Sulfidolysis of Tetrathionate and Spectrophotometric Determination of Tetrathionate, Thiosulfate and Sulfide in Their Mixtures

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A spectrophotometric method has been developed for the determination of tetrathionate, thiosulfate and sulfide in mixtures. The conditions for tetrathionate to be stoichiometrically converted to thiosulfate were established by varying reaction time, reaction temperature, pH and amount of sulfide. The present method consists of three procedures: I, II and III. The absorbance obtained by Procedure I corresponds to the sum of the thiosulfate and twice the tetrathionate in the mixture. The absorbance obtained by Procedure II, where tetrathionate was not sulfidolyzed and sulfide was removed, corresponds to the amount of thiosulfate only. The absorbance obtained by Procedure III corresponds to the sum of the amount of thiosulfate and twice that of sulfide. The method is applicable to the determination of tetrathionate, thiosulfate and sulfide in amounts more than 0.1 μmol and gave a relative standard deviation of 1.2% at 1 μmol level of tetrathionate in the presence of 1 μmol of sulfide and 2 μmol of thiosulfate.

Keywords Tetrathionate sulfidolysis, sulfur anions determination, tetrathionate-thiosulfate-sulfide mixture, spectrophotometry

Polythionates have been detected in metallurgical effluents as a result of incomplete oxidation of metal sulfides.¹ They are also formed with other sulfur species in Wackenroder's solution obtained by passing hydrogen sulfide into a solution of sulfite.² From the standpoint of sulfur chemistry, there is a growing interest in accurate determination of polythionates in mixture with the other sulfur species. Numerous methods have been proposed for the determination of polythionates in their mixture with the other sulfur compounds. These methods are based on the cyanolysis³⁻⁶ and sulfitolysis⁷⁻⁹ and sulfidolysis¹⁰ of polythionates to form thiocyanate and/or thiosulfate, which is spectrophotometrically measured. However, no consideration has been given to the sulfidolysis of tetrathionate, followed by the spectrophotometry of the thiosulfate formed for the determination of tetrathionate in mixture with the other sulfur species.

In the present study, the following reaction:

was investigated in detail, and the conditions under which tetrathionate is stoichiometrically converted to thiosulfate were established. The present method is based on the formation of thiosulfate equivalent to tetrathionate and on the spectrophotometric measure-

ment of excess iodine for the reaction of the iodine with the thiosulfate formed. A procedure for the determination of tetrathionate, thiosulfate and sulfide in a mixture is also described.

Experimental

Apparatus and reagents

All spectrophotometric measurements were made with a Shimadzu Model QV-50 spectrophotometer with 10-mm quartz cells. Desired temperatures were controlled by a Taiyo Coolnit Model CL-15 thermoregulator. pH was measured with a Hitachi-Horiba Model M-7 pH meter.

All chemicals used, except tetrathionate, were of analytical grade and were used without further purification. The water used in the present experiment was redistilled. Potassium tetrathionate was prepared by the reaction of sulfurous acid with sulfur monochloride (disulfur dichloride).¹¹ The tetrathionate obtained was further recrystallized with water at temperatures below 60°C and then dried at room temperature before storage at $-10 \pm 2^\circ\text{C}$. A standard tetrathionate solution (1×10^{-3} M) was prepared by dissolving 151.3 mg of the potassium tetrathionate (water content: 0.07%) in water and diluting it to 500 ml; then it was

stored at $5 \pm 2^\circ\text{C}$. A stock solution of thiosulfate 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 iodimetry² a week after preparation. Working standard thiosulfate solutions were prepared by suitable dilution. These standards were used to ascertain the stoichiometry and completion of the reaction of tetrathionate with sulfide. The sulfide solution (0.02 M) used for sulfidolysis of tetrathionate was prepared by dissolving 1 g of sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), whose surface was washed with oxygen-free water (the water on the solid sulfide was removed by absorption with filter paper), in water which was being continuously deaerated with nitrogen gas, and diluting the solution to 200 ml. This sulfide solution was not standardized but was prepared every time just before use, and the passing of nitrogen gas continued throughout the experiments. A 0.05 M standard sulfide solution prepared as described above was standardized by iodimetry¹², and working standard sulfide solutions were obtained by suitable 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 iodate-iodide solution was prepared by adding 50.0 ml of 1.00×10^{-2} N ($=1.67 \times 10^{-3}$ M) standard iodate solution to a solution containing 0.2 g of sodium carbonate and 72.6 g of potassium iodide (99.5%), and diluting this mixture to 500 ml to give a 1.00×10^{-3} N iodate and 0.87 M iodide.

Buffer solutions required for adjusting the pH of reaction solutions were prepared by the mixing of acetic acid (0.2 M) and sodium acetate (0.2 M) solutions, sodium hydrogenmaleate (0.2 M) and sodium maleate (0.2 M) solutions, and ammonium nitrate (0.2 M) and ammonia (0.2 M) solutions, respectively, in various volume ratios. In addition, acetic acid, ammonia, sodium carbonate and sodium hydroxide solutions of various concentrations were also used for the adjustment of pH. The buffer solutions of pH 6.9 used in Procedure I and pH 6.2 in Procedures II and III were prepared by mixing 20 ml of 0.2 M sodium hydrogenmaleate solution with 200 ml of 0.2 M sodium maleate solution, and 100 ml of 0.2 M sodium hydrogenmaleate solution with 200 ml of 0.2 M sodium maleate solution. A suspension of zinc carbonate hydroxide was prepared by mixing 5% (w/v) zinc acetate and 7.5% (w/v) sodium carbonate solutions in equal volume ratio immediately before use.

Procedure

The procedures for the determination of tetrathionate, thiosulfate and sulfide in a mixture are as follows.

Procedure I. For total amounts of tetrathionate and thiosulfate in the mixture. Pipette 2.5 ml of the maleate buffer solution (pH 6.9) and a 10-ml aliquot of sample solution containing tetrathionate, thiosulfate and sulfide into a 50-ml beaker, and allow the beaker

to stand in a thermostat at 10°C for at least 15 min. To this mixture, add 1 ml of the 0.02 M sodium sulfide solution maintained at a temperature of 10°C ; the solution is thereby brought to pH 7.5. Allow the mixture to stand at 10°C for 20 min, to convert tetrathionate completely into thiosulfate. Then add 1.1 ml of 0.2 M acetic acid and 1 ml of the zinc carbonate hydroxide suspension; this solution is buffered at pH 7.2, and an excess of sulfide is completely precipitated. Filter off the precipitate through Toyo No. 6 filter paper, wash it thoroughly with water, and transfer the filtrate and washings to a 50-ml volumetric flask. To this mixture, add 5 ml of 5 M acetic acid and 4.8 ml of the standard 1.00×10^{-3} N iodate-0.87 M iodide solution, then fill the flask to the mark with water. Mix the contents well, and measure the absorbance of a solution of iodine-iodide complex against water at 350 nm of maximum absorption for triiodide ion.

Procedure II. For amount of thiosulfate in the mixture. Pipette 1 ml of the maleate buffer (pH 6.2), 3 drops of the zinc carbonate hydroxide suspension, and a 10-ml aliquot of sample solution to a 50-ml beaker. Then filter off the precipitate through Toyo No. 6 filter paper, wash it with water, and transfer the filtrate and washings to a 50-ml volumetric flask.

Procedure III. For total amount of thiosulfate and sulfide in the mixture. Pipette 1 ml of the maleate buffer (pH 6.2), 3 drops of the zinc carbonate hydroxide suspension and a 10-ml aliquot of sample solution to a 50-ml volumetric flask.

To these two solutions from Procedures II and III, add 2 ml of 2 M acetic acid and 4.8 ml of the standard 1.00×10^{-3} N iodate-0.87 M iodide solution, then fill the flask to the mark with water. Mix the contents of the flask, and measure the absorbance of the solution against water at 350 nm. In Procedure III, it is necessary to add the standard iodate-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 tetrathionate and thiosulfate were treated as in Procedure I. According to Eq. (1), when 1 mol of tetrathionate undergoes sulfidolysis, 2 mol of thiosulfate are formed. Therefore, if tetrathionate is converted to thiosulfate stoichiometrically, the calibration graph of tetrathionate should coincide with that of thiosulfate when the molar concentration scale for tetrathionate is drawn to twice the scale for thiosulfate concentration. Figure 1 proves that tetrathionate was quantitatively converted to thiosulfate according to Eq. (1). The calibration graph of thiosulfate obtained by Procedure I was also in complete agreement with that of thiosulfate obtained by both Procedures II and III. Under the conditions of

Fig. 1 Calibration graphs for tetrathionate and thiosulfate obtained by Procedure I. ○, $S_4O_6^{2-}$; ◻, $S_2O_3^{2-}$.

Procedure III, the calibration graph of sulfide accorded with that of thiosulfate, even in the presence of tetrathionate when the molar concentration scale for sulfide is drawn to twice the scale for thiosulfate concentration. These experimental facts reveal that tetrathionate, thiosulfate and sulfide in a mixture can be individually determined by solving simultaneous equations derived from Procedures I, II and III.

Effect of temperature and pH on the sulfidolysis of tetrathionate

The polysulfide formed by the reaction of sulfide with the free sulfur produced by the sulfidolysis of tetrathionate might undergo air-oxidation to form thiosulfate at higher temperatures than 15°C; tetrathionate gave absorbances in accord with the expected value when sulfidolyzed at 5, 10 and 15°C, but gave lower absorbances at 20 and 25°C. The reaction rate of tetrathionate with sulfide was therefore investigated at 10°C and at various pH values ranging from 6.6 to 9.5. The absorbance for 2×10^{-4} M tetrathionate reached that for 4×10^{-4} M thiosulfate, which is the expected value, in 30 min at pH 6.6, in 20 min at pH 7.0 and in 10 min at pH both 7.5 and 9.5, and then remained constant over different intervals of time. Lower absorbance then ensued, due to the thiosulfate formed by the air-oxidation of polysulfide.

In order to establish the optimum pH range for the sulfidolysis, tetrathionate was allowed to react with sulfide for 20 min at 10°C and at various pH values. There were no measurable changes in the reagent blank over the pH range of 5.5–10.5. Figure 2 shows that tetrathionate was stoichiometrically converted to thiosulfate according to Eq. (1) over the pH range of 7.0–9.5. The decrease in absorbance above pH 9.5 could be attributed to the formation of thiosulfate by the air-

Fig. 2 Effect of pH on the sulfidolysis of tetrathionate. The conditions except pH are as described in Procedure I. ○, reagent blank; ◐, 2×10^{-4} M $S_4O_6^{2-}$; ◑, 4×10^{-4} M $S_2O_3^{2-}$ in the absence of sulfide.

oxidation of polysulfide.

Effect of amount of sulfide

In measuring the effect of amount of sodium sulfide on the sulfidolysis of tetrathionate, various amounts of the 0.02 M sodium sulfide solution ranging from 0.3 to 1.5 ml were used. In all cases, tetrathionate (2 μmol) was allowed to react with sulfide in the solutions buffered to a pH of 7.0–9.5 for 20 min at 10°C. The results show that the reaction did not go to stoichiometric completion with 0.3 to 0.6 ml of 0.02 M sulfide solution because of the shortage of its amount. But when 0.8 to 1.5 ml of 0.02 M sulfide solution were used, the absorbances for tetrathionate were in full agreement with the expected value obtained for thiosulfate. Therefore, 1 ml of 0.02 M sodium sulfide was used in Procedure I.

Removal of sulfide

The excess sulfide used for the sulfidolysis of tetrathionate must be eliminated completely, because it consumes iodine. An attempt was made to precipitate the sulfide with freshly precipitated zinc carbonate hydroxide and to filter off the precipitate through filter paper. Figure 3 shows how the sulfide could be removed by varying the pH of the mixture solution. The reagent blank gave constant absorbances over the pH range of 4.0–11.9; excess sulfide was completely removed within this pH range. On the other hand, the absorbance for tetrathionate reached the expected value over the pH range of 5.5–8.9, and the absorbance for thiosulfate over the pH range of 5.5–11.9. Consequently, the pH of the mixture solution was adjusted to 7.2 in Procedure I. Higher absorbances for both tetrathionate and thiosulfate below pH 5.5 could

Fig. 3 Effect of pH on the removal of excess sulfide with zinc carbonate hydroxide suspension. The conditions except pH are as described in Procedure I. $\circ$, reagent blank; $\odot$, 2×10^{-4} M $S_4O_6^{2-}$; $\ominus$, 4×10^{-4} M $S_2O_3^{2-}$; $\bullet$, 4×10^{-4} M $S_2O_3^{2-}$ in the absence of sulfide (expected value).

Fig. 4 Effect of pH on the removal of sulfide fixed by zinc carbonate hydroxide. The conditions except pH are as described in Procedure II. $\circ$, 2.4×10^{-4} M S^{2-} in the absence of tetrathionate; $\odot$, 4×10^{-4} M $S_2O_3^{2-}$ in the presence of sulfide and tetrathionate of 2.4×10^{-4} M; $\bullet$, 4×10^{-4} M $S_2O_3^{2-}$ in the absence of sulfur species (expected value).

be attributed to the incomplete transference of thiosulfate into the filtrate because the precipitate is gelatinous at the lower pH range. Lower absorbances for tetrathionate above pH 8.9 are due to the thiosulfate formed by the air-oxidation of polysulfide. In measuring the effect of the amount of the zinc carbonate hydroxide suspension on the removal of the excess of sulfide, various volumes of the suspension prepared by mixing 5% (w/v) zinc acetate and 7.5% (w/v) sodium carbonate solutions in equal volume ratio were added, and the mixture solutions were buffered to pH 5.5–8.9, which is the optimum range for the elimination of sulfide. The excess sulfide was completely removed when 0.4 to 1.5 ml of the suspension were used.

In Procedure II, where the sulfidolysis of tetrathionate is not carried out, the sulfide ions in sample solution must be removed before they react with tetrathionate. The sulfide fixed by addition of 3 drops of the suspension in Procedure II was found to be stable for 2 h even in the presence of tetrathionate at pH values between 7.0 and 8.3. The sulfide could be completely removed by filtration over the pH range of 5.6–11.3 in the absence of tetrathionate (symbol $\circ$ in Fig. 4), and over the pH range of 6.6–9.2 in its presence (symbol $\odot$ in Fig. 4), respectively. It was therefore concluded that the amount of thiosulfate in the mixture with sulfide and tetrathionate can be determined by Procedure II without any time-dependent change in chemical composition of sample over the pH range of 6.6–9.2. The decrease in absorbance for thiosulfate above pH 9.2 (symbol $\ominus$ in Fig. 4) is probably due to the thiosulfate formed by the sulfidolysis of tetrathionate as well as its alkaline decomposition.¹³

Effect of amount of acetic acid

Iodine–iodide complex is formed in an acid medium

from an iodate–iodide mixture. Experimental results showed that 3 to 7 ml of 5 M acetic acid were sufficient for the complete liberation of iodine in Procedure I. In Procedures II and III, the absorbance remained constant over the volume range of 1–3 ml of 2 M acetic acid. When more amounts of acetic acid were added in Procedure III, the absorbance for sulfide increased due to the evolution of hydrogen sulfide. In Procedure III, it is necessary to add the standard iodate–iodide solution immediately after the addition of acetic acid.

Determination of tetrathionate, thiosulfate and sulfide in a mixture

These three sulfur species in the mixture give the following equivalents in the three procedures:

The absorbance obtained by Procedure I corresponds to the sum of the thiosulfate and twice the tetrathionate (see Eq. (1)) in the mixture, sulfide being removed by the addition of the zinc carbonate hydroxide suspension. The absorbance obtained by Procedure II, where sulfidolysis of tetrathionate was not carried out, corresponds to the amount of thiosulfate in the mixture only. The absorbance obtained by Procedure III corresponds to the sum of the thiosulfate and twice the sulfide in the mixture. Moreover, the calibration graphs for tetrathionate, thiosulfate and sulfide were in full agreement when plotted in terms of equivalent concentrations. The following equations can thus be obtained: $[S_4O_6^{2-}] = (I - II)/2$, $[S_2O_3^{2-}] = II$, and $[S^{2-}] = (III - II)/2$, where I, II and III denote the molar concentration of thiosulfate which was determined

Table 1 Determination of tetrathionate, thiosulfate and sulfide mixed in various ratios in 100-ml solution

Taken/ μmol			Found/ μmol		
$\text{S}_4\text{O}_6^{2-}$	$\text{S}_2\text{O}_3^{2-}$	S^{2-}	$\text{S}_4\text{O}_6^{2-}$	$\text{S}_2\text{O}_3^{2-}$	S^{2-}
1.50	0.70	1.70	1.51	0.71	1.72
1.50	0.75	1.40	1.50	0.75	1.41
1.30	0.50	1.80	1.32	0.51	1.79
1.10	1.00	0.60	1.08	0.99	0.62
0.70	0.30	1.00	0.71	0.32	0.98

Table 2 Effect of foreign ions

Ion	Added as ^a	Concn, ppm	Absorbance	
			Reagent blank	$1.2 \times 10^{-4} \text{ M } \text{S}_4\text{O}_6^{2-}$
none			1.220	0.608
Na^+	Na_2SO_4	1000	1.219	0.610
K^+	K_2SO_4	1000	1.219	0.605
NH_4^+	NH_4Cl	1000	1.218	0.611
Ca^{2+}	CaCl_2	1000	1.220	0.610
Ba^{2+}	BaCl_2	1000	1.219	0.604
Mg^{2+}	MgSO_4	1000	1.219	0.610
Zn^{2+}	ZnSO_4	100	1.220	0.615
Pb^{2+}	$\text{Pb}(\text{CH}_3\text{COO})_2$	50	1.208	0.550
Cu^{2+}	CuSO_4	5	1.172	0.550
Cd^{2+}	$\text{Cd}(\text{CH}_3\text{COO})_2$	5	1.218	0.531
Mn^{2+}	MnSO_4	5	1.020	0.395
Fe^{2+}	FeSO_4	5	1.178	0.554
Fe^{3+}	$\text{Fe}_2(\text{SO}_4)_3$	5	1.177	0.578
Al^{3+}	$\text{Al}_2(\text{SO}_4)_3$	50	1.219	0.686
F^-	NaF	1000	1.218	0.599
Cl^-	KCl	1000	1.221	0.604
Br^-	KBr	1000	1.219	0.612
I^-	KI	1000	1.219	0.610
NO_3^-	KNO_3	1000	1.218	0.610
SO_4^{2-}	Na_2SO_4	1000	1.219	0.607
CO_3^{2-}	Na_2CO_3	1000	1.220	0.604
BO_3^{3-}	H_3BO_3	1000	1.219	0.607
PO_4^{3-}	Na_3PO_4	100	1.187	0.566
HAsO_4^{2-}	Na_2HAsO_4	100	1.183	0.587

a. Water of hydration is omitted for brevity.

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 tetrathionate, thiosulfate and sulfide mixed in various ratios with an error below $\pm 0.02 \mu\text{mol}$.

The precision was obtained from six repeated determinations by the procedures I, II and III for

sample solution containing $1 \mu\text{mol}$ of tetrathionate, $2 \mu\text{mol}$ of thiosulfate and $1 \mu\text{mol}$ of sulfide. The present method gave a mean value of $1.00 \mu\text{mol}$ with a standard deviation of $0.012 \mu\text{mol}$ and a relative standard deviation of 1.2% for tetrathionate, $2.00 \mu\text{mol}$ with 0.013 and 0.67% for thiosulfate, and $1.01 \mu\text{mol}$ with 0.006 and 0.59% for sulfide.

Effect of diverse ions

A 10-ml aliquot containing various amounts of diverse ions, both in the presence of tetrathionate ($1.2 \times 10^{-4} \text{ M}$) and in its absence, was treated according to Procedure I. The results are given in Table 2. Heavy metal ions such as lead(II), copper(II), cadmium(II), manganese(II), iron(II) and iron(III) interfered, in small amounts, with the determination of tetrathionate presumably because their colloidal sulfides could pass through the filter paper. The negative errors in absorbance in the presence of phosphate and arsenate were due to an incomplete removal of the excess sulfide, owing to the shortage of zinc caused by precipitation of its phosphate and arsenate. About 1000 ppm of almost all the other ions listed in Table 2 could be tolerated.

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