Indirect complexometric determination of mercury(II) in synthetic alloys and complexes using ethanethiol as a selective masking agent

J. KARTHIKEYAN[1], P. PARAMESHWARA[1], A. NITYANANDA SHETTY[1,*] and PRAKASH SHETTY[2]

[1]*Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Srinivasnagar 575 025, India and* [2]*Department of Chemistry, Manipal Institute of Technology, Manipal 576 119, India (e-mail: nityashreya@rediffmail.com)*

Abstract: A complexometric method for the determination of mercury(II) in presence of other metal ions, based on the selective masking action of ethanethiol towards mercury(II) is described. Mercury(II) present in a given sample solution is first complexed with an excess of EDTA and the unreacted EDTA is titrated against zinc sulphate solution at pH 5–6 (hexamine buffer) using xylenol orange as the indicator. An excess of a 0.3 % solution of ethanethiol is then added to displace EDTA from the Hg(II)–EDTA complex. The released EDTA is titrated with a standard zinc sulphate solution. Reproducible and accurate results are obtained for 4–85 mg of mercury(II) with a relative error of less than ± 0.46 % and coefficient of variation of not more than 0.47 %. The effects of the presence of various ions were studied. The method can be used for the analysis of mercury in its synthetic alloy mixtures and also in complexes.

Keywords: mercury(II) determination, ethanethiol, complexometric determination.

INTRODUCTION

Mercury plays an important role in chemical and biological processes. Mercury forms useful amalgams with many metals. These amalgams find various applications in diverse fields such as Cd–Hg in the Weston cadmium cell and Zn–Hg as a reducing agent in chemical synthesis. In most of these applications, a simple, rapid and accurate analytical method for determining the mercury content in the samples is often essential.

Mercury(II) is not normally determined by direct EDTA titration, particularly in the presence of other metal ions,[1] as EDTA is a unselective complexing agent and forms stable complexes with most metal ions. The usual practice is to complex mercury(II) together with the associated metal ions with EDTA and then to decompose selectively the

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*   Corresponding author.

Hg(II) –EDTA complex with an appropriate masking agent. The released EDTA is titrated with a standard metal ion solution. Singh[2] described the determination of mercury(II) in the presence of various cations with thiourea as the masking agent. In this method, the interference of copper(II) was avoided by controlling the pH at 5.5 followed by cooling the solution at 15 °C before the addition of thiourea. Good results in the presence of copper(II) were obtained with thiourea as the masking agent when it was present in a slight excess over the required amount. This causes problem when a sample of unknown composition is required to be analysed. Selective determination of mercury using *N*-allylthiourea[3] as the masking agent requires heating to decompose the Hg–EDTA complex and some precipitation of HgS is also obtained. In the selective determination of mercury using thiosemicarbazide[4] as the masking agent, copper causes serious interference. Ueno[5] suggested potassium iodide as the masking agent in alkaline medium for the determination of mercury in the presence of copper, but many other cations interfered. 2-Mercaptoethanol,[6] 3-mercapto-1,2-propanediol,[7] 1,10-phenanthroline,[8] DL-cystein,[9] cysteamine hydrochloride,[10] thioglycolic acid,[11] potassium bromide,[12] glutathione[13] have also been used as selective masking agents for the determination of mercury(II). Some of the other masking agents, such as 4-amino-5-mercapto-3-*n*-propyl-1,2,4-triazole,[14] 2-imidazolidinethione,[15] hexahydropyrimidine-2-thione,[16] require tedious and time consuming synthesis procedures for their preparation, as they are not readily available.

The present investigation describes the use of ethanethiol as the masking agent for the selective and quantitative determination of mercury(II). The effects of foreign ions and the application of the method in the analysis of synthetic mixtures of metal ions and mercury complexes are also reported in this paper.

EXPERIMENTAL

Reagents

All employed reagents were of analytical or chemically pure grade.

Mercury(II) chloride solution. The mercury(II) chloride solution was prepared by dissolving a known weight of $HgCl_2$ in the minimum amount of water and making it up to a known volume with distilled water. The stock solution was standardized by the ethylene-diamine method.[17]

Zinc sulphate solution (0.02 M). The zinc sulphate solution was prepared by dissolving a known amount of zinc sulphate in the minimum amount of water and then making it up to a known volume with distilled water. The stock solution was standardizing gravimetrically by the oxinate method.[17]

EDTA solution (≈0.04 M). The EDTA solution was prepared by dissolving the disodium salt of EDTA in distilled water.

Xylenol orange indicator. A freshly prepared 0.5 % aqueous solution of the indicator was used.

Ethanethiol was used as 0.3 % aqueous solution.

Preparation of foreign ions. Solutions of various metal ions were prepared by dissolving the appropriate metal salts in water or suitable acids.

Procedure

To an aliquot of sample solution containing 4–85 mg of mercury(II) and varying amounts of diverse metal ions, an excess of 0.04 M EDTA was added and the solution was diluted with 25 ml of dis-

tilled water. The pH of the solution was adjusted to 5–6 by adding solid hexamine. The surplus EDTA was back titrated with standard zinc sulphate solution to a sharp color change of xylenol orange from yellow to red. To this, a freshly prepared 0.3 % solution of ethanethiol was added in the required amount. The contents were mixed well and allowed to stand for 5 min in order to ensure the quantitative release of EDTA. The liberated EDTA was then titrated with the standard zinc sulphate solution as before. The second titre value is equivalent to the amount of mercury(II) present in the aliquot.

Analysis of mercury complexes

Mercury complexes with thiourea, ethylenediamine and thiocarbohydrazide were prepared and purified by the reported methods.[17–19] A known weight of the complex was carefully decomposed with *aqua regia* by evaporation to near dryness. The residue was then cooled, dissolved in distilled water and made up to a known volume. Aliquots of this solution were used for estimation as per the proposed procedure.

RESULTS AND DISCUSSION

Masking action of ethanethiol

Ethanethiol acts as a mono-dentate ligand and can form a 1:2 (M:L) complex with mercury(II). According to the HSAB theory,[20,21] mercury(II) ions form strong bond through the soft sulphur atoms of the mercapto group. The Hg(II) is bonded in the complex with deprotonated sulphur atoms of the thiol group, the formed Hg–S bonds having partial double bond character due to the weak π-interaction between the filled 3p orbital of the sulphur atoms and the empty 6p orbital of the mercury atoms, which results in the formation of a stable complex.[22,23] The quantitative release of EDTA from Hg–EDTA complex by ethanethiol indicates that the $Hg(SR)_2$ (R = $-C_2H_5$) complex is more stable than the Hg–EDTA complex under the employed conditions. The release of EDTA is quantitative and instantaneous at room temperature. The formed $Hg(SR)_2$ complex is soluble under the experimental conditions and the detection of the end point is very sharp.

Effect of the ethanethiol concentration

It was observed that for instantaneous and quantitative release of EDTA from the Hg(II)–EDTA complex, the amount of ethanethiol required was in the mole ratio of 1:8 (M:L). Further, it was noticed that the addition of excess ethanethiol, as much as 10-fold excess over the required mole ratio does not have any adverse effect on the obtained results. In all subsequent determinations, the concentration of ethanethiol was maintained at slight excess over the 1:8 (M:L) mole ratio.

Accuracy and precision

In order to check the accuracy and precision of the method, mercury in the concentration range 4–85 mg was determined under the optimized experimental conditions. These results are presented in Table I. The results show that the maximum relative error and coefficient of variation ($n = 6$) of the method were $\pm$ 0.46 % and 0.47 %, respectively. From these results, it is reasonable to infer that the proposed method is precise and accurate.

TABLE I. Precision and accuracy in the determination of mercury(II) ($n = 6$)

Mercury/mg		Relative error/%	Standard deviation/mg	Coefficient of variation/%
Taken	Found			
4.26	4.24	− 0.46	0.02	0.47
8.53	8.55	+0.23	0.04	0.46
12.79	12.82	+0.23	0.04	0.31
21.32	21.35	+0.14	0.04	0.18
42.65	42.59	− 0.14	0.04	0.09
63.98	63.92	− 0.09	0.05	0.07
85.31	85.20	− 0.12	0.03	0.03

Effect of foreign ions

The effect of various cations and anions on the quantitative determination of Hg(II) was studied by estimating 12.96 mg of Hg(II) in the presence of different metal ions. No interference was observed for the ions in the amounts shown in Table II. However, Pd(II), Tl(III) and Sn(IV) interfere severely with a positive error. The interference of Pd(II), Tl(III) and Sn(IV) is due to the release of EDTA from their respective EDTA complexes on addition of the reagent. However, the interference of Pd(II), Tl(III) and Sn(IV) can be avoided by using a suitable premasking agent, such as histidine, hydrazine sulphate and sodium fluoride, respectively.

TABLE II. Determination of 12.96 mg of Hg(II) in the presence of diverse metal ions ($n = 4$)

Metal ions	Quantity added/mg	Mercury found/mg	Relative error/%
Mg(II)	100	12.92	− 0.30
Mn(II)	30	12.94	− 0.15
Co(II)	125	12.94	− 0.15
Ni(II)	125	12.93	− 0.23
Cu(II)	125	12.94	− 0.15
Zn(II)	300	12.96	0.00
Cd(II)	150	12.97	+ 0.07
Pb(II)	350	12.97	+ 0.07
Pd(II)	10	12.94	− 0.15
La(III)	300	12.95	− 0.07
Y(III)	300	12.92	− 0.30
Ir(III)	100	12.92	− 0.30
Al(III)	50	12.96	0.00
Bi(III)	250	12.92	− 0.30
Rh(III)	100	12.96	0.00
Ru(III)	5	12.96	0.00

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TABLE II. Continued

Metal ions	Quantity added/mg	Mercury found/mg	Relative error/%
As(III)	30	12.96	0.00
Tl(III)♠	30	12.97	+ 0.07
Sn(IV)♣	10	12.96	0.00
Sb(IV)	25	12.90	− 0.46
Pt(IV)	75	12.96	0.00
Se(IV)	250	12.97	+ 0.07
U(VI)	40	12.93	− 0.23
W(VI)	150	12.93	− 0.23
Chloride	200	12.94	− 0.15
Phosphate	150	12.97	+ 0.07
Citrate	150	12.97	+ 0.07
Tartarate	200	12.96	0.00
Acetate	200	12.94	− 0.15
Borate	200	12.92	− 0.30
Sulphate	100	12.93	− 0.23
Oxalate	150	12.90	− 0.46

[*] Histidine (10 %, 10 – 20 ml); [♠]Hydrazine sulphate (5 %, 10 – 20 ml); [♣]Sodium fluoride (saturated solution, 10 – 15 ml)

Applications

In order to explore the practical application of the proposed method, it was extended for the determination of mercury in its complexes and in synthetic alloy mixtures of metal ions. The experimental results of these analyses are presented in Tables III and IV, respectively. It is evident from these results that the method can be conveniently employed in the analysis of mercury in its complexes and alloys with a fair degree of accuracy.

TABLE III. Analysis of mercury complexes ($n = 3$)

Complex	Hg calculated/%	Hg found/%	Relative error/%
$Hg(CH_4N_2S)Cl_2$[a]	57.69	57.64	− 0.08
$Hg(CH_4N_2S_2)_2Cl_2$[b]	47.34	47.30	− 0.08
$[Cu(en)_2][HgI_4]$[c]	50.05	49.98	− 0.14
$Hg(CH_6N_4S)_2Cl_2$[d]	41.46	41.40	−0.14

Mercury complexes of [a,b]thiourea, [c]ethylenediamine, [d]thiocarbohydrazide

TABLE IV. Determination of mercury(II) in synthetic mixtures of metal ions ($n=3$)

Mixture	Hg present/%	Hg found/%	Relative error/%
Hg + Zn + Cd	27.09	27.01	− 0.29
Hg + Pb + La	14.66	14.68	− 0.13

TABLE IV. Continued

Mixture	Hg present/%	Hg found/%	Relative error/%
Hg + Y + Ir	9.32	9.32	0.00
Hg + Bi + Cu	74.36	74.39	+0.04
Hg + Cu + Se	4.44	4.44	0.00
Hg + Co + Cu	14.66	14.67	+ 0.06
Hg + Se + W	9.32	9.30	− 0.21
Hg + Zn + Cd + La	4.44	4.44	0.00

CONCLUSIONS

The proposed method is simple, as it does not require any pH adjustment after the addition of the reagent or heating for the quantitative release of EDTA. The absence of any precipitate during the titration facilitates easy detection of a sharp end point. Since, many metal ions do not interfere, the method is fairly selective for the rapid analysis of mercury in the presence of these metal ions.

извод

ИНДИРЕКТНО КОМПЛЕКСОМЕТРИЈСКО ОДРЕЂИВАЊЕ ЖИВЕ(II) У СИНТЕТИЧКИМ ЛЕГУРАМА И КОМПЛЕКСИМА КОРИШЋЕЊЕМ ЕТАНТИОЛА

J. KARTHIKEYAN[1], P. PARAMESHWARA[1], A. NITYANANDA SHETTY[1] и PRAKASH SHETTY[2]

[1]Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Srinivasnagar 575 025, India u [2]Department of Chemistry, Manipal Institute of Technology, Manipal 576 119, India

Описана је комплексометријска метода за одређивање живе(II) у присуству других металних јона, заснована на селективном маскирању живе(II) етантиолом. Жива(II) у узорку комплексирана је најпре вишком EDTA и непрореагована количина EDTA титрисана цинк-сулфатом при pH 5–6 (хексамински пуфер) уз ксиленол оранж као индикатор. Вишак 0,3 % раствора етантиола је затим додаван да би истиснуо EDTA из жива(II) – EDTA комплекса. Ослобођени EDTA титрисан је стандардним раствором цинк-сулфата. За опсег 4–85 mg живе(II) добијени су репродуктивни и тачни резултати са релативном грешком мањом од ± 0,46 % и коефицијентом варијације не већим од 0,47 %. Испитивани су ефекти присуства различитих јона. Метода може да се користи за анализу живе у смешама синтетичких легура и, такође, у комплексима.

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