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Spectrophotometric Determination of Micro Amounts of Pentathionate via Permanganate Reaction

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A method has been developed for the determination of micro amounts of pentathionate. It is based on the reaction of pentathionate with a given amount of permanganate in a dilute sulfuric acid medium and on the spectrophotometric measurement of iodine as triiodide, which is formed by the oxidation of iodide with an excess of permanganate. The analytical conditions were established by varying the temperature, reaction time, and amounts of sulfuric acid and permanganate. The present method can be successfully applied to a determination of pentathionate in the range 2×10^{-7} to 1.4×10^{-5} mol dm^{-3} (0.5—35.9 μg $S_5O_6^{2-}$ in 10 cm^3) and gives a higher sensitivity than any previous method without solvent extraction. In eleven determinations for 10 cm^3 sample solutions containing 0.080 μmol of pentathionate, the present method gave a mean value of 0.080 μmol, with a standard deviation of 0.0006 μmol and a relative standard deviation of 0.75%.

A simple, accurate and sensitive determination of polythionates (tri-, tetra-, penta-, and hexathionate) is increasingly desirable from the viewpoint of sulfur chemistry. When polythionates react with cyanide, sulfite, hydroxide or mercury(II) thiocyanate, thiocyanate or thiosulfate (or both species equivalent to each of polythionates) is formed. Thiocyanate and thiosulfate can easily be measured spectrophotometrically with iron(III) and iodine, respectively. Therefore, various investigations have been made concerning the cyanolysis,[1–7)] the sulfitolysis,[8–11)] the alkaline decomposition[12,13)] and the mercury(II) thiocyanate reaction[14)] of polythionates and have led to the development of spectrophotometric methods for the determination of polythionates at concentrations as low as the 10^{-4} mol dm^{-3} level. Moreover, a sensitive method has been proposed for the determination of tetra-, penta-, and hexathionate, based on the solvent extraction of thiocyanate formed by their cyanolysis as an ion pair with Methylene Blue.[15)] The cyanolysis and sulfitolysis of polythionates have also played a critical role in the development of methods for the analysis of mixtures of polythionates[16–20)] as well as mixtures of sulfite, thiosulfate and each of the polythionates.[8–11)] High-performance liquid chromatography (HPLC)[21–25)] has been used for the separation of mixtures of polythionates. Takano et al.[24)] sulfitolyzed polythionates prior to HPLC separation and determined even tri- and tetrathionate in mixtures with the other polythionates (which can not be separated chromatographically).

In a previous paper,[26)] the present authors devised a sensitive method for the determination of thiocyanate up to 4×10^{-5} mol dm^{-3}; it was based on the consumption of permanganate by its reaction with thiocyanate in an acid medium. It has been found that pentathionate is also oxidized by permanganate. No consideration was given to the spectrophotometric determination of polythionates by means of their reactions with permanganate. In the present study, the optimal conditions under which pentathionate can be oxidized quantitatively by permanganate were established. The proposed method is based on the reaction of pentathionate with a given amount of permanganate in dilute sulfuric acid and on the spectrophotometric measurement of any formed iodine (as triiodide) after a reaction of excess permanganate with iodide to form iodine.

Experimental

Apparatus. All spectrophotometric measurements were made at 350 nm using a Shimadzu Model UV-240 recording spectrophotometer with 10-mm quartz cells. Desired temperatures were controlled by a Taiyo Coolnit Model CL-15 thermoregulator. In all the experiments, redistilled water was used, which was freed from any permanganate-consuming impurities with a Nippon Millipore, Ltd., Model Milli-QII apparatus.

Reagents. All chemicals were of analytical grade and were used without further purification.

Potassium pentathionate. Potassium pentathionate was prepared as described by Goehring and Feldmann.[27)] The obtained pentathionate ($K_2S_5O_6\cdot1.5H_2O$) was recrystallized twice in an acid medium of 0.5 mol dm^{-3} hydrochloric acid, and then dried at room temperature before storage at -10 ± 2 °C. The pentathionate was confirmed to be sufficiently pure for the present purpose; its purity was estimated by the sulfitolysis method[10)] to be 92.5% as $K_2S_5O_6$.

Standard Pentathionate Solution. A 1×10^{-3} mol dm^{-3} pentathionate solution was prepared by dissolving 180.8 mg of potassium pentathionate in water and diluting to 500 cm^3. The stock solution of 1×10^{-3} mol dm^{-3} standard pentathionate could be used for at least four months without any measurable changes as long as it was stored at 5 ± 2 °C. The working solution was prepared by suitable dilution.

Standard Permanganate Solution.[28)] A 0.02 mol dm^{-3} permanganate solution was prepared by heating a potassium permanganate solution to boiling, keeping it at a temperature slightly below the boiling point for 1 h, and then allowing it to stand for 3 d at room temperature. After manganese dioxide had been filtered off by suction with a sintered glass filter (3SG4), the filtrate was standardized by titration with standard sodium oxalate. The stock solution of 0.02 mol dm^{-3} standard permanganate proved to be stable; even after six months, no measurable change was found by the present method when it was stored at room temperature in the dark. A working solution of 2×10^{-4} mol dm^{-3} permanganate could be used for 2 d.

Standard Thiosulfate Solution. A 0.1 mol dm^{-3} thiosulfate solution was prepared by dissolving sodium thiosulfate pentahydrate in freshly boiled and cooled water containing a small amount of sodium carbonate as a stabilizer. The thiosulfate solution was standardized by iodimetry a week after preparation. A 5×10^{-4} mol dm^{-3} thiosulfate solution was obtained by diluting the standardized thiosulfate solution.

Iodide Solution. A 0.5 mol dm^{-3} iodide solution was prepared by dissolving 41.7 g of potassium iodide in water containing 200 mg of sodium carbonate as a stabilizer and by then diluting it to 500 cm^3.

Recommended Procedure. A mixture of 1.5 cm^3 of 1 mol dm^{-3} sulfuric acid and 4 cm^3 of 2×10^{-4} mol dm^{-3} standard potassium permanganate solution was placed in a 25 cm^3 volumetric flask. To this mixture, 10 cm^3 of a sample solution containing pentathionate up to 0.140 μmol was added. The mixture was then allowed to stand for 20 min at temperatures ranging from 5 to 40 °C to complete the oxidation of pentathionate. Then, 1 cm^3 of 0.5 mol dm^{-3} potassium iodide was added to form iodine equivalent to excess permanganate, and 3 cm^3 of 5×10^{-4} mol dm^{-3} sodium thiosulfate was added to decrease the absorbance of the iodine as triiodide to an appropriate value, otherwise the absorbance for the reagent blank becomes so high as much as 1.94. The flask was filled to the mark with water. The absorbance of a solution of the triiodide complex, thus formed, was measured against water at 350 nm about 5 min after the dilution.

A permanganate-free reagent blank was prepared by adding 1.5 cm^3 of 1 mol dm^{-3} sulfuric acid, 14 cm^3 of water in place of both 4 cm^3 of 2×10^{-4} mol dm^{-3} permanganate and 10-cm^3 of a sample solution containing pentathionate, and 1 cm^3 of 0.5 mol dm^{-3} iodide in a 25-cm^3 volumetric flask. After the flask had been filled to the mark with water, the absorbance was measured against water at 350 nm after about 5 min. This absorbance value was subtracted from each of the absorbances for pentathionate and the reagent blank, for iodide is susceptible to air-oxidation in an acid medium.

Results and Discussion

Reaction of Pentathionate with Permanganate. In order to determine the stoichiometric relationship between pentathionate and permanganate in an acid medium, the reaction was investigated by the molar-ratio method. For the application of this method, 4 cm^3 of permanganate with various molar concentrations and 10-cm^3 of each of 0.3×10^{-5}, 0.6×10^{-5}, 1×10^{-5} and 1.4×10^{-5} mol dm^{-3} pentathionate solutions were used with varying the molar ratio of permanganate to pentathionate. Pentathionate was allowed to react with permanganate for 20 min, where sodium thiosulfate was not added. The results are shown in Fig. 1. When straight portions of each graph were extrapolated, each line (dotted lines) intersected the abscissa at a point of 3.5. This fact proves that 2 mol of pentathionate reacted exactly with 7 mol of permanganate under the conditions of the recommended procedure.

Calibration Plots. Figure 2 shows the calibration graphs obtained by treating a series of standard solutions of pentathionate according to the recommended procedure, and the plots obtained by treating a series of standard permanganate solutions according to the recommended procedure except that 4 cm^3 of redistilled water was used instead of 4 cm^3 of 2×10^{-4} mol dm^{-3} permanganate. The graph for permanganate was prepared to confirm the stoichiometry and the completion

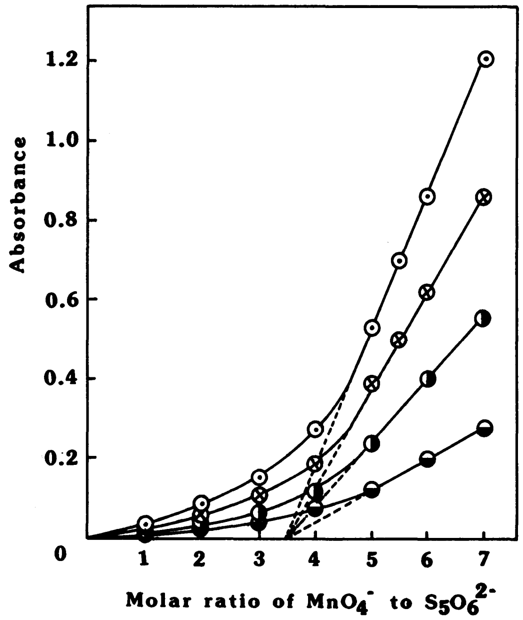

Fig. 1. Molar ratio plots for the reaction of pentathionate with permanganate.
⊙: 1.4×10^{-5} mol dm^{-3} $S_5O_6^{2-}$, ⊗: 1×10^{-5} mol dm^{-3} $S_5O_6^{2-}$, ◑: 0.6×10^{-5} mol dm^{-3} $S_5O_6^{2-}$, ⊖: 0.3×10^{-5} mol dm^{-3} $S_5O_6^{2-}$.

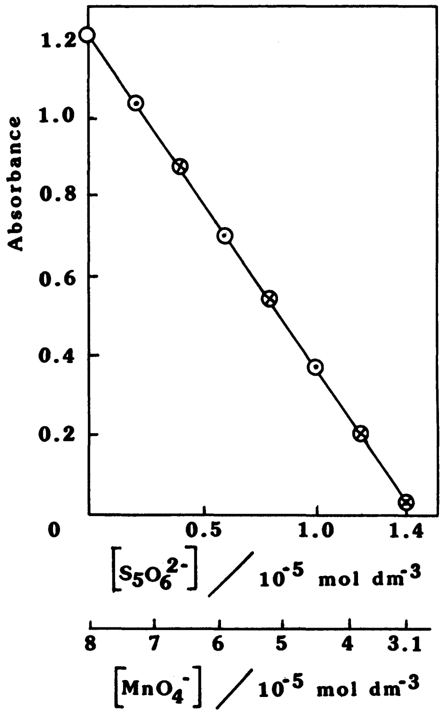

Fig. 2. Calibration plots.
O: Reagent blank, ⊙: $S_5O_6^{2-}$, ⊗: MnO_4^- (expected value).

of the reaction of pentathionate with permanganate. As described above, if 2 mol of pentathionate reacts with 7 mol of permanganate stoichiometrically, the graph for pentathionate should coincide with that for permanganate (the expected graph). Figure 2 proves that the reaction proceeded to stoichiometric completion under the conditions of the recommended procedure.

The precision was estimated from eleven results for 10-cm³ aliquots of a solution containing 0.080 μmol of pentathionate. The present method gave a mean value of 0.080 μmol, with a standard deviation of 0.0006 μmol and a relative standard deviation of 0.75%. This method gives a higher sensitivity than previous methods without any need for solvent extractions.

Rate of Reaction of Pentathionate with Permanganate. The reaction rate was investigated at temperatures ranging from 5 to 40 °C. The amounts of the reagents and the addition order were the same as in the above procedure. The results are given in Table 1. The reaction was gradually accelerated by an increase in the temperature. The absorbances for 1.2×10^{-5} mol dm^{-3} pentathionate reached those for 3.8×10^{-5} mol dm^{-3} permanganate, which are the expected values, in 20 min at 5 °C, in 10 min at 10 and 20 °C, in 5 min at 30 °C and in 3 min at 40 °C, and then kept constant until 60 min had passed. These facts confirm that the reaction proceeds to completion as long as the reaction is carried out for 20 min at temperatures of 5 to 40 °C. On the other hand, when pentathionate was allowed to react with permanganate in a low-acidity solution using 1.5 cm³ of 0.6 mol dm^{-3} sulfuric acid, the reaction did not proceed to completion. Therefore, the effect of acidity was investigated at 20 °C. The results are shown in Table 2.

Table 1. Reaction Rate of Pentathionate with Permanganate at Various Temperatures

t / min	Absorbance of I_3^- (350 nm)				
	1.2×10^{-5} mol dm^{-3} $S_5O_6^{2-}$				
	5 °C	10 °C	20 °C	30 °C	40 °C
	0.206$^{a)}$	0.205$^{a)}$	0.205$^{a)}$	0.206$^{a)}$	0.204$^{a)}$
1	0.249	0.243	0.242	0.231	0.229
3	0.237	0.235	0.236	0.221	0.203
5	0.226	0.225	0.222	0.211	0.205
10	0.218	0.210	0.206	0.206	0.203
20	0.208	0.205	0.205	0.208	0.204
30	0.203	0.203	0.204	0.205	0.203
45	0.203	0.204	0.205	0.203	0.205
60	0.204	0.205	0.203	0.205	0.204

a) Absorbances for 3.8×10^{-5} mol dm^{-3} permanganate which are expected values.

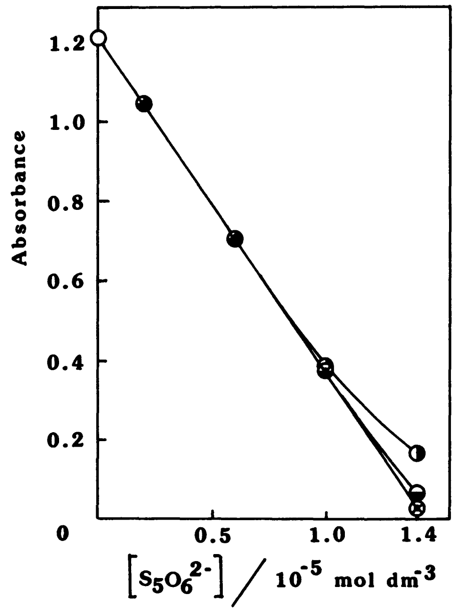

Fig. 3. Effect of amounts of permanganate on the reaction with pentathionate.
○: Reagent blank, ◑: $S_5O_6^{2-}$ with 2.5 cm³ of 2×10^{-4} mol dm^{-3} MnO_4^-, ◒: $S_5O_6^{2-}$ with 3.0 cm³ of 2×10^{-4} mol dm^{-3} MnO_4^-, ⊗: $S_5O_6^{2-}$ with 3.5, 4.0, or 4.5 cm³ of 2×10^{-4} mol dm^{-3} MnO_4^-, ⊙: $S_5O_6^{2-}$ obtained under the conditions of the recommended procedure.

Table 2. Effect of Various Amounts of Sulfuric Acid on the Reaction of Pentathionate with Permanganate at 20 °C

t / min	Absorbance of I_3^- (350 nm)			
	1.2×10^{-5} mol dm^{-3} $S_5O_6^{2-}$			
	0.6 mol dm^{-3} H_2SO_4	0.8 mol dm^{-3} H_2SO_4	1 mol dm^{-3} H_2SO_4	2 mol dm^{-3} H_2SO_4
	0.207$^{a)}$	0.205$^{a)}$	0.207$^{a)}$	0.204$^{a)}$
1	0.261	0.250	0.242	0.248
3	0.243	0.240	0.236	0.238
5	0.229	0.227	0.222	0.223
10	0.224	0.208	0.206	0.209
20	0.222	0.203	0.205	0.208
30	0.220	0.204	0.204	0.209
45	0.220	0.205	0.205	0.207
60	0.218	0.207	0.203	0.205

a) Absorbances for 3.8×10^{-5} mol dm^{-3} permanganate which are expected values. The volume of sulfuric acid used was 1.5 cm³.

Table 3. Effect of Diverse Ions

Foreign ion	Added as	Amount	Amount of $S_5O_6^{2-}$ found	Error	Foreign ion	Added as	Amount	Amount of $S_5O_6^{2-}$ found	Error
		μg	μg	%			μg	μg	%
None			20.5		Cr^{3+}	$Cr(NO_3)_3 \cdot 9H_2O$	500	20.4	−0.5
Na^+	Na_2SO_4	10000	20.6	0.5	F^-	NaF	30000	20.5	0
K^+	K_2SO_4	10000	20.6	0.5	Cl^-	NaCl	10000	20.5	0
NH_4^+	$(NH_4)_2SO_4$	10000	20.5	0	Br^-	KBr	500	20.6	0.5
Mg^{2+}	$Mg(NO_3)_2 \cdot 6H_2O$	10000	20.5	0	I^-	KI	100	20.5	0
Ca^{2+}	$Ca(NO_3)_2 \cdot 4H_2O$	10000	20.5	0	NO_3^-	KNO_3	10000	20.6	0.5
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	10000	20.5	0	NO_2^-	KNO_2	1	20.7	1.0
Cd^{2+}	$Cd(OAc)_2 \cdot 2H_2O$	10000	20.6	0.5			1000[b]	20.2	−1.5
Mn^{2+}	$MnSO_4 \cdot 5H_2O$	50	20.5	0	CO_3^{2-}	Na_2CO_3	10000	20.5	0
Co^{2+}	$CoSO_4 \cdot 7H_2O$	10000	20.5	0	S^{2-}	$Na_2S \cdot 9H_2O$	0.1	20.6	0.5
Ni^{2+}	$NiSO_4 \cdot 6H_2O$	10000	20.5	0	HSO_3^-	$NaHSO_3$	1	20.7	1.0
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	1000	20.1	−2.0	$S_2O_3^{2-}$	$Na_2S_2O_3 \cdot 5H_2O$	0.1	20.6	0.5
Pb^{2+}	$Pb(NO_3)_2$	1000	20.1	−2.0	$H_2PO_4^-$	$NaH_2PO_4 \cdot 2H_2O$	10000	20.5	0
Fe^{2+}	$FeSO_4 \cdot 7H_2O$	1	20.8	1.5	Borate ion	H_3BO_3	10000	20.6	0.5
Fe^{3+}	$Fe(NO_3)_3 \cdot 9H_2O$	1	20.5	0	Silicate ion	(as SiO_2)	10000	20.5	0
		1000[a]	20.2	−1.5	OAc^-	$NaOAc \cdot 3H_2O$	10000	20.6	0.5
Al^{3+}	$Al(NO_3)_3 \cdot 9H_2O$	10000	20.5	0	$H_2NSO_3^-$	$HOSO_2NH_2$	5000	20.5	0

a) Three cm^3 of 0.5 mol dm^{-3} NaF was added. b) One cm^3 of 0.05 mol dm^{-3} sulfamic acid was added.

The absorbances for 1.2×10^{-5} mol dm^{-3} pentathionate coincided with the expected value in 10 min with respect to 1.5 cm^3 of each of 0.8, 1, and 2 mol dm^{-3} sulfuric acid, and then remained constant. Consequently, 1.5 cm^3 of 1 mol dm^{-3} sulfuric acid was employed in this experiment.

Effect of Amounts of Permanganate. For measuring the effect of amounts of permanganate, pentathionate was allowed to react with various amounts of potassium permanganate for 20 min at 20 °C. In this experiment, thiosulfate, which is used in order to reduce the absorbance in the recommended procedure, was not added. The absorbance, therefore, increased with increasing amounts of permanganate employed. The resulting graphs given in Fig. 3 were normalized in such way that each calibration graph for pentathionate with various amounts of permanganate was permitted to shift in parallel fashion to cause each reagent blank to accord with that obtained under the conditions of the recommended procedure. When 2.5 and 3 cm^3 of 2×10^{-4} mol dm^{-3} permanganate were used, the reaction did not go to completion because the amounts of permanganate were insufficient; even in this case, the reagent blank gave high absorbances of 1.215 and 1.453, respectively. When 3.5, 4.0, or 4.5 cm^3 of the permanganate solution were used, the graphs for pentathionate yielded a straight line and coincided exactly with that obtained under the conditions of the recommended procedure. Consequently, 4 cm^3 of 2×10^{-4} mol dm^{-3} permanganate was employed, and 3 cm^3 of 5×10^{-4} mol dm^{-3} thiosulfate was added to decrease the reagent blank to an appropriate value by reducing the iodine formed.

Effect of Diverse Ions. A 10-cm^3 portion of a solution containing 20.5 μg of pentathionate and various amounts of diverse ions was treated exactly as in the recommended procedure. For the determination of pentathionate with an error of below 2% by the present method, foreign ions can be tolerated at the levels given in Table 3. Iron(II), nitrite, thiosulfate, sulfide, and sulfite gave positive errors, even when present in trace amounts, because they reduce permanganate. However, the interference of nitrite could be eliminated by decomposing it with sulfamic acid. Iron(III) gave a negative interference in amounts of 10 μg because it oxidizes iodide to form iodine, but its interference was removed by masking with fluoride. Trithionate gave a very weak interference, but tetrathionate and hexathionate gave strong interferences with the determination of pentathionate because they also were oxidized by permanganate.

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