Siloxene as a Chemiluminescent Indicator in Titration

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The indicator described emits light in the presence of an oxidant. When a minute excess of oxidant is added beyond the stoichiometric point, the entire liquid emits light. This is taken as the end point. Highly colored components such as cobaltous ion do not interfere in the titration of ferrous ion with ceric sulfate solution.

OHLER in 1863 treated calcium silicide with concentrated hydrochloric acid and obtained a yellow, insoluble product which he called "silicone" (13). The silicone consisted of bright, orange-yellow leaflets, insoluble in all inert solvents, and pseudomorphic with the calcium silicide. On heating in air it burst into flame. On heating, while enclosed, it evolved hydrogen and silicon hydrides. If prepared with more dilute hydrochloric acid, it was lighter in color. In sunlight it bleached. Under water, in sunlight, it evolved a steady stream of bubbles of hydrogen and was oxidized to a white product which Wöhler called "leucone." Since Wöhler, several investigators have attempted to elucidate the structure of the various silicon derivatives involved (12), but most of our knowledge of their structures is due to Kautsky (3, 4).

NOMENCLATURE

The name "silicone," unfortunately, is the same as that now universally applied to the technically important, polymeric $R_2Si=0$ compounds (R = organic radical or hydrogen) as given by Kipping (11).

The silicones of Wöhler and Kautsky, which are the ones discussed in this paper, contain covalent silicon-silicon bonds in rings of six silicon atoms, also silicon-oxygen, silicon-chlorine, and silicon-hydrogen bonds, and no organic constituents, whereas the industrial silicones contain no silicon-silicon bonds, but do contain silicon-carbon bonds as well as silicon-oxygen bonds. Wöhler's silicone, which is used in this research as an indicator is referred to here as siloxene indicator,

SILOXENE INDICATOR

Structure and Reactions. According to Kautsky (3, 4) a solid, yellow "silicone" consists of thin sheets of atoms, one molecule

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thick. These sheets are stacked one upon the other to form a solid pseudocrystal pseudomorphic with the original calcium silicide crystal. Actually, there is sufficient space between the sheets to allow a reagent solution to penetrate almost instantly from their edges toward their centers. The looseness, or interlamellar distance of the sheets, varies with methods of preparation, a propyl alcohol preparation giving considerable distance. and the method described herein making them rather tightly bound (6). Throughout most reactions of substitution, hydrolysis, and oxidation the lamellar structure remains the same. the dimensions and shape of the crystal altering little. The silicon atoms are arranged in hexagons which are all connected in one network plane, forming one lamella. Each hexagon is bridged to an adjacent one by oxygen atoms (4, 7). The plane is probably folded periodically along its surface to accommodate oxygen atoms. The reactive groups-e.g., hydroxyl, chlorine, or hydrogen—are on both sides of this plane (1, 4). Wöhler's silicone is not a compound having a definite chemical composition, but is a variable mixture of siloxene, polyhydroxysiloxenes, polychlorosiloxenes, and various oxidized siloxenes in which oxygen atoms have been inserted between silicon atoms of silicon 6-rings previously joined with silicon-silicon bonds. Figure 1 shows siloxene, chlorosiloxene, hydroxysiloxene, and an oxidized siloxene.

Siloxene is the first product formed by the interaction of calcium silicide and hydrochloric acid (4, 5). The reaction for a single lamella (4) is:

 $6n \mathrm{H}^{+} + 3n \mathrm{CaSi}_{2} + 3n \mathrm{H}_{2}\mathrm{O} \longrightarrow (\mathrm{Si}_{6}\mathrm{H}_{6}\mathrm{O}_{3})_{n} + 3n \mathrm{H}_{2} + 3n \mathrm{Ca}^{++}$ (Siloxene)

Kautsky states that unless the acid is diluted with much alcohol, and the reaction is carried out over a period of many hours, at





b

a. Siloxene (colorless, weakly fluorescent). Three identical six-membered rings are drawn in two different ways. The open circles indicate oxygen atoms (4, 7). The small cross-hatched circles in rings II and III indicate silicon atoms (4, 7), which are in a plane probably at least 1A, above the plane of the silicon atoms represented by the small black circles (4, 7). The hydrogen atoms (4, 7). Which are in a plane probably at least 1A, above the plane of the silicon atoms represented by the small black circles (4, 7). The hydrogen atoms are omitted in rings II and III. In ring I three of the hydrogens are above and three are below the silicon atoms (4).
b. c. chorosiloxene [colored, fluorescent (8), chemiluminescent]
c. Hydroxysiloxene [colored, fluorescent, chemiluminescent) (8)]. Several additional hydroxy groups increase the color and the fluorescence.
d. Oxidized hydroxysiloxene (colorless, nonfluorescent). After complete oxidation there is no Si—Si bond. Silicic acid is the final product (4, 10).

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the solid crystal. Kautsky has estimated (6) that 100 mg. of siloxene have a reactive surface of about 2736 square feet. The hydrogens in it are replaceable analogously to the hydrogens in benzene.

The silicon 6-ring is a chromophore and a luminophore (4). The colors of the silicones depend upon the number and extent of substitution of the hydroxysiloxene rings present. The pure hydroxysiloxenes have the following colors: $Si_{6}H_{6}O_{3}$ (colorless), $Si_6H_5O_3(OH)$ (yellow), $Si_6H_4O_3(OH)_2$ (brown-red), $Si_6H_3O_3(OH)_3$ (red), $\rm Si_6H_2O_3(OH)_4$ (brown-violet), and $\rm Si_6O_3(OH)_6$ (black). Kautsky states (4, 9, 10) that the colors, fluorescences, and chemiluminescences of the silicones depend on the number and extent of substitution of the hydroxysiloxene rings present, and that these properties are more pronounced for silicone than for a pure specimen of an individual hydroxysiloxene. He states further that silicones possibly contain small areas of hydroxysiloxenes surrounded by oxidized siloxenes and that these hydroxysiloxene areas function as chemiluminescence centers when energy reaches them as a result of oxidation of another part of the silicone network. The energy for the activation of the chemiluminescence centers can be supplied by treating a suspension of silicone in dilute acid with strong oxidizing agents such as chromic acid, potassium permanganate, nitric acid, ceric solutions, and per compounds.

The "oxidation-potential" required for light emission of silicone has not heretofore been determined, but should be rather high, as strong oxidizing agents are required. The oxidation reaction appears to be strictly nonreversible; once oxidized, the reduced forms cannot be regenerated.

Preparation. "Siloxene indicator" is the name applied in this research to Wöhler's silicone. Its preparation is extremely simple.

Calcium silicide (Eimer & Amend, technical grade) was well powdered with a mortar and pestle. Five grams of this powder were placed in an 800-ml. beaker in a hood. The room was not darkened. Concentrated hydrochloric acid (50 ml.) was added and the mixture was agitated and stirred for several minutes with a long stirring rod. A vigorous reaction gradually developed, with spontaneous heating, foaming, and evolution of much hydrogen chloride vapor. After it subsided, 25 ml. more of concentrated hydrochloric acid were added, and the mixture was boiled gently and stirred for 5 minutes. Then 150 ml. of water were added, and it was boiled 5 minutes longer. The suspension of yellow silicone was decanted from any gray, unreacted calcium silicide onto a Büchner filter funnel. It was washed on the filter with water, then with 95% ethyl alcohol, and finally with ether. The yellow product was spread out on a porous plate to dry, and stored in a brown bottle.

It is stable for only a few days when dry, but for a longer time if kept under dilute hydrochloric acid. If prepared by this method, the material obtained is neither spontaneously flammable nor explosive. The time required for preparation of 5 grams of indicator was 20 minutes.

Use and Advantages. There are many situations in the field of analytical chemistry in which a titration cannot be made because the color of the solution makes it impossible to observe the color change of any indicator which might be selected. The authors have demonstrated that in such situations chemiluminescence can be used to locate the end point. Several types of titration are possible.

One situation in which the chemiluminescent siloxene indicator can be used to advantage is the oxidimetric titration of solutions, the color of which would interfere with the detection of the end point of any of the known redox indicators or with the end point of potassium permanganate.

When a very slight excess of oxidant is present in the solution being titrated, light is emitted by the indicator. If the excess is merely local, a momentary bright spot is produced in the solution. A minute excess of oxidant beyond the stoichiometric point will cause the entire solution to emit light. When the titrations are carried out in the dark, the end point is taken as the point at which the outline of the entire liquid is visible. For the research in hand the amount of siloxene indicator used in each titration was approximately 100 mg. Titrations employing different amounts of indicator showed that variations of several milligrams had little or no effect upon the end point. The effect on the end point of extremely small or extremely large amounts of indicator is being investigated and will be reported later.

A desirable feature of siloxene indicator is its prompt reaction to excess of oxidant. Consequently, no indicator catalyst is required.

EXPERIMENTAL

Use of Siloxene Indicator in the Titration of Ferrous Ion with Ceric Sulfate Solution. Approximately 0.1 M solutions of ferrous ammonium sulfate and ceric sulfate were prepared and were compared by titrating 25.00-ml. portions of the ferrous solution with the ceric sulfate. A vacuum tube potentiometer of the type described by Garman and Droz (2) was used to locate the end point. The meter readings could be made to within 2 mv. on a scale which had been carefully calibrated against a series of potentials measured with a Leeds & Northrup 7660-A vacuum tube potentiometer. A saturated calomel reference electrode and a gold indicator electrode were used. The cell temperature was not controlled thermostatically. The maximum variation of the laboratory temperature, however, was about 2°, which corresponds to a variation of about 2 mv.



Figure 2. Titration Curves Used in Locating Stoichiometric Point



Figure 3. Average Curve Showing Range of End Points without Cobalt and with Cobalt Using Siloxene

in the voltage of the cell. The darkroom in which the titration was carried out was equipped with a convenient light which could be turned on or off as the occasion demanded.

The results of eight titrations of the ferrous solution with the ceric solution are given in Figure 2.

Because the curve for the reaction

$$Fe^{++} + Ce^{++++} \rightarrow Fe^{+++} + Ce^{+++}$$

is symmetrical with respect to the stoichiometric point, the midpoint of the nearly vertical portion of each curve was taken as the end point. The results of this graphical method are given in Table I, together with the corresponding potentiometer readings and oxidation potentials. The latter are referred to the normal hydrogen electrode.

With respect to the buret readings, the average deviation of a single observation was thus 0.01 ml., which for the case in hand yields a precision of 0.50 part per 1000.

The mean end point potential of 1087 mv. agrees fairly well with theoretically calculated values and with the results of numerous experimenters.

Because the jump in potential near the stoichiometric point is

| Table I. | Volume of Mi. | Ceric Sol of Ferrous | ution Eq Solution | uivalent 1 | to 25.00 |
|--|---|---|--|--|---|
| | (At 30° ± 2° | C. and corre | sponding p | otentials) | |
| Titration | Ceric Solution | Deviation from Mean | Potential Difference | Oxidation Potential | Deviation from Mean |
| | Ml. | Ml. | Mv. | Mv. | Mv. |
| S1 S2 S3 S56 S56 S7 S8 | $\begin{array}{c} 26.47\\ 26.48\\ 26.48\\ 26.48\\ 26.48\\ 26.48\\ 26.48\\ 26.48\\ 26.48\\ 26.48\\ 26.43\end{array}$ | $\begin{array}{c} 0 & 01 \\ 0 & 00 \\ 0 & 00 \\ 0 & 03 \\ 0 & 00 \\ 0 & 00 \\ 0 & 00 \\ 0 & 00 \\ 0 & 05 \end{array}$ | 886 845 833 832 834 834 834 851 | $1128\\1087\\1087\\1075\\1074\\1076\\1076\\1093$ | $ \begin{array}{c} 41 \\ 0 \\ 12 \\ 13 \\ 11 \\ 11 \\ 6 \end{array} $ |
| Mean | 26.48 | 0.01 | 845 | 1087 | 12 |

Table II. Volume of Ceric Solution Equivalent to 25.00 Ml. of Ferrous Solution

(Siloxene indicator at $30^\circ \pm 2^\circ$ C. and corresponding potentials)

| Titration | Ceric Solution Ml. | Deviation from Mean <i>Ml</i> . | Potenti- ometer Reading Mv. | Oxidation Potential Mv. | Deviation from Mean Mv. |
|-----------|--------------------------|---------------------------------------|--------------------------------------|-------------------------------|-------------------------------|
| 1 | 26,50 | 0.02 | 980 | 1222 | 41 |
| 2 | 26.50 | 0.02 | 850 | 1092 | 71 |
| 3 | 26.55 | 0.03 | 920 | 1162 | 1 |
| 4 | 26.55 | 0.03 | 925 | 1167 | 4 |
| 5 | 26.50 | 0.02 | 970 | 1212 | 49 |
| 6 | 26.50 | 0.02 | 955 | 1197 | 34 |
| 7 | 26.45 | 0.07 | 920 | 1162 | 1 |
| 8 | 26.56 | 0.04 | 920 | 1162 | 1 |
| 9 | 26.55 | 0.03 | 950 | 1192 | 27 |
| Mean | 26.52 | 0.03 | 932 | 1174 | 25 |

about 30 mv. per 0.02 ml. of ceric solution, the precision of the potential measurements in this region is not high. This, of course, can be improved by control of temperature and by the use of a microburet.

From the results shown in Table I, the average curve shown in Figure 3 was plotted. In order to test the performance of siloxene indicator in the titration of ferrous ion with ceric ion, eighteen 25.00-ml. portions of ferrous solution were titrated. In each case the end point was determined in the dark, the indicator being added in a lighted room about 2 ml. prior to the end point.

In order to test the effectiveness of the indicator in the presence of a highly colored solution, half of the titrations were of the ferrous solution alone and half were of the same ferrous solution to which 5 ml. of 0.5 M cobaltous nitrate solution had been added. These solutions were approximately 0.10 M with respect to cobaltous ion and at the end point they were approximately 0.05 M. The depth of color due to cobalt at the end point was decidedly more pronounced than the usual permanganate end point and sufficiently deep to prevent the use of permanganate or the use of the common redox indicators. The concentration of cobaltous ion employed was purely arbitrary and is not to be construed as the upper limit of concentration permissible. Work is in progress to determine this upper limit, if any, and also to determine the application of chemiluminescent indicators to other titrations involving the presence of various colored components.

The results of the titrations of the ferrous solutions containing no cobalt are shown in Table II and those of the solution containing cobalt are shown in Table III. The potentiometer readings and corresponding oxidation potentials are given for each titration. The intensity of the light emitted at the end point did not seem to be materially affected by the presence of the cobalt. To test a more extreme case of interference with light emission, a titration was carried out on a ferrous solution containing 10 ml. of India ink. A satisfactory end point was obtained in this solution.

The limits between which the end points lie for ferrous solutions that contain cobalt and for those that do not contain cobalt are shown in Figure 3.

With respect to the buret readings of Table II, the average deviation of a single observation was thus 0.03 ml., which for the case in hand yields a precision of 1.1 parts per 1000. The indicator

| Table III. | Volume of Ceric Solution Equivalent to 25.00 |
|------------|--|
| | Ml. of Ferrous Solution |

(5 ml. of 0.5 M cobaltous nitrate added, using siloxene indicator at $30^\circ = 2^\circ$ C, and corresponding potentials)

| Titration | Ceric Solution Ml. | Deviation from Mean Ml. | Potenti- ometer Reading Mv. | Oxidation Potential Mv. | Deviation from Mean Mv. |
|-----------|--------------------------|-------------------------------|--------------------------------------|-------------------------------|-------------------------------|
| 10 | 26.60 | 0.05 | 895 | 1137 | 36 |
| 11 | 26.55 | 0.00 | 940 | 1182 | - 9 |
| 12 | 26.56 | 0.01 | 970 | 1212 | 39 |
| 13 | 26.55 | 0.00 | 935 | 1177 | 4 |
| 14 | 26.60 | 0.05 | 965 | 1207 | 34 |
| 15 | 26.54 | 0.01 | 960 | 1202 | 29 |
| 16 | 26.50 | 0.05 | 910 | 1152 | 21 |
| 17 | 26.55 | 0.00 | 940 | 1182 | 3 |
| 18 | 26.55 | 0.00 | 860 | 1102 | 71 |
| Mean | 26.55 | 0.02 | 931 | 1173 | 27 |

error—namely, 26.52 - 26.48 or 0.04 ml.—corresponded to less than 1 drop from the buret, and for the case in hand amounts to 1.5 parts per 1000.

The potential at which the indicator emits enough light to give the end point appears to be about 87 mv. higher than the stoichiometric potential.

In the titrations of Table II and in all subsequent titrations the volume of solution at the end point was approximately 55 to 60 ml.

With respect to the buret readings of Table III, the average deviation of a single observation was thus 0.02 ml., which for the case in hand yields a precision of 0.75 part per 1000. The indicator error is 26.55 - 26.48 or 0.07 ml., 0.03 ml. more than in the absence of cobalt. The end-point potential appears to be about 86 mv. above the stoichiometric potential.

Table IV. Volume of Ceric Solution Equivalent to 25.00 Ml. of Ferrous Solution

| (Siloxene indicator added prio | r to titration | and at 2 ml. | before end point) |
|--------------------------------|----------------|--------------|-------------------|
|--------------------------------|----------------|--------------|-------------------|

| | Prior Addition of Indicator | | | Indicator Added 2 Ml. before End Point | | |
|---|----------------------------------|--|---|---|---|--|
| Titration | Time of ex- posure Min. | Ceric solution Ml. | Dev. from mean Ml. | Time of ex- posure Min. | Ceric solution <i>Ml</i> . | Dev. from mean Ml. |
| 1 2 3 4 5 6 7 8 9 10 | 4656585856 | $\begin{array}{c} 27.05\\ 27.10\\ 27.05\\ 26.98\\ 26.94\\ 27.03\\ 27.01\\ 27.00\\ 26.95\\ 27.06\\ \end{array}$ | $\begin{array}{c} 0.03 \\ 0.08 \\ 0.03 \\ 0.04 \\ 0.08 \\ 0.01 \\ 0.01 \\ 0.02 \\ 0.07 \\ 0.04 \end{array}$ | 3343232372 | $\begin{array}{c} 27.00\\ 27.05\\ 27.02\\ 27.02\\ 27.02\\ 26.98\\ 26.97\\ 26.98\\ 26.96\\ 27.00\end{array}$ | $\begin{array}{c} 0.00\\ 0.05\\ 0.02\\ 0.02\\ 0.00\\ 0.02\\ 0.03\\ 0.02\\ 0.03\\ 0.02\\ 0.04\\ 0.00\\ \end{array}$ |
| Mean | 6 | 27.02 | 0,04 | 3 | 27.00 | 0.02 |

If the results of Table III and Table IV are combined, the eighteen samples yield an average deviation of 0.02 ml., an end point of 26.54 ml. of ceric solution, an indicator error of 0.05 ml., and an accuracy of 1.9 parts per 1000. With samples requiring 40.00 ml. of ceric solution instead of 26.54 ml. the accuracy would be 1.3 parts per 1000. If, of course, the indicator error was applied as a correction, a decidedly higher degree of accuracy would be obtainable. In many instances it would be possible to use siloxene indicator in the standardization of the ceric solution and thereby eliminate most or all of the indicator error. The potential required to give the light at the end point is approximately 86 mv. above the stoichiometric potential. The oxidation potential at the end point appears to be about 1173 mv.

In order to determine what effect, if any, is produced on the end point by adding the indicator at the beginning of the titration instead of at a point 2 ml. prior to the end point, ten titrations of each sort were carried out on 25.00-ml. portions of a ferrous solution. The time of exposure of the indicator to the solution was noted in each case (Table IV).

ANALYTICAL CHEMISTRY

In Table IV it is seen that exposure of the indicator to the solution throughout the entire titration increased the time of exposure by about 3 minutes but had little or no effect on the end point.

A determination was made of the pH of the iron solution at the end point of the indicator, as well as the pH of a suspension of the indicator in 50 ml. of distilled water. These measurements, made with a glass electrode and a Leeds & Northrup 7660-A vacuum tube potentiometer, yielded 0.23 for the pH of the former and 3.59 for the pH of the latter The pH at the end point of the iron solution would, of course, vary with the acidity of the ferrous and ceric solutions and the volumes of each used. Attempts by the authors to obtain satisfactory light emission of siloxene indicator in neutral or basic solutions have failed. Experiments to determine the minimum acidity necessary are in progress and will be reported on later. However, preliminary results indicate that the value is in the neighborhood of pH 2.

The decidedly acid pH of the suspension of siloxene indicator in distilled water probably results from the presence of residual hydrochloric acid in the indicator as well as hydrolysis of the chlorosiloxenes present.

A direct determination of the indicator correction was carried out by preparing a solution of sulfuric acid having the same pH as that of the end point solution—namely, 0.23—by diluting 5.8 ml. of 18 *M* sulfuric acid to 250 ml. One hundred milligrams of indicator were added to 50-ml. portions of the solution and titrated with ceric solution from a microburet, the readings of which could be estimated to 0.001 ml. Half of the solutions tested were also 0.05 *M* with respect to cobaltous ion, whereas the other half contained no cobalt. The results are shown in Table V.

In Table II the indicator correction was shown to be 0.04 ml. for solutions containing no cobalt, which is substantially the same as the directly measured value of 0.035 ml. given in Table V.

In Table III the indicator correction was shown to be 0.03 ml. more in a solution which is 0.05 M with respect to cobaltous ion than in a solution containing no cobalt. Thus, the total correction is seen to be 0.07 ml. This is substantially the same as the directly measured value of 0.068 ml. shown in Table V.

SUMMARY

This paper describes a new method of titration which employs a chemiluminescent material as indicator. When siloxene indicator is used in titrating ferrous ion, a precision of 0.02 ml. is obtained which corresponds to 0.75 part per 1000.

An indicator error of 0.04 ml. was determined for solutions containing no cobalt. Without the use of this correction, iron was titrated with an accuracy of 1.5 parts per 1000. This would correspond with an accuracy of 1.0 part per 1000 if sufficient ferrous solution were taken to require 40.00 ml. of ceric solution. By applying the indicator correction or by using siloxene indicator in standardizing the ceric solution, a more accurate result could be obtained.

The presence at the end point of 0.05 M cobaltous solution increased the end point by only 0.03 ml. and had little effect on the end point potential.

Table V. Direct Determination of Indicator Correction with Ceric Solution

(On 100-mg. portions of indicator in sulfuric acid solutions having end point pH, with and without 0.05~M cobaltous ion)

| | Ceric S | Ceric Solution Used | | | |
|---------------|--------------------------------------|---|--|--|--|
| Titration | Sclutions containing no cobalt | Solutions containing 0.05 M cobaltous ion | | | |
| | 112 14 | | | | |
| $\frac{1}{2}$ | 0.035 | 0.071 | | | |
| 3 | 0.038 | 0.067 | | | |
| 5 | 0.030 | 0.060 | | | |
| Mean | 0.035 | 0.068 | | | |

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No indicator catalyst is required

Potential measurements in the vicinity of the stoichiometric point yielded an oxidation potential at the end point of $1173 \pm$ 26 my., referred to the normal hydrogen electrode.

The siloxene indicator, to function properly, must be used in acid solution.

Methods described may be applicable to many determinations involving the presence of a highly colored or opaque component.

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Determination of Boron in Magnesite and Fused Magnesia

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A method for the determination of boron in magnesite and fused magnesia is described. The method is direct, requires very little time, and is subject to no interference from the usual impurities found in magnesite. Data are presented showing the accuracy and precision obtainable. The method entails the solution of the sample in hydrochloric acid under

AGNESITE from some foreign deposits, especially India, VL contains only a few parts per million of boron. Mugnesite from some domestic deposits contains boron, and magnesites produced from the extraction and calcination of magnesium hydroxide from sea water contain very appreciable amounts of boron.

The increased use of high grade periclase for the embedding medium of resistor elements in hot plates, immersion heaters, stove units, etc., has resulted in an investigation of the various factors affecting the conductivity of this embedding medium. It has been found that the presence of even small amounts of boron is detrimental to periclase used for this purpose.

The presence of boron in the periclase gives a marked increase in the slope of the curve of resistance versus temperature at the higher temperatures of operation. At low temperatures the effect is not so great. The change of the slope of this curve means that as the amount of boron increases, the conductivity of the periclase becomes greater. It actually becomes dangerous and undesirable as an insulator material, especially when used in household appliances. When boron is present in this material it also has a tendency to glaze over the individual grains, causing sintering of the insulating medium. During sintering the resistor itself is attacked, resulting in early failure of the element.

Because many of the available magnesites contain appreciable boron, it has been necessary to develop an accurate and reliable method for determining boron in all concentrations in incoming magnesite, and in all the resultant fusions of this material.

In the authors' laboratory, it has been the practice to determine the boron content of these products by spectrographic methods when the concentrations are low, and by wet chemical methods when the boron is high. Boron determinations up to 1000 p.p.m. (0.10% boron) are carried out spectrographically by a method developed in the laboratory, which is intended for publication at a later date.

a reflux condenser, and precipitation of the iron, titanium, calcium, and magnesium with sodium carbonate and sodium hydroxide. The solution containing the precipitate is made up to a definite volume and filtered, and an aliquot is taken for the boron titration. This is made with 0.1 N sodium hydroxide after the addition of mannitol.

An accurate determination of boron is not a simple test for the analyst. Many methods have been proposed (1, 2, 6, 8), but most are subject to long tedious separations in which boron is lost, to high blanks from the reagents used, and to volatility of the boric acid in aqueous and acid solutions. The classical method of Chapin (2) is perhaps the most widely used procedure, but the high unreliable blanks obtained by this method make the determination of small amounts of boron exceedingly difficult and unreliable. These high blanks are occasioned, no doubt, by the fact that the calcium chloride, which is used as a dehydrating agent before the distillation of the boric acid as methyl borate, contains appreciable amounts of boron. The large amount of the dehydrating agent necessary makes this method rather inaccurate, especially for smaller amounts of boron.

Many thousands of boron analyses have been made in this laboratory on all types of materials including elemental boron. The authors have consistently tried to develop fast, accurate, and dependable methods for boron. From their experience in this type of work, the method here described has been worked out. They feel that it satisfies all the above requirements for the determination of boron in magnesite and fused magnesia products.

EXPERIMENTAL

A sample of very high grade India magnesite was selected as e starting material. . his sample contained less than 0.5 the starting material. p.p.m. of boron by spectrographic analysis, and was a part of the magnesite from which spectrographic standards are prepared. Besides the boron, the material contained as impurities about 1.50% silica, 0.06% ferric oxide, 1.70% calcium oxide, and traces of minor constituents such as alumina, titania, manganese oxide, sodium oxide, and sulfate. This material, because of its negligible boron content and the noninterference of the other constituents, made an excellent starting material for preliminary study.

A standard solution of boric acid was made from recrystallized T. Baker's reagent grade boric acid. Chemical analysis