Spectrophotometric Determination of Thiocyanate by Its Oxidation with Iodate

Tomozo Koh,* Yasunobu Yonemura, and Hiroaki Kanai
Department of Chemistry, Faculty of Science, Tokai University,
Hiratsuka, Kanagawa 259-12

(Received June 30, 1992)

A simple method for the determination of thiocyanate has been proposed, based on the oxidation of thiocyanate to sulfate with iodate in a sulfuric acid medium and on the spectrophotometric measurement of the iodine as triiodide at 350 nm, formed from the excess iodate with iodide added. The complete oxidation of thiocyanate to sulfate using iodate was achieved in a medium containing varying amounts of sulfuric acid at 30 °C. Thiocyanate reacted with iodate with a mole ratio of 1 : 1 under the conditions employed here. The proposed method is approximately 20-fold more sensitive than the conventional method using iron(III) and can be applied to the determination of thiocyanate in the concentration range 5.6×10^{-7}—5.2×10^{-5} mol dm^{-3} (0.31—30.2 μg of SCN^- in 10 cm^3). The relative standard deviation (n=11) was 0.44% at the 3×10^{-5} mol dm^{-3} thiocyanate (17.4 μg of SCN^- in 10 cm^3) level.

The spectrophotometric method for thiocyanate using iron(III)[1] is very simple, rapid and precise, and has been extensively used for the determination of sulfur compounds, in which the thiocyanate, formed from thiosulfate,[2-4] polythionates,[5-10] and sulfide[11,12] by their reactions with cyanide and mercury(II) thiocyanate, was measured. Several other methods using pyridine–pyrazolone,[13,14] pyridine–benzidine,[15] and Methylene Blue[16] have been proposed for a highly sensitive determination of thiocyanate; pyridine–pyrazolone reagent has drawbacks regarding preparation and stability, and benzidine has a carcinogenic property. A Methylene Blue method[16] has played a critical role in the development of sensitive methods for the determination of polythionates.[17,18] However, this procedure is somewhat complicated, mainly because it involves the extraction of thiocyanate produced from the polythionate as an ion pair with Methylene Blue into an organic solvent.

The formal potential for the redox couples, which involves a large number of hydrogen-ions, is expected to increase, from the Nernst expression, with an increase in the hydrogen ion concentration. Hence, a method using permanganate has been proposed for the determination of thiocyanate,[19] based on the oxidation of thiocyanate with permanganate in a strong acid medium and on a measurement of the iodine as triiodide formed by the oxidation of iodide with excess permanganate. In previous papers it was mentioned that thiosulfate[20] and tetrathionate[21] can be quantitatively oxidized by iodate to sulfate in a strong acidic medium. In this work we attempted to oxidize thiocyanate with iodate in a medium of sulfuric acid, and to establish the conditions under which thiocyanate can be stoichiometrically oxidized to sulfate according to the following equation:

$$SCN^- + IO_3^- + H_2O \longrightarrow SO_4^{2-} + HCN + I^- + H^+. \quad (1)$$

Experimental

Reagents and Apparatus. All of the chemicals used were of analytical-reagent grade and were used without further purification. The water used in these experiments was redistilled. An approximately 0.1 mol dm^{-3} thiocyanate solution was prepared by dissolving a known amount of potassium thiocyanate in water. This solution was standardized by the Volhard's method. Working standards were prepared by suitable dilution. A 0.100/6 mol dm^{-3} standard iodate solution was prepared by dissolving 3.567 g of potassium iodate (99.98%) in water and diluting to 1000 cm^3. Working standard iodate solutions were prepared by appropriate dilution with water.

A Shimadzu Model UV-100-02 spectrophotometer with 10-mm quartz cells was used for all of the absorbance measurements. The desired temperatures were controlled by a Taiyo Coolnit Model CL-15 thermoregulator.

Procedure. Procedure I for the Determination of Thiocyanate: Pipette a 10 cm^3 of a sample solution of up to 6.5×10^{-5} mol dm^{-3} thiocyanate into a 50-cm^3 calibrated flask, and add 3 cm^3 of 3 mol dm^{-3} sulfuric acid and 4.2 cm^3 of a $1\times10^{-3}/6$ mol dm^{-3} standard iodate solution. Allow the flask to stand in a thermostat at 30 °C for 30 min in order to oxidize the thiocyanate completely to sulfate according to Eq. 1. Then add 5 cm^3 of 5 mol dm^{-3} acetic acid, 3 cm^3 of 6 mol dm^{-3} sodium hydroxide and 5 cm^3 of 1 mol dm^{-3} potassium iodide solution; the iodine equivalent to the excess iodate is thus formed. After diluting the mixture to the mark with water, mix the contents well and measure the absorbance of the formed triiodide against water at 350 nm, which is the wavelength of the maximum absorption for triiodide.[22]

Prepare an iodate-free reagent blank by adding 4.2 cm^3 of water in place of 4.2 cm^3 of $1\times10^{-3}/6$ mol dm^{-3} standard iodate solution and treat it exactly the same; correct it for all of the absorbances measured in the Procedure-I section.

Procedure II for the Determination of Iodate: Place 10 cm^3 of a standard solution of up to 7×10^{-5} mol dm^{-3} iodate, 5 cm^3 of 1 mol dm^{-3} potassium iodide and 5 cm^3 of 5 mol dm^{-3} acetic acid in a 50-cm^3 calibrated flask; in this case the iodine equivalent to the amount of the iodate is formed. After diluting to the mark with water, mix the contents well and measure the absorbance of the triiodide against water at 350 nm. Subtract the reagent blank from the measured absorbances.

Results and Discussion

Calibration Graphs. A series of standard solutions (10 cm^3) of thiocyanate were treated as described in the Procedure-I section. After the reaction of thiocyanate with iodate went to completion, the iodine which formed from the excess iodate with iodide added was spectrophotometrically measured as triiodide. The proposed method gave a linear calibration graph with a negative slope for an increase in the concentration of thiocyanate. The positive deviation from a straight line in the higher concentration range of thiocyanate was attributed to an incomplete oxidation of thiocyanate. The calibration graph for thiocyanate is shown in Fig. 1, together with the calibration graph for iodate obtained by Procedure II. The calibration graphs for both thiocyanate and iodate were parallel to each other up to 5.2×10^{-5} mol dm^{-3} thiocyanate, when the molar concentration scale for iodate was drawn in a way opposite to the scale for the thiocyanate concentration. The lower reagent blank obtained by Procedure I can probably be ascribed to the oxidation of trace amounts of impurities in the reagents by the iodate and to higher temperatures caused by the neutralization heat of a strong acid; at higher temperatures the absorbance of triiodide decreases due to its dissociation. When the absorbance for 7×10^{-5} mol dm^{-3} iodate obtained by Procedure II was normalized to the reagent blank obtained by Procedure I, the calibration graph for thiocyanate was in complete agreement with that for iodate up to 5.2×10^{-5} mol dm^{-3} thiocyanate. This proves that the reaction between thiocyanate and iodate proceeded to stoichiometric completion according to Eq. 1 under the conditions described in the Procedure-I section.

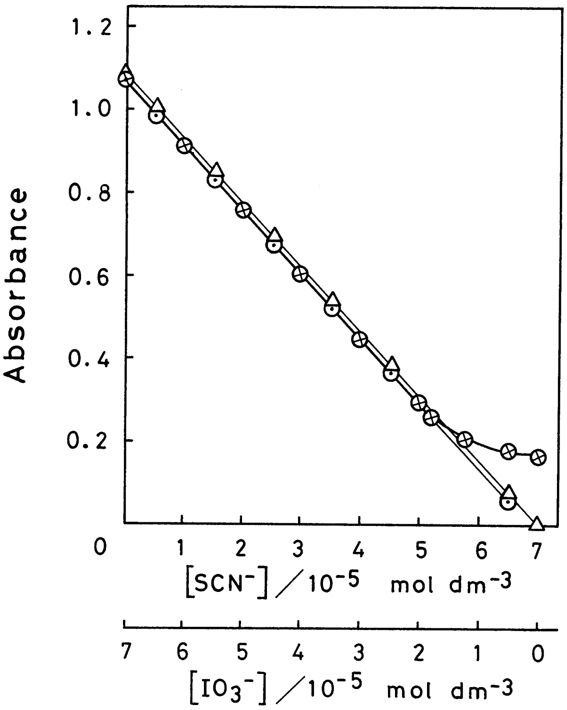

Fig. 1. Calibration graphs for thiocyanate and iodate. ⊗, Thiocyanate by Procedure I; △, iodate by the Procedure II; ⊙, expected graph (the absorbance for 7×10^{-5} mol dm^{-3} iodate obtained by the Procedure II was normalized to the reagent blank obtained by the Procedure I).

The proposed method is approximately 20-fold more sensitive than a conventional method using iron(III),[1] and is applicable to the determination of thiocyanate in 0.31—30.2 μg in 10 cm^3. The precision was determined from 11 results obtained for a 10-cm^3 aliquot of a 3×10^{-5} mol dm^{-3} standard thiocyanate solution (17.4 μg of SCN^-); the mean value of the thiocyanate found was 17.4 μg, with a standard deviation of 0.077 μg of SCN^- and a relative standard deviation of 0.44%.

Reaction Rate of Thiocyanate with Iodate. The formal potential for the reduction of iodate ion to iodide ion is expected to increase with an increase in the hydrogen-ion concentration. Hence, we attempted to oxidize thiocyanate to sulfate with iodate in a strong acid medium of sulfuric acid.[20] Thiocyanate (10 cm^3 of 5×10^{-5} mol dm^{-3}) was allowed to react with iodate (4.2 cm^3 of $1 \times 10^{-3}/6$ mol dm^{-3}) in a medium containing varying amounts of sulfuric acid at 30 °C for various periods of time. The resulting graphs are shown in Fig. 2. Here, all of the absorbances obtained were normalized to those obtained using 3 cm^3 of 3 mol dm^{-3} sulfuric acid (all the reagent blanks had been normalized to that obtained by Procedure I). The reaction rate was accelerated by an increase in the concentration of sulfuric acid; the reaction went to stoichiometric completion according to Eq. 1 within 90 min in a 0.17-mol dm^{-3}

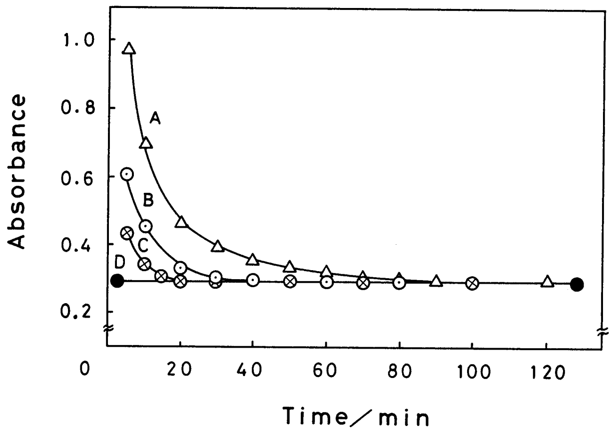

Fig. 2. Reaction rate of thiocyanate with iodate in a medium containing varying amounts of sulfuric acid at 30 °C. A 10-cm^3 solution of 5×10^{-5} mol dm^{-3} thiocyanate was used. A, 3-cm^3 addition of 1 mol dm^{-3} H_2SO_4; B, 3-cm^3 addition of 2 mol dm^{-3} H_2SO_4; C, 3-cm^3 addition of 3 mol dm^{-3} H_2SO_4; D, expected value obtained by the Procedure II using a 10-cm^3 solution of 2×10^{-5} mol dm^{-3} IO_3^-.

sulfuric acid medium (3-cm^3 addition of 1 mol dm^{-3} H_2SO_4), within 40 min in a 0.35-mol dm^{-3} sulfuric acid medium (3-cm^3 addition of 2 mol dm^{-3} H_2SO_4), and within 20 min in a 0.52-mol dm^{-3} sulfuric acid medium (3-cm^3 addition of 3 mol dm^{-3} H_2SO_4); the absorbances then remained constant. Therefore, 3 cm^3 of 3 mol dm^{-3} sulfuric acid was used in the Procedure-I section and thiocyanate was allowed to react with iodate in the 0.52-mol dm^{-3} sulfuric acid medium for 30 min at 30 °C. The reaction proceeded to completion according to Eq. 1 in 60 min at 10 °C and in 40 min at 20 °C, respectively.

Stoichiometric Relationship for the Reaction of Thiocyanate with Iodate. The stoichiometric relationship for the oxidation of thiocyanate with iodate in a medium of sulfuric acid was investigated by the method of continuous variations. Figure 3 shows the resulting plots of absorbance vs. mole fraction of iodate; all three lines intersected at a 0.5 mole fraction of iodate. Further, the absorbance at this point appeared exactly on that obtained for the amount of the iodate employed additionally. From a consideration of these results it was concluded that 1 mol of thiocyanate reacted stoichiometrically with 1 mol of iodate according to Eq. 1 under the conditions described in the Procedure-I section.

Effect of Foreign Ions. A 10-cm^3 solution containing 17.4 μg of thiocyanate (3×10^{-5} mol dm^{-3}) and various amounts of foreign ions was treated as described in the Procedure-I section. The results are given in Table 1. Ionic species, such as copper(II), iron(III) and nitrite which oxidize iodide, gave negative errors. However, iron(III) could be tolerated in amounts of up to 1000 μg and nitrite up to 10000 μg; the former was masked by the addition of 2 cm^3 of 0.2 mol dm^{-3} fluoride solution, and the latter was decomposed by the addition of 1 cm^3 of 0.5 mol dm^{-3} amidosulfuric acid solution. Lead(II), manganese(II), and iodide also gave negative

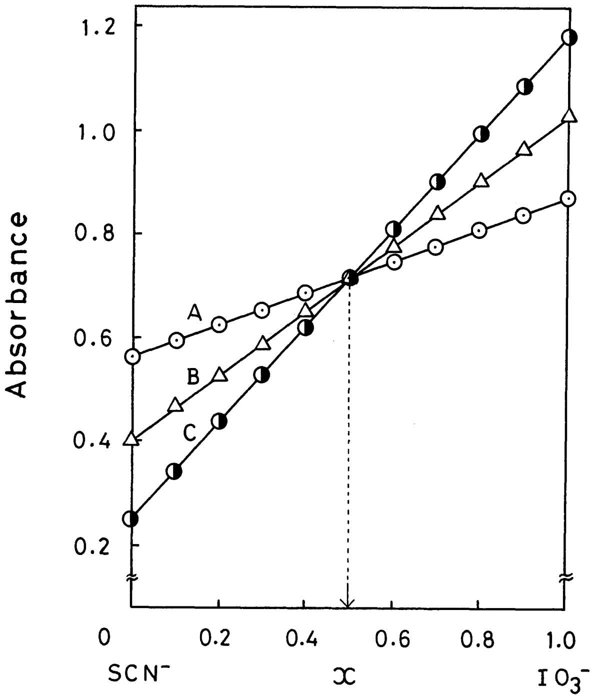

Fig. 3. Continuous variation graphs for the reaction of thiocyanate with iodate. A, $[IO_3^-]+[SCN^-]=1\times10^{-5}$ mol dm^{-3}; B, $[IO_3^-]+[SCN^-]=2\times10^{-5}$ mol dm^{-3}; C, $[IO_3^-]+[SCN^-]=3\times10^{-5}$ mol dm^{-3}. A 2.8-cm^3 solution of $1\times10^{-3}/6$ mol dm^{-3} iodate was used additionally.

Table 1. Effect of Foreign Ions on the Determination of 17.4 μg of Thiocyanate in a 10-cm^3 Sample Solution

Ion	Added as[a]	Amount	Amount of SCN$^-$ found	Error
		μg	μg	%
None			17.4	
Pb^{2+}	$Pb(NO_3)_2$	1000	15.6	−10.3
		100	17.4	0
Mn^{2+}	$MnSO_4$	100	13.9	−20.1
		10	17.8	2.3
Cu^{2+}	$CuSO_4$	100	12.1	−30.5
		10	17.2	−1.1
Fe^{3+}	$Fe(NH_4)(SO_4)_2$	1000	12.7	−27.0
		1000	17.2[b]	−1.1
I$^-$	KI	1000	6.0	−65.5
		100	17.9	2.9
CN$^-$	NaCN	1000	18.9	8.6
		1000	17.6[c]	1.1
NO_2^-	$NaNO_2$	10	5.6	−67.8
		10000	17.2[d]	−1.1
HSO_3^-	$NaHSO_3$	10	21.2	21.8
		100	17.6[c]	1.1
S^{2-}	Na_2S	1	19.2	10.3
		100	17.9[c]	2.9

a) Water of crystallization is omitted for brevity. b) Two cm^3 of 0.2 mol dm^{-3} sodium fluoride solution were added. c) The nitrogen gas at a flow rate of 300 cm^3 min^{-1} was bubbled for 30 min. d) One cm^3 of 0.5 mol dm^{-3} amidosulfuric acid was added.

Table 2. Recovery of Thiocyanate Added to Sewage Works Samples

Samples	Thiocyanate content/ppm			Recovery
	Added	Found	Found in samples	%
Sample A		0.23	0.29	
	0.58	0.82		101.7
	1.45	1.69		100.7
	2.32	2.55		100.0
Sample B		0.19	0.24	
	0.58	0.78		101.7
	1.45	1.65		100.7
	2.32	2.53		100.9
Sample C		0.26	0.23	
	0.58	0.85		101.7
	1.45	1.72		100.7
	2.32	2.60		100.9
Sample D		0.22	0.28	
	0.58	0.80		100.0
	1.45	1.67		100.0
	2.32	2.54		100.0

interferences, due to the turbidity produced by the precipitate of lead sulfate, the oxidation of the iodide by the manganese oxidized to higher oxidation state, and the formation of iodine as a result of the reaction of iodide with the iodate, respectively. Sulfide, sulfite, and cyanide, which reduce iodate, gave positive errors when present in small amounts. Their interferences, however, could be eliminated to some extent by bubbling nitrogen gas through the sample solution for 30 min at a flow rate of 300 $cm^3\ min^{-1}$ after the addition of 3 cm^3 of 3 $mol\ dm^{-3}$ sulfuric acid. Magnesium(II), calcium(II), zinc(II), cadmium(II), aluminium(III), fluoride, chloride, bromide, nitrate, sulfate, carbonate, phosphate, and arsenate were tolerated in amounts of up to 10000 μg.

Application to Real Samples. The proposed method was applied to the determination of thiocyanate in sewage works effluents. The thiocyanate content in the samples was determined as follows, using the standard addition method. Known amounts of thiocyanate, 1.5 cm^3 of 6.67 $mol\ dm^{-3}$ sodium hydroxide solution[23] and 8.5 g of sodium nitrate were added to 80-cm^3 sample solutions and the mixtures were diluted to 100 cm^3 with water to be 0.1 $mol\ dm^{-3}$ NaOH and 1 $mol\ dm^{-3}$ $NaNO_3$, respectively; a 1 $mol\ dm^{-3}$ $NaNO_3$ was confirmed not to interfere with the proposed method. After centrifuging the mixture at a rate of 2000 rpm for 5 min, a 10-cm^3 aliquot of the supernatant obtained was treated according to the Procedure-I section, in which 1 cm^3 of 0.1 $mol\ dm^{-3}$ amidosulfuric acid solution was added to eliminate the interference of the nitrites formed by oxidation of ammonium ions with nitrite bacteria in the samples. The results are summarized in Table 2. The recoveries for the thiocyanate added to the samples ranged from 100 to 101.7% with an average of 100.8%.

References

1) L. G. Hargis, "Colorimetric Determination of Nonmetals," ed by D. F. Boltz and I. A. Howell, John Wiley & Sons, New York (1978), p. 78.

2) B. Sörbo, *Biochim. Biophys. Acta,* **23**, 412 (1957).

3) T. Koh, Y. Miura, and M. Katoh, *Talanta,* **24**, 759 (1977).

4) Y. Miura and T. Koh, *Anal. Chim. Acta,* **173**, 33 (1985).

5) T. Koh, *Bull. Chem. Soc. Jpn.,* **38**, 1510 (1965).

6) T. Koh and I. Iwasaki, *Bull. Chem. Soc. Jpn.,* **38**, 2135 (1965).

7) T. Koh and I. Iwasaki, *Bull. Chem. Soc. Jpn.,* **39**, 359 (1966).

8) T. Koh and I. Iwasaki, *Bull. Chem. Soc. Jpn.,* **39**, 703 (1966).

9) Y. Miura and T. Koh, *Anal. Chem.,* **52**, 1855 (1980).

10) T. Koh, Y. Miura, M. Ishimori, and N. Yamamuro, *Anal. Sci.,* **5**, 79 (1989).

11) T. Koh, Y. Miura, N. Yamamuro, and T. Takaki, *Analyst* (*London*), **115**, 1133 (1990).

12) T. Koh, N. Yamamuro, and Y. Miura, *Anal. Sci.,* **6**, 917 (1990).

13) J. Epstein, *Anal. Chem.,* **19**, 272 (1947).

14) S. Nagashima, *Anal. Chem.,* **55**, 2086 (1983).

15) F. Wagner, *Fresenius' Z. Anal. Chem.,* **162**, 106 (1958).

16) T. Koh and I. Iwasaki, *Bull. Chem. Soc. Jpn.,* **40**, 569 (1967).

17) T. Koh, N. Saito, and I. Iwasaki, *Anal. Chim. Acta,* **61**, 449 (1972).

18) T. Koh, Y. Aoki, and I. Iwasaki, *Analyst* (*London*), **104**, 41 (1979).

19) Y. Miura and T. Koh, *Bull. Chem. Soc. Jpn.,* **59**, 741 (1986).

20) T. Koh, K. Kitami, and Y. Yonemura, *Anal. Sci.,* **7**, 81 (1991).

21) T. Koh and M. Yajima, *Bull. Chem. Soc. Jpn.,* **64**, 1854 (1991).

22) T. Ozawa, *Nippon Kagaku Zasshi,* **87**, 573 (1966).

23) T. Imanari, S. Tanabe, and T. Toida, *Chem. Pharm. Bull.,* **30**, 3800 (1982).