The Purification of Silicon Tetrachloride from Traces of Boron with N, N-Diphenylacetamide

By Masanao NAKAGAWA

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During the past decade many studies have been made of the purification of silicon for use as a semiconductor and of its raw materials, particularly from traces of boron. The purification of silicon tetrachloride and trichlorosilane,[1,2] the raw materials, from the boron, however, has not been fully studied because of the lack of any appropriate method for chemical analysis, although a report[3] on it has recently been published.

In previous papers[4] it has been shown that the boron in silicon tetrachloride can be decreased by the addition of many Lewis bases, such as nitriles, amides, aniline derivatives and some others, followed by distillation. Among those bases, *N, N*-diphenylacetamide appeared to be a particularly effective reagent, because the amide gave a stable addition compound[5,6] with boron trichloride, with an equilibrium constant[7] of more than an order of 10^3, the heating of which up to 100°C evolves no detectable volatile boron compounds, as has also been reported previously.[8]

On the other hand, an analytical method[9] for traces of boron based on the extraction of a boron tetrafluoride ion-methylene blue complex, followed by spectrophotometric determination, appeared to be a useful and convenient method for the present study.

Thus, the present work was undertaken to clarify the effects of *N,N*-diphenylacetamide in the purification from boron (1 p.p.m. or 1 p.p.b. order) by a slight modification of the methylene blue method.

Experimental

Reagents.—Pure silicon tetrachloride was prepared by refluxing its crude chloride with copper powder (3%), followed by fractional distillation. Boron trichloride was obtained as a liquefied gas (a purity of 99.5%) in a steel cylinder from the American Potash and Chemical Corp. Carbon tetrachloride was distilled in the presence of phosphorus pentoxide. Dichloroethane, methylene blue and *N, N*-diphenylacetamide were purified by the normal procedure.

The Procedure for the 1 p. p. m. Order.—The standard solution of boron trichloride in carbon tetrachloride (1.125 M) was prepared by dissolving the vapor from the steel cylinder in the solvent; the concentration of the solution was determined by the titration, with a standard sodium hydroxide solution, of an aqueous solution obtained by hydrolyzing a portion of the solution in carbon tetrachloride.

The standard solution of boron in silicon tetrachloride (1.1 μg./ml.) was also prepared by diluting the standard solution in carbon tetrachloride (1.125 M) with pure silicon tetrachloride. The standard solution (25 ml.) and the amide (1/400 mol.)[10] were taken into a distillation flask (100 ml.), and, after having been stirred or refluxed for a stated number of times, the silicon tetrachloride was completely distilled off at 62~65°C, and dry nitrogen was passed through the flask overnight. The residue was hydrolyzed by stirring in a dilute sodium hydroxide solution (25 ml. of distilled water and 2 ml. of 5% sodium hydroxide) for 1 hr. The solution was filtered from the amide, and the filtrate was concentrated to about 5 ml.

The concentrate was diluted in a volumetric flask (25 ml.), and the solution (10 ml.) was taken into a polyethylene bottle (100 ml.) and acidified with phosphoric acid (1 ml. of a 1 : 10 solution). After the successive addition of hydrofluoric acid (5 ml. of a 5% solution) and distilled water (10 ml.), the bottle was tightly stoppered and kept at room temperature for 2 hr. Then ferrous ammonium sulfate (2 ml. of a 4% solution), distilled water (78 ml.) and methylene blue (2 ml. of a 1/1000 M aqueous solution) were successively added to the bottle, and the solution was vigorously shaken for 2 min. with dichloroethane (25 ml.). After the solution had stood for 30 min. the dichloroethane layer (1 ml.) was pipetted off and diluted with pure dichloroethane (5 ml.).

The dichloroethane solution was taken into a quartz cell (1 cm.), and the absorbance at 660 mμ

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2) E. g., G. Rosenberger, German Pat. 955415; *Chem. Zblt.* **128**, 6864 (1957); G. A. Wolf. U. S. Pat. 2857249; *Chem. Abstr.*, **53**, 4673 (1959).
3) M. Miyamoto, *Japan Analyst*, **12**, 233 (1963).
4) M. Nakagawa, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 135, 2115 (1960).
5) W. Gerrard, M. F. Lappert and J. W. Wallis, *J. Chem. Soc.*, **1960**, 2141.
6) M. J. Frazer, W. Gerrard and J. K. Patel, ibid., **1960**, 726.
7) M. Nakagawa, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), to be published.
8) M. Nakagawa, ibid., **66**, 168 (1963).
9) L. Pasztor and J. D. Bode, *Anal. Chem.*, **32**, 277 (1960).
10) The amount was favorable in a preliminary test with a standard solution of boron (25 ml. of 0.045 M) in carbon tetrachloride, in silicon tetrachloride or in a mixture of them.

was measured by a Shimadzu QR-50 type photoelectric spectrophotometer. After the reagent blank with pure silicon tetrachloride had been subtracted from the absorbance, the amount of boron taken out with *N*, *N*-diphenylacetamide was obtained by the calibration curve made up with the standard aqueous solution of boron.

The Procedure for the 1 p.p.b. Order.—The standard solution of boron in silicon tetrachloride (0.009 μg./ml.) was prepared as has been described above, and the solution (100 ml.) was taken into a polypropylene beaker (100 ml.). After the addition of *N*, *N*-diphenylacetamide (0.1 g.), the beaker was placed in a vacuum desiccator equipped with two stopcocks, which were connected to a scrubbing bottle with concentrated sulfuric acid, through which dry air could be admitted, and to a vacuum pump via a phosphorus pentoxide column, two scrubbing bottles with a sodium hydroxide solution (1 : 2), and a calcium chloride column.

The vacuum desiccator was evacuated by heating it by two lamps (60 W.) above the desiccator, and the silicon tetrachloride was completely distilled off. The residue was taken out and hydrolyzed with distilled water (10 ml.). After the mixture had stood overnight in order to complete the hydrolysis the aqueous solution was filtered from the amide, and the beaker was washed two times with distilled water (5 ml.). The washing solution was also filtered by the filter paper previously used, and those filtrates were taken into a polyethylene bottle (100 ml.). The aqueous solution was submitted to extraction, followed by the measurement of the absorbance, which was as described previously except for the following points: dichloroethane, 10 ml., the shaking time for the extraction, 10 min., the quartz cell, 3 mm., and the absorbance was measured without the dilution of the extracts.

Results and Discussion

Figure 1 gives the calibration curve for the

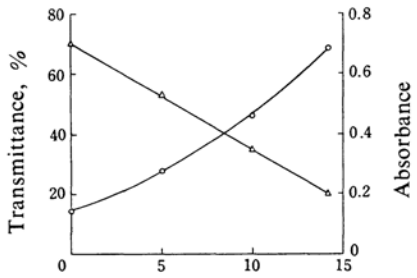

Fig. 1. Calibration curve for 1 p.p.m. order.
△ Transmittance ○ Absorbance

boron of the 1 p.p.m. order, which rather deviates from Beer's law, but which gives a good reproducibility and an accuracy within ± 0.3 μg. The deviation observed might be due to certain interference by the amide slightly dissolved in the aqueous solution.

It had been reported[9] that the extraction oculd be well carried out with dichloroethane (25 ml.) and methylene blue (1/1000 M, 10 ml.). In the present study, however, a smaller amount of methylene blue (1/1000 M, 2 ml.) was used to decrease the blank value of the absorbance; the use of more was unfavorable for sensitive analyses.

The effects of the reaction factors on the recovery of boron (1 p.p.m. order) are shown in Fig. 2. The stirring at room temperature

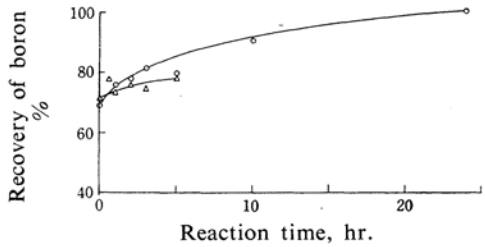

Fig. 2. Effect of the reaction time of the recovery of the boron (1.08 μg./ml.).
○ Stirring △ Refluxing

gave a slightly high recovery, and the stirring for 24 hr. led to a recovery of about 100%, which suggests that the boron contents in the silicon tetrachloride distilled off should be 0.06 μg./ml. or less, as could be estimated from the maximum experimental error involved.

Figure 3 represents the calibration curve for

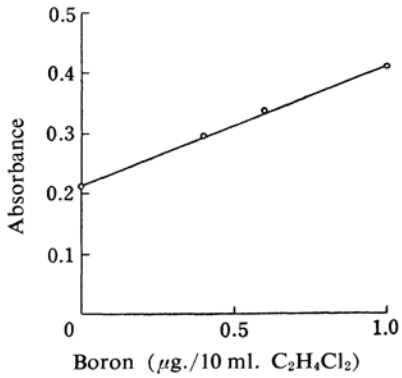

Fig. 3. Calibration curve for 1 p.p.b. order.

the 1 p.p.b. order, which obeys Beer's law. The analytical method herein used was sensitive, but the curve was less reproducible, and all the curves in the repeated experiments slightly varied parallel with one another from day to day. The lesser reproducibility appeared to be due to the slight variation in contamination involved. The respective calibration curve, therefore, was prepared in every experiment.

Table I reports on the recovery of the boron from the standard solution in silicon tetrachloride (100 ml. of 0.009 μg./ml.) by the vacuum

TABLE I. RECOVERY OF THE BORON OF 1 p.p.b. ORDER*

No.	A from pure $SiCl_4$ μg.	B from boron soln. μg.	(A-B) μg.	Recovery %
1	0.08	1.86	1.78	
2	0.14	1.07	0.93	
3	0.05	0.58	0.53	
4	0.17	0.93	0.76	
5	0.25	1.78	1.53	
Mean	0.14	1.2	1.1	1.2×100

* The recovery from the standard silicon tetrachloride soln. (100 ml. of 0.009 μg./ml.) with the amide (0.1 g.).

distillation carried out immediate after the addition of the amide (0.1 g.). Every numerical value given in the table varied, with some error, but the effects of the amide were apparent, and the amount of amide required was less than could be estimated by the equilibrium constant reported previously.[7]

The effects of the reaction factors were also studied, but similar results were obtained within the range of experimental error. For the purification, however, the stirring with amide, followed by the distillation, appeared to be more favorable, as could be expected by analogy with the results obtained with the solution of boron of the 1 p.p.m. order.

Summary

A standard solution of boron in silicon tetrachloride (1 p.p.m. or 1 p.p.b. order) has been distilled in the presence of *N*, *N*-diphenylacetamide. The residue of the distillation has been analyzed for boron by the spectrophotometric measurement of the methylene blue complex of boron tetrafluoride ions. The boron of an order of 1 p.p.m. has been about 100% recovered when the solution in silicon tetrachloride has been distilled after being stirred for 24 hr. with the amide. The recovery of the boron of an order of 1 p.p.b. has also been satisfactory. The silicon tetrachloride distilled off in the presence of the amide, therefore, believed to be almost free of boron.

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Government Chemical Industrial Research Institute, Tokyo
Shibuya-ku, Tokyo