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Spectrophotometric Determination of Cyanide Ion with Mercury(II)-Methylthymolblue Complex

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Cyanide ion reacted with mercury(II)-methylthymolblue (Hg-MTB) complex to form a mixed ligand complex. Since the resulting mixed ligand complex had a considerable absorption at 615 mμ, the spectrophotometric determination of cyanide ion was performed by measuring the increase in absorption of mercury(II)-methylthymolblue complex caused by formation of this mixed ligand complex. After excess MTB methanol and mercury(II) nitrate solutions were added to a cyanide sample solution which was adjusted to a definite pH value between pH 7.3 and 7.6 with phosphate buffer solution, it was diluted to exactly 50 m*l* with water. After standing for about 25 min, the absorbance of this solution was measured at 615 mμ against the reagent blank solution. Beer's law was obeyed in the concentration range of cyanide ion from 5 to 80 μg per 50 m*l*, and the molar extinction coefficient was found to be about 5100. Taking 55.0 μg of cyanide ion, the standard deviation and variation coefficient of absorbances in the mean value of 10 runs were 0.0019 and 0.90%, respectively. The molar ratio of cyanide ion to Hg-MTB in the mixed ligand complex was found to be 1 : 1.

Mercury(II) reacts with organic reagents having two diacetic amino groups to form mercury(II) complexes which further react with anions such as SCN^-, CN^-, I^- and Br^-, *etc.*, to form mixed ligand complexes. Nomura *et al.*, reported that ethylenediaminetetraacetate (EDTA),[1] cyclohexanediaminetetraacetate (CyDTA),[2] and cresolphthalein complexone (PC),[3] *etc.*, have the above property among organic reagents. Also, Hashitani[4] reported that alizarin complexone reacts with cerium or lanthanum to form a complex which reacts with fluoride ion to form the same mixed ligand complex.

Methylthymolblue (MTB), having two diacetic amino groups, reacts with mercury(II) to form a mercury(II)-methylthymolblue complex (Hg-MTB or $HgMe^{4-}$),[5] having a considerable absorption at 620 mμ, and the molar ratio of MTB to mercury(II) in this complex is 1 : 1. It was found that cyanide ion also reacted similarly with Hg-MTB to form a mixed ligand complex as thiocyanate ion.[6] Therefore, making use of this fact, the author has developed a rapid method for spectrophotometrically determinating small amounts of cyanide ion by measuring the absorbance of this cyano mixed ligand complex.

Experimental

Reagents. All analytical grade reagents were used without further purification.

Standard Cyanide Solution. The exact concentration of the stock solution of cyanide ion, prepared by dissolving potassium cyanide in water, was obtained through indirect chelatometric titration with $[HgY(CN)]^{3-}$[7] before use. The working standard solutions were prepared by diluting this stock solution to the concentrations required for experiment.

Methylthymolblue (MTB) Methanol Solution. The MTB methanol solution of 1×10^{-3} M was prepared by dissolving 390 mg of Dotite MTB in a small amount of water, followed by the addition 250 m*l* of methanol, and dilution to exactly 500 m*l* with water. This solution, stored in a brown glass bottle, was stable at least for about three months.

Mercury(II) Solution. The stock solution mercury(II) was prepared by dissolving mercury(II) nitrate in a small amount of concentrated nitric acid and water, and diluting to exactly 1 *l* with water. The exact concentration of this solution was obtained through titration with 0.01 M standard EDTA solution using Cu-PAN as indicator. The working solution of 1×10^{-3} M (F=0.983) was prepared by dilution with water.

Buffer Solution. Buffer solutions having a definite pH were prepared by properly mixing 0.2 M potassium dihydrogen phosphate and 0.2 M disodium hydrogen phosphate solutions.

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[1] S. Komatsu and T. Nomura, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 841 (1966); **87**, 845 (1966); **88**, 63 (1967).

[2] T. Nomura, *ibid.*, **88**, 199 (1967).

[3] T. Nomura, *ibid.*, **88**, 635 (1967).

[4] H. Hashitani, *Dotite News Letter*, **13**, 3 (1965).

[5] N. Iritani and T. Miyahara, *Bunseki Kagaku (Japan Analyst)*, **12**, 1183 (1963).

[6] T. Nomura, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **88**, 961 (1967).

[7] S. Komatsu and T. Nomura, *ibid.*, **87**, 1060 (1966).

Apparatus. Spectrophotometric measurements were made with a Hitachi Perkin Elmer 139 type spectrophotometer with 10.0 mm glass cells. The pH measurements were made with a Hitachi-Horiba 4 type pH meter.

Procedure. The sample solution containing from 5 to 80 μg of cyanide ion was adjusted to a definite pH value between pH 7.3 and 7.6 with 10 m*l* of buffer solution, to each of which 5 m*l* of 1×10^{-3} M MTB methanol solution and aqueous mercury(II) solution were added and the total volume adjusted to 50 m*l* with water. After standing for about 25 min, the absorbance of this solution was measured at 615 mμ against a reagent blank solution which was prepared similarly without the addition of cyanide solution.

Results and Discussion

Absorption Spectra of Hg-MTB and Cyano Mixed Ligand Complex. Spectra are shown in Fig. 1. The maximum absorbances of Hg-MTB were found at 420 mμ and 610 mμ, respectively. However, the absorbance decreased at 420 mμ and increased at 610 mμ when cyanide ion was added to this complex solution. Then, the measurement of increase in the absorbance at 610 mμ caused by the formation of a cyano mixed ligand complex could be made to determine cyanide ion. The wavelength of 615 mμ, at which the cyanide mixed ligand complex had a maximum absorbance, was used practically in all subsequent measurements, because the difference in absorbance between Hg-MTB and the mixed ligand complex was greater at 615 mμ than at 610 mμ, as shown in Fig. 1.

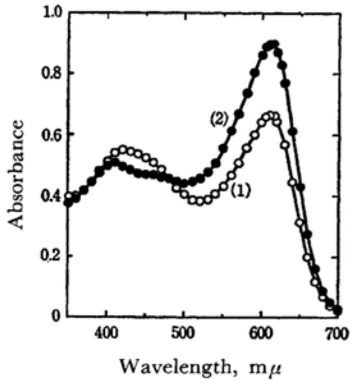

Fig. 1. Absorption spectra of Hg-MTB and cyano mixed ligand complex.
(1) Hg-MTB complex containing each 5 m*l* of 1×10^{-3} M MTB methanol and mercury(II) solutions at pH 7.4.
(2) Cyano mixed ligand complex containing above solutions and 66.0 μg of cyanide ion at pH 7.4.

Effect of pH. This complex was stable between pH 7.3 and 7.6, as shown in Fig. 2. Since the absorbance of Hg-MTB increased with pH,[6] the pH in a practical procedure should be adjusted to a definite value between pH 7.3 and 7.6.

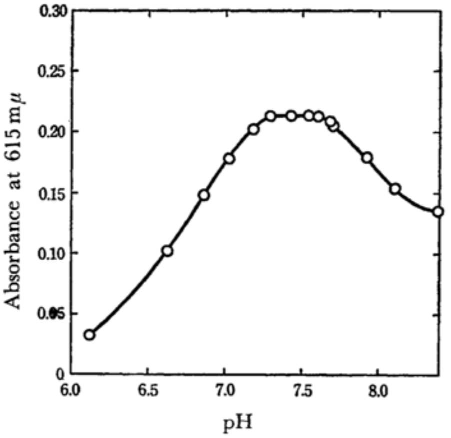

Fig. 2. Effect of pH.
The every absorbances of the mixed solution containing each 5 m*l* of 1×10^{-3} M$\cdot$MTB methanol and mercury(II) solutions and 55.0 μg of cyanide ion were measured against a reagent blank solution after adjusting to the pH needed with phosphate buffer solution.

Effect of Standing Times. The time required for the complete formation of this mixed ligand complex (blue color) was about 20 min, and the color of this complex showed no change for at least three hours. The procedure for color development was carried out at room temperatures.

Molar Ratio of Hg-MTB to Cyanide Ion. The results are shown in Fig. 3. When Hg-MTB reacted with cyanide ion to form the mixed ligand complex, the molar ratio of Hg-MTB to cyanide ion was found to be 1 : 1. But, above the equivalent point, the mixed ligand complex reacted subsequently with cyanide ion in the same way as the cyano mixed liquid complex $[HgY(CN)]^{3-}$

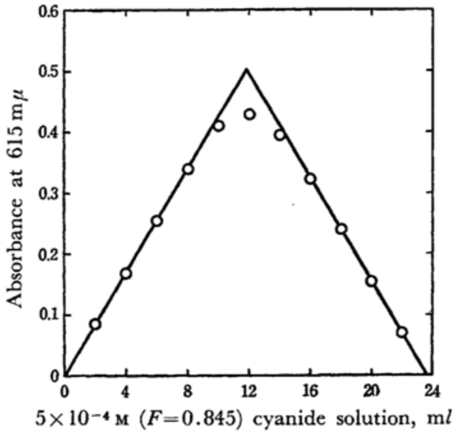

Fig. 3. Molar ratio of Hg-MTB to cyanide ion.
The every absorbances of the mixed solution containing each 5 m*l* of 1×10^{-3} M$\cdot$MTB methanol and mercury(II) solutions were measured against a reagent blank solution after adding cyanide solution at pH 7.5.

(abbreviated Hg-EDTA as HgY^{2-}) reacted with cyanide ion to form mercury(II) cyanide and EDTA.7)

$$[HgMe(CN)]^{5-} + CN^- + 2H^+ \rightarrow Hg(CN)_2 + H_2Me^{4-}$$

Hence, the absorbances of this mixed ligand complex solution decreased when an excess amount of cyanide ion (compared with Hg-MTB, in molar ratio) was added. The absorbances of the solutions which were prepared by the addition of different amounts of cyanide sample solution should be measured in order to avoid erroneous measurements, which may be made above the equivalent point.

Calibration Curve. The relationship between cyanide ion content and the absorbance was linear from 5 μg up to 80 μg cyanide ion content per 50 m*l*, as shown in Fig. 4. The molar extinction coefficient was found to be about 5100. Taking 55.0 μg of cyanide ion, the standard deviation and variation coefficient for the mean absorbances of 10 analyses were 0.0019 and 0.90%, respectively.

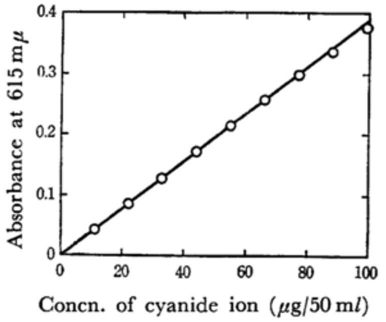

Fig. 4. Calibration curve for cyanide ions. pH 7.4

Effect of Diverse Ions. Results are given in Table 1. Taking 55.0 μg of cyanide ion, the absorbances were measured according to the above procedure in the co-existence of a number of various foreign ions. Measurements that differed from the expected absorbance by more than ±2% were taken as criterion for interference.

Anions such as SCN^-, S^{2-}, I^- and Br^- interfered in this method, because S^{2-} reacted with mercury(II) to form mercuric sulfide, and SCN^-, I^- and Br^- reacted with Hg-MTB to form mixed ligand complexes, as did cyanide ion. Cations, such as Mn^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Bi^{3+}, Ni^{2+} and NH_4^+, interfered since these cations, except NH_4^+, reacted with MTB to form metal-MTB complexes. These interfering ions should be separated or masked properly for the determination of cyanide ion. A method of separation has been reported by Okutani *et al.*8)

TABLE 1. EFFECT OF DIVERSE IONS

Ion	Added as	Tolerance limit	
SCN^-	KSCN	1.2 μg	+
Br^-	KBr	2.5 μg	+
I^-	KI	3.5 μg	+
S^{2-}	$Na_2S \cdot 9H_2O$	10 μg	−
Cl^-	NaCl	20 μg	+
F^-	NaF	>10 mg	
NO_3^-	KNO_3	>10 mg	
SO_4^{2-}	K_2SO_4	>10 mg	
ClO_4^-	$NaClO_4$	>10 mg	
Ni^{2+}	$NiSO_4 \cdot 7H_2O$	1.0 μg	+
Co^{2+}	$CoSO_4 \cdot 7H_2O$	1.2 μg	+
Mn^{2+}	$MnSO_4$	4 μg	+
NH_4^+	$(NH_4)_2SO_4$	4 μg	+
Bi^{3+}	$Bi(NO_3)_3$	5 μg	−
Cd^{2+}	$CdSO_4$	6 μg	+
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	9 μg	−
Pb^{2+}	$Pb(NO_3)_2$	18 μg	−
Fe^{3+}	$Fe(NO_3)_3 \cdot 9H_2O$	50 μg	−
Al^{3+}	$Al_2(SO_4)_3$	50 μg	−
Ag^+	$AgNO_3$	50 μg	+
Mg^{2+}	$MgSO_4$	120 μg	+
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	120 μg	+
Ca^{2+}	$Ca(NO_3)_2$	350 μg	+
Hg^{2+}	$Hg(NO_3)_2$	350 μg	+
Th^{4+}	$Th(NO_3)_4$	900 μg	−
Sr^{2+}	$Sr(NO_3)_2$	>2 mg	
Ba^{2+}	$Ba(NO_3)_2$	>2 mg	

(+): positive error (−): negative error

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8) T. Okutani and S. Utsumi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 444 (1966).