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DETERMINATION OF OXYGEN IN LITHIUM METAL*

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DETERMINATION OF OXYGEN IN LITHIUM METAL

The corrosive properties of liquid lithium have recently been examined. By analogy with the effect of oxygen in sodium, it was expected that oxide and other trace contaminants would have a major effect on the corrosiveness of liquid lithium. A suitable analytical procedure for the determination of oxygen in lithium in the range of 0.001 to 0.1% was therefore required.

The mercury amalgamation procedure, developed for the determination of oxygen in sodium[1,2] can, with some modifications, be adapted for lithium. This method involves the extraction of the metallic sodium or lithium with mercury. The mercury-insoluble material is then dissolved in water and titrated with standard acid. With sodium, the assumption is often made that the oxide is the only mercury-insoluble impurity that reacts with water to form base. This assumption cannot be applied to lithium. Lithium nitride for one, also reacts with water to yield base, and is generally present in amounts of the same order of magnitude as the lithium oxide. In order to determine the oxide in lithium by the mercury amalgamation procedure, it would be necessary to make a separate determination of the nitride content and to correct for it. In addition, if the hydride, carbide, or phosphide are present in appreciable amounts in the lithium, corrections for them must be applied to the apparent oxide content as determined by the mercury extraction method. It was therefore decided to develop an analytical procedure that is specific for oxide.

A successful method was developed based on the conversion of the oxide oxygen to water and determination of the water thus formed with Karl Fischer reagent. This principle has been used by other workers for the determination of oxygen in calcium metal.[3] The sample of calcium was dissolved in methanol and the resulting solution combined with salicylic acid-pyridine mixture. The water, which is formed stoichiometrically from the oxide present, is determined by the Karl Fischer method. Samples of calcium with oxide contents of 0.4 to 2.0% were analyzed by this method. In the case of

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[1] Pepkowitz, L. P., and Judd, W. C., Anal. Chem., 22, 1283 (1950).

[2] Williams, D., and Miller, R. R., Anal. Chem., 23, 1865 (1951).

[3] Eberle, A. R., Lerner, M. W., and Petretic, G. J., Anal. Chem., 27, 1431 (1955).

lithium, the pertinent chemical equations are:

(1) $2\ Li + 2\ CH_3OH \rightarrow 2\ LiOCH_3 + H_2$.

(2) $Li_2O + 2\ CH_3OH \rightarrow LiOH + LiOCH_3$.

(3) $LiOCH_3 + C_6H_4 \cdot OH \cdot COOH \rightarrow LiC_6H_4 \cdot OH \cdot COO + CH_3OH$.

(4) $LiOH + C_6H_4 \cdot OH \cdot COOH \rightarrow LiC_6H_4 \cdot OH \cdot COO + H_2O$.

(5) $SO_2 + I_2 + 3C_5H_5N + CH_3OH + H_2O \rightarrow C_5H_5NH \cdot SO_4 \cdot CH_3 + 2C_5H_5N \cdot HI$.

In applying the above method to the determination of oxygen in lithium, various modifications were made. The range of interest is 10 to 1000 ppm of oxygen in lithium. This requires a higher sensitivity than is normally attained in Karl Fischer determinations. A micro procedure for the Karl Fischer determination has been reported.[4] A limiting sensitivity of 10 μg of water in a maximum volume of about 10 ml of titrated solution was attained. This was accomplished by using a diluted reagent and by being careful to protect the reagent and the titrated solution from atmospheric moisture.

Procedure

The diluted Karl Fischer reagent was prepared by diluting stock Karl Fischer reagent 1:5 with anhydrous methanol. The water equivalent of this diluted reagent was in the range of 0.25 – 0.50 mg/ml. The stock reagent was prepared according to the directions of Mitchell and Smith.[5] The titer of the diluted reagent, which was protected from moisture, did not change more than 1% in a week. The anhydrous methanol was dried by magnesium turnings and then distilled.[6]

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[4] Wiberly, J. S., Anal. Chem., 23, 656 (1951).

[5] Mitchell, J., and Smith, D. M., Aquametry (Interscience Publishers, Inc., New York, 1948) p. 19.

[6] Weissburger, A. et al., Organic Solvents (Interscience Publishers, Inc., New York, 1955) p. 334.

The apparatus used for the analysis is shown in Figure 1. The system is designed so that it can be sealed off from the atmosphere and the solutions manipulated by means of excess pressure of purified argon. A lithium sample of 0.5 – 1.0 g is dropped into the reaction flask (item 20). This sample can be exposed to air prior to putting it into the reactor flask because in this procedure, the oxide on the exposed surfaces of the lithium is washed off with methanol before the analysis is started. This is done by transferring anhydrous methanol from the burette (item 3) to the reaction flask, and then discarding the washings. This is satisfactory for cast lithium because the oxygen figure desired is the per cent present in the bulk of the metal. After the washing operation, a measured quantity of anhydrous methanol (usually 60 ml) is transferred by means of gas pressure to the reaction flask, and the sample allowed to react with the methanol. The hydrogen gas generated by the reaction of the lithium and the methanol is vented to the atmosphere, while the sample of lithium is dissolving. A portion of a 50% solution of salicylic acid in pyridine (usually 40 ml) is pipetted into the titration flask (item 7) through the vent (item 11). The solution of salicylic acid is pre-titrated to an end point with the Karl Fischer reagent. The methylate solution is then combined with the salicylic acid in the titration flask. Any lithium oxide present in the sample liberates water which is then titrated with the Karl Fischer reagent. The blank for the methanol is determined separately and is subtracted from the final titration.

The sample size can be determined by a flame photometric determination of the lithium content of the titrated solution. If a flame photometer is not readily available, the sample size can be determined by an alternate procedure. From a knowledge of the acid equivalence of the salicylic acid solution and the Karl Fischer reagent, the number of moles of acid added to the titrated solution can be calculated. The actual number of moles of acid present in the titrated solution is determined with standard base. The difference between the calculated moles of acid and the moles of acid actually found is equal to the number of moles of lithium in the sample.

FIGURE 1

Oxygen Analysis Setup

1. P_2O_5 on asbestos.
2. 12/2 ball and socket joint.
3. 2-liter automatic burette with anhydrous alcohol.
4. 12/2 ball and socket joint.
5. 12/18 standard taper joint.
6. To purified argon and vacuum.
7. Titration flask.
8. Stirring bar.
9. Magnetic stirrer.
10. Platinum electrodes.

10a. Leads to dead-stop indicator.

11. Vent to atmosphere.
12. 1-liter automatic burette with Karl Fischer reagent.
13. Sample to be analyzed.
14. 18-mm stopcock.
15. 35/20 ball and socket joint.
16. Condenser.
17. Vycor to pyrex graded seal.
18. Vycor frit.
19. Capillary constriction.
20. Reaction flask.

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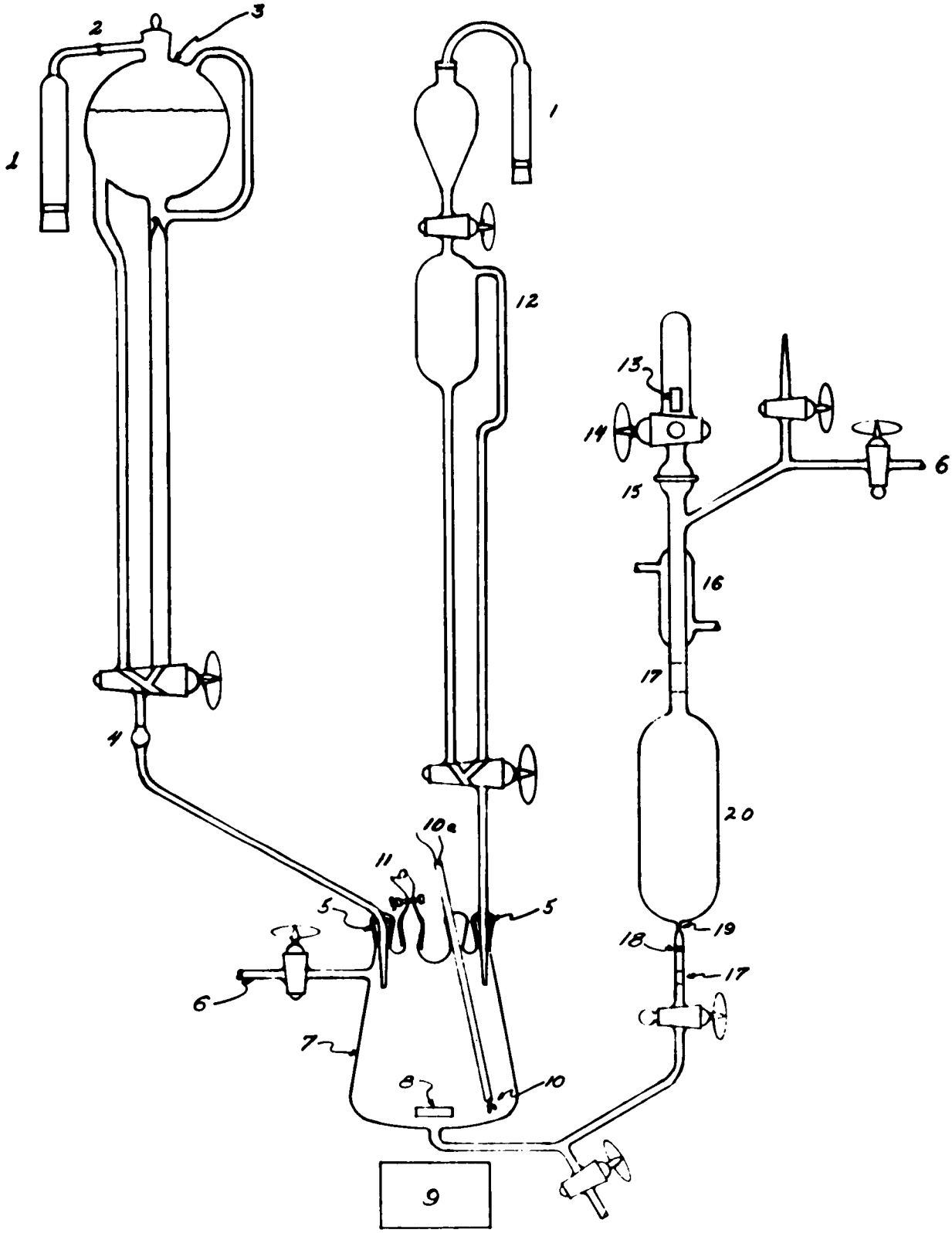

Oxygen analysis set-up

Discussion and Experimental Results

In order to achieve the desired accuracy and sensitivity in this procedure, introduction of interfering contaminants into the system must be prevented. Air and moisture are excluded by using a closed system and manipulating the solutions with gas pressure. When the apparatus is not in use, a solution of methanol containing a large excess of concentrated Karl Fischer reagent is kept in the reaction and titration flasks. This minimizes the amount of moisture adsorbed on the walls of the apparatus.

Preliminary experiments were run in which lithium or standard sodium samples were dissolved in a pyrex reaction flask. The analytical results were somewhat higher than expected. This was attributed to leaching of oxides from the glass by the methylate solution. Substitution of a vycor reaction flask resulted in more consistent results.

The methanol used, as well as the other reagents, was carefully dried. However, the blank for the 60 – 80 ml of methanol used to dissolve the sample was usually equivalent to 0.5 – 1.0 mg of oxygen. The oxygen present in the various samples of lithium and sodium were usually in the range of 0.01 – 0.50 mg. This means that the oxygen content of a sample is determined by a small difference between two relatively large numbers. It was, therefore, necessary that the titrations have a high degree of reproducibility and sensitivity.

The Karl Fischer titration was done by the dead-stop direct-titration method. The detection circuit was devised by Wiberly and consisted simply of a 2-v battery, a 0 – 50 microammeter and two resistors. A voltage of 100 mv was applied across the terminals of a pair of platinum electrodes, immersed in the solution to be titrated. The current passing through the electrodes was measured by the microammeter.

When the direct dead-stop end-point titration is applied to solutions of normal concentrations, an abrupt rise in current occurs at the end point. Because of the high dilutions used in this work, the current was observed to rise very gradually with increasing amounts of reagent added to the titrated solution. The following procedure was found to yield reproducible titrations. The salicylic acid-pyridine mixture was pretitrated by adding it to Karl Fischer reagent until a small current (10 μa) was passing through the indicating electrodes. The solution of lithium methylate in

methanol was combined with the pretitrated solution of salicylic acid. This combined solution was then titrated with the Karl Fischer reagent until the current was restored to its original value (10 μa). The methanol blank analysis was performed in a similar manner.

Another consequence of the high dilutions used, is that the reaction between the Karl Fischer reagent and the water is slow, and sufficient time must be allowed for completion of the reaction. In spite of all precautions, there is a fairly constant apparent pickup of water by the titrated solution at the rate of about 1 μg/min. A constant titration time of 15 min was used and this provided sufficient time for completion of the reaction between the Karl Fischer reagent and the water, and also made it possible to eliminate errors due to water pickup.

The platinum electrodes were made of 30-mil wire or small plates. The use of relatively large area electrodes resulted in improved sensitivity.

Testing of the validity of the method was handicapped because of the unavailability of standard lithium samples, or lithium samples of very low oxygen content. A validity test was devised based on the principle of dividing a lithium sample in two parts and adding a known amount of lithium oxide to one of the parts. The difference in titer of the two samples was then due to the added lithium oxide.

Known amounts of lithium oxide were made by adding a measured quantity of lithium hydroxide solution to a platinum plate. This was dried and then heated with a Meker burner to 700 – 800°C for 10 sec. At this temperature, the hydroxide is converted to the oxide (p H_2O at 700°C = 91 mm.[7] The plate with the oxide was dropped, while hot, into the reaction flask. Several tests were made in which the product resulting from the heating of the hydroxide was analyzed for oxygen content. The amount of oxygen found agreed with that expected of lithium oxide rather than that of lithium hydroxide. These results are tabulated in Table I.

Samples of distilled sodium were analyzed for oxygen content. The oxygen contents found were in range of 10 – 30 ppm, which is in agreement with the results obtained with the mercury-extraction procedure.

[7] Gmelin's Handbuch der Anorganische Chemie, "Lithium" (Verlag Chemie, Berlin) (1927).

TABLE I

Lithium Oxide Recoveries

Oxygen in Lithium (mg)	Oxygen added (mg)	Calculated Total Oxygen (mg)	Oxygen Found (mg)
0 (no lithium)	0.119	0.119	0.123 ± 0.005
0 (no lithium)	0.060	0.060	0.053 ± 0.004
0.066	0.119	0.185	0.190
0.087	0.119	0.206	0.202
0.115	0.119	0.234	0.217
0.203	0.119	0.322	0.286
0.309	0.119	0.428	0.441

Conclusion

A method for the determination of the oxide content of lithium has been developed. This method is specific for oxygen and of sufficient sensitivity to perform analysis in the range of 10 – 100 ppm of oxide.

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