Indirect Complexometric Determination of Mercury(II) Using Guanidine Nitrate as a Selective Masking Agent

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The direct EDTA titration¹ of mercury(II) exhibits poor selectivity, because of the co-titration of other metal ions. The usual practice is to determine the sum of mercury and associated cations, and then to decompose the Hg-EDTA complex selectively with masking agents, such as thiosemicarbazide² or cysteine,³ and titrate the liberated EDTA. In these methods copper causes serious interference. Although Ueno suggested potassium iodide⁴ as a masking agent in an alkaline medium for determining mercury in the presence of copper, many other cations interfered. Thiosulfate⁵ has also been reported as a masking agent for mercury in an alkaline medium, but the effect of copper was not studied. Barcza and Kores⁶ used thiocyanate to mask mercury during the titration of bismuth at a pH of 1.0. The mercury thiocyanate complex could then be decomposed with silver ions, and the liberated mercury was titrated with EDTA at pH 5.0 to 6.0 in the same solution. Singh described the determination of mercury in the presence of various cations with thiourea⁷ as a masking agent. In this method, a minimal excess of thiourea should be used. This restriction causes a problem in the analysis of samples of completely unknown composition. The selective determination of mercury using *N*-allylthiourea⁸ as a masking agent requires heating to decompose the Hg-EDTA complex; some precipitation of HgS is also obtained. The method of mercury determination by Gadiyar *et al.*⁹ using 4-amino-5-mercapto-3-*n*-propyl-1,2,4-triazole as a replacing agent is inconvenient because the masking agent requires a tedious and time-consuming preparation. Although 2-imidazolidinethione¹⁰ and hexahydropyrimidine-2-thione¹¹ as replacing agents were found to be accurate and reliable, these reagents require tedious and time-consuming preparations. Also, they are not readily available. Even though 2-mercaptoethanol¹² was used as a good masking agent, it is unpleasant to use because of its smell; also, Cu(II) interfered with excess reagent. Although sulfite as a masking agent¹³ overcomes all these difficulties, a large excess of the reagent affects the pH of the solution. The use of acetylacetone¹⁴ and sodium nitrite¹⁵ as masking agents for the indirect determination of mercury(II) was found to be convenient. Ions like Pd(II), Sn(II) and Cu(II) do not interfere in this method. 1,10-Phenanthroline¹⁶ and DL-cysteine¹⁷ were used as masking reagents for the determination of mercury(II). In these methods ions like Cu(II), Pd(II), Tl(III) interfere. Cysteamine hydrochloride is also used as a selective masking agent,¹⁸ but ions like Tl(III) and Cu(II) are found to interfere.

In the present investigation, guanidine nitrate was used for the selective and quantitative determination of mercury(II) in the pH range of 5.0 to 6.0

Experimental

Reagents and solutions

All of the reagents used were of analytical reagent grade or chemically pure grade. A mercury nitrate solution (0.01 M) was prepared by dissolving a known amount of mercuric nitrate in distilled water and standardized by the ethylene diamine method.¹⁹ A zinc sulfate solution (0.02 M) was prepared from an analytical reagent-grade sample, and was standardized by a quinolate method.¹⁹ Verifications of the standard mercury(II) and zinc(II) solutions were done by comparing the results with standard reference materials supplied by National Institute of Standards and Technology (NIST) Gaithersburg, MD. Solutions of various metal ions were prepared by dissolving calculated amounts of the metal nitrate/sulfate in distilled water. An EDTA solution (0.02 M) was prepared by dissolving the disodium salt of EDTA in distilled water. Xylenol Orange indicator was prepared by grinding 1 g of Xylenol Orange with 100 g of potassium nitrate crystals, and used as such. Guanidine nitrate was used as a 5% solution in distilled water.

Procedure

To an aliquot of acidic solution containing 2.01 to 160 mg of mercury(II), 5 to 50 ml of EDTA solution was added and diluted to about 60 to 130 ml. About 0.03 g of Xylenol Orange indicator was added and the pH of the solution was adjusted to 5.0 to 6.0 using hexamine (10 ± 2 g). Excess EDTA was titrated with a zinc sulfate solution. To this solution, 1 to 20 ml of 5% guanidine nitrate solution was added and mixed well by shaking. The liberated EDTA was then titrated with a zinc sulfate solution. This second titer value corresponds to the mercury(II) present.

Results and Discussion

The absolute formation constant ($\log \beta$) of Hg-EDTA¹⁹ complex is 21.9, yielding a log conditional stability constant of 15.3 at pH 5.0. Mercury(II) forms a stable soluble complex with guanidine nitrate as $[\text{Hg}(\text{NH}_2\text{-CH}(\text{NH})\text{-NH}_2)_2]^{2+}$ with a log β value²⁰ of 24.96. The sensitivity of this method is established by the effects of various quantities of 5% guanidine nitrate

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Fig. 1 Effect of 5% guanidine nitrate solution used in the determination of mercury(II) (40.12 mg).

Table 1 Determination of mercury(II) in mercuric nitrate solution

Mercury present/mg	Mercury found ^a /mg	Relative error, %	Standard deviation/mg	Students' "t" value ^b
2.01	2.01	0.00	0.01	0.00
4.02	4.01	-0.25	0.02	1.12
8.02	8.03	0.12	0.03	0.75
10.04	10.01	-0.30	0.04	1.68
20.59	20.56	-0.15	0.07	0.96
50.15	50.08	-0.14	0.13	1.2
100.29	100.17	-0.12	0.26	1.03
140.41	140.34	-0.05	0.21	0.75
160.47	160.30	-0.11	0.22	1.73

a. Average of five determinations.

b. Students' "t" test for 5% level of significance = 2.78.

solution used for the recovery of 40.12 mg of Hg, as shown in Fig. 1. It is found that 1 ml of 5% guanidine nitrate solution is required for each 9 mg of mercury(II).

Accuracy and precision

The determinations of mercury in mercuric nitrate solutions were performed at different concentrations of mercury(II) using the above-mentioned reagents. The results are given in Table 1. It shows that the relative error did not exceed $\pm 0.30\%$ and that the standard deviation is ≤ 0.26 mg. On comparing the computed value of students' "t" (2.78 for 5% level of significance) with the tabulated values, it can be observed that in most cases there is no significant difference between the reference values and the value obtained by the proposed method.

Effect of foreign ions

The effect of different cations and anions in the quantitative determination of Hg(II) was investigated at 40.12 mg of Hg(II) in a solution using guanidine nitrate as a masking agent. There was no interference by the ions listed in Table 2. The reduction of Au(III) by EDTA and hydrolysis of Sn(IV) was avoided by using fluoride (10% NH_4F ; 20 ml) for 10 mg of Au(III) and 15 mg of Sn(IV).

Applications

Analysis of alloys of mercury(II). Mercury forms solid alloys with zinc and tin containing 42% and 15% mercury,

Table 2 Determination of mercury(II) in the presence of diverse ions (40.12 mg)

Diverse ion	Amount of diverse ion/mg	Mercury found ^b /mg	Relative error, %
Na(I)	275	40.10	-0.05
Ag(I)	50	40.17	0.12
Zn(II)	100	40.10	-0.05
Co(II)	100	40.11	-0.03
Ni(II)	100	40.17	0.12
Pb(II)	150	40.12	0.00
Pd(II)	15	40.07	-0.12
Cu(II)	75	40.14	0.04
Mn(II)	10	40.16	0.09
Cd(II)	200	40.14	0.04
Mg(II)	150	40.20	0.19
Fe(III)	75	40.12	0.00
Au(III) ^a	15	40.07	-0.12
Al(III)	125	40.07	-0.12
Bi(III)	100	40.12	0.00
Ce(III)	50	40.16	0.09
Cr(III)	50	40.17	0.12
Tl(III)	100	40.10	-0.05
V(IV)	75	40.12	0.00
Ti(IV)	100	40.20	0.19
Pt(IV)	15	40.09	-0.07
Sn(IV) ^a	325	40.11	-0.03
U(VI)	100	40.16	0.09
CH_3COO^-	300	40.12	0.00
NO_3^-	300	40.13	0.02
Cl^-	15	40.11	-0.03
Br^-	30	40.10	-0.05
F^-	300	40.11	-0.03
SO_4^{2-}	350	40.12	0.00
BO_3^{3-}	400	40.14	0.04
PO_4^{3-}	300	40.12	0.00

a. Masked using fluoride.

b. Average of five determinations.

Table 3 Determination of mercury in alloys

Alloy composition	Expected percentage of mercury	Mercury found ^a , %	Relative error, %	Standard deviation, %
Hg + Zn	42.00	41.98	-0.05	0.12
Hg + Cu	83.49	83.47	-0.02	0.09
Hg + Mg	50.00	49.97	-0.06	0.20
Hg + Sn ^b	15.00	15.04	0.27	0.12
Hg + Na	67.70	67.71	0.01	0.11
Hg + Mn	90.13	90.09	-0.04	0.20
Hg + Ni	93.19	93.24	0.05	0.14
Hg + Pb	33.30	33.32	0.06	0.11
Hg + Cd	37.00	37.19	0.51	0.45

a. Average of five determinations.

b. Fluoride is used as secondary masking agent.

respectively. About 1.5 g to 3.0 g of accurately weighed pure alloy samples containing metals like Zn, Cu, Mg, Sn, Na, Mn, Ni, and Pb were taken and heated with 5–10 ml conc. nitric acid; the oxides of nitrogen were expelled by using of 0.5–1.0 ml conc. sulfuric acid until the evolution of brown fumes ceased. The residue was extracted with distilled water and made up to 100 ml in a standard flask. Aliquots of 5–10 ml were used for titration by the recommended procedure. The

Table 4 Analysis of mercury(II) complexes

Complex	Mercury present, %	Mercury found ^f , %	Relative error, %	Standard deviation, %
Hg(C ₃ H ₆ N ₄ S) ₂ ^a	43.74	43.51	-0.53	0.57
Hg(C ₃ H ₆ N ₃ S) ₂ Cl ₂ ^b	42.17	42.15	-0.05	0.27
Hg(C ₄ H ₈ N ₃ S) ₂ Cl ₂ ^c	39.83	39.79	-0.10	0.38
Hg(C ₁₀ H ₁₁ N ₄ OS) ₂ ^d	29.91	29.99	0.27	0.39
Hg(C ₉ H ₇ N ₄ O ₃) ₂ ^e	31.41	31.66	0.80	0.32

Mercury complexes of (a) 4-amino-5-mercapto-3-methyl-1,2,4-triazole; (b) 2-imidazolidinethione; (c) hexahydropyrimidine-2-thione; (d) 4-amino-5-mercapto-3-(*o*-tolylloxymethyl)-1,2,4-triazole; (e) 4-amino-3-mercapto-6-phenyl-1,2,4-triazin(4*H*)-5-one; (f) average of five determinations.

solution was analyzed for the concentration of Hg(II). The results are tabulated in Table 3.

Analysis of mercury(II) in complexes. A number of Hg(II) complexes with sulfur donor ligands²¹ were prepared by the conventional method, and their purity was checked by elemental analysis. About 0.1 to 0.2 g of the complex was decomposed by evaporation to near dryness with concentrated nitric acid and a few drops of conc. sulfuric acid. The residue was then cooled and dissolved in water, and made up to 100 ml with water. Aliquots of 10 ml were used for titration by the proposed method using guanidine nitrate as a masking agent. The results are tabulated in Table 4.

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