Spectrophotometric Method for the Determination of Small Amounts of Sulfate Ions

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(Received February 28, 1957)

A more rapid and accurate method for determining sulfate of low concentration in natural waters is desirable. An indirect colorimetric determination of sulfate, using solid barium chromate and diphenylcarbazide was previously reported by us[1]. However, this method can only be applied to the determination in the range 0.2 to 10 p. p. m. Recently, T. Kato, Y. Nomizo and K. Shinra[2] studied a photometric method of determination of 2 to 120 p. p. m. of sulfate using a perchloric acid solution of barium chromate and ammonia. The authors have devised an improved method for the determination of sulfate over the range 0.3 to 100 p. p. m., using barium chromate suspended in an acid solution.

Experimental Results and Discussion

Reagents

(1) *Standard solution of sulfate* (1,000 p. p. m. SO_4^{2-}): —Recrystallized potassium sulfate (guaranteed reagent) 1.815 g. is dissolved and diluted to 1 l. with distilled water. Solutions of various concentrations can be prepared by diluting this stock solution. All solutions are stored in polyethylene bottles.

(2) *Barium chromate suspension.*—One hundred cc. of a hot solution of barium chloride containing 10 g. of $BaCl_2$-$2H_2O$ is added slowly to 800 cc. of a hot solution of potassium chromate containing 8 g. of K_2CrO_4 to obtain a yellow precipitate of barium chromate. This precipitate is washed three times by decantation with about 500 cc. portions of hot water, dissolved in 100 cc. of hot 2 M hydrochloric acid, and diluted to 700 cc. with hot water. A 105∼110 cc. portion of 2 M ammonia water is added slowly in order to reprecipitate the barium chromate. The precipitate thus obtained is washed again in the same way as mentioned above, and after drying at 105°C for about one hour, it is pulverized in an agate motar. Barium chromate suspension is prepared by adding 2.5 g. of the barium chromate in 200 cc. of the aqueous solution consisting of 0.5 M acetic acid and 0.01 M hydrochloric acid. The pH of this suspension is about 2.4. The reagent is stored in a polyethylene bottle.

(3) *Ammonia water containing calcium ions.*—

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[1] I. Iwasaki, S. Utsumi and T. Tarutani, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **74**, 400 (1953).

[2] T. Kato, Y. Nomizo and K. Shinra, ibib., **76**, 373 (1955).

The reagent is prepared by dissolving 1.85 g. of $CaCl_2 \cdot 2H_2O$ in 500 cc. of purified 6 M ammonia water (1 mg. Ca^{2+}/cc.). The solution is stored in a container shown in Fig. 1.

(4) *Diphenylcarbazide reagent.*—The reagent is prepared by dissolving 1 g. of diphenylcarbazide in a mixture of 100 cc. of ethanol and 1 cc. of 1 M hydrochloric acid. This reagent is stable for 2∼3 weeks in a brown bottle.

(5) Ethanol (guaranteed reagent) is used after being purified by distillation.

(6) Hydrochloric acid (6 M).

Apparatus

(1) Measurements were carried out with the Hitachi Type E. P. U. 2 spectrophotometer and with 5 mm. absorption cells.

(2) Centrifuge (about 4,000 r. p. m.).

(3) Glass filter (15 cc., No. 4),

(4) Centrifuge tube (15 cc.) with a glass stopper[3].

(5) Apparatus for storing ammonia water. To keep ammonia water free from carbon dioxide in the air, a polyethylene bottle attached with a buret and two soda-lime tubes as shown in Fig. 1 was used.

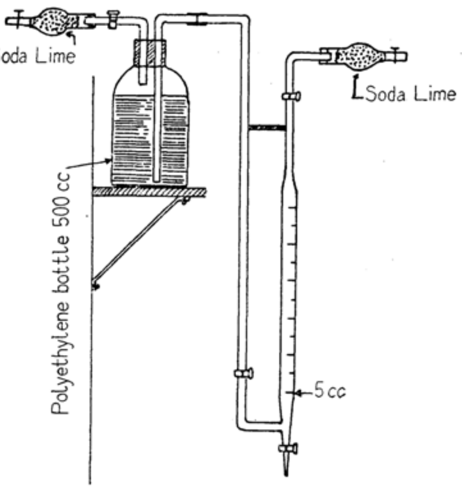

Fig. 1. Apparatus for storing ammonia water.

Procedure

Pipet 5 cc. of a sample solution into a centrifuge tube, add 2 cc. of a uniformly suspended solution of barium chromate and mix. After standing for 2∼3 minutes, add 0.5 cc. of ammonia water containing calcium ions and mix. Add 5 cc. of ethanol and shake for about one minute (pH of the solution is about 9.8). Let the mixture stand for about ten minutes.

When the sulfate concentration of a sample solution is higher than 20 p. p. m., measure the absorbance of the supernatant solution at 370 mμ directly after the centrifugation (Procedure A).

For the cases of concentration lower than 20 p. p. m., filter the supernatant solution of the centrifugate gradually through a glass filter, add 1 cc. of diphenylcarbazide reagent and 0.7 cc. of 6 N hydrochloric acid to the filtrate and mix well. After five minutes, measure the absorbance of this violet colored solution at 545 mμ (Procedure B).

Absorption Spectral Curves

The absorption of the yellow color due to the chromate ion replaced in the solution was measured over the wave length range 230 to 450 mμ. The absorption spectral curve is shown in Fig. 2, in which there are two absorption maxima at about 275 mμ and 370 mμ.

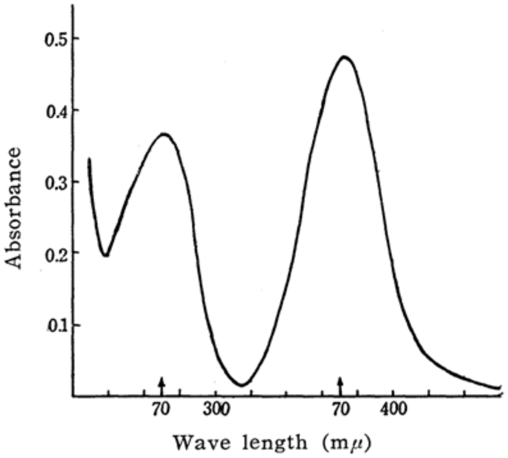

Fig. 2. Absorption spectral curve of chromate.

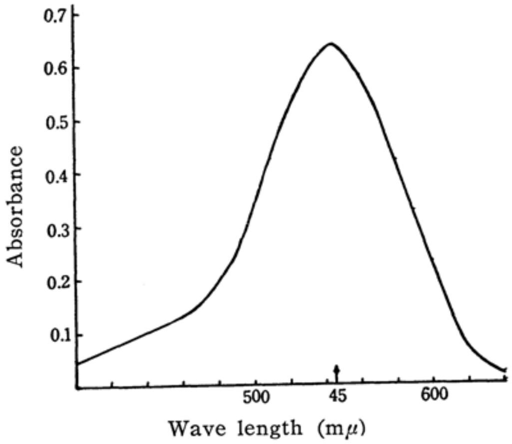

Fig. 3. Absorption spectral curve of Cr(VI)-Diphenylcarbazide.

The chromate ion reacted with diphenylcarbazide in an acidified solution to give a violet coloration. The absorption of the violet color was measured over the range 400 to 640 mμ, as shown in Fig. 3, in which there is one absorption maximum at about 545 mμ.

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[3] S. Utsumi, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **74**, 35 (1953).

The maximum color development of the solution(chromium(VI)-diphenylcarbazide) was obtained after letting it stand for five minutes at room temperature. The violet color was stable for a long time.

Calibration Curves

(1) *For concentrations lower than 20 p. p. m. of sulfate.* — The calibration curve(I) shown in Fig. 4 was obtained by Procedure B with standard sulfate solutions of known concentration. The absorbance and the concentration were in a good linear relationship for the range 2 to 20 p. p. m. SO_4^{2-}, but were not good for concentrations lower than 2 p. p. m.

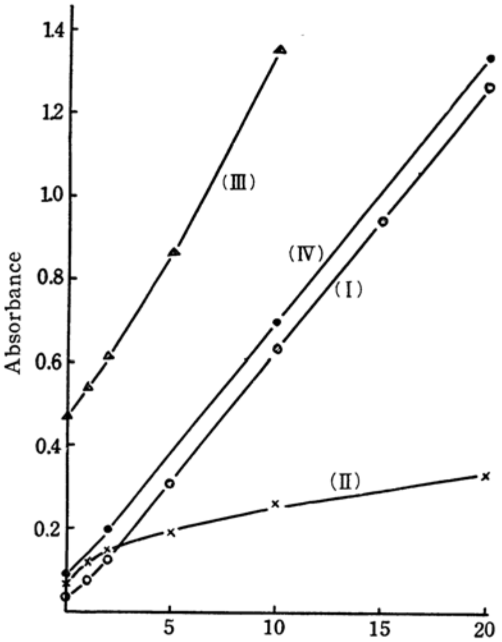

Fig. 4. Calibration curves at 545 mμ, 5 mm cells.

The calibration curve had to be renewed whenever solid barium chromate was newly prepared. In order to obtain reproducible results, it was necessary to use barium chromate suspension which had been stored for a few days after preparation.

When a blank test was made with redistilled water, a faint coloration appeared. The absorbance of the blank test solution was small and constant. The lowest concentration of sulfate, whose coloration could be distinguished from that of the blank test was 0.3 p. p. m. SO_4^{2-} (3.1×10^{-6} M/l).

The calibration curve(I) shown in Fig. 4 was reproducible within the error of ±0.2 p. p. m. SO_4^{2-}. Thus, the method may be available for determining sulfate over the range from 0.3 to 20 p. p. m.

(2) *For concentrations higher than 20 p. p. m.* SO_4^{2-}.—The calibration curve shown in Fig. 5 was obtained by Procedure A using standard sulfate solutions.

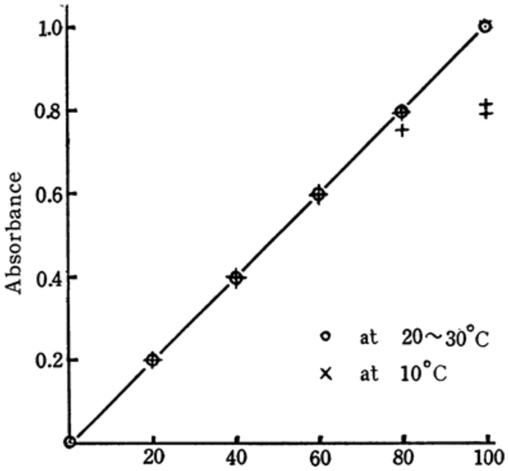

Fig. 5. Calibration curve at 370 mμ, 5 mm cells.

As can be seen in Fig. 5, Beer's law was conformable up to 100 p. p. m. and 70—80 p. p. m. of sulfate respectively at 20—30°C and 10°C. Since barium chromate was more soluble at higher temperatures and hence a sufficient amount of barium ion was available for the precipitation of barium sulfate, it seemed that sulfate of higher concentrations could be determined at higher temperatures.

The absorbance of the blank solution was negligible. The calibration curve was reproducible within 1%.

Conditions for the Analysis

(1) *Reasons for the use of barium chromate suspension.*—When a dilute solution of barium chromate in acidic medium was used instead of its suspension, there was a tendency to form a colloidal solution after the addition of ammonia water. Moreover, the calibration curve was not reproducible. For an accurate determination of a small amount of sulfate, the use of barium chromate suspension was better than that of its solution, because particles of barium chromate in the suspension carried colloidal precipitates of barium

chromate, formed by the addition of ammonia water.

(2) *Influence of acids in barium chromate suspension on the determination of sulfate.*—When a barium chromate suspended in distilled water was used in Procedure B, instead of the suspension mentioned above, the calibration curve(II) as shown in Fig. 4 was obtained, which was not linear with respect to the concentration. When a barium chromate suspended in 0.5 M acetic acid was used, sulfate ions could be determined only up to the concentration of 40—50 p. p. m. at 20—30°C (Procedure A).

On the other hand, when a barium chromate suspended in 0.01 M hydrochloric acid was used, the clear solution, once obtained after the addition of ammonia water containing calcium ion followed by centrifugation, gradually became turbid owing to the formation of calcium carbonate with carbon dioxide in the air.

(3) *Effect of the amounts of barium chromate.*—It was found that the coincident results were obtained by the use of between 2 to 3 g. of reprecipitated barium chromate in 200 cc. of the acid solution (0.5 M acetic and 0.01 M hydrochloric acid). Therefore, the authors would like to recommend the use of 2.5 g. of barium chromate.

(4) *Effect of alcohol.* — Since barium chromate was much less soluble in ethyl alcohol than in water, the influence of ethanol upon the determination of sulfate was examined. The experiment was carried out under the following conditions: 10 cc. of a sample solution was pipetted into a centrifuge tube, then 2 cc. of barium chromate suspension was added and mixed. After being set aside for 2—3 minutes, 0.5 cc. of ammonia water containing calcium ions was added and shaken for about one minute without ethanol. The subsequent treatment was done in the same way as procedure B, by which the calibration curve(III) in Fig. 4 was obtained. Not only was the absorbance of the blank solution larger owing to the greater solubility of barium chromate, but the calibration curve did not give a linear relationship, bending upward though slightly.

In order to decrease the solubility of barium chromate, 5 cc. of ethanol was used for 5 cc. of the sample solution.

(5) *Effect of the calcium ion in ammonia water.*—Since barium carbonate was also difficultly soluble, the absorbance would be considerably affected by the presence of carbonate in ammonia water. Without calcium ions, calibration curve(IV) shown in Fig. 4 was obtained. The curve was influenced by the concentration of carbonate in ammonia water. In order to remove the dissolved carbonate, the authors recommend the addition of some calcium ions into the ammonia water.

(6) *Effect of temperature.* — Since the concentration range of determination was affected by temperature, as shown in Fig. 5, it was desirable to carry out Procedure A at 20—30°C in order to determine the sulfate up to 100 p. p. m. satisfactorily. On the other hand, in the case of Procedure B the effect of temperature was negligible.

Influence of Various Ions.

The effect of different kinds of ion on this method was examined in the presence of 10 p. p. m. SO_4^{2-} and in its absence. The experimental results were summarized as follows.

(1) Neither sodium nor chloride ions interfere even when present in the amount of 5,000 p. p. m.

(2) One thousand p. p. m. of potassium or ammonium ions do not interfere, but 5,000 p. p. m. of each ion gives lower results.

(3) One thousand p. p. m. of perchlorate and 50 p. p. m. of silicate ions have no effect.

(4) The presence of nitrate ions gives somewhat higher results at 50 p. p. m. and considerably higher results at 1,000 p.p.m.

(5) The presence of carbonate or bicarbonate does not interfere at 50 p.p.m. but at 100 p. p. m. slightly higher results are obtained. When larger amounts of these substances are present, it is necessary to remove them beforehand. Carbonate (or bicarbonate) can easily be expelled by boiling a sample solution for a short time after neutralization with dilute hydrochloric acid. The necessary amount of hydrochloric acid may be determined by neutralizing an aliquot portion of the same sample, using methyl orange as indicator.

(6) Neither 100 p. p. m. of magnesium or calcium ions, nor 10 p. p. m. of strontium ion interfere.

(7) Each 10 p. p. m. of Ag^+, Zn^{2+}, Hg^{2+}, Fe^{3+}, Al^{3+} or Mn^{2+} ions does not interfere.

(8) Since lead chromate is difficultly soluble, lead ions interfere even in small amounts.

(9) As the copper ion also reacts with diphenylcarbazide, the presence of copper is undesirable. When the copper ion is present in a sample solution, 0.1 cc. of E·

D. T. A. (0.2 M) should be added before the addition of diphenylcarbazide.

(10) Phosphate, vanadate and selenate give remarkably higher results even in small amounts, because barium salts of these anions are also insoluble in water.

(11) Also arsenate, molybdate, selenite and thiosulfate give some interference even at 10 p. p. m.

However, the undesirable substances described above are not usually contained in common natural waters (rain water, river water etc.) in such concentrations as would give a serious error, therefore this rapid analytical method of sulfate may be applicable to the ordinary water analysis with satisfactory results.

Summary

The authors have devised a new method for the determination of small amounts of sulfate. Sulfate is precipitated as barium sulfate using barium chromate suspension in an acid solution (0.5 M acetic, 0.01 M hydrochloric acid), and the excess of barium is almost completely precipitated as barium chromate by adding ammonia water (containing calcium ion) and ethanol. Finally the amount of chromate which is exchanged with sulfate is estimated.

The proposed method may be applicable to the determination of 0.3—100 p. p. m. sulfate with satisfactory results.

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