Spectrophotometric Determination of Tetrathionate by Its Oxidation with Iodate

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(Received January 25, 1991)

The conditions under which tetrathionate is oxidized stoichiometrically to sulfate by iodate have been established by investigating the reaction rate of tetrathionate with iodate in a medium containing varying amounts of sulfuric acid at room temperature and 40 °C. Tetrathionate reacted with iodate with a tetrathionate : iodate mole ratio of 3 : 7 under the conditions of the usual procedure. After a complete reaction, the iodine, formed from excess iodate by the addition of iodide, was spectrophotometrically measured as triiodide. A 14-fold chemical amplification was achieved for the determination of tetrathionate by using the proposed method, compared with the conventional methods via the sulfitolysis and cyanolysis of tetrathionate. A linear calibration graph with a negative slope was obtained over the concentration range 2.5×10^{-7}—2.5×10^{-5} mol dm^{-3} tetrathionate (0.56—56 μg of $S_4O_6^{2-}$ in 10 cm^3); the relative standard deviation was 0.42% at the 1.5×10^{-5} mol dm^{-3} tetrathionate level.

The identification and determination of polythionates in their mixtures are difficult owing to similarities in their chemical and physical properties.[1] Hence, various reactions of individual polythionates, such as cyanolysis,[2–7] sulfitolysis[8–10] and sulfidolysis,[11,12] have been investigated in detail in order to determine a specific polythionate in the presence of other polythionates. These reactions have played an important role in the development of methods for the analysis of mixtures of polythionates.[13–17] All of these methods have been based on the formation of thiosulfate and/or thiocyanate equivalent to the polythionates, and on the spectrophotometric measurements of the reaction products.

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

$$IO_3^- + 8I^- + 6H^+ \longrightarrow 3I_3^- + 3H_2O. \quad (1)$$

Further, the molar absorptivity of triiodide at 350 nm is much higher than that of iodine in carbon tetrachloride at 515 nm.[18] With regard to reactions involving oxoacid ions, such as the iodate ion, the potential for its reduction to the iodide ion is expected to increase with an increase in the hydrogen-ion concentration. In a previous paper[19] it was mentioned that thiosulfate can be oxidized by iodate to sulfate in a strong acidic medium, and that a simple, precise method has been developed for the determination of thiosulfate. In this study we attempted to oxidize tetrathionate with iodate in a strong acid medium, and established the conditions under which tetrathionate can be stoichiometrically oxidized to sulfate according to the following equation:

$$3S_4O_6^{2-} + 7IO_3^- + 9H_2O \longrightarrow 12SO_4^{2-} + 7I^- + 18H^+. \quad (2)$$

The proposed method for the determination of tetrathionate, in which the formed iodine equivalent to the excess iodate is measured spectrophotometrically, is very simple and is 14-fold more sensitive than previous methods for tetrathionate by its cyanolysis[15] and sulfitolysis.[8]

Experimental

Apparatus and Reagents. A Shimadzu Model UV-240 recording spectrophotometer with 10-mm quartz cells was used for all of the absorbance measurements. The desired temperatures were controlled by a Taiyo Model M-1 incubator.

All of the chemicals used, except for tetrathionate, were of analytical-reagent grade and were used without further purification. The water used in these experiments was redistilled.

Standard Tetrathionate Solution: Potassium tetrathionate was prepared according to a procedure described by Stamm and Goehring.[20] The obtained tetrathionate was recrystallized with water at temperatures below 60 °C and then dried at room temperature before storage at −10±2 °C. A standard tetrathionate solution (1×10^{-3} mol dm^{-3}) was prepared by dissolving 151.3 mg of the potassium tetrathionate (water content: 0.07%) in water and diluting it to 500 cm^3; it was then stored at 5±2 °C. Working standards were prepared by suitable dilultion.

Standard Iodate Solution: A 0.100/6 mol dm^{-3} iodate solution was prepared by dissolving 3.567 g of potassium iodate (99.98%) in water and diluting to 1000 cm^3. Working standard iodate solutions were prepared by appropriate dilution.

Standard Thiosulfate Solution: An approximately 0.1 mol dm^{-3} solution was prepared by dissolving a known amount of 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 (0.01% w/v Na_2CO_3) were prepared by suitable dilution of the standard with oxygen-free water.

Procedure. Pipette 10 cm^3 of a sample solution of up to 2.86×10^{-5}mol dm^{-3} tetrathionate into a 50-cm^3 calibrated flask, and add 3 cm^3 of 5 mol dm^{-3} sulfuric acid and 4.2 cm^3 of $1\times10^{-3}/6$ mol dm^{-3} standard iodate solution. Allow the flask to stand in a thermostat at 40 °C for 30 min in order to oxidize the tetrathionate completely to sulfate according to Eq. 2. Then add 5 cm^3 of 5 mol dm^{-3} acetic acid, 5 cm^3 of 6 mol dm^{-3} sodium hydroxide and 5 cm^3 of 1 mol dm^{-3} potassium iodide, whereupon the iodine equivalent to the excess iodate is quantitatively formed. After diluting to the mark with water, mix the contents well and measure the absorbance of a solution of the triiodide against water at 350 nm.

Prepare an iodate-free reagent blank by adding 4.2 cm^3 of water in place of 4.2 cm^3 of $1\times10^{-3}/6$ mol dm^{-3} standard iodate solution and treating it exactly the same, and correct it for all the absorbances measured in this study.

Results and Discussion

Calibration Graphs. A series of standard solutions (10 cm^3) of tetrathionate were treated as described in the Procedure section. After the complete reaction of tetrathionate with iodate, the iodine which formed from the excess iodate was spectrophotometrically measured as triiodide. Hence, the proposed method gave a linear calibration graph with a negative slope for an increase in the concentration of tetrathionate. In previous methods, the thiosulfate formed by the sulfitolysis[8] and cyanolysis[15] of tetrathionate was measured by the consumption of iodine according to the following equation:

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-, \qquad (3)$$

in which 1 mol of thiosulfate furnishes 1 mol of electrons. On the other hand, according to Eq. 2, tetrathionate is oxidized to sulfate by iodate; 1 mol of tetrathionate furnishes 14 mol of electrons. Therefore, when the amount of liberated iodine equivalent to the excess iodate for tetrathionate is measured, a 14-fold chemical amplification can be achieved for the determination of tetrathionate. The calibration graph for tetrathionate obtained by the proposed method is shown, together with the calibration graph obtained for thiosulfate using iodine,[21] in Fig. 1, in which the molar concentration scale for tetrathionate was drawn to 14-times the scale for the thiosulfate concentration. The calibration graph for tetrathionate and that for thiosulfate were parallel to each other; the lower reagent blank obtained by the proposed method can be probably attributed to the oxidation of trace amounts of impurities in the reagents by the iodate and to the higher temperatures caused by the heat of neutralization of a strong acid; at higher temperatures the absorbance of triiodide decreases owing to its dissociation. When the reagent blank obtained for thiosulfate was normalized to that for tetrathionate, both the calibration graphs coincided completely with each other. This confirms that tetrathionate is quantitatively oxidized to sulfate by iodate according to Eq. 2 under the conditions described in the Procedure section.

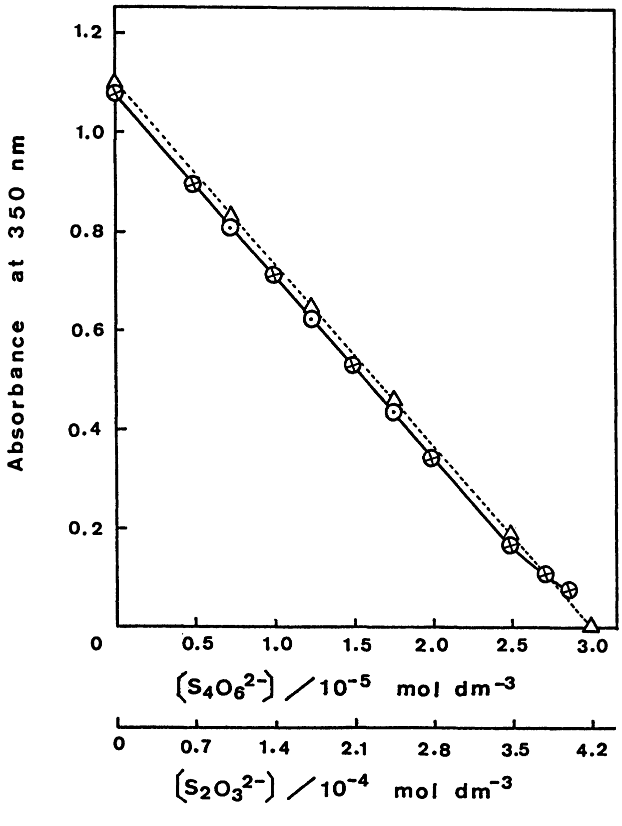

Fig. 1. Calibration graphs for tetrathionate and thiosulfate. ⊗, Tetrathionate by the proposed method; △, thiosulfate by iodine method;[21] ⊙, expected graph (the reagent blank obtained by the iodine method was normalized to that by the proposed method).

The proposed method can be applied to the determination of tetrathionate in the concentration range 2.5×10^{-7}—2.5×10^{-5} mol dm^{-3} (0.056—5.6 ppm). The precision of the method was based on 11 replicate analyses of a 10-cm^3 aliquot of a 1.5×10^{-5} mol dm^{-3} standard tetrathionate solution (33.6 μg of $S_4O_6^{2-}$ in 10 cm^3); the mean value of tetrathionate was found to be 33.5 μg, with a standard deviation of 0.14 μg of $S_4O_6^{2-}$ and a relative standard deviation of 0.42%.

Reaction Rate of Tetrathionate with Iodate. It is normally known that the potential for the redox couples, which involve a large number of hydrogen ions, is strongly dependent on the hydrogen-ion concentration. We therefore made an attempt to oxidize tetrathionate with iodate in an acidic medium of various strong acids: hydrochloric, nitric, perchloric, and sulfuric. Among these acids, only sulfuric acid proved suitable as a medium for the reaction of tetrathionate with iodate.[19] Therefore, the reaction rate was investigated in a medium containing varying amounts of sulfuric acid at 21 °C (i.e., room temparature); tetrathionate was allowed to react with iodate for various periods of time; the amount of iodine liberated from the excess of the iodate by the addition of iodide was then measured. The resulting graphs are shown in Fig. 2. Here, all of the absorbances obtained were normalized to those obtained using 3 cm^3 of 5 mol dm^{-3} sulfuric acid (i.e., all the reagent blanks were normalized to that obtained under the Procedure section). The reaction did not go to completion, even within 2 h in a 0.52 mol dm^{-3} sulfuric acid medium (3-cm^3 addition of 3 mol dm^{-3} H_2SO_4). Still, the reaction rate was accelerated by an increase in the amount of sulfuric acid; the reaction proceeded to stoichiometric completion according to Eq. 2 within 80 min in a 0.70 mol dm^{-3} sulfuric acid

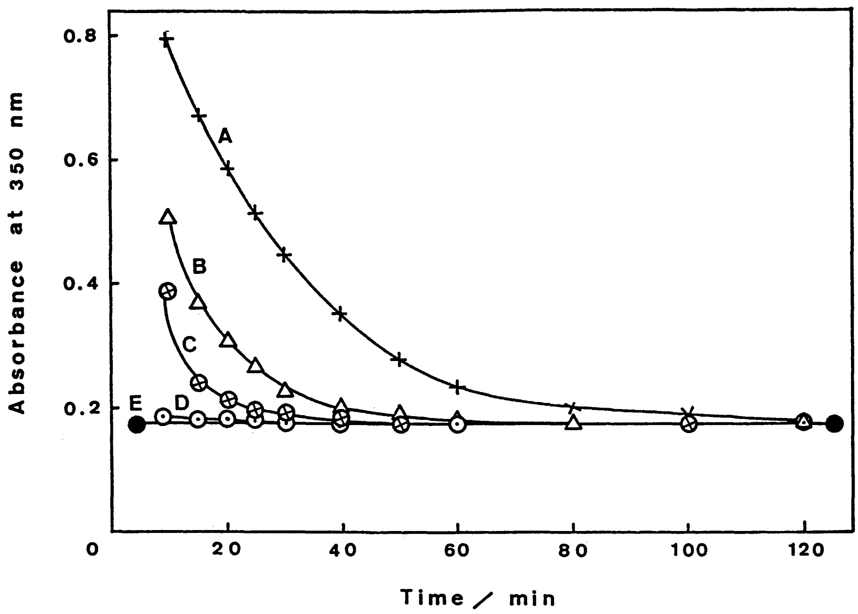

Fig. 2. Reaction rate of tetrathionate with iodate in a medium containing varying amounts of sulfuric acid at 21 °C (i. e., room temperature). A 10-cm^3 solution of 2.5×10^{-5} mol dm^{-3} tetrathionate was used. A, 3-cm^3 addition of 3 mol dm^{-3} H_2SO_4; B, 3-cm^3 addition of 4 mol dm^{-3} H_2SO_4; C, 3-cm^3 addition of 5 mol dm^{-3} H_2SO_4; D, 3-cm^3 addition of 8 mol dm^{-3} H_2SO_4; E, expected value obtained for 3.5×10^{-4} mol dm^{-3} $S_2O_3^{2-}$ using iodine method.[21]

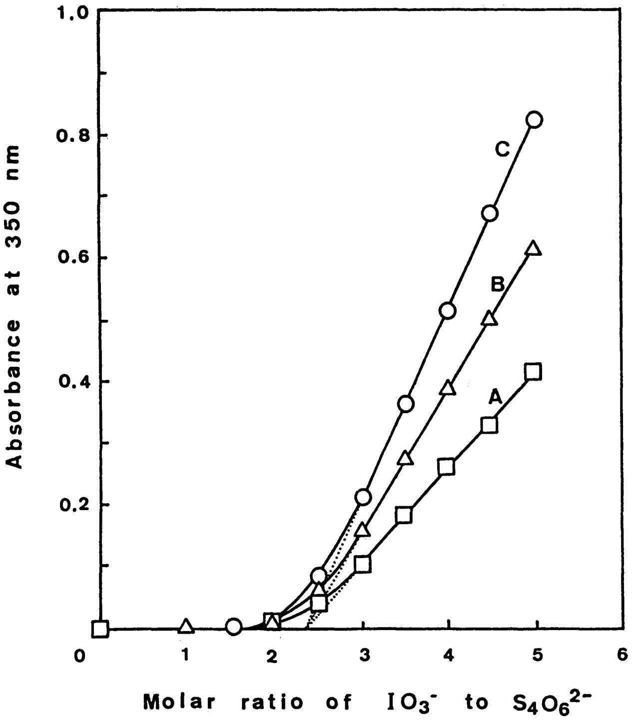

Fig. 3. Molar ratio graphs for the reaction of tetrathionate with iodate. A 10-cm^3 tetrathionate solution with various concentrations was used. A, 1×10^{-5} mol dm^{-3} $S_4O_6^{2-}$; B, 1.5×10^{-5} mol dm^{-3} $S_4O_6^{2-}$; C, 2×10^{-5} mol dm^{-3} $S_4O_6^{2-}$.

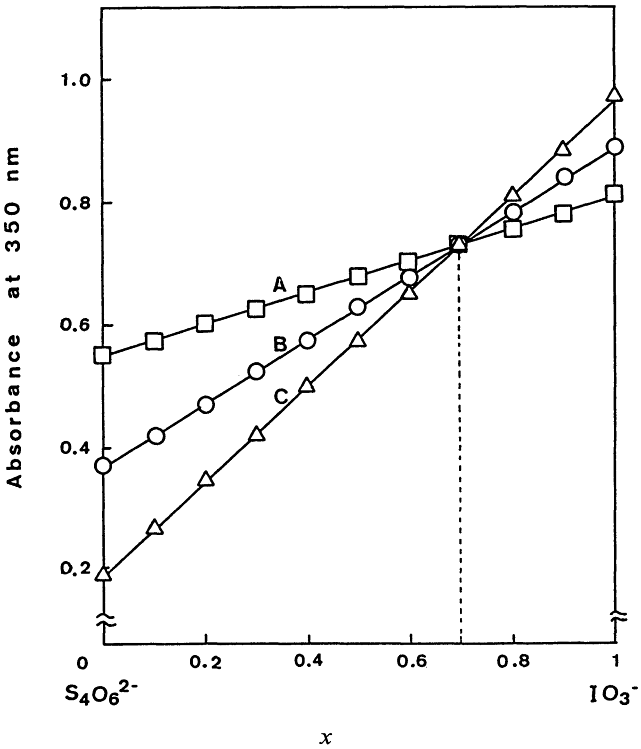

Fig. 4. Continuous variation graphs for the reaction of tetrathionate with iodate. A, $[IO_3^-]+[S_4O_6^{2-}]=5\times10^{-6}$ mol dm^{-3}; B, $[IO_3^-]+[S_4O_6^{2-}]=1\times10^{-5}$ mol dm^{-3}; C, $[IO_3^-]+[S_4O_6^{2-}]=1.5\times10^{-5}$ mol dm^{-3}. A 2.8-cm^3 solution of $1\times10^{-3}/6$ mol dm^{-3} iodate was additionally used.

Table 1. Effect of Foreign Ions on the Determination of 33.6 μg of Tetrathionate in 10 cm^3 of Sample Solution

Ion	Added as[a)]	Amount μg	Amount of $S_4O_6^{2-}$ found μg	Error %
None			33.6	
Na^+	Na_2SO_4	10000	33.6	0
K^+	K_2SO_4	10000	33.6	0
NH_4^+	$(NH_4)_2SO_4$	10000	33.6	0
Mg^{2+}	$MgSO_4$	10000	33.6	0
Zn^{2+}	$ZnSO_4$	10000	33.8	0.6
Ca^{2+}	$Ca(NO_3)_2$	10000	33.2	−1.2
Cd^{2+}	$CdSO_4$	10000	33.6	0
Al^{3+}	$K_2Al_2(SO_4)_4$	10000	33.8	0.6
Pb^{2+}	$Pb(NO_3)_2$	1000	31.6	−6.0
		100	33.6	0
Mn^{2+}	$MnSO_4$	100	22.4	−33.3
		10	33.8	0.6
Cu^{2+}	$CuSO_4$	100	26.9	−19.9
		10	33.8	0.6
Fe^{2+}	$FeSO_4$	1000	22.2	−33.9
		100	34.0	1.8
Fe^{3+}	$Fe(NH_4)(SO_4)_2$	100	25.6	−24.1
		100	33.2[b)]	−1.2
F^-	NaF	10000	33.8	0.6
Cl^-	KCl	10000	34.0	1.8
Br^-	KBr	10000	34.7	3.3
I^-	KI	1000	14.1	−58.0
		100	34.5	2.7
SO_4^{2-}	Na_2SO_4	10000	33.6	0
NO_3^-	KNO_3	10000	33.4	−0.6
HPO_4^{2-}	Na_2HPO_4	10000	33.6	0
HCO_3^-	$NaHCO_3$	10000	33.6	0
$HAsO_4^{2-}$	Na_2HAsO_4	10000	33.8	0.6
NO_2^-	$NaNO_2$	10	29.4	−12.5
		10000	33.8[c)]	−0.6
HSO_3^-	$NaHSO_3$	10	37.4	11.3
		100	34.0[d)]	1.8
S^{2-}	Na_2S	1	35.6	6.0
		10	34.5[d)]	2.7

a) Water of crystallization is omitted for brevity. b) Iron(III) was masked by adding 1 cm^3 of 0.2 mol dm^{-3} sodium fluoride. c) Nitrite was decomposed by adding 1 cm^3 of 0.5 mol dm^{-3} amidosulfuric acid. d) The nitrogen gas at a flow-rate of 400 cm^3 min^{-1} was bubbled for 30 min.

medium (3-cm^3 addition of 4 mol dm^{-3} H_2SO_4), within 50 min in a 0.87 mol dm^{-3} sulfuric acid medium (3-cm^3 addition of 5 mol dm^{-3} H_2SO_4) and within 30 min in a 1.4 mol dm^{-3} sulfuric acid medium (3-cm^3 addition of 8 mol dm^{-3} H_2SO_4); the absorbances remained constant. At 40 °C, the reaction rate was accelerated much more and the reaction went to completion within 40 min in a 0.52 mol dm^{-3} sulfuric acid medium, within 30 min in a 0.70 mol dm^{-3} sulfuric acid medium and within 20 min in both 0.87 and 1.4 mol dm^{-3} sulfuric acid media. Hence, for the usual procedure, 3 cm^3 of 5 mol dm^{-3} sulfuric acid was employed and tetrathionate was allowed to react with iodate in the 0.87 mol dm^{-3} sulfuric acid medium for 30 min at 40 °C.

The sulfuric acid used had to be neutralized with a strong base; otherwise, the absorbance of triiodide increased greatly and rapidly with time owing to the formation of iodine in a strong acid medium, as the result of air-oxidation of the iodide added for the liberation of iodine from the excess iodate. Accordingly, each amount of the sulfuric acid used was neutralized with a strong base equivalent to the amount of the sulfuric acid. Further, 5 cm^3 of 5 mol dm^{-3} acetic acid was added to make the solution weakly acidic. However, it was desirable to measure the absorbance of the triiodide as soon as possible after its formation. A 4—8 cm^3 volume of 1 mol dm^{-3} potassium iodide solution proved to be sufficient for the complete liberation of iodine; in the Procedure section, a 5-cm^3 volume of 1 mol dm^{-3} potassium iodide solution was employed.

Stoichiometric Relationship for the Reaction of Tetrathionate with Iodate. An attempt was made to determine the stoichiometric relationship for the reaction of tetrathionate with iodate in a medium of sulfuric acid using both the molar ratio method and the continuous variation method. For applying the molar ratio method, 10 cm^3 each of 1×10^{-5}, 1.5×10^{-5}, and 2×10^{-5} mol dm^{-3} tetrathionate solutions, and 4.2 cm^3 of each of iodate solutions (with varying concentrations) were used with a varying mole ratios of iodate to tetrathionate. After the addition of 3 cm^3 of 5 mol dm^{-3} sulfuric acid to each mixture, the mixture was allowed to stand for 30 min at 40 °C. The absorbance of the series of the solutions obtained was then measured according to the Procedure section. The resulting graphs are shown in Fig. 3. In order to determine the stoichiometric relationship of iodate to tetrathionate involved in the determination of tetrathionate, straight portions of each graph were extrapolated to the abscissa, since the proposed method gave a straight calibration graph over the concentration range of up to 2.5×10^{-5} mol dm^{-3} tetrathionate. Each dotted line intersected the abscissa at the point 2.3 (7/3). This proves that 3 mol of tetrathionate reacted with 7 mol of iodate under the conditions of the usual procedure.

For the method of continuous variations, each $10x$ (x=mole fraction of iodate) cm^3 of 5×10^{-6}, 1×10^{-5}, and 1.5×10^{-5} mol dm^{-3} iodate solutions, and each $10(1-x)$ cm^3 of 5×10^{-6}, 1×10^{-5}, and 1.5×10^{-5} mol dm^{-3} tetrathionate solutions were used to prepare a series of 10-cm^3 solutions with a varying iodate–tetrathionate mole ratio. To each mixture, 2.8 cm^3 of $1\times10^{-3}/6$ mol dm^{-3} iodate solution was added in order to obtain the absorbance of iodine (as triiodide), even in the region of the excess of tetrathionate ($x<0.7$). Then, 3 cm^3 of 5 mol dm^{-3} sulfuric acid and 1.4 cm^3 of water were added; the resulting volume of the solution was 17.2 cm^3 (as described in the Procedure section). The mixture was allowed to stand for 30 min at 40 °C; then, the absorbance of a series of the solutions was measured at 350 nm against water. Figure 4 shows the resulting plots of absorbance vs. mole fraction of iodate; all three graphs intersected at the point indicating a 0.7 [7/(7+3)] mole fraction of iodate. Further, this point appeared just on the absorbance obtained for the amount of the iodate used additionally. These results signify that tetrathionate reacted with iodate stoichiometrically with a tetrathionate : iodate mole ratio of 3 : 7 under the conditions described in the Procedure section, according with the results obtained by the method of molar ratios.

Effect of Foreign Ions. A 10-cm^3 solution containing 33.6 μg of tetrathionate (1.5×10^{-5} mol dm^{-3} tetrathionate) and various amounts of foreign ions was treated as described in the Procedure Section. The results are given in Table 1. The proposed method is based on the oxidation of tetrathionate with iodate in a strong acid medium, followed by spectrophotometric measurements of the iodine (as triiodide) formed (by the addition of iodide) from the excess iodate. Hence, the ions which oxidize iodide or reduce iodate are thought to interfere with the determination of tetrathionate. Copper(II), iron(III), and nitrite (which oxidize iodide), and sulfite and sulfide (which reduce iodate) gave serious errors when present in small amounts. Still, the nitrite was tolerated in amounts of up to 10000 μg by decomposing it by the addition of 1 cm^3 of 0.5 mol dm^{-3} amidosulfuric acid solution.

References

1) T. Koh, *Anal. Sci.*, **6**, 3 (1990).

2) P. J. Urban, *Fresenius' Z. Anal. Chem.*, **179**, 422 (1961).

3) T. Koh, A. Wagai, and Y. Miura, *Anal. Chim. Acta*, **71**, 367 (1974).

4) O. A. Nietzel and M. A. DeSesa, *Anal. Chem.*, **27**, 1839 (1955).

5) T. Koh and I. Iwasaki, *Bull. Chem. Soc. Jpn.*, **39**, 352 (1966).

6) T. Koh, *Bull. Chem. Soc. Jpn.*, **38**, 1510 (1965).

7) T. Koh and I. Iwasaki, *Bull. Chem. Soc. Jpn.*, **38**, 2135 (1965).

8) T. Koh, K. Taniguchi, Y. Miura, and I. Iwasaki, *Nippon Kagaku Kaishi*, **1979**, 348.

9) T. Koh, K. Taniguchi, and I. Iwasaki, *Bull. Chem. Soc. Jpn.*, **51**, 164 (1978).

10) T. Koh and K. Taniguchi, *Anal. Chem.*, **46**, 1679 (1974).

11) T. Koh, Y. Miura, and M. Suzuki, *Anal. Sci.*, **4**, 267 (1988).

12) T. Koh, Y. Miura, and M. Suzuki, *Analyst* (*London*), **113**, 949 (1988).

13) T. Koh and I. Iwasaki, *Bull. Chem. Soc. Jpn.*, **39**, 703 (1966).

14) D. P. Kelly, L. A. Chambers, and P. A. Trudinger, *Anal. Chem.*, **41**, 898 (1969).

15) T. Koh and K. Taniguchi, *Anal. Chem.*, **45**, 2018 (1973).

16) T. Koh, Y. Aoki, and I. Iwasaki, *Analyst* (*London*), **104**, 41 (1979).

17) T. Koh, Y. Miura, M. Ishimori, and N. Yamamuro, *Anal. Sci.*, **5**, 79 (1989).

18) T. Ozawa, *Nippon Kagaku Zasshi*, **87**, 573 (1966).

19) T. Koh, K. Kitami, and Y. Yonemura, *Anal. Sci.*, **7**, 81 (1991).

20) H. Stamm and M. Goehring, *Z. Anorg. Allg. Chem.*, **250**, 226 (1942).

21) T. Ozawa, *Nippon Kagaku Zasshi*, **87**, 576 (1966).