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A New Spectrophotometric Method for the Determination of Micro Amounts of Sulfite*[1]

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A new spectrophotometric method for the determination of a minute quantity of sulfite was studied. When a definite amount of aqueous solution of mercuric nitrate mixed with potassium bromide and an ethanol solution of diphenylcarbazone are added to the sample solution kept at pH 7.0, sulfite reacts with mercuric reagent and the excess of the mercuric reagent forms the reddish-violet complex with diphenylcarbazone which may be easily extracted by benzene. Sulfite is determined by measuring the absorbancy of the benzene phase which decreases upon an increase in the concentration of sulfite, at the wavelength of 562 mμ, The method which is applicable to the determination of both sulfite and sulfide has also been established, because sulfide as well as sulfite reacts with mercuric reagent. By this proposed method, sulfite (0.1—2.5 ppm) and sulfide (0.01—0.5 ppm) could be determined at the same time rapidly and accurately. The composition of the complex formed between mercury(II) and sulfite was also studied.

Sulfur dioxide is the most important substance of all air pollutions. Steigmann[1)] has proposed a colorimetric method for the determination of sulfur dioxide using funchsine reagent. Grant,[2)] Atkin,[3)] Uron and Boggs[4)] have studied various

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[*1] Presented at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.

1) A. Steigmann, *J. Soc. Chem. Ind.*, **61**, 18 (1942).

2) W. M. Grant, *Anal. Chem.*, **19**, 345 (1947).

3) S. Atkin, *ibid.*, **22**, 947 (1950).

4) P. F. Uron and W. E. Boggs, *ibid.*, **23**, 1517 (1951).

modifications of this method for the determination of sulfur dioxide in the atmosphere.

West and Gaeke[5] have indicated that the use of tetrachloromercurate(II) as an absorber for sulfur dioxide formed disulfitomercurate(II) $[Hg(SO_3)_2]^{2-}$. Nauman *et al.*[6] have elucidated the mechanism of the reaction between sulfur dioxide, pararosaniline and formaldehyde. They have suggested that the composition of the mercury(II) - sulfur dioxide complex was dichlorosulfitomercurate(II) $[HgCl_2SO_3]^{2-}$ and was not disulfitomercurate(II) $[Hg(SO_3)_2]^{2-}$.

Burke and Davis,[7] and Goto, Kakita and Manabe[8] have also used fuchsine for the determination of sulfur in the metals.

The present authors have previously reported a spectrophotometric determination of minute quantities of chloride,[9] thiosulfate,[10] sulfide[11] and cyanide ions,[12] in which these ions reacted with mercuric reagent, and the excess of the reagent forms also reddish-violet complex with diphenylcarbazone which was easily extracted by benzene.

In the present work, it has been found that a very small amount of sulfite could be determined by a procedure similar to that used for above ions.

The proposed method is sufficiently rapid and accurate to be used for the determination of sulfite ranging from 0.1 to 2.5 ppm concentration.

Experimental

Apparatus. The spectrophotometric measurments were made with a Hitachi spectrophotometer, Model EPU-2 with 10 mm cells.

The separation of organic layer from the aqueous layer was carried out with a brown separatory funnel approximately 50 m*l*.

Materials. Guaranteed reagent benzene was used as extracting agent.

Standard Sulfite Solution. A sulfite solution was prepared by dissolving about 0.324 g of sodium bisulfite in 500 m*l* of water (about 500 ppm). This was then standardized according to iodometry and stored in a brown glass bottle. The working standard solutions were prepared by diluting this stock solution with sulfuric acid of 2.5×10^{-5} mol/*l* properly. The solution of 10 ppm of sulfite proved to be stable for about 60 min.

Standard Sulfide Solution. A sulfide solution was prepared by dissolving about 0.4 g of sodium sulfide ($Na_2S\cdot9\,H_2O$) in 500 m*l* of a 0.1 N sodium hydroxide solution (about 100 ppm). It was then standardized by iodometry and stored in a brown glass bottle. This solution was diluted to the concentration required for the experiments. The solution of 1 ppm of sulfide was stable for about 60 min.

Mercuric Nitrate Solution. A mercuric nitrate solution was prepared by dissolving 8.5 g of mercuric nitrate in water containing 2 m*l* of concentrated nitric acid and then diluting it to 500 m*l* (about 0.05 mol/*l*). This solution was standardized by Volhard's method, and was stored in a brown glass bottle. The working solutions were prepared by diluting the stock solution properly.

Potassium Bromide and Potassium Iodide Solution. Potassium bromide and potassium iodide solutions (0.1 mol/*l*) were standardized by Volhard's method, which were stored in a brown glass bottle. More dilute solutions were prepared by diluting aliquots of these solutions to a definite volume.

Mixed Reagent Solution. The working mixed reagent solution was prepared by mixing equal volumes of mercuric nitrate solution (4.0×10^{-4} mol/*l*) and potassium bromide solution (4.0×10^{-4} mol/*l*) with each other.

Buffer Solution. Buffer solution (pH 7.0) was prepared by mixing 0.1 mol/*l* sodium dihydrogen phosphate solution and 0.1 mol/*l* potassium monohydrogen phosphate solution.

Formaldehyde Solution. Two and a half milliliters of 40% formaldehyde was diluted to 1000 m*l* with water.

Diphenylcarbazone Solution. 0.05 g of diphenylcarbazone was dissolved in 100 m*l* of ethanol.

All the chemicals used were of analytical grade.

Procedure and Calibration Curve. Ten milliliters of the standard sulfite solution are placed in a brown separatory funnel. Then 1.0 m*l* of the mixed reagent solution (2.0×10^{-4} mol/*l* mercuric nitrate-2.0×10^{-4} mol/*l* potassium bromide) and 2.0 m*l* of the buffer solution (pH 7.0) are added. To this mixture, 10 m*l* of benzene and 1.0 m*l* of ethanol solution of diphenylcarbazone (0.05 g/100 m*l*) are added. The separatory funnel is shaken for about 1 min; the complex formed between mercuric reagent and diphenylcarbazone is thereby extracted into the organic layer. The absorbancy of the organic layer is measured at 562 mμ, using pure water as a reference.

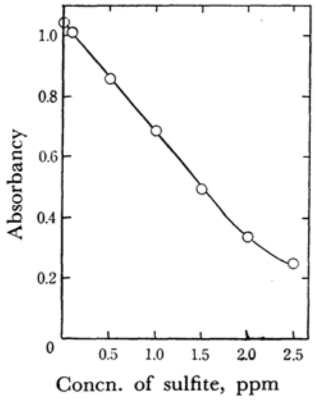

Fig. 1. Calibration curve at 20°C.

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[5] P. W. West and G. C. Gaeke, *Anal. Chem.*, **28**, 1816 (1956).

[6] N. V. Nauman, P. W. West, F. Tron and G. C. Gaeke, *ibid.*, **32**, 1307 (1960).

[7] K. E. Burke and C. M. Davis, *ibid*, **34**, 1747 (1962).

[8] S. Goto Y. Kakita and Manabe, *Anal. Chem. Japan.*, **14**, 244 (1965).

[9] S. Utsumi and T. Okutani, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **85**, 543 (1965).

[10] T. Okutani, S. Utsumi, K. Shibata and I. Iwasaki, *ibid.*, **86**, 831 (1965).

[11] T. Okutani and S. Utsumi, *ibid.*, **86**, 1149 (1965).

[12] T. Okutani and S. Utsumi, *ibid.*, **87**, 444 (1966).

The calibration curve shown in Fig. 1 was obtained by the above procedure with standard sulfite solutions of known concentrations at 20°C. As can be seen in Fig. 1 the absorbancy decreases with the increase in the concentration of sulfite, moreover calibration curve is linear up to 2 ppm concentration of sulfite.

Results and Discussion

Calibration Curves with Mercuric Reagent Solutions. The mixed solution of mercuric nitrate - potassium bromide was used for the determination of chloride,9) while mixed solution of mercuric nitrate - potassium iodide was employed for the determination of thiosulfate,10) sulfide11) and cyanide12) at a pH value of 2.5 or 7.0.

The calibration curves of sulfite with these mixed reagent solutions or mercuric nitrate solution at pH 7.0 are shown in Fig. 2.

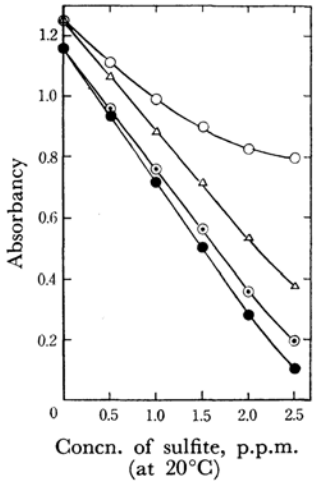

Fig. 2. Calibration curves with mixed reagent solutions at pH 7.0.
-○- 2.5×10⁻⁴ mol/*l* $Hg(NO_3)_2$ and 2.5×10⁻⁴ mol/*l* KI
-△- 2.5×10⁻⁴ mol/*l* $Hg(NO_3)_2$ and 2.5×10⁻⁴ mol/*l* KBr
-●- 2.5×10⁻⁴ mol/*l* $Hg(NO_3)_2$
-⊙- 2.5×10⁻⁴ mol/*l* $(HgCl_4)^{2-}$

As can be seen in Fig. 2, the mixed solution of mercuric nitrate - potassium iodide was not suitable for the determination of sulfite. On the other hand, satisfactory results were obtained by using mercuric nitrate, tetrachloromercurate or mixed solution of mercuric nitrate - potassium bromide.

The calibration curves of sulfite at pH 2.5 with these solutions are also shown in Fig. 3.

From the experimental facts shown in Figs. 2 and 3, it has been confirmed that the sulfite could be determined more sensitively at pH 2.5 than at pH 7.0. But chloride interfered with the determination of sulfite at pH 2.5.

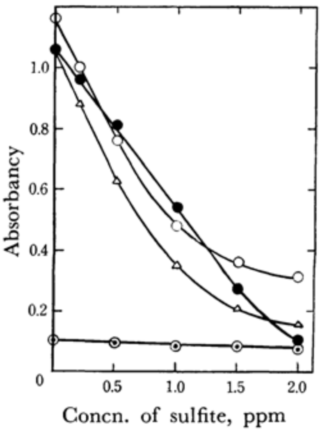

Fig. 3. Calibration curves with mixed reagent solutions at pH 2.5.
-○- 2.5×10⁻⁴ mol/*l* $Hg(NO_3)_2$ and 2.5×10⁻⁴ mol/*l* KI
-△- 2.5×10⁻⁴ mol/*l* $Hg(NO_3)_2$ and 2.5×10⁻⁴ mol/*l* KBr
-●- 2.5×10⁻⁴ mol/*l* $Hg(NO_3)_2$
-⊙- 2.5×10⁻⁴ mol/*l* $(HgCl_4)^{2-}$

The Effect of the Temperature and the Light. The effects of the temperature on this method were examined by using mercuric reagent solutions.

The experimental results of the reagent blank are given in Table 1. These results show that the complex formed between the mixed solution of mercuric nitrate - potassium bromide (or potassium iodide) and diphenylcarbazone is only slightly affected by the temperature.

From both the results shown in the Figs. 2 and 3, and the above facts listed in Table 1, the mixed reagent solution of mercuric nitrate - potassium bromide is used in this work. The higher the concentration of the mixed reagent solution was, the deeper the color of benzene phase was. Therefore the working mixed reagent solution was made by mixing equal volumes of mercuric nitrate of 4.0×10⁻⁴ mol/*l* and potassium bromide of 4.0×10⁻⁴ mol/*l* with each other.

In regard to the effect of light, it has been previously reported9) that the complex between mercuric solution mixed with potassium bromide and diphenylcarbazone is stable for at least 20 min in the brown separatory funnel.*2

The Effect of the Chloride. In the previous papers, the present authors have reported that thiosulfate10) can be determined even in the presence of 100 ppm of chloride at pH 7.0. It was investigated how the chloride affected the determination of sulfite. Table 2 shows that the chloride

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*2 The complex of Hg(II)-Br-diphenylcarbazone is more stable than that of Hg(II)-diphenylcarbazone although the composition is not yet known. These complexes are more stable at pH 7.0 than at pH 2.5.9,10)

Table 1. Effect of temperature

pH	Mercuric reagent	Hg^{2+}-Concn. in the mixed soln. mol/l	Absorbancy		
			20°C	12°C	Difference
2.5	$Hg(NO_3)_2$	2.5×10^{-4}	1.075	1.164	0.089
			1.086	1.173	0.087
7.0	$Hg(NO_3)_2$	2.5×10^{-4}	1.156	1.221	0.065
			1.161	1.214	0.053
7.0	$(HgCl_4)^{2-}$	2.5×10^{-4}	1.170	1.229	0.059
			1.161	1.234	0.073
7.0	$Hg(NO_3)_2$-KI	2.5×10^{-4}	1.251	1.244	0.007
			1.251	1.251	0.000
7.0	$Hg(NO_3)_2$-KBr	2.5×10^{-4}	1.251	1.259	0.008
			1.244	1.259	0.015
7.0	$Hg(NO_3)_2$-KBr	2.0×10^{-4}	1.045	1.065	0.020
			1.050	1.060	0.010

Table 2. Effect of chloride

Cl^- ppm	Absorbancy	
	Reagent blank	2.0 ppm SO_3^{2-}
None	1.045	0.349
25	1.036	0.344
50	1.036	0.341
100	1.036	0.346

ions of up to 100 ppm have no any effect on this method.

Stability of the Complex between Mercury(II) and Sulfite. A stability of the mercury(II) - sulfite complex was examined by the following procedure. One milliliter of mixed reagent solution and 2.0 ml of buffer solution (pH 7.0) are added to 10.0 ml of the standard sulfite solution of 2 ppm in a brown separatory funnel. Then benzene and diphenylcarbazone solution are added after standing for a various period of time, and the absorbancy of benzene layer is measured.

The experimental results show that the absorbancy remains constant even after 2 hr from the addition of a mercuric reagent to the sulfite solution.

These experiments indicate that the mercury(II) reacts immediately with sulfite and the complex formed is stable.

The Determination of Sulfite and Sulfide Simultaneously Present. Hydrogen sulfide is generally present together with sulfur dioxide in the air. Sulfur dioxide (sulfite) alone can not be determined in the presence of hydrogen sulfide, because sulfide as well as sulfite reacts with mercury(II).

The calibration curve for the sulfide which is obtained by exactly the same procedure as that used for sulfite is shown in Fig. 4 (-●-).

Several methods were tried to determine the minute amount of sulfite in the presence of sulfide; it was found that each of them could be determined by the following procedure.

In the first place, the absorbancy was measured according to the above procedure when both sulfite and sulfide were present simultaneously (absorbancy=A).

On the other hand, 10 ml of the sample solution were taken into a separatory funnel. Then 1.0 ml of a 0.1% formaldehyde solution was added in order to mask sulfite and the absorbancy was measured (absorbancy=B).

The absorbancy for the sulfite was calculated from these two absorbancies by the following equation:

$$C=B1-\{(B1-A)-(B1-B)\}=B1-B+A$$

C: Absorbancy for a sulfite
$B1$: Absorbancy for a reagent blank

The sulfite could be determined by using this absorbancy (C) and the calibration curve shown in Fig. 4.

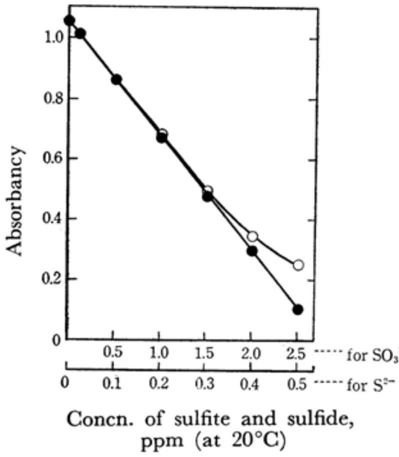

Fig. 4. Calibration curves of sulfite and sulfide.
-○- Sulfite, -●- Sulfide

TABLE 3. DETERMINATION OF SULFITE AND SULFIDE PRESENT TOGETHER

Taken, ppm			Absorbancy			Found (ppm)	
Concn. of SO_3^{2-}	Concn. of S^{2-}	Concn. of Cl^-	A	B	C	Concn. of SO_3^{2-}	Concn. of S^{2-}
0.5	0.1	0	0.673	0.853	0.870	0.50	0.10
	0.3	0	0.319	0.508	0.867	0.50	0.29
1.0	0.1	0	0.511	0.823	0.744	0.90	0.12
	0.3	0	0.209	0.515	0.744	0.90	0.29
2.0	0.3	0	0.795	0.928	0.913	2.0*	0.30*
	0.6	0	0.710	0.835	0.925	1.9*	0.60*
	2.0	0	0.627	0.681	0.996	1.8**	2.00**
5.0	0.5	0	0.795	0.958	0.887	4.9**	0.50**
	2.0	0	0.521	0.694	0.877	5.0**	1.90**
0.5	0.1	50	0.657	0.841	0.866	0.50	0.10
1.0	0.3	50	0.182	0.507	0.725	0.90	0.29
2.0	1.0	100	0.527	0.688	0.889	2.2*	0.98*
5.0	2.0	100	0.508	0.705	0.853	5.2**	1.90**

Absorbancy for the reagent blank: 1.050

* 2 m*l* of a sample solution was diluted to 10 m*l*.

** 1 m*l* of a sample solution was diluted to 10 m*l*.

The effect of the presence of a 0.1% formaldehyde solution on the determination of sulfide was negligible up to 3 m*l* and sulfite ranging from 0.1 to 2.5 ppm concentration was completely masked with 1 m*l* of a 0.1% formaldehyde solution.

The results listed in Table 3 were obtained by the procedure described above, in the presence of various amounts of both sulfide and sulfite of known concentrations at 20°C.

As will be in Table 3, small amounts of them can be determined.

The Effect of Divers Ions. The effects of the divers ions on this method were examined. Thiosulfate, cyanide and iodide ions interfere remarkably even at 1 ppm. Bromide, ferrous, cupric and silver ions at a concentration of 10 ppm interfere with the determination of sulfite.

The Composition of the Complex between Mercury(II) and Sulfite. Feigl[13] has reported that disulfitomercurate ion, which was formed when sulfite were added to mercuric ion, was very stable, and even permanganate failed to oxidize the complex at a very slow rate. On the other hand, it has been reported by Nauman[6] that there was a 1 to 1 mol ratio between tetrachloromercurate(II) $[HgCl_4]^{2-}$ and sulfite, therefore, the chemical formula of the complex was not disulfitemercurate(II) $[Hg(SO_3)_2]^{2-}$ but dichlorosulfitomercurate(II) $[HgCl_2SO_3]^{2-}$.

The present authors have investigated in greater detail the composition of the mercury(II) - sulfite complex using mercuric nitrate, mercuric chloride, tetrachloromercurate and mixed solution of mercuric nitrate - potassium bromide at pH 2.5 and pH 7.0 by the mole ratio method. The resulting curves are shown in Fig. 5.

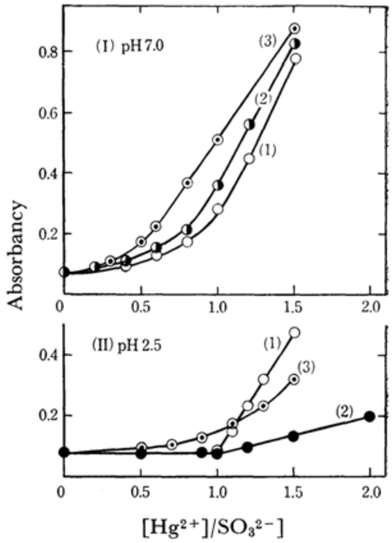

Fig. 5. Mole ratio method.
Concentrations of sulfite; 2.5×10^{-5} mol/*l*
-○- $Hg(NO_3)_2$ -◑- $(HgCl_4)^{2-}$
-●- $HgCl_2$ -⊙- $Hg(NO_3)_2$ and KBr

As can be seen in Fig. 5 (II), the curves of (1) or (2) indicate that there is a 1 to 1 mol ratio between mercuric nitrate (or mercuric chloride) and sulfite at pH 2.5, but the curve (3) does not seem to indicate a clear 1 to 1 mol ratio complex between the mixed solution (mercuric nitrate - potassium bromide) and sulfite.

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13) F. Feigl, "Chemistry of Specific, Selective and Sensitive Reactions," Academic Press, New York (1949), p. 75.

As can be seen in Fig. 5 (I), the curve (3) indicates that there seems to be a 1 to 2 mol ratio between mixed solution (mercuric nitrate - potassium bromide) and sulfite at pH 7.0, while the curve of (1) or (2) does not indicate a definite mole ratio.

Recently, the present authors*[3] have found according to the measurement of ultraviolet absorption that mercury(II) forms both 1 to 1 and 1 to 2 complexes with sulfite.

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*[3] The study will be reported on in another paper.