Microcolorimetric Determination of Sulfate by Reduction to Hydrogen Sulfide with Tin(II)—Strong Phosphoric Acid

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In a previous paper[1] from the authors' laboratory it was shown that both soluble and insoluble sulfates could be quantitatively reduced to hydrogen sulfide by heating with tin(II)-strong phosphoric acid, a new powerful and stable reducing agent first described by the authors. The discovery of this reagent led the authors to the development of a new rapid and simple method for the determination of semimicro quantities of sulfate sulfur. The established method[1] consists of the following three succesive steps: (a) reduction of sulfate to hydrogen sulfide by tin(II)-strong phosphoric acid, (b) absorption of the hydrogen sulfide by zinc acetate solution, (c) iodometric titration of the resulting zinc sulfide by ordinary procedures.

The present report concerns a later investigation in which the above method has been extended to the microgram scale by adopting the sensitive methylene blue method for sulfides[2]. The rapidity and simplicity of the original method are still retained in this new colorimetric procedure, by which 1 to 35 micrograms of sulfate sulfur can be estimated.

Apparatus

Reduction and Absorption Apparatus.—The apparatus for the reduction of the sulfate and the absorption of the hydrogen sulfide evolved is shown in Fig. 1. The reaction vessel (A) is of fused silica. Unexpectedly high values of sulfur were occasionally obtained when glass vessels were used, probably owing to minute amounts of sulfur in the glass. A bent glass tube (F) is attached to the outlet arm of the reaction vessel with a short piece of rubber tubing (G). A detachable delivery tube (D) is connected with another rubber tubing to the bent tube (F) and inserted into the absorbing vessel (C). Since zinc sulfide adheres to that part of the tube immersed in the solution, it must be disconnected and allowed to remain in the absorbing vessel during the development of the methylene blue color. A Kipp's apparatus is employed for the production of carbon dioxide, which is purified by six-washing bottles (not shown in Fig. 1.) and introduced into the reaction vessel through the inlet arm. Solutions used for the purification of carbon dioxide are described below.

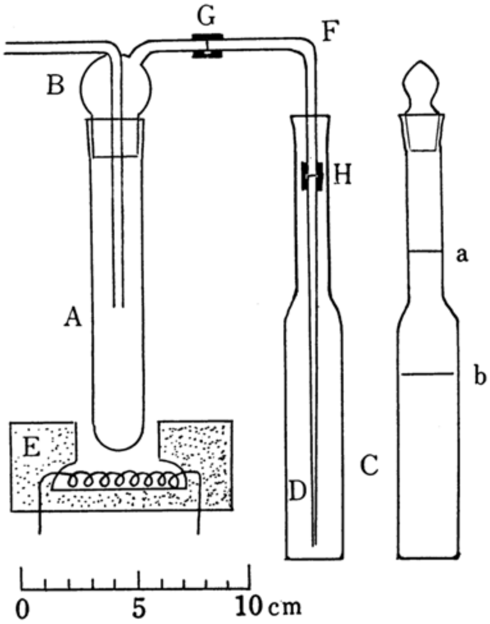

Fig. 1. Apparatus for reduction and absorption.
A: Reaction vessel of fused silica
B: Glass cap fitted to the reaction vessel
C: Absorbing vessel a: the mark of 50 ml.
b: the mark of 35 ml.
D: Detachable delivery tube (4 mm. in outside diameter)
E: Electric heater
F: Gas leading tube
G, H: Short pieces of rubber tubing

Photoelectric Colorimeter. — A "Hirama" photoelectric colorimeter with 1 cm. cells and a filter 655 mμ were used throughout this work.

Reagents

Tin(II)-Strong Phosphoric Acid.—Prepare from 250 g. of strong phosphoric acid and 50 g. of tin(II) chloride dihydrate of extra pure grade as described in the previous paper[1].

Carbon Dioxide.—Purify carbon dioxide produced in the Kipp's apparatus by passing through five gas-washing bottles containing respectively

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[1] T. Kiba et al., This Bulletin, **28**, 641 (1955).

[2] J. F. Fogo and M. Popowsky, *Anal. Chem.*, **21**, 732 (1949).

[3] S. Nakayama, *J. Chem. Soc. Japan*, **47**, 197 (1926).

water, 1% potassium permanganate in 10% sodium carbonate solution, vanadium (II) sulfate in sulfuric acid, 5% barium chloride, and zinc acetate absorbing solution. Place a sixth, empty bottle to equalize the flow of the gas and to intercept mist. The vanadium (II) sulfate solution is employed to remove oxygen completely from the carbon dioxide. To prepare it, dissolve 2 g. of ammonium vanadate in 200 ml. of water, add 20 ml. of 6 N sulfuric acid, and shake vigorously with 3% zinc amalgam in an atmosphere of carbon dioxide until the violet color of vanadium (II) appears. Transfer the solution quickly into a gas-washing bottle containing a small amount of the amalgam.

Zinc Acetate Absorbing Solution.— Dissolve 20 g. of zinc acetate dihydrate of extra pure grade in 1 l. of redistilled water. If necessary, add two or three drops of glacial acetic acid to clarify the solution, but the pH of the solution should not be below 5. The redistilled water is prepared by distilling ordinary distilled water with a small amount of sodium hydroxide in an all-glass still.

***p*-Amino Dimethyl Aniline Solution.**—Dissolve 1.4 g. of *p*-amino dimethyl aniline sulfate crystals of pure grade in 200 ml. of 1:1 sulfuric acid.

Ferric Chloride Solution.—Dissolve 10 g. of ferric chloride hexahydrate in 100 ml. of distilled water.

Standard Sulfate Solution.—Dissolve 4.4299 g. of anhydrous sodium sulfate of extra pure grade in 1 l. of sulfur-free water. Take 20 ml. of this solution with a pipet and dilute it to 1 l., so that the final solution contains 20 micrograms of sulfur in 1 ml. Pipet accurately required amounts of this stock solution for the analysis.

Barium Chloride Solution. — Dissolve 1 g. of barium chloride dihydrate in 100 ml. of sulfur-free water, and use 0.5 ml. of this solution in each test.

Procedure

When the sample is a solution, pipet accurately an aliquot containing 1 to 35 micrograms of sulfur. When it is a solid, take an accurately weighed quantity containing the same range of sulfur. Put the measured sample into the reaction vessel (A) (Fig. 1.), add 0.5 ml. of the barium chloride solution to fix the sulfate as barium sulfate, and evaporate the content to dryness at the bottom of the vessel. Pour 5 ml. of tin (II)-strong phosphoric acid over the dried residue from a pipet. Fill the absorbing vessel up to the 35 ml. mark with the zinc acetate solution. Connect all the apparatus as shown in Fig. 1. Pass carbon dioxide very rapidly through the apparatus for five minutes. The passage of the gas should be rapid enough to cause strong agitation of the surface of the liquid in the absorbing vessel, and the end of the gas delivery tube should reach to the bottom of the vessel. After five minutes, reduce the flow of the gas to a rate of one bubble per second. Heat the bottom of the reaction vessel on a small etectric heater, which is regulated by a variable transformer, until white fumes of phosphoric acid appear. Continue the heating for about fifteen minutes. It is unnecessary to keep the reaction temperature strictly constant, but it should be high enough to ensure that the mixture exhibits a white turbidity near the end of the reaction. Stop the heating and continue to pass carbon dioxide for about five minutes.

Remove the absorbing vessel, leaving the gas delivery tube in it. Stopper the vessel and place it in a thermostat kept at 24°C for several minutes. Add quickly 1.5 ml. of *p*-amino dimethyl aniline solution using a rapid delivery pipet, stopper the vessel, shake it vigorously, and then quickly add 0.5 ml. of the ferric chloride solution. Stopper and shake the vessel again. After keeping the vessel in the thermostat at 24°C for fifteen minutes, add more distilled water till the liquid reaches the 50 ml. mark, while the delivery tube is hung up from the solution with washing. Stopper and shake the vessel so as to make the solution homogeneous. Read the absorbancy of the solution in the colorimeter at 655 mμ within thirty minutes.

Results and Discussion

Standard Sulfate Calibration Curve.— As shown in Fig. 2, the linear relationship was obtained between the amount of sulfate and the absorbancy of the resulting methylene blue solutions in the range 1 to 35 micrograms of sulfur. Measurements were made in 1-cm. cells at 655 mμ, using

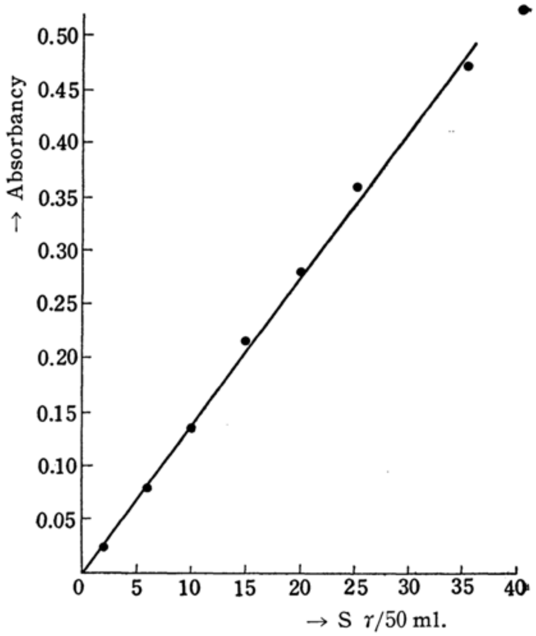

Fig. 2. Standard sulfate calibration curve.

a mixture of the absorbing solution and the reagent of the same amounts as reference. For more than 40 micrograms of sulfur the linearity is not held, because of mutual interaction of the light-absorbing molecules or of spectral purity of the instrument. According to the authors' experience, the main sources of error in this method seemed to be imperfect removal of oxygen from the carbon dioxide and careless delay in adding the reagents, viz., *p*-amino dimethyl aniline and ferric chloride.

A comparison of the standard curve with that drawn for sodium sulfide by direct coloration with *p*-amino dimethyl aniline, indicated that the two curves coincided with each other satisfactorily. Both curves could be expressed by the equation, $x=a+by$, where x is the absorbancy measured and y the amount of sulfur in micrograms. The average values of a and b computed from the sulfate curves were 0.00614 and 0.01084, respectively, whereas those obtained from the sulfide curves were 0.00245 and 0.01087, respectively. These numerical values were calculated by the method of the least square. It may be concluded from this fact that the sulfate was completely reduced to hydrogen sulfide under the given condition.

Interferences and their Elimination.—The effect of chloride was examined by the addition of various amounts of sodium chloride to sodium sulfate solutions, containing 1 to 35 micrograms of sulfur through the standard procedure. It was found that, when the amount of the sulfate sulfur was less than 20 micrograms, the presence of as much as 36.9 mg. of the chloride ion does not interfere with the determination. When the amount of coexisting chloride ions was decreased to 12 mg., the linearity of the curve was recovered for a wider range of sulfur, i. e., from 1 to 35 micrograms.

The presence of nitrate in the sample, on the other hand, was found to result in apparently low values for sulfate sulfur.

As the sulfate ion is customarily separated from other anions with barium chloride, the effect of the barium ion was examined. By the addition of 1 ml. of 1% barium chloride solution to sodium sulfate solutions containing 1 to 40 micrograms of sulfur, the determination of sulfate sulfur was carried out. Although in this case a large excess of the barium ion was always present, it did not bring about any deviation from the linear relationship as shown in the standard sulfate sulfur curve. The experiment conclusively showed that the barium ion does not affect the accuracy of the method.

The collector action of ferric hydroxide may have great importance in analytical procedures, particularly in a micro analysis. Minute amounts of the sulfate ion, coexisting with other interfering soluble ions, may also be separated by centrifugation or filtration as barium sulfate, which is occluded in the ferric hydroxide precipitate. So the effect of the ferric ion was examined as follows. To sodium sulfate solution containing 1 to 40 micrograms of sulfur were added 0.5 ml. of 1% solution of barium chloride and 3.35, 5.58, and 11.17 mg. of ferric ion as iron(III) chloride, respectively. After the drying of the mixed solutions in the reaction vessels, the entire procedure was carried out and the absorbancy of the resulting methylene blue solution was measured. As illustrated in Fig. 3, the solution containing 11.17 mg. of the ferric ion showed lower sulfur values. Moreover, even by the use of 5.58 mg. of ferric ions, the linearity of the curve could not be preserved for more than 20 micrograms of sulfur content. As it might be considered that the effect was caused by both ferric and chloride

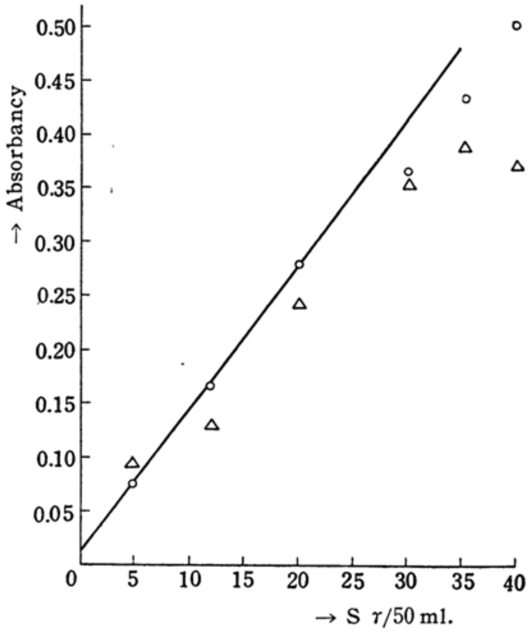

Fig. 3. Effect of ferric and chloride ions on the sulfate calibration curve.

○: 5.5_8 mg. Fe and 12.2 mg. Cl
△: 11.1_7 mg. Fe and 22.9_5 mg. Cl

ions, the following experiments were carried out to eliminate their interference. To the sulfate solution taken in the reaction vessels were added 11.2 mg. of ferric ion as ferric chloride, 0.5 ml. of 1% barium chloride solution, and 0.5 ml. of aqueous ammonia (d=0.88). The mixture was evaporated to dryness, and heated in an electric oven to 500°C. By this treatment all acidic components but sulfate would be decomposed, unless too large amounts of alkali or alkaline earth metal ions were present. The ferric chloride was eventually converted into ferric oxide. Then the reduction of the sulfate to hydrogen sulfide was carried out according to the procedure without further addition of barium chloride. The linear relationship between the amount of the sulfate and the absorbancy of the resulting methylene blue solution was obtained. So it was found that the elimination of the effects of ferric and chloride ions could be completed by this treatment.

Determination of Sulfur in Commercial Ferric Chloride Reagent.—The method described above can be readily applied to the determination of sulfate in various substances. For example, weigh accurately about 27 g. of ferric chloride hexahydrate, and dissolve it in 500 ml. of distilled water. Pipet 1 ml. of the solution into a reaction vessel, and after the treatment described above, the analysis is similarly carried out. In the course of the treatment some ferric chloride volatilizes, but barium sulfate is stable at as high as 900°C[3] and most of the ferric chloride is converted into ferric oxide at 500°C[4]. The experimental data of the analysis are given in Fig. 4 showing satisfactory recovery of the sulfate added. The absorbancy measured in the absence of sulfate was 0.052, which is the sum of the absorbancy of 0.039 for the blank of ammonia and that of 0.019 for sulfur in the ferric chloride tested. So the amount of sulfur in 54 mg. of ferric chloride hexahydrate is estimated to be as small as 1 microgram and that contained in 0.5 ml. of aqueous ammonia 2.4 micrograms.

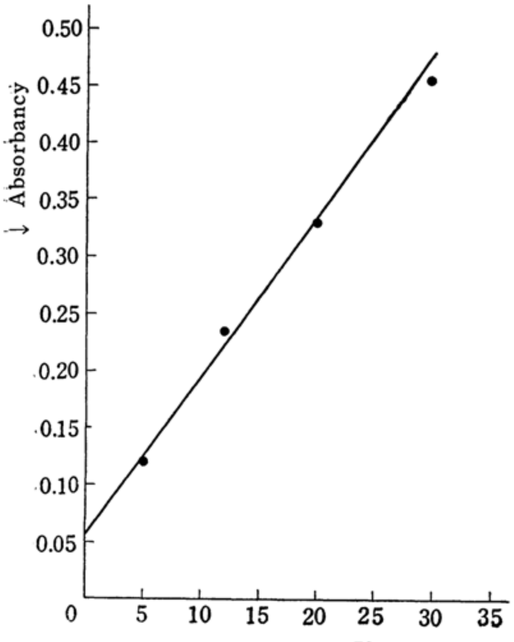

Fig. 4. Sulfate calibration curve after treatment with ammonia, in the presence of 54 mg. of ferric chloride hexahydrate.

Determination of Sulfur in Japanese Acid Clay.—A 0.1 to 0.5 g. portion of air-dried clay was weighed directry in a reaction vessel. The analysis was similarly carried out without any preliminary treatment. As shown in Table I, a linear relationship was obtained between the amount of the clay and that of sulfur found. Moreover, it was verified that as little as 4 micrograms of sulfur in 0.1 g. of the clay could be estimated accurately and rapidly with satisfactory reproducibility.

TABLE I

DETERMINATION OF SULFUR IN JAPANESE ACID CLAY

Acid Clay Taken g.	Absorbancy	Sulfur Found μg.	Sulfur Content %
0.1000	0.056	3.8	0.0038
0.2175	0.119	8.6	0.0039
0.3825	0.195	14.3	0.0037

Summary

A new reagent, "Tin(II)-strong phosphoric acid" has been prepared to permit a rapid and simple determination of sulfate sulfur by reduction to hydrogen sulfide. The procedure for the determination of semi-micro quantities of sulfate sulfur, previously devised by the authors, has been extended to the microgram scale by adopting the sensitive methylene blue colorimetric method. The rapidity and simplicity of the original method are still retained in this new colorimetric method,

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[4] L. Marvin, *Ind. Eng. Chem. Anal. Ed*, **17**, 554 (1945).

by which 1 to 35 micrograms of sulfate sulfur can be estimated. The apparatus is very simple, a test-tube of fused silica being employed as the reaction vessel. The standard calibration curve for colorimetric determination of sulfate sulfur by this method coincides well with that drawn for sodium sulfide by direct coloration with *p*-amino dimethyl aniline and ferric chloride. Interference of other anions can be kept out of consideration, because the sulfate ion is easily separated by addition of barium chloride solution and coprecipitation with ferric hydroxide. Large amounts of ferric hydroxide do not affect the method. Some examples of the determination of sulfate sulfur in ferric chloride reagent and Japanese acid clay are described.

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