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Quantitative Complexometric Determination of Mercury(II) in Synthetic Alloys and Complexes Using 2-Thiazolinethiol as a Masking Agent

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A simple, rapid and selective complexometric method is proposed for the determination of mercury(II). Mercury(II) and other related metal ions are first complexed with an excess of EDTA and the surplus EDTA is back-titrated with a standard lead nitrate solution at pH 5.0-6.0 (hexamine buffer) using xylenol orange as an indicator. A 0.2% solution of 2-thiazolinethiol in acetone is then added to displace EDTA from the Hg(II)-EDTA complex. The released EDTA is titrated with a standard lead nitrate solution as before. Reproducible and accurate results are obtained in the range of 0.8 g l^{-1}-15.8 g l^{-1} of mercury with a relative error less than ±0.25% and a coefficient of variation (n = 6) not higher than 0.28%. The interference of various ions was studied and the method was employed for the analysis of mercury in its synthetic alloy mixtures and in complexes.

Keywords: Complexometric methods, EDTA-titrations, Masking agents, Mercury(II) determination, 2-Thiazolinethiol

INTRODUCTION

Mercury plays an important role in biological and chemical processes. It also forms useful amalgams with many metals, which find various applications in diverse fields. Due to the numerous applications and the toxic nature of amalgams and mercury compounds, there is a need for simple and accurate analytical methods that allow for the rapid determination of mercury content in samples.

Mercury(II) is normally not determined by direct EDTA titration, especially when other metal ions are present [1]. Usual practice is to complex mercury(II) together with the associated metal ions by EDTA and then selectively decompose the Hg(II)-EDTA complex with an appropriate masking agent. The released EDTA is titrated with a standard metal ion solution. Singhhas described the determination of mercury(II) in the presence of various cations with thiourea as masking agents [2]. In this method, the interference of copper(II) was avoided by fixing the pH at 5.5, and then cooling the solution to 15 °C before the addition of thiourea. Good results in the presence of copper(II) were obtained with thiourea as a masking agent when this metal was present in concentrations above a critical limit. This raises a problem when samples of unknown composition need to be analyzed. Selective determination of mercury using N-allylthiourea [3] as a masking agent requires heating to decompose the Hg-EDTA complex. In this method, some precipitation of HgS is also observed. In the selective determination of mercury using thiosemicarbazide [4] as a masking agent, copper causes serious interference. Ueno suggested employing potassium iodide [5] as a masking agent in an alkaline medium for determining mercury in the presence of copper, but many

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other cations interfered.

Thiocyanate [6], 2-mercaptoethanol [7], acetyl acetone [8], 3-mercapto-1,2-propanediol [9], 1,10-phenanthroline [10], DL-cystein [11], cysteamine hydrochloride [12], thioglycolic acid [13], potassium bromide [14], glutathione [15], and 2-mercaptopropionic acid [16] were also used as selective masking agents for the determination of mercury(II). Some other masking agents, such as 4-amino-5-mercapto-3-*n*-propyl-1,2,4-triazole [17], 2-imidazolidinethione [18], and hexahydropyrimidine-2-thione [19] require tedious and time-consuming syntheses, as they are not readily available. In many of these methods, Cu(II) or other metal ions show interference.

The present investigation describes the use of 2-thiazolinethiol as a masking agent for the selective and quantitative determination of mercury(II) in the pH range 5-6. In this work, we study the effects of foreign ions and report the application of this method in the analysis of mixtures of ions and mercury complexes.

EXPERIMENTAL

Reagents

All chemicals used were of analytical or chemically pure grade. A mercury(II) chloride solution was prepared by dissolving mercuric chloride in distilled water and then diluting the solution to a known volume. The solution was standardized by the ethylene diamine method [20]. A lead nitrate solution (0.02 M) was prepared by dissolving lead nitrate in distilled water and then diluting the solution to a known volume. This solution was standardized by the chromate method [20].

An EDTA solution (~0.03 M) was prepared by dissolving the disodium salt of EDTA in distilled water. The xylenol orange indicator was prepared just before use as a 0.5% aqueous solution. Only freshly prepared solutions of 2-thiazolinethiol (0.2%) were used.

Procedure

To an aliquot (5 to 15 ml) of the sample solution, containing mercury(II) (0.004 to 0.078 M; 0.8 to 15.8 g l^{-1}; 4 to 78 mg) and varying amounts of diverse metal ions, an excess of 0.03 M EDTA was added and the solution was diluted to 25 ml with distilled water. The pH of the solution was adjusted to 5.0-6.0 by adding solid hexamine. The EDTA surplus was back titrated with a standard lead nitrate solution, using the sharp color change, from yellow to red, of xylenol orange to determine the endpoint. To this the required amount of a freshly prepared solution of 2-thiazolinethiol was added. The contents were mixed and allowed to stand for 5 min in order to ensure the quantitative release of EDTA. The liberated EDTA was then titrated with a standard lead nitrate solution as above. The second titration value is equivalent to the amount of mercury(II) present in the aliquot.

Analysis of Mercury Complexes

Mercury(II) complexes were prepared and purified by previously reported methods [21-25]. A precise amount of the complex was carefully decomposed with aqua regia upon which the corresponding solution was evaporated by heating to dryness. The residue was then cooled, dissolved in distilled water and diluted to a known volume. Aliquots of this solution were used for evaluation according to the proposed procedure.

RESULTS AND DISCUSSION

Masking Property of the Reagent

A comparison of the previously reported methods with that described in this work is given in Table 1.

The 2-thiazolinethiol reagent acts as a monodentate ligand and forms a 1:2 complex with mercury(II) ion. According to the HSAB theory, mercury(II) is expected to form strong bonds through the soft sulfur of the mercapto group [26,27]. In fact, the bonding of Hg(II) occurs *via* the deprotonated thiol group, the resulting Hg-S bond having a partial double bond character due to the weak π-interaction between the filled 3p orbital of sulfur and the empty 6p orbital of mercury, hence leading to the formation of a stable complex [28,29]. The quantitative release of EDTA from the Hg(II)-EDTA complex after the addition of 2-thiazolinethiol indicates that the $Hg(SR)_2$ complex [R = C_3H_4NS] is more stable than Hg(II)-EDTA under the conditions employed. The $Hg(SR)_2$ complex formed is soluble under the experimental conditions. The detection of the endpoint is very sharp.

Table 1. Comparison of Previously Reported Masking Agents with 2-Thiazolinethiol

Reagent	Interfering ions	Ref.
Thiosemicarbazide	Cu(II) and Fe(II)	[4]
Potassium iodide	Cu(II), Zn(II), Ni(II), Co(II), alkaline earth metal ions, nitrate and ferrocyanide ions	[5]
Thiocyanate	Pd(II), Tl(III), and Sn(IV)	[6]
2-Mercaptoethanol	Cu(II)	[7]
Acetyl acetone	Cu(II), Pd(II), and Tl(III)	[8]
3-Mercapto 1,2-propanethiol	Pd(II), Tl(III), Sn(IV), Bi(III), and Sn(IV)	[9]
1,10-Phenanthroline	Pd(II), Cd(II), Cu(II), and Tl(III)	[10]
DL-Cysteine	Pd(II), Cu(II), and Tl(III)	[11]
Cysteamine hydrochloride	Cu(II) and Tl(III)	[12]
Thioglycolic acid	Cu(II), Pd(II), Hg(II), Tl(III), and Sn(IV)	[13]
Potassium bromide	Ag(I), Hg(II), Pd(II), Au(III), Sb(IV), and Sn(IV)	[14]
Glutathione	Pd(II), Cu(II), Tl(III), and Sn(IV)	[15]
2-Mercaptopropionic acid	Pd(II), Cu(II), Tl(III), and Sn(IV)	[16]
4-Amino-5-mercapto-3-n-propyl-1,2,4-triazole	Less popular reagent requiring tedious and time-consuming preparation.	[17]
2-Imidazolidinethione	Reagent is carcinogenic and requires tedious and time-consuming preparations	[18]
Hexahydropyrimidine-2-thione	Less popular reagent requiring tedious and time-consuming preparations	[19]
2-Thiazolinethiol	Pd(II), Tl(III) and Sn(IV) and Hg(II) The interference of Pd(II), Tl(III), and Sn(IV) can be eliminated by premasking these ions with L-histidine, hydrazine sulfate and sodium fluoride, respectively.	Proposed reagent

Effect of Reagent Concentration

It was observed that for an instantaneous and quantitative release of EDTA from the Hg(II)-EDTA complex, the amount of 2-thiazolinethiol required corresponded to a M:L ratio of 1:2. It was further noticed that the addition of a 20-fold excess of reagent had no impact on the results obtained. In all our subsequent determinations, the concentration of 2-thiazolinethiol was therefore maintained slightly above a 1:2 (M:L) molar ratio.

Accuracy and Precision

In order to assess the accuracy and precision of the proposed method, the determination of Hg(II) was carried out at different concentrations. The corresponding results, presented in Table 2, show that the relative error (*i.e.* the absolute error divided by the true or most probable value; usually expressed in terms of percentage or parts per thousand) and the coefficient of variation (n = 6) of the method do not exceed 0.25% and 0.28%, respectively. Thus, the proposed method is precise and accurate.

Effect of Diverse Ions

The effect of the presence of various ions on the accuracy and precision of the method was studied by carrying out the determination of 19.54 mg of Hg(II). The presence of the following ions did not interfere below a critical amount (given in parentheses; in mg): Pb(II) (100), Zn(II) (60), Cd(II), Mg(II) (50), Ni(II) (35), Cu(II) (20), Co(II) (20), Mn(II) (5),

Table 2. Precision and Accuracy in the Determination of Mercury(II)

Hg (mg)		Relative error	Standard deviation	Coefficient of variation
Taken	Found[a]	(%)		(%)
3.91	3.92	+ 0.25	0.01	0.18
7.82	7.83	+ 0.12	0.02	0.19
11.72	11.73	+ 0.08	0.03	0.28
19.54	19.54	0.00	0.05	0.24
39.08	39.01	-0.18	0.07	0.17
58.62	58.66	+ 0.07	0.10	0.18
78.16	77.99	-0.22	0.15	0.20

[a]Average of six determinations.

Table 3. Analysis of Mercury Complexes

Complex	Mercury calculated (%)	Mercury found (%)[a]	Relative error (%)	Standard deviation
$Hg(CH_4N_2S)Cl_2.1/2\ H_2O$[b]	56.18	56.36	+ 0.32	0.010
$Hg(CH_4N_2S)_2Cl_2$[c]	47.28	47.10	– 0.38	0.007
$Hg(CH_4N_2S)_3Cl_2$[d]	40.15	40.27	+ 0.32	0.010
$Hg(C_2H_2N_3S)_2$[e]	49.55	49.36	– 0.38	0.070

[a]Average of three determinations

Mercury complexes with [b]monothiourea, [c]dithiourea, [d]trithiourea and [e]1,2,4-triazole-3(5)-thiol.

Table 4. Determination of Mercury in Synthetic Mixtures

Mixture	Composition (%)	Mercury found (%)[a]	Relative error (%)	Standard deviation
Hg + Zn + Pb	20.2 + 42.5 + 37.3	20.21	+ 0.05	0.014
Hg + Zn + Cu	25.6 + 40.4 +34.0	25.59	– 0.05	0.010
Hg + Zn + Ni	20.2 + 63.8 + 16.0	20.25	+ 0.25	0.014
Hg + Co + Cd	29.7 + 39.0 + 31.3	29.79	+ 0.30	0.014

[a]Average of five determinations.

La(III) (80), Y(III) (80), Ce(III) (30), Al(III) (20), Fe(III) (20), Rh(III) (20), Ir(III) (20), Bi(III) (5), Pt(IV) (50), As(IV) (5), W(VI) (25), U(VI) (15), chloride (120), oxalate (40), tartrate (130), acetate (150), sulfate, borate (200) and citrate (170). However, metal ions such as Pd(II), Cr(III), Tl(III), Sn(IV) and phosphate showed interference. The interference of Pd(II), Tl(III) and Sn(IV) is due to the reagent-induced liberation of EDTA from the corresponding EDTA complexes as well as from the Hg-EDTA complex. However, the interference of Pd(II) (up to 15 mg), Tl(III) (40 mg), and Sn(IV) (10 mg) can be eliminated by premasking these ions with L-histidine, hydrazine sulfate and sodium fluoride, respectively. The interference of Cr(III) is apparent due to the deep purple color of its EDTA complex, which makes detection of the end point difficult.

APPLICATIONS

In order to explore its usefulness, the proposed method was applied to the analysis of mercury complexes and synthetic mixtures of metal ions. The results of the analyses are presented in Tables 3 and 4. Our findings indicate that the method is suitable for the analysis of such samples and shows good accuracy.

CONCLUSIONS

The proposed method is simple, rapid and does not require heating for the release of EDTA from the Hg(II)-EDTA complex. The method further tolerates the presence of many metal ions and anions. The method does not require adjustment of pH after addition of the reagent. It can be conveniently employed for the rapid analysis of mercury in its complexes and in alloys with a fair degree of accuracy.

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