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The Chemical Behavior of Low Valence Sulfur Compounds. IX.[1] Photometric Determination of Thiosulfate, Trithionate and Tetrathionate in Mixture

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The cyanolysis and photometric determination of thiosulfate, trithionate and tetrathionate have been investigated under the various conditions. The cyanolysis of thiosulfate catalyzed by cupric ions proceeded quantitatively in the presence of acetate buffer solution of pH 4.5, while the degree of cyanolysis of trithionate and that of tetrathionate were 0.3 and 0.6%, respectively. The degree of cyanolysis of trithionate was not so depressed as to a negligible extent by the methods previously proposed, but was depressed to 0.7% or less by the addition of such organic solvents as acetone, methanol, *etc.* The determination of thiosulfate, trithionate and tetrathionate in the concomitant presence of them could be made with a high accuracy.

A simple analytical method for 0—10 μmol of thiosulfate and polythionates has been a subject in the study on the chemical behavior of low valence sulfur compounds in biological systems. The classical iodometric method for the determination of these compounds,[2] which was used in our previous studies, has been found inapplicable to the analysis of systems in which reducing organic compounds are contained. A colorimetric method depending on the photometric determination of thiocyanate formed in the reaction with cyanide seems superior in the possibility of fractional determination of these compounds, to many other methods proposed previously.[3,4] This method was proposed by Nietzel *et al.*[5] to determine tetrathionate, and was then extended to the colorimetric determination of thiosulfate by Sörbo.[6] Urban has described the cyanolysis of thiosulfate[7] and polythionates,[8,9] obtaining only the mean value *n* in the formula $S_nO_6^{2-}$.[10] Koh *et al.* have fully investigated the cyanolysis and photometric determination of trithionate,[11] tetrathionate,[12] pentathionate[13] and hexathionate,[14] and also have reported a highly sensitive analytical method for thiosulfate[15] and polythionates[16] by means of solvent extraction. The application, however, has been restricted to the determination of two-component mixtures excluding trithionate.[17] Kelly *et al.*[18] have proposed a fractional determination method for thiosulfate, trithionate and tetrathionate, but the measured values fluctuate within 10 to 20%, requiring a more accurate analytical method to investigate the reaction mechanism of low valence sulfur compounds.

The reactions of thiosulfate and polythionates with cyanide are given by Eqs. (1)—(4). As the velocity of the reactions largely depends on the conditions applied,

$$S_2O_3^{2-} + CN^- \overset{Cu^{2+}}{=} SCN^- + SO_3^{2-} \tag{1}$$

$$S_3O_6^{2-} + CN^- + 2OH^- = SCN^- + SO_3^{2-} + SO_4^{2-} + H_2O \tag{2}$$

$$S_4O_6^{2-} + CN^- + 2OH^- = SCN^- + S_2O_3^{2-} + SO_4^{2-} + H_2O \tag{3}$$

$$S_4O_6^{2-} + 2CN^- + 2OH^- \overset{Cu^{2+}}{=} 2SCN^- + SO_3^{2-} + SO_4^{2-} + H_2O \tag{4}$$

it may be expected that special reactions proceed exclusively under the suitable conditions. However, it has not been shown systematically to what degree the side reactions can be depressed.

From a result of investigation of the respective reaction under the various conditions, it has become clear that three sorts of procedures shown in Table 1 can be employed with satisfactory accuracy, and that the determination of thiosulfate, trithionate and tetrathionate in mixtures can be made by those procedures. The present paper is concerned with the result of this investigation.

Experimental

Materials. All chemicals, except polythionates, were analytical reagent grade, and were used without further purification. Potassium trithionate and potassium tetra-

Table 1. Procedures and the equivalents of thiocyanate expected

Procedure	Outline of the procedure	Reactions	Equivalents of SCN⁻ expected
A	Cupric ion-catalyzed cyanolysis of thiosulfate at pH 4.5	(1)	$S_A{}^{a)} = (S_2O_3^{2-})^{a)}$
B	Cyanolysis of tetrathionate in the presence of acetone followed by cupric ion-catalyzed cyanolysis of thiosulfate	(1), (4)	$S_B = (S_2O_3^{2-}) + 2(S_4O_6^{2-})$
C	Cyanolysis of trithioate and tetrathioate in boiling water bath followed by cupric ion-catalyzed cyanolysis of thiosulfate	(1), (2), (4)	$S_C = (S_2O_3^{2-}) + (S_3O_6^{2-}) + 2(S_4O_6^{2-})$

a) Denotes the amount in mole unit.

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Table 2. Analysis of polythionate samples (wt%)

	$K_2S_3O_6$		$K_2S_4O_6$	
	K[a]	S[b]	K	S
Theoretical values	28.92	35.57	25.86	42.40
Measured values	28.97	35.74	25.85	42.93

a) Determined by gravimetry as potassium sulfate after ignition at 700 °C. b) Determined by gravimetry as barium sulfate after oxidation with potassium chlorate.

thionate were prepared by Stamm's method[19] and Martin's method[20], respectively, and were found to be free from thiosulfate as well as other polythionates by paper chromatography.[21] The results of analyses of the polythionates are shown in Table 2, indicating that these polythionate samples are pure enough for the purpose of this study.

Standard Trithionate Solution (0.01 M*)*: Dissolve 0.5407 g of potassium trithionate in distilled water, and dilute to 200 ml. Prepare working solutions by suitable dilution.

Standard Tetrathionate Solution (0.01 M*)*: Dissolve 0.6049 g of potassium tetrathionate in distilled water, and dilute to 200 ml. Prepare working solutions by suitable dilution.

Standard Thiocyanate Solution (0.05 M*)*: Dissolve potassium thiocyanate in distilled water, and standardize by Volhard's method. Prepare working solutions by suitable dilution.

Standard Thiosulfate Solution (0.01 M*)*: Dissolve sodium thiosulfate pentahydrate in distilled water, and standardize by iodometry. Prepare working solutions by suitable dilution.

Potassium Cyanide Solution (0.5 M*)*: Dissolve 17.2 g of potassium cyanide in distilled water and dilute to 500 ml.

Cupric Chloride Solution (0.2 M*)*: Dissolve 17.6 g of cupric chloride dihydrate in distilled water, dilute to 500 ml, and add a drop of concentrated hydrochloric acid to prevent the hydrolysis of cupric ions.

Buffer Solutions: Buffer solutions of desired pH values are obtained by mixing the following two solutions in a suitable ratio.

2 M acetate buffer solution: 2 M acetic acid with 2 M ammonium acetate,
0.2 M phosphate buffer solution: 0.2 M sodium dihydrogen phosphate with 5 M sodium hydroxide.

Ferric Nitrate-Perchloric Acid Solution:[13] Dissolve 303 g of ferric nitrate, $Fe(NO_3)_3 \cdot 9H_2O$, in a small volume of distilled water containing 217 ml of concentrated perchloric acid (60 wt%), and then dilute to 500 ml with distilled water.

Recommended Procedures. *Procedure A. Cupric Ion-Catalyzed Cyanolysis of Thiosulfate at pH 4.5*: Transfer an aliquot of the sample solution to a 50-ml volumetric flask. To this, add 10 ml of acetate buffer of pH 4.5, 1 ml of 0.5 M potassium cyanide solution, and 1.5 ml of 0.2 M cupric chloride solution, in this order, with mixing. Finally, add 5 ml of ferric nitrate-perchloric acid solution with continuous mixing, and make up to 50 ml with distilled water. Measure the absorbance of the solution against reagent blank at 460 nm in a glass cell of 10 mm thick. The content must be kept at 20 °C or lower to prevent the cyanolysis of higher polythionates. The thiocyanate equivalent can be obtained from the calibration curve prepared by using standard thiosulfate or thiocyanate solutions.

Procedure B. Cyanolysis of Tetrathionate in the Presence of Acetone Followed by Cupric Ion-Catalyzed Cyanolysis of Thiosulfate: Transfer an aliquot of the sample solution to a 50-ml volumetric flask, and add water to give a total volume of about 15 ml. Neutralize with 1 M ammonia water to thymolphtalein, add 10 ml of acetone, and cool to 20 °C. Add 2 ml of 0.5 M potassium cyanide solution and maintain at 20 °C for 20 min. Add 1.5 ml of 0.2 M cupric chloride solution, and apply the same ensuing manipulation as that in Procedure A.

Procedure C. Cyanolysis of Trithionate and Tetrathionate in Boiling Water Bath Followed by Cupric Ion-Catalyzed Cyanolysis of Thiosulfate: Transfer an aliquot of the sample solution to a 50-ml volumetric flask. Add a few drops of 0.1% thymolphtalein as well as 2 ml of 0.5 M potassium cyanide solution, and also 1 M ammonia water until a blue color comes out. Keep the flask in a boiling water for 30 min, and then cool to room temperature. Add 1.5 ml of 0.2 M cupric chloride solution and apply the same ensuing manipulation as that in Procedure A.

Unless otherwise stated, the concentrations mentioned in this report are values presented when the solutions are made up to 50 ml. The term of "cyanolysis" denotes "cyanolysis in the absence of cupric ions", and is distinct from "cupric ion-catalyzed cyanolysis". The degree of cyanolysis in each procedure is expressed as the ratio of equivalents of thiocyanate obtained to those expected to be obtained which are shown in Table 1. The concentrations of the stock solution of trithionate and of tetrathionate were determined on the assumption that the purities of both samples were 100%, since the impurities are not correctly determined by any of the methods previously reported. A Hitachi spectrophotometer model 101 was used to measure the absorbance.

Results and Discussion

Procedure A. Cupric Ion-Catalyzed Cyanolysis of Thiosulfate at pH 4.5. In Procedure A, the reaction shown by Eq. (1) is expected to proceed exclusively.

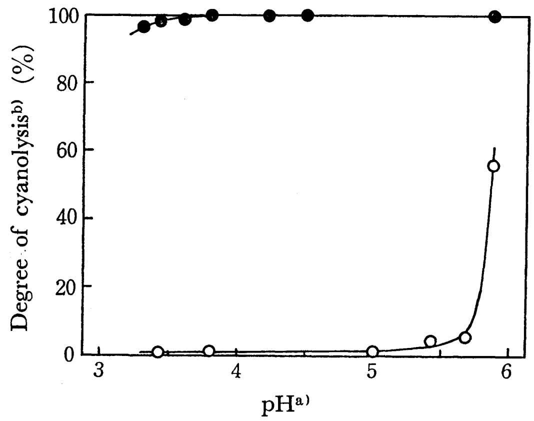

Fig. 1. Effect of pH on the cyanolysis of thiosulfate and tetrathionate.

Concn of KCN: 10 mM, concn. of $CuCl_2$: 6 mM, $S_2O_3^{2-}$(●) and $S_4O_6^{2-}$(○) taken: 5.00 µmol/50 ml.

a) pH values are those shown after $CuCl_2$ addition, which differed from those of the buffer solutions used by less than 0.2.

b) The degree of cyanolysis at each pH value was calculated by [(the absorbance obtained when such solutions as sample, buffer, KCN, $CuCl_2$ and $Fe(NO_3)_3$-$HClO_4$ were mixed in this order)/(the absorbance obtained when such solutions as sample, KCN, $CuCl_2$, $Fe(NO_3)_3$-$HClO_4$ and buffer were mixed in this order)] × 100. In the cyanolysis of tetrathionate, the reaction mixtures were maintained at the room temperature for 5 min before an addition of $CuCl_2$ solution.

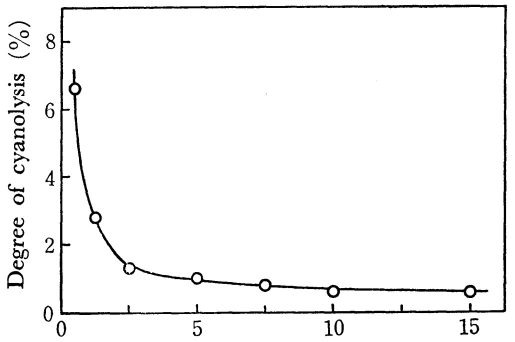

Fig. 2. Effect of the amount of acetate buffer solution of pH 4.5 on the cyanolysis of tetrathionate.
Concn. of KCN: 10 mM, concn. of $CuCl_2$: 6 mM, $S_4O_6^{2-}$ taken: 5.00 μmol/50 ml.

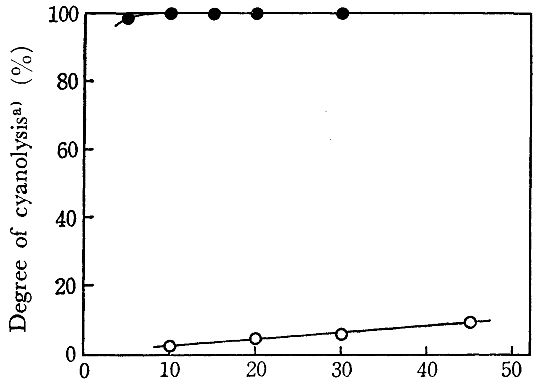

Fig. 3. Cyanolysis of trithionate and tetrathionate by Kelly's method.
○: trithionate, ●: tetrathionate.
Temp.: 5 °C, concn. of KCN: 20 mM, cyanolysis pH: 9.7, $S_3O_6^{2-}$ taken: 10.13 μmol/50 ml, $S_4O_6^{2-}$ taken: 5.00 μmol/50 ml.
a) Determined by using a calibration curve prepared from a standard thiocyanate solution. See Table 1 for the theoretical equivalents of thiocyanate.

It has been cleared by Urban⁷⁾ that the reaction shown by Eq. (1), catalyzed by cupric ions, proceeds selectively if the pH is carefully controlled, but the procedure is complicated. Figure 1 shows the results of the cyanolysis of thiosulfate and tetrathionate in the presence of acetate buffer solutions of various pH values. It is clear that the reaction shown by Eq. (1) takes place quantitatively above the pH value of 4, while the cyanolysis of tetrathionate hardly proceeds below the pH value of 5. These results are almost consistent with those by Urban.⁷⁾ Koh *et al.*¹⁷⁾ have reported that thiosulfate is not converted quantitatively to thiocyanate below the pH value of 5. This discrepancy may be attributed to their determination of pH values after an addition of cyanide solution. Figure 2 shows the effect of the amount of buffer solution added on the degree of cyanolysis of tetrathionate. It is clear that the addition of more than 5 ml has little effect. The amount added in the recommended procedure has been decided to be 10 ml per 50 ml so as to depress the fluctuation of pH in the analysis of practical samples.

The cyanolysis degree of 10 μmol of trithionate and that of 5 μmol of tetrathionate were 0.3 and 0.6%, respectively, showing that the cyanolysis of thiosulfate shown by Eq. (1) proceeds exclusively in the presence of acetate buffer of pH 4.5.

Procedure B. Cyanolysis of Tetrathionate in the Presence of Acetone Followed by Cupric Ion-Catalyzed Cyanolysis of Thiosulfate. In Procedure B, the reactions shown by Eqs. (1) and (4) are expected to proceed, while the cyanolysis of trithionate shown by Eq. (2) must be depressed. Kelly *et al.*¹⁸⁾ have described that the cyanolysis of trithionate can be depressed under the conditions of reaction temperature 5 °C and pH 9.65, but the actual degree of cyanolysis of trithionate is not shown.

The procedure proposed by Kelly *et al.* (Treatment I) was applied to analyses of trithionate and tetrathionate. The results in Fig. 3 show that tetrathionate undergoes a quantitative conversion according to Eq. (3), while the degree of cyanolysis of trithionate cannot be ignored. One of the reasons why recoveries of tetrathionate in the analysis of mixtures tend to be high, and those of thiosulfate correspondingly low by their method, may be that the cyanolysis of trithionate is not depressed quantitatively.

Several sorts of organic solvents were added to lower the dielectric constant of the solution, so as to prevent the cyanolysis of trithionate. Organic solvents were added after the regulation of pH. As is evident from the results shown in Table 3, the degree of cyanolysis of trithionate is depressed greatly by the addition of organic solvents, which, however, cannot be related simply to the dielectric constant of the solution. The cyanolysis in the presence of methanol and acetone was

TABLE 3. EFFECT OF ORGANIC SOLVENTS ON THE CYANOLYSIS OF TRITHIONATE AND TETRATHIONATE IN THE ABSENCE OF CUPRIC IONS

Organic solvent added (vol.%)	Degree of cyanolysis^a) (%)	
	$S_3O_6^{2-}$	$S_4O_6^{2-}$
None	24.4	100.0
Methanol (20)	2.9	100.4
Ethanol (20)	3.4	100.2
Isopropanol (20)	3.8	99.6
Ethylene glycol (20)	4.9	98.2
Dioxane (10)	6.2	117.5
(20)	3.4	133.8
(30)	2.3	144.0
Acetone (20)	4.2	100.4

Temp.: 25 °C, time: 30 min, concn. of KCN: 20 mM, $S_3O_6^{2-}$ taken: 9.90 μmol/50 ml, $S_4O_6^{2-}$ taken: 5.02 μmol/50 ml. Ferric nitrate–nitric acid solution⁶⁾, which is obtained by dissolving 50 g of ferric nitrate in water containing 100 ml of concentrated nitric acid followed by diluting to 500 ml with water, was used. a) Determined by using a calibration curve prepared from a standard thiocyanate solution. See Table 1 for the theoretical equivalent of thiocyanate.

TABLE 4. CYANOLYSIS OF TRITHIONATE AND TETRATHIONATE IN THE PRESENCE OF METHANOL

Concn. of KCN (mM)	Concn. of MeOH (vol.%)	Temp. (°C)	Time (min)	Absorbance[a]	
				$S_3O_6^{2-}$	$S_4O_6^{2-}$
10	20	10	30	0.0005	0.402
10	20	30	15	0.013	0.409
10	20	30	60	0.037	0.410
10	30	10	30	0.000	0.377
10	30	20	30	0.0045	0.423
10	30	30	30	0.012	0.425
10	40	30	30	0.007	0.434
15	30	20	15		0.416, 0.418
15	30	20	30	0.000	0.420
20	20	25	30	0.012	0.410
20	30	10	5		0.293
20	30	10	10		0.379
20	30	10	15		0.407
20	30	10	20		0.418
20	30	10	30	0.001	0.420
20	30	20	15	0.001, 0.000	0.423, 0.424
20	30	20	30	0.006	0.423
20	30	25	15	0.008, 0.008	
20	30	30	30	0.026	0.422
20	40	30	30	0.016	0.437

$S_3O_6^{2-}$ taken: 9.90 μmol/50 ml, $S_4O_6^{2-}$ taken: 5.04 μmol/50 ml. a) Ferric nitrate-nitric acid solution was used. Optimum conditions: methanol 30 vol.%, KCN 20 mM, temp. 20 °C, time 15 min.

TABLE 5. CYANOLYSIS OF TRITHIONATE AND TETRATHIONATE IN THE PRESENCE OF ACETONE

Concn. of KCN (mM)	Concn. of acetone (vol.%)	Time (min)	Absorbance	
			$S_3O_6^{2-}$	$S_4O_6^{2-}$
15	20	10	0.0035	0.421
15	20	15		0.447
15	20	20	0.005	0.456
15	20	25		0.460
15	20	30	0.0085	0.460
15	20	40	0.010	
20	20	5		0.400
20	20	10	0.004	0.4525
20	20	15		0.4615
20	20	20	0.007	0.4615
20	20	30	0 0125	
20	20	40	0.014	
20	30	10	0.003	0.419
20	30	15		0.453
20	30	20	0.005	0.467
20	30	25		0.472
20	30	30	0.0075	0.471
20	30	35		0.472
20	30	40	0.009	

$S_3O_6^{2-}$ taken: 9.90 μmol/50 ml, $S_4O_6^{2-}$ taken: 5.04 μmol/50 ml. Optimum conditions: acetone 20 vol.%, KCN 20 mM, temp. 20 °C, time 20 min.

investigated in detail, results of which being shown in Tables 4 and 5, respectively. Under each table are described the optimum conditions, where at as near as 20 °C, in a short time, the cyanolysis of tetrathionate is saturated, and that of trithionate shows its minimum.

In the case when methanol was added, ferric nitrate–nitric acid solution[6] was used instead of ferric nitrate–perchloric acid solution, so as potassium perchlorate not to precipitate. As is evident from Table 6, the conditions shown under Table 5 seem to be superior to those shown under Table 4, in respect that the ab-

TABLE 6. EFFECT OF FOREIGN SUBSTANCES ON THE CUPRIC ION-CATALYZED CYANOLYSIS OF THIOSULFATE IN THE PRESENCE OF METHANOL AND ACETONE

		Organic solvent added (vol.%)	
Fe reagent		Methanol (30) $Fe(NO_3)_3$-HNO_3[6]	Acetone (20) $Fe(NO_3)_3$-$HClO_4$[13]
Na_2SO_4	50 mg/50 ml	93.3%[a]	100.0%
	100	88.5	100.4
	200	80.4	100.9
Na_2HPO_4	4	98.9	99.8
	20	97.5	99.8
	40	80.3	97.2
	100	40.7	95.6
	200	7.6	88.9
NaCl	50	98.6	100.6
	100	97.9	102.8
	250	95.5	111.9
	500	96.5	134.2
Na_2SO_3	1	94.4	99.2
	2	91.7	96.1
	5	87.5	92.4
	10	85.4	91.9

$S_2O_3^{2-}$ taken: 5.00 μmol/50 ml, concn. of KCN: 20 mM, concn. of $CuCl_2$: 6 mM. a) The figures show the recoveries of thiosulfate in per cent.

Table 7. Cyanolysis of thiosulfate, trithionate and tetrathionate under the optimum conditions

Organic solvent		MeOH	Acetone
Amount added (vol.%)		30	20
Concn. of KCN (mM)		20	20
Temp. (°C)		20	20
Time (min)		15	20
Degree of cyanolysis (%)	$S_2O_3^{2-}$	0.6	0.8
	$S_3O_6^{2-}$	0.1	0.7
	$S_4O_6^{2-}$	100.4	100.4

Amount of sample taken (μmol/50 ml): $S_2O_3^{2-}$ 10.00, $S_3O_6^{2-}$ 9.90, $S_4O_6^{2-}$ 5.04.

sorbance is not affected so much by co-existing ions. Accordingly, the authors have concluded that acetone is superior to methanol as a solvent to be added for depressing the cyanolysis of trithionate. Nietzel *et al.*[5] have reported that the sensitivity of analysis is increased by the addition of acetone in the cyanolysis of tetrathionate. However, it may be a new finding that the degree of cyanolysis of trithionate is depressed by the addition of organic solvents.

The degrees of cyanolysis of thiosulfate, trithionate and tetrathionate under the recommended conditions are given in Table 7. It is clear that the degree of cyanolysis of trithionate is extremely low, compared with the value of 4.7% under the conditions proposed by Kelly *et al.* (see Ref. 18, Treatment I). On the other hand, the degree of cyanolysis of tetrathionate was almost 100%. However, it may be well considered that 1% of thiosulfate formed as shown by Eq. (3) is converted to thiocyanate, since the purity of tetrathionate sample is not necessarily pure, and the cyanolysis of thiosulfate proceeds by 0.8% under these above-mentioned conditions. The reason why the discrepancy between expected value and obtained value in Treatment I is much larger than the discrepancies obtained in Treatments II and III proposed by Kelly *et al.*, may be also related to the phenomena of partial cyanolysis of thiosulfate as described above. On the other hand, the error due to the partial cyanolysis of thiosulfate may be eliminated, if all of the thiosulfate are converted to thiocyanate in the presence of cupric ions.

Now Procedure B′ will be discussed below. This procedure denotes the cyanolysis procedure for only tetrathionate in the absence of cupric ions and is identical, in principle, with Treatment I proposed by Kelly *et al.* As a relation of $S_B=S_A+2S_{B'}$ exists between the thiocyanate equivalents(S) of three sorts of procedures, one of the three procedures can be omitted for the determination of thiosulfate, trithionate and tetrathionate. It seems that Procedure B′ is most apt to produce error among the three procedures, so the authors have not adopted this procedure as one of the recommended procedures. Procedure B′, however, is useful for judging if higher polythionates are present or not in the sample solutions.

In Table 8, the thiosulfate concentration obtained in the presence of acetone is compared with that obtained in the absence of acetone, showing that the cyanolysis of thiosulfate proceeds quantitatively in Procedure B. The purity of potassium tetrathionate sample used in the present study was found to be 99.0% by means of Procedure B.

Table 8. Effect of acetone on the cupric ion-catalyzed cyanolysis of thiosulfate[a)]

Addition (vol.%)	$S_2O_3^{2-}$ obtained (mM)
None	1.042
Acetone (20) (=Procedure B)	1.036

Concn. of KCN: 20 mM, concn. of $CuCl_2$: 6 mM, $S_2O_3^{2-}$ concn. determined by iodometry: 1.035 mM. a) The calibration curves were prepared by using a standard thiocyanate solution. The figures are the means of three measurements.

Procedure C. Cyanolysis of Trithionate and Tetrathionate in Boiling Water Bath Followed by Cupric Ion-Catalyzed Cyanolysis of Thiosulfate. In Procedure C, not only thiosulfate and tetrathionate but also trithionate must be converted to thiocyanate. Urban[8)] has reported the conditions under which the cyanolysis of trithionate proceeds quantitatively. These conditions, however, are not practical due to the extremely long reaction time. Kelly *et al.*[18)] have proposed a procedure for the determination of trithionate by means of its cyanolysis at 100 °C and pH 9.6, followed by cupric ion-catalyzed cyanolysis of thiosulfate formed by the side reaction shown by Eq. (5).

$$S_3O_6^{2-} + H_2O = S_2O_3^{2-} + SO_4^{2-} + 2H^+ \qquad (5)$$

The principle of Procedure C in the present study is wholly identical with that proposed by Kelly *et al.* The addition of a large amount of phosphate, however, decreased the absorbance, as in the case of Procedure B, so the present authors decided to adopt the recommended procedure as shown above. There seems to be sufficient probability that thiosulfate and tetrathionate undergo the quantitative cyanolysis under the conditions of Procedure C.

The cyanolysis of trithionate without cupric ions was investigated at various temperatures, the results of which are shown in Fig. 4. It is obvious that the maximum

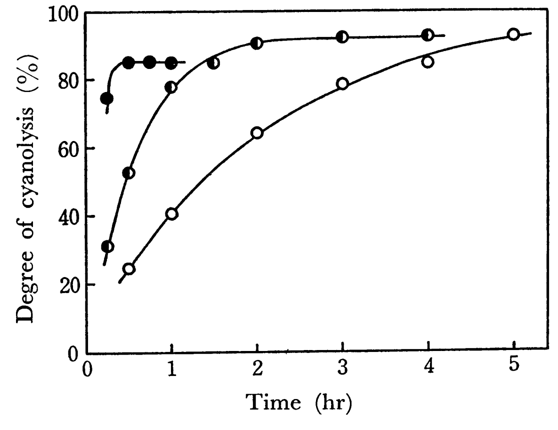

Fig. 4. Cyanolysis of trithionate at various temperatures.

Temp. (°C): ○ 50, ◐ 70, ● 90—95.

Concn. of KCN: 20 mM, $S_3O_6^{2-}$ taken: 4.95 μmol/50 ml.

recovery of trithionate decreases gradually with the increase of the cyanolysis temperature. On the other hand, the recoveries of trithionate under the following two sorts of cyanolysis conditions for 3 hr at 50 °C and 30 min at 95 °C, were the same and amounted to 97.6%, in the case when cupric ions were added after the cyanolysis. A difference of 2.4% between the expected value and the found value may be attributed to the impurities of the sample. Accordingly, it seems that trithionate undergoes the side reaction as shown by Eq. (5) during the cyanolysis at high temperature, and that Procedure C can be performed with a satisfactory accuracy for trithionate as well as thiosulfate and tetrathionate, as having been shown by Kelly *et al.* The purity of potassium tetrathionate sample used in the present study was found to be 99.3% by means of Procedure C.

Precision and Range of Determination. The precisions of Procedures A, B and C were evaluated by determining the concentrations of thiosulfate, tetrathionate and trithionate solutions, respectively, the results of which are shown in Table 9. An absorbance of 1.0 was obtained, when Procedures A, B and C were carried out, taking 12, 11 and 12 μ equivalents of thiocyanate in a 50-ml volumetric flask, respectively. Absorbance and concentration showed a good linear relation between them within this concentration range.

Table 9. Replicate determination of the concentrations of thiosulfate, tetrathionate and trithionate solutions

Sample solution Procedure applied		$S_2O_3^{2-}$ A	$S_4O_6^{2-}$ B	$S_3O_6^{2-}$ C
Analysis	1	0.495 mM	0.495 mM	0.489 mM
	2	0.496	0.495	0.488
	3	0.496	0.496	0.487
	4	0.495	0.495	0.487
	5	0.495	0.495	0.488
	6	0.495	0.494	0.488
Average		0.4953	0.4950	0.4878
CV (%)		0.23	0.28	0.34

Table 10. Application to the analysis of mixtures of thiosulfate, trithionate and tetrathionate (unit: mM)

		$S_2O_3^{2-}$	$S_3O_6^{2-}$	$S_4O_6^{2-}$	Procedures
Expt. 1	Expected	0	0	0.494	
	Found	0.002	0.004	0.486	A, B, C
2	Expected	0.364	0	0.368	
	Found	0.371	0.008	0.358	A, B, C
3	Expected	0.414	0.393	0.401	
	Found	0.418	0.382	0.395	A, B, C
		0.418	0.358	0.407	A, B′, C
		0.394	0.382	0.407	B′, B, C

The sample solutions were prepared by mixing the individual stock solutions. Procedure B′ is identical with Procedure B; the only difference is that cupric chloride is not added in Procedure B′. In the case when Procedure B′ is adopted, the amount of thiosulfate, trithionate and tetrathionate are given as follows: $(S_2O_3^{2-})=S_B-2S_{B'}$, $(S_3O_6^{2-})=S_C-S_A-2S_{B'}$, $(S_4O_6^{2-})=S_{B'}$.

Application to the Analyses of Mixtures. From the results described above, it is concluded that Procedures A, B and C can be performed without any noticeable side reactions. The following equivalents of thiocyanate(S) are formed by the three procedures (see Table 1):

$$S_A = (S_2O_3^{2-})$$
$$S_B = (S_2O_3^{2-}) + 2(S_4O_6^{2-})$$
$$S_C = (S_2O_3^{2-}) + (S_3O_6^{2-}) + 2(S_4O_6^{2-}).$$

Then, the amount of the species are given as follows:

$$(S_2O_3^{2-}) = S_A$$
$$(S_3O_6^{2-}) = S_C - S_B$$
$$(S_4O_6^{2-}) = \frac{1}{2}(S_B - S_A).$$

Table 10 shows the results of analyses of the mixtures consisting of thiosulfate, trithionate and tetrathionate. The values determined by Procedures A, B and C agree well with the expected values with a maximum discrepancy of 3%. This discrepancy seems to arise mainly by assuming that the polythionate samples are pure. On the other hand, it is noted that in the case when Procedure B′ is adopted, recoveries of tetrathionate tend to be high, while those of thiosulfate or trithionate tend to be correspondingly low. This phenomena may be explained by the fact that the cyanolysis of thiosulfate and trithionate cannot be depressed completely in Procedure B′.

In the analytical method described here, polythionates above tetrathionate were not considered. Investigation on the photometric determination method for thiosulfate, trithionate, tetrathionate and pentathionate are currently under way. If polythionates above tetrathionate react with cyanide quantitatively in Procedure B as shown in Eq. (6), the value of $1/2(S_B-S_A)$

$$S_nO_6^{2-} + (n-2)CN^- + 2OH^- = (n-2)SCN^- + SO_3^{2-} + SO_4^{2-} + H_2O \quad (6)$$

would be as follows: $((S_4O_6^{2-}) + 3/2(S_5O_6^{2-}) + 2(S_6O_6^{2-}) + \cdots\cdots\cdots)$. Paper chromatography[21] may be useful for judging the presence of such higher polythionates.

In the reaction of low valence sulfur compounds, a few sorts of polythionates often appear together with the familiar compounds such as thiosulfate, sulfite and sulfate. However, the analysis of sulfite and sulfate is not a serious problem. Accordingly, the present analytical method, by which the determination of thiosulfate, trithionate and tetrathionate in the concomitant presence of them can be made with a great simplicity and a high accuracy, may be used widely in various fields.

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