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Volumetric Determination of the Iodide Ion with Mercury(II) Ethylenediaminetetraacetate Using Mercury(II)-Methylthymolblue as an Indicator

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After 5 m*l* portions of 1×10^{-4} M methylthymolblue (MTB or H_2Me^{4-}) and mercury(II) nitrate solutions had been added to an iodide sample solution adjusted to pH 7.3—8.8, it was diluted to about 50 m*l* with water. This solution was titrated with a 1×10^{-2} M standard mercury(II) ethylenediaminetetraacetate (Hg-EDTA or HgY^{2-}) solution until it turned blue from greenish yellow. The iodide-ion content was calculated by applying the volume of the standard Hg-EDTA solution on the calibration curve determined with solutions of known iodide-ion contents. The iodide ion reacts with HgY^{2-} and with greenish-yellow $HgMe^{4-}$ to form colorless $[HgY(I)]^{3-}$ and blue $[HgMe(I)]^{5-}$ complexes respectively. The $[HgMe(I)]^{5-}$ complex reacts subsequently with the iodide ion to form mercury(II) iodide and greenish-yellow H_2Me^{4-}. It has been found that, except when an excess amount of the iodide ion existed, the $[HgMe(I)]^{5-}$ complex is the most stable among these mixed ligand complexes and mercury(II) iodide. Therefore, the iodide ion can be titrated directly with a Hg-EDTA solution by using $HgMe^{4-}$ as an indicator according to the following equation:

$$HgI_2 + H_2Me^{4-} + HgY^{2-} \rightarrow [HgMe(I)]^{5-} + [HgY(I)]^{3-} + 2H^+$$

Mercury(II) reacts with ethylenediaminetetraacetate (EDTA) to form mercury(II) ethylenediaminetetraacetate (Hg-EDTA or HgY^{2-}), which has no absorption in the visible region. Hg-EDTA reacts further with the iodide ion to form a colorless mixed ligand complex $[HgY(I)]^{3-}$, which does not react with the excess iodide ions any more.[1]

$$HgY^{2-} + I^- \rightarrow [HgY(I)]^{3-} \qquad (1)$$

Mercury(II) reacts with colored methylthymolblue (MTB or H_2Me^{4-}) to form mercury(II)-methylthymolblue (Hg-MTB or $HgMe^{4-}$),[2] which has a color similar to that of MTB, and then further reacts with the iodide ion by means of the formation of a blue-colored mixed ligand complex $[HgMe(I)]^{5-}$:[3]

$$HgMe^{4-} + I^- \rightarrow [HgMe(I)]^{5-} \qquad (2)$$

The $[HgMe(I)]^{5-}$ complex reacts subsequently with the iodide ion to form mercury(II) iodide and MTB, as the following equation shows:

$$[HgMe(I)]^{5-} + I^- + 2H^+ \rightarrow HgI_2 + H_2Me^{4-} \qquad (3)$$

in the way similar to that in which the cyano mixed ligand complex $[HgMe(CN)]^{5-}$ reacts with the cyanide ion to form mercury(II) cyanide and MTB:[4]

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

The order of the stability constants of these iodo mixed ligand complexes and mercury(II) iodide is:

$$[HgMe(I)]^{5-} > [HgY(I)]^{3-} > HgI_2$$

except when excess iodide ions are present in the solution.[5]

When an iodide-ion solution containing a small amount of $HgMe^{4-}$ is titrated with a Hg-EDTA solution, the reaction proceeds as follows.

When a small amount of $HgMe^{4-}$ is added to the iodide-ion solution before the titration, mercury(II) iodide and greenish-yellow H_2Me^{4-} are formed as in Eq. (5), since the excess iodide ions are present:

$$HgMe^{4-} + 2I^- + 2H^+ \rightarrow HgI_2 + H_2Me^{4-} \qquad (5)$$

In the begining of the titration of this solution with the Hg-EDTA solution, the free iodide ion reacts with HgY^{2-} to form the $[HgY(I)]^{3-}$ complex as Eq. (1). After the excess iodide ions have been consumed by the Hg-EDTA, the (6) reaction begins and the blue color of $[HgMe(I)]^{5-}$ appears.

$$HgI_2 + HgY^{2-} + H_2Me^{4-} \rightarrow [HgY(I)]^{3-} + [HgMe(I)]^{5-} + 2H^+ \qquad (6)$$

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

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

[3] T. Nomura and S. Komatsu, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)* **90**, 168 (1969).

[4] T. Nomura, This Bulletin, **41**, 1619 (1968).

[5] T. Nomura and S. Komatsu, unpublished work.

Therefore, the iodide-ion contents in a solution can be titrated with a Hg-EDTA solution, using Hg-MTB as an indicator, if one considers the point at which the color changes from greenish yellow to blue as the end point of the titration.

As a representative method of the volumetric determination of iodide ions, Volhard's method (suitable for a 0.1 M iodide concentration)[6] and iodometry with hypochlorite (suitable for a 0.01 M iodide concentration)[7] have been reported. However, the present, newly-proposed method is especially suitable for the determination of about 0.01 M iodide. It is satisfactorily simple and reproducible.

Experimental

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

Methylthymolblue (MTB) Solution of 1×10^{-4} *M.* The stock 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 of 250 m*l* of methanol and by the exact dilution to 500 m*l* with water. This solution was stored in a brown glass bottle.[8] The working solution of 1×10^{-4} M was prepared by dilution with water.

Mercury(II) Nitrate Solution of 1×10^{-4} *M.* The stock solution of mercury(II) nitrate was prepared by dissolving 3.35 g of mercury(II) nitrate in a small amount of concentrated nitric acid and water, followed by dilution to 1 *l* with water. The precise concentration of this solution was obtained through titration with a 0.01 M standard EDTA solution, using Cu-PAN as an indicator.[9] The working solution of 1×10^{-4} M ($F=1.052$) was prepared by dilution with water.

Standard Iodide Ion Solution of 1×10^{-2} *M.* The stock solution was prepared by dissolving 16.6 g of potassium iodide and by then diluting to 1 *l* with water. The precise concentration of this solution was determined through titration with Volhard's method.[6] The working solution of 1×10^{-2} M ($F=1.000$) was prepared by dilution with water.

Standard Mercury(II) Ethylenediaminetetraacetate (Hg-EDTA) Solution of 1×10^{-2} *M.* This solution was prepared by the dissolution of 6.07 g of Dotite Hg-EDTA and by subsequent exact dilution to 1 *l* with water.

Buffer Solutions. Buffer solutions with definite pHs were prepared by properly mixing 0.2 M disodium hydrogenphosphate and 0.2 M potassium dihydrogenphosphate solutions.

Apparatus. The titration of the iodide ion solutions was 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. Sample solutions containing up to 30 mg of iodide ions were adjusted to pH 7.3—8.8 with a buffer solution, to which a 5 m*l* portion of both a 1×10^{-4} M MTB and a mercury(II) nitrate solution were added; then they were diluted to about 50 m*l* with water. This solution (greenish yellow) was titrated with a 1×10^{-2} M standard Hg-EDTA solution until the color changed from greenish yellow to blue. The iodide-ion content was calculated by applying the titrated volume of the standard Hg-EDTA solution to the calibration curve obtained from solutions of known iodide-ion contents.

Results and Discussion

$HgMe^{4-}$ Indicator. The molar ratio of mercury(II) to MTB to form $HgMe^{4-}$ is 1 : 1, as has previously been mentioned.[2] Therefore, these reagents should be added to an iodide solution at a 1 : 1 molar ratio. However, because mercury(II) nitrate is insoluble in methanol and MTB is insoluble in water, it is difficult to make a solution which contains the reagents in a 1 : 1 molar ratio in a methanol-water mixture. Although it has been found that these reagents dissolve together in an aqueous buffer solution adjusted at pH 7.0, this solution can not be maintained for a long time because of its unstability. Therefore, each reagent solution should kept separately and added to the sample solution at every titration.

The Amount of Mercury(II) Nitrate Solution. In order to examine the suitable ratio of the mercury(II) nitrate solution to the MTB solution, various amounts of a mercury(II) nitrate solution and 5 m*l* of a MTB solution were added to an iodide solution which had been adjusted to pH 7.5 and which contained 6.345 mg of iodide ions. The mixture was then diluted to about 50 m*l* with water. This solution was titrated according to the procedure described in the Experimental section. Below 1 m*l* of a mercury(II) nitrate solution, the end point was not clear because the weak blue color of the

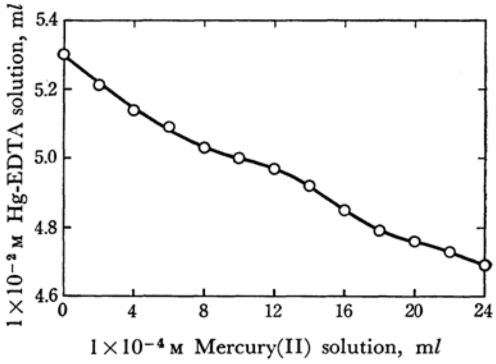

Fig. 1. Amount of mercury(II) solution as an indicator, 6.345 mg of iodide ion, 5 m*l* of 1×10^{-4} M MTB solution, pH 7.5.

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[6] W. J. Blaedel and V. W. Meloche, "Elementary Quantitative Analysis," Second Edition, John Weatherhill Inc., Tokyo (1966) p. 302.

[7] S. Utsumi, T. Okutani, Y. Tamura and I. Iwasaki, *Bunseki Kagaku (Japan Analyst)*, **12**, 951 (1963).

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

[9] H. Flaschka and H. Abdine, *Chemist-Analyst*, **45**, 58 (1956).

mixed ligand complex was contradicted by the strong greenish-yellow color of the excess MTB. In the region from 2 m*l* to 5 m*l* of a mercury(II) nitrate solution, the end point was clearly observed despite the excess MTB giving a greenish-yellow color to the solution. From 5 m*l* to 15 m*l* of the mercury(II) nitrate solution, the end point was also clear in spite of the appearance of a yellow-green color just before the end point. However, the amount of the standard Hg-EDTA solution required in the titration was decreased in inverse proportion to the amount of the mercury(II) nitrate solution added. This situation is shown in Fig. 1. Therefore, the amount of the mercury(II) nitrate solution should be kept definite throughout a series of titrations.

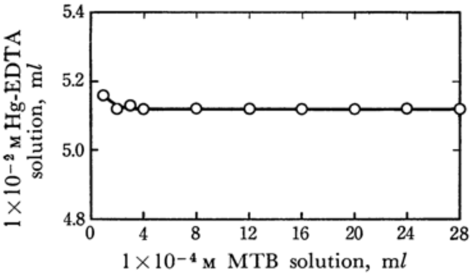

Fig. 2. Amount of MTB solution as an indicator. 6.345 mg of iodide ion, 5 m*l* of 1×10^{-4} M mercury(II) solution, pH 7.5.

The Amount of the MTB Solution. For the same purpose as in the preceding paragraph, various amounts of a MTB solution and 5 m*l* of a mercury(II) nitrate solution were added to the iodide solution under conditions identical to those described above, and this solution was treated similarly. When up to 1 m*l* of the MTB solution was added, the end point could not be determined because scarcely no color change in the solution could be observed. In the range from 6 m*l* to 15 m*l* of the MTB solution added, the greenish-yellow color of the excess MTB remained after the end point had been reached. However, the end point was clearly observed. Over 15 m*l*, however, the end point was not clear because of the strong greenish-yellow color of the excess MTB remaining after the end point. These results are shown in Fig. 2. Therefore, when 5 m*l* of a mercury(II) nitrate solution of 1×10^{-4} M is added, 2 m*l* to 15 m*l* of the MTB solution of 1×10^{-4} M should be added to the iodide sample solution before titration.

As a result of the above examination, the amount of a mercury(II) nitrate solution should be between 2 m*l* and 15 m*l* and the amount of the MTB solution should be from a half to 3 times that of the mercury(II) nitrate solution. In the following experiments, 5 m*l* portions of both mercury(II) nitrate and MTB solutions of 1×10^{-4} M were used.

Effect of pH. After a solution containing 6.345 mg of iodide ions had been adjusted to various pH values with buffer solutions, the solution was treated with the above procedure. The results are shown in Fig. 3. Up to pH 6.7, the end point could not be detected because the yellow of MTB did not change; that is, the mixed ligand complex did not form. Between pH 6.9 and 7.1, the end point could be detected with difficulty. The color change from greenish yellow to blue was very clear between pH 7.3 and 8.8. Furthermore, an identical amount of the standard Hg-EDTA solution was necessary in this pH range. Above pH 8.9, the blue color of MTB in the high-pH region made the end point unobservable. Therefore, the titration should be performed between pH 7.3 and 8.8.

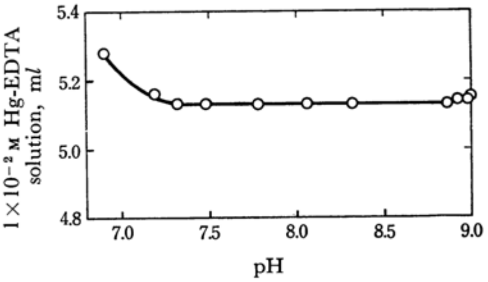

Fig. 3. Effect of pH.
Each 5 m*l* of 1×10^{-4} M MTB and mercury(II) solutions, 6.345 mg of iodide ion.

Effect of Standing Time. The interval between the preparation of a sample solution and titration with a standard Hg-EDTA solution was changed in order to study the effect of the standing time. No effect was observed, however, even at titration after 60 min. Therefore, the titration was carried out after a few minutes.

Calibration Curve and Reproducibility of Analytical Results. It is common, in a titration, for the quantity of an ion present in an unknown sample solution to be calculated by multiplicating the Titer by the volume of the standard solution required (titer). In the present method, however, because the standard Hg-EDTA solution contains free mercury(II), the Titer can not be calculated from the volume of the Hg-EDTA solution required to titrate a known amount of iodide ions. If the quantity of iodide ions were calculated with the usual Titer method, any error in the analytical results might be increased in proportion to the difference between a titer and the volume of the standard solution required to determine the Titer. In this experiment, therefore, a calibration curve was made by a procedure which proposed to express the relationship between the iodide-ion content and the volume of the 1×10^{-2} M standard Hg-EDTA solution required (titer). The reap-

Table 1. Reappearance of titer (ml) with the proposed procedure

Iodide ions added (mg)	0.317	0.635	1.269	2.538	6.345	12.69	19.04	25.38	31.73
1	0.12	0.41	0.92	1.99	5.13	10.34	15.57	20.83	26.08
2	0.15	0.42	0.94	2.00	5.13	10.33	15.59	20.87	26.12
3	0.15	0.41	0.94	1.99	5.12	10.33	15.61	20.84	26.09
4	0.15	0.41	0.93	1.98	5.12	10.32	15.57	20.83	26.10
5	0.16	0.42	0.93	2.00	5.13	10.33	15.58	20.82	26.10
Standard deviation	0.0063	0.0063	0.0077	0.0077	0.0063	0.0063	0.016	0.017	0.013
Variation coefficient (%)	4.21	1.54	0.83	0.39	0.12	0.06	0.10	0.08	0.05

pearance of titers on the calibration curve was examined; the results are shown in Table 1. The calibration curve is linear from a 0.3 to a 32 mg iodide ion content.

A minor additional comment is necessary regarding this titration. If the sample does not contain any iodide ions at all, the greenish-yellow color of the solution does not change to blue. Therefore, it is recommended that a preliminary test for the presence of iodide ions be made by means of the addition of 5 ml of a 1×10^{-4} M iodide solution to the sample. When no iodide is present in the sample, the color of the solution is blue before any of the standard solution is dropped in.

Effect of Diverse Ions. A solution containing 6.345 mg of iodide ions and various foreign ions was titrated by means of the proposed procedure. The results are shown in Table 2. The results that differed more than ±2% from the expected volume of the standard Hg-EDTA solution were taken as the criterion for the interference.

The interference of such anions as CN^-, S^{2-}, SCN^-, and Br^- in this titration can be interpreted as originating as follows. The cyanide ion reacts with Hg-EDTA to form mercury(II) cyanide and EDTA, S^{2-} reacts with mercury(II) to form mercury(II) sulfide, and SCN^- and Br^- react with Hg-EDTA or Hg-MTB to form mixed ligand complexes. Cations, such as Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Ca^{2+} and Ag^+, also interfere, since these cations react with MTB to form metal-MTB complexes.

These interfering ions should be separated or masked properly when this procedure is used. A method of separation employing ion-exchange resin has been reported by Takiura *et al.*10) for anions, and by the author for cations.8)

Table 2. Effect of diverse ions

Ions	Added as	Tolerance limit	
CN^-	KCN	3 μg	+
S^{2-}	$Na_2S\cdot 9H_2O$	7 μg	+
SCN^-	KSCN	150 μg	+
Br^-	KBr	360 μg	+
Cl^-	NaCl	>20 mg	
F^-	KF	>20 mg	
ClO_4^-	$NaClO_4$	>20 mg	
SO_4^{2-}	K_2SO_4	>20 mg	
NO_3^-	$NaNO_3$	>20 mg	
Co^{2+}	$CoSO_4\cdot 7H_2O$	20 μg	−
Ni^{2+}	$NiSO_4\cdot 7H_2O$	40 μg	−
Cu^{2+}	$CuSO_4\cdot 5H_2O$	50 μg	−
Mn^{2+}	$MnSO_4$	80 μg	−
Zn^{2+}	$ZnSO_4\cdot 7H_2O$	100 μg	−
Ca^{2+}	$Ca(NO_3)_2$	100 μg	−
Ag^+	$AgNO_3$	200 μg	−
NH_4^+	$(NH_4)_2SO_4$	320 μg	+
Cd^{2+}	$CdSO_4$	350 μg	−
Bi^{3+}	$Bi(NO_3)_3\cdot 5H_2O$	600 μg	+
Pb^{2+}	$Pb(NO_3)_2$	1.5 mg	−
Al^{3+}	$Al_2(SO_4)_3$	1.8 mg	+
Fe^{3+}	$Fe(NO_3)_3\cdot 9H_2O$	4.3 mg	+
Mg^{2+}	$MgSO_4$	6 mg	+
Ba^{2+}	$Ba(NO_3)_2$	>10 mg	
Sr^{2+}	$Sr(NO_3)_2$	>10 mg	
Th^{4+}	$Th(NO_3)_4\cdot 4H_2O$	>10 mg	

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

The author wishes to thank Professor S. Komatsu for his many helpful discussions and suggestions during this work.

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10) K. Takiura and Y. Takino, *Bunseki Kagaku (Japan Analyst)*, **10**, 493 (1961).