GRAVIMETRIC ESTIMATION OF LITHIUM
AS TRILITHIUM PHOSPHATE

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ABSTRACT

A method has been developed for the gravimetric estimation of lithium as trilithium phosphate, by precipitating it from a homogeneous medium of 60 per cent ethanol employing a reagent of pH 9.5, prepared by mixing β-diethyl amino ethyl alcohol and orthophosphoric acid. By this method, it is possible to estimate lithium in solution containing 5 to over 100 mg. even in the presence of sodium and/or potassium to the extent of five times the weight of lithium. The method works satisfactorily in the presence of anions such as chloride, sulphate, phosphate and nitrate.

Caley and Simmons[1] recently employed phosphate of choline (a quaternary ammonium base) for the gravimetric estimation of lithium by precipitating it as trilithium phosphate from 50 % isopropanol medium. They, however, pointed out that it was difficult to obtain, commercially, quarternary ammonium bases in sufficient purity for use as quantitative analytical reagents. Efforts were, therefore, made to find out suitable alternative bases. For this purpose, phosphate reagents of bases of β-dimethyl amino ethyl alcohol, β-diethyl amino ethyl alcohol, 2-amino ethanol, diethanol amine and triethanol amine in the pH range of 8 to 10 were tried for the precipitation of trilithium phosphate. It was found that the phosphate reagents of the first two bases gave quantitative values for lithium when suitable precautions were taken ; in the case of 2-amino ethanol and diethanol amine, the analytical data indicated lower values for the lithium content but in the case of triethanolamine, the results were not satisfactory. β-diethyl amino ethyl alcohol was selected for the development of the gravimetric method since lithium phosphate was least soluble in presence of this reagent.

When the phosphate reagent of β-diethyl amino ethyl alcohol of pH higher than 9.5 was used, larger quantities of the reagent were required for quantitative precipitation of lithium, although the error in the estimation was -0.27 mg. of lithium ; while with the reagent of pH lower than 9, the error due to the enhanced solubility of lithium phosphate was larger, the error ranging from -0.46 to -0.71 mg. of lithium. To strike the mean, a phosphate reagent of pH 9 to 9.5, with which the error was -0.37 to -0.35 mg. of lithium, was used for the standardisation of the procedure.

REAGENTS EMPLOYED

1.   *Lithium chloride solution*:—Lithium chloride was prepared from lithium carbonate (B. D. H. laboratory reagent), purified by the method of Caley and Elving.[2]   Purified Li_2CO_3 was found to be free from other alkali metal salts when tested spectrographically.   10.0 ml. of the neutral solution contained 24.40 mg. of lithium as determined gravimetrically by converting it into anhydrous lithium sulphate.

2.   *Orthophosphoric acid*:—Guaranteed pure 'Merck' reagent having the specific gravity of 1.75.

3.   *Ethyl alcohol*:—Absolute ethyl alcohol further purified by the method of Lund and Bjerrum[3] was employed.

4.   *β-diethyl amino ethyl alcohol*:—"Eastman organic chemical" having B. pt. 161–163°C. was used.

5.   *Trilithium phosphate*:—It was prepared by reacting lithium chloride solution with the phosphate of β-diethyl amino ethyl alcohol from a homogeneous medium of 60 % ethyl alcohol at 68°C as described later.   The purified monohydrate was dried at 110°C for about 24 hours.

6.   *Wash liquor*:—Sixty per cent ethyl alcohol (by volume) was shaken mechanically with trilithium phosphate for about 12 hours to prepare a saturated solution.   The clear filtrate was used for washing the precipitate.

7.   *Phosphate reagent of β-diethyl amino ethyl alcohol*:—One hundred ml. of the amino alcohol was diluted with 300 ml. of distilled water and orthophosphoric acid was added to it till the pH of the solution was 9.5.

PROCEDURE

The method is based on the procedure of Caley and Simmons[1] with some modifications.   10 ml. of the solution of lithium chloride containing 24.4 mg. of lithium was taken in a 250 ml. pyrex beaker and diluted to 14 ml. with distilled water.   6 ml. of the phosphate reagent was added to the solution.   To minimise the losses of the solution due to evaporation, the beaker was covered with a pyrex glass dish containing cold water, which was changed frequently.   The mixture was heated on a water bath between 65°C and 70°C.   One hour after the first appearnce of the precipitate in the beaker, 30 ml. of absolute alcohol were added to it to bring about the precipitation to completion.   The contents in the beaker were stirred well occasionally.   Two hours after the addition of the alcohol, the precipitate was filtered hot through a medium porosity sintered porcelain crucible, previously ignited, cooled and weighed.   The precipitate was washed with small portions of wash liquor until a total of about 50 ml. was used.   Air was then drawn in through the crucible for a few minutes to remove most of the wash liquor.   The precipitates were then washed with hot 80 % ethanol (2 ml).   The crucible containing the precipitate was then heated in an electric muffle between 650°–700°C for about half an hour, when the monohydrate of trilithium phosphate was converted

into Li_3PO_4. The weight of the crucible with trilithium phosphate was determined and the lithium content calculated. The results could be reproduced within ± 0.02 mg. of lithium.

Variables Studied

1. *Choice of alcohol for the precipitating medium* : —Caley and Simmons[1] employed 50 % 2-propanol medium. Since 2-propanol is comparatively expensive and has highly irritating odour[4], it was thought desirable to find out the suitability of using ethyl alcohol medium for the precipitation studies. A comparative estimation of trilithium phosphate by the method described above, showed that the negative errors for 50 % 2-propanol and 60 % ethanol media were respectively 0.37 mg. and 0.35 mg. of lithium. This shows that ethyl alcohol medium can be used for the precipitation of lithium phosphate.

2. *Concentration of ethyl alcohol medium* :—Experiments carried out with 40, 50, 60, and 80 % alcohol gave a constant negative error of 1.1, 0.46, 0.35 and 0.23 mg. of lithium respectively, even though the amount of lithium employed for the precipitation was varied from 5.5 to 24.4 mg. Although 80 % alcohol medium gave the best quantitative results for lithium, yet 60 % alcohol medium was preferred for subsequent experiments since such a medium can permit the precipitation of lithium in presence of comparatively larger amounts of sodium and potassium salts without any coprecipitation.

Table I

Effect of total voulme of the precipitating medium in the estimation of lithium

Final vol. of the precipitating medium of 60 % alcohol, ml.	Amount of reagent employed in ml.	Lithium in mg.		Difference in mg.
		Taken	Found	
25	6	2.75	2.45	— 0.30
25	6	5.50	5.30	— 0.20
25	6	22.00	21.82	— 0.18
50	6	2.75*		
50	6	5.50	5.12	— 0.38
50	6	11.00	10.65	— 0.35
50	6	49.50	49.15	— 0.35
100	16	49.50	48.74	— 0.76
100	16	99.00	98.30	— 0.70
100	24	110.00	109.28	— 0.72
100	24	121.00	120.24	— 0.76
100	24	154.00	153.22	— 0.78

* Colloidal precipitate was obtained.

3.   *Effect of the total volume of the precipitating medium*:—For this purpose, different amounts of lithium in solution were taken and calculated amounts of the reagent and alcohol were added in the usual way so that the final composition of the medium was 60% ethyl alcohol.   Subsequent volume was then adjusted by adding 60% ethyl alcohol.   The remaining procedure was the same as already described.   It was noticed that when the amount of lithium was less than 5 mg. in 50 ml. of the medium, colloidal precipitate was obtained.   The precipitate was coagulated by the addition of 0.1 ml. of KCl solution containing 0.55 mg. of potassium.   In general, the pH of the precipitating medium was found to be about 8.5.   The results are given in Table I and show that the negative error is more or less proportional to the volume of the solution, indicating thereby that the error is due to slight solubility of lithium phosphate in the precipitating medium.   Hence the necessary correction could be applied during the estimation of lithium as phosphate.   It is seen from the table that the method could be employed for the estimation of lithium from 5 to over 150 mg.

4.   *Effect of temperature*:—At room temperature, the first appearance of trilithium phosphate took considerably long time from an aqueous solution of lithium chloride, when the phosphate reagent was added to it.   The value of lithium precipitated was low even from 60% alcohol medium, when the mixture was allowed to stand for a period of six hours.   At the temperature of $65-70^{\circ}$C, the precipitate appeared within 3—5 minutes and it increased on the addition of alcohol.   The precipitates formed at higher temperatures were granular and easy to filter.   Moreover, the solubility of trilithium phosphate decreases with the rise in temperature both in water and in aqueous alcohol, while that of other alkali metal phosphates increases.   It is, therefore, beneficial to carry out the precipitation at $65-70^{\circ}$C.

SUGGESTED PROCEDURE FOR THE ESTIMATION OF LITHIUM

The procedure described here was standardised after a number of preliminary experiments.   When the aqueous solution is expected to contain 5 to 50 mg. of lithium, the volume of the solution is adjusted to 14 ml. with distilled water in a 250 ml. pyrex beaker and 6 ml. of the phosphate reagent (pH 9 to 9.5) are added to it.   If the solution contains 51 to 100 mg. of lithium, the volume of the solution is made to 24 ml. and 16 ml. of the phosphate reagent are added to it.   When the amount of lithium expected is from 100 to over 150 mg., the volume of the solution is made to 36 ml. and 24 ml. of the phosphate reagent are added to the solution and the beaker is heated on the waterbath at $65-70^{\circ}$C as described already.   One hour after the first appearance of the precipitate, calculated amount of absolute alcohol is added, while stirring, to bring up the concentration of the alcohol to 60%.   For amounts of lithium up to about 50 mg., the volume is adjusted to 50 ml.; while beyond 50 mg., to 100 ml. with 60% alcohol.   The rest of the procedure is the same as described earlier.   A solubility correction factor of 0.35 mg. of lithium should be added to the value of lithium

obtained for every 50 ml. of the precipitating medium employed. The same procedure is employed even in the presence of sodium and/or potassium. As shown later, the present method is applicable when the ratio of lithium: sodium or potassium does not exceed 1 : 5, and the ratio of lithium: sodium : potassium is not beyond 1 : 3 : 3 in the case of the mixture of the three alkali metals in the solution.

TABLE II
Estimation of lithium in presence of potassium chloride

No.	Approximate ratio of Li : K	Lithium in mg.		Difference in mg.	Percentage error
		Taken	Estimated		
1	1 : 0	5.20	5.20	0.00	0.00
2	1 : 5	5.20	5.17	− 0.03	− 0.57
3	1 : 6	5.20	5.05	− 0 15	− 2.7
4	1 : 10	5.20	4.37	− 0.83	− 16.0
5	1 : 4	12.40	12.40	0.00	0.0
6	1 : 5	12.40	12.38	− 0.02	− 0.16
7	1 : 10	12.40	11.65	− 0.75	− 6.0
8	1 : 5	24.80	24.80	0.00	0.0
9	1 : 6	24.80	23.65	− 0.15	− 0.60
10	1 : 10	24.80	24.01	− 0.79	− 3.2
11	1 : 1	124.00	123.98	− 0.02	− 0.02

TABLE III
Estimation of lithium in presence of sodium chloride

No.	Approximate ratio of Li : Na	Lithium in mg.		Difference in mg.	Percentage error
		Taken	Estimated		
1	1 : 0	5.20	5.20	0.00	0.00
2	1 : 5	5.20	5.18	− 0.02	− 0.38
3	1 : 10	5.20	4.35	− 0.85	− 16.3
4	1 : 5	12.40	12.39	− 0.01	− 0.08
5	1 : 10	12.40	11.52	− 0.88	− 7.1
6	1 : 5	24.80	24.79	− 0.01	− 0.04
7	1 : 6	24.80	24.60	− 0.20	− 0.80
8	1 : 1	124.00	123.94	− 0.06	− 0.05

5. *Estimation of lithium in the presence of sodium and/or potassium chloride and some anions*:—The results of Tables II to V indicate that the method gives quite accurate values of lithium in the presence of potassium and/or sodium

TABLE IV

Estimation of lithium in presence of a mixture of sodium and potassium chlorides

No.	Approximate ratio of Li : K : Na	Lithium in mg.		Difference in mg.	Percentage error
		Taken	Estimated		
1	1 : 0 : 0	9.90	9.90	0.00	0.00
2	1 : 1 : 1	9.90	9.90	0.00	0.00
3	1 : 3 : 3	9.90	9.89	− 0.01	− 0.10
4	1 : 4 : 4	9.90	9.80	− 0.10	− 1.01
5	1 : 5 : 5	9.90	9.13	− 0.77	− 7.76
6	1 : 2 : 2	23.40	23.40	0.00	0.00
7	1 : 3 : 3	23.40	23.39	− 0.01	− 0,04
8	1 : 5 : 5	23.40	22.60	− 0.80	− 3.42

TABLE V

Influence of anions in the estimation of lithium

Amount of lithium taken in the solution=24.80 mg.

Alkali salt added	Anion in mg.	Lithium estimated, mg.	Difference in mg.	Percentage error
Na_2SO_4	52.0	24.79	− 0.01	− 0.04
$NaNO_3$	80.5	24.80	0.00	0.00
Na_3PO_4	50.5	24.79	− 0.01	− 0.04
Na_2HPO_4	70.4	24.79	− 0.01	− 0.04
NaCl	55.5	24.80	0.00	0.00
$Na\overline{AC}$	55.0	24.75	− 0.05	− 0.20
K_2SO_4	50.5	24.79	− 0.01	− 0.04
KNO_3	60.0	24.79	− 0.01	− 0.04
KCl	35.0	24.80	0 00	0.00
K_3PO_4	75.0	24.80	0.00	0.00

salts within the limits pointed out already. In these tables, the solubility correction has been applied for the lithium estimated. Spectroscopic examination of samples of Li_3PO_4 precipitated in the presence of potassium (Li : K as 1: 5 or less) showed no indication for potassium while that with sodium in this range indicated less than 0.1 % of sodium. When samples of Li_3PO_4 precipitated in the presence of seven times the amount of potassium or sodium, potassium was found to be less than 0.1 % while sodium was less than 1 % in the respective samples.

The results of Table V indicate that the presence of sulphate, chloride, nitrate and phosphate ions does not materially interfere in the estimation of lithium. In the case of sodium acetate, the result is slightly lower.

DISCUSSION

It is seen that the phosphate reagent prepared from β-diethyl amino ethyl alcohol can be used successfully for the estimation of lithium as trilithium phosphate, even in the presence of sodium and potassium salts. The accuracy obtained in the presence of these salts is, in general, greater than that obtained by Caley and Simmons.[1] In the present method, the accuracy is not affected even when sodium and/or potassium are present to the extent of 5 times the quantity of lithium. In Caley and Simmons method, the analytical values have always a positive error in presence of other alkali metal salts. This indicates that the precipitate in their method might have been contaminated with the alkali salts. In the present method, on the other hand, the error is negative in presence of the alkali metal salts and spectrographic analysis of trilithium phosphate reveals very little contamination.

Use of organic phosphate reagent in the precipitation of lithium as trilithium phosphate has some advantages over an alkali phosphate reagent employed by Mayer.[5] An organic phosphate hydrolyses more slowly, thus providing the PO_4 radicals gradually for the formation of trilithium phosphate. There are, therefore, less chances of co-precipitation of other alkali metal phosphates along with lithium phosphate. Since the precipitation takes place from the homogeneous medium of 60% ethyl alcohol at a temperature of 65-70°C, adsorption of sodium and potassium ions by lithium phosphate is prevented and the precipitate is more granular.

It is interesting to note that in presence of large proportions of alkali chlorides, there is a negative error, indicating higher solubility of the trilithium phosphate. This is probably due to the equilibrium between the chloride and the lithium ions, resulting in the formation of small amounts of lithium chloride.

ACKNOWLEDGMENT

REFERENCES

1. Caley, E. R. and Simmons,   *Anal. Chem.*, 1953, **25**, 1380.
    G. A.

2. Caley, and E. R. Elving, P. J.   *Inorganic Synthesis*, 1939, **1**, 1, Editor: H. S. Booth
                                      (New York: (McGraw-Hill).

3. Lund, H. and Bjerrum, J   ... *Ber.*, 1931, **64**, 210.

4. Karrer, Paul   ... *Organic Chemistry*, 1947, 93 (New York: Elsevier)

5. Mayer,   ... *Ann.*, 1856, **98**, 193.