Spectrophotometric Determination of Micro Amounts of Sulfide, Sulfite and Thiosulfate

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The present method is based on the spectrophotometric measurement of an excess amount of iodine for the reaction of iodine with sulfide, sulfite and thiosulfate in a mixture after proper chemical treatments; it consists of three Procedures: I, II and III. The absorbance obtained by Procedure I corresponds to the sum of the thiosulfate and twice the sulfide and sulfite in the mixture. The absorbance obtained by Procedure II, where sulfite was masked by formaldehyde, corresponds to the sum of the thiosulfate and twice the sulfide. The absorbance obtained by Procedure III corresponds to only the amount of thiosulfate, because sulfite was masked by formaldehyde and sulfide was eliminated with the suspension of zinc carbonate hydroxide. The conditions under which all the three sulfur species in a mixture can be stable and react stoichiometrically with iodine were established. The method is applicable to the determination of sulfur species in amounts more than 0.05 μmol and gave a relative standard deviation of 3% at 0.4 μmol level. It has been applied to the determination of sulfide, sulfite and thiosulfate in various amounts in several fumarolic condensate samples.

Keywords Sulfur anions determination, sulfide-sulfite-thiosulfate mixture, iodine, spectrophotometry, fumarolic condensates

Sulfur forms various species, which can be classified into two types; the first group consumes iodine in an acid medium and the other does not. The former group includes sulfides, sulfites and thiosulfates. The identification and determination of these sulfur species are difficult, particularly when mixed with one another in a solution, because they are labile and participate in complex equilibria with the other sulfur compounds formed by their auto-redox reactions. Various investigations have been made regarding the determination of either one or two sulfur species in mixture of two species such as sulfide (polysulfide included) and thiosulfate¹⁻⁵, sulfide and sulfite^{6,7}, and sulfite and thiosulfate.⁸⁻¹² Recently, ion chromatography has been applied to the separation of sulfite, thiosulfate and sulfate¹³, and also to the analysis of mixtures of sulfite, thiosulfate, sulfate and thiocyanate.¹⁴ However, no consideration has been given to the determination of sulfide, sulfite and thiosulfate in a mixture.

In the past, classical iodimetric titration methods^{15,16} have been extensively employed for the determination of sulfide, sulfite and thiosulfate in a mixture. Kilroy¹⁷ has proposed a titrimetric method for the mixture of sulfide, sulfite, thiosulfate and dithionite. However, these methods are not suitable for micro amounts of sulfur species. In addition, the procedure¹⁷ for the determination of thiosulfate is too complicated and time-consuming. Ono¹⁸ has devised a method for the determination of sulfide, sulfite and thiosulfate in the leaching solution of blast-furnace slags by ion exchange chromatography. In the present study, the conditions

of stabilization of sulfide and sulfite mixed with each other were investigated to avoid time-dependent change in chemical composition of the sample solution containing soluble sulfide, sulfite and thiosulfate. The present paper is based on the spectrophotometric measurement of an excess amount of iodine for the reaction of iodine with sulfide, sulfite and thiosulfate after proper chemical treatments.

Experimental

Reagents and apparatus

All chemicals used were of analytical grade and were used without further purification. The water was redistilled. A sulfide solution (0.05 M) was prepared by dissolving 2.4 g of sodium sulfide nonahydrate whose surface was washed with oxygen-free water (the water on the solid sulfide was removed by absorption with filter paper) in 200 ml of water. The solution was continuously deaerated with nitrogen gas, and then standardized by iodimetry.¹⁹ Working standard sulfide solutions were prepared by appropriate dilution with oxygen-free water. These standards must be used within 30 min after standardization, because the concentration of sulfide decreases due to its oxidation on further standing. A standard sulfite solution was prepared by dissolving sodium hydrogensulfite in oxygen-free water, and was standardized by iodimetry.²⁰ Working standards were obtained by suitable dilution. A standard thiosulfate solution was prepared

by dissolving a given amount of sodium thiosulfate pentahydrate in oxygen-free water containing a small amount of sodium carbonate as a stabilizer, and standardized by iodimetry²⁰ a week after preparation. Working standard thiosulfate solutions were prepared by appropriate dilution as required.

A standard iodate-iodide solution was prepared by adding 50.0 ml of 1.00×10^{-2} N ($=1.67 \times 10^{-3}$ M) standard iodate to a solution containing 0.2 g of sodium carbonate and 72.6 g of potassium iodide, and diluting it to 500 ml to give a 1.00×10^{-3} N iodate in 0.87 M iodide solution. An iodide solution of 0.87 M was prepared by dissolving 72.6 g of potassium iodide in water containing 0.2 g of sodium carbonate and diluting it to 500 ml. This solution was used for the correction of air-oxidation of iodide. Suspension of zinc carbonate hydroxide was prepared by mixing 5%(w/v) zinc acetate and 7.5%(w/v) sodium carbonate in equal volume ratio immediately before use.

Buffer solutions required for adjusting the pH of reaction solutions were prepared by the mixing of formic acid (0.2 M) and sodium hydroxide (0.2 M), acetic acid (0.2 M) and sodium acetate (0.2 M), sodium hydrogenmaleate (0.2 M) and sodium maleate (0.2 M), boric acid (0.2 M) containing potassium chloride (0.2 M) and sodium hydroxide (0.2 M), sodium hydrogen-carbonate (0.2 M) and sodium carbonate (0.2 M), and ammonium chloride (0.2 M) and ammonia (0.2 M), in various volume ratios. In addition, sodium carbonate and sodium hydroxide solutions were used for the adjustment of pH. The buffer solutions of pH 5.0 used in Procedure I and pH 6.2 in both Procedures II and III were obtained by mixing 100 ml of 0.2 M acetic acid with 200 ml of 0.2 M sodium acetate, and 100 ml of 0.2 M sodium hydrogenmaleate with 200 ml of 0.2 M sodium maleate, respectively.

All spectrophotometric measurements were made with a Shimadzu Model UV-100-02 spectrophotometer with 10-mm quartz cells. pH was measured with a Hitachi-Horiba Model M-7 pH meter.

Procedure

Prepare the following three reaction mixtures for the determination of sulfide, sulfite and thiosulfate in mixtures.

Procedure I. Determination of sulfide, sulfite and thiosulfate in the mixture. Place 1 ml of 0.2 M acetate buffer (pH 5.0), 1 ml of 0.1%(w/v) zinc acetate, and then a 10.0-ml aliquot of the sample solution containing sulfide, sulfite and thiosulfate to a 25-ml volumetric flask. The pH of the solution is thereby brought to 5.1.

Procedure II. Determination of sulfide and thiosulfate in the mixture. Place 1 ml of 0.2 M maleate buffer (pH 6.2), 1 ml of 0.1%(w/v) zinc acetate, and a 10.0-ml aliquot of the sample solution to a 25-ml volumetric flask. Then add 1 ml of 1.5×10^{-2} M formaldehyde, and allow the mixture to stand for at least 1 min. The pH of the solution is thereby brought to 6.2.

Procedure III. Determination of thiosulfate in the mixture. Place 1 ml of 0.2 M maleate buffer (pH 6.2), 1 ml of 1.5×10^{-2} M formaldehyde, and then a 10.0-ml aliquot of the sample solution to a 50-ml beaker. Allow the mixture to stand for 1 min, then add two drops of suspension of freshly precipitated zinc carbonate hydroxide. In this case, the pH of the solution was adjusted to 6.8, and the sulfide in the mixture was precipitated. Filter off the precipitate through Toyo No. 6 filter paper, wash it thoroughly with water, and transfer the filtrate and washings to a 25-ml volumetric flask.

To these three mixtures of Procedures I, II and III, add 2 ml of 2 M acetic acid and 2.4 ml of 1.00×10^{-3} N standard iodate in 0.87 M iodide solution, then fill the flask to the mark with water. Mix the contents of the flasks well, and measure the absorbance of the solution against water at 350 nm of maximum absorption for triiodide ion. In Procedures I and II, it is necessary to add standard iodate in iodide solution immediately after the addition of acetic acid, otherwise hydrogen sulfide is evolved.

Results and Discussion

Calibration graphs

A series of standard solutions (10.0 ml) of thiosulfate, sulfide and sulfite were treated according to Procedure I. It is well known that thiosulfate, sulfide and sulfite react with iodine in an acid medium as follows²¹:

Fig. 1 Calibration graphs for thiosulfate, sulfide, sulfite and iodine obtained by Procedure I. (○) $S_2O_3^{2-}$, (○) S^{2-} , (○) SO_3^{2-} , (●) I_2 .

As can be seen in Fig. 1, the calibration graphs for thiosulfate, sulfide and sulfite obtained by procedure I coincided with one another when the molar concentration scale for sulfide and sulfite was drawn to twice the scale for thiosulfate concentration. Moreover, these graphs accorded with that for iodine when the molar concentration scale for iodine was drawn oppositely to that for sulfur species. The calibration plots for both sulfide and thiosulfate in the presence of sulfite (1.2×10^{-4} M) obtained by Procedure II and that for thiosulfate in the presence of both sulfide (1.2×10^{-4} M) and sulfite (1.2×10^{-4} M) by Procedure III were also in complete accordance with the calibration graph for iodine in Fig. 1. These experimental facts show that any species of sulfide, sulfite and thiosulfate can react stoichiometrically with iodine even in the presence of others without changes in the chemical composition under the conditions given in Procedures I, II and III.

Stability of sulfide and sulfite in their mixture

Sulfide is a very unstable species, particularly in an aqueous solution; low results were obtained in the determination of sulfide because of its evolution and/or oxidation. Therefore, an attempt was made to fix sulfide as zinc sulfide¹⁹ for its stabilization. The amounts of 1 ml of 0.06–0.3% (w/v) zinc acetate were sufficient to stabilize sulfide. When 1 ml of 0.1% zinc acetate was added as in Procedure I, the sulfide was stable for 10 min at pH 4.5, for 30 min at pH 5.1 and for 15 min at pH 7.8. On the other hand, sulfite was stable for 15 min at pH 4.5, for 20 min at pH 5.1 and for 10 min at pH 6.2. Figure 2 shows that sulfide and sulfite are stable for 5 min over the pH range 4.5–7.8 and over the pH range 3.8–6.4, respectively. An increase in absorbance for sulfide below pH 4.5 and for sulfite below pH 3.8 is thought to be predominantly caused by the evolution of hydrogen sulfide and sulfur

dioxide. An increase in absorbance for sulfide above pH 7.8 and for sulfite above pH 6.4 is probably due to the oxidation of sulfide and sulfite. Sulfide proved not to react with sulfite when fixed as zinc sulfide, and even the mixtures with various molar ratios of sulfide to sulfite were stable for at least 15 min at pH 5.1 and could be stable for 5 min over the pH range 4.5–6.4. It was therefore concluded that each sulfide, sulfite and thiosulfate in a mixture can react quantitatively with iodine under the conditions given in Procedure I without time-dependent changes in the chemical composition of sample.

Masking of sulfite with formaldehyde

In order to obtain the absorbance for total amounts of both sulfide and thiosulfate in the presence of sulfite according to Procedure II, the reaction of sulfite with iodine must be completely prevented. An attempt was made to mask the sulfite with formaldehyde.⁹ It was confirmed that sulfite was completely masked in the pH range 5.6–8.6, when 1 ml of 1.5×10^{-2} M formaldehyde was added and the mixture was allowed to stand for 1 min. As mentioned above, the sulfide fixed as zinc sulfide was stable over the pH range 4.5–7.8. Consequently, iodine reacted with only both sulfide and thiosulfate even in the presence of sulfite when the sulfite was masked by formaldehyde over the pH range of 5.6–7.8.

Removal of sulfide

In Procedure III, the reaction of both sulfide and sulfite with iodine must be prevented in order to obtain the absorbance for thiosulfate. Sulfide was precipitated with 2 drops of suspension of zinc carbonate hydroxide and eliminated by filtering off the precipitate. Figure 3 shows how the sulfide could be removed by varying the pH of mixture solution. The absorbance for sulfide coincided with the reagent blank

Fig. 2 Effect of pH on the stability of sulfide, sulfite and thiosulfate. Standing time: 5 min. The conditions are as described in Procedure I, except pH and standing time. (○) 7.5×10^{-5} M S^{2-} , (◐) 7.5×10^{-5} M SO_3^{2-} , (●) 1.5×10^{-4} M $\text{S}_2\text{O}_3^{2-}$.

Fig. 3 Effect of pH on the removal of sulfide. The conditions are as described in Procedure III, except pH. (○) reagent blank, (◐) 1.2×10^{-4} M S^{2-} , (●) 1.5×10^{-4} M $\text{S}_2\text{O}_3^{2-}$, (◐) 1.5×10^{-4} M $\text{S}_2\text{O}_3^{2-}$ in the presence of S^{2-} (1.2×10^{-4} M).

over the pH range 5.7–10.9. On the other hand, the absorbance for thiosulfate in the presence of sulfide was in complete agreement with the absorbance for thiosulfate in the absence of sulfide over the pH range 6.5–10.9. Higher absorbances for thiosulfate below pH 6.5 could be attributed to the incomplete transference of thiosulfate into the filtrate, probably owing to the occlusion of thiosulfate in the precipitate. The maximum determinable amount (1.2 μmol) of sulfide was completely removed by adding 1 to 5 drops of the above-mentioned suspension. As stated above, the reactions of sulfite and sulfide with iodine could be prevented over the pH ranges of 5.6–8.6 and 6.5–10.9, respectively. Therefore, we could obtain the absorbance for thiosulfate in the presence of sulfite and sulfide by Procedure III, where the solution was buffered at the pH range 6.5–8.6 after the addition of the suspension.

Determination of sulfide, sulfite and thiosulfate in their mixture

The three sulfur species in their mixture give the following equivalents in three Procedures:

The absorbance obtained by Procedure I corresponds to the sum of twice the sulfide (see Eq. 2) and sulfite (Eq. 3), and the thiosulfate (Eq. 1) in the mixture. The absorbance obtained by Procedure II, where sulfite was masked by formaldehyde, corresponds to the sum of the thiosulfate and twice the sulfide in the mixture. The absorbance obtained by Procedure III corresponds to only the amount of the thiosulfate in the mixture solution, because sulfite was masked by formaldehyde and sulfide was eliminated by the suspension of zinc carbonate hydroxide. Moreover, the calibration graphs for sulfide, sulfite and thiosulfate

Table 1 Determination of each sulfur species in 10-ml mixture solution of sulfide, sulfite and thiosulfate

Taken/ μmol			Found/ μmol		
S^{2-}	SO_3^{2-}	$\text{S}_2\text{O}_3^{2-}$	S^{2-}	SO_3^{2-}	$\text{S}_2\text{O}_3^{2-}$
0.35	0.50		0.35	0.51	
0.80	0.20		0.80	0.21	
	0.80	0.40		0.81	0.39
	0.40	1.00		0.40	1.00
0.70		0.50	0.72		0.50
0.60		0.90	0.61		0.90
0.50	0.40	0.30	0.52	0.40	0.28
0.25	0.25	0.50	0.25	0.24	0.51
0.30	0.45	0.65	0.30	0.46	0.64
0.40	0.40	0.40	0.40	0.41	0.30

were in complete agreement with one another when plotted in terms of equivalent concentrations. The following equations can thus be obtained: $[\text{S}^{2-}] = (\text{II} - \text{III})/2$, $[\text{SO}_3^{2-}] = (\text{I} - \text{II})/2$ and $[\text{S}_2\text{O}_3^{2-}] = \text{III}$, where I, II and III denote the molar concentration of thiosulfate which was determined from the calibration graph for thiosulfate in Fig. 1 using the absorbance obtained by Procedures I, II and III, respectively. Table 1 shows that the present method can be successfully applied to the determination of sulfide, sulfite and thiosulfate mixed in various ratios with an error below $\pm 0.02 \mu\text{mol}$.

The precision was obtained from six results for three 10-ml aliquots of sample solution containing 0.4 μmol of each species of sulfide, sulfite and thiosulfate. The method gave a mean value of 0.4 μmol with a standard deviation of 0.01 μmol and a relative standard deviation of 2.5% for sulfide, 0.41 μmol with 0.0063 and 1.5% for sulfite, and 0.39 μmol with 0.013 and 3.2% for thiosulfate.

Effect of diverse ions

Three aliquots (10 ml) of solution containing various amounts of foreign ions and 0.4 μmol of sulfide, sulfite and thiosulfate respectively were treated according to Procedures I, II and III. The amounts of diverse ions that caused errors below 5% are listed in Table 2 except Cu(II) and Fe(III). The interference of Mn(II) was due to the incomplete masking of sulfite in its presence under the conditions given in Procedure II. All the other ions could be tolerated in amounts of about 1000 ppm.

Table 2 Effect of diverse ions on the determinations of 0.4 μmol of sulfide, sulfite and thiosulfate in 10-ml mixture solution

Ion	Added as ^a	Conc, ppm	Found/ μmol		
			S^{2-}	SO_3^{2-}	$\text{S}_2\text{O}_3^{2-}$
Na^+	Na_2SO_4	1000	0.41	0.38	0.41
K^+	K_2SO_4	1000	0.42	0.38	0.40
NH_4^+	NH_4NO_3	1000	0.41	0.39	0.41
Mg^{2+}	$\text{Mg}(\text{NO}_3)_2$	1000	0.41	0.39	0.39
Ca^{2+}	$\text{Ca}(\text{NO}_3)_2$	1000	0.42	0.38	0.39
Zn^{2+}	ZnSO_4	1000	0.41	0.39	0.40
Cd^{2+}	CdSO_4	1000	0.41	0.39	0.39
Mn^{2+}	MnSO_4	1	0.41	0.38	0.41
Cu^{2+}	CuSO_4	1	0.30	0.39	0.42
Pb^{2+}	$\text{Pb}(\text{NO}_3)_2$	10	0.40	0.40	0.40
Fe^{3+}	$\text{Fe}(\text{NO}_3)_3$	10	0.42	0.32	0.41
Al^{3+}	$\text{Al}(\text{NO}_3)_3$	100	0.42	0.39	0.38
F^-	NaF	1000	0.42	0.38	0.39
Cl^-	NaCl	1000	0.40	0.38	0.42
Br^-	KBr	1000	0.41	0.38	0.40
I^-	KI	1000	0.42	0.38	0.39
NO_3^-	NaNO_3	1000	0.41	0.38	0.40
HCO_3^-	NaHCO_3	1000	0.42	0.38	0.40
SO_4^{2-}	Na_2SO_4	1000	0.41	0.38	0.41
H_2PO_4^-	NaH_2PO_4	1000	0.39	0.39	0.42
HAsO_4^{2-}	Na_2HAsO_4	1000	0.42	0.38	0.40

a. Water of hydration was omitted for brevity.

Table 3 Determination of sulfide, sulfite and thiosulfate in 10-ml sample solution of fumarolic condensates

Sample	S ²⁻ / μmol	SO ₃ ²⁻ / μmol	S ₂ O ₃ ²⁻ / μmol
A	7.12	314	1.96
B	ND ^a	0.06	0.36
C	0.07	0.12	0.52
D	7.58	44.1	0.64

a. ND means "not detected".

Determination of sulfide, sulfite and thiosulfate in fumarolic condensates

The present method was applied to the determination of sulfide, sulfite and thiosulfate in several fumarolic condensates. The results are shown in Table 3. Acetate buffers and maleate buffers of various pH and ammonia were used to adjust pH of the sample solutions to the optimal pH ranges in Procedures I, II and III. The amounts of formaldehyde used to mask the sulfite in samples A and D were much more than those in the recommended Procedures II and III. Table 3 shows that the present method is applicable to the determination of sulfide, sulfite and thiosulfate in various amounts in fumarolic condensates.

We wish to express our thanks to Dr. Minoru Yoshida of Tokyo Institute of Technology for supplying the fumarolic condensate samples.

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(Received August 21, 1987)

(Accepted October 7, 1987)