.05 N K⁺, and 0.01 N K⁺ standards as references, reading all samples containing K⁺ in amounts up to and including the concentration of the standard. Repeat for lithium. Plot percent emission vs. meq/ml as for example:

pure potassium -	0.5 N std. reference	
	0.1 N "	"
	0.05 N "	"
	0.01 N "	"

Use all readings obtained for samples containing only potassium chloride.

Pure lithium - repeat as for potassium using readings obtained for lithium.

3 K ⁺ :1 Li ⁺	-	0.5 N std. reference
		0.1 N " "
		0.05 N " "
		0.01 N " "

Use readings obtained with 3 K⁺:1 Li⁺ solutions read against pure potassium standards.

Repeat for 3 K⁺ : 1 Li⁺ (Li⁺ readings), 3 Li⁺ : 1 K⁺ (K⁺ + Li⁺ readings), 5 K⁺ : 1 Li⁺ (K⁺ - Li⁺ readings), 1 K⁺ : 1 Li⁺ (K⁺ + Li⁺ readings), and 5 Li⁺ : 1 K⁺ (K⁺ + Li⁺ readings). (Note 2). In this manner, 40 graphs can be obtained.

Note 2. All graphs will not read from 0-100% emission. For example, for 5 K⁺ : 1 Li⁺, using 0.01 K⁺ as reference, readings will probably be obtained only from 50-100% because the ratio limits the range of the Li⁺ and therefore the K⁺. The reverse is also true, in that the Li⁺ curve, using the 0.5 N Li⁺, will probably only go from 0-50% emission.

PROCEDURE

6. (a) Transfer the resin sample to a column saving all washings. If the resin fills more than one-half of the column, remove the excess and place in a tared beaker. Wash the resin in the column with 100 ml of water and save the washings. Add 125 ml of 2.0 N hydrochloric acid to the delivery flask and allow the acid to pass through the resin very slowly. Always keep the resin under liquid. Collect the effluent in a 250-ml volumetric flask. When 125 ml of acid has passed through the resin, change the receiving flask for a clean one and pass a second 125-ml portion of 2.0 N hydrochloric acid through the resin. Wash with 100 ml of distilled water, collecting the effluent in the second flask.

Transfer the resin to a tared beaker using distilled water to wash from one container to the other. Dry the resin overnight at 105°C and cool in a dessicator. Weigh rapidly (Note 3).

The solutions are diluted to exactly 250 ml using the original washings first to make the dilutions and then distilled water. Obtain readings for potassium and lithium using the proper standards on the flame photometer. Obtain the potassium and lithium values by reading from the proper graphs and interpolating where necessary.

If excess resin has been removed, dry this portion at 105°C overnight and weigh. Report separately in addition to sample weight as total weight of resin.

Note 3. The resin will pick up moisture in weighing and therefore speed in weighing is essential.

CALCULATIONS

7. (a) Calculate the meq/ml of potassium and lithium in the solutions as follows:

- (1) Read the value for potassium from the proper "pure potassium" graph.
- (2) Repeat for lithium.
- (3) Determine the potassium-lithium or lithium-potassium ratio, using the smaller quantity as the denominator.
- (4) Reread the potassium and lithium results from the proper ratio graphs interpolating where necessary.

(b) Using the corrected meq/ml values, calculate the meq/g as follows:

$$\text{meq/g} = \frac{(A)250 + (B)250}{(C)}$$

where:

- A = corrected meq/ml for first portion,
 B = corrected meq/ml for second portion,
 C = weight of resin used.

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