BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 703—708 (1966)

The Determination of Micro Amounts of Polythionates. V.* A Photometric Method for the Determination of Polythionates When Two Species of Them, Tetra-, Penta- and Hexathionate, are Present Together[1]

By Tomozo KOH and Iwaji IWASAKI

Laboratory of Analytical Chemistry and Geochemistry, Tokyo Institute of Technology, Ookayama, Tokyo

(Received July 28, 1965)

In the previous papers of this series, the present authors have found the conditions under which all three polythionates (n=4, 5 and 6) are quantitatively converted into thiocyanate. When one mole of polythionate undergoes cyanolysis, one mole of thiosulfate and ($n-3$) moles of thiocyanate are formed. The thiosulfate formed from polythionate is then converted into thiocyanate by the addition of a cupric chloride solution. A photometric method for the determination of polythionate when two species of polythionates, tetra-, penta- and hexathionate, are present toghther has been devised; it depends upon the determination of the different amounts of thiocyanate formed from the cyanolysis of polythionates both in the presence of cupric ions and in their absence. The mean number of sulfur atoms, n, in the formula, $S_nO_6^{2-}$, for polythionate, was determined; the polythionate composition of the solution was also evaluated from the n value

In the previous papers[2-4] of this series, the present authors have established excellent methods for the determination of polythionates, tetra-, penta- and hexathionate. These methods are based on the reaction:

$$S_nO_6^{2-}+(n-1)CN^-+H_2O= \\ S_2O_3^{2-}+SO_4^{2-}+2HCN+(n-3)SCN^- \quad (A) \\ (n=4,\ 5\ \text{and}\ 6)$$

followed by the photometric determination of the thiocyanate thus formed with ferric iron when tetra-, penta- or hexathionate is present by itself alone. They also have found the conditions under which all these polythionates are quantitatively converted into thiocyanate.

Iwasaki and his co-worker[5] have proposed a method for the determination of tetrathionate by means of its decomposition with sulfite.

It would be important and interesting, from the analytical and the geochemical viewpoints, to determine micro quantities of polythionates mixed with one another, but no satisfactory method has yet been devised for when they are present together. In the present paper, an attempt has been made, as the initial step, to determine polythionate when two species of polythionates, tetra-, penta- and hexathionate, are present together. It has been stated in the literature[6] that cupric ion has a catalytic effect on the conversion of thiosulfate into thiocyanate. Consequently, if the cupric chloride is added after the above Eq. A has been completed, then the thiosulfate formed from polythionate is further converted into thiocyanate. The overall reaction of polythionates, accordingly, is as follows:

$$S_nO_6^{2-}+nCN^-+H_2O= \\ SO_3^{2-}+SO_4^{2-}+2HCN+(n-2)SCN^- \quad (B) \\ (n=4,\ 5\ \text{and}\ 6)$$

Urban[7] has evaluated n in the formula, $S_nO_6^{2-}$, for polythionates by means of the photometric determination of different amounts of the thiocyanate formed in accordance with Eq. A and B. However, penta- and hexathionate, as has been pointed out in the previous papers,[2,3] are not quantitatively converted into thiocyanate under the conditions of Urban's method,[7] because of the partial alkaline decomposition arising from the higher pH value caused by the addition of a sodium cyanide solution. Therefore, Urban's method is inapplicable to the evaluation of n in the formula, $S_nO_6^{2-}$, for polythionates.

The present authors will here investigate, in greater detail, a photometric method for the determination of thiosulfate which is based on the formation of thiocyanate from thiosulfate by reaction with cyanide in the presence of cupric ions; they will propose a method for the determination of micro amounts of polythionates when two species of them are present together by means of the photometric determination of different amounts

---

* Part IV: This Bulletin, **39**, 576 (1966).

[1] Presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

[2] T. Koh, This Bulletin, **38**, 1510 (1965).

[3] T. Koh and I. Iwasaki, ibid., **38**, 2135 (1965).

[4] T. Koh and I. Iwasaki, ibid., **39**, 352 (1966).

[5] I. Iwasaki and S. Suzuki, ibid., **39**, 576 (1966).

[6] B. Sörbo, *Biochim. Biophysica Acta*, **23**, 412 (1957).

[7] P. J. Urban, *Z. anal. Chem.*, **180**, 110 (1961).

of the thiocyanate formed in accordance with Eqs. A and B. They will also determine n, the mean number of sulfur atoms in the formula, $S_nO_6^{2-}$, for polythionates above trithionate, and, at the same time, will evaluate the polythionate composition of the solution from the n values.

Experimental

Apparatus and Materials.—Unless stated otherwise, the apparatus and materials used in this investigation were the same as those described in previous papers.[2-4)]

The Standard Thiosulfate Solution.—The stock solution of thiosulfate was prepared by dissolving guaranteed sodium thiosulfate pentahydrate in freshly-boiled and cooled redistilled water containing a small amount of sodium carbonate; it was then standardized with a standard potassium iodate solution. The working thiosulfate solutions were prepared by diluting the stock solution properly.

The Cupric Chloride Solution.—The working cupric chloride solutions were prepared by diluting a 1 M solution properly.

Buffer Solution.—The solutions of acetic acid - sodium acetate (0.1 M), sodium dihydrogen phosphate-sodium hydroxide (0.2 M), borax - hydrochloric acid (0.2 M—0.1 N) and disodium phosphate - sodium hydroxide (0.1 M) were mixed with each other, at various ratios, in order to obtain buffer solutions from pH 3.2 to 5.0, from pH 6.0 to 8.0, from pH 8.8 to 10.0, and from pH 11.2 to 12.0 respectively.

Procedure A.—A sample solution of 10.0 ml. is placed in a 25 ml. volumetric flask. To this solution are added, first, 4.0 ml. of a phosphate buffer solution of pH 7.0, and then 2.5 ml. of a 0.1 M sodium cyanide solution; the pH of the solution is thereby brought to 8.7. The volumetric flask is kept in the thermostat at 40°C for 30 min.; polythionates are thereby quantitatively converted into thiocyanate according to Eq. A. Then 3.0 ml. of a 1.5 M ferric nitrate - perchloric acid solution is added. After the flask has been filled with redistilled water to the mark, the contents are mixed well. The absorbancy of the solution of the ferric-thiocyanate complex thus formed is measured at the wavelength of 460 mμ, using the reagent blank as a reference.

Procedure B.—To 10.0 ml. of a sample solution in a 25-ml. volumetric flask there are added, first, 4.0 ml. of a buffer solution of pH 7.0, and then 2.5 ml. of a 0.1 M sodium cyanide solution. After the volumetric flask has been kept in the thermostat at 40°C for 30 min., 1.5 ml. of a 0.05 M cupric chloride solution is added; the pH of the solution is thereby brought to 7.1. The mixture is shaken vigorously, whereupon polythionates are converted into thiocyanate quantitatively in accordance with Eq. B. Then 3.0 ml. of a perchloric acid solution of ferric nitrate is added; after filling the flask with redistilled water to the mark, the contents are mixed well. The absorbancy of the solution of the ferric-thiocyanate formed is measured at 460 mμ against the reagent blank.

Results and Discussion

Calibration Curves.—The calibration curves shown in Fig. 1 were obtained by the procedure B, using the standard solutions of thiosulfate and thiocyanate.

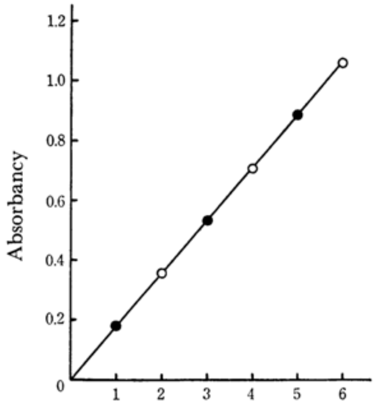

Fig. 1. Calibration curves.

○ Thiosulfate, ● Thiocyanate

When one ion of thiosulfate undergoes cyanolysis, one ion of thiocyanate is formed. Therefore, if thiosulfate is converted into thiocyanate quantitatively and completely, the calibration curve of thiosulfate should be in full accord with that of thiocyanate when plotted by the mole concentrations for thiosulfate and thiocyanate. Figure 1 shows that the reaction of thiosulfate with cyanide in the presence of cupric ions is stoichiometric and goes well to completion under the conditions mentioned above.

The standard solutions containing various amounts of tetra-, penta-, hexathionate and thiocyanate were treated by the procedure B described above; the experimental results are plotted in Figs. 2 and 3.

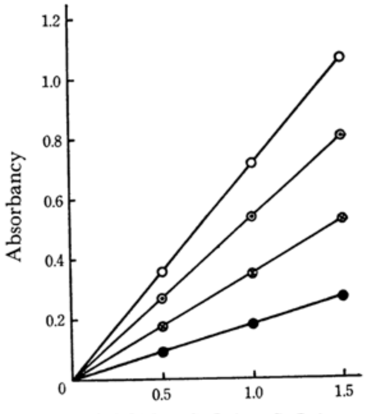

Fig. 2. Calibration curves.

● Thiocyanate, ⊗ Tetrathionate

⊙ Pentathionate, ○ Hexathionate

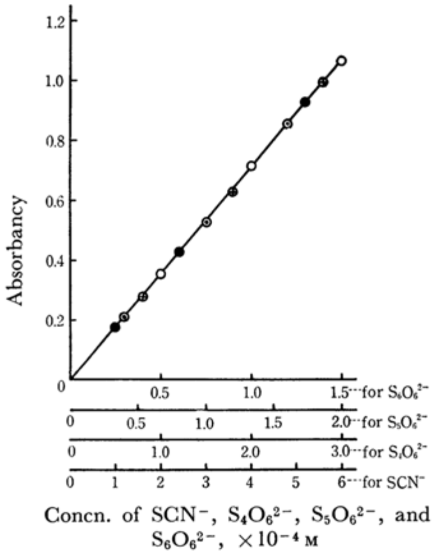

Fig. 3. Calibration curves.

● Thiocyanate, ⊗ Tetrathionate
⊙ Pentathionate, ○ Hexathionate

According to Eq. B, when one ion of polythionate, $S_nO_6^{2-}$ (n=4, 5 and 6), undergoes cyanolysis, ($n-2$) ions of thiocyanate are formed. As a matter of fact, Fig. 2 shows that the calibration curves of tetra-, penta- and hexathionate are, respectively, twice, three times and four times as sensitive as that of thiocyanate when plotted by the molar concentration.

As can also be seen in Fig. 3, their calibration curves are in exact accordance with that of thiocyanate when the scales of the concentrations of thiocyanate, tetrathionate and pentathionate are made to one-fourth, two-fourths and three-fourths of the hexathionate concentration, demonstrating that all three of these polythionates are quantitatively converted into thiocyanate according to Eq. B.

The Effect of the pH.—In order to study the effect of the pH on the cyanolysis, the reaction of thiosulfate with cyanide in the presence of cupric ions was carried out at various pH values. Figure 4 shows that the optimum pH value for the complete and stoichiometric reaction is within a range from 5.0 to 9.0 under the conditions of the procedure B described above.

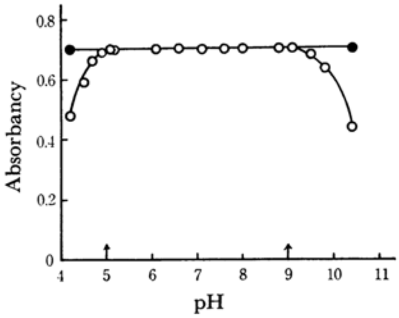

Fig. 4. The effect of the pH.

● 4.0×10^{-4} M SCN^-, ○ 4.0×10^{-4} M $S_2O_3^{2-}$

The pH of the solution, after the cyanolysis of polythionates in accordance with Eq. A, was brought from 8.7 to 7.1 by the addition of a 0.05 M cupric chloride solution in the procedure B.

The decreases in absorbancy below the pH value of 4.9 and above pH 9.1 may be attributed to the decrease in the concentration of cyanide ions with the lowering of the pH, and to the decrease of the concentration of cupric ions due in all probability to the formation of the cuprous-cyanide complex⁸⁾ which might result from the increase in the concentration of cyanide ions with the elevation of the pH.

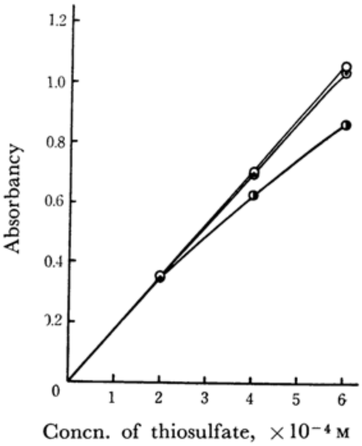

Fig. 5. The effect of the amount of sodium cyanide. The pH was adjusted to the range from 5.0 to 9.0 in all cases.

○ 0.1 M NaCN 1.2, 1.5, and 2.5 ml. (III)
◑ 0.1 M NaCN 0.5 ml. (I)
⊙ 0.1 M NaCN 1.0 ml. (II)

The Effect of the Amount of Sodium Cyanide.—In measuring the effect of the amount of sodium cyanide on the conversion of thiosulfate into thiocyanate, a volume of from 0.5 to 2.5 ml. of 0.1 M sodium cyanide was employed; in all cases the solution was buffered to the optimum pH range. The resulting effect is shown in Fig. 5.

The calibration curves with 0.5 and 1.0 ml. do not form straight lines (see I and II), indicating that the conversion of thiosulfate is not quantitative because of insufficient amounts of cyanide. Figure 5 shows that 1.2 ml. of a 0.1 M sodium cyanide solution is sufficient for the quantitative conversion and that the amount of sodium cyanide does not have any effect on the method as long as

---

8) E. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley & Sons, New York (1935), p. 667.

Table I. The effect of the amount of cupric chloride

Time min.	Sample	Absorbancy							
		4.0×10^{-4} M				6.0×10^{-4} M			
		0.05 M $CuCl_2$ 0.5 ml.	0.05 M $CuCl_2$ 1.0 ml.	0.05 M $CuCl_2$ 1.5 ml.	0.05 M $CuCl_2$ 2.0 ml.	0.05 M $CuCl_2$ 0.5 ml.	0.05 M $CuCl_2$ 1.0 ml.	0.05 M $CuCl_2$ 1.5 ml.	0.05 M $CuCl_2$ 2.0 ml.
	SCN^-	0.705	0.705	0.705	0.705	1.055	1.055	1.055	1.055
0.5	$S_2O_3^{2-}$	0.150	0.328	0.705	0.696	0.231	0.530	1.053	1.053
1	$S_2O_3^{2-}$	0.158	0.335	0.699	0.703	0.236	0.519	1.058	1.053
3	$S_2O_3^{2-}$	0.149	0.348	0.701	0.698	0.236	0.522	1.053	1.053
60	$S_2O_3^{2-}$	0.163	0.348	0.704	0.697	0.232	0.510	1.054	1.054

it is sufficient and the pH is adjusted to an optimum value. From a consideration of the cyanolysis of polythionate prior to the cyanolysis of the thiosulfate formed from the reaction of polythionate with cyanide, 2.5 ml. of a 0.1 M sodium cyanide solution was added in the present work.

The Effect of the Amount of Cupric Chloride.—In order to investigate the effect of the quantity of cupric ions, a solution of from 0.5 to 2.0 ml. of 0.05 M cupric chloride was employed; in all cases the solution was buffered to a pH value from 5.0 to 9.0. The results listed in Table I show that 1.5 ml. of a 0.05 M cupric chloride solution is sufficient for quantitative cyanolysis and that thiosulfate is instantly converted into thiocyanate in the pre- sence of cupric ions.

The Effect of Shaking on the Cyanolysis of Thiosulfate.—Table II shows that the shaking has to be made after the addition of a cupric chloride solution in order that the cyanolysis of thiosulfate may be stoichiometric and may go well to completion; otherwise the quantitative reaction does not occur.

Table II. Effect of shaking on cyanolysis of thiosulfate

Sample	Concn., $\times10^{-4}$ M	Absorbancy			
		No shaking		Shaking	
SCN^-	4.0	0.704	0.706	0.705	0.705
$S_2O_3^{2-}$	4.0	0.592	0.538	0.705	0.705

The Evaluation of n in $S_nO_6^{2-}$ for Polythionates.—Suppose A and B are the absorbancies obtained by the two procedures, A and B, described above, then:

$$A/B = (n-3)/(n-2)$$

When rearranged:

$$n = A/(B-A)+3 \quad \text{or} \quad n = (3B-2A)/(B-A)$$

The former, being the simpler for determining the n value, was used in this work. The results obtained when applied to solutions of tetra-, penta- and hexathionate are listed in Table III.

Table III. The evaluation of n in $S_nO_6^{2-}$ for polythionates

Sample	Concn. $\times10^{-4}$ M	Absorbancy A	Absorbancy B	n
$S_4O_6^{2-}$	1.5	0.268	0.525	4.04
$S_5O_6^{2-}$	1.5	0.522	0.801	4.87
$S_6O_6^{2-}$	1.5	0.801	1.063	6.06

Urban⁷⁾ has pointed out that polythionates, with the exception of tetrathionate, are mixtures containing the other polythionates; he deduced this from the n values, which he estimated to be from 4.29 to 4.34 for pentathionate and from 4.87 to 5.35 for hexathionate. However, his results do not seem reasonable, because these polythionates, as has been mentioned above, undergo a partial alkaline decomposition besides cyanolysis under the conditions of Urban's method.

From Table III, it may be seen that the n value, the mean number of sulfur atoms in the formula, $S_nO_6^{2-}$, for polythionate, could be sufficiently accurately determined by the present method.

The Evaluation of the Composition of Polythionates Simultaneously Present.—The composition of polythionates can be easily evaluated from the n value and Figs. 6 and 7 when two species of polythionates from among tetra-, penta- and hexathionate are simultaneously present.

The experimental results are given in Table IV.

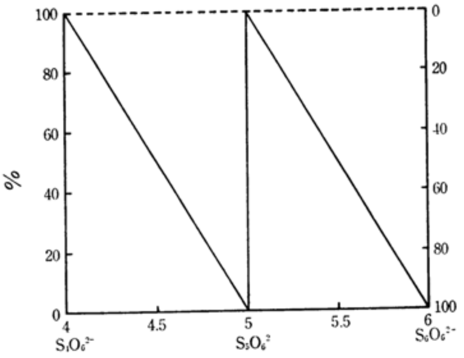

Fig 6.

Table IV. Evaluation of composition of polythionates present together

Concn. ×10⁻⁴ M		Composition calcd., %		n	Composition evaluated, %		Difference %	
$S_4O_6{}^{2-}$	$S_5O_6{}^{2-}$	$S_4O_6{}^{2-}$	$S_5O_6{}^{2-}$		$S_4O_6{}^{2-}$	$S_5O_5{}^{2-}$	$S_4O_6{}^{2-}$	$S_5O_6{}^{2-}$
1.5	0.5	75	25	4.21	79	21	+4	−4
1.0	1.0	50	50	4.44	56	44	+6	−6
0.5	1.0	33.3	66.7	4.60	40	60	+6.7	−6.7
$S_5O_6{}^{2-}$	$S_6O_6{}^{2-}$	$S_5O_6{}^{2-}$	$S_6O_6{}^{2-}$		$S_5O_6{}^{2-}$	$S_6O_6{}^{2-}$	$S_5O_6{}^{2-}$	$S_6O_6{}^{2-}$
1.0	0.6	62.5	37.5	5.33	67	33	+4.5	−4.5
0.8	0.8	50	50	5.44	56	44	+6	−6
0.4	1.2	25	75	5.73	27	73	+2	−2
$S_4O_6{}^{2-}$	$S_6O_6{}^{2-}$	$S_4O_6{}^{2-}$	$S_6O_6{}^{2-}$		$S_4O_6{}^{2-}$	$S_6O_6{}^{2-}$	$S_4O_6{}^{2-}$	$S_6O_6{}^{2-}$
1.4	0.2	87.5	12.5	4.24	88	12	+0.5	−0.5
1.0	0.6	62.5	37.5	4.75	62.5	37.5	0	0
1.0	1.0	50	50	5.09	45.4	54.6	−4.6	+4.6
0.5	1.0	33.3	66.7	5.29	35.8	65.2	+2.5	−2.5

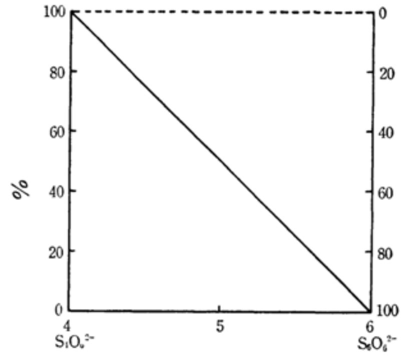

Fig. 7.

As may be seen in Table IV, there is a remarkable agreement between the experimental and the calculated compositions.

The Determination of Tetrathionate and Pentathionate Simultaneously Present.—The method consists of the determination of the different amounts of thiocyanate formed from Eqs. A and B on two separate aliquots of the sample; one is treated by the procedure A, and the other, by the procedure B. Then:

$$(S_4O_6{}^{2-}) = 2B-3A \text{ and } (S_5O_6{}^{2-}) = 2A-B,$$

where $(S_4O_6{}^{2-})$ and $(S_5O_6{}^{2-})$ indicate the absorbancy corresponding to the same concentration of thiocyanate as those of tetrathionate and pentathionate; A and B are the absorbancies obtained by the procedures A and B.

Tetrathionate and pentathionate simultaneously present can be readily determined by reference to the calibration curve in Fig. 1. The results listed in Table V show that this method can be accurately applied to the determination of tetrathionate and pentathionate simultaneously present at various ratios.

The Determination of a Tetrathionate-Hexathionate Mixture and a Pentathionate-Hexathionate Mixture.—The following equations can also be obtained: for a tetrathionate-hexathionate mixture, $(S_4O_6{}^{2-}) = (3B-4A)/2$ and $(S_6O_6{}^{2-}) = (2A-B)/2$; for a pentathionate-hexathionate mixture, $(S_5O_6{}^{2-}) = 3B-4A$ and $(S_6O_6{}^{2-}) = 3A-2B$. These polythionates can be determined in the same way as that used for a tetrathionate-pentathionate mixture, by using the above equations when two species of polythionates are simultaneously present. The results of the deter-

Table V. Determination of tetrathionate and pentathionate present together

Polythionates taken, ×10⁻⁴ M		Polythionates found, ×10⁻⁴ M		Difference ×10⁻⁴ M	
$S_4O_6{}^{2-}$	$S_5O_6{}^{2-}$	$S_4O_6{}^{2-}$	$S_5O_6{}^{2-}$	$S_4O_6{}^{2-}$	$S_5O_6{}^{2-}$
0.50	1.00	0.63	0.91	+0.13	−0.09
0.50	1.60	0.57	1.54	+0.07	−0.06
1.00	1.00	1.14	0.91	+0.14	−0.09
1.00	1.50	1.02	1.45	+0.02	−0.05
1.50	0.50	1.56	0.45	+0.06	−0.05
1.50	1.00	1.56	0.92	+0.06	−0.08
2.00	0.60	2.04	0.54	+0.04	−0.06

Table VI. Determination of tetrathionate and hexathionate present together

Polythionates taken, ×10⁻⁴ M		Polythionates found, ×10⁻⁴ M		Difference ×10⁻⁴ M	
$S_4O_6{}^{2-}$	$S_6O_6{}^{2-}$	$S_4O_6{}^{2-}$	$S_6O_6{}^{2-}$	$S_4O_6{}^{2-}$	$S_6O_6{}^{2-}$
0.50	0.50	0.56	0.46	+0.06	−0.04
0.50	1.00	0.58	0.96	+0.08	−0.04
0.50	1.20	0.52	1.18	+0.02	−0.02
1.00	0.50	0.96	0.51	−0.04	+0.01
1.00	0.60	0.99	0.60	−0.01	0
1.00	1.00	0.92	1.02	−0.08	+0.02
1.50	0.50	1.54	0.47	+0.04	−0.03
1.50	0.70	1.66	0.73	+0.16	+0.03
2.00	0.40	1.96	0.40	+0.04	0

TABLE VII. DETERMINATION OF PENTATHIONATE AND HEXATHIONATE PRESENT TOGETHER

Polythionates taken, $\times 10^{-4}$ M		Polythionates found, $\times 10^{-4}$ M		Difference $\times 10^{-4}$ M	
$S_5O_6^{2-}$	$S_6O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$	$S_5O_6^{2-}$	$S_6O_6^{2-}$
0.30	0.50	0.41	0.40	+0.11	−0.10
0.30	1.00	0.39	0.93	+0.09	−0.07
0.30	1.20	0.28	1.19	−0.02	−0.01
0.40	1.20	0.42	1.16	+0.02	−0.04
0.50	0.50	0.68	0.36	+0.18	−0.14
0.50	1.00	0.65	0.88	+0.15	−0.12
0.50	1.20	0.36	1.28	−0.14	+0.08
0.80	0.80	0.90	0.72	+0.10	−0.08
1.00	0.40	1.18	0.26	+0.18	−0.14
1.00	0.60	1.08	0.54	+0.08	−0.06
1.00	0.80	0.98	0.80	−0.02	0
1.50	0.40	1.54	0.37	+0.04	−0.03

mination of polythionates mixed in various ratios are given in Tables VI and VII.

As will be seen in Tables V, VI and VII, the results are reproducible within an error of $\pm 0.2 \times 10^{-4}$ M of polythionates.

Summary

The photometric method for the determination of a small amount of thiosulfate has been investigated in greater detail; it is based on the formation of thiocyanate from the reaction of thiosulfate with cyanide in the presence of cupric ions, and on the determination of the thiocyanate with an excess of ferric iron.

The polythionates are first converted into thiocyanate with cyanide; one ion of thiosulfate is also thereby formed. The thiosulfate formed is then converted into thiocyanate by the addition of a cupric chloride solution. A method for the determination of micro amounts of polythionates mixed with each other has been devised; it is based on the determination of the different amounts of thiocyanate formed from the cyanolysis of polythionates in the presence of cupric ions and in their absence.

The present method was reproducible to $\pm 0.2 \times 10^{-4}$ M of polythionates when applied to the determination of polythionates simultaneously present at various ratios.

The authors wish to express their gratitude to Dr. Satori Utsumi of Nihon University, and to Mr. Takejiro Ozawa and Dr. Minoru Yoshida of the Tokyo Institute of Technology, for their valuable advice during this study.