BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 569—575 (1967)

A New Spectrophotometric Method for the Determination of Micro Amounts of Thiocyanate by Solvent Extraction[1]

Tomozo KOH and Iwaji IWASAKI

Laboratory of Analytical Chemistry and Geochemistry, Tokyo Institute of Technology, Ookayama, Tokyo

(Received August 17, 1966)

A study was made aimed at devising a new spectrophotometric method for the determination of ultramicro amounts of thiocyanate. A methylene blue is slightly extracted into a dichloroethane layer from an acid aqueous solution. However, if methylene blue is added to an acid aqueous solution containing thiocyanate, the complex formed in a 1 : 1 ratio between methylene blue and thiocyanate is well extracted into dichloroethane, the amount of extraction being proportional to the amount of thiocyanate present. Thiocyanate is determined by measuring the absorbancy of the dichloroethane solution of the complex at the wavelength of 657 mμ. This method is suitable for the determination of thiocyanate within the concentration range from 2.0×10^{-7} to 6.0×10^{-6} M by employing a 5.0-m*l* portion of dichloroethane for extraction, and in the range from 3.0×10^{-7} to 1.0×10^{-5} M by employing a 10.0-m*l* portion of it.

Many investigations have been made regarding the analysis of the thiocyanate. Direct titrimetric methods for the oxidation of thiocyanate by ceric sulfate[2] and sulfatoceric acid[3] have been proposed. An indirect titrimetric method[4] for the oxidation of thiocyanate by ceric sulfate, in which an excess of ceric sulfate was back-titrated with Mohr's salt solution, has also been reported. Plowman and Wilson[5] have studied a polarographic method. Recently, Ganchev and Koev[6] have devised a method which is based on the use of filter paper evenly impregnated with silver chromate. None of these methods, however, is suitable for micro

---

[1] Presented at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.

[2] G. S. Desmukh and A. L. J. Rao, *Z. anal. Chem.*, **185**, 376 (1962).

[3] S. Singh and J. R. Siefker, *Anal. Chim. Acta*, **27**, 489 (1962).

[4] G. S. Desmukh and M. K. Joshi, *J. Indian Chem. Soc.*, **31**, 413 (1954).

[5] R. A. Plowman and I. R. Wilson, *Analyst*, **85**, 222 (1960).

[6] N. Ganchev and K. Koev, *Mikrochim. Acta*, **1964**, 87.

quantities of thiocyanate.

For very low concentrations of thiocyanate, the copperpyridine,[7] the pyridine-benzidine[8,9] and the pyridine-pyrazolone procedures[9,10] are generally known; the latter two procedures are based on the photometric determination of the complex formed between the cyanogen halide obtained from thiocyanate by reaction with bromine or chloramine-T, and the pyridine-benzidine or pyridine-pyrazolone reagent. The pyridine-benzidine reagent does not form a stable complex with cyanogen halide, while the pyridine-pyrazolone reagent has the disadvantages of being complicated to prepare and being unstable.

On the other hand, the present authors[11,12] have previously reported a spectrophotometric determination of perchlorate depending on the extraction of the methylene blue-perchlorate complex with organic solvents; they have found that a very small amount of thiocyanate can be determined by a procedure similar to that used for perchlorate. In preceding papers[13-16] the present authors have also described methods for the determination of polythionates based on the formation of thiocyanate equivalent to the polythionate by reaction with cyanide, and on the photometric determination of thiocyanate with an excess of ferric iron. A new method for determining an ultramicro amount of thiocyanate has now been investigated in order to make the determination of polythionate more sensitive by applying this method to the determination of the thiocyanate formed from the polythionates. The present method for the determination of thiocyanate appears to be more sensitive than any photometric method previously reported.

Experimental

Apparatus. The spectrophotometric measurements were made with a Hitachi Perkin-Elmer Model 139 spectrophotometer with 10.0 mm cells, at a spectral band width of 2 mμ.

The pH measurements were made with a Toa Denpa Model HA-5A pH meter.

The shaking was done with a Tokiwa Model TS shaker.

The organic layer was separated from the aqueous layer with an approximately 50 m*l* separatory funnel fitted with a short leg. The organic layer was then transferred from the separatory funnel into an about 15 m*l* glass tube equipped with a glass stopper.

Materials. All the chemicals used were of an analytical grade and were used without any further purification.

The Standard Thiocyanate Solution. The stock solution of thiocyanate was prepared by dissolving potassium thiocyanate in redistilled water; it was then standardized according to Volhard's method. The working standard solutions were obtained by diluting this stock solution to the concentrations required for the experiments.

The Methylene Blue Solution. The methylene blue solution of a 8.0×10^{-3} M was prepared by dissolving 600 mg. of methylene blue ($C_{16}H_{18}N_3ClS\cdot3H_2O$) in redistilled water, and then diluting it to 200 m*l*. This stock solution was diluted to the concentration required for the individual experiments.

1, 2-*Dichloroethane.* This solvent was used as the extracting agent.

Sulfuric Acid. A 0.4 N sulfuric acid solution was used for making the aqueous solution acid.

Anhydrous Sodium Sulfate. This salt was used as the dehydrating agent for making the organic layer transparent.

Procedure. A sample solution (10.0 m*l*) is placed in a separatory funnel. Then 0.5 m*l* of a 0.4 N sulfuric acid solution, 3.0 m*l* of a 8.0×10^{-4} M methylene blue solution, and 5.0 or 10.0 m*l* of dichloroethane are added. The separatory funnel is shaken by the shaker for about 40 sec; the complex formed between methylene blue and thiocyanate is thereby extracted into the organic layer. When the two layers have settled down, the organic layer is transferred into a glass tube equipped with a glass stopper, and about 0.5 g of the anhydrous sodium sulfate is added; then the mixture is shaken vigorously by hand to make it transparent. The absorbancy of the clear solution is measured at the wavelength of 657 mμ, using dichloroethane as a reference.

Results and Discussion

Calibration Curves. The calibration curves shown in Fig. 1 were obtained by the above procedure with 5.0-m*l* or 10.0-m*l* portions of dichloroethane, using standard thiocyanate solutions of known concentrations. As can be seen in Fig. 1, the absorbancy and the concentration were in a good linear relationship.

It has been observed in the present study that the calibration curve obtained using a 5.0-m*l* portion of dichloroethane is much more sensitive than that obtained using a 10.0-m*l* portion, though the extraction rate by the 5.0-m*l* portion is less than that by the 10.0-m*l* portion, as will be reported below.

Spectral Absorbancy Curves. The spectral absorbancy curves obtaining using dichloroethane as a reference are shown in Fig. 2. They were measured for a dichloroethane solution obtained by extraction both from an aqueous solution which contained thiocyanate and another solution which did not. It was confirmed that both

---

[7] J. M. Kruse and M. G. Mellon, *Anal. Chem.*, **25**, 446 (1953).

[8] W. N. Aldridge, *Analyst*, **69**, 262 (1944).

[9] W. N. Aldridge, *ibid.*, **70**, 474 (1945).

[10] J. Epstein, *Anal. Chem.*, **19**, 272 (1947).

[11] I. Iwasaki, S. Utsumi and T. Koh (C. K.), *Kogyo Yōsui (Industrial Water)*, **37**, 37 (1961).

[12] I. Iwasaki, S. Utsumi and T. Koh (C. K.), This Bulletin, **36**, 325 (1963).

[13] T. Koh, *ibid.*, **38**, 1510 (1965).

[14] T. Koh and I. Iwasaki, *ibid.*, **38**, 2135 (1965).

[15] T. Koh and I. Iwasaki, *ibid.*, **39**, 352 (1966).

[16] T. Koh and I. Iwasaki, *ibid.*, **39**, 703 (1966).

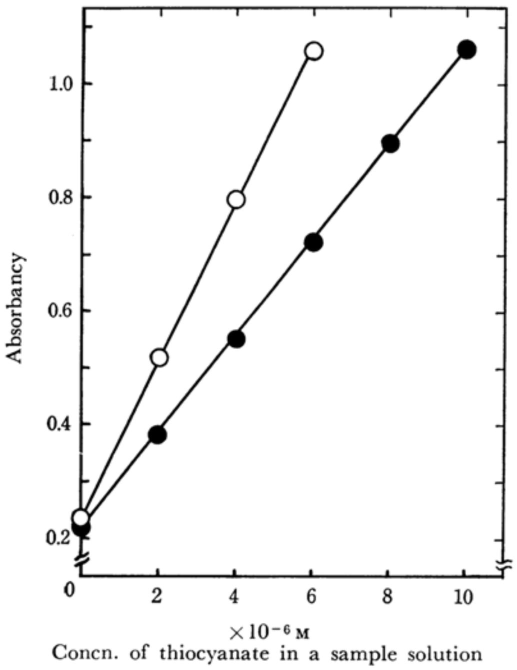

Fig. 1. Calibration curves.
○ 5.0 m*l* of dichloroethane (I)
● 10.0 m*l* of dichloroethane (II)

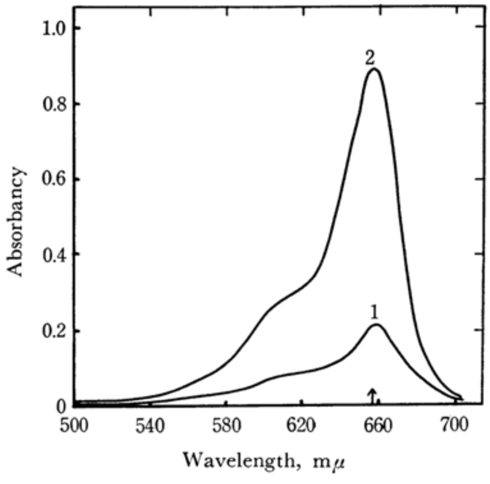

Fig. 2. Spectral absorbancy curves. Extraction was done with 10.0 m*l* of dichloroethane.
Curve 1: Spectrum of dichloroethane phase extracted from an aqueous solution consisting of 10.0 m*l* of redistilled water, 0.5 m*l* of a 0.4 N H_2SO_4 and 3.0 m*l* of a 8.0×10^{-4} M methylene blue solution.
Curve 2: Spectrum of dichloroethane phase extracted from an aqueous solution consisting of 10.0 m*l* of a 8.0×10^{-6} M SCN^-, 0.5 m*l* of a 0.4 N H_2SO_4 and 3.0 m*l* of a 8.0×10^{-4} M methylene blue solution.

curves have a maximum absorbancy at the wavelength of 657 mμ; this peak was used in all subsequent measurements because the difference in the absorbancy between the reagent blank and the methylene blue - thiocyanate complex is the greatest at this wavelength. This maximum did not shift with a change in the acidity or in the kind of acid in either the reagent blank and the complex.

The Stability of the Color. The color intensity of the extract was very stable; no measurable change was found ever after it had stood, for 24 hr at room temperature in diffused light, in a glass tube equipped with a glass stopper for protection against the evaporation of the dichloroethane.

Extraction by Organic Solvents. Many organic solvents, such as 1, 2-dichloroethane, 1, 1-dichloroethane, 1, 1, 1-trichloroethane, 1, 1, 2-trichloroethane, 1, 1, 2, 2 - tetrachloroethane, *n* - butyl alcohol, isoamyl alcohol, ethyl ether, isopropyl ether, butyl acetate, amyl acetate, methylisobutyl ketone, chloroform, carbon tetrachloride, tributyl phosphate, benzene, toluene, nitrobenzene, and chlorobenzene, were tried as the extracting solvent. Of these, 1, 2-dichloroethane, 1, 1, 2-trichloroethane and 1, 1, 2, 2 - tetrachloroethane proved useful. The first one was chosen for the present work because it gives the greatest difference in absorbancy between the reagent blank and the

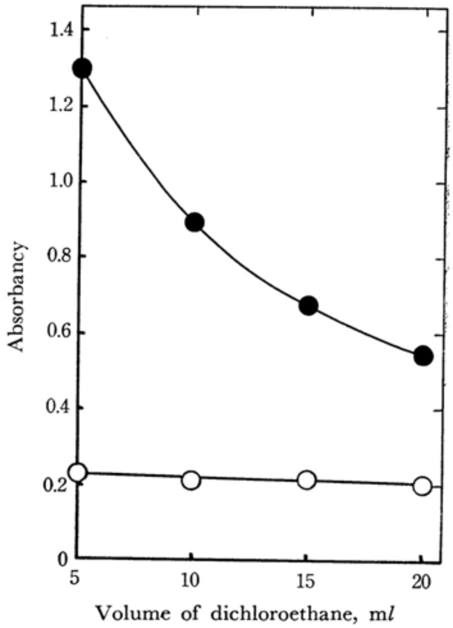

Fig. 3. Effect of the volume of dichloroethane on extraction.
○ Reagent blank extracted from an aqueous solution consisting of 10.0 m*l* of redistilled water, 0.5m*l* of a 0.4 N H_2SO_4, and 3.0 m*l* of a 8.0×10^{-4} M methylene blue solution.
● Complex extracted from an aqueous solution consisting of 10.0 m*l* of a 8.0×10^{-6} M SCN^-, 0.5 m*l* of a 0.4 N H_2SO_4, and 3.0 m*l* of a 8.0×10^{-4} M methylene blue solution.

methylene blue-thiocyanate complex, and, moreover, a lower absorbancy of the reagent blank.

The Effect of the Volume of Dichloroethane on the Extraction. The volume of dichloroethane was found to have a considerable effect on the absorbancy. In measuring this effect on the extraction, from 5.0 m*l* to 20.0 m*l* of dichloroethane was employed. The experimental results are shown in Fig. 3. The absorbancy of the reagent blank remains nearly constant, while that of the complex decreases significantly with an increase in the volume of dichloroethane. Therefore, the extraction in the present study was done with a 5.0 m*l* or a 10.0 m*l* portion of dichloroethane.

The Effect of the Times of Extraction. Two aqueous solutions, one containing a definite amount of thiocyanate and an optimum amount of the reagents, and the other containing only an optimum amount of the reagents, were prepared. The extraction was then carried out with successive 10.0-m*l* portions of dichloroethane. The absorbancy at 657 mμ was measured for the dichloroethane solution obtained by each extraction, using dichloroethane as a reference. Figure 4 shows how the methylene blue and the methylene blue-thiocyanate complex were extracted into a dichloroethane layer from an aqueous solution with 10.0 m*l* of dichloroethane. The reagent blank does not undergo any measurable change in absorbancy as a result of the successive extractions.

The second extract shows a considerable difference in absorbancy between the reagent blank and the complex, but the absorbancy of the third extract for the complex coincides with that for the reagent blank. These facts indicate that two extractions with 10.0-m*l* portions of this solvent have to be carried out in order to extract the complex formed between methylene blue and thiocyanate almost completely from an aqueous solution. However, it is not desirable for two extractions to be made because of the complexity of doing so and the lack of sensitivity as a result of an increase in the total volume of the dichloroethane phase. It was found most practical to use one 5.0-m*l* or one 10.0-m*l* portion of the solvent in the extraction; good reproducibility could be obtained by a single extraction in this study. The extraction rate using 10.0 m*l* of dichloroethane was about 84%, while that using 5.0 m*l* was calculated to be about 64% from both Figs. 3 and 4.

The Effect of the Amount of Methylene Blue. The formation of extractable species may be governed mainly by the concentration of methylene blue. Therefore, the effect of the amount

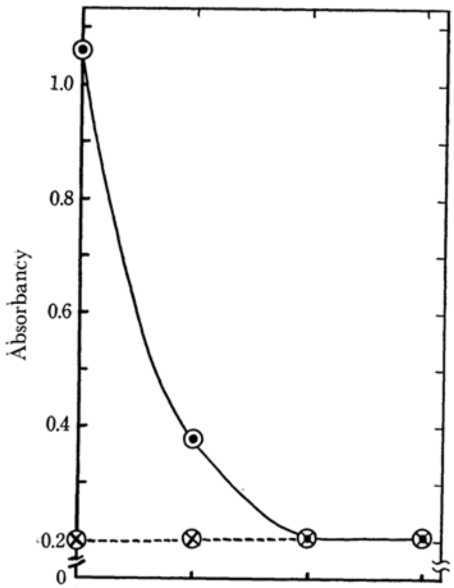

Fig. 4. Effect of the times of extraction.

⊗ Reagent blank obtained by each extraction from an aqueous solution consisting of 10.0 m*l* of redistilled water, 0.5 m*l* of a 0.4 N H_2SO_4, and 3.0 m*l* of a 8.0×10^{-4} M methylene blue solution.

⊙ Complex obtained by each extraction from an aqueous solution consisting of 10.0 m*l* of a 10.0×10^{-6} M SCN^-, 0.5 m*l* of a 0.4 N H_2SO_4, and 3.0 m*l* of a 8.0×10^{-4} M methylene blue solution.

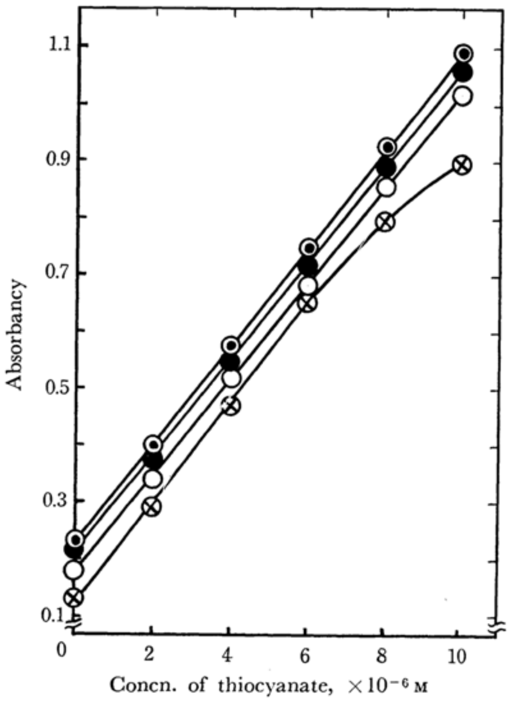

Fig. 5. Effect of the amount of methylene blue. Extraction was done with 10.0 m*l* of dichloroethane.

⊗ 1.0 m*l*	(I)	○ 2.0 m*l*	(II)
● 3.0 m*l*	(III)	⊙ 4.0 m*l*	(IV)

of methylene blue was investigated in order to establish the optimum amount for methylene blue. From 1.0 m*l* to 4.0 m*l* of a 8.0×10^{-4} M methylene blue solution was added to a standard thiocyanate solution containing 0.5 m*l* of a 0.4 N sulfuric acid solution; the extraction was then carried out according to the procedure described above.

The results are shown in Fig. 5, where the calibration curve with 1.0 m*l* does not form a straight line because of insufficient amounts of methylene blue (see I), while the calibration curves with 2.0, 3.0 and 4.0 m*l* do form straight lines, lines which are parallel with one another (see II, III and IV). Consequently, 3.0 m*l* of a 8.0×10^{-4} M methylene blue solution was employed in this work.

The Effect of the Amount of Sulfuric Acid. When the aqueous solution is alkaline, the extracts in dichloroethane become purple, so the procedure should be carried out below a pH value of 7. As will be described below, it was observed that the presence of small amounts of chloride and nitrate has a considerable effect on this method. Therefore, sulfuric acid was used for making the aqueous solution acid.

The calibration curve using 2.0 m*l* of a 0.4 N sulfuric acid solution is less sensitive than that using 0.5 m*l* (see I and II in Fig. 6). In order to clarify these effects, 0.5 m*l* and 2.0 m*l* portions of a 0.4 N sodium sulfate solution were employed in place of the sulfuric acid solution, where the pH of each aqueous solution was 5.8. The differences between one set of two calibration curves (I and III in Fig. 6) and between another set (II and IV in Fig. 6) may be attributed to the pH of the aqueous solution, because the amounts of sulfate ions are equal; only the pH values vary. On the other hand, the difference between the two calibration curves (III and IV in Fig. 6) in which the reagent blank remains constant depends only upon the amount of sulfate ions, because the pH values of the aqueous solution are equal; only the amounts of sulfate ions vary. On the basis of these experimental facts, it has been concluded that both the increase in the concentration of sulfate ions and the decrease in the pH of the aqueous solution cause a less sensitive calibration curve.

The Effect of the Shaking Time on Extraction. The shaking time was varied from 15 to 60 sec, while the other variables were kept constant. These variations in the shaking time showed that a 30 sec shaking was sufficient for the extraction. Thus, the shaking time was fixed at 40 sec in this work.

The Composition of the Methylene Blue-Thiocyanate Complex. By the method of continuous variations,[17-21] we attempted to determine whether or not more than one complex was formed from methylene blue and thiocyanate.

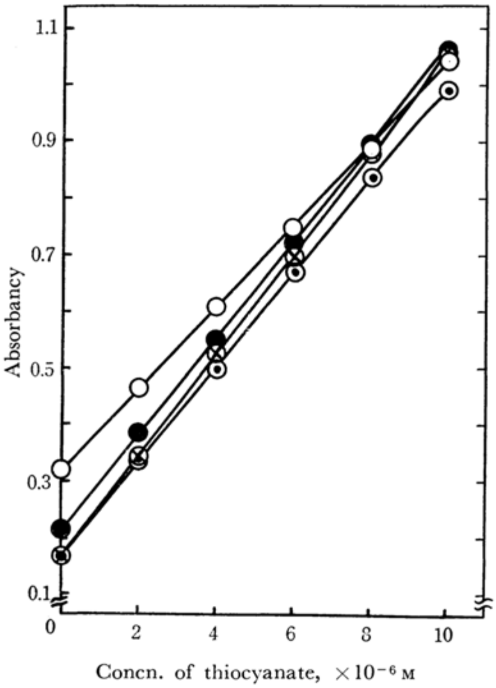

Fig. 6. Effect of the amount of sulfuric acid. Extraction was done from an aqueous solution consisting of 10.0 m*l* of sample solution and a definite amount of sulfuric acid or sodium sulfate solution, with 10.0 m*l* of dichloroethane. Concentration of both sulfuric acid and sodium sulfate solutions is 0.4 N respectively.

● (I) 0.5 m*l* of sulfuric acid solution (pH 2.0)
○ (II) 2.0 m*l* of sulfuric acid solution (pH 1.5)
⊗ (III) 0.5 m*l* of sodium sulfate solution } (pH 5.8)
⊙ (IV) 2.0 m*l* of sodium sulfate solution }

Methtylene blue and thiocyanate solutions, both at a concentration of 4.0×10^{-5} M, were prepared; $10X$ m*l* of a methylene blue solution was mixed with $10(1-X)$ m*l* of a thiocyanate solution containing 0.5 m*l* of a 0.4 N sulfuric aicd in the proportions of 1 : 1, 1 : 3 and 9 : 1, then the extraction was done as in the procedure described above. The absorption spectra of the resulting extracts were measured to be as shown in Fig. 7. The curves are of the same shape and do not cross. A series of mixtures was, therefore, measured at three arbitrarily-selected wavelengths. The resulting curves, in which the reagent blank was subtracted, are shown in Fig. 8. At all three

---

[17] Y. Shibata, T. Inoue and Y. Nakatsuka, *Nippon Kagaku Kaishi (J, Chem. Soc. Japan)*, **42**, 983 (1921).

[18] P. Job, *Ann. Chim.*, [10] **9**, 113 (1928).

[19] W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

[20] R. K. Gould and W. C. Vosburgh, *ibid.*, **64**, 1630 (1942).

[21] R. T. Foley and R. C. Anderson, *ibid.*, **70**, 1195 (1948).

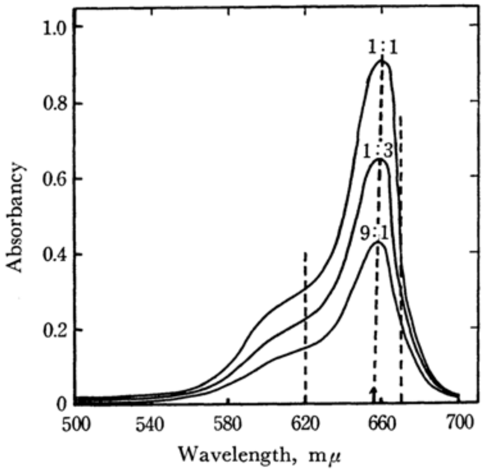

Fig. 7. Absorption spectra of dichloroethane phase extracted from aqueous solutions containing methylene blue and thiocyanate in the ratios, 1 : 1, 1 : 3, and 9 : 1.

Extraction was done with 10.0 m*l* of dichloroethane. Dotted lines represent arbitrarily selected wavelengths.

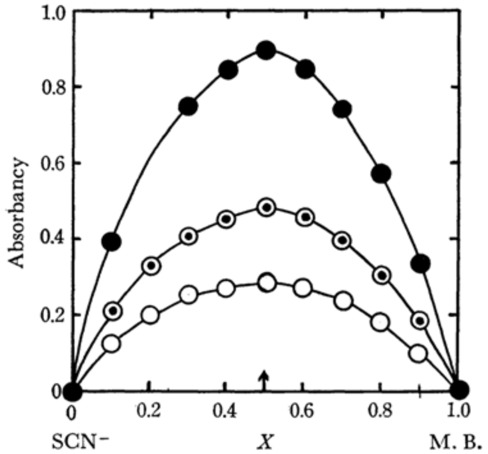

Fig. 8. Method of continuous variations.

Extraction was done from the aqueous solutions consisting of $10X$ ml of a 4.0×10^{-5} M methylene blue solution, $10(1-X)$ ml of a 4.0×10^{-5} M thiocyanate solution and 0.5 ml of a 0.4 N sulfuric acid solution, with 10.0 ml of dichloroethane.

○ 620 mμ ● 657 mμ ⊙ 670 mμ

wavelengths the maximum comes at $X=0.5$, at which point equal volumes of the equimolar solutions of methylene blue and thiocyanate have been mixed; this indicates that the only chemical species extracted into dichloroethane from an aqueous solution is a complex formed in a 1 : 1 ratio from methylene blue and thiocyanate.

The Effect of Diverse Ions. The effect of a series of anions on the extraction with dichloroethane was also studied. The extraction was done with 10.0 m*l* portions of dichloroethane on aqueous solutions containing various amounts of diverse anions, both with 4.0×10^{-6} M (0.23 ppm) of thiocyanate and without it. The results are given in Table 1.

TABLE 1. EFFECT OF DIVERSE ANIONS

Anion	Added as	Concn. ppm	Absorbancy	
			Reagent blank	0.23 ppm SCN^-
None		0	0.220	0.556
F^-	NaF	100	0.242	0.575
Cl^-	NaCl	10	0.268	0.582
Br^-	KBr	1	0.276	0.588
I^-	KI	0.1	0.268	0.618
ClO_3^-	$KClO_3$	1	0.490	0.775
BrO_3^-	$KBrO_3$	1	0.242	0.536
IO_3^-	KIO_3	10	0.381	0.443
		100	0.243	0.592
		1000	0.219	0.509
ClO_4^-	$KClO_4$	0.1	0.309	0.682
IO_4^-	$NaIO_4$	1	0.280	0.572
NO_2^-	$NaNO_2$	1	0.228	0.575
NO_3^-	KNO_3	1	0.490	0.770
$S_2O_3^{2-}$	$Na_2S_2O_3\cdot5H_2O$	1	0.366	0.623
SO_4^{2-}	K_2SO_4	1000	0.219	0.547
CN^-	KCN	10	0.216	0.562
		100	0.269	0.633
$H_2PO_4^-$	$NaH_2PO_4\cdot H_2O$	100	0.232	0.580

It is of great interest that the halide, when listed in the order of increasing interference with this method, are chloride, bromide and iodide, while the oxyacid and the peracid of the halogens are listed, on the contrary, as iodate, bromate and chlorate, and periodate and perchlorate. As to iodate and bromate, the difference in absorbancy between the reagent blank and the methylene blue - thiocyanate complex decreases with a further increase in their amount. Fluoride, iodate, cyanide, and phosphate interfere with the determination of thiocyanate when present in molar quantities more than 100 times that of thiocyanate, while iodide and perchlorate, when present in amounts corresponding to that of thiocyanate, interfere remarkably with this method.

Summary

A new spectrophotometric method for the determination of an ultramicro amount of thiocyanate has been proposed. It is based on the extraction of the complex formed between methylene blue and thiocyanate with dichloroethane and on the measurement of the absorbancy

of the organic phase. In order to establish the optimum conditions for the determination of thiocyanate, various factors, the amounts of the solvent and the reagents, the times of extraction, the shaking time, and the presence of diverse anions, were studied. The only chemical species extracted into dichloroethane proved to be a complex formed in a 1 : 1 ratio from methylene blue and thiocyanate; Beer's law was applicable in the range from 2.0×10^{-7} to 1.0×10^{-5} M of thiocyanate.