The Determination of Micro Amounts of Polythionates. I.* A Photometric Method for the Determination of Pentathionate by Means of Its Cyanolysis

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Although it is important and desirable, from the viewpoints of geochemistry and medical science, to determine the amounts of polythionates in hot springs, there have been no suitable procedures for determining the polythionates in such micro amounts as are present in hot springs. Many investigations[1-15] have been made regarding the analysis of the polythionates. None of these methods, however, is suitable for micro quantities of polythionates.

Nietzel and DeSesa[16] have proposed a method for the estimation of a small amount of tetrathionate which is based on the reaction:

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1) F. Raschig, *Z. angew. Chem.*, **33**, 260 (1920).
2) A. Kurtenacker and A. Fritsch, *Z. anorg. Chem.*, **117**, 262 (1921).
3) A. Kurtenacker, ibid., **134**, 265 (1924).
4) A. Kurtenacker and E. Goldbach, *Z. anorg. u. allgem. Chem.*, **166**, 177 (1927).
5) M. Goehring, *Z. anal. Chem.*, **128**, 6 (1948).
6) M. Goehring, U. Feldmann and W. Helbing, ibid., **129**, 346 (1949).
7) A. Kurtenacker and K. Bittner, *Z. anorg. u. allgem. Chem.*, **142**, 119 (1925).
8) R. Lang and H. Kurtenacker, *Z. anal. Chem.*, **123**, 169 (1942).
9) B. Singh and I. Ilahi, *J. Indian Chem. Soc.*, **14**, 376 (1937).
10) W. Feld, *Z. angew. Chem.*, **24**, 290 (1911).
11) R. R. Jay, *Anal. Chem.*, **25**, 288 (1953).
12) H. Ishikawa and T. Murooka, *Rikagaku Kenkyuzyo Iho (Sci. Rep. Res. Inst. Phys. Chem.)*, **6**, 407 (1927).
13) T. Murayama, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zassi)*, **74**, 349 (1953).
14) W. Furness and W. C. Davies, *Analyst*, **77**, 697 (1952).
15) A. Iguchi, This Bulletin, **31**, 597 (1958).
16) O. A. Nietzel and M. A. DeSesa, *Anal. Chem.*, **27**, 1839 (1955).

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

followed by the photometric determination of the thiocyanate with ferric iron. They have pointed out that their method might also be suitable for pentathionate and hexathionate, because the higher polythionates react more easily with cyanide to form thiocyanate. Recently, Urban[17] has improved the Nietzel and DeSesa's method and applied it to the evaluation of *n*, the mean number of sulfur atoms in the formula, $S_nO_6^{2-}$, for polythionate above trithionate, in order to indicate the polythionate composition of the solution.

In the present investigation, it is confirmed that pentathionate is not quantitatively converted into thiocyanate under the conditions of the Nietzel-DeSesa's and the Urban's methods,[16,17] because of the partial alkaline decomposition arising from the higher pH value caused by the addition of a sodium cyanide solution. Consequently, their methods are not suitable for the higher polythionate, pentathionate. The present author has, therefore, investigated, in greater detail, a photometric method for the determination of a small amount of pentathionate which is dependent on the reaction:

$$S_5O_6^{2-} + 4CN^- + H_2O = S_2O_3^{2-} + SO_4^{2-} + 2HCN + 2SCN^-$$

and he has established an excellent method, finding the most suitable conditions for the reaction of pentathionate with cyanide to go well to completion and to be stoichiometric.

This paper will be concerned with the results of this investigation and with the determination of pentathionate by means of its cyanolysis.

Experimental

Apparatus.—The photometric measurements were made with a Hirama photometer with a 460 mμ filter (maximum transmission at 460 mμ) and with 10.0 mm. cells.

All pH measurements were made with a Toa Denpa Model HM-5A pH meter.

The desired temperatures were controlled by a Taiyo Model K-II thermostat.

The standard pentathionate solution was kept in a Hitachi Model R-104K refrigerator, the temperature of which was maintained at 5±2°C.

Potassium pentathionate was kept in a Sanyo Model HF-33 freezer in which the temperature was maintained at −8±2°C.

Volumetric flasks of 25 ml. were coated with black paint, except for small vertical areas on opposite sides near the top graduation.

17) P. J. Urban, *Z. anal. Chem.*, **180**, 110 (1961).

Materials.—Potassium pentathionate was prepared according to the procedure of Goehring and Feldmann.[18] The pentathionate obtained was recrystallized twice with 0.5 N hydrochloric acid and dried at room temperature for 4 days. The total water content in the pentathionate, including the water of crystallization, was estimated to be 8.2% by the Karl Fischer method. This result indicates that some moisture is adsorbed on the pentathionate besides the water of crystallization of one and a half molecules which corresponds to 7.5%.

The Purity of the Potassium Pentathionate.—The purity of this salt was estimated by determining the total sulfur and potassium as follows. The pentathionate was oxidized[19,20] by bromine in an alkaline medium on heating; the sulfate ion formed was determined by the usual gravimetric method.

The potassium pentathionate is decomposed into potassium sulfate by heating;

$$K_2S_5O_6 \rightarrow K_2SO_4$$

The potassium was determined by weighing[19] the potassium sulfate thus formed.

Table I. Determination of S for the potassium pentathionate* used in the present study

Sample taken	As $K_2S_5O_6$	Found as $BaSO_4$	K found for $K_2S_5O_6$	K calcd. for $K_2S_5O_6$
mg.	mg.	mg.	%	%
133.1	122.1	423.7	47.65	47.92
101.5	93.1	322.3	47.54	

* Total water content including the water of crystallization was 8.2%.

Table II. Determination of K for the potassium pentathionate* used in the present study

Sample taken	As $K_2S_5O_6$	Found as K_2SO_4	S found for $K_2S_5O_6$	S calcd. for $K_2S_5O_6$
mg.	mg.	mg.	%	%
310.2	284.8	148.8	23.44	23.38
215.4	197.7	103.2	23.43	

* Total water content including the water of crystallization was 8.2%.

The results listed in Tables I and II show that this potassium pentathionate is pure enough for the purpose of this study.

The Standard Pentathionate Solution.—182.2 mg. of the potassium pentathionate was dissolved in redistilled water and diluted to 500 ml. to give a 1.0×10^{-3} M solution. This standard solution proved to be stable; even after four months, no measurable change was found by the present method when it was kept in a refrigerator at the temperature of

18) M. Goehring and U. Feldmann, *Z. anorg. Chem.*, **257**, 223 (1948).

19) F. Martin and L. Metz, *Z. anorg. u. allgem. Chem.*, **127**, 83 (1923).

20) C. Mishima, *Bull. Tokyo Inst. Tech.*, No. 1, 27 (1951).

5±2°C. This was diluted to the concentration required for the experiments.

The Standard Thiocyanate Solution. — The stock solution of thiocyanate was prepared by dissolving guaranteed potassium thiocyanate in redistilled water; it was then standardized acording to Volhard's method. The working thiocyanate solutions were prepared by diluting the stock solution properly; they were used as standards to ascertain whether or not the reaction of pentathionate with cyanide went to completion and was stoichiometric.

Buffer Solutions.—A 0.2 M sodium dihydrogenphosphate solution was mixed with a 0.2 N sodium hydroxide solution, at various ratios, in order to obtain the buffer solutions from pH 6.0 to 8.0.

The Sodium Cyanide Solution.—The working cyanide solutions were prepared by diluting a 1 M solution properly.

The Ferric Nitrate - Perchloric Acid Solution. — 303.0 g. of guaranteed ferric nitrate, $Fe(NO_3)_3 \cdot 9H_2O$, was dissolved in a small volume of redistilled water containing 217.4 ml. of concentrated perchloric acid; then the mixture was diluted to 500 ml. to give a 1.5 M ferric nitrate - 4 N perchloric acid solution.

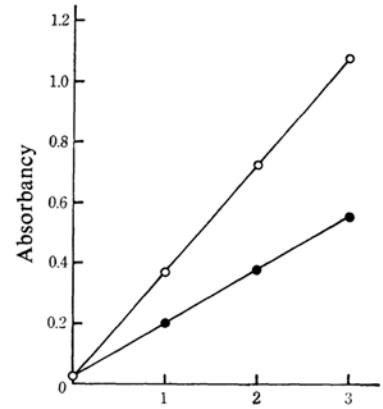
Procedure. — 10.0 ml. of the standard pentathionate solution is placed in a 25 ml. volumetric flask. To this solution are added first 4.0 ml. of the buffer solution of pH 7.4, and then 2.6 ml. of 0.05 M sodium cyanide; the pH of the solution is thereby brought to 8.6.

The volumetric flask is kept in the thermostat at 40°C for 30 min.; pentathionate is thereby converted into thiocyanate quantitatively. Then, 3.0 ml. of 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 distilled water as a reference.

Results and Discussion

Calibration Curves. — The calibration curves shown in Figs. 1 and 2 were obtained by a procedure using standard pentathionate and thiocyanate solutions of known concentrations.

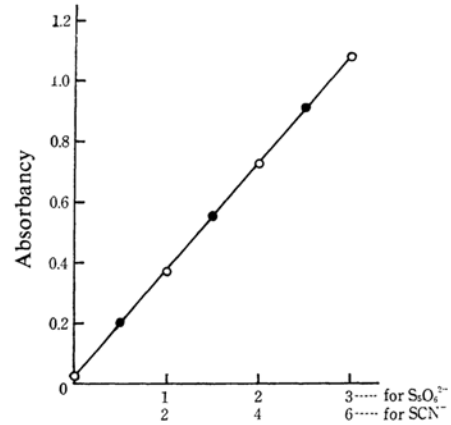
As can be seen in Figs. 1 and 2, the absorbancy and the concentration were in a good linear relationship. When one ion of pentathionate undergoes cyanolysis, two ions of thiocyanate are formed. Consequently, if the pentathionate is pure enough and if it is, moreover, converted into thiocyanate quantitatively, the sensitivity of the pentathionate should be just twice as much as that of thiocyanate. In fact, Fig. 1 shows that the calibration curve for pentathionate is twice as sensitive as that for thiocyanate. As can also be seen in Fig. 2, the calibration curve of pentathionate exactly coincides with that of thiocyanate when the scale of thiocyanate concentration is made to a half of the pentathionate concentration, demonstrating that a stoichiometric reaction has occurred.



Concn. of $S_5O_6^{2-}$ and SCN^-, $\times 10^{-4}$ M

Fig. 1. Cablibration curves.

○ Pentathionate, ● Thiocyanate



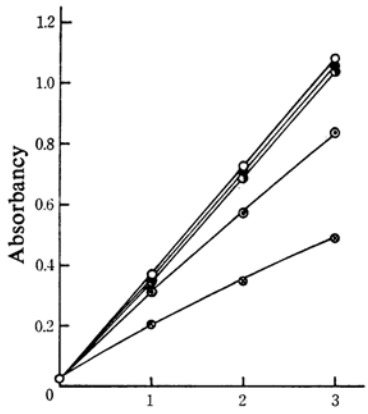
Concn. of $S_5O_6^{2-}$ and SCN^-, $\times 10^{-4}$ M

Fig. 2. Calibration curves.

○ Pentathionate, ● Thiocyanate

The Effect of the Amount of Sodium Cyanide. — In measuring the effect of the amount of sodium cyanide on the cyanolysis, from 0.5 to 6.0 ml. of a 0.05 M sodium cyanide solution was added to a standard pentathionate solution containing 4.0 ml. of the buffer solution of pH 7.4. Then, the mixiture was kept in the thermostat at 40°C for 30 min. and then treated as in the procedure described above. The experimental results are shown in Fig. 3.

When up to 2.6 ml. of a sodium cyanide solution, the more of it was added, the more the calibration curves approach the theoretical curve (see I, II and III). On the contrary, when more than 3.0 ml. was added, the more the absorbancies deviated from the theoretical value (see IV and V), except for the absorbancy of

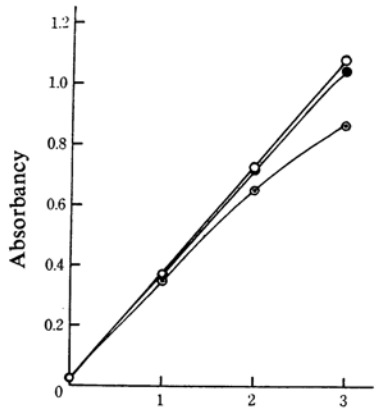


Concn. of pentathionate, $\times 10^{-4}$ M

Fig. 3. Effect of sodium cyanide amount.

Use is made of 4.0 ml. of the buffer solution of pH 7.4 in all cases.
Concn. of sodium cyanide solution: 0.05 M
Cyanolysis time: 30 min. at 40°C
⊗ 0.5 ml. (I) ⊙ 1.0 ml. (II)
○ 2.6 ml. (III) ● 4.0 ml. (IV)
◑ 6.0 ml. (V)

the reagent blank, which remains constant (see I—V). These facts led the author to the conclusion that the pH has a great effect on the cyanolysis and that pentathionate undergoes a partial alkaline decomposition as a result of the higher pH caused by the addition of the cyanide. As will be disclosed below, it was confirmed that the optimum pH for the reaction of pentathionate with cyanide is within a range from 8.0 to 8.8 under the conditions of the above procedure. A solution of from 0.5 to 4.0 ml. of 0.05 M sodium cyanide was employed; in all cases the solution is buffered over the optimum pH. The effect of the amount of sodium cyanide on the cyanolysis is shown in Fig. 4. The calibration curves with 0.5 and 1.0 ml. do not form straight lines (see I and II), indicating that the conversion of pentathionate is not quantitative because of the insufficient amounts of cyanide. Figure 4 shows that 2.0 ml. of a 0.05 M sodium cyanide solution is sufficient for the quantitative cyanolysis and that the amount of sodium cyanide does not have any effect on the method as long as it is sufficient and the pH is adjusted to an optimum value.



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

Fig. 4. Effect of sodium cyanide amount.

The pH was adjusted over a range from 8.0 to 8.8 in all cases.
Cyanolysis time: 30 min. at 40°C
⊙ 0.5 ml. (I) ● 1.0 ml. (II)
○ 2.0, 2.6 and 4.0 ml. (III)

The Effect of the pH.—At higher pH levels, pentathionate also undergoes the alkaline decomposition, so the procedure should be carried out below a pH value of 8.8. Figure 5 shows the dependence of the rate of cyanolysis on the pH of the solutions at 20°C.

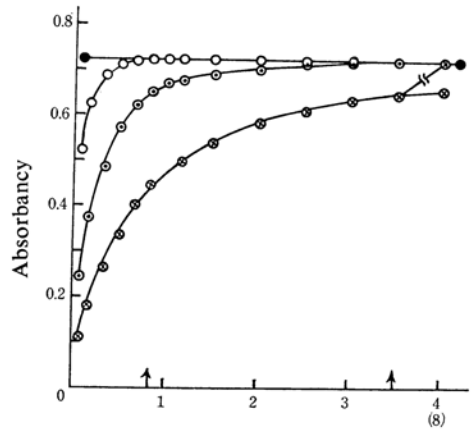


Fig. 5. Effect of pH on the rate of cyanolysis at 20°C.

● 4.0×10^{-4} M SCN^-
○ pH 8.7 (I)
⊙ pH 8.0 (II) } 2.0×10^{-4} M $S_5O_6^{2-}$
⊗ pH 7.5 (III)

The maximum absorbancy, which means the quantitative cyanolysis, is reached in 50 min. at pH 8.7; then it remains constant (see I). The reaction at pH 7.5 does not go to completion in 4 hr.; however, it goes stoichiometrically to completion after 8 hr. (see III).

In order to accelerate the rate of cyanolysis, the reaction temperature was raised from 20°C to 40°C and 70°C. At 40°C, the reaction goes well to completion and is stoichiometric in 15 min. at pH 8.7 (see I in Fig. 6); the reactions at pH 8.0 and 7.5 go well to completion in 30 min. and 1 hr. 20 min. respectively (see II and III in Fig. 6). At 70°C, thermodecomposition occurs in addition to cyanolysis, so

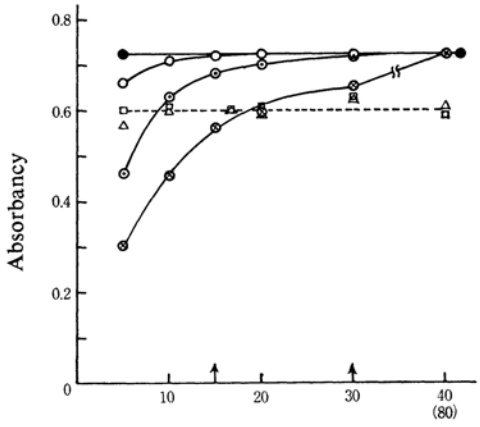


Fig. 6. Effect of pH on the rate of cyanolysis.

—●— 4.0×10^{-4} M SCN^-
—○— pH 8.7 (I) } at 40°C
—⊙— pH 8.0 (II) } at 40°C
—⊗— pH 7.5 (III) } at 40°C
--△-- pH 8.7 (IV) } at 70°C
--□-- pH 8.0 (IV) } at 70°C
} 2.0×10^{-4} M $S_5O_6^{2-}$

the reaction is not stoichiometric (see IV in Fig. 6).

In order to study the effect of the pH on the cyanolysis, the reaction of pentathionate with cyanide was carried out both at 20°C for 70 min. and at 40°C for 30 min. The results are shown in Fig. 7, where the reaction at 20°C for 70 min. gives maximum absorbancies over the pH range from 8.8 to 8.4 (see I) and that at 40°C for 30 min., over the pH range from 8.8 to 8.0 (see II). The decrease in absorbancy above the pH value of 9.0 may be attributed to the alkaline decomposition of pentathionate. The optimum pH range for the reaction with cyanide can be extended from both 8.0 and 8.4 to a lower pH value by making the cyanolysis time longer, because the rate of cyanolysis decreases with the lowering of the pH.

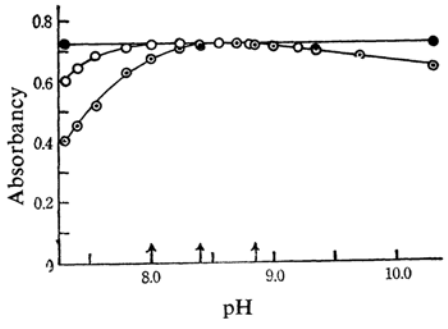


Fig. 7. Effect of pH.

● 4.0×10^{-4} M SCN^-
○ 30 min. at 40°C (II) } 2.0×10^{-4} M $S_5O_6^{2-}$
⊙ 70 min. at 70°C (I) } 2.0×10^{-4} M $S_5O_6^{2-}$

The Amount of Ferric Ntirate. — It is well known that the phosphate interferes with the color development of ferric-thiocyanate because of the formation of a ferric-phosphate complex.

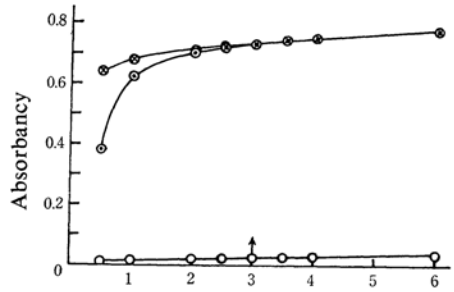


Fig. 8. Effect of ferric nitrate amount.
Use is made of 1.5 M ferric nitrate - 4 N perchloric acid solution
⊗ 4.0×10^{-4} M thiocyanate without buffer solution.
⊙ 4.0×10^{-4} M thiocyanate with 4.0 ml. of 0.2 M phosphate buffer solution of pH 7.4.
○ Reagent blank with 4.0 ml. of 0.2 M phosphate buffer solution of pH 7.4

Figure 8 shows how the phosphate buffer solution interferes; it also shows that 3.0 ml. of a 1.5 M ferric nitrate - perchloric acid solution is sufficient in the recommended procedure.

A similar method for the determination of micro amounts of hexathionate will be reported on in another paper. Moreover, the effect of diverse ions on the method and a detailed study regarding the stability of polythionate solutions will also be reported on.

Summary

The photometric method for the determination of a small amount of pentathionate has been developed; it is based on the formation of thiocyanate equivalent to the pentathionate, and on the determination of thiocyanate with an excess of ferric iron.

The buffer solution is first added to the standard pentathionate solution so that the pH values of the mixture solution after the addition of the cyanide solution may be over an optimum range; othewise the pentathionate undergoes alkaline decomposition because of the higher pH value which results from the addition of the cyanide.

The conditions under which the reaction of pentathionate with cyanide is rapid and goes well to completion have been established by varying the cyanide amount, the pH, the reaction time, and the temperature.

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