302. *A New Method for the Quantitative Separation of Lithium, with Reference to its Determination in Insoluble Silicates.*

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Lithium, like sodium, is said to form complex triple acetates with uranyl acetate and the acetate of a bivalent metal such as zinc (Barber and Kolthoff, *J. Amer. Chem. Soc.*, 1929, **51**, 3233) or magnesium (Kahane, *Bull. Soc. chim.*, 1933, **53**, 555), but, although the first two authors suggested the possibility, the acetates have apparently not been utilised quantitatively.

The determination of lithium in an insoluble silicate has usually depended on the assembling of the alkali chlorides apart from all other constituents, followed by the separation of lithium chloride from sodium and potassium chlorides, and its conversion into sulphate; and recent research has been directed towards finding the most suitable organic solvents for the separation. We sought a method whereby lithium could be precipitated quantitatively as a complex triple acetate, and then applied it to the determination of the metal in an insoluble silicate.

In preliminary experiments with mixtures of solutions of uranyl acetate and another bivalent metal acetate, prepared and used for lithium chloride exactly as zinc uranyl acetate (Barber and Kolthoff, *J. Amer. Chem. Soc.*, 1928, **50**, 1625) is used for sodium chloride, it was found that precipitates were readily obtained in presence of zinc and nickel acetates, the yields of triple acetate based on the formula $LiM(UO_2)_3(C_2H_3O_2)_9,6H_2O$ ($M =$ Zn or Ni) being of the order of 50% of the theoretical. Further experiments showed that the yields varied with the proportions of zinc (or nickel) acetate, uranyl acetate, and acetic acid in the reagent, as indicated below.

Solvent. Acetic acid, ml./100 ml.	Solution (a).	Solution (b).	Reagent (satd. with triple acetate).			Li recovered %.
			(a), %.		(b), %.	
5	Solvent satd. with $UO_2(OAc)_2$	Solvent satd. with $Ni(OAc)_2$	9	+	91	0
			50	+	50	30
			75	+	25	69
50	ditto	ditto	9	+	91	0
			50	+	50	66
			75	+	25	92
25	ditto	Soln. (a) satd. with $Ni(OAc)_2$	70	+	30	Small or negligible
			76	+	24	
			86	+	14	
50	ditto	ditto	70	+	30	60
			76	+	24	94
			86	+	14	92
			91	+	9	55
75	ditto	ditto	60	+	40	61
			75	+	25	64
			86	+	14	60
50	ditto	Soln. (a) satd. with $Zn(OAc)_2$	68	+	32	93
			72	+	28	94
			75	+	25	100
			86	+	14	88

It was evident that the conditions for complete precipitation were critical. As the best results were obtained with zinc acetate in presence of high concentrations of uranyl acetate and acetic acid, a few experiments were made in a slightly different manner. Various amounts of zinc acetate were dissolved in 40%, 50%, and 60% aqueous acetic acid as solvents. All were saturated with uranyl acetate and then with the triple acetate, and applied as before. The results are shown below.

Solvent. Acetic acid, ml./100 ml.	G. of zinc acetate per 100 ml. of solvent.				
	5	7·5	10	12·5	15
	Lithium recovered, %.				
40	76	94	100	96	—
50	86	97	98	97	95
60	98	100	99	100	—

As theoretical results, based on the formula previously given, were obtained, within the limits of experimental error, over a considerable range of zinc acetate concentration with 60% acetic acid as solvent, this was used for all subsequent work, 12·5 g. of zinc acetate being added per 100 ml., and the resultant solution further treated as stated above. All operations were conducted at constant temperature (*ca.* 20°) with the aid of a thermostat.

Precipitates formed with this reagent were pale yellow, crystalline, and rather more finely divided than the corresponding sodium salt. The solubility in water was roughly 30% greater than that of the sodium analogue. In absolute and 95% aqueous ethyl alcohol, the respective solubilities of the lithium complex salt were 0·22 g. and 0·19 g. per 100 ml. Prolonged heating at 40—50° was without influence, but slight losses in weight occurred above 70°. The complex was stable when kept in a desiccator containing calcium chloride. When placed in air, under a bell-jar, it gained about 0·1%, the weight then remaining constant. Analyses of the precipitates gave the following results:

	Wt. of mixed sulphates from 0·66 g. of salt.	Zn, %.	UO_2. %.	$C_2H_3O_2$, %.	H_2O, %.
Found	0·5702	4·37	53·2	34·7, 34·9	—
	0·5692	4·38	53·2	35·0, 34·9	—
Calc. for $LiZn(UO_2)_3(C_2H_3O_2)_9,6H_2O$	0·5702	4·30	53·2	34·9	7·1
Calc. for $LiZn(UO_2)_3(C_2H_3O_2)_9,7H_2O$	0·5636	4·25	52·6	34·5	8·2

Attempts to determine water by dehydrating the complex with phosphoric oxide at 90°, in evacuated, sealed, all-glass apparatus, gave unreliable results, owing to slight decomposition, for which an accurate correction could not be applied. The losses observed after 2 and 4 days, 8·0 and 7·8% respectively, were undoubtedly not entirely due to water, and were unacceptable as evidence for the heptahydrate composition. Prolonged heating (6—8 weeks) under similar conditions at 50° might give the required information. The above data, however, were regarded as sufficient justification for the acceptance of the hexahydrate formula.

Quantitative experiments made with lithium chloride solutions, with and without other added chlorides, yielded the results shown below. All precipitations were effected in volumes of solution of 1 ml. or less.

LiCl used, mg.	LiCl, found, mg.	
	One pptn.	Two pptns.
10·00	9·95, 9·97, 9·99	9·97, 10·06
2·00	2·01, 1·96	1·96, 2·01
0·60	0·60, 0·60	0·57, 0·61

Added salt, and wt., g.	LiCl used, mg.	LiCl, found, mg.	
		One pptn.	Two pptns.
KCl, 0·003	10·00	10·05	—
NaCl, 0·0005	10·00	10·59	—
$CaCl_2,6H_2O$, 1·2	10·00	7·89	—
,, 0·12	10·00	10·34, 10·28	10·01
,, 0·12	2·00	—	2·07, 1·94
,, 0·12	0·60	—	0·55, 0·56

Amounts of lithium chloride ranging from 10 to 0·6 mg. may be determined with fair accuracy in absence of other salts, and two precipitations do not materially affect the results, showing that the precipitation of lithium is quantitative. A small amount of potassium chloride has no important influence on the determination of lithium, but it is obvious that lithium chloride must be quantitatively separated from sodium chloride, prior to its precipitation as the triple acetate. The presence of 1·2 g. of calcium chloride prevents complete precipitation, and 0·12 g. causes the precipitate to be contaminated, necessitating a double precipitation. Results based on two precipitations are, on the whole, less consistent than those based on one.

In view of the composition of the aqueous solution obtained after decomposing 0·5 g. of a silicate by the Lawrence Smith method (see preceding paper, p. 1390), and of the fact that precipitation of lithium in presence of 1·2 g. of calcium chloride is not feasible without modification of the analytical method, it is evident that lithium must be determined in one-tenth of the aqueous extract, and quantitatively separated from sodium. On this basis, lithium was determined in two ways in solutions containing sodium, potassium, and calcium chlorides, such as might be derived from silicates with a lithia content of 7—0·4%.

In the first method the anhydrous chlorides were extracted twice with minimal amounts of *iso*amyl alcohol, in which sodium and potassium chlorides are sparingly soluble (cf. Gooch, *Chem. News*, 1887, **55**, 18 *et seq.*). Lithium and calcium chlorides were dissolved, the alcohol removed from the separated solution, and lithium determined as lithium zinc uranyl acetate after two precipitations. The following results refer to solutions in which 0·12 g. of calcium chloride and 10 mg. each of potassium and sodium chlorides were present in addition to lithium chloride :

Wt. of LiCl taken (mg.)	10·00	2·00	0·60
Wt. of LiCl found (mg.)	10·07, 10·03	2·12, 2·13	0·74, 0·65, 0·62

The positive errors were undoubtedly due to the slight solvent effect of the alcohol on sodium chloride.

The second method involved extraction by anhydrous acetone (Brown and Reedy, *Ind. Eng. Chem., Anal.*, 1930, **2**, 304), in which lithium chloride is fairly soluble, calcium chloride slightly soluble, and sodium and potassium chlorides insoluble. Repeated extractions with small amounts of acetone were much more effective than one extraction with a large amount. The solutions used were as in the preceding case, except that only 5 mg. each of sodium and potassium chlorides were present. Four extractions were necessary when the amount of lithium chloride was 10 mg., and three when it was 2—0·5 mg. As the amount of calcium chloride extracted was small, only one precipitation of the triple acetate was required. The results are given below. The figures in the last column refer to solutions containing, in addition to the other salts, 5 mg. of sodium sulphate.

Wt. of LiCl taken (mg.)	10·00	2·00	0·60	0·50
Wt. of LiCl found (mg.)	9·95, 9·91	2·05, 1·99	0·57, 0·60	0·51, 0·49

As anticipated, the errors were mainly negative. This method was preferred to the first, partly because one precipitation of the triple salt sufficed. It was superior for the determination of small amounts of lithium.

It might be thought that the precipitation of calcium as calcium carbonate would be more expeditious than the repeated extractions with acetone, but this is not so. Further, direct experiments showed that, even if the precipitation method were adopted, two extractions with acetone would still be necessary to remove 10 mg. of lithium chloride from the same weight of sodium and potassium chlorides.

The determination of soda, potash, and lithia in silicates is now described. Since (preceding paper) sodium as well as lithium is frequently determinable in one-tenth of the aqueous extract already referred to (p. 1396), and a quantitative separation of sodium and lithium chlorides is essential, sodium may be determined in the residue after removal of lithium chloride. When acetone is used to extract lithium chloride, this residue contains most of the calcium chloride, and two precipitations of sodium zinc uranyl acetate are requisite. Another method is available, however, *viz.*, the removal of the bulk of the calcium chloride from the residue by means of the minimal amount of *iso*amyl alcohol, and the separation of sodium in the residue by a single precipitation as the triple salt. In determining 5 mg. of sodium chloride in presence of 5 mg. of potassium chloride, 0·12 g. of calcium chloride, and lithium chloride, 99·4% recoveries were achieved. This method is recommended for silicates containing both soda and lithia.

For the determination of potash, the methods described in the preceding paper are applicable in presence of lithia.

Finally, two 0·5-g. portions of a lithia-containing silicate, lepidolite, of undetermined composition, were decomposed according to Lawrence Smith's procedure. In one experiment the alkali chlorides were separated and weighed, exactly as described by Washington (" The Chemical Analysis of Rocks," 1930, p. 222). In the other, lithia and soda were determined in 10% of the acidified aqueous extract of the decomposed silicate, lithium chloride being extracted with acetone prior to the determination of soda as already outlined; potash was determined in 90% of the extract, according to method 3 of the preceding paper. The sum of the weights of the corresponding chlorides was computed. The results for the two experiments, referred to exactly 0·5 g. of the silicate, and suitably corrected for alkali chlorides in the reagents, were as follows :

G. of alkali chlorides by direct determination	. . . .	0·1232
G. of LiCl, 0·0483; NaCl, 0·0015; KCl, 0·0739.	Total . . .	0·1237

The agreement is satisfactory, although the amount of sodium chloride was rather small for determination in only 10% of the silicate extract.

EXPERIMENTAL.

The glassware was Jena or Pyrex. Neutral solutions of lithium chloride were prepared by decomposing a known amount of Merck's " extra pure " lithium carbonate with hydrochloric acid in a platinum basin, evaporating to dryness, dissolving in water, and weighing. The lithium carbonate, after spectroscopic examination, was guaranteed by Dr. S. Judd Lewis to contain not more than 0·014% of sodium. It lost no weight on heating to 200°. The reagents mentioned in the preceding paper were again employed, and others were, as far as possible, of A.R. quality. Kahlbaum's glacial acetic acid " for analysis " was used. Pure anhydrous acetone and *iso*amyl alcohol were prepared according to standard methods, and absolute ethyl alcohol and anhydrous ether were redistilled. Evaporations were conducted on an adjustable grid placed over an electric boiler. A thermostat at about 20° was employed.

The Zinc Uranyl Acetate Reagent for the Precipitation of Lithium.—In 600 ml. of acetic acid, diluted to 1000 ml. with water, 125 g. of zinc acetate trihydrate were dissolved. To the solution, uranyl acetate dihydrate was added in slight excess, and then more than enough of the complex lithium salt to saturate it. The mixture was briskly shaken, and thereafter kept at constant temperature. Immediately before use, suitable portions were stirred mechanically for ½ hour to avoid supersaturation, and filtered. It was important to preserve the reagent in a dark bottle, as it deteriorated in the light, and to renew it once a month.

Quantitative Precipitation of Lithium Zinc Uranyl Acetate.—A weighed amount of the lithium chloride solution was evaporated just to dryness in a 50-ml. beaker. 10 Ml. of the filtered reagent were added, and the mixture was stirred mechanically for 15 mins., and allowed to settle for 15 mins. The precipitate was collected in a Jena sintered-glass filtering crucible (No. 10 G 3), on the disc of which was a thin layer of asbestos, and washed with the precipitating reagent (5 × 2 ml.), 95% aqueous ethyl alcohol saturated with the triple salt (5 × 2 ml.), and finally with a little anhydrous ether. All operations were carried out at the temperature at which the reagent had been prepared. The precipitate was heated at 40° for 10 mins., cooled in a desiccator containing calcium chloride, and weighed. When two precipitations were necessary, and the weight of the first precipitate was not required, the ether washing of the latter was omitted, and the number of alcohol washings was reduced to two. The precipitate was then dissolved in 10 ml. of 0·1*N*-hydrochloric acid, and the solution evaporated in a beaker until a solid film just formed. If the mixture was taken to dryness the final results were high. The second precipitation was made similarly to the first, and the triple salt was separated and weighed.

Analysis of Lithium Zinc Uranyl Acetate Precipitates.—The determination of zinc with 8-hydroxyquinoline was based on Wiggins and Wood's method (*J. Soc. Chem. Ind.*, 1934, **53**, 254T), in which malic acid is employed to prevent interference from uranium. 0·7 G. of the complex acetate was used, and two precipitations were made, the first precipitate being dissolved in dilute hydrochloric acid, and reprecipitated with a few drops of the reagent solution and 2*N*-sodium hydroxide. The second precipitate was collected in a Jena-glass filtering crucible (No. 10 G 4), heated at 120°, and weighed as the anhydrous complex. As a check, experiments were made simultaneously with standard solutions of zinc sulphate containing uranyl acetate, corresponding to that under test. A correction of − 0·8% was required.

Gladding's distillation method (*Ind. Eng. Chem.*, 1909, **1**, 250) for acetate, which gave exact results with a standardised solution of acetic acid, was used for the determination of acetate in 0·85 g. of lithium zinc uranyl acetate.

In the determination of uranium in 0·63 g. of the triple acetate, acetate was first removed (on the recommendation of Dr. A. M. Ward) by distillation with 8*N*-sulphuric acid, water being added to maintain the volume constant. Uranium was then determined with a standard solution of potassium dichromate (Kolthoff and Lingane, *J. Amer. Chem. Soc.*, 1933, **55**, 1871).

For the conversion of lithium zinc uranyl acetate into the mixed sulphates, 0·6—0·7 g. in a platinum crucible was dissolved in 10 ml. of dilute sulphuric acid, and carefully evaporated to dryness. The residue was dissolved in water, the solution re-evaporated, the sulphates heated to 500°, and weighed.

Determination of Lithium in a Mixture of Calcium, Sodium, Lithium, and Potassium Chlorides.—*Method* (a). *Extraction of lithium chloride by* isoamyl *alcohol.* A capillary immersion filter was made by widening 1-mm. internal-diam. capillary tubing to a small bell-shaped end. A short spiral of very fine platinum wire was inserted in the capillary to prevent blocking, and a little asbestos in suspension was drawn up. As finely divided precipitates tended to clog the asbestos, a plug of paper cut from an ashless filtration accelerator was placed in the wider part of the filter. The tubing was bent twice at right angles, so that the filtering end could be held vertically in the mixture to be filtered, and the other, which was drawn off to a slanting point, placed vertically against a receiving beaker within a bell-jar that could be evacuated.

The solution of chlorides in a 30-ml. beaker was evaporated to dryness, and the residue re-evaporated with 1 ml. of *iso*amyl alcohol to ensure complete dehydration. 2 Ml. of the alcohol and a small drop of concentrated hydrochloric acid (to convert any lithium hydroxide formed into chloride) were added, the mixture heated to boiling, and the hard mass thoroughly broken up with a glass rod. After cooling, the supernatant liquid was drawn by gentle suction through the immersion filter into another beaker, and the residue was washed with the solvent (3 × 0·5 ml.). Any residue adhering to the filter was returned to the beaker containing the main portion of the residue, by putting this beaker inside the bell-jar and drawing hot water through the filter. The latter was made ready for use again by treatment with a little absolute ethyl alcohol, and then *iso*amyl alcohol. The residue was next dissolved in water, and the evaporation, extraction (1 ml. of alcohol), and washing (5 × 0·5 ml.) processes were repeated. From the combined extracts, *iso*amyl alcohol was removed, and lithium zinc uranyl acetate was precipitated twice under the stipulated conditions.

Method (b). *Extraction of lithium chloride by acetone.* The apparatus was the same as for method (a), except that the paper plug was omitted from the immersion filter. The solution of mixed chlorides was evaporated to dryness, and the residue, dehydrated by heating at 150°, was cooled in a desiccator containing phosphoric oxide. 5 Ml. of acetone and a small drop of concentrated hydrochloric acid were added, the mixture was warmed to soften the solid mass, and then again transferred to the desiccator to cool (lithium chloride is more soluble in the cold solvent). Filtration was effected as before, but with reduced suction to prevent loss of acetone by volatilisation and the deposition of lithium chloride on the filter, and the residue was washed with the solvent (3 × 1 ml.). Re-extractions were made as described in method (a), but with the appropriate modifications for acetone as solvent. In the last extraction 5 ml. of wash liquid were used. Lithium zinc uranyl acetate was precipitated once in the combined extracts, from which acetone had previously been removed by evaporation.

Determination of Sodium Chloride in a Mixture of Sodium, Lithium, Potassium, and Calcium Chlorides.—From the anhydrous chlorides lithium chloride was removed by means of acetone, as just described. The residue was evaporated to dryness and dehydrated by heating with 1 ml. of *iso*amyl alcohol. A few ml. of the latter were then added, the mixture heated, the residue broken up, and the supernatant liquid containing calcium chloride removed, when cold, by means of the capillary immersion filter. Any residue adhering to the filter was washed through with hot water into the beaker containing the main portion of the residue. After evaporation to dryness, the residue was dissolved in 1 ml. of water, and sodium zinc uranyl acetate was precipitated once in the customary manner.

This work is being continued.

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