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Spectrophotometric Determination of Thiosulfate Based on an Oxidation Reaction in the Presence of Formaldehyde with Iodine in the Organic Phase

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Aqueous thiosulfate was shaken in the presence of large amounts of sulfuric acid and formaldehyde with iodine in carbon tetrachloride; thereby, one mol of thiosulfate reacted with one mol of iodine. The organic phase was separated, the excess of iodine was extracted into an aqueous iodide solution as triiodide and the absorbance of the liberated triiodide was measured at 350 nm. The calibration plot obtained for thiosulfate did not form a linear graph and was not affected by a change in the volume of 10 to 27 cm^3 of the sample solution. The proposed method could be applied to the determination of thiosulfate in the concentration ranges 5×10^{-7}—3.4×10^{-5} mol dm^{-3} (0.056—3.81 ppm) for a 10 cm^3 thiosulfate solution and 1.9×10^{-7}—1.36×10^{-5} mol dm^{-3} (0.021—1.52 ppm) for a 25 cm^3 thiosulfate solution. Good recoveries of thiosulfate from hot-spring and lake-water samples, to which various known amounts of thiosulfate had been added, was achieved and the relative standard deviation was 0.86% at the 5.42×10^{-6} mol dm^{-3} (0.608 ppm) thiosulfate level when applied to a hot-spring sample.

It has been stated that iodate can be used as an excellent primary standard for iodine,[1)] because a mixture solution of standard iodate and an excess amount of iodide is extremely stable and produces iodine equivalent to the iodate, by the addition of acid, according to the following equation:

$$\mathrm{IO_3^- + 8I^- + 6H^+ \longrightarrow 3I_3^- + 3H_2O.} \qquad (1)$$

Further, the molar absorptivity of triiodide at 350 nm is much higher than that of iodine in carbon tetrachloride at 515 nm.[2)] Ozawa[3)] has proposed an excellent method for the determination of thiosulfate, based on the reaction of thiosulfate with the iodine produced from the mixture of standard iodate and iodide,

$$\mathrm{2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-,} \qquad (2)$$

followed by a spectrophotometric measurement of the excess amount of iodine (as triiodide). This method has been extensively used for the determination of polythionates, in which the thiosulfate formed from the polythionates by their cyanolysis,[4)] sulfitolysis,[5—7)] alkalinolysis,[8,9)] and sulfidolysis[10—12)] was measured.

It is well known that thiosulfate is decomposed into sulfite and free sulfur in a strong acid medium and that sulfite reacts with formaldehyde to form formaldehyde hydrogensulfite:

$$\mathrm{S_2O_3^{2-} + 2H^+ \longrightarrow H_2SO_3 + S} \qquad (3)$$

$$\mathrm{SO_3^{2-} + HCHO + H^+ \longrightarrow HCHO{\cdot}HSO_3^-.} \qquad (4)$$

The thiosulfate in a strong acid medium is therefore supposed to react with formaldehyde to yield an adduct according to the following equation:

$$\mathrm{S_2O_3^{2-} + 2H^+ + HCHO \longrightarrow HCHO{\cdot}HSO_3H + S.} \qquad (5)$$

When the adduct is oxidized by iodine, the reaction is

$$\mathrm{HCHO{\cdot}HSO_3H + I_2 + H_2O \longrightarrow SO_4^{2-} + HCHO + 2I^- + 4H^+,} \qquad (6)$$

and the overall reaction of Eqs. 5 and 6 is as follows:

$$\mathrm{S_2O_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + S + 2I^- + 2H^+.} \qquad (7)$$

In this work, a new reaction has been found: thiosulfate reacts with iodine in carbon tetrachloride in the presence of large amounts of sulfuric acid and formaldehyde according to Eq. 7. The excess iodine in the carbon tetrachloride is extracted into an aqueous iodide solution as triiodide, and the formed triiodide is measured spectrophotometrically at 350 nm with reference to the determination of thiosulfate. The proposed method has advantages over the former method[3)] in terms of sensitivity and selectivity, and has been successfully applied to the determination of thiosulfate in hot-spring and lake-water samples.

Experimental

Reagents and Apparatus. All of the reagents used were of analytical-reagent grade and were used without further purification. Doubly distilled water was used in all of the experiments. An approximately 0.1 mol dm^{-3} thiosulfate solution was prepared by dissolving sodium thiosulfate pentahydrate in oxygen-free water containing a small amount of sodium carbonate (0.01% w/v) as a stabilizer. This solution was standardized by iodimetry 1 week after preparation. Working standard thiosulfate solutions (in 0.01% w/v Na_2CO_3) were prepared by appropriate dilution with oxygen-free water. An approximately 0.05 mol dm^{-3} iodine solution was prepared by dissolving a known amount of iodine in carbon tetrachloride. This 10 cm^3 solution was pipetted into a 200 cm^3 conical beaker containing 10 cm^3 of water, and then standardized against a standard thiosulfate solution by iodimetry, in which the beaker was shaken during the titration and the disappearance of the purple color due to iodine in the organic phase was taken to be the endpoint of the titration. Working standards were prepared by suitable dilution with carbon tetrachloride. Standard solutions of 5×10^{-2} and 8.5×10^{-5} mol dm^{-3} iodine in carbon tetrachloride were stable for up to 2 weeks and 1 week, respectively, after preparation.

A Shimadzu Model UV-160A recording spectrophotometer with 10 mm quartz cells was used for all of the absorbance measurements. An Iwaki Model KM shaker was used to encourage both the reaction of iodine with thiosulfate in the presence of sulfuric acid and formaldehyde in the two different phases and the extraction of the iodine in carbon tetrachloride into the aqueous phase as triiodide.

Procedure. Pipette a 10 cm^3 sample solution containing up to 3.4×10^{-5} mol dm^{-3} thiosulfate, 1 cm^3 of 2 mol dm^{-3} sulfuric acid (1 cm^3 of 4.5 mol dm^{-3} sulfuric acid for a 25 cm^3 sample solution) and 2.5 cm^3 of 37% commercial formaldehyde into a 50 cm^3 separating funnel. For samples containing sulfite and sulfide, purge the mixture with nitrogen gas at a flow-rate of 400 cm^3 min^{-1} for 20 min[13] after the addition of the sulfuric acid, in order to completely remove the sulfite and sulfide. Then add 4 cm^3 of 8.5×10^{-5} mol dm^{-3} iodine in carbon tetrachloride and shake the funnel for 4 min to allow the iodine to react with the thiosulfate in the aqueous phase. Transfer the organic phase into another 50 cm^3 separating funnel and add 5 cm^3 of 1 mol dm^{-3} potassium iodide (in 0.04% w/v Na_2CO_3). After introducing nitrogen gas into the funnel for 2 min to displace the air, add 3 cm^3 of 1.2 mol dm^{-3} acetic acid and shake the funnel for 1 min to extract the excess iodine into the aqueous phase as triiodide. Measure the absorbance of the solution of triiodide against water at 350 nm using 10 mm quartz cells. An iodine-free reagent blank was subtracted from all of the absorbances measured in Procedure.

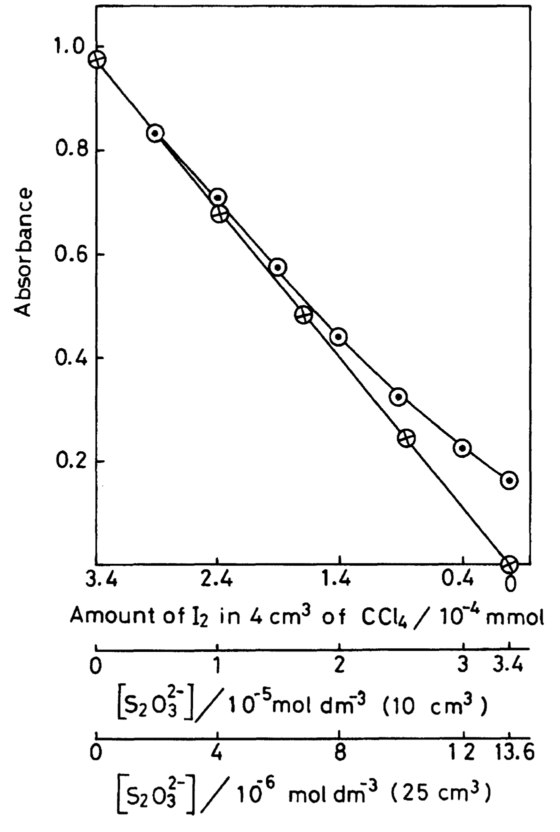

Fig. 1. Calibration graphs for thiosulfate and iodine. ⊙, $S_2O_3^{2-}$ in a 10 or 25 cm^3 solution; ⊗, I_2 (expected) by using a 10 or 25 cm^3 water.

Results and Discussion

Calibration Graphs. A series of standard solutions of thiosulfate were treated as described in Procedure. After the complete reaction of thiosulfate with the iodine in carbon tetrachloride, the excess iodine was extracted into an aqueous iodide solution, and the formed triiodide was measured spectrophotometrically. Hence, if the reaction proceeds to stoichiometric completion according to Eq. 7, the calibration graph for thiosulfate should coincide with that obtained for iodine by using a series of standard solutions (4 cm^3 carbon tetrachloride solution) of iodine and 10 cm^3 water (in place of 10 cm^3 thiosulfate solution) in Procedure. In this instance, the amount scale for iodine is drawn in a way that is opposite from the scale for the thiosulfate concentration, as shown in Fig. 1. The calibration graph for thiosulfate accorded well with that for iodine (expected graph) up to 5×10^{-5} mmol thiosulfate and then gradually and positively deviated from the linear graph of iodine. These experimental results show that, under the conditions of Procedure, the reaction of thiosulfate with iodine in carbon tetrachloride did not proceed to stoichiometric completion according to Eq. 7 over the entire thiosulfate concentration range. The calibration graph for thiosulfate was not affected by a change in the volume of 10 to 27 cm^3 of the sample solution. The proposed method could be applied to the determination of thiosulfate in the concentration ranges 5×10^{-7}—3.4×10^{-5} mol dm^{-3} (0.056—3.81 ppm) for a 10 cm^3 thiosulfate solution and 1.9×10^{-7}—1.36×10^{-5} mol dm^{-3} (0.021—1.52 ppm) for a 25 cm^3 thiosulfate solution. The precision was ascertained from 11 results obtained for a 10 cm^3 aliquot of a 1.7×10^{-5} mol dm^{-3} standard thiosulfate solution (19.1 µg of $S_2O_3^{2-}$); the mean value of thiosulfate was found to be 19.0 µg, with a standard deviation of 0.14 µg of $S_2O_3^{2-}$ and a relative standard deviation of 0.74%.

Effect of the Amounts of Sulfuric Acid and Formaldehyde on the Reaction of Thiosulfate with Iodine in Carbon Tetrachloride. In order to prevent iodine in carbon tetrachloride from transferring into an aqueous phase as the result of iodine hydrolysis, a strong acid of sulfuric acid[13] had to be added to the aqueous phase. Further, sulfuric acid proved to participate directly in the reaction of Eq. 7. With a small amount of sulfuric acid, the reagent blank increased slightly and the absorbance for thiosulfate decreased; then, both of them remained constant over the concentration range of 0.037 to 0.37 mol dm^{-3} sulfuric acid. Hence, 1 cm^3 of 2 mol dm^{-3} sulfuric acid was added to a 10 cm^3 sample solution to give a 0.15 mol dm^{-3} sulfuric acid solution in Procedure.

Table 1. Volume Effect of Organic Phase Containing Iodine on Its Reaction with Thiosulfate in a 10 cm^3 Aqueous Solution

Volume of organic phase/cm^3	$[I_2]/10^{-5}$ mol dm^{-3}	Reagent blank	Absorbance$^{a)}$ expected	Absorbance for 5×10^{-6} mol dm^{-3} $S_2O_3^{2-}$	$[I_2]/[S_2O_3^{2-}]$	$S_2O_3^{2-}$ reacted, %
4	8.5	0.989	0.843	0.844	17	99.3
4.5	7.6	0.986	0.841	0.856	15.2	98.7
5	6.8	0.975	0.832	0.854	13.6	84.6
7	4.9	0.960	0.818	0.840	9.8	84.5
10	3.4	0.925	0.788	0.811	6.8	83.2
20	1.7	0.820	0.702	0.724	3.4	81.4

a) Read out from the calibration graphs obtained for iodine by using a series of standard iodine in each volume of organic phase.

Table 2. Extraction of Iodine in Organic Phase into Aqueous Phase

Shaking time	Absorbance					
	Under the atmosphere			Under an atmosphere of nitrogen		
min	5 mmol of I^-	$I_2^{a)}$ plus 5 mmol of I^-	$IO_3^{-b)}$ plus 5 mmol of I^-	5 mmol of I^-	$I_2^{a)}$ plus 5 mmol of I^-	$IO_3^{-b)}$ plus 5 mmol of I^-
0.5	0.024	1.118	1.116	0.005	1.106	1.104
1	0.029	1.119	1.117	0.006	1.104	1.104
1.5	0.030	1.122	1.121	0.006	1.106	1.102
2	0.030	1.129	1.129	0.007	1.106	1.103
3	0.032	1.150	1.149	0.009	1.105	1.103

a) 3.4×10^{-4} mmol I_2 (against 5 mmol of I^-). b) 1.13×10^{-4} mmol IO_3^- (against 5 mmol of I^-).

It is well known that thiosulfate is oxidized by iodine to tetrathionate in an acidic medium, according to Eq. 2. In this study, a new reaction has been found, in which thiosulfate is oxidized by iodine in carbon tetrachloride, according to Eq. 7, in a medium containing a strong acid comprising sulfuric acid and a large amount of formaldehyde. In determining the optimum amount of formaldehyde required, various volumes of up to 5 cm^3 of 37% commercial formaldehyde were added to a solution containing 10 cm^3 of 1.7×10^{-5} mol dm^{-3} thiosulfate and 1 cm^3 of 2 mol dm^{-3} sulfuric acid in a 50 cm^3 separating funnel. Then, to this mixture 4 cm^3 of 8.5×10^{-5} mol dm^{-3} iodine in carbon tetrachloride was added (4 cm^3 of 4.25×10^{-5} mol dm^{-3} iodine in carbon tetrachloride was added to a solution containing 10 cm^3 of water and 1 cm^3 of 2 mol dm^{-3} sulfuric acid for the expected value); the mixture was then treated as described in Procedure. The results are shown in Fig. 2. The absorbance for thiosulfate decreased upon the addition of formaldehyde, and then remained constant with the addition of 2 to 5 cm^3 of 37% formaldehyde. In contrast, the reagent blank and the absorbance for iodine (expected value) remained constant throughout. Though the absorbance for thiosulfate did not completely coincide with the expected value, the added formaldehyde was found to take part directly in the reaction of Eq. 7. In Procedure 2.5 cm^3 of 37% formaldehyde was used.

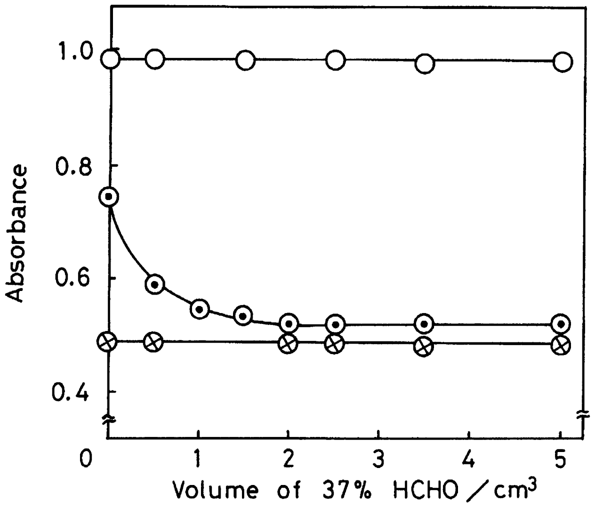

Fig. 2. Effect of the amount of formaldehyde on the reaction of thiosulfate$_{(aq)}$ with iodine$_{(org)}$. A volume of the aqueous phase was adjusted to be 13.5 cm^3. ○, Reagent blank; ⊙, 1.7×10^{-5} mol dm^{-3} $S_2O_3^{2-}$ (10 cm^3); ⊗, expected value (1.7×10^{-4} mmol of iodine in 4 cm^3 carbon tetrachloride).

Volume Effect of Organic Phase Containing Iodine on Its Reaction with Thiosulfate. A preliminary experiment revealed that, the higher was the concentration of iodine, the more completely did the reaction of thiosulfate with the iodine in an organic phase proceed, even though the amount of the iodine used remained unchanged. In order to investigate this effect, an attempt was made to cause 0.05 µmol of $S_2O_3^{2-}$ in 10 cm^3 to react with 0.34 µmol of I_2 in carbon tetrachloride of various volumes under the conditions of Procedure. The results are presented in Table 1. The reagent

Table 3. Effect of Foreign Ions on the Determination of 19.1 μg of Thiosulfate in a 10 cm^3 solution

Ion	Added as[a]	Amount μg	Amount of $S_2O_3^{2-}$ found μg	Error %
None			19.1	
Na^+	Na_2SO_4	10000	19.2	0.5
K^+	K_2SO_4	10000	19.3	1.0
NH_4^+	$(NH_4)_2SO_4$	10000	19.1	0
Mg^{2+}	$MgSO_4$	10000	19.0	−0.5
Ca^{2+}	$Ca(NO_3)_2$	10000	19.1	0
Ba^{2+}	$Ba(NO_3)_2$	10000	19.0	−0.5
Zn^{2+}	$ZnSO_4$	10000	19.0	−0.5
Cd^{2+}	$CdSO_4$	10000	18.6	−2.6
Pb^{2+}	$Pb(NO_3)_2$	10000	19.2	0.5
Mn^{2+}	$MnSO_4$	10000	19.1	0
Fe^{2+}	$Fe(NH_4)_2(SO_4)_2$	10000	18.0	−5.8
		1000	18.6	−2.6
Cu^{2+}	$CuSO_4$	1000	18.4	−3.7
		100	19.2	0.5
Al^{3+}	$Al(NO_3)_3$	10000	18.9	−1.0
Fe^{3+}	$FeNH_4(SO_4)_2$	10000	18.2	−4.7
		1000	18.9	−1.0
F^-	NaF	10000	19.2	0.5
Cl^-	KCl	10000	26.4	38.2
		1000	19.2	0.5
Br^-	KBr	1000	21.8	14.1
		100	19.3	1.0
I^-	KI	100	17.5	−8.4
		10	19.1	0
NO_3^-	KNO_3	10000	19.1	0
NO_2^-	$NaNO_2$	10	16.5	−13.6
		10000[b]	18.7	−2.1
HCO_3^-	$NaHCO_3$	10000	18.7	−2.1
HSO_3^-	$NaHSO_3$	10000[c]	20.6	7.9
		1000[c]	19.6	2.6
SO_4^{2-}	Na_2SO_4	10000	19.3	1.0
$S_3O_6^{2-}$	$K_2S_3O_6$	100	20.6	7.9
		10	19.0	−0.5
$S_4O_6^{2-}$	$K_2S_4O_6$	1000	27.6	44.5
		100	19.1	0
$S_5O_6^{2-}$	$K_2S_5O_6$	1000	21.1	9.9
		100	19.0	−0.5
HPO_4^{2-}	Na_2HPO_4	10000	18.9	−1.0
$HAsO_4^{2-}$	Na_2HAsO_4	10000	18.9	−1.0

a) Water of crystallization is omitted for brevity. b) Nitrite was decomposed by adding 1 cm^3 of 0.5 mol dm^{-3} amidosulfuric acid. c) Nitrogen gas was bubbled through the solution according to Procedure.

blank decreased with an increase in the volume of carbon tetrachloride, because of its capability to dissolve iodine; this led to a low sensitivity for the determination of thiosulfate. Table 1 shows that thiosulfate reacted quantitatively with iodine according to Eq. 7 when the concentration for iodine in the organic phase (4 cm^3) became 17-times the concentration for thiosulfate. The reaction went to a less quantitative completion with an increase in the volume of carbon tetrachloride. In the result, the calibration graph (Fig. 1) obtained for thiosulfate under the conditions of Procedure was curved, and deviated positively with an increase in the concentration for thiosulfate.

The shaking time for facilitating the reaction of thiosulfate with iodine was varied from 0.5 to 10 min, while the other variables were kept constant. These variations in the shaking time gave a great decrease in the absorbance for up to 3 min, and then did not produce any change in the absorbance; thus, a 4-min shaking time was used in this work.

Extraction of Iodine in Organic Phase into Aqueous Phase. An attempt was made to extract the iodine in carbon tetrachloride into the aqueous phase as triiodide using iodide and acetic acid solutions.

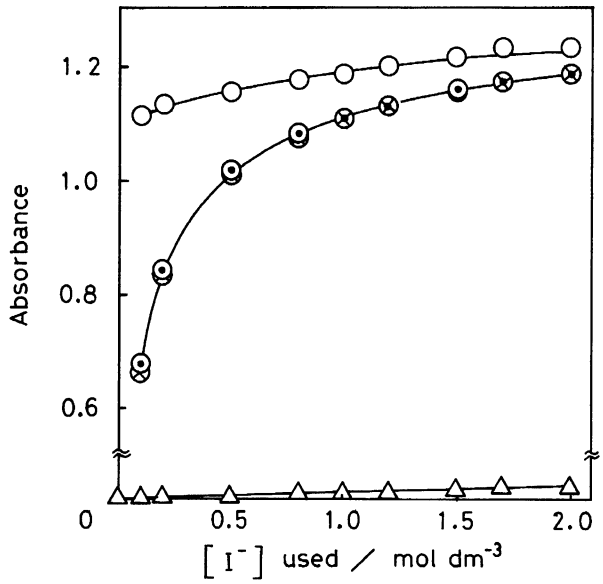

Fig. 3. Effect of the amount of iodide on extraction of iodine into the aqueous phase. A 5 cm^3 solution of iodide was used. Each absorbance (△) for the iodide in the absence of iodine was subtracted from the absorbances obtained for iodine and iodate. ⊙, 3.4×10^{-4} mmol of I_2 in 4 cm^3 carbon tetrachloride; ⊗, 1.13×10^{-4} mmol of IO_3^- in the presence of 4 cm^3 carbon tetrachloride; ○, 1.13×10^{-4} mmol of IO_3^- in the absence of 4 cm^3 carbon tetrachloride.

After a solution containing iodide (5 mmol) and acetic acid (3.6 mmol) was placed in three 50 cm^3 separating funnels, 1.13×10^{-4} mmol of iodate (equivalent to 3.4×10^{-4} mmol of iodine) were added to one of the funnels. After diluting the three mixtures up to 8 cm^3, each 4 cm^3 of carbon tetrachloride was added to the mixture containing the iodate and to the second mixture; a 4 cm^3 solution of 8.5×10^{-5} mol dm^{-3} iodine in carbon tetrachloride was added to the third mixture. These three mixtures were shaken under an atmosphere of air or nitrogen for various periods of time, and the absorbance of the aqueous phase was measured at 350 nm. The results are given in Table 2. Under the atmosphere, the absorbance obtained for iodine in each shaking time coincided well with that for iodate; this shows that the iodine in carbon tetrachloride was completely extracted into the aqueous phase as triiodide. The absorbances for both iodine and iodate increased perceptibly along with an increase in the shaking time due to the easier oxidation of iodide in the presence of iodine. However, under an atmosphere of nitrogen, the absorbance obtained for iodine accorded well with that for iodate throughout the period of the shaking time; further, the absorbance for iodide was lower and remained constant. Hence, nitrogen gas at a flow-rate of 250 cm^3 min^{-1} was introduced into a separating funnel for 2 min in order to displace air after the addition of iodide in Procedure.

In determining the optimum amount of iodide required for the extraction of iodine, each 5 cm^3 solution of various concentrations of iodide and 3 cm^3 of 1.2 mol dm^{-3} acetic acid solution were added to a 4 cm^3 solution of 8.5×10^{-5} mol dm^{-3} iodine in carbon tetrachloride in a 50 cm^3 separating funnel and the funnel was shaken for 1 min after displacement of the air with nitrogen. As can be seen in Fig. 3, the absorbance thus obtained for iodine coincided well with that for iodate equivalent to the iodine in the presence of 4 ml of carbon tetrachloride, even when a 0.5 mmol of iodide was used. Both of the absorbances for iodine and iodate increased greatly, and then gradually with an increase in the amount of iodide, and eventually remained almost parallel to the absorbance obtained for the iodate in the absence of carbon tetrachloride. Further, a 3 cm^3 solution of 1.2 mol dm^{-3} acetic acid proved to be sufficient to suppress the hydrolysis of iodine. Hence, 5 cm^3 of a 1 mol dm^{-3} iodide solution and 3 cm^3 of a 1.2 mol dm^{-3} acetic acid solution were used to extract the iodine into the aqueous phase, in Procedure.

Effect of Foreign Ions. A 10 cm^3 solution containing 19.1 μg of thiosulfate (1.7×10^{-5} mol dm^{-3}) and various amounts of foreign ions was treated as described in Procedure. The results are presented in Table 3. In the proposed method, copper(II) up to 100 μg, iron(III) up to 1000 μg and nitrite up to 10000 μg were tolerated. The nitrite was decomposed by the addition of 1 ml of 0.5 mol dm^{-3} amidosulfuric acid solution. Further, sulfite and iron(II) were tolerated in amounts of up to 1000 μg, tetrathionate and pentathionate up to 100 μg and trithionate up to 10 μg. Chloride, bromide, and iodide gave positive errors, probably because of the formation

Table 4. Recoveries of Thiosulfate Added to Hot-Spring and Lake-Water Samples

Samples	Thiosulfate content/ppm			Recovery
	Added	Found	Found in samples	%
Sample A[a)]		0.09	0.11	
	0.27	0.37		103.7
	0.54	0.65		103.7
	1.12	1.21		100
Sample B[b)]		0.07	0.09	
	0.27	0.33		96.3
	0.54	0.61		100
	1.12	1.18		99.1
Sample C[c)]		0.08	0.10	
	0.27	0.34		96.3
	0.54	0.61		98.1
	1.12	1.19		99.1
Sample D[d)]		1.03	4.12	
	0.67	1.73		104.5
	1.35	2.04		101.5
	2.24	3.30		101.3

a) Yunohanazawa at Hakone. b) Yubatake at Kusatsu-Shirane. c) Yubatake at Manza. d) Yugama lake-water at Kusatsu-Shirane.

of diiodine monohalogenide ions. The other ions listed in Table 3 were tolerated in amounts as large as 10000 μg with an error of less than 3%.

Application to Real Samples. As mentioned above, a change in the volume of the sample solutions (10 to 27 cm^3) did not have any effect on the calibration curve for thiosulfate when the amounts of sulfuric acid in the aqueous phase were sufficient. Hence, a 10 or 25 cm^3 sample solution was used for the determination of thiosulfate, according to its content. For use with the proposed method, nitrogen was bubbled through the sample solutions for 20 min at a flow-rate of 400 cm^3 min^{-1} after the addition of sulfuric acid to remove sulfide. Potential matrix interferences from unknown species in real samples were investigated by adding known amounts of thiosulfate to the sample solutions and then treating the mixtures as described in Procedure. The results are given in Table 4, in which a 25 cm^3 solution of samples A, B, and C diluted 1.25-fold and a 10 cm^3 solution of sample D diluted 4-fold were used, respectively. The recoveries ranged from 96.3 to 104.5% with an average of 100.3%, which is adequate for the analysis of environmental samples. The precision of the method was determined from 11 results obtained for 25 cm^3 solution of sample A diluted 1.25-fold, to which a known amount of thiosulfate (13.5 μg) had been added after removal of the sulfide. The mean concentration of the thiosulfate found was 0.608 ppm with a standard deviation of 0.0052 ppm and a relative standard deviation of 0.86%.

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