Determination of Tetrathionate, Thiosulfate, Sulfite and Trithionate in Their Mixtures by Spectrophotometry

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The proposed method consists of four procedures; excess iodine for reactions with thiosulfate and/or sulfite under Procedures I, II and III, and the thiocyanate formed under Procedure IV are measured spectrophotometrically after proper chemical treatments. The absorbance obtained by Procedure I corresponds to the sum of the amount of tetrathionate and that of thiosulfate in the mixture. The absorbance obtained by Procedure II corresponds only to the amount of thiosulfate in the mixture. The absorbance obtained by Procedure III corresponds to the sum of the amount of thiosulfate and twice that of sulfite in the mixture. The absorbance obtained by Procedure IV corresponds to the sum of the amount of both thiosulfate and trithionate and twice that of tetrathionate in the mixture. The proposed method was applied to the determination of tetrathionate, thiosulfate, sulfite and trithionate mixed in various ratios in amounts of more than 0.05 μmol with an error below $\pm 0.02 \mu\text{mol}$.

Keywords Polythionates determination, tetrathionate sulfitolysis, trithionate cyanolysis, tetrathionate-trithionate-thiosulfate-sulfite mixture, spectrophotometry

The determination of various sulfur anion species in their mixtures is desirable for interpreting their redox chemistry in aqueous solution systems. However, this is difficult owing to similarities in their chemical and physical properties. Spectrophotometric methods^{1,2} for the determination of trithionate, thiosulfate and tetrathionate in a mixture, based on the formation of thiocyanate by their cyanolysis, have been proposed. In an experiment the cyanolysis of trithionate was carried out at pH 9.6 for 30 min at a temperature of boiling water. Under these conditions, only 87% of trithionate was converted into thiocyanate, the rest into thiosulfate. Accordingly, these methods can not be considered accurate. Recently, a number of publications dealing with high performance liquid chromatography (HPLC) for the separation of mixtures of polythionates have appeared.³⁻¹⁰ However, no consideration has been given to the determination of tetrathionate, thiosulfate, sulfite and trithionate in a mixture.

The present authors have developed methods for the determination of tetrathionate¹¹, pentathionate¹² and hexathionate¹³ by means of their sulfitolysis. On the other hand, lanthanum(III) has been found to have a catalytic effect on the conversion of trithionate¹⁴ and thiosulfate¹⁵ into thiocyanate. In this work, the conditions under which both thiosulfate and trithionate are simultaneously and completely converted into thiocyanate were established. This paper is concerned with the sulfitolysis of tetrathionate and the cyanolysis of both thiosulfate and trithionate for the determination

of four sulfur species of tetrathionate, thiosulfate, sulfite and trithionate in a mixture.

Experimental

Reagents and apparatus

All chemicals used, except tetrathionate and trithionate, were of analytical grade and used without further purification. The water used in these experiments was redistilled. Potassium tetrathionate was prepared according to a procedure described by Stamm *et al.*¹⁶ The obtained tetrathionate 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 ($1 \times 10^{-3} \text{ M}$) was prepared by dissolving 151.3 mg of the potassium tetrathionate (water content: 0.07%) in water and diluting to 500 ml. The concentration of the tetrathionate solution was checked by the sulfitolysis method¹¹ and the solution stored at $5 \pm 2^\circ\text{C}$. A stock solution of thiosulfate was prepared by dissolving a known amount of sodium thiosulfate pentahydrate in oxygen-free water containing a small amount of sodium carbonate as a stabilizer. It was standardized by iodometry¹⁷ one week after preparation. Working standard thiosulfate solutions were prepared by suitable dilution with oxygen-free water. These standards were used to ascertain the stoichiometry and completion of the sulfitolysis of tetrathionate. A sulfite solution was

prepared by dissolving sodium hydrogen sulfite in oxygen-free water and standardized by iodometry.¹⁷ Working standards were obtained by suitable dilutions with oxygen-free water. A 0.15 M sulfite solution, which was not standardized, proved to be useful for the sulfitolysis of tetrathionate for 2 weeks after its preparation. A thiocyanate solution was standardized by the Volhard method¹⁸, and working standards were prepared by suitable dilution. These standards were used to ascertain the stoichiometry of the cyanolysis of thiosulfate and trithionate. Potassium trithionate was prepared according to a procedure described by Stamm *et al.*¹⁶ The obtained trithionate was recrystallized with water at a temperature below 35°C and then dried at room temperature before storage at $-10 \pm 2^\circ\text{C}$. A trithionate solution was standardized against a standard thiocyanate solution by the cyanolysis method;¹⁴ the solution was stored at $5 \pm 2^\circ\text{C}$. 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 a 0.87 M iodide solution.

Then, 1.5 M iron(III) in a 4 M perchloric acid solution was prepared by dissolving 306.05 g of iron(III) nitrate nonahydrate (99%) in a small volume of water containing 217.4 ml of 60% perchloric acid and diluting it to 500 ml. The buffer solutions of pH 9.9 used in Procedures I, II and IV and of pH 3.5 used in Procedures I and II were prepared by mixing 100 ml of 0.3 M sodium hydrogencarbonate with 100 ml of 0.3 M sodium carbonate, and 160 ml of 0.5 M acetic acid with 10 ml of 0.5 M sodium acetate, respectively.

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

Procedure

The proposed method for the determination of tetrathionate, thiosulfate, sulfite and trithionate in mixtures consists of the following four procedures.

Procedure I. For total amounts of tetrathionate and thiosulfate in the mixture. Pipette 1.8 ml of the carbonate buffer solution (pH 9.9), 2 ml of the 0.15 M sulfite solution, and then a 10-ml aliquot of a sample solution containing tetrathionate, thiosulfate, sulfite and trithionate, into a 25-ml volumetric flask. The pH of the solution is thereby brought to 8.0. Allow the mixture to stand at room temperature for 20 min, to completely convert tetrathionate into thiosulfate. Add 2 ml of 0.5 M formaldehyde solution and 1.5 ml of the acetate buffer solution (pH 3.5) to the reaction mixture. In this case, the solution was buffered to a pH of 5.0. Allow the mixture to stand for 5 min to completely mask any excess sulfite.

Procedure II. For amounts of thiosulfate in the mixture. Place 1.8 ml of the carbonate buffer solution (pH 9.9), a 10-ml aliquot of the above sample solution,

2 ml of the 0.5 M formaldehyde solution and 1.5 ml of the acetate buffer solution (pH 3.5) in a 25-ml volumetric flask. Then allow the mixture to stand for 5 min to completely mask any sulfite in the sample.

Procedure III. For total amounts of thiosulfate and sulfite in the mixture. Pipette a 10-ml aliquot of the sample solution into a 25-ml volumetric flask.

To these three mixture solutions from Procedures I, II and III, add 2 ml of 5 M acetic acid and 2.4 ml of the standard 1.00×10^{-3} N iodate in a 0.87 M iodide solution; then dilute to the mark with water. Mix the contents of the flask well and measure the absorbance of the solution against water at 350 nm of maximum absorption for triiodide ion.

Procedure IV. For total amounts of tetrathionate, thiosulfate and trithionate in the mixture. Pipette 1.8 ml of the carbonate buffer solution (pH 9.9), 2 ml of the 0.15 M sulfite solution and a 10-ml aliquot of the sample solution into a 50-ml volumetric flask. Allow the mixture to stand for 20 min in order to sulfitolize the tetrathionate completely. Then add 0.6 ml of 0.5 M acetic acid and 2 ml of 0.5 M formaldehyde to the reaction mixture, and allow the mixture to stand for 5 min to mask the sulfite. To this mixture add 2 ml of 1 M acetic acid, 1.5 ml of 1.5 M lanthanum(III) nitrate and 4.5 ml of 4 M cyanide solution; the resulting solution has a pH of 9.5. Allow the mixture to stand at 15°C for 1.5 h in order to completely convert both the thiosulfate and the trithionate into thiocyanate. Then add 1 ml of 0.01 M iodine in methanol, 4 ml of 60% perchloric acid and 3 ml of 1.5 M iron(III) nitrate in a 4 M perchloric acid solution. Dilute to the mark with water, mix the contents well and measure the absorbance of the solution of the iron(III)-thiocyanate complex, thus formed, against water at 460 nm.

Results and Discussion

Calibration graphs

It is well known that polythionates do not consume iodine, but that thiosulfate and sulfite react with iodine in an acidic medium as follows:

In a previous paper¹¹, the conditions under which tetrathionate is converted into thiosulfate according to

have been established, in which 1 mol of thiosulfate is formed by the sulfitolysis of 1 mol of tetrathionate. It can be seen in Fig. 1 that the calibration graph for the tetrathionate obtained by Procedure I, that for the thiosulfate obtained by Procedure II and that for the sulfite obtained by Procedure III were, respectively, in good agreement with one another when the molar

Fig. 1 Calibration graphs for tetrathionate, thiosulfate and sulfite obtained by Procedures I, II and III. O, reagent blank obtained by Procedures I, II and III; ◐, $S_4O_6^{2-}$ by Procedure I; ⊗, $S_2O_3^{2-}$ by Procedures I, II and III; ●, SO_3^{2-} by Procedure III.

Table 1 Effect of formaldehyde on the cyanolysis of thiosulfate and trithionate

Sample	Absorbance			
	In the absence of HCHO 8×10^{-4} M	12×10^{-4} M	0.5 M HCHO 2 ml ^a 8×10^{-4} M	12×10^{-4} M
SCN^-	0.675 ^b	1.011 ^b	0.670 ^b	1.005 ^b
$S_2O_3^{2-}$	0.668	0.987	0.670	1.000
$S_3O_6^{2-}$	0.677	1.011	0.670	1.000

a. Under the same conditions as in Procedure IV.

b. The expected values obtained for thiocyanate.

concentration scale for sulfite was drawn to twice the concentration scale for tetrathionate and thiosulfate. Experimental results revealed that tetrathionate does not react at all with the sulfite in the sample solution under Procedures II and III, but is stoichiometrically converted into thiosulfate according to Eq. (3) under Procedure I.

According to Eq. (3), when 1 mol of tetrathionate undergoes sulfitolysis, 1 mol of thiosulfate and trithionate, each, is formed. Lanthanum(III) has been found to have a catalytic effect on the following reactions of thiosulfate¹⁵ and trithionate:¹⁴

The results obtained for the cyanolysis of thiosulfate and trithionate are shown in Table 1. When a 2-ml volume of 0.5 M formaldehyde was deleted from

Fig. 2 Calibration graphs for tetrathionate and thiocyanate obtained by Procedure IV. O, reagent blank; ◐, $S_4O_6^{2-}$; ⊗, SCN^- .

Procedure IV, thiosulfate gave lower absorbances than the expected values, in which the excess sulfite used for the sulfitolysis of tetrathionate interfered with the cyanolysis of thiosulfate. Thiosulfate and trithionate were quantitatively converted into thiocyanate over the pH ranges 9.3–9.6 and 8.9–9.6, respectively, when cyanolyzed for 1.5 h¹⁵ at 15°C¹⁴ after complete masking of the excess sulfite with formaldehyde in the solution buffered at the pH range 4.0–9.1.¹² Consequently, both of the thiosulfate and trithionate formed from tetrathionate and those in the sample could be stoichiometrically converted into thiocyanate over the pH range 9.3–9.6. The overall reaction for tetrathionate under Procedure IV is as follows:

Here, 1 mol of tetrathionate produces 2 mol of thiocyanate. Hence, if tetrathionate is quantitatively converted into thiocyanate according to Eq. (6), the calibration graph for tetrathionate obtained by measuring the thiocyanate formed from tetrathionate should coincide with that for thiocyanate when the molar concentration scale for tetrathionate is drawn to twice the scale for the thiocyanate concentration. Figure 2 confirms that tetrathionate is completely converted into thiocyanate according to Eq. (6) and that the thiosulfate and trithionate in the sample can be converted into thiocyanate according to Eqs. (4) and (5), respectively.

Stability of iron(III)-thiocyanate complex

It is known that the absorbance of iron(III)-thiocyanate decreases with time because of the reduction of iron(III) by thiocyanate.¹⁹ The iron(III)-

thiocyanate can be greatly stabilized by the addition of persulfate, hydrogen peroxide¹⁹ and nonionic surfactants.²⁰ As can be also seen in Table 2, the absorbance of the iron(III)-thiocyanate complex, obtained under Procedure A in which 1 ml of 0.01 M iodine in methanol was not added, gradually decreased with the time of standing. On the other hand, the absorbance remained constant for 2 h under the conditions of both Procedure B and Procedure IV in which iodine was added as an oxidizing agent. Hence, 1 ml of 0.01 M iodine in methanol was used as a stabilizer for an iron(III)-thiocyanate complex under Procedure IV.

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These four sulfur compounds in their mixture give the following equivalents in the four procedures:

Table 2 Stability of iron(III)-thiocyanate complex

Time/ min	Absorbance ^a for 8×10^{-4} M SCN ⁻		
	Procedure A ^b	Procedure B ^c	Procedure IV
1	0.685	0.701	0.672
10	0.675	0.695	0.672
20	0.666	0.695	0.674
30	0.663	0.695	0.677
40	0.660	0.695	0.679
60	0.652	0.695	0.676
80	0.645	0.695	0.679
100	0.638	0.693	0.684
120	0.635	0.693	0.680

a. The reagent blank was subtracted.

b. An 1-ml volume of methanolic solution of 0.01 M iodine was deleted from Procedure IV.

c. Each 2-ml volume of 0.15 M sulfite and 0.5 M formaldehyde solutions was deleted from Procedure IV.

The absorbance obtained by Procedure I corresponds to the sum of the amount of tetrathionate [see Eq. (3)] and that of thiosulfate [Eq. (1)] in the mixture. The absorbance obtained by Procedure II, in which the sulfitolysis of tetrathionate was not carried out and the sulfite in the sample was masked by formaldehyde, corresponds only to the amount of thiosulfate in the mixture. The absorbance obtained by Procedure III, in which neither the sulfitolysis of tetrathionate nor the masking of sulfite was carried out, corresponds to the sum of the amount of thiosulfate and twice that of sulfite [Eq. (2)] in the mixture. The absorbance obtained by Procedure IV, in which tetrathionate was converted into both thiosulfate and trithionate, followed by their conversion into thiocyanate by the cyanolysis, corresponds to the sum of the amount of thiosulfate [Eq. (4)], that of trithionate [Eq. (5)] and twice that of tetrathionate [Eq. (6)] in the mixture. The calibration graphs obtained for tetrathionate, thiosulfate and sulfite by, respectively, Procedures I, II and III were in complete agreement with one another when plotted in terms of equivalent concentrations. In addition, the calibration graph for tetrathionate obtained by Procedure IV coincided with those for thiosulfate and trithionate when plotted in terms of equivalent concentrations. Hence, the following equations can be obtained: $[\text{S}_4\text{O}_6^{2-}] = \text{I} - \text{II}$, $[\text{S}_2\text{O}_3^{2-}] = \text{II}$, $[\text{SO}_3^{2-}] = (\text{III} - \text{II})/2$ and $[\text{S}_3\text{O}_6^{2-}] = \text{IV} - 2\text{I} + \text{II}$. Here, I, II and III denote the molar concentrations of thiosulfate determined from the calibration graph for thiosulfate shown in Fig. 1 using the absorbance obtained by Procedures I, II and III, respectively. The Roman numeral IV indicates the molar concentration of thiocyanate determined from the calibration graph for thiocyanate shown in Fig. 2 using the absorbance obtained by Procedure IV. Table 3 shows that the proposed method can be successfully applied to the determination of tetrathionate, thiosulfate, sulfite and trithionate

Table 3 Determination of tetrathionate, thiosulfate, sulfite and trithionate mixed in various ratios in a 10-ml solution

Amount taken/ μmol				Amount found/ μmol			
$\text{S}_4\text{O}_6^{2-}$	$\text{S}_2\text{O}_3^{2-}$	SO_3^{2-}	$\text{S}_3\text{O}_6^{2-}$	$\text{S}_4\text{O}_6^{2-}$	$\text{S}_2\text{O}_3^{2-}$	SO_3^{2-}	$\text{S}_3\text{O}_6^{2-}$
0.80	0.50	0.50	0.80	0.81	0.49	0.50	0.82
0.70	0.70	0.45	0.80	0.71	0.69	0.44	0.82
0.85	0.95	0.10	0.90	0.86	0.95	0.10	0.91
0.60	0.60	0.15	1.00	0.58	0.61	0.16	0.99
0.20	0.30	0.75	2.00	0.20	0.30	0.75	1.99
1.50	0.40	0.90	2.50	1.50	0.40	0.89	2.50
0.65	0.50	0.50	3.50	0.65	0.50	0.50	3.49
0.40	1.50	0.25	4.50	0.41	1.50	0.26	4.48
0.75	0.75	0.75	5.00	0.76	0.75	0.74	5.00
1.25	0.75	0.60	6.50	1.25	0.75	0.61	6.49
0.95	0.30	1.00	7.00	0.95	0.30	1.00	7.00
0.90	1.00	0.35	7.50	0.90	1.00	0.36	7.50

mixed in various ratios with an error less than $\pm 0.02 \mu\text{mol}$.

The precision of the method was obtained from 11 results for a 10-ml aliquot of a sample solution containing $0.75 \mu\text{mol}$ of each species of tetrathionate, thiosulfate and sulfite, and $5 \mu\text{mol}$ of trithionate. The proposed method gave a mean value of $0.76 \mu\text{mol}$ with a standard deviation (SD) of $0.005 \mu\text{mol}$ and a relative standard deviation (RSD) of 0.67% for tetrathionate, $0.74 \mu\text{mol}$ (SD= $0.005 \mu\text{mol}$ and RSD= 0.70%) for thiosulfate, $0.74 \mu\text{mol}$ (SD= $0.004 \mu\text{mol}$ and RSD= 0.54%) for sulfite and $5.0 \mu\text{mol}$ (SD= $0.01 \mu\text{mol}$ and RSD= 0.22%) for trithionate.

Recovery of tetrathionate, thiosulfate, sulfite and trithionate added to natural water samples

Potential matrix interferences from unknown species in natural water samples were investigated using a 10-ml aliquot of sample solutions followed by the addition of known amounts of tetrathionate, thiosulfate, sulfite and trithionate; the mixture solutions were treated according to Procedures I, II, III and IV. The results are given in Table 4. Iron(III) interferes with Procedures I, II and III because it oxidizes iodide to iodine; iron(II) also interferes with the measurement of absorbance of iron(III)-thiocyanate complex under Procedure IV as a result of the formation of hexacyanoferrate(II). Therefore, the iron(III) present in hot-spring water samples, (A) and (C), and the iron(II) in lake water sample were removed by a batch operation²¹ of cation-exchange, in which 1 g of Amberlite IR-120B (100–200 mesh) was used for each 25 ml of samples. The resin was filtered off by suction with a Millipore SM filter (pore size, $5 \mu\text{m}$) prior to the addition of the

four sulfur species to the samples. For lake water sample which contained a large amount of iron(II), this cation-exchange procedure was repeated twice. The total polythionates (tetra-, penta- and hexathionate) content in the hot-spring water sample (C) was determined to be $3.2 \times 10^{-5} \text{ M}$ by the cyanolysis method²² using the standard addition method. When the iron in the samples was removed after the addition of the four sulfur species to the samples, a low recovery only for sulfite was obtained, owing to the evolution of sulfur dioxide from the sulfite in the strong acid media of the samples during the ion-exchange operation. The accuracy of the proposed method was checked by adding varying known amounts of tetrathionate, thiosulfate, sulfite and trithionate to the natural-water samples, the iron in which had been removed. The higher recovery for tetrathionate in hot-spring water (C) can probably be attributed to the presence of higher polythionates, such as penta- and hexathionate in the sample. The other recoveries ranged with an error below $\pm 0.03 \mu\text{mol}$ maximal for tetrathionate, thiosulfate and sulfite and below $\pm 0.2 \mu\text{mol}$ for trithionate. When the method was applied to the natural water samples, the precision was determined from 11 results obtained for a 10-ml aliquot of the hot-spring water sample (A), to which known amounts of tetrathionate ($0.65 \mu\text{mol}$), thiosulfate ($0.50 \mu\text{mol}$), sulfite ($0.50 \mu\text{mol}$) and trithionate ($3.5 \mu\text{mol}$) were added. The proposed method gave a mean value of $0.66 \mu\text{mol}$ with a standard deviation of $0.009 \mu\text{mol}$ and a relative standard deviation of 1.4% for tetrathionate, $0.50 \mu\text{mol}$ (SD= $0.006 \mu\text{mol}$ and RSD= 1.1%) for thiosulfate, $0.50 \mu\text{mol}$ (SD= $0.007 \mu\text{mol}$ and RSD= 1.4%) for sulfite and $3.4 \mu\text{mol}$ (SD= $0.03 \mu\text{mol}$ and RSD= 0.99%) for trithionate.

Table 4 Recovery of tetrathionate, thiosulfate, sulfite and trithionate added to natural water samples

Amount taken/ μmol				Amount found/ μmol				Recovery, %			
$\text{S}_4\text{O}_6^{2-}$	$\text{S}_2\text{O}_3^{2-}$	SO_3^{2-}	$\text{S}_3\text{O}_6^{2-}$	$\text{S}_4\text{O}_6^{2-}$	$\text{S}_2\text{O}_3^{2-}$	SO_3^{2-}	$\text{S}_3\text{O}_6^{2-}$	$\text{S}_4\text{O}_6^{2-}$	$\text{S}_2\text{O}_3^{2-}$	SO_3^{2-}	$\text{S}_3\text{O}_6^{2-}$
Hot spring water A ^a											
0.85	0.95	0.10	0.90	0.86	0.95	0.10	0.75	101	100	100	83.3
0.20	0.30	0.75	2.00	0.21	0.31	0.75	1.85	105	103	100	92.5
0.65	0.50	0.50	3.50	0.65	0.50	0.51	3.42	100	100	102	97.7
Hot spring water B ^b											
0.85	0.95	0.10	0.90	0.87	0.96	0.10	0.76	102	101	100	84.4
0.20	0.30	0.75	2.00	0.22	0.33	0.74	1.81	110	110	98.7	90.5
0.65	0.50	0.50	3.50	0.68	0.51	0.51	3.33	105	102	102	95.1
Hot spring water C ^c											
—	—	—	—	0.32 ^e	—	—	—	—	—	—	—
0.85	0.95	0.10	0.90	1.03 ^f	0.93	0.10	0.83	121	97.9	100	92.2
0.20	0.30	0.75	2.00	0.37 ^f	0.30	0.75	2.02	185	100	100	101
0.65	0.50	0.50	3.50	0.83 ^f	0.49	0.50	3.56	128	98.0	100	102
Lake water ^d											
0.80	0.50	0.50	0.80	0.80	0.50	0.49	0.73	100	100	98.0	91.3
0.70	0.70	0.45	0.80	0.69	0.70	0.44	0.75	98.6	100	97.8	93.8
0.60	0.60	0.15	1.00	0.61	0.60	0.15	0.92	102	100	100	92.0

a. Yubatake at Kusatsu-Shirane. b. Yunohanazawa at Hakone. c. Yubatake at Manza. d. Yugama lake water at Kusatsu-Shirane. e. Total polythionates (tetra-, penta- and hexathionate) content. f. Determined as tetrathionate.

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