# Determination of Micro Amounts of Polythionates. X. Spectrophotometric Determination of Micro Amounts of Pentathionate in Mixtures with Thiosulfate and Sulfite by Means of Its Sulfitolysis

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An accurate method has been proposed for the determination of pentathionate in mixtures with thiosulfate and sulfite. The method is based on the formation of thiosulfate equivalent to the pentathionate, and the spectrophotometric determination of excess iodine for the reaction with the thiosulfate formed. The conditions for pentathionate to be quantitatively converted into thiosulfate were established by varying pH, reaction time, and amounts of sulfite. The method can be successfully applied to the determination of pentathionate, thiosulfate, and sulfite when they are mixed in various ratios, giving a relative standard deviation of 0.82% at the 0.5 μmol level of pentathionate in a 10.0 $cm^3$ sample solution in the presence of 0.5 μmol of thiosulfate and 0.25 μmol of sulfite.

When polythionates are formed in nature like hot springs, or in Wackenroder's solution obtained when hydrogen sulfide is passed into a solution of sulfite, various sulfur species, such as sulfite, thiosulfate, sulfide, sulfate, and free sulfur, can be simultaneously present with polythionates.[1] Renewed interest has arisen in the procedure for determination of micro amounts of polythionates in mixtures with other sulfur compounds, for the clarification of the chemical behavior of sulfur compounds in hot springs or in Wackenroder's solutions. Chapman and Beard have proposed a procedure[2] for the separation and determination of the polythionates in Wackenroder's solution by high-speed liquid chromatography, and Blasius and Münch a coulometric method[3] for polythionates. The reactions of polythionates (tri-, tetra-, penta-, and hexathionate) with cyanide, sulfite, sulfide, and hydroxide should be studied in detail for determining a specific polythionate in the presence of other polythionates.[4]

In regard to the cyanolysis of polythionates, various investigations have been made, the methods for the determination of trithionate,[5-8] tetrathionate,[7-12] pentathionate,[12,13] and hexathionate,[12,14] based on the formation of thiocyanate, being proposed. As a result of these investigations, a method[15] for the determination of polythionates in mixtures with each other was developed, based on the photometric determination of different amounts of thiocyanate formed by the cyanolysis of polythionate in the presence or in the absence of copper(II) ions. A method for determining total amounts of polythionates in mixtures,[16] based on the spectrophotometric measurement of excess iodine for thiosulfate formed by the cyanolysis of polythionates, was also devised.

With respect to the sulfitolysis of polythionates, methods have been described for the determination of tetrathionate[17] and hexathionate,[4] based on the consumption of iodine by the thiosulfate formed. However, no consideration has been given to the spectrophotometric determination of pentathionate by means of its sulfitolysis. The reaction

$$S_5O_6^{2-} + 2SO_3^{2-} = 2S_2O_3^{2-} + S_3O_6^{2-} \quad (1)$$

was investigated in detail and the conditions under which pentathionate is completely converted into thiosulfate were established. Simultaneous sulfitolysis of both pentathionate and hexathionate could be quantitative only under strict conditions. The present method is based on the formation of thiosulfate equivalent to pentathionate, and on the spectrophotometric measurement of excess iodine for the thiosulfate. A procedure for the analysis of mixtures of pentathionate, thiosulfate and sulfite is also described.

## Experimental

*Apparatus.* Spectrophotometric measurements were carried out with a Shimadzu Model QV-50 spectrophotometer with 10-mm quartz cells. pH Measurements were made with a Hitachi-Horiba Model M-7 pH meter.

*Reagents.* All chemicals except for pentathionate, were of analytical grade and used without further purification.

*Potassium Pentathionate* was prepared as described by Goehring and Feldmann.[18] The pentathionate obtained was recrystallized twice in an acid medium of 0.5 M (M=mol/$dm^3$) hydrochloric acid, and then dried at room temperature before storage at $-10\pm2$ °C. The water content was estimated by Karl Fischer method to be 10.48% including the water of crystallization. The pentathionate was confirmed to be pure enough for the present purpose; its purity was estimated by determining the total potassium and sulfur contents.[13]

*Standard Pentathionate Solution* of $1.0\times10^{-3}$ M was prepared by dissolving 186.8 mg of the potassium pentathionate (water content 10.48%) in redistilled water, and then diluting it to 500 $cm^3$. The standard pentathionate solution was stored at $5\pm2$ °C.

*Standard Sulfite Solution* was prepared by dissolving sodium hydrogensulfite in freshly boiled and cooled redistilled water, and standardized by iodimetry. Working standards were obtained by appropriate dilution. The sulfite solution (0.15 M), which was not standardized, proved useful for the sulfitolysis of pentathionate 2 weeks after its preparation.

*Standard Thiosulfate Solution* was prepared by dissolving sodium thiosulfate pentahydrate in freshly boiled and cooled redistilled water containing a small amount of sodium carbonate as a stabilizer, and standardized by iodimetry a week after preparation. Working solutions were prepared by suitable dilution. These standards were used to confirm stoichiometry and completion of the reaction of pentathionate with sulfite.

*Standard Iodate-Iodide Solution* was prepared by adding 50.0 $cm^3$ of $1.67\times10^{-3}$ M standard iodate to a solution containing 0.2 g of sodium carbonate and 72.2 g of potassium iodide,

and diluted to 500 cm³ to give $1.67\times10^{-4}$ M iodate in a 0.87 M iodide solution.

*Iodide Solution* of 0.87 M was prepared by dissolving 72.2 g of potassium iodide in redistilled water containing 0.2 g of sodium carbonate, and then diluting it to 500 cm³.

*Buffer Solution* series are as follows: acetic acid (0.1, 0.5, or 1 M) and sodium acetate (0.1, 0.5, or 1 M), sodium dihydrogenphosphate (0.2 M) and sodium hydroxide (0.2 M), sodium hydrogencarbonate (0.1, 0.3, or 0.5 M) and sodium carbonate (0.05, 0.3, or 0.5 M), and sodium monohydrogenphosphate (0.5 M) and sodium hydroxide (0.5 M). The buffer solutions (pH 9.9 and 3.5) used in Procedures A and B were prepared by mixing 50 cm³ of 0.3 M sodium carbonate with 50 cm³ of 0.3 M sodium hydrogencarbonate, and by mixing 80 cm³ of 0.5 M acetic acid with 5 cm³ of 0.5 M sodium acetate, respectively.

*Acetic Acid Solution* was prepared by diluting glacial acetic acid as required.

*Formaldehyde Solution* was prepared by suitable dilution of formalin.

*Procedure A for the Amount of Pentathionate Alone.* 1.8 cm³ of a carbonate buffer solution (pH 9.9), 2.0 cm³ of 0.15 M sulfite, and 10.0 cm³ of a sample solution containing pentathionate were placed in a 25-cm³ volumetric flask, the pH of the solution becoming 8.0. The mixture was allowed to stand at room temperature for 10 min, to convert pentathionate completely into thiosulfate, Then, 1.5 cm³ of an acetate buffer solution (pH 3.5) and 2.0 cm³ of 0.5 M formaldehyde were added to the reaction mixture. The pH of the solution was kept at 5.8. The mixture was then allowed to stand for 5 min to mask excess sulfite with formaldehyde completely. To this mixture were added 2.0 cm³ of 15 M acetic acid and 2.4 cm³ of $1.67\times10^{-4}$ M standard iodate in a 0.87 M iodide solution, and the flask was filled to the mark with redistilled water. The contents were mixed well, and the absorbance of the solution of iodine-iodide complex was measured against distilled water at 350 nm within 10 min after the addition of the standard iodate-iodide solution.

An iodate-free reagent blank was prepared by addition of 2.4 cm³ of 0.87 M iodide in place of 2.4 cm³ of $1.67\times10^{-4}$ M standard iodate in a 0.87 M iodide solution and by the same treatment as in the above procedure. The absorbance of this blank was subtracted from all the absorbances obtained.

*Procedure B for Mixtures of Pentathionate, Thiosulfate, and Sulfite.* Three reaction mixtures were prepared in 25-cm³ volumetric flasks as follows.

*Procedure B-I for Total Amount of Pentathionate and Thiosulfate in the Mixtures*: A 10.0-cm³ aliquot of the sample solution containing pentathionate, thiosulfate, and sulfite was treated as in Procedure A, in order to convert the pentathionate completely into thiosulfate. 1.5 cm³ of an acetate buffer solution (pH 3.5) and 2.0 cm³ of 0.5 M formaldehyde were then added to the reaction mixture, which was allowed to stand for 5 min to mask the sulfite completely.

*Procedure B-II for the Amount of Thiosulfate in the Mixtures*: 1.8 cm³ of a carbonate buffer solution (pH 9.9), a 10.0-cm³ aliquot of the sample solution, 1.5 cm³ of an acetate buffer solution (pH 3.5), and 2.0 cm³ of 0.5 M formaldehyde were placed in a 25-cm³ volumetric flask, and the resulting mixture was allowed to stand for 5 min.

*Procedure B-III for Total Amount of Thiosulfate and Sulfite in the Mixtures*: A 10.0-cm³ aliquot of the sample solution and 1.5 cm³ of an acetate buffer solution (pH 3.5) were placed in a 25-cm³ volumetric flask.

Finally, 2.0 cm³ of 15 M acetic acid and 2.4 cm³ of $1.67\times10^{-4}$ M standard iodate in a 0.87 M iodide solution were added to each mixture. The three flasks were then filled to the mark with redistilled water. The contents were mixed thoroughly and the absorbance of the solution of iodine-iodide complex was measured against distilled water at 350 nm.

## Results and Discussion

*Calibration Plots.* A series of standard solutions of pentathionate and thiosulfate were treated as in Procedure A. The resulting graphs are shown in Fig. 1. According to Eq. 1, when 1 mol of pentathionate undergoes sulfitolysis, 2 mol of thiosulfate are formed. Thus, if pentathionate is completely converted into thiosulfate stoichiometrically, the calibration plot of pentathionate should coincide with that of thiosulfate when the molar concentration scale for thiosulfate is drawn to one second of the scale for pentathionate concentration. Figure 1 shows that pentathionate is quantitatively converted into thiosulfate according to Eq. 1.

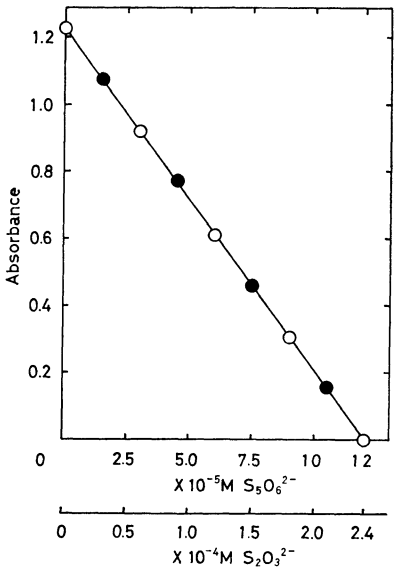


Fig. 1. Calibration plots for pentathionate and thiosulfate.
○: $S_5O_6^{2-}$; ●: $S_2O_3^{2-}$.

*Rate of Sulfitolysis of Pentathionate.* The rate was studied at both 5 °C and room temperature. The results are given in Tables 1 and 2. At pH 6.5, 8.0, and 8.2, the absorbance which was in complete agreement with the expected value was reached in 20 min at both 5 °C and room temperature, in 4 min at 5 °C and in 3 min at room temperature, and in 3 min at both 5 °C and room temperature, respectively, and then remained constant over different intervals of time. Higher absorbances then ensued as a result of the reaction of thiosulfate formed with the excess sulfite as shown in Eq. 2:

$$S_2O_3^{2-} + 4SO_3^{2-} + 6H^+ = 2S_3O_6^{2-} + 3H_2O \quad (2)$$

deviating from the expected value. The rate of sulfitolysis of pentathionate was little affected by temperature. Thus, pentathionate was allowed to react with sulfite at room temperature.

Table 1. Rate of sulfitolysis of pentathionate at 5°C

| $t$ / min | Absorbance: pH 6.5 $7.5\times10^{-5}$ M $S_5O_6^{2-}$ | pH 8.0 $7.5\times10^{-5}$ M $S_5O_6^{2-}$ | pH 8.2 $7.5\times10^{-5}$ M $S_5O_6^{2-}$ |
|---|---|---|---|
| | 0.456[a)] | 0.454[a)] | 0.456[a)] |
| 1 | 0.737 | 0.546 | 0.504 |
| 3 | 0.653 | 0.478 | 0.459 |
| 4 | 0.612 | 0.460 | 0.456 |
| 5 | 0.584 | 0.455 | 0.455 |
| 10 | 0.469 | 0.456 | 0.455 |
| 20 | 0.455 | 0.454 | 0.454 |
| 30 | 0.456 | 0.456 | 0.455 |
| 40 | 0.455 | 0.455 | 0.456 |
| 50 | 0.457 | 0.458 | 0.455 |
| 60 | 0.458 | 0.460 | 0.458 |
| 70 | 0.458 | 0.462 | 0.460 |
| 80 | 0.466 | 0.467 | 0.465 |
| 90 | 0.480 | 0.470 | 0.469 |

a) Absorbance for $1.5\times10^{-4}$ M $S_2O_3^{2-}$.

Table 2. Rate of sulfitolysis of pentathionate at room temperature

| $t$ / min | Absorbance: pH 6.5 $7.5\times10^{-5}$ M $S_5O_6^{2-}$ | pH 8.0 $7.5\times10^{-5}$ M $S_5O_6^{2-}$ | pH 8.2 $7.5\times10^{-5}$ M $S_5O_6^{2-}$ |
|---|---|---|---|
| | 0.454[a)] | 0.455[a)] | 0.455[a)] |
| 1 | 0.636 | 0.490 | 0.482 |
| 3 | 0.536 | 0.460 | 0.457 |
| 4 | 0.524 | 0.457 | 0.456 |
| 5 | 0.503 | 0.455 | 0.454 |
| 10 | 0.465 | 0.455 | 0.455 |
| 20 | 0.455 | 0.455 | 0.455 |
| 30 | 0.455 | 0.455 | 0.455 |
| 40 | 0.458 | 0.456 | 0.455 |
| 50 | 0.460 | 0.459 | 0.460 |
| 60 | 0.461 | 0.460 | 0.460 |
| 70 | 0.468 | 0.466 | 0.465 |
| 80 | 0.474 | 0.473 | 0.466 |
| 90 | 0.486 | 0.480 | 0.475 |

a) Absorbance for $1.5\times10^{-4}$ M $S_2O_3^{2-}$.

*Effect of pH.* In measuring the effect of pH on the sulfitolysis of pentathionate, the reaction was carried out for 10 min at various pH values. Figure 2 shows that pentathionate was quantitatively converted into thiosulfate in the pH range 6.9—8.2. A decrease in absorbance at higher pH levels was thought to be caused by the alkaline decomposition of pentathionate,[19] in addition to its sulfitolysis, as follows.

$$2S_5O_6^{2-} + 6OH^- = 5S_2O_3^{2-} + 3H_2O \quad (3)$$

The optimal pH range could be extended to a lower pH value by lengthening the sulfitolysis time; for instance, it was in the pH range 6.5—8.2 when sulfitolyzed for 20 min. However, the sulfitolysis time cannot be made any longer at the lower pH value, since the lower the pH of the solution, the faster the reaction rate of thiosulfate formed with the sulfite.

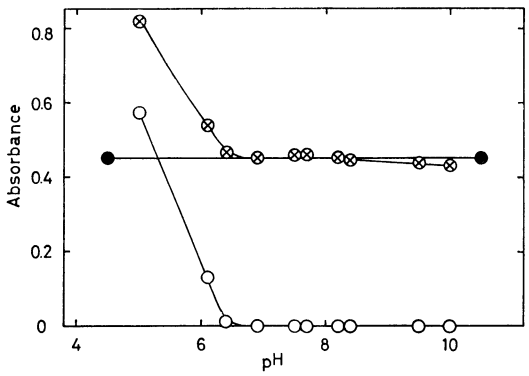


Fig. 2. Effect of pH on the sulfitolysis of pentathionate.
●: $1.5\times10^{-4}$ M $S_2O_3^{2-}$; ⊗: $7.5\times10^{-5}$ M $S_5O_6^{2-}$; ○: $1.2\times10^{-4}$ M $S_5O_6^{2-}$.

The conditions under which sulfitolysis of polythionates goes to stoichiometric completion must be established to determine specific polythionate in mixtures of the polythionates. An optimal pH for the sulfitolysis of hexathionate was found to be in the range 7.5—9.5[4] when sulfitolyzed for 10 min. Therefore, in so far as the pH of the reaction solution is kept in the range 7.5—8.2, the sulfitolysis of both penta- and hexathionate will be quantitative. In fact, the calibration plots for penta- and hexathionate were, respectively, in exact accordance with that for thiosulfate when plotted in terms of equivalent concentrations, demonstrating the fact that sulfitolysis of both the polythionates attained stoichiometric completion.

*Effect of Amount of Sulfite.* The extent of sulfitolysis of pentathionate can be affected by the concentra-

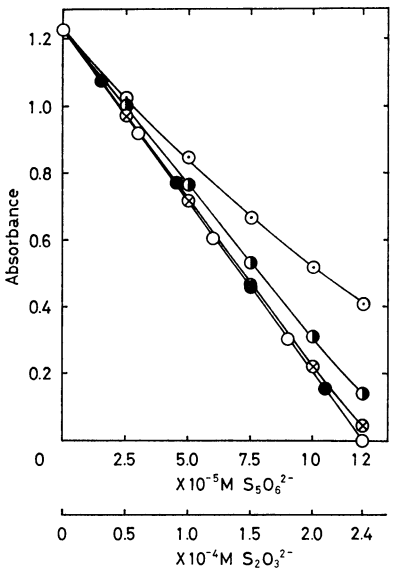


Fig. 3. Effect of amount of sulfite on the sulfitolysis of pentathionate.
⊙: $S_5O_6^{2-}$ with 2.0 cm³ of 0.01 M $SO_3^{2-}$; ◑: $S_5O_6^{2-}$ with 2.0 cm³ of 0.02 M $SO_3^{2-}$; ⊗: $S_5O_6^{2-}$ with 2.0 cm³ of 0.03 M $SO_3^{2-}$; ○: $S_5O_6^{2-}$ with 2.0 cm³ of 0.07, 0.1, or 0.15 M $SO_3^{2-}$; ●: $S_2O_3^{2-}$ with 2.0 cm³ of 0.15 M $SO_3^{2-}$.

tion of sulfite. In measuring the effect of the amount of sulfite on the conversion of pentathionate into thiosulfate, 2.0 $cm^3$ of 0.01, 0.02, 0.03, 0.07, 0.1, and 0.15 M sodium hydrogensulfite were employed, respectively. In all cases, the solutions were kept at pH 6.9—8.2, which is the optimal range for the sulfitolysis of pentathionate when sulfitolyzed for 10 min. As can be seen in Fig. 3, the sulfitolysis of pentathionate was incomplete with 2.0 $cm^3$ of 0.01, 0.02, or 0.3 M sulfite, because of an insufficient amount of sulfite. However, when 2.0 $cm^3$ of 0.07, 0.1, or 0.15 M was used, the calibration graph of pentathionate was linear and coincided exactly with that of standard thiosulfate. 2.0 $cm^3$ of 0.15 M sulfite was therefore used.

The sulfite used for the sulfitolysis consumed iodine completely, as a result of its reaction with iodine. However, it was confirmed that the excess sulfite was completely masked in the pH range 4.0—9.1, when 2.0 $cm^3$ of 0.5 M formaldehyde was added and the mixture solution was allowed to stand for 5 min. It is desirable to carry out spectrophotometric measurements within at least 10 min after the addition of standard iodate–iodide solution, because the reaction of iodine–iodide complex with the adduct formed ensued slowly.[4]

*Analysis of Mixtures of Pentathionate, Thiosulfate, and Sulfite.* The three sulfur compounds in mixtures give the following equivalents in three procedures:

Procedure B-I $\triangleq 2S_5O_6^{2-} + S_2O_3^{2-}$

Procedure B-II $\triangleq S_2O_3^{2-}$

Procedure B-III $\triangleq S_2O_3^{2-} + 2SO_3^{2-}$

The absorbance obtained by Procedure B-I corresponds to the sum of twice the pentathionate (see Eq. 1) and the thiosulfate in the mixtures, because sulfite is masked by the formaldehyde added for the removal of excess sulfite. The absorbance obtained by Procedure B-II, in which no sulfitolysis of pentathionate was carried out, corresponds to only the amount of thiosulfate in the mixtures. The absorbance obtained by Procedure B-III corresponds to the sum of the thiosulfate and twice the sulfite in the mixture solution.

Table 3. Analysis of pentathionate, thiosulfate, and sulfite in 10.0 $cm^3$

| Taken (μmol) | | | Found (μmol) | | |
|---|---|---|---|---|---|
| $S_5O_6^{2-}$ | $S_2O_3^{2-}$ | $SO_3^{2-}$ | $S_5O_6^{2-}$ | $S_2O_3^{2-}$ | $SO_3^{2-}$ |
| 0.10 | 0.30 | 0.75 | 0.11 | 0.30 | 0.75 |
| 0.35 | 0.50 | 0.50 | 0.35 | 0.51 | 0.50 |
| 0.75 | 0.40 | 0.10 | 0.76 | 0.40 | 0.10 |
| 0.30 | 1.00 | 0.15 | 0.30 | 1.02 | 0.14 |
| 0.45 | 0.50 | 0.25 | 0.45 | 0.51 | 0.25 |
| 0.50 | 0.50 | 0.25 | 0.50 | 0.51 | 0.25 |

Table 4. Effect of diverse ions

| Ion | Added as | Concn ppm | Absorbance: Reagent blank | Absorbance: $6.0\times10^{-5}$ M $S_5O_6^{2-}$ |
|---|---|---|---|---|
| None | | 0 | 1.224 | 0.610 |
| $Na^+$ | $Na_2SO_4$ | 1000 | 1.224 | 0.609 |
| $K^+$ | $K_2SO_4$ | 1000 | 1.223 | 0.608 |
| $NH_4^+$ | $(NH_4)_2SO_4$ | 1000 | 1.224 | 0.613 |
| $Cu^{2+}$ | $CuSO_4\cdot5H_2O$ | 10 | 1.415 | 0.801 |
| $Mg^{2+}$ | $MgSO_4\cdot5H_2O$ | 1000 | 1.224 | 0.607 |
| $Ca^{2+}$ | $CaCO_3$ | 1000 | 1.234 | 0.615 |
| $Zn^{2+}$ | $ZnSO_4\cdot7H_2O$ | 1000 | 1.225 | 0.610 |
| $Cd^{2+}$ | $Cd(CH_3COO)_2\cdot2H_2O$ | 1000 | 1.224 | 0.610 |
| $Mn^{2+}$ | $MnSO_4\cdot5H_2O$ | 1000 | 1.223 | 0.612 |
| $Pb^{2+}$ | $Pb(CH_3COO)_2\cdot3H_2O$ | 10 | 1.264 | 0.652 |
| $Fe^{2+}$ | $Fe(NH_4)_2(SO_4)_2\cdot6H_2O$ | 50 | 1.654 | 0.936 |
| $Fe^{3+}$ | $Fe(NH_4)(SO_4)_2\cdot12H_2O$ | 10 | 1.341 | 0.747 |
| | | 1 | 1.251 | 0.640 |
| $Al^{3+}$ | $Al_2(SO_4)_3\cdot18H_2O$ | 500 | 1.237 | 0.631 |
| $F^-$ | NaF | 1000 | 1.224 | 0.611 |
| $Cl^-$ | NaCl | 1000 | 1.224 | 0.608 |
| $Br^-$ | KBr | 1000 | 1.225 | 0.608 |
| $I^-$ | KI | 1000 | 1.223 | 0.609 |
| $NO_3^-$ | $KNO_3$ | 1000 | 1.246 | 0.631 |
| $NO_2^-$ | $KNO_2$ | 1 | 1.424 | 0.755 |
| $S^{2-}$ | $Na_2S\cdot9H_2O$ | 0.5 | 1.062 | 0.462 |
| $SO_4^{2-}$ | $Na_2SO_4$ | 1000 | 1.223 | 0.607 |
| $SO_3^{2-}$ | $NaHSO_3$ | 1000 | 1.223 | 0.610 |
| $HAsO_4^{2-}$ | $Na_2HAsO_4\cdot7H_2O$ | 1000 | 1.223 | 0.606 |
| $PO_4^{3-}$ | $Na_3PO_4\cdot12H_2O$ | 1000 | 1.224 | 0.608 |
| Borate | $H_3BO_3$ | 1000 | 1.225 | 0.613 |
| Silicate | (as $SiO_2$) | 500 | 1.230 | 0.614 |

Moreover, the calibration graphs for pentathionate, thiosulfate, and sulfite were in full agreement with one another when plotted in terms of equivalent concentrations. Thus, the following equations can be obtained: $(S_5O_6^{2-})=(I-II)/2$, $(S_2O_3^{2-})=II$, and $(SO_3^{2-})=(III-II)/2$, where I, II, and III denote the molar concentration which was determined from the calibration graph for thiosulfate in Fig. 1 using the absorbance obtained by Procedures B-I, B-II, and B-III, respectively. Table 3 shows that the above technique can be successfully applied to the determination of a mixture of pentathionate, thiosulfate, and sulfite at various ratios.

The precision was estimated from six results for three 10.0-cm$^3$ aliquots of sample solutions containing 0.5 μmol of pentathionate, 0.5 μmol of thiosulfate, and 0.25 μmol of sulfite. The method gave a mean value of 0.498 μmol with a standard deviation of 0.0041, and a ralative standard deviation of 0.82% for pentathionate, 0.503 μmol with 0.0052 and 1.0% for thiosulfate, and 0.257 μmol with 0.0052 and 2.0% for sulfite.

*Effect of Diverse Ions.* The interference of various ions was checked under the conditions of Procedure A, both in the presence of pentathionate ($6.0\times10^{-5}$ M) and in its absence. The results are given in Table 4.

The present method is based on the spectrophotometric measurement of excess iodine such as triiodide for the thiosulfate formed by the sulfitolysis of pentathionate. Therefore, iron(III), copper(II), nitrite, or sulfide which can oxidize iodide or reduce iodine, interferes seriously with the determination of pentathionate. In the case of both lead(II) and iron(II), the positive error in absorbance may be attributed to the formation of lead–iodide complex which exhibits its absorption at 350 nm, and to the oxidation of iodide by the iron(III) ion produced by the air-oxidation of iron(II). Approximately 1000 ppm of almost all the other ions listed in Table 4 is allowable.

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