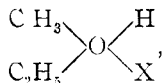


This ether dissolves readily in the hydrogen bromide or iodide with the development of a large quantity of heat. White crystals separate out, which melt sharply at  $-30^{\circ}$  in the case of hydrobromic acid compounds, and at  $-22^{\circ}$  in the other. One molecule of acid unites with one molecule of the ether—a result to be expected from the composition of di-methyl and di-ethyl acid compounds. These compounds, if the oxygen is tetravalent, have the composition



and here the oxygen is asymmetric. Attempts to separate these compounds into their optically active isomers have not been successful.

The melting points of the various ether compounds with hydrobromic and hydriodic acids are given in the following table:

Compounds.	M. P.
$(\text{CH}_3)_2\text{OHI}$ .....	-15
$(\text{CH}_3)_2\text{OHBBr}$ .....	-22
$(\text{C}_2\text{H}_5)_2\text{OHI}$ .....	-18
$(\text{C}_2\text{H}_5)_2\text{OHBBr}$ .....	-40
$\begin{array}{l} \text{C H}_3 \\ \diagdown \\ \text{O} \\ \diagup \\ \text{C}_2\text{H}_5 \end{array} \text{OHI}$ .....	-22
$\begin{array}{l} \text{C H}_3 \\ \diagdown \\ \text{O} \\ \diagup \\ \text{C}_2\text{H}_5 \end{array} \text{OHBBr}$ .....	-30

McGILL UNIVERSITY, MONTREAL,  
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## A NEW METHOD OF SEPARATING LITHIUM CHLORIDE FROM THE CHLORIDES OF THE OTHER ALKALIS, AND FROM THE CHLORIDE OF BARIUM.

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It is well known that the separation of lithium from the other alkali metals presents considerable difficulty. In his investigations of the mineral water of Karlsbad, Berzelius<sup>1</sup> sought to separate lithium from sodium and potassium by adding phosphoric acid to the solution and then neutralizing with sodium carbonate in slight excess. On evaporating this alkaline solution to dryness and then extracting with cold water a residue was obtained, which he regarded as a double phosphate of sodium and lithium, which, upon ignition, yielded the pyrophosphates of sodium and lithium in equimolecular proportions. Later Rammelsberg<sup>2</sup> demonstrated that upon evaporating the alkaline solution prepared accord-

<sup>1</sup> *Pogg. Ann.*, 4, 245 (1825).

<sup>2</sup> *Ibid.*, 66, 79 (1845).

ing to Berzelius, a tribasic phosphate is obtained in which the relative amounts of sodium and lithium are quite variable, so that the method could not be used for the estimation of lithium.

Eleven years later W. Mayer<sup>1</sup> showed that trilitium phosphate,  $\text{Li}_3\text{PO}_4$ , quite free from sodium may be secured by washing the residue obtained upon evaporation according to Berzelius's directions. However, on account of the sodium carbonate employed the lithium phosphate was always contaminated with lithium carbonate. To obviate this Mayer neutralized with sodium hydroxide instead of sodium carbonate. Nevertheless, there was always some lithium carbonate formed due to absorption of carbon dioxide from the air, which was difficult to prevent; and again, in freeing the precipitate of lithium phosphate from sodium phosphate by washing with water, an appreciable amount of the former was always dissolved. For these reasons this method of estimating lithium yielded inaccurate results.

Rammelsberg<sup>2</sup> was the first to use non-aqueous solvents in separating lithium from sodium and potassium. His method consisted of extracting the lithium chloride from the mixed chlorides of the alkalis by means of a mixture of equal volumes of anhydrous ether and alcohol. Small quantities of water remaining in this solution cause the chlorides of sodium and potassium to pass into the solution somewhat. As it is difficult to keep the ether alcohol mixture perfectly anhydrous, this constitutes an inherent difficulty in the method. Again, in drying the chlorides perfectly, some of the lithium chloride is apt to be converted into lithium hydroxide, and consequently rendered insoluble in the solvent employed.

In 1887 F. A. Gooch<sup>3</sup> sought to effect the separation of lithium chloride from the chlorides of sodium and potassium by means of amyl alcohol. When a concentrated aqueous solution of lithium chloride is treated with amyl alcohol, two layers of liquid are formed, the alcoholic layer being above. On gently warming the whole to the boiling point of the alcohol, the water will gradually be boiled off, and the lithium chloride will remain in form of a clear solution in amyl alcohol. In this process a few drops of hydrochloric acid are added to prevent the formation of lithium hydroxide. The chlorides of sodium and potassium are almost completely insoluble under the same conditions; that is, they crystallize out as the water is driven off, thus affording the basis for the separation in question.

Gooch found that on boiling sodium chloride in amyl alcohol, 1 gram of the salt is dissolved by 3000 parts of the alcohol; or 100 cc. of the latter dissolve 0.0041 gram of sodium chloride. Similarly, 1 gram of potassium

<sup>1</sup> *Ann. Chem. u. Pharm.*, 98, 193 (1856).

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Chem. News*, 55, 18-79 (1887).

chloride is dissolved in 24,000 parts of amyl alcohol; or 100 cc. of the latter take up about 0.0051 gram potassium chloride. In washing the chlorides of potassium and sodium with amyl alcohol at room temperature, but very small amounts of these salts are dissolved. In his analytical method Gooch corrects for this very slight solubility by making note of the amount of amyl alcohol employed in washing the residues of the sodium and potassium chlorides. The results obtained by Gooch were much more satisfactory than those that had been obtained before.

Carnot<sup>1</sup> sought to separate lithium from sodium and potassium by precipitating the lithium as fluoride by means of ammonium fluoride in ammoniacal solution. After standing for twelve hours the lithium fluoride was filtered off and washed with an ammoniacal solution of ammonium fluoride. The lithium was weighed as fluoride or as sulphate. The washing solution used, however, dissolved lithium fluoride slightly, so that it was found necessary to introduce a correction of 2 mg. of lithium fluoride for every 7 cc. of filtrate and washings.

It is well known that lithium chloride is quite soluble in pyridine. In his researches on pyridine solutions one of us has found that the chlorides of the other alkalis are practically completely insoluble in this solvent. Recently A. Neumann and J. Schroeder<sup>2</sup> tested the solubility of some of the common salts in pyridine. They state that the chlorides of lithium, barium, magnesium, strontium and calcium are soluble, and that potassium chloride is difficultly soluble. The chlorides of sodium, caesium, rubidium and ammonium are mentioned as being insoluble. Having good reasons to question the correctness of some of these results, solubility tests of all of the salts mentioned were made in pyridine and also in pyridine containing small amounts of water.

The pyridine used in this work and also in the subsequent determinations was obtained from Kahlbaum. It was dried thoroughly over fused caustic potash and redistilled. The fraction passing over between 114° and 116° was employed. The salts, with the exception of the lithium chloride, were of Kahlbaum's manufacture and were spectroscopically free from other salts. The lithium chloride used was obtained from de Haen. It was free from other metals, but contained a small amount of sulphate which was removed by dissolving the chloride away from it by means of pyridine, the sulphate of lithium being insoluble in pyridine.

In making the solubility tests a minute crystal of the anhydrous salt was placed in a test tube in a few cubic centimeters of anhydrous pyridine, which was then heated to boiling. The test tube was then securely stoppered and allowed to stand for a day or two. The crystal was examined from time to time with the aid of a hand lens. If the edges of

<sup>1</sup> *Compt. rend.*, **107**, 237-40 (1888).

<sup>2</sup> *Berichte*, **37**, 4609 (1904).

the crystal or particle remained perfectly sharp and unchanged, no solvent action was taking place. In cases where any doubt whatever existed as to the results by this method a weighed quantity of the anhydrous salt was treated with 100 cc. of pyridine at a boiling heat. After standing for thirty minutes, the salt was filtered off and the filtrate evaporated to dryness by distilling off the pyridine. Any residue remaining was weighed and tested with the spectroscope. The undissolved salt which was filtered off was dried and weighed and any loss of weight carefully noted. Thus in the important cases of sodium and potassium chlorides no solubility was noted in absolute pyridine. In a solvent consisting of 95 per cent. pyridine and 5 per cent. water by volume, apparently a very slight solvent action took place; the matter was consequently tested quantitatively as just described with the following results:

Amount of NaCl taken.....	0.3769 g.
Amount of NaCl left undissolved.....	0.3753
Loss in weight.....	0.0016
Weight of residue from pyridine.....	0.0018
Amount of KCl taken.....	0.3471
Amount of KCl left undissolved.....	0.3459
Loss in weight.....	0.0012
Weight of residue from pyridine.....	0.0015

It is thus evident that these salts are but very slightly soluble even in 95 per cent. pyridine. When 97 per cent. pyridine was used no solvent action whatever could be detected when the experiment was similarly carried out.

In Table 1, the headings of which are self-explanatory, are given the results obtained from the solubility tests carried out as described. The figures showing the composition of the solvent used indicate percentages by volume at 20°.

TABLE 1.

	Anhydrous pyridine,	Pyridine, 97% Water, 3%.	Pyridine, 95% Water, 5%.	Pyridine, 93% Water, 7%.
LiCl	soluble	soluble	soluble	soluble
NaCl	insoluble	insoluble	very slightly soluble	slightly soluble
KCl	insoluble	insoluble	very slightly soluble	slightly soluble
NH <sub>4</sub> Cl	insoluble	soluble	soluble	soluble
RbCl	insoluble	insoluble	very slightly soluble	slightly soluble
CsCl	insoluble	insoluble	very slightly soluble	slightly soluble
BaCl <sub>2</sub>	insoluble	insoluble	insoluble	slightly soluble
SrCl <sub>2</sub>	slightly soluble	soluble	soluble	soluble
CaCl <sub>2</sub>	slightly soluble	soluble	soluble	soluble
MgCl <sub>2</sub>	slightly soluble	soluble	soluble	soluble

An inspection of Table 1 at once reveals that it ought to be possible to separate the chloride of lithium from the chlorides of sodium, potassium, rubidium, caesium and barium by using pyridine which is either anhydrous or contains not over 3 per cent. of water. Now this has actually

been realized, and the new method of making the separation mentioned is described in detail below. From Table 1 it would also appear that the chloride of lithium might be separated from the chloride of ammonium by means of anhydrous pyridine. However, as the chloride of ammonium becomes soluble as soon as only a small amount of moisture is present, and as it is difficult to keep the pyridine perfectly anhydrous while exposing it to the air during the analytical operations, it was not thought worth while to separate ammonium chloride from lithium chloride by the solvent action of pyridine on the latter salt. Furthermore, the separation is far more readily made by volatilizing the ammonium chloride in the usual way. Table 1 also shows that it would be possible to separate the chlorides of sodium, potassium, caesium, rubidium and barium from ammonium chloride by the use of about 97 per cent. pyridine as solvent. For the reason that in this case too, the separation is more readily effected by driving off the chloride of ammonium by means of heat, the matter has not been pursued further.

Since the solubility of lithium chloride in pyridine and the insolubility of the chlorides of the other alkalis and the chloride of barium in this solvent constitutes the basis of the analytical method described in this paper, it seemed very desirable to investigate the solubility of lithium chloride in pure pyridine, and also in 97 per cent. pyridine, for during ordinary analytical processes, it is well nigh impossible to keep this solvent perfectly anhydrous, and fortunately even 3 per cent. of water in pyridine does not increase the solvent action on the chlorides of sodium, potassium, rubidium, caesium and barium appreciably, as Table 1 shows. The solubility determinations of lithium chloride in pure pyridine and in 97 per cent. pyridine were made by essentially the same method as that used by Meyerhoffer and van't Hoff in their researches on the Stassfurt salts. The method is sufficiently well described in Findlay's "Practical Physical Chemistry." The bath used was a high-boiling petroleum oil, in order to avoid the water vapors, which are always present about a bath of aqueous character. The determinations were made at intervals of from  $10^{\circ}$  to  $15^{\circ}$  between  $10^{\circ}$  and  $100^{\circ}$ , a standard thermometer graduated to hundredths of a degree being employed, though no attempt was made to hold the bath constant to more than a tenth of a degree. The results obtained are presented in Table 2, and also in graphic form in Figs. 1 and 2. It will be noted that the results are given in amount of salt in 100 grams of the solution and also in amount of salt in 100 grams of solvent.

When anhydrous pyridine is added to dry powdered lithium chloride heat is evolved and a compact mass results, indicating that an addition product is formed. On account of the formation of this hard addition product, care had to be used in the solubility determinations to secure

TABLE 2.

(a) Solubility of lithium chloride in anhydrous pyridine.

Temperature.	Grams LiCl in 100 g. solution.	Grams LiCl in 100 g. solvent.
8° C.	11.31	12.71
20	11.81	13.39
28	11.87	13.47
40	11.60	13.10
49	11.43	12.90
60	11.38	12.84
80	11.71	13.27
100	13.01	14.98

(b) Solubility of lithium chloride in a mixture of 97 per cent. pyridine and 3 per cent. water by volume.

22° C.	12.50	14.31
32	13.79	15.98
45	15.58	18.46
58	16.72	20.08
72	17.12	20.66
97	18.35	22.48

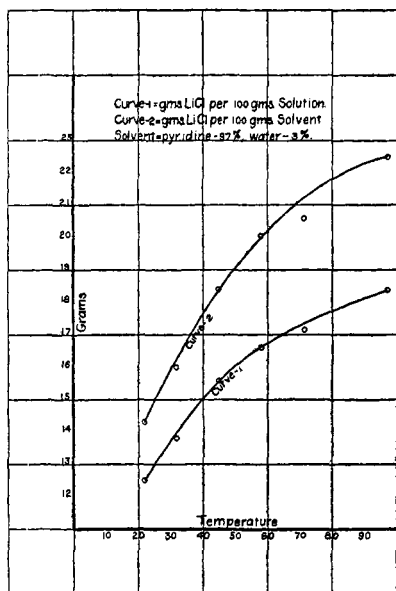


Fig. 1.

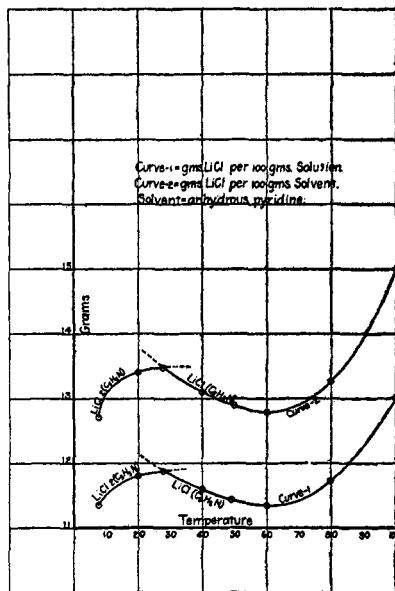


Fig. 2.

perfectly saturated solutions. The solid phase was, of course, always present in large excess and the solution was stirred continuously at constant temperature by means of a motor, till it had a perfectly constant composition; as a rule this required from six to twelve hours. At 28° the curve representing the solubility of lithium chloride in pure pyridine, Fig. 1, shows a maximum. At this temperature we have a transition

point, for it was found by analysis that below  $28^{\circ}$  the solid in equilibrium with the saturated solution is  $\text{LiCl} \cdot 2\text{C}_5\text{H}_5\text{N}$  and above  $28^{\circ}$  the solid phase in equilibrium with the solution has the composition  $\text{LiCl} \cdot \text{C}_5\text{H}_5\text{N}$ . The former salt has crystals of rhombohedral habit, while the latter consists of crystals that are apparently monoclinic.

It is evident from Fig. 2 that when 97 per cent. pyridine is used as the solvent the solubility curve shows no transition point, the solubility increasing with the temperature in a regular manner. On cooling the hot solution to room temperature the whole almost completely solidifies to a mass of needle-shaped crystals which, upon analysis, showed very approximately the composition corresponding to the formula  $\text{LiCl} \cdot \text{H}_2\text{O} \cdot 2\text{C}_5\text{H}_5\text{N}$ . If a film of saturated solution of dry lithium chloride in anhydrous pyridine is exposed to the air for a few seconds these same needle-like crystals form. In all of these cases the crystals were extremely hygroscopic, and it was consequently very difficult to free them perfectly from adhering mother-liquor. They were carefully drained without exposing them to moisture, then quickly pressed between layers of filter paper, and transferred to weighing bottles. The lithium in them was weighed as sulphate; in a separate sample the pyridine was titrated with tenth-normal hydrochloric acid, using methyl orange as indicator, and the water was estimated by difference. In determining the strength of the saturated solutions the lithium was also weighed as sulphate and the pyridine titrated as described.

The difficulties encountered in separating lithium chloride from the chlorides of the other alkalis by means of pyridine are perhaps best presented by giving the details of the experiments by means of which a satisfactory method of securing the desired result was finally found.

The first method adopted consisted of dissolving known quantities of the chloride of lithium and the chloride of the other metal from which it was to be separated in water in a small beaker and evaporating the solution to dryness on a sand bath heated by a steam coil. The residue was then treated with about fifty times its weight of pyridine at a boiling temperature. With the blunt end of a glass stirring rod the salt crystals were carefully pulverized in this liquid. After allowing the insoluble portion to settle which required but a few seconds, the supernatant liquid was poured off through a small filter. The residue was treated with hot pyridine in the manner described, four or five times, and the filter was then carefully washed with hot pyridine. Finally, the residue on the filter was washed with water into the beaker containing the residue of undissolved salt. All was then transferred to a platinum crucible, evaporated to dryness, carefully ignited, cooled and weighed as chloride. The pyridine solution containing the lithium chloride was freed from pyridine by distillation from a small flask. The residue was

taken up with a little water, transferred to a platinum crucible, evaporated to dryness with a little sulphuric acid, carefully ignited, cooled and weighed as lithium sulphate. By this process the lithium chloride formed was invariably a little too low in quantity and the chloride of the other metal correspondingly high. The latter salt, therefore, always contained appreciable amounts of lithium, which was confirmed by spectroscopic tests; the lithium chloride, however, was invariably free from the other alkali chloride as indicated by the spectroscope.

The procedure failed to yield a complete separation for the reason that some of the lithium chloride was occluded in the crystals of the other chlorides and hence escaped contact with the pyridine. To avoid this difficulty the process was somewhat altered. After two successive extractions with pyridine, the residue was dissolved in a small amount of water; this solution was then evaporated barely to dryness and treated three or four times with pyridine as before described. In this way the lithium chloride was separated practically completely from the other chlorides. The latter, to be sure, still showed a spectroscopic test for lithium, but the chloride of that element was no longer present in estimable quantity.

In Table 3 are given the results that were obtained by thus effecting the separation of lithium chloride from the chlorides of sodium, potassium, rubidium, caesium and barium. It will be noted that the deviations lie well within the limits of experimental error.

TABLE 3.

(a) LiCl taken.....	0.1532 g.	NaCl taken.....	0.4047 g.
LiCl found.....	0.1229	NaCl found.....	0.4051
	<hr/>		<hr/>
Difference.....	-0.0003	Difference.....	+0.0004
(b) LiCl taken.....	0.1532	KCl taken.....	0.4359
LiCl found.....	0.1528	KCl found.....	0.4358
	<hr/>		<hr/>
Difference.....	-0.0004	Difference.....	+0.0001
(c) LiCl taken.....	0.3353	RbCl taken.....	0.3020
LiCl found.....	0.3348	RbCl found.....	0.3021
	<hr/>		<hr/>
Difference.....	-0.0005	Difference.....	+0.0001
(d) LiCl taken.....	0.2996	CsCl taken.....	0.5015
LiCl found.....	0.2993	CsCl found.....	0.5016
	<hr/>		<hr/>
Difference.....	-0.0003	Difference.....	+0.0001
(e) LiCl taken.....	0.1532	BaCl <sub>2</sub> taken.....	0.4013
LiCl found.....	0.1531	BaCl <sub>2</sub> found.....	0.4011
	<hr/>		<hr/>
Difference.....	-0.0001	Difference.....	-0.0002



In order to ascertain whether lithium chloride could thus be successfully separated from the chlorides of barium, potassium and sodium, if the latter were present in relatively larger amounts, additional experiments were performed, the results of which are given in Table 4. It will be observed that in these cases too, the separation was quite successful.

In the work presented in Tables 2, 3 and 4, anhydrous pyridine was used. From Table 1 it appears that a mixture of 97 volumes pyridine to 3 volumes water would also serve the purpose. This was found to be the case in a series of experiments in which 97 per cent. pyridine was employed. The results are given in Table 5, inspection of which shows that the separations can be made satisfactorily.

TABLE 4.

(a) LiCl taken.....	0.1532	NaCl taken.....	0.8094
LiCl found.....	0.1529	NaCl found.....	0.8096
Difference.....	0.0003	Difference.....	+0.0002
LiCl taken.....	0.0908	NaCl taken.....	0.8270
LiCl found.....	0.0907	NaCl found.....	0.8271
Difference.....	0.0001	Difference.....	+0.0001
(b) LiCl taken.....	0.1532	KCl taken.....	0.8718
LiCl found.....	0.1528	KCl found.....	0.8723
Difference.....	0.0004	Difference.....	+0.0005
LiCl taken.....	0.1532	KCl taken.....	1.3077
LiCl found.....	0.1532	KCl found.....	1.3081
Difference.....	0.0000	Difference.....	+0.0004
(c) LiCl taken.....	0.1532	BaCl <sub>2</sub> taken.....	0.8026
LiCl found.....	0.1528	BaCl <sub>2</sub> found.....	0.8032
Difference.....	0.0004	Difference.....	+0.0006
LiCl taken.....	0.1551	BaCl <sub>2</sub> taken.....	1.2039
LiCl found.....	0.1546	BaCl <sub>2</sub> found.....	1.2037
Difference.....	0.0005	Difference.....	-0.0002

TABLE 5.

(a) LiCl taken.....	0.1551	NaCl taken.....	0.4047
LiCl found.....	0.1550	NaCl found.....	0.4048
Difference.....	-0.0001	Difference.....	+0.0001
LiCl taken.....	0.1551	LiCl taken.....	0.4047
LiCl found.....	0.1546	LiCl found.....	0.4040
Difference.....	0.0005	Difference.....	-0.0007

(b) LiCl taken.....	0.1551	KCl taken.....	0.4359
LiCl found.....	0.1549	KCl found.....	0.4367
	<hr/>		<hr/>
Difference.....	-0.0002	Difference.....	+0.0008
LiCl taken.....	0.1551	KCl taken.....	0.4359
LiCl found.....	0.1554	KCl found.....	0.4361
	<hr/>		<hr/>
Difference.....	+0.0003	Difference.....	+0.0002

In reviewing the various methods of determining lithium, E. Waller<sup>1</sup> states that Gooch's method is reliable only for quantities of lithium chloride under 0.2000 gram. In order to test the pyridine method here proposed, further in this direction, experiments were performed in which approximately twice as much lithium chloride was used as before. We found that one extra evaporation to dryness and two or three additional washings with pyridine served to secure a satisfactory separation, as the results which are recorded in Table 6 show.

TABLE 6.

(a) LiCl taken.....	0.3064	NaCl taken.....	0.4056
LiCl found.....	0.3066	NaCl found.....	0.4059
	<hr/>		<hr/>
Difference.....	+0.0002	Difference.....	+0.0003
(b) LiCl taken.....	0.3064	KCl taken.....	0.4376
LiCl found.....	0.3061	KCl found.....	0.4380
	<hr/>		<hr/>
Difference.....	-0.0003	Difference.....	+0.0004

Since the chief error in the method described lies in the tenacity with which lithium chloride is held or occluded by the crystals of the other chlorides present, the following procedure was tried. The aqueous solution containing the mixed chlorides was carefully evaporated to the point where crystals just began to separate out. Pyridine was then added in such an amount that the solvent mixture would contain at least 97 per cent. of pyridine. Thus the insoluble chlorides were precipitated out. They were washed with pyridine and weighed as before, while the filtrate containing the lithium chloride was evaporated to dryness and the lithium determined as sulphate as before. However, by this method lithium chloride remains occluded in the crystals of potassium and sodium chloride to quite an appreciable extent as the results accorded in Table 7 show, so that there is no gain in conducting the process as last described. The precipitations were made at different temperatures, and the manner of adding the pyridine was also varied, but there were always appreciable amounts of lithium chloride carried down with the other chlorides and this lithium chloride was very hard to remove by simple repeated washing with pyridine.

<sup>1</sup> THIS JOURNAL, 12, 214 (1890).

TABLE 7.

(a) LiCl taken.....	0.1856	NaCl taken.....	0.4997
LiCl found.....	0.1841	NaCl found.....	0.5015
Difference.....	-0.0015	Difference.....	-0.0018
LiCl taken.....	0.0907	NaCl taken.....	0.4874
LiCl found.....	0.0896	NaCl found.....	0.4885
Difference.....	+0.0011	Difference.....	+0.0011
(b) LiCl taken.....	0.1856	KCl taken.....	0.5004
LiCl found.....	0.1836	KCl found.....	0.5024
Difference.....	+0.0020	Difference.....	+0.0016
LiCl taken.....	0.0907	KCl taken.....	0.4874
LiCl found.....	0.0895	KCl found.....	0.4885
Difference.....	-0.0012	Difference.....	-0.0011

In order to test the method proposed still further, known amounts of the chlorides of lithium, potassium, sodium and barium were dissolved together in water. The solution was evaporated to dryness and the lithium chloride separated from the other chlorides by the method used in obtaining the results recorded in Table 6. The results obtained are given in Table 8. It will be noted that the separation was successful, within the limits of ordinary experimental error.

TABLE 8.

## Lithium Chloride from the Chloride of Potassium, Sodium and Barium.

LiCl taken.....	0.0958	KCl taken.....	0.3020
LiCl found.....	0.0956	NaCl taken.....	0.3082
Difference.....	-0.0002	BaCl <sub>2</sub> taken.....	0.0905
		Total.....	0.6007
		Total found.....	0.6001
		Difference.....	-0.0006
LiCl taken.....	0.0907	KCl taken.....	0.1933
LiCl found.....	0.0903	NaCl taken.....	0.2913
Difference.....	0.0004	BaCl <sub>2</sub> taken.....	0.1021
		Total taken.....	0.5867
		Total found.....	0.5873
		Difference.....	+0.0006

Table 1 shows that the chlorides of strontium, calcium, and magnesium are slightly soluble in pure pyridine and more so in 97 per cent. pyridine. These chlorides could consequently not be separated successfully from lithium chloride by the process described. Even when first heated to

dull redness, at the risk of rendering them slightly alkaline, the chlorides of calcium, strontium and magnesium are somewhat soluble in anhydrous pyridine.

In making attempts to separate the chloride of ammonium from the chloride of lithium, it was found that the thorough desiccation required, before extracting the mixed chlorides with pyridine, had to be conducted at such a temperature that small losses of ammonium salt invariably resulted. The attempts to separate the latter salt from lithium chloride by the use of pyridine were consequently abandoned.

### Summary.

It has been shown that the chlorides of sodium, potassium, rubidium, caesium and barium are practically insoluble in pyridine containing less than five per cent. water, while lithium chloride is quite soluble even in pure pyridine. In consequence of these facts lithium may be directly and completely separated from the other alkalis or from barium by treating the chlorides with pyridine.

From the experiments above detailed, the best method of procedure is the following: Evaporate the aqueous solution of the mixed chlorides just to dryness and digest the residue, weighing two grams or less, with about 25 cc. of pyridine at a boiling temperature for a few minutes, breaking up any large pieces with the end of a stirring rod. Allow the insoluble part to settle, which takes but a few seconds, decant the clear liquid through a small filter, and wash the residue twice with small amounts of hot pyridine. Dissolve the residue in a small amount of water, evaporate barely to dryness, and repeat the extraction with hot pyridine. Combine the pyridine filtrates containing the lithium chloride; distil off the pyridine and finally convert the lithium chloride into sulphate and weigh. Wash the filter with water into the beaker containing the residue of chlorides insoluble in pyridine, evaporate to dryness, and weigh as chlorides. In cases where the amounts of the chlorides insoluble in pyridine are relatively large as compared with the lithium chloride present, it is advisable to make a third extraction with pyridine.

The method is simple, direct and easily carried out, and is particularly adapted to obtain lithium free from other alkalis. After the treatment described, the lithium chloride remaining with the chlorides that are insoluble in pyridine is an unweighable quantity, though traces of lithium may still be detected in the residue by means of the spectroscope. As the pyridine can be readily recovered by distillation, the method is not an expensive one. On account of the unpleasant odor of pyridine the work should be done under a well ventilated hood.