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The Determination of Micro Amounts of Polythionates. III.* A Photometric Method for the Determination of Tetrathionate by Means of Its Cyanolysis[1]

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A photometric method capable of determining tetrathionate by exactly the same procedure as that used for pentathionate and hexathionate has been established. The optimum pH ranges for the reactions of tetrathionate, pentathionate and hexathionate with cyanide are 8.3—12.1, 8.0—8.8, and 7.8—8.9 respectively for the recommended procedure. From a consideration of the above experimental facts, it has been concluded that tetrathionate can be determined accurately by exactly the same procedure as that used for pentathionate and hexathionate when the pH value is within the range from 8.3 to 8.8. To the standard tetrathionate solution first the buffer solution and then a solution of sodium cyanide are added in order that the pH value of the mixture solution after the addition of the cyanide solution may be within the 8.3—8.8 range. The mixed solution is kept in the thermostat at 40°C for 30 min.; the tetrathionate is thereby converted into thiocyanate quantitatively. After the addition of a ferric nitrate - perchloric acid solution, the absorbancy of the solution of ferric-thiocyanate complex formed is measured at the wavelength of 460 mμ.

Nietzel and DeSesa[2] have presented a spectrophotometric method for the determination of low concentrations of tetrathionate, a method which is based on the formation of thiocyanate from tetrathionate by reaction with cyanide in an alkaline medium, and on the subsequent formation of a ferric-thiocyanate complex with ferric iron. At the same time, they have pointed out that their method can also be used for pentathionate and

* Part II: This Bulletin, **38**, 2135 (1965).

1) Presented at the Scientific Meeting on Chemistry, Tokyo, November, 1964.

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

hexathionate, because the higher polythionates react more easily with cyanide to form thiocyanate.

On the other hand, Urban[3] has modified the Nietzel-DeSesa method and applied it to the evaluation of *n*, the mean number of sulfur atoms in the formula, $S_nO_6^{2-}$, for polythionates above trithionate, on the assumption that pentathionate and hexathionate would react with cyanide to be quantitatively converted into thiocyanate under the same conditions as those used for the estimation of tetrathionate.

However, the higher polythionates, as has been reported in the first paper of this series,[4] undergo a partial alkaline decomposition under the conditions of the Nietzel-DeSesa and the Urban methods,[2,3] because of the higher pH value arising from the addition of a sodium cyanide solution. Therefore, their methods are not suitable for the higher polythionates.

The present authors[5] have previoulsy reported a method for the determination of a small amount of hexathionate, a method based on the reaction of hexathionate with cyanide, with the subsequent formation of thiocyanate from hexathionate, and on the photometric determination of the thiocyanate with ferric iron. In the above investigation, it has been found that the hexathionate can be determined sufficiently rapidly, precisely, and accurately by the very same procedure as is used for pentathionate.[4]

The present authors have now investigated, in greater detail, a method for the determination of tetrathionate using the reaction:

$$S_4O_6^{2-} + 3CN^- + H_2O = S_2O_3^{2-} + SO_4^{2-} + 2HCN + SCN^-$$

followed by the photometric determination of the thiocyanate thus formed with ferric iron; they have thus established an excellent method for determining a small amount of tetrathionate by the very same procedure as is used for pentathionate[4] and hexathionate[5]; they have found the conditions under which tetrathionate is also quantitatively converted into thiocyanate under the same conditions as are used for pentathionate and hexathionate, by varying the cyanide amount, the pH, the reaction time, and the temperature.

The present investigation was undertaken to see if the method for the determination of pentathionate[4] and hexathionate[5] could be used for tetrathionate also; the authors have their ultimate object analyzing the polythionates when they are mixed with one another.

Experimental

Apparatus and Materials.—Unless otherwise stated, the apparatus and materials used in this study were the same as those described in the first paper of this series.[4]

Potassium Tetrathionate.—This salt was prepared according to the directions of Stamm and Goehring.[6] The raw tetrathionate obtained was recrystallized with redistilled water at a temperature below 60°C and dried at room temperature for 4 days. The water content physically adsorbed in the tetrathionate was estimated to be 0.6% by the Karl Fischer method.

The purity of this salt was estimated by determining the total potassium and sulfur as follows. The potassium tetrathionate was decomposed into potassium sulfate by heating it at about 800°C; $K_2S_4O_6 \rightarrow K_2SO_4$. The potassium was determined by weighing[7] the potassium sulfate thus formed.

As for the sulfur, the tetrathionate was oxidized[4,5,7] by bromine in an alkaline medium upon heating; the sulfate ions formed were determined by the usual gravimetric method.

Table I. Determination of K for the potassium tetrathionate* used in the present study

Sample taken mg.	As $K_2S_4O_6$ mg.	Found as K_2SO_4 mg.	K found for $K_2S_4O_6$ %	K calcd. for $K_2S_4O_6$ %
261.6	260.0	149.8	25.86	25.86
198.7	197.5	113.7	25.83	

Table II. Determination of S for the potassium tetrathionate* used in the present study

Sample taken mg.	As $K_2S_4O_6$ mg.	Found as $BaSO_4$ mg.	S found for $K_2S_4O_6$ %	K calcd. for $K_2S_4O_6$ %
273.2	271.6	832.2	42.09	42.40
233.2	231.8	710.5	42.10	

* Water content was estimated to be 0.6%.

Tables I and II show that this potassium tetrathionate is pure enough for the purposes of this investigation.

The Standard Tetrathionate Solution.—The standard solution, a 1.0×10^{-3} M stock solution of tetrathionate, was prepared by dissolving 152.1 mg. of the potassium tetrathionate (water content: 0.6%) in redistilled water, and then diluting it to 500 ml. This stock solution proved to be stable; even after six months, no measurable change was found by the present method when it was kept at 5±2°C in a refrigerator. The working standard solutions were prepared by diluting the stock solution properly.

Buffer Solution.—Phosphate buffer (0.2 M) and sodium hydroxide (0.01 to 1 N) solutions were employed to adjust the pH to the values required.

Procedure.—A sample solution of 10.0 ml. is placed in a 25 ml. volumetric flask. To this solution there are added, first 4.0 ml. of the phosphate buffer solution of pH 7.4, and then 2.6 ml. of 0.05 M sodium cyanide; the pH of the solution is thereby brought to 8.6.

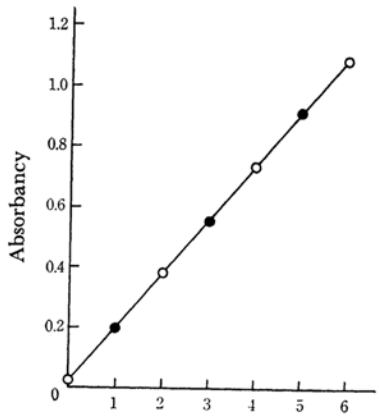
The volumetric flask is kept in the thermostat at 40±1°C for 30 min.; the tetrathionate is thereby converted into thiocyanate quantitatively. Then 3.0 ml. of a 1.5 M ferric nitrate - perchloric acid solution is

3) P. J. Urban, *Z. anal. Chem.*, **180**, 110 (1961).
4) T. Koh, This Bulletin, **38**, 1510 (1965).
5) T. Koh and I. Iwasaki, ibid., **38**, 2135 (1965).
6) H. Stamm and M. Goehring, *Z. anorg. u. allgem. Chem.*, **250**, 226 (1942).
7) F. Martin and L. Metz, ibid., **127**, 83 (1923).

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 distilled water as a reference.

Results and Discussion

Calibration Curves.—The calibration curves shown in Fig. 1 were obtained by the procedure described above, using standard tetrathionate and thiocyanate solutions.

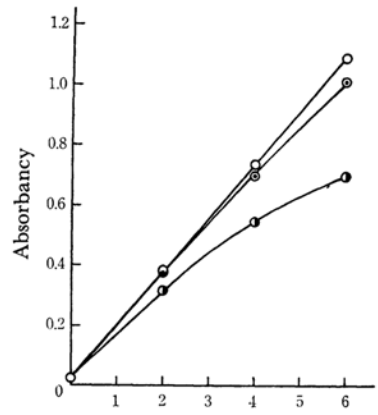


Concn. of $S_4O_6^{2-}$ and SCN^-, $\times 10^{-4}$ M

Fig. 1. Calibration curves.
○ Tetrathionate ● Thiocyanate

The absorbancy and the concentration were in a good linear relationaship, as can be seen in Fig. 1. When one ion of tetrathionate undergoes cyanolysis, one ion of thiocyanate is formed. Therefore, if the tetrathionate is pure enough and if it is, moreover, converted into thiocyanate stoichiometrically and quantitatively, the calibration curve of tetrathionate should be in full accord wtih that of thiocyanate when plotted by the mole concentration for tetrathionate and thiocyanate. In fact, Fig. 1 shows that the calibration curve for tetrathionate is in exact accordance with that for thiocyanate, demonstrating that the reaction of tetrathionate with cyanide goes well to completion and that it is stoichiometric.

The Effect of the Amount of Sodium Cyanide.—As will be disclosed below, it was confirmed that the optimum pH value for the reaction of tetrathionate with cyanide ranges from 8.3 to 12.1 under the conditions of the procedure mentioned above. 0.5 ml. of a 0.025 M sodium cyanide solution and from 0.5 to 4.0 ml. of a 0.05 M sodium cyanide solution were employed, in all cases the final solution being buffered to the optimum pH value. The resulting effect of the amount of sodium cyanide upon the cyanolysis is shown in Fig. 2.

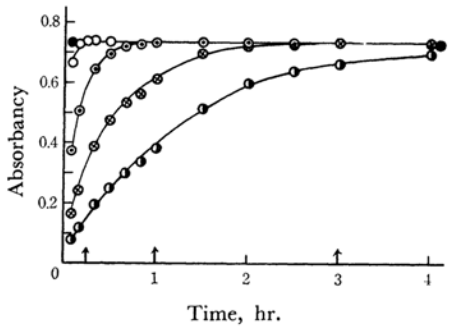


Concn. of tetrathionate, $\times 10^{-4}$ M

Fig. 2. The effect of the amount of sodium cyanide.
The pH was adjusted to 8.4—12.1 in all cases.
Cyanolysis time: 30 min. at 40°C
◑ 0.025 M NaCN 0.5 ml. (I)
⊙ 0.05 M NaCN 0.5 ml. (II)
○ 0.05 M NaCN 1.0, 2.0, 2.6, and 4.0 ml. (III)

The calibration curves with 0.5 ml. portions of 0.025 and 0.05 M sodium cyanide solutions do not form straight lines (see I and II), indicating that tetrathionate is not completely converted into thiocyanate because of insufficient amounts of cyanide. It can be concluded from Fig. 2 that 1.0 ml. of a 0.05 M sodium cyanide solution is sufficient for the complete conversion of tetrathionate into thiocyanate, and that the amount of sodium cyanide does not have any effect on this method as long as it is sufficient and the pH is adjusted to an optimum value.

The Effect of the pH.—The reaction should be carried out below a pH value of 12.1, because tetrathionate undergoes alkaline decomposition in addition to cyanolysis at higher pH levels.



Time, hr.

Fig. 3. Effect of pH on the rate of cyanolysis at 25°C.
● 4.0×10^{-4} M SCN^-
○ pH 10.3 and 11.8 (I)
⊙ pH 8.7 (II)
⊗ pH 8.0 (III)
◑ pH 7.5 (IV)
} 4.0×10^{-4} M $S_4O_6^{2-}$

Figure 3 shows the dependence of the rate of cyanolysis on the pH of the solution at 25°C.

The maximum absorbancy, which corresponds to the complete and stoichiometric reaction of tetrathionate with cyanide, is attained in 15 min. at pH 10.3 and 11.8, and thereafter remains constant (see I), while the reactions at pH 8.7 and 8.0 go to completion in 1 hr. and 3 hr. respectively (see II and III). However, the reaction at pH 7.5 does not reach completion even within 4 hr. (see IV).

As can also be seen from Fig. 3, the higher the pH of the solution, the more rapid the rate of cyanolysis; therefore, it is desirable that the procedure is carried out at a higher pH level as long as it is below 12.1. However, pentathionate and hexathionate, as has been reported in previous papers,[4,5] undergo a partial alkaline decomposition at pH levels higher than pH 9.0. Consequently, we made our study at pH values below 8.7. In order to accelerate the rate of cyanolysis, the reaction temperature was raised from 25°C to 40°C. Figure 4 shows how the pH of the solution affects the rate of cyanolysis at 40°C.

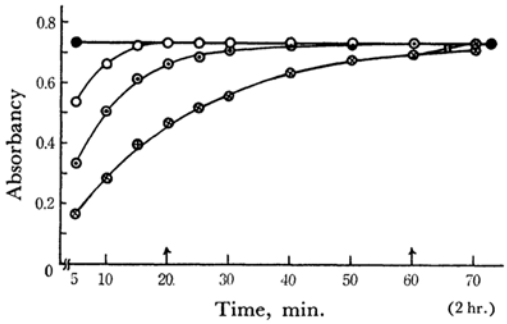


Fig. 4. Effect of pH on the rate of cyanolysis at 40°C.

● 4.0×10^{-4} M SCN^-
○ pH 8.7 (I)
⊙ pH 8.0 (II)
⊗ pH 7.5 (III)
} 4.0×10^{-4} M $S_4O_6^{2-}$

The reactions at pH 8.7 and 8.0 go well to completion, and are stoichiometric, in 20 min. and 1 hr. respectively (see I and II in Fig. 4). On the other hand, the reaction at pH 7.5 goes stoichiometrically to completion in 2 hr. (see III).

It was observed that tetrathionate also undergoes thermal decomposition as well as cyanolysis at 70°C, as do pentathionate and hexathionate.

The reaction of tetrathionate with cyanide at various pH values was carried out both at 25°C for 70 min. and at 40°C for 30 min. The results are shown in Fig. 5, where the complete and stoichiometric reaction occurs over the pH range from 8.5 to 12.1 at 25°C for 70 min. (see I) and over the pH range from 8.3 to 12.1 at 40°C for 30 min. (see II).

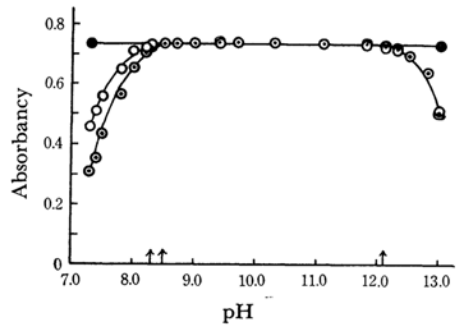


Fig. 5. Effect of pH.

● 4.0×10^{-4} M SCN^-
○ 30 min. at 40°C (II)
⊙ 70 min. at 25°C (I)
} 4.0×10^{-4} M $S_4O_6^{2-}$

The decrease in absorbancy above the pH value of 12.2 may be due to the alkaline decomposition of tetrathionate. The optimum pH range for the reaction of tetrathionate with cyanide can be extended from either 8.3 or 8.5 to a lower pH by making the cyanolysis time longer, because the rate of cyanolysis decreases with a lowering of the pH value.

Figure 6 shows how the pH affects the cyanolysis of tetrathionate, pentathionate, and hexathionate under the conditions of the procedure described above.

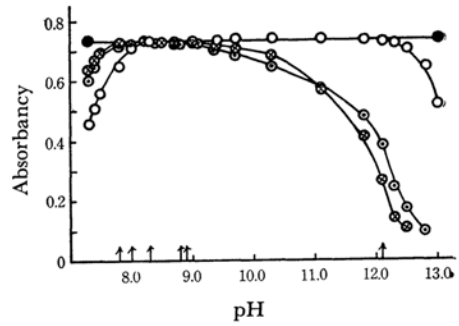


Fig. 6. Effect of pH.
Cyanolysis time: 30 min. at 40°C

● 4.0×10^{-4} M SCN^-
○ 4.0×10^{-4} M $S_4O_6^{2-}$
⊙ 2.0×10^{-4} M $S_5O_6^{2-}$
⊗ 1.33×10^{-4} M $S_6O_6^{2-}$

As can be seen in Fig. 6, the optimum pH ranges for tetrathionate, pentathionate, and hexathionate are between 8.3 and 12.1, 8.0 and 8.8, and 7.8 and 8.9 respectively. In view of the experimental results shown in Fig. 6, it may be concluded that tetrathionate can be determined accurately by the very same procedure as that used for pentathionate and hexathionate, where the pH value is 8.6.

Calibration Curves of Tetrathionate, Pentathionate, and Hexathionate.—Solutions

containing various amounts of thiocyanate, tetrathionate, pentathionate, and hexathionate were treated by the preceding procedure; the results are shown in Figs. 7 and 8. When one ion of tetrathionate, pentathionate, and hexathionate undergoes cyanolysis, one, two, and three ions of thiocyanate are, respectively, formed.

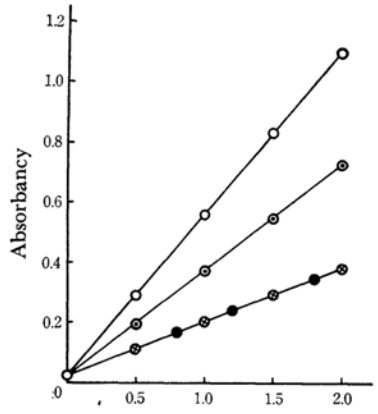


Fig. 7. Calibration curves
● Thiocyanate ⊗ Tetrathionate
⊙ Pentathionate ○ Hexathionate

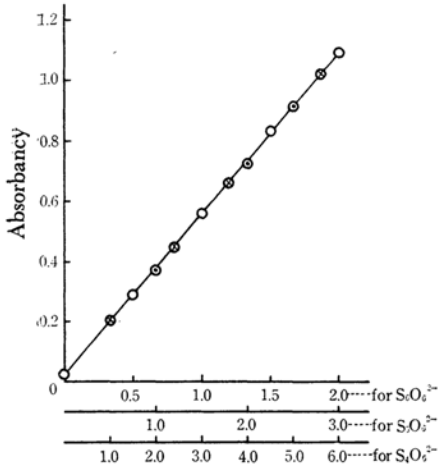


Fig. 8. Calibration curves.
⊗ Tetrathionate ⊙ Pentathionate
○ Hexathionate

In fact, Fig. 7 shows that the calibration curves of tetrathionate, pentathionate, and hexathionate are once, twice, and three times, respectively, as sensitive as that of thiocyanate. As can also be seen in Fig. 8, their calibration curves exactly coincide with one another when the scales of the concentration of tetrathionate and pentathionate are made one-third and two-thirds of the hexathionate concentration, indicating that all three of these polythionates can be easily determined by the same procedure.

A similar method, one suitable for the determination and for the evaluation of the composition of the polythionates mixed with each other, will be reported on in another paper.

Summary

The photometric method for the determination of a small amount of tetrathionate has been developed; it is based on the formation of thiocyanate equivalent to the tetrathionate, and on the determination of the thiocyanate with an excess of ferric iron. The conditions capable of determining a small quantity of tetrathionate by the very same procedure as that used for pentathionate and hexathionate have been established by varying the cyanide amount, the pH, the reaction time and the temperature.

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