

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE UNIVERSITY OF NORTH CAROLINA]

DETERMINATION OF ALUMINUM. FORMATION OF LITHIUM ALUMINATE

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Introduction

The formation of lithium aluminate has been studied by D. Proci¹. He used the method of J. Hegrousky,² for preparing acid lithium aluminate. This method consists of dissolving strips of amalgamated aluminum in normal and tenth normal solutions of lithium hydroxide. He states also that lithium aluminate is precipitated by the addition of a solution of lithium hydroxide to a solution of aluminum salts, or by adding a solution of lithium salt to a solution of alkaline aluminate. In all cases the composition of the compound was expressed by the formula $\text{LiH}(\text{AlO}_2)_2 \cdot 5\text{H}_2\text{O}$, which upon moderate ignition was transformed into $\text{Li}_2\text{O} \cdot 2\text{Al}_2\text{O}_3$. The solubility of lithium aluminate was found by Proci¹ to be 1.2×10^{-4} gr. eq. per liter at 25°. This suggests a possible method of determining aluminum quantitatively by addition of an excess of lithium salt solution to the aluminum solution and making the solution alkaline.

Reagents

Solution of Lithium Chloride.—A 10% solution is made by dissolving 100 g. of lithium chloride in distilled water and making the volume up to 1 liter with water, or by dissolving the required amount of lithium carbonate in a small amount of water, adding hydrochloric acid and making the volume up to 1 liter with water.

Ammonium Hydroxide Solution.—Approximately *N*/10 solution is used as it is easier to secure the exact alkalinity of the solution by adding the very dilute solution dropwise.

Indicator.—Phenolphthalein is used as indicator. The required alkalinity of the solution is a faint pink that is just perceptible.

Standard Aluminum Nitrate Solution.—The solution is made by dissolving 30 g. of aluminum nitrate and making up to 1000 cc. This solution is standardized by evaporating 25 cc. to dryness, igniting and weighing the resulting Al_2O_3 .

Procedure

Aliquot portions of the aluminum salt, sufficient to give approximately 0.1 g. of lithium aluminate, are placed in a beaker and the volume made up to 100 cc. with water. To this solution are added a few drops of phenolphthalein and lithium chloride solution in excess of that required to precipitate the estimated amount of aluminum in the sample. Dilute ammonium hydroxide is added drop by drop with stirring until a very faint pink color is detected. If too much ammonium hydroxide is added, dilute hydrochloric acid is added until the desired pink tint is obtained. A voluminous, flocculent precipitate is formed that filters very rapidly and washes easily. The precipitate is allowed to settle

¹ Proci, *Collection des Travaux de Czechoslovak*, 1, 95 (1929).

² Hegrousky, *J. Chem. Soc.*, 118, 1013 (1920).

for five minutes, filtered and washed with distilled water until free from chlorides. An 11-cm. filter paper is required for a sample giving a precipitate weighing approximately 0.1 g. After washing is complete, the filter paper with the precipitate is transferred to a crucible and placed in a low temperature oven until dry. Then the temperature is raised and the precipitate is ignited, at a high temperature, to constant weight. The precipitate is weighed and aluminum calculated from the formula $2\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$.

Experimental Results

The results, expressed in grams of $2\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$, obtained from samples of pure aluminum nitrate solution are given in Table I.

TABLE I

EXPERIMENTAL RESULTS			
I $2\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$, g.	II $2\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$, g.	III $2\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$, g.	IV $2\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$, g.
0.1084	0.1071	0.0996	0.1031
.1090	.1073	.0994	.1028
.1084	.1066	.0997	.1027
.1084	.1080	.0998	.1029
.1082	.1070	.0999	.1034
Av. .1085	Av. .1072	Av. .0997	Av. .10298
Calcd. .1083	Calcd. .1070	Calcd. .0996	Calcd. .1030

Discussion of Results

Since the precipitate is very voluminous this method requires the use of a large filter paper. The precipitate comes down in a flocculent form that filters and washes very rapidly. The time required to filter and wash a series of twelve samples of lithium aluminate precipitate is not more than an hour. At the same time a large volume of water will have passed through the precipitate. These facts render this method much more desirable than the accepted method in which the aluminum is precipitated with ammonium hydroxide.

The method gives more concordant results than those obtained by the ammonium hydroxide process.

The most satisfactory results are obtained when the weight of lithium aluminate is not more than 0.1 g. A little experience will enable one to determine the size of aliquot to use in order to obtain approximately this weight. Precipitates weighing very much more than 0.1 gram are so bulky that they are unwieldy in transferring and washing.

D. Prociv suggested this as a method for the determination of lithium, but said the precipitate, after ignition, is weighed as $\text{Li}_2\text{O} \cdot 2\text{Al}_2\text{O}_3$. From his solubility determinations he concluded that the precipitate contains lithium and aluminum in the ratio of 0.8Li : 2Al, which, he says, is an atomic ratio of approximately 1Li : 2Al. In fact, this is an atomic ratio of 2Li : 5Al. This corresponds to the formula $2\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$ which was found in this investigation.

The precipitation should be made in solutions just alkaline to phenolphthalein. Ammonium hydroxide is used instead of sodium hydroxide or potassium hydroxide since it is volatile and in case some ammonium salt remains in the precipitate after washing, it will be volatilized during ignition of the precipitate.

The method has been used, with excellent results, in some alum investigations. It is applicable under any conditions in which the ammonium hydroxide method can be used.

Summary

1. Aluminum may be determined quantitatively as lithium aluminate.
2. Lithium aluminate precipitate is filtered and washed much more rapidly than aluminum hydroxide.
3. More concordant results are obtained by this process than by the ammonium hydroxide method.

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AN OVERLOOKED SOURCE OF ERROR IN THE FERROCYANIDE TITRATION OF ZINC

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The ferrocyanide method of determining zinc proposed by Fahlberg,¹ and modified by Low² and Demorest,³ includes the addition of hydrogen sulfide or hydrogen sulfide water just before the titration.

Hydrogen sulfide is added to precipitate copper and to reduce any bromine, chlorine or chlorate which might be present in the zinc solution. The fact that ferricyanide is also reduced by hydrogen sulfide has apparently been overlooked.

When a solution of ferrocyanide stands, a small amount of ferricyanide is formed. According to Kolthoff,⁴ this change is hastened by light. Even in freshly prepared solutions of ferrocyanide there is usually a little ferricyanide. During the zinc titration, if hydrogen sulfide is present, this ferricyanide is reduced to ferrocyanide, which reacts with the zinc. If no hydrogen sulfide is present, there is no reaction between

¹ Fahlberg, *Z. anal. Chem.*, **13**, 379 (1874).

² Low, "Technical Methods of Ore Analysis," 9th ed., John Wiley and Sons, Inc., New York, 1922, p. 252.

³ Lord and Demorest, "Metallurgical Analysis," 5th ed., McGraw-Hill Book Co., Inc., New York, 1924, p. 203.

⁴ Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, Inc., New York, 1928, Vol. I, p. 239.