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The Determination of Micro Amounts of Polythionates. IV.* A Photometric Method for the Determination of Tetrathionate by Decomposition with Sodium Sulfite[1]

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A new photometric method for the determination of tetrathionate by means of its decomposition with sulfite has been developed. It is based on the formation of thiosulfate equivalent to the tetrathionate, and on the photometric determination of thiosulfate by measuring its decoloration of an iodine solution. 5×10^{-6}—1×10^{-3} M (1 mg./l.—0.2 g./l.) of tetrathionate can be determined easily and rapidly within a range of error of $\pm2\times10^{-6}$—2×10^{-5} M (0.4 mg./l.—4 mg./l.) by using 20 ml. of a sample. The tetrathionate solution is decomposed with sodium sulfite in a slightly alkaline medium. After the completion of the decomposition reaction, a formaldehyde solution is added to mask the interference of the excess sulfite remaining and this solution is acidified with acetic acid. Then the standard iodine solution is added. The absorbancy of the solution is measured at the wavelength of 372 or 440 mμ 20 min. after the addition of an iodine solution. By this method tetrathionate can be determined, even when it is coexistent with thiosulfate and sulfite in up to similar amounts. Many substances, such as aluminum, calcium, cadmium, magnesium, zinc, silicate, nitrate, sulfate, phosphate, chloride and fluoride, do not interfere, but iron(II, III), manganese(II), copper(II) and sulfide do interfere.

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* T. Koh and I. Iwasaki, This Bulletin, **39**, 352 (1966).

[1] Presented at the Scientific Meeting on Chemistry, Tokyo, November, 1961.

There have been no suitable procedures for the determination of the polythionates in such micro amounts as are present in hot springs, although a more rapid and accurate method for determining polythionates of low concentrations is desirable for the studies of the hydrolysis and oxidation products of sulfur and sulfide.

The reactions of polythionates with sulfite, cyanide and sulfide have been reported by Kurtenacker and Goldbach.[2] Goehring, Feldmann and Helbing[3] have then applied these reactions to the determination of polythionates, depending on the iodometric titration of the thiosulfate obtained. Nietzel and DeSesa[4] determined colorimetrically the thiocyanate obtained from the reactions between tetrathionates and cyanide. In our own series of studies[5-7] of determination of micro amounts of polythionates, many fundamental processes in the reaction of polythionates with cyanide have been studied in detail.

In the present investigation, it will be confirmed that micro amounts of tetrathionate from 5×10^{-6} to 10^{-3} M can be determined photometrically by measuring the degree of the decoloration of iodine, which depends on the amounts of thiosulfate formed from the reaction of tetrathionate with sulfite. Polythionates react with sulfite in an alkaline medium to form thiosulfate as follows[2,3]:

$$\begin{aligned}&S_nO_6{}^{2-} + (n-3)SO_3{}^{2-}\\&\quad = (n-3)S_2O_3{}^{2-} + S_3O_6{}^{2-} \qquad (1)\\&\qquad (n=4,\ 5,\ \text{and}\ 6)\end{aligned}$$

In this reaction 1 mol. of thiosulfate is formed from 1 mol. of tetrathionate. The thiosulfate thus formed reacts quantitatively with iodine in an acid medium. Therefore, the degree of the decoloration of iodine indicates the amount of tetrathionate in the original solution.

This paper will be concerned with the presentation of the results of this investigation and with the determination of small amounts of tetrathionate in the presence of sulfite and thiosulfate by means of its decomposition with sodium sulfite.

Experimental

Apparatus and Reagents.—A Hirama electrophotocolorimeter model II, with 10.0 mm. cells and filters of 372 and 440 mμ (maximum transmission at 372 and 440 mμ respectively), was used to measure the absorbancy.

The Standard Potassium Tetrathionate Solution.—30.25 g. of potassium tetrathionate ($K_2S_4O_6$) was dissolved in water, the mixture was then diluted to 1 l. (M/10). This stock solution was standardized by iodometric titration after decomposing it with sulfite or cyanide,[2,3] and then diluted to an adequate concentration. Potassium tetrathionate was prepared by the reaction of potassium thiosulfate with iodine; it was recrystallized with aqueous alcohol and dried in a desiccator containing sulfuric acid.[8]

The Standard Iodine Solution.—A standardized N/10 iodine solution was diluted to a desirable concentration; in all cases the concentration of potassium iodide was N/5.

The Standard Sodium Thiosulfate Solution.—24.82 g. of guaranteed reagent sodium thiosulfate pentahydrate ($Na_2S_2O_3\cdot5H_2O$) was dissolved in water and diluted to 1 l. (N/10). This solution was standardized with potassium iodate and then diluted to a concentration required.

Procedure.—20.0 ml. of a sample solution is placed in a 50 ml. volumetric flask. Then 1.0 ml. of a 0.5 M sodium sulfite solution is added and mixed in well. When this solution does not show a pink color with a phenolphthalein indicator, a 1 N sodium or potassium hydroxide solution is added drop by drop until the pink color appears. After this mixture has stood for 5 min. or longer, 1.0 ml. of a 20% formaldehyde solution[2,9] is added; this solution is then acidified with 10 ml. of a 20% acetic acid solution. 5.00 ml. of N/2000 or N/200 standard iodine solution is then added. After the flask has been filled with water to the mark, the absorbancy of the solution is measured at the wavelength of 372 or 440 mμ 20 min. after the addition of an iodine solution.

Thiosulfate and sulfite can also be determined when both are present in the sample solution. Three 20.0-ml. aliquots of the sample solution are placed in three 50-ml. volumetric flasks. The first 20.0-ml. aliquot is treated by the procedure described above. To the second, 10 ml. of a 20% acetic acid solution and 5.00 ml. of the standard iodine solution are added. To the third, after the addition of 1.0 ml. of a 20% formaldehyde solution, a 1 N alkali hydroxide solution is added drop by drop until the solution becomes alkaline to a phenolphthalein indicator. Then the solution is acidified with 10 ml. of 20% acetic acid and 5.00 ml. of the standard iodine solution is added.

The degree of the decoloration of iodine observed in the first aliquot corresponds to the sum of the amount of tetrathionate and that of thiosulfate in the solution; that observed in the second, to the sum of the amount of thiosulfate and twice the amount to sulfite in the solution, and that observed in the third, to only the amount of thiosulfate in the solution.

Results and Discussion

Working Curves.—As the final purpose of this series of investigations is to determine the polythionates to such micro amounts as are present in hot springs, the working curves were prepared with the standard sodium thiosulfate solution

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[2] A. Kurtenacker and E. Goldbach, *Z. anorg. u. allgem. Chem.*, **166**, 177 (1927). A. Kurtenacker, "Analytische Chemie der Sauerstoffsauren des Schwefels," Stuttgart (1938).

[3] M. Goehring, U. Feldmann and W. Helbing *Z. anal. Chem.*, **129**, 346 (1949).

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

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

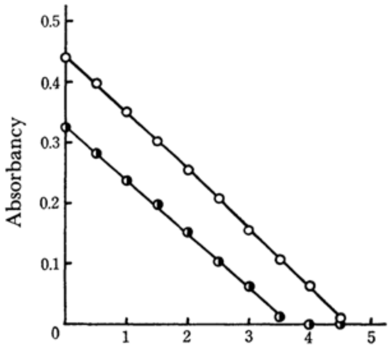
[6] T. Koh and I. Iwasaki, ibid., **38**, 2135 (1965).

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

[8] G. Bauer, "Handbuch der Preparativen Anorganischen Chemie," (1954), p. 311.

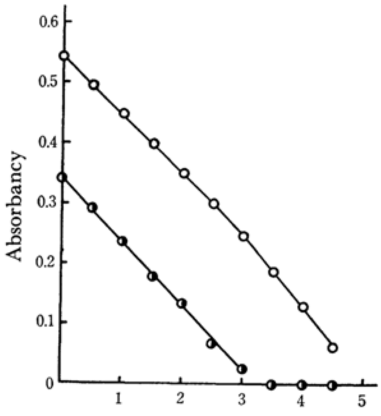
[9] A. Kurtenacker, *Z. anal. Chem.*, **64**, 56 (1924).

instead of the standard potassium tetrathionate solution. Examples of the working curves are shown in Figs. 1 and 2.



ml. of a 5.0×10^{-4} N standard thiosulfate solution

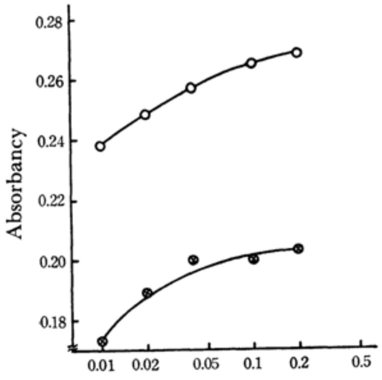
Fig. 1. Working curves.
Use is made of 5.0 ml. of a 5.0×10^{-4} N iodine standard solution. Absorbancy was measured at 372 mμ 20 and 90 min. respectively after the addition of a standard iodine solution.
—○— 20 min., —◑— 90 min.



ml. of a 5.0×10^{-3} N standard thiosulfate solution

Fig. 2. Working curves.
Use is made of 5.0 ml. of a 5.0×10^{-3} N iodine standard solution. Absorbancy was measured at 440 mμ 20 min. and 22 hr. respectively after the addition of a standard iodine solution.
—○— 20 min., —◑— 22 hr.

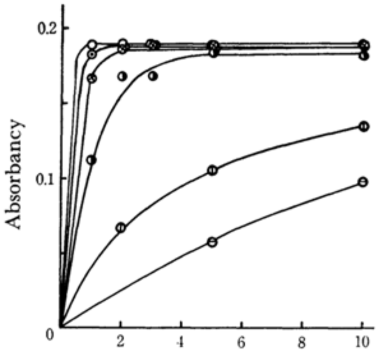
The Effect of the Concentration of Iodide on the Absorbancy.—The absorbancies of iodine solutions become higher with an increase in the concentration of iodide at the wavelengths of both 372 and 440 mμ. Therefore, it is necessary to keep the concentration of iodide constant in the final solutions. However, no significant difference could be found between iodide concentrations of N/5 and N/50. In this study, N/50 of iodide was used as the final iodide concentration.



Concn. of iodide, normality

Fig. 3. Effect of the concentration of iodide on the absorbancy.
—○— 2.0×10^{-4} N iodine, at 440 mμ
—⊗— 2.0×10^{-5} N iodine, at 372 mμ

Time of Reaction.—The concentration of sodium sulfite seriously affects the velocity of the decomposition reaction of tetrathionate (Eq. 1), as is shown in Fig. 4. When 0.2 ml. of a 0.5 M sodium sulfite solution is used, it takes about 20 min. for the complete reaction, but it takes only 2 or 3 min. when 1.0 ml. of it is used. The absorbancies of the solutions obtained show the nearly constant value which is to be expected from Eq. 1. From these results it may be concluded that tetrathionate can be decomposed completely and that thiosulfate equivalent to the tetrathionate is formed quantitatively under these experimental conditions. Consequently, 1.0 ml. of a 0.5 M sodium sulfite solution was used in this study. However, when the pH value of the solution rises locally, there other



Time of reaction, min.

Fig. 4. Effect of the amount of sodium sulfite on the velocity of decomposition reaction.
2.0 ml. of a 5.0×10^{-3} M tetrathionate, 5.0 ml. of 20% formaldehyde, 10 ml. of 20% acetic acid, and 5.0 ml. of 5.0×10^{-3} N iodine were used. The absorbancy was measured at 440 mμ.
Concn. of sodium sulfite: 0.5 M

⊖ 0.1 ml. ⦶ 0.2 ml.
◑ 0.5 ml. ⊗ 1.0 ml.
⊙ 1.5 ml. ○ 2.0 ml.

decomposition reactions[2,3] occur; this may be a cause of error.

The Effect of Formaldehyde.—Since sulfite, as well as thiosulfate, reacts with iodine in an acid medium, it must be masked with formaldehyde, as has been proposed by Kurtenacker.[9] Figure 5 shows the decoloration of iodine solutions with formaldehyde on standing after the standard iodine solution has been added to sulfite solutions when thiosulfate and tetrathionate are absent. As may be seen in Fig. 5, the differences among the effects of 0.2 ml., 1.0 ml. and 5.0 ml. of a 20% formaldehyde solution are negligible. However, both when no formaldehyde was added and when it was added in an acidified medium, the iodine was completely consumed by the reaction with the excess sulfite remaining in the solution. Therefore, formaldehyde must be added to the solution in order to mask the action of the excessive sulfite before the solution is acidified with acetic acid.

On the other hand, the decoloration of the iodine solution proceeds when it stands after the addition of iodine, especially in its lower concentrations. From the results obtained in this study, 1.0 ml. of a 20% formaldehyde solution was used, and the absorbancies of the iodine solutions obtained were measured 20 min. after the addition of an iodine solution.

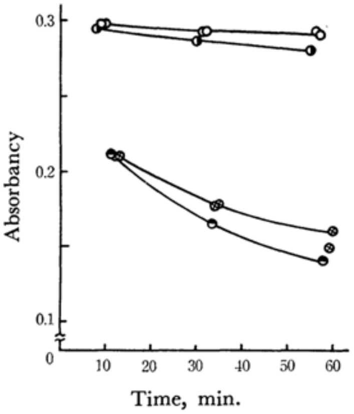


Fig. 5. Effect of formaldehyde on stability of color. 1.0 ml. of 0.5 M sodium sulfite and 10 ml. of acetic acid were used.

Concn. of formaldehyde: 20%

○ 1.0 and 5.0 ml. } 5.0×10^{-3} N I_2 2.5 ml.,
◑ 0.2 ml. } at 440 mμ
⊗ 1.0 and 5.0 ml. } 5.0×10^{-4} N I_2 2.5 ml.,
◓ 0.2 ml. } at 372 mμ

The Amounts of Acetic Acid.—It is necessary to acidify the solution for the reaction of thiosulfate with iodine. Figure 6 shows the absorbancies of the solutions against the amounts of acetic acid when 2.50 ml. of a N/2000 standard sodium thiosulfate solution and 5.00 ml. of a N/2000 standard iodine solution were used.

As will be seen in Fig. 6, when more than 5 ml. of 20% acetic acid were employed the absorbancies of the solutions reached a constant value; 10 ml. of 20% acetic acid was used in this study.

The Results of the Analyses of the Synthetic Solutions.—From the experimental results, the analytical procedures described above have been established. The working curves shown in Figs. 1 and 2 were obtained by these procedures.

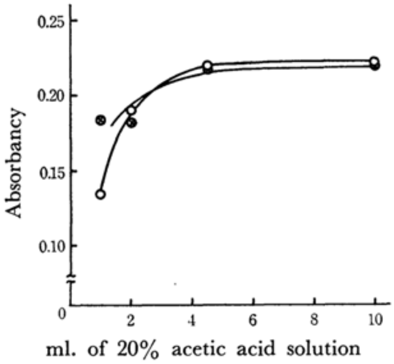


Fig. 6. Effect of the amount of acetic acid. 1.0 ml. of a 0.5 M sodium sulfite was used. Absorbancy was measured 20 min. after the addition of iodine solution at 372 mμ.
○ 20% formaldehyde 1.0 ml.
⊗ 20% formaldehyde 5.0 ml.

TABLE I. DETERMINATION OF TETRATHIONATE IN THE SYNTHETIC SOLUTIONS*

	Present($\times10^{-4}$ M)			Found($\times10^{-4}$ M)		
No.	$S_4O_6^{2-}$	$S_2O_3^{2-}$	SO_3^{2-}	$S_4O_6^{2-}$	$S_2O_3^{2-}$	SO_3^{2-}
1	0.09	—	—	0.10	—	—
2	0.34	—	—	0.34	—	—
3	0.80	—	—	0.79	—	—
4	1.08	—	—	1.07	—	—
5	0.05	1.00	—	0.03	0.99	—
6	0.05	0.50	—	0.03	0.51	—
7	0.10	0.90	—	0.07	0.90	—
8	0.10	0.80	—	0.05	0.82	—
9	0.10	0.45	—	0.10	0.46	—
10	0.25	0.45	—	0.24	0.45	—
11	0.50	0.15	—	0.48	0.17	—
12	0.90	0.05	—	0.88	0.06	—
13	0.10	0.05	0.50	0.10	0.06	0.50
14	0.20	0.50	0.20	0.22	0.49	0.20
15	0.50	0.05	0.50	0.48	0.07	0.50
16	0.50	0.10	0.10	0.49	0.12	0.10
17	0.50	0.50	0.05	0.50	0.51	0.05
18	0.60	0.10	0.40	0.59	0.12	0.40
19	0.50	—	10	0.51	0.00	—
20	0.50	—	100	0.52	0.02	—
21	0.10	0.80	10	0.04	0.79	—
22	0.10	0.80	100	0.06	0.80	—
23	0.80	0.10	10	0.75	0.11	—
24	0.80	0.10	100	0.81	0.12	—

* : 5×10^{-6} to 10^{-4} M at 372 mμ
— : Absent or not determined

TABLE II. DETERMINATION OF TETRATHIONATE IN THE SYNTHETIC SOLUTIONS*

No.	Present ($\times 10^{-3}$ M) $S_4O_6^{2-}$	Present $S_2O_3^{2-}$	Present SO_3^{2-}	Found ($\times 10^{-3}$ M) $S_4O_6^{2-}$	Found $S_2O_3^{2-}$	Found SO_3^{2-}
1	0.20	—	—	0.20	—	—
2	0.58	—	—	0.59	—	—
3	0.73	—	—	0.74	—	—
4	0.95	—	—	0.96	—	—
5	0.10	0.90	—	0.10	0.89	—
6	0.20	0.50	—	0.21	0.48	—
7	0.50	0.25	—	0.51	0.24	—
8	0.80	0.10	—	0.79	0.11	—
9	0.10	0.10	0.10	0.10	0.11	0.10
10	0.10	0.10	0.50	0.12	0.10	0.50
11	0.20	0.20	0.20	0.19	0.21	0.19
12	0.30	0.30	0.10	0.29	0.31	0.10
13	0.30	0.50	0.20	0.28	0.50	0.20
14	0.50	0.10	0.30	0.48	0.12	0.29
15	0.50	—	1.0	0.54	0.00	—
16	0.50	—	10	0.50	0.00	—
17	0.25	0.80	1.0	0.24	0.80	—
18	0.25	0.80	10	0.24	0.80	—
19	0.80	0.25	1.0	0.79	0.25	—
20	0.80	0.25	10	0.77	0.26	—

* : 5×10^{-5} to 10^{-3} M at 440 mμ

— : Absent or not determined

TABLE III. EFFECT OF DIVERSE IONS

No.	Ionic species	Concn., w/v %	Form of salt	Absorbancy 372 mμ	Absorbancy 440 mμ
0	—	—	—	0.309[a]	0.320[b]
1	Fe^{2+}	0.05	$FeSO_4\cdot 7H_2O$	—[c]	0.457
2	Fe^{3+}	0.05	$Fe(NO_3)_3\cdot H_2O$	—[c]	0.502
3	Al^{3+}	0.05	$AlCl_3\cdot 6H_2O$	0.312	0.320
4	Ca^{2+}	0.10	$CaCO_3$(HCl)	0.309	0.320
5	Mg^{2+}	0.06	MgO(HCl)	0.318	0.320
6	Mn^{2+}	0.01	$MnSO_4\cdot nH_2O$	—[c]	0.540
7	Zn^{2+}	0.5	$ZnSO_4\cdot 7H_2O$	0.314	0.320
8	Cu^{2+}	0.013	$CuSO_4\cdot 5H_2O$	0.364	0.338
9	Cd^{2+}	6.3[e]	$8CdSO_4\cdot 3H_2O$	0.312	0.320
10	SiO_3^{2-}	0.02	$Na_2SiO_3\cdot nH_2O$	0.321	0.318
11	Cl^-	1.2	NaCl	0.301	0.317
12	SO_4^{2-}	1.0	Na_2SO_4	0.317	0.321
13	NO_3^-	0.9	KNO_3	0.306	0.321
14	S^{2-}	0.8	Na_2S	0.04[d]	0.01[d]
15	PO_4^{3-}	0.4	$Na_2HPO_4\cdot 12H_2O$	0.310	0.319
16	F^-	0.005	NaF	0.310	0.320

a) 3×10^{-5} M concentration of tetrathionate.

b) 5×10^{-4} M concentration of tetrathionate.

c) Higher than 2.0 of absorbancy.

d) Slightly turbid.

e) Preliminary test for removal of sulfide.

The results of the analyses by the present method of the samples containing tetrathionate only, tetrathionate and thiosulfate, or tetrathionate, thiosulfate and sulfite are listed in Tables I and II. Very good agreements are seen, even in the lower concentrations of these chemical species.

The Influence of Diverse Ions.—The other polythionates would interfere,[2,3] but these, as well as thiosulfate and sulfite, might be individually determined by solving the simultaneous equations derived from Eq. 1 and the following reactions[2,3]:

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

$$S_nO_6^{2-}+S^{2-}=2S_2O_3^{2-}+(n-3)S \quad (n=3,\ 4,\ 5,\ \text{and}\ 6) \qquad (3)$$

$$2S_nO_6^{2-}+6OH^-=(2n-5)S_2O_3^{2-}+(10-2n)SO_3^{2-}+3H_2O \quad (n=3,\ 4,\ \text{and}\ 5) \qquad (4)$$

$$2S_6O_6^{2-}+6OH^-=5S_2O_3^{2-}+2S+3H_2O \qquad (4')$$

The influence on this method of the other ions commonly present in hot springs are given in Table III. Sulfide liberates colloidal sulfur. Iron(II) and manganese(II) are oxidized in an alkaline solution, and the iron(III) and manganese(IV) thus formed oxidize the iodide to produce iodine. The elimination of the interfering matter must be studied before we can apply this procedure to the various samples in their natural state.