Spectrophotometric Determination of Micro Amounts of Thiocyanate via Permanganate Reaction

Yasuyuki Miura* and Tomozo Koh
Department of Chemistry, Faculty of Science, Tokai University, 1117,
Kitakaname, Hiratsuka, Kanagawa 259-12

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A method has been developed for the determination of micro amounts of thiocyanate. It is based on the reaction of thiocyanate with a given amount of permanganate as an oxidizing agent 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 for its reaction with thiocyanate. The conditions for the thiocyanate to be quantitatively oxidized were established by varying the temperature, reaction time, and amounts of sulfuric acid and permanganate. The present method can be successfully applied to the determination of thiocyanate in the range from 7×10^{-7} to 4×10^{-5} mol dm^{-3} (0.4—23.2 μg SCN$^-$ in 10 cm^3). In eleven determinations for 10-cm^3 sample solutions containing 0.250 μmol of thiocyanate, the present method gave a mean value of 0.251 μmol, with a standard deviation of 0.0022 μmol and a relative standard deviation of 0.88%. Chloride, bromide, iodide, and cyanide did not interfere with the determination of 14.5 μg of thiocyanate in the presence of 1000 μg, 500 μg, 100 μg, and 50 μg, respectively.

Iron(III) reacts easily with thiocyanate to give a red iron(III)-thiocyanate complex in an acid medium. Therefore, iron(III)[1] is widely used for the photometric determination of small amounts of thiocyanate. However, in measuring thiocyanate at concentrations as low as the 10^{-5} mol dm^{-3} level, the iron(III) method is not considered useful because of its low sensitivity. For the sensitive spectrophotometric determination of thiocyanate, the pyridine-pyrazolone,[2,3] the pyridine–benzidine,[4,5] and the pyridine-barbituric acid[6] methods have been devised. Moreover, extraction methods using copper–pyridine,[7] tris(1,10-phenanthroline)iron(II),[8] Neutral Red,[9] mercury(II) Methylthymol Blue-zephiramine,[10] and mercury(II)-quinoline[11] reagents have been proposed. These methods[2–11] have, however, some disadvantages: pyridine is unpleasant and noxious, benzidine has a carcinogenic property, and solvent extraction is generally troublesome. Koh and Iwasaki[12] have previously reported a very sensitive method of determining thiocyanate (3×10^{-7}—1×10^{-5} mol dm^{-3}) based on the extraction of thiocyanate with Methylene Blue into 1,2-dichloroethane and the spectrophotometric measurement of the organic phase.

The purpose of this work, using the reaction of thiocyanate with permanganate, is to develop a method for the sensitive determination of thiocyanate without any solvent extractions or poisonous reagents. The optimal conditions under which thiocyanate can be oxidized by permanganate were established. The proposed method is based on the reaction of thiocyanate with a given amount of permanganate in an acidic medium[13] according to following Eq. 1, and then on the spectrophotometric measurement of the iodine thus formed, after converting the permanganate in excess for its reaction with thiocyanate into iodine[14] according to Eq. 2:

$$5SCN^- + 6MnO_4^- + 8H^+ \longrightarrow 6Mn^{2+} + 5SO_4^{2-} + 5CN^- + 4H_2O \tag{1}$$

$$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O \tag{2}$$

Experimental

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

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

Standard Thiocyanate Solution. A 0.1 mol dm^{-3} thiocyanate solution was prepared by dissolving potassium thiocyanate in redistilled water. The solution was standardized by Volhard's method. The working solutions were prepared by suitable dilution.

Standard Permanganate Solution.[15] A 0.02 mol dm^{-3} permanganage solution was prepared by heating the solution in which potassium permanganate had been dissolved 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 the manganese dioxide thus obtained had been filtered off by suction with a sintered glass filter(3SG4), the filtrate was standardized by oxidation-reduction titration using 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 dark. A working solution of the 2×10^{-4} mol dm^{-3} permanganate solution obtained by the appropriate dilution of the stock solution 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 redistilled 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 exactly.

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

Recommended Procedure. A 1.5 cm^3 of 0.8 mol dm^{-3} sulfuric acid and 4 cm^3 of a 2×10^{-4} mol dm^{-3} standard potassium permanganate solution were placed in a 25-cm^3 volumetric flask. To this mixture, 10-cm^3 of a sample solution containing thiocyanate up to 0.400 µmol were added. The mixture was then allowed to stand for 10 min in the temperature range from 15 to 40 °C to complete the oxidation of thiocyanate. Then, 1 cm^3 of 0.5 mol dm^{-3} potassium iodide was added to form iodine equivalent to the excess permanganate, and 3 cm^3 of 5×10^{-4} mol dm^{-3} sodium thiosulfate were added to decrease the absorbance of the iodine as triiodide to an appropriate value. The flask was filled to the mark with redistilled water. The absorbance of a solution of the triiodide complex thus formed was measured against distilled water at 350 nm in about 5 min after the dilution.

A permanganate-free reagent blank was prepared by placing 1.5 cm^3 of 0.8 mol dm^{-3} sulfuric acid, 14 cm^3 of redistilled 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 thiocyanate, and 1 cm^3 of 0.5 mol cm^{-3} iodide in a 25-cm^3 volumetric flask. After the flask had been filled to the mark with redistilled water, the absorbance was measured against distilled water at 350 nm in about 5 min. This absorbance value was subtracted from each of the absorbances for thiocyanate and the reagent blank, for iodide is susceptible to air-oxidation in an acid medium.

Results and Discussion

Calibration Plots. Figure 1 shows the calibration graphs obtained by treating a series of standard solutions of thiocyanate according to the recommended procedure and permanganate according to a procedure where 4 cm^3 of redistilled water were 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 of the reaction of thiocyanate with permanganate. According to Eq. 1, if 5 mol of thiocyanate react with 6 mol of permanganate completely and stoichiometrically, the graph for thiocyanate should coincide with that for permanganate (the expected graph) in excess amounts for the reaction with thiocyanate, when each of the molar concentration scales for thiocyanate and permanganate is drawn as in Fig. 1. Figure 1 proves that the reaction proceeded to stoichiometric completion under the conditions of Procedure.

The precision was estimated from 11 results for 10-cm^3 aliquots of a solution containing 0.250 µmol of thiocyanate. The present method gave a mean value of 0.251 µmol, with a standard deviation of 0.0022 µmol and a relative standard deviation of 0.88%. This method give a higher sensitivity than the copper(II) diethyldithiocarbamate-silver(I)[16] and the rhenium[17] methods without any need for solvent extractions or poisonous reagents.

Rate of Reaction of Thiocyanate with Permanganate. The reaction rate was investigated at temperatures ranging from 10 to 40 °C. The amount of the reagents and the addition order were 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

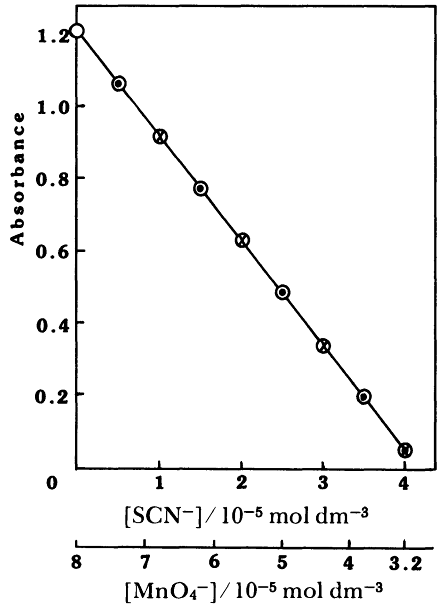

Fig. 1. Calibration plots.
○: Reagent blank, ⊙: SCN$^-$, ⊗: MnO$_4^-$ (the expected value).

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

$\frac{t}{\text{min}}$	Absorbance			
	4×10^{-5} mol dm^{-3} SCN$^-$			
	10 °C	15 °C	25 °C	40 °C
	0.055[a]	0.053[a]	0.056[a]	0.055[a]
1	0.083	0.075	0.073	0.068
3	0.072	0.068	0.065	0.056
5	0.070	0.063	0.054	0.054
10	0.066	0.057	0.055	0.051
20	0.053	0.053	0.057	0.056
30	0.052	0.055	0.053	0.057

a) Absorbances for 3.2×10^{-5} mol dm^{-3} permanganate (the expected values).

4×10^{-5} mol dm^{-3} thiocyanate reached those for 3.2×10^{-5} mol dm^{-3} permanganate, which are the expected values, in 20 min at 10 °C, in 10 min at 15 °C, in 5 min at 25 °C, and in 3 min at 40 °C, and then kept constant until 30 min had passed. These facts confirm that the reaction proceeds to completion as long as it is carried out for 10 min at temperatures from 15 to 40 °C. On the other hand, when thiocyanate was allowed to react with permanganate in a solution of a low acidity using 1.5 cm^3 of 0.3 mol dm^{-3} sulfuric acid, the reaction did not proceed to completion according to Eq. 1. Therefore, the effect of acidity was investigated at 20 °C. The results are shown in Table 2. The absorbances for 4×10^{-5} mol dm^{-3} thiocyanate coincided with the expected value in 10 min with 1.5 cm^3 of 0.6 mol dm^{-3} sulfuric acid, in 5 min with 1.5 cm^3 of each 0.8 and 1.0 mol dm^{-3} sulfuric acid, and in 3 min with 1.5 cm^3 of 1.5 mol dm^{-3} sulfuric acid. Consequently, 1.5 cm^3 of 0.8 mol dm^{-3} sulfuric acid was employed in this experiment.

Effect of Amounts of Permanganate. For measuring the effects of the amounts of permanganate, thiocyanate was allowed to react with various amounts of potassium permanganate for 10 min at 20 °C. In this experiment, the thiosulfate, which is used in order to reduce the absorbance, was not added. The absorbance, therefore, increased with the increase in the amounts of permanganate employed. The resulting graphs (given in Fig. 2) were normalized in such a way that each calibration graph for thiocyanate 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 Procedure. When 2.5 and 3.0 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. However, when 3.5, 4.0, or 4.5 cm^3 of the permanganate solution were used, the graphs for thiocyanate formed a straight line and coincided completely with that obtained under the conditions

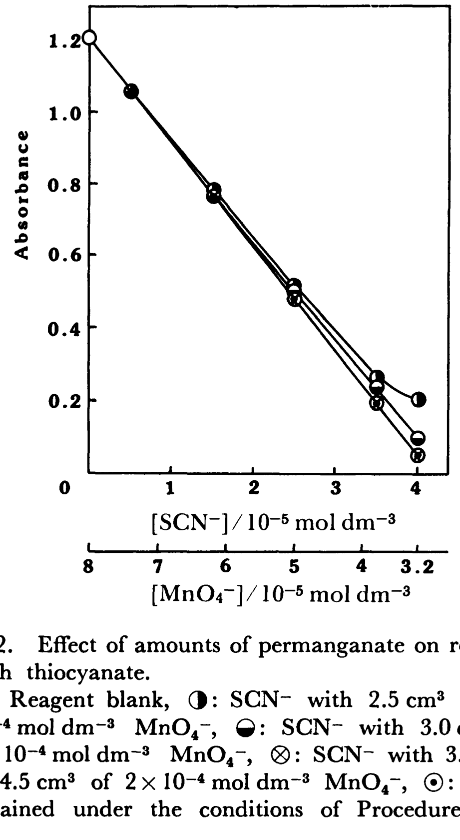

Fig. 2. Effect of amounts of permanganate on reaction with thiocyanate.
○: Reagent blank, ◑: SCN^- with 2.5 cm^3 of 2×10^{-4} mol dm^{-3} MnO_4^-, ⊖: SCN^- with 3.0 cm^3 of 2×10^{-4} mol dm^{-3} MnO_4^-, ⊗: SCN^- with 3.5, 4.0, or 4.5 cm^3 of 2×10^{-4} mol dm^{-3} MnO_4^-, ⊙: SCN^- obtained under the conditions of Procedure.

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

$\frac{t}{\text{min}}$	Absorbance			
	4×10^{-5} mol dm^{-3} SCN^-			
	0.6 mol dm^{-3} H_2SO_4	0.8 mol dm^{-3} H_2SO_4	1.0 mol dm^{-3} H_2SO_4	1.5 mol dm^{-3} H_2SO_4
	0.056[a)]	0.053[a)]	0.056[a)]	0.055[a)]
1	0.085	0.077	0.072	0.070
3	0.078	0.066	0.062	0.060
5	0.068	0.056	0.059	0.054
10	0.056	0.056	0.058	0.053
20	0.054	0.052	0.055	0.056
30	0.053	0.055	0.058	0.051

a) Absorbances for 3.2×10^{-5} mol dm^{-3} permanganate (the expected values). The volume of the sulfuric acids used was 1.5 cm^3.

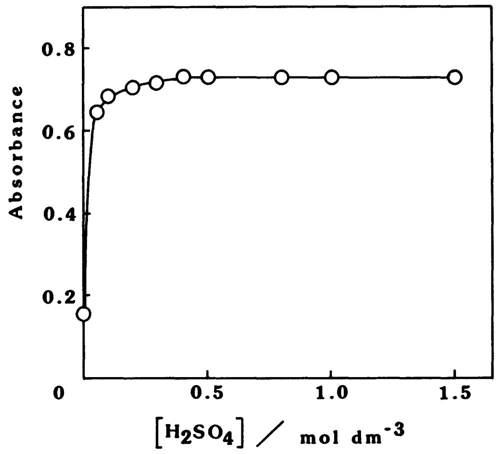

Fig. 3. Effect of amounts of sulfuric acid on liberation of iodine by oxidation with permanganate. A 10 cm^3 of 6×10^{-5} mol dm^{-3} permanganate was treated as in procedure, where 1.5 cm^3 sulfuric acid solution in various molar concentrations were used and 4 cm^3 of redistilled water were employed instead of 4 cm^3 of 2×10^{-4} mol dm^{-3} permanganate.

Table 3. Effect of Standing Time of Triiodide Solution

$\frac{t}{\text{min}}$	Absorbance	
	Reagent blank	4×10^{-5} mol dm^{-3} SCN$^-$
1	1.179	0.048
3	1.203	0.053
5	1.205	0.057
7	1.208	0.059
10	1.213	0.063
15	1.226	0.077
20	1.233	0.084

Table 4. Effect of Diverse Ions

Ion	Added as	Amount / μg	Amount of SCN$^-$ found / μg	Error / %
None			14.5	
Na^+	Na_2SO_4	10000	14.5	0
K^+	K_2SO_4	10000	14.5	0
NH_4^+	$(NH_4)_2SO_4$	10000	14.5	0
Mg^{2+}	$Mg(NO_3)_2\cdot6H_2O$	10000	14.4	−0.7
Ca^{2+}	$Ca(NO_3)_2\cdot4H_2O$	10000	14.5	0
Zn^{2+}	$ZnSO_4\cdot7H_2O$	10000	14.6	+0.7
Cd^{2+}	$Cd(NO_3)_2\cdot4H_2O$	10000	14.5	0
Mn^{2+}	$MnSO_4\cdot5H_2O$	100	14.5	0
Co^{2+}	$CoSO_4\cdot7H_2O$	10000	14.5	0
Ni^{2+}	$NiSO_4(NH_4)_2SO_4\cdot6H_2O$	10000	14.5	0
Cu^{2+}	$CuSO_4\cdot5H_2O$	1000	14.4	−0.7
Pb^{2+}	$Pb(NO_3)_2$	1000	14.5	0
Fe^{2+}	$FeSO_4(NH_4)_2SO_4\cdot6H_2O$	1	14.4	−0.7
Fe^{3+}	$Fe(NO_3)_3\cdot9H_2O$	1	14.4	−0.7
		5000[a)]	14.6	+0.7
Al^{3+}	$Al(NO_3)_3\cdot9H_2O$	10000	14.6	+0.7
F^-	NaF	30000	14.7	+1.4
Cl^-	NaCl	10000	14.5	0
Br^-	KBr	500	14.8	+2.1
I^-	KI	100	14.2	−2.1
CN^-	NaCN	50	14.6	+0.7
NO_3^-	KNO_3	10000	14.5	0
NO_2^-	KNO_2	1	14.6	+0.7
		1000[b)]	14.5	0
S^{2-}	$Na_2S\cdot9H_2O$	0.5	14.8	+2.1
HSO_3^-	$NaHSO_3$	1	14.8	+2.1
CO_3^{2-}	Na_2CO_3	10000	14.5	0
$HAsO_4^{2-}$	$Na_2HAsO_4\cdot7H_2O$	10000	14.4	+0.7
$H_2PO_4^-$	$NaH_2PO_4\cdot2H_2O$	10000	14.5	0
Borate ion	H_3BO_3	10000	14.5	0

a) 3 cm^3 of 0.5 mol dm^{-3} NaF were added. b) 1 cm^3 of 0.05 mol dm^{-3} sulfamic acid was added.

of Procedure. Consequently, 4.0 cm^3 of 2×10^{-4} mol dm^{-3} permanganate were employed.

Effect of Amounts of Iodide. In order to estimate the optimal amount of iodide on the formation of iodine equivalent to excess amounts of permanganate for the reaction of Eq. 1, 1 cm^3 of 0.1, 0.3, 0.5, 0.7, or 1.0 mol dm^{-3} iodide solution was used in Procedure. In all cases, calibration graphs for thiocyanate gave straight lines with a good reproducibility, and the sensitivity increased with the increase in the amounts of iodide used. In the recommended procedure, 1 cm^3 of a 0.5 mol dm^{-3} iodide solution was used, for it gives the appropriate absorbance value for the reagent blank.

Effect of Amounts of Sulfuric Acid on Liberation of Iodine. For measuring the effects of the amounts of sulfuric acid on the oxidation of iodide by permanganate to iodine, 1.5 cm^3 of a sulfuric acid solution in various molar concentrations were employed in Procedure. As can be seen in Fig. 3, when 1.5 cm^3 of 0.4—1.5 mol dm^{-3} sulfuric acid were used, the absorbance reached the maximum value and subsequently remained constant. Therefore, 1.5 cm^3 of 0.8 mol dm^{-3} sulfuric acid were used in Procedure.

Stability of Triiodide Complex Solution. The absorbance of the triiodide complex solution increased progressively with time because iodine is formed by the air-oxidation of iodide in an acidic solution. The triiodide complex solution prepared according to Procedure was allowed to stand for various periods of time at room temperature. The results are given in Table 3. The absorbances for the reagent blank and 4×10^{-5} mol dm^{-3} thiocyanate gave nearly constant values over the range from 3 to 7 min. Therefore, all the absorbances were measured in about 5 min after the contents had been diluted to 25 cm^3 by the recommended procedure.

Effect of Diverse Ions. A 10-cm^3 portion of a solution containing 14.5 μg of thiocyanate and various amounts of diverse ions was treated exactly as in Procedure. Iron(II), nitrite, sulfide, and sulfite gave positive errors for the determination of thiocyanate, 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 the presence of 10 μg because it reacts with iodide to form iodine, but its interference was eliminated by masking with fluoride. For the determination of 14.5 μg of thiocyanate with an error of below 2.1% by the present method, foreign ions can be tolerated at the levels given in Table 4. Anions such as chloride, bromide, iodide, and cyanide, which interfere seriously in the conventional determination of thiocyanate are tolerated in amounts of 10000 μg, 500 μg, 100 μg, and 50 μg, respectively, in the present method.

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