~~M. J. Skinner~~

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SUBJECT: Spectrophotometric Determination of Lithium Carbide in Metallic Lithium as the Acetylene-Silver Perchlorate Complex

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FROM: T. W. Gilbert, Jr., A. S. Meyer, Jr., and J. C. White

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SPECTROPHOTOMETRIC DETERMINATION OF LITHIUM CARBIDE IN METALLIC LITHIUM AS THE ACETYLENE-SILVER PERCHLORATE COMPLEX

ABSTRACT

Lithium carbide and lithium nitride in lithium metal are determined simultaneously by measuring the quantities of acetylene and ammonia that are evolved when a sample of lithium is dissolved in water. Ammonia is absorbed in a solution of boric acid and is determined by the conventional Nessler's method. Available methods for the determination of small amounts of acetylene either lacked the required sensitivity or were not suited to this application. Accordingly, a new spectrophotometric method was devised for the determination of 50 to 2500 µg of acetylene with a coefficient of variation of 2.7 per cent. The acetylene is absorbed in 1.5 M silver perchlorate; the ultraviolet absorption of the soluble silver-acetylene complex that is formed is then utilized for the determination of acetylene.

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SPECTROPHOTOMETRIC DETERMINATION OF LITHIUM CARBIDE IN METALLIC LITHIUM AS THE ACETYLENE-SILVER PERCHLORATE COMPLEX

T. W. Gilbert, Jr., A. S. Meyer, Jr., and J. C. White

Lithium metal is ordinarily contaminated by oxygen, nitrogen, and carbon which exist in the combined forms of lithium oxide, Li_2O, lithium nitride, Li_3N, and lithium carbide, Li_2C_2, respectively. When the metal is dissolved in water, the nitride is hydrolyzed quantitatively to ammonia and the carbide to acetylene. Since hydrogen is also a product of the dissolution of metallic lithium in water, methods for the determination of carbon in lithium involve the determination of traces of acetylene in hydrogen. The purpose of this investigation was to develop a simple and rapid method for the determination of acetylene in hydrogen that would also allow simultaneous determination of the ammonia released by the hydrolysis of lithium nitride.

Small amounts of acetylene are generally determined by measuring the absorbance of colloidal suspensions of cuprous acetylide.[1,3,4] Purser[5] reported, however, that this absorbance is a function of the conditions of mixing the reagents and, accordingly, for each determination a comparison with standard acetylene solutions is mandatory. A method was sought, therefore, which would be less subject to the difficulties usually encountered when making spectrophotometric measurements of colloidal suspensions.

Shaw and Fisher[6] observed that when acetylene is passed into a "35 per cent solution of silver nitrate," no precipitate of silver acetylide is formed; however, on dilution with water, the double salt, $Ag_2C_2 \cdot AgNO_3$, is precipitated and can be used as a weighing form for the gravimetric determination of acetylene.

The existence of a complex of acetylene that is soluble in concentrated solutions of silver suggested the possibility of a spectrophotometric determination based on the ultraviolet absorption of the silver-acetylide complex. Due to the strong absorption of nitrate, it was necessary to substitute silver perchlorate for silver nitrate as the absorbent for acetylene.

Solutions of acetylene in silver perchlorate have been previously studied by Vestin and Ralf.[7] By means of solubility measurements they postulated that the silver acetylene complexes were of the type $(C_2Ag_2)_n(Ag^+)_p$, where for $n = 1$, the most likely values of p were 4 to 6. They investigated the ultraviolet absorption of the silver-acetylene complexes and stated that they do not absorb light at wavelengths greater than 270 mμ. Contrary to their findings, however, the authors observed absorption at longer wavelengths and that this absorption was useful for the spectrophotometric determination of acetylene.

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REAGENTS

Calcium carbide - Baker and Adamson, 3/8-inch lumps.

Acetylene - Acetylene was prepared by the method of Shaw and Fisher[6] by adding a mixture of water and ethanolamine dropwise on calcium carbide. The gas is passed through two scrubbers, the first of which contains a solution of chromic acid, while the second contains a solution of 30-per cent potassium hydroxide. Acetylene prepared in this manner was reported to exceed 99.5 per cent in purity.

Silver perchlorate, anhydrous - G. Fredrick Smith Chemical Company. Solutions of this compound were prepared by dissolving a weighed amount in water, diluting to the required volume, and then filtering through two thicknesses of Whatman No. 42 paper. Only in this manner was it possible to obtain solutions which were free enough from turbidity for spectrophotometric work. Most of the solutions used in this study were 1.5 M in silver perchlorate and were prepared in this way.

These solutions, unfortunately, have an objectionable characteristic in that on dilution with water a turbidity develops which invalidates any absorbance measurements. For certain experiments, therefore, it was necessary to use a solution of silver perchlorate prepared by precipitating silver oxide from silver nitrate solutions, washing the oxide free of nitrate, and then dissolving the product in an equivalent amount of perchloric acid. No turbidity was observed on dilution of solutions prepared in this manner.

The silver solutions were standardized by a titration with potassium thiocyanate in which ferric alum was utilized as the indicator.

APPARATUS

The apparatus used for the determination of carbide and nitride in lithium metal is shown schematically in Figure 3. Its principal parts consist of a stainless steel pressure vessel in which the sample is dissolved in water, a cylinder that contains 100 ml of 4 per cent boric acid to absorb ammonia, and three bubblers, each of which contains 5 ml of 1.5 M silver perchlorate.

All absorption measurements were made with a Beckman Model DU Spectrophotometer which was equipped with thermospacers to maintain the temperature in the cell compartment at 25 ± 0.2° C. Both hydrogen and mercury vapor lamps were used as light sources.

EXPERIMENTAL

Absorption Spectra

The absorption spectra of solutions of silver perchlorate that contained acetylene, measured against silver perchlorate of equal concentration, are shown in Figure 1. In addition, the spectrum of a solution of silver perchlorate that was measured against water is shown. It is obvious that absorption due to the silver ion does not interfere with the measurement of the absorption caused by the silver acetylene complex.

Preparation of a Standard Solution of Acetylene in Silver Perchlorate

A standard solution of acetylene in silver perchlorate was prepared as follows: Silver acetylide, Ag_2C_2, was precipitated by passing acetylene through a strongly ammoniacal solution containing a weighed amount of silver nitrate. The mixture was filtered through a tared, sintered-glass crucible, after which the precipitate was washed several times with water. (Caution: Do not allow a glass stirring rod to scratch the sintered glass filter since the silver acetylide is easily detonated.) Acidification of the filtrate and washings with hydrochloric acid should produce a negligible turbidity indicative of a quantitative precipitation of the silver. The silver acetylide is dissolved by passing 60 ml of 2.5 M silver perchlorate slowly through the filter. The filter is washed with water, and hydrochloric acid is added to the crucible to convert any undissolved Ag_2C_2 to AgCl. Hydrochloric acid is likewise added to the original beaker, used in the precipitation, for the same purpose. The silver chloride residues are combined, dried, and weighed. The quantity of Ag_2C_2 which dissolved in the concentrated solution of silver perchlorate solution is then calculated by difference. One hundred ml of a 1.5 M solution of silver perchlorate that contained 0.4084 mg of acetylene per ml was prepared in this manner.

Calibration Curves

It is seen from Figure 1 that the spectrum of the silver acetylene complex does not have a maximum at which absorbance measurements can be made. If a hydrogen lamp is used as the source of excitation for the measurement of the absorbance of the solutions on the slope of the absorption band, a satisfactory calibration curve can be obtained; however, the use of a mercury vapor lamp instead of a hydrogen lamp is superior in two respects. First, the curve, obtained with the hydrogen source, slopes downward at higher absorbance values due to non-monochromatic incident light. The use of a mercury spectral line was found to improve this condition greatly. Second, because measurements are made on the slope of an absorption band, the setting of the wavelength dial is critical. A mercury spectral line provides an absolute wavelength standard. Thus, a calibration curve can be constructed which can be used with any instrument without the necessity of calibrating

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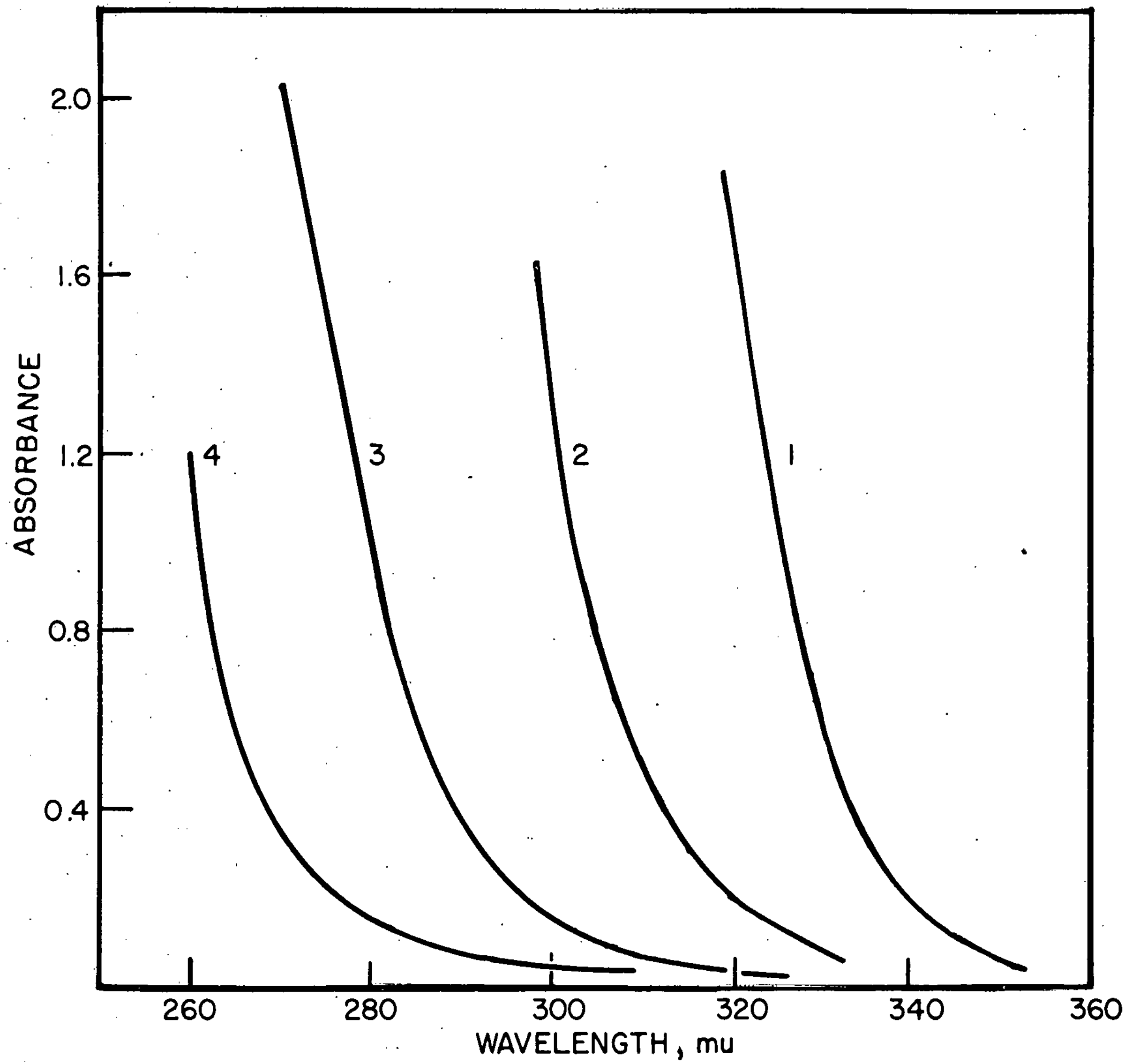

1. 2.0 M $AgClO_4$, saturated with acetylene vs 2.0 M $AgClO_4$
2. 2.0 M $AgClO_4$, 1/10 saturated with acetylene v.s. 2.0 M $AgClO_4$
3. 2.0 M $AgClO_4$, 1/100 saturated with acetylene v.s. 2.0 M $AgClO_4$
4. 1.5 M $AgClO_4$, v.s. water

FIGURE 1, ABSORPTION SPECTRA OF ACETYLENE IN SILVER PERCHLORATE

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the wavelength scale or referring to standard acetylene solutions.

The conformity of the system to Beer's Law when the mercury lines at 296.7 and 313.2 mμ are used is shown in Figure 2. As can be seen, Beer's Law is obeyed even at high absorbance values. These solutions were prepared by dilution of the standard acetylene solution described previously with 1.5 M silver perchlorate. Absorbance measurements were carried out at two temperatures since the system has an abnormally high dependence on temperature. For careful work the use of a thermostatically controlled cell compartment on the spectrophotometer is recommended. The results are summarized in Table 1.

Table 1

Effect of Temperature on the Absorbance of 1.5 M Silver Perchlorate Solutions Containing Dissolved Acetylene

1-cm Silica Cells
Beckman Model DU Spectrophotometer, Mercury Vapor Lamp
Reference Solution, 1.5 M $AgClO_4$

Acetylene μg/ml	Absorbance 25° C 296.7 mμ	Absorbance 25° C 313.2 mμ	Absorbance 30° C 296.7 mμ	Absorbance 30° C 313.2 mμ
8.17	0.063	--	0.059	--
20.42	0.144	--	0.141	--
40.84	0.287	--	0.275	--
61.26	0.435	0.082	0.424	0.078
102.1	0.750	0.140	0.727	0.135
122.5	0.894	0.167	0.874	0.162
204.2	1.48	0.286	1.44	0.271
306.3	--	0.429	--	0.423
408.4	--	0.572	--	0.549

It is seen that the use of two spectral lines permits a wide range of concentrations of acetylene to be determined directly without the necessity of taking aliquots and making dilutions.

As a check on the validity of the method devised for the preparation of standard acetylene solutions, measured volumes of pure acetylene gas under atmospheric pressure and temperature were bubbled through single 5-ml aliquots of 1.5 M silver perchlorate. The weight of acetylene added in each case was calculated and the absorbances of the solutions were measured. Comparison of the results obtained with the absorbances of solutions prepared from precipitated silver acetylide showed that on the average, the absorbances observed on the addition of gaseous acetylene were 3 per cent lower than those obtained from the standard acetylene solutions.

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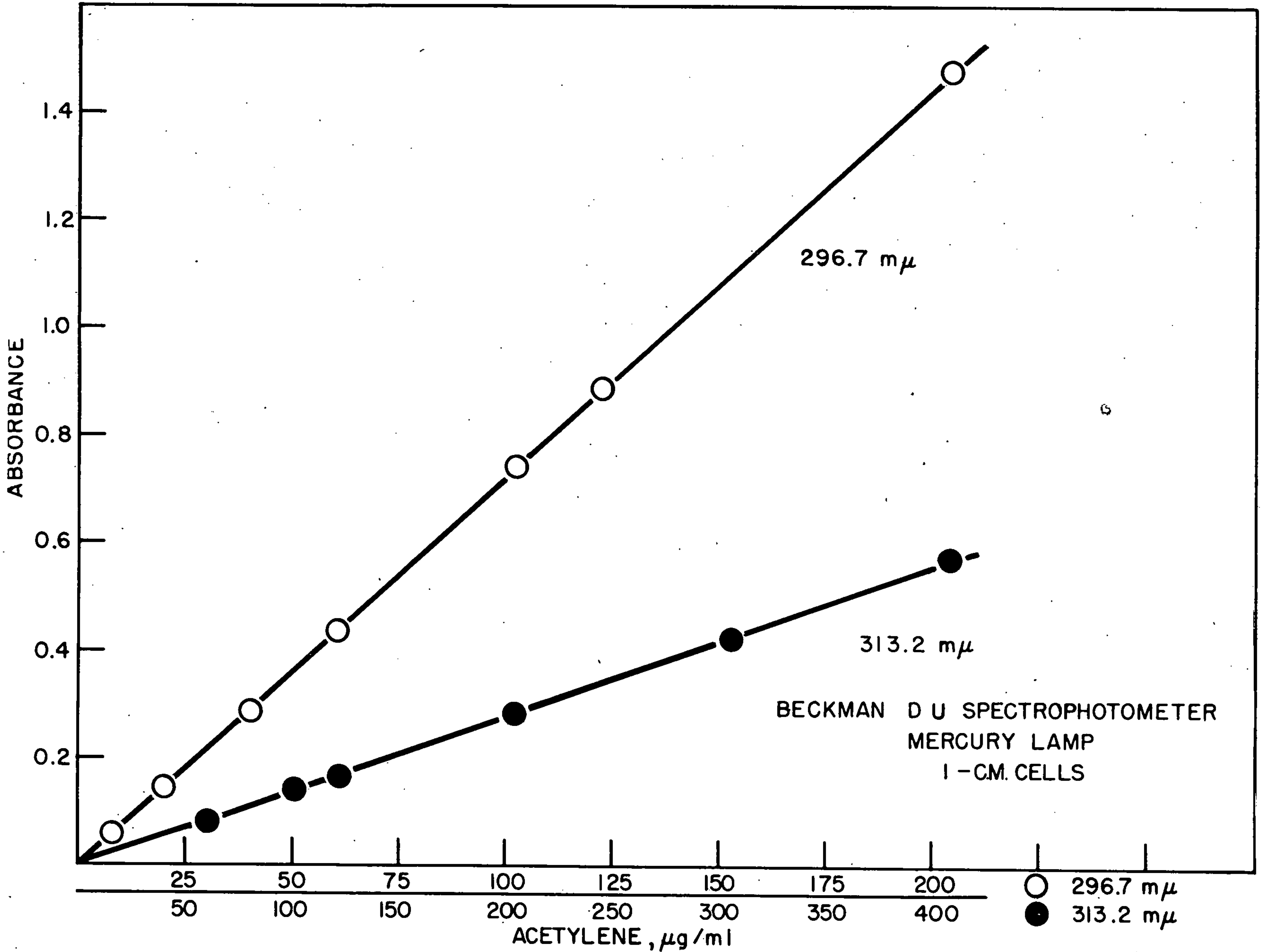

FIGURE 2, CALIBRATION CURVES FOR THE DETERMINATION OF ACETYLENE AS THE SILVER-ACETYLENE COMPLEX.

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This is considered to be satisfactory agreement especially since some of the acetylene undoubtedly escaped absorption (v.i.).

The Efficiency of the Absorption of Acetylene in Silver Perchlorate Solutions

A small volume of pure acetylene was allowed to pass through three absorption tubes that were connected in series, each of which contained 5 ml of 1.5 M silver perchlorate. The absorbance of each portion of silver perchlorate was then measured against the original solution. The results are shown in Table 2.

Table 2

The Efficiency of Absorption of Acetylene in 1.5 M Silver Perchlorate

1-cm Silica Cells
Beckman Model DU Spectrophotometer
Reference Solution, 1.5 M $AgClO_4$

Tube Number	Absorbance, 297 mμ
1	0.467
2	0.009
3	-0.002

The data show that only approximately two per cent of the acetylene escaped absorption in the first tube. This figure was found to increase when a small amount of acetylene was absorbed from a large volume of hydrogen. Under these conditions about 10 per cent of the acetylene was found in the second tube.

The Effect of the Concentration of Silver Perchlorate

In order to ascertain whether the concentration of the silver perchlorate solution, used for the absorption of acetylene, has a pronounced effect on the absorbance observed, small equal volumes of acetylene were bubbled into 5-ml portions of silver perchlorate of various concentrations. The absorbances of these solutions were then measured against solutions of equal silver concentrations. The results are shown in Table 3.

Table 3

The Effect of Silver Ion Concentration on the Absorption of Light by the Silver Acetylene Complex

1-cm Silica Cells
Beckman Model DU Spectrophotometer, Hydrogen Lamp

$AgClO_4$, Molarity	Absorbance, 297 $m\mu$
2.51	0.461
2.01	0.433
1.51	0.385
1.00	0.320
0.50	0.300*

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*Very slightly turbid

The absorption was found to become more intense with increasing concentrations of silver perchlorate. The effect is not pronounced enough to cause serious difficulty, however.

Interferences

In the application of this method to the determination of small amounts of acetylene formed from the hydrolysis of lithium carbide, the only interference encountered was that of hydrogen. At room temperature, hydrogen slowly reduces silver to metallic silver which remains in suspension and interferes with the spectrophotometric measurements. The extent of this reduction was found to be minimized by cooling the silver perchlorate solutions to 0° C during the absorption of the acetylene. Small amounts of dissolved hydrogen are made to react following the absorption step by heating the solutions for 5 to 10 minutes on a steam bath. The precipitated silver metal is then removed by centrifugation.

Precision

The precision of the method was determined by passing known volumes of acetylene through 1.5 M silver perchlorate and measuring the absorbance of the solution. The coefficient of variation is 3 per cent for 25 to 2500 ppm of carbon in lithium.

Application of Method to the Determination of Carbide in Lithium Metal

The proposed method was applied to the determination of carbide in metallic lithium. Since lithium reacts readily with oxygen and nitrogen, samples are usually sealed in evacuated glass tubes. More intricate sampling devices are also available in which the specimen can be transferred directly into the reaction vessel in an inert atmosphere. In this case, however, the samples, which weigh approximately 2.5 g, are sealed in evacuated glass ampules and placed in the reaction bomb, shown in Figure 3, which contains 200 ml of freshly boiled water. After the bomb is deaerated with argon, the valves are closed and the sample vial is broken by shaking the bomb vigorously. When the lithium has completely reacted as indicated by a constant reading on the pressure gauge, the bomb is connected to the rest of the system. (Figure 3). Valve B is then opened partially to allow the gases to pass slowly through the absorbing solutions.

The cylinder, C, contains 100 ml of a 4 w/v per cent solution of boric acid. The absorption tubes, D, D', and D", which contain 5 ml of 1.5 M silver perchlorate, are cooled to 0° C in an ice bath. When the flow of gases ceases, the valve, E, is opened; then the system is flushed for 15 minutes with argon. With argon still flowing slowly, approximately 60 ml of water is distilled from the bomb into the absorption cylinder C.

The absorption tubes D, D', and D" are then disconnected from the train, fitted with rubber stoppers to prevent evaporation, and heated on a steam bath for 10 minutes. They are next cooled to room temperature, after which the contents of the tubes are transferred to centrifuge tubes to be centrifuged. The tubes are then placed in a water bath at 25° C for 15 minutes. The solutions are transferred to 1-cm silica cells; then their absorbances are measured at 297 and 313 mμ with a Beckman Model DU Spectrophotometer fitted with thermospacers to maintain the temperature of the cell compartment at 25 ± 0.2° C. The reference solution is 1.5 M silver perchlorate.

The contents of cylinder C are diluted to 200 ml in a volumetric flask, and a suitable aliquot is taken for the determination of ammonia with Nessler's reagent.[2] Some typical results are shown in Table 4 for lithium of varying purity.

Table 4

Determination of Carbon and Nitrogen in Lithium Metal

1-cm Silica Cells
Beckman Model DU Spectrophotometer, Mercury Vapor Lamp
Reference Solution, 1.5 M $AgClO_4$

Sample	Carbon, ppm	Nitrogen, Per Cent
1	4	1.2
2	53	2.1
3	1	0.055
4	22	-
5	310	-

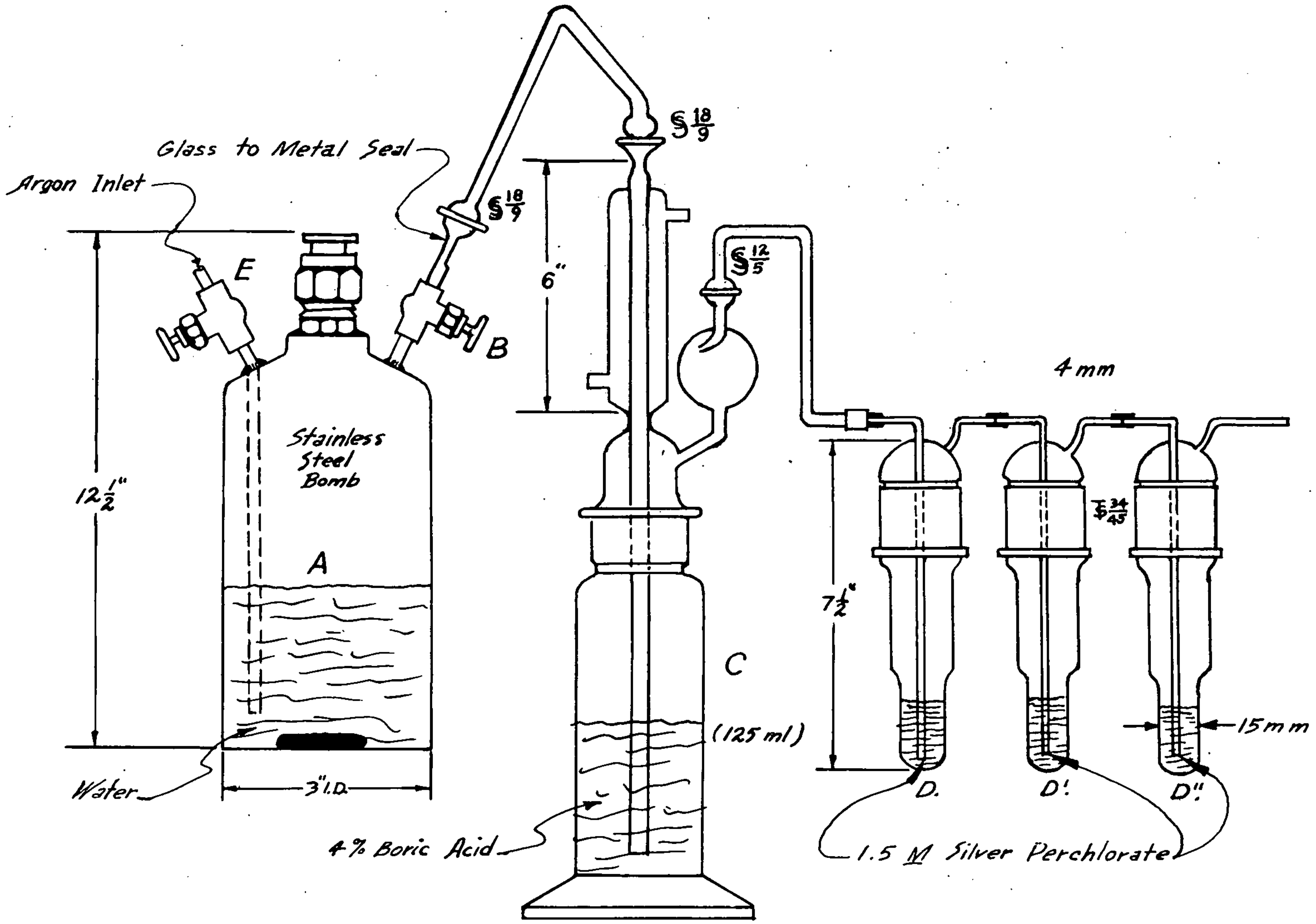

FIGURE 3, APPARATUS FOR DETERMINATION OF Li_2C_2 and Li_3N IN METALLIC LITHIUM.

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