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Volumetric Determinations of Cyanide, Thiocyanate, and Iodide Ions with Mercury(II) Ethylenediaminetetraacetate Using These Mixed-ligand Complexes as Indicators

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Mercury(II) complexes of EDTA, methylthymolblue, or cresolphthaleincomplexone form mixed-ligand complexes with cyanide, thiocyanate, or iodide ions. These anions can be determined with mercury(II) ethylenediaminetetraacetate, using the other mercury(II) complexes as indicators, because of the difference between the stability constant of the mixed-ligand complex of EDTA and that of the other complexes. The previously reported methods, however, require a calibration curve. The determination was simplified by Titer methods, using these mixed-ligand complexes as indicators. To the anion-sample solutions adjusted to a given pH value with a buffer solution, 5 m*l* portions of 1×10^{-4}M mercury(II), an organic reagent, and anion solutions were added, these mixtures were then titrated with a 1×10^{-2}M standard mercury(II) ethylenediaminetetraacetate solution. These solutions change in color from pale pink (PC) or yellow (MTB) to red-violet (PC) or blue (MTB) by the end point. The Titer values were determined by the use known of standard anion solutions.

Mercury(II) reacts with ethylenediaminetetraacetate (EDTA) to form mercury(II) ethylenediaminetetraacetate (Hg-EDTA). This colorless complex was found to react with cyanide, thiocyanate, iodide, bromide, *etc.* to form colorless mixed-ligand complexes.1) The cyano complex among these mixed-ligand complexes reacts with an

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1) S. Komatsu and T. Nomura, *Nippon Kagaku Zasshi*, **87**, 841 (1966); **87**, 845 (1966); **88**, 63 (1967).

excess cyanide to form mercury(II) cyanide and EDTA.[2]

Cresolphthaleincomplexone (PC, pale pink) reacts with mercury(II) to form mercury(II)-cresolphthaleincomplexone (Hg-PC),[3] which is red-violet in color and which reacts with cyanide[4] or iodide. The solutions containing the mixed-ligand complex produced with Hg-PC and cyanide or iodide ions are pale pink.

Mercury(II)-methylthymolblue (Hg-MTB, yellow or yellowish green)[5] reacts with cyanide, thiocyanate,[6] iodide, bromide, or chloride[7] to form these mixed-ligand complexes, which are blue in color. The cyano or iodo mixed-ligand complexes among these complexes react with excess cyanide or iodide to form mercury(II) cyanide or iodide and MTB.

Some of these mixed-ligand complexes have low stability constants, and dissociate to mercury(II) anion complexes and organic reagents in the presence of an excess amount of anions. Therefore, the volumetric determination of anions can be achieved with a standard Hg-EDTA solution using the mercury(II)-organic reagent complex as indicator,[8-10] in just the same fashion as in the volumetric determination of metal ions with EDTA using metal indicators.[11] In these methods, the required volume (equivalent weight) of the standard Hg-EDTA solution is not equal to the equivalent weight of anions in the sample solution, because the color change of the solution at the end point is caused by the appearance of the color of the mixed-ligand complex of the mercury(II)-organic reagent-anion, *i. e.*, the required volume of the standard Hg-EDTA solution corresponds to the equivalent weight of anions minus the equivalent weight of the mixed-ligand complex formed in the sample solution. Therefore, the usual Titer method, in which the anions are determined by multiplying the required volume of the standard solution by the weight of anions necessary to titrate one m*l* of the standard Hg-EDTA solution, can not be applied to this procedure; the calibration curves are necessary for the determination. However, if one uses a mixed-ligand complex as an indicator, the Titer method can be used for the determination of these anions. This paper will describe this method, in which the anions can be determined with a good reproducibility. The proposed methods are especially suitable for anion concentrations of the order of 0.01 M and are satisfactorily simple and reproducible. The interfering anions will also be discussed.

Experimental

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

1×10^{-4} M Cresolphthaleincomplexone (PC) Solution. The stock solution of 1×10^{-3} M was prepared by dissolving 320 mg of Dotite PC and by then diluting to 500 m*l* with methyl alcohol. This solution was stored in a brown glass bottle. The working solution of 1×10^{-4} M was prepared by dilution with water.

1×10^{-4} M Methylthymolblue (MTB) and 1×10^{-2} M Standard Thiocyanate-ion Solution. These solutions were prepared as in a preceding experiment.[9]

1×10^{-2} M Standard Cyanide-ion Solution. This solution was prepared as in a preceding experiment.[8]

1×10^{-2} M Standard Iodide-ion and Standard Hg-EDTA Solutions. These solutions were prepared as in a preceding experiment.[10]

1×10^{-4} M Hg-SCN, Hg-CN, and Hg-I Solutions. These solutions were prepared by the addition of 10 m*l* portions of mercury(II) nitrate and the corresponding standard anion solutions of 1×10^{-2} M and by subsequent dilution to 1 *l* with water.

Buffer Solutions. Buffer solutions having a given pH value were prepared by properly mixing the following solutions; $pH<8$, 0.1 M potassium dihydrogen phosphate and 0.1 M disodium hydrogen phosphate solutions; between pH 8 and 9, 0.1 M potassium dihydrogen phosphate and 0.05 M borax solutions; $pH>9$, 0.1 M sodium carbonate and 0.1 M sodium hydrogen carbonate solutions or 0.1 M disodium hydrogen phosphate and 0.1 M sodium hydroxide solutions.

Apparatus. The titrations of anion solutions were carried out with a 1/20 graduated microburette. A Hitachi-Horiba M-4-type pH meter was used for the measurement of the pH values.

Procedure. The pH values of the anion sample solutions were adjusted to an appropriate value with a buffer solution, to which 5 m*l* portions of organic-reagent (MTB for SCN^- or I^-, PC for CN^- or I^-) and Hg-X ($X=\text{anion}=SCN^-$, CN^- or I^-) solutions of 1×10^{-4} M were added. Then the solutions were diluted to about 50 m*l* with water. The solutions were titrated with a standard 1×10^{-2} M Hg-EDTA solution until the solutions changed in color from yellow or a greenish-yellow (MTB) or pale pink (PC) to blue (MTB) or red-violet (PC) with respect to the blank solution, which had been prepared by the same procedure as has been described above, except for the addition of the anion sample solution. The amount of the anion in the sample solution was calculated by multipling the required vol-

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

[3] S. Komatsu and T. Nomura, *ibid.*, **88**, 542 (1967).

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

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

[6] T. Nomura, This Bulletin, **41**, 1619 (1968); *Nippon Kagaku Zasshi*, **88**, 961 (1967).

[7] T. Nomura and S. Komatsu, *ibid.*, **90**, 168 (1969).

[8] T. Nomura, K. Takeuchi and S. Komatsu, *ibid.*, **89**, 291 (1968).

[9] T. Nomura and S. Komatsu, *Bunseki Kagaku*, **17**, 1406 (1968).

[10] T. Nomura, This Bulletin, **42**, 952 (1969).

[11] K. Ueno, "Kireito Tekiteiho," Nankodo, Tokyo (1960).

ume of the standard Hg-EDTA solution (*titer*) by the Titer which was determined on a solution with a known concentration.

Results and Discussion

Determination of the Thiocyanate Ion Using the Hg-MTB-SCN Complex as an Indicator. In the volumetric determination of the thiocyanate ion using the Hg-MTB complex as an indicator,[9] the optimum pH range being 6.3—6.8. A sample solution containing up to 11.0 mg of thiocyanate ion was titrated by the standard procedure at pH 6.7 in the presence of MTB and Hg-SCN. The color change by the end point was from yellow to blue. The Titer was calculated from the volume of the standard Hg-EDTA solution required to titrate 2.745 mg of the thiocyanate ion:

$$1\ \mathrm{m}l \text{ of a } 1\times10^{-2}\mathrm{M} \text{ standard Hg-EDTA solution} = 0.5434 \text{ mg of SCN}^- \qquad (1)$$

The results are shown in Table 1. The *titer* value was an average of two titrations. In the determination of a small amount of the thiocyanate ion, the relative error was large, while in the determination of a larger amount of the thiocyanate ion (above 11 mg), the color change at the end point became indistinct, resulting in an even greater error.

TABLE 1. DETERMINATION OF THE THIOCYANATE ION BY MEANS OF THE TITER METHOD

Taken (mg)	*Titer* (m*l*)	Found (mg)	Error (mg)	Error (%)
0.137	0.25	0.136	−0.001	0.73
0.274	0.50	0.272	−0.002	0.73
0.549	1.02	0.554	+0.005	0.91
1.098	2.02	1.098	0	0
2.745	5.05	2.744	−0.001	0.04
5.489	10.08	5.477	−0.012	0.22
8.234	15.10	8.205	−0.029	0.35
10.98	20.12	10.93	−0.05	0.41

1 m*l* of a 1×10^{-2}M standard Hg-EDTA solution = 0.5434 mg of SCN^-

In the previous method,[9] the end point was determined visually by the color change from yellow to blue, without any standard color reference, so there was a relatively large error. In addition to this, a preliminary test for the existence of an excess of the thiocyanate ion was necessary. In the present method, however, the color at the end point is compared with that of the reference blank solution. Therefore, the individual error is smaller than that in the previous method. In addition to this advantage, no preliminary test is necessary. When the thiocyanate ion is not present in the sample, the color of the solution before the titration is blue, while when the thiocyanate ion is present, the color is yellow, as is shown in Eq. (2):

$$\underset{\text{blue}}{\text{Hg-MTB-SCN}} + \mathrm{SCN}^- \rightleftharpoons \mathrm{Hg(SCN)_2} + \underset{\text{yellow}}{\text{MTB}} \qquad (2)$$

The blue color at the end point, however, gradually changes to green upon the addition of an excess of the Hg-EDTA solution because the Hg-EDTA-SCN complex is more stable than the Hg-MTB-SCN complex. That is, at the end point:

$$\mathrm{Hg(SCN)_2} + \text{MTB} + \text{Hg-EDTA} \rightleftharpoons \text{Hg-EDTA-SCN} + \underset{\text{blue}}{\text{Hg-MTB-SCN}} \qquad (3)$$

and after the addition of an excess amount of the standard solution:

$$\text{Hg-MTB-SCN} + \text{Hg-EDTA} \rightleftharpoons \text{Hg-EDTA-SCN} + \underset{\text{green}}{\text{Hg-MTB}} \qquad (4)$$

However, this color change does not disturb the end-point determination.

Determination of the Iodide Ion Using the Hg-MTB-I Complex as an Indicator. The method used here was virtually identical with that described in a previous paper,[10] but here the Hg-MTB-I complex was used as an indicator.

A sample solution containing up to 31 mg of the iodide ion was titrated at pH 7.5 in the presence of MTB and Hg-I. The color change at the end point was form greenish yellow to blue. The Titer was calculated from the volume of the standard Hg-EDTA solution required to titrate 6.225 mg of the iodide ion:

$$1\ \mathrm{m}l \text{ of a } 1\times10^{-2}\mathrm{M} \text{ standard Hg-EDTA solution} = 1.186 \text{ mg of I}^- \qquad (5)$$

The results are shown in Table 2. The *titer* value was an average of two titrations. This method had the same advantages as in the case of the determination of thiocyanate described above.

The blue color appearing after the end point did not change upon the addition of the *titer*, for the stability of Hg-MTB-I is greater than that of Hg-EDTA-I. When an excess of iodide existed in the solution, the color was greenish yellow, as is shown in Eq. (6):

$$\text{Hg-MTB-I} + 2\mathrm{I}^- + \text{Hg-EDTA} \rightleftharpoons \text{Hg-EDTA-I} + \mathrm{HgI_2} + \underset{\text{greenish yellow}}{\text{MTB}} \qquad (6)$$

Hg-MTB-I dissociated to mercury(II) iodide and MTB with an excess of iodide, but Hg-EDTA-I did not.

Interfering anions, such as sulfide, cyanide, and thiocyanate,[10] could be removed the hydrogen peroxide method, which will be described in the section concerned with the determination of iodide.

Table 2. Determination of the iodide ion by means of the Titer method

Taken (mg)	*Titer* (m*l*)	Found (mg)	Error (mg)	Error (%)
0.311	0.26	0.308	−0.003	0.96
0.623	0.52	0.617	−0.006	0.96
1.245	1.04	1.233	−0.012	0.96
2.490	2.10	2.491	+0.001	0.04
6.225	5.25	6.227	+0.002	0.03
12.45	10.52	12.48	+0.03	0.24
18.68	15.77	18.70	+0.02	0.11
24.90	21.13	25.06	+0.16	0.64
31.13	26.31	31.20	+0.07	0.22

1 m*l* of a 1×10^{-2}M standard Hg-EDTA solution
= 1.186 mg of I$^-$

Bromide could not, however, be removed by this method.

Determination of Cyanide Using the Hg-PC-CN Complex as an Indicator. The method used here was virtually identical with that described in a previous paper,[8] but the Hg-PC-I complex was used as an indicator.

A cyanide-sample solution (up to 6.2 mg) was titrated at pH 11.2 in the presence of PC and Hg-CN. The color change at the end point was from a pale pink to red-violet. The Titer was calculated from the volume of the standard Hg-EDTA solution required for 1.241 mg of cyanide. The results are shown in Table 3.

$$1\ \mathrm{m}l \text{ of a } 1\times10^{-2}\mathrm{M} \text{ standard Hg-EDTA solution} = 0.2434 \text{ mg of } \mathrm{CN}^- \tag{7}$$

Table 3. Determination of the cyanide ion by means of the Titer method

Taken (mg)	*Titer* (m*l*)	Found (mg)	Error (mg)	Error (%)
0.062	0.25	0.061	−0.001	1.61
0.124	0.50	0.122	−0.002	1.61
0.248	1.02	0.248	0	0
0.496	2.05	0.499	+0.003	0.60
1.241	5.10	1.241	0	0
2.482	10.22	2.488	+0.006	0.24
3.723	15.30	3.724	+0.001	0.03
4.964	20.36	4.956	−0.008	0.16
6.205	25.40	6.182	−0.023	0.37

1 m*l* of a 1×10^{-2}M standard Hg-EDTA solution
= 0.2434 mg of CN$^-$

Determination of Iodide Using the Hg-PC-I Complex as an Indicator. Iodide could also be determined using the Hg-PC-I complex as an indicator.

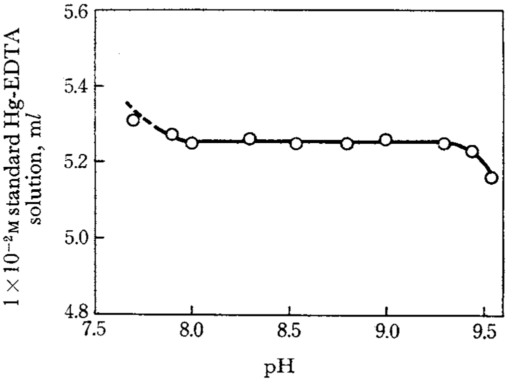

Fig. 1. Effect of pH.
Each 5 m*l* of PC and Hg-I solutions of 1×10^{-4}M, 6.225 mg of iodide ion.

Hg-PC-I Complex. The iodide ion reacts with Hg-PC (red-violet) to form a mixed-ligand complex. The color of this complex was a pale pink. The molar ratio of Hg-PC to iodide in the mixed-ligand complex was found to be 1 : 1 by the molar ratio method and by the continuous variation method. The mixed-ligand complex does not dissociate to mercury(II) iodide and PC in the presence of the excess iodide.

Effect of pH. The effect of the pH on the titration of iodide was investigated by the same method as in the case of cyanide. The sample solution containing 6.225 mg of iodide was adjusted to an appropriate pH value with a buffer solution, to which 5 m*l* portions of PC and 1×10^{-4}M Hg-I solutions were added. The results are shown in Fig. 1.

At pH values below 7.9 it was difficult to distinguish the end point. At pH values above 9.5, however, the solution gradually changed from a pale pink to violet at the beginning of the end point. Between pH 8.0 and 9.3, the color of the solution at the end point changed from pink to red-violet.

Table 4. Determination of the iodide ion by means of the Titer method

Taken (mg)	*Titer* (m*l*)	Found (mg)	Error (mg)	Error (%)
0.311	0.27	0.320	+0.009	2.89
0.623	0.53	0.629	+0.006	0.96
1.245	1.04	1.233	−0.012	0.96
2.490	2.10	2.491	+0.001	0.04
6.225	5.25	6.227	+0.002	0.03
12.45	10.48	12.43	−0.02	0.16
18.68	15.69	18.61	−0.07	0.37
24.90	21.01	24.92	+0.02	0.08
31.13	26.25	31.13	0	0

1 m*l* of a 1×10^{-2}M standard Hg-EDTA solution
= 1.186 mg of I$^-$

Titer Method. Iodide was determined by titration at pH values between 8.0 and 9.3 in the presence of PC and Hg-I. The color change at the end point was from a pale pink to red-violet. The Titer was calculated from the volume of the standard Hg-EDTA solution required for 6.225 mg of iodide.

1m*l* of a 1×10^{-2}M standard Hg-EDTA solution

$$= 1.186 \text{ mg of } I^- \qquad (8)$$

The results are shown in Table 4.

Diverse Ions. In this method, various cations interfered, as in the case reported in a previous paper.[10] Some anions, such as sulfide, cyanide, and thiosulfate, interfered in minute amounts. Bromide, chloride, fluoride, thiocyanate, sulfate, nitrate, and perchlorate, however, did not interfere at all. The interfering anions could be removed by the following procedure.

TABLE 5. REMOVAL OF INTERFERING ANIONS

Iodide ion taken in (mg)	Interfering anions added			Iodide ion found (mg)
	S^{2-} (mg)	CN^- (mg)	$S_2O_3^{2-}$ (mg)	
2.490	—	—	—	2.491
2.490	0.32	0.52	0.56	2.467
6.225	—	—	—	6.227
6.225	0.32	0.52	0.56	6.215

To an iodide-ion sample solution (pH 8.0—9.3), 2 m*l* of 3% hydrogen peroxide were added. This solution was then boiled until large bubbles appeared, it was then cooled to room temperature, and 5 m*l* portions of PC and Hg-I soultion of 1×10^{-4}M were added, and the solution was treated in the usual way.

Some representative results of this method are shown in Table 5. Excess hydrogen peroxide did not interfere.

TABLE 6. SIMULTANEOUS DETERMINATION OF CYANIDE AND IODIDE IONS

Taken		Found	
CN^- (mg)	I^- (mg)	CN^- (mg)	I^- (mg)
0.238	1.245	0.241	1.242
0.238	6.225	0.239	6.224
1.191	1.245	1.193	1.240
1.191	6.225	1.198	6.219

1 m*l* of a 1×10^{-2}M standard Hg-EDTA solution
$= 0.2434$ mg of CN^- $= 1.186$ mg of I^-

Simultaneous Determination of Cyanide and Iodide Ions. When cyanide and iodide ions were both present in the same sample, the simultaneous determination of these ions was performed with a standard Hg-EDTA solution, using the Hg-PC-I complex as an indicator. However, when iodide ions did not exist in the sample solution, cyanide could not be determined by this method.

An aliquot of a sample solution containing cyanide and iodide was titrated with the standard Hg-EDTA solution using the Hg-PC-I complex according to the procedure of iodide determination (*titer* A). Another, identical aliquot was treated according to the procedure described in the Diverse Ions section for the determination of iodide ion, also using the Hg-PC-I complex (*titer* B). The volume of the standard Hg-EDTA solution required for cyanide is given by, (A—B) and the volume for iodide, B. These results are shown in Table 6.

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