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Notes

Indirect complexometric determination of mercury(II) using 2-mercaptopropionic acid (2-MPA) as a selective masking agent

J Karthikeyan[a], P Parameshwara[a], A Nityananda Shetty[a*] & Prakash Shetty[b]

[a]Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Srinivasnagar 575 025, India
[b]Department of Chemistry, Manipal Institute of Technology, Manipal 576 104, India

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A complexometric method for the determination of mercury(II) in presence of other metal ions is described based on the selective masking action of 2-mercaptopropionic acid towards mercury(II). 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. A 0.5% aqueous solution of 2-mercaptopropionic acid is then added to displace EDTA from the Hg(II)-EDTA complex. The released EDTA is estimated. Reproducible and accurate results are obtained for 4-88 mg of mercury(II) with relative error less than ± 0.46% and coefficient of variation not more than 0.34%. The effects of various ions were studied. The method is used for the analysis of mercury in its synthetic alloy mixtures and also in complexes.

Keywords: Mercury(II), 2-mercaptopropionic acid, complexometric titration

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Mercury plays an important role in chemical and biological processes. Because of the extensive applications and toxic nature of mercury compounds, there is need for a simple and rapid analytical method for the determination of mercury in samples.

Mercury(II) is not determined normally by direct EDTA titration, particularly in the presence of other metal ions[1] as EDTA is an unselective complexing agent, forms stable complexes with most of the metal ions. 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 standard metal ion solution. Singh[2] has described the determination of mercury(II) in the presence of various cations with thiourea as 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 masking agent when it was present in slight excess over the required amount. This causes problem when a sample of unknown composition needs to be analysed. Selective determination of mercury using N-allylthiourea[3] as 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 masking agent, copper causes serious interference. Ueno[5] suggested potassium iodide as masking agent in alkaline medium for determining 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] were also used as 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 2-mercaptopropionic acid as a masking agent for the selective and quantitative determination of mercury(II). The effects of foreign ions are studied and the application of the method in the analysis of mixture of ions and mercury complexes is also reported in this paper.

Experimental Procedure

All reagents used were of analytical or chemically pure grade. The stock solutions of mercury(II)chloride, EDTA(~0.04 M) (sodium salt) and zinc sulphate(0.02 M) were prepared by dissolving a requisite amount of salt in minimum amount of water, making up to the mark with distilled water and standardizing the solution by the standard methods[17]. Freshly prepared (0.5%) aqueous solutions of xylenol

*For correspondence (E-mail: nityshreya@rediffmail.com; Fax: 0824–2474033)

orange (indicator) and 2-mercaptopropionic acid (masking agent) (Acros organics, USA) were prepared by dissolving the requisite amount of reagents in distilled water. Solutions of various metal ions were prepared by dissolving calculated amounts of the metal chlorides/nitrates/sulphates in distilled water and then making up to a known volume.

Method

To an aliquot of sample solution containing 4-88 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 distilled 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 0.5% solution of 2-mercaptopropionic acid was added in 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, thiocyanate, 1,2,4-triazole-3(5)-thiol, thiocarbohydrazide, were prepared and purified by the reported methods[18-22]. 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 2-mercaptopropionic acid

2-Mercaptopropionic acid acts as a bidentate ligand and forms a 1:2 complex with mercury(II). According to HSAB theory[23,24] mercury(II) forms strong bond through soft sulphur of mercapto group. Therefore, it is reasonable to expect the bonding of Hg(II) with deprotonated sulphur of thiol group and hydroxyl oxygen of carboxyl group, which results in the formation of a stable five membered chelate[25]. The quantitative release of EDTA from Hg-EDTA complex by 2-MPA indicates that $Hg(2\text{-}MPA)_2$ chelate is more stable than Hg-EDTA complex under the conditions employed. The release of EDTA is quantitative and instantaneous at room temperature itself. The $Hg(2\text{-}MPA)_2$ complex formed is soluble under the experimental conditions and the detection of the end point is very sharp.

Effect of 2-MPA concentration

It was observed that for instantaneous and quantitative release of EDTA from the Hg(II)-EDTA complex, the amount of 2-MPA required was in the molar ratio of 1:2(M:L). Further, it was noticed that the addition of excess 2-MPA, as much as 20-fold excess over the required molar ratio does not have adverse effect on the results obtained. In all subsequent determinations, the concentration of 2-MPA was maintained at slight excess over the 1:2(M: L) molar ratio.

Accuracy and precision

In order to check the accuracy and precision of the method, determinations of mercury in the concentration range 4-88mg were carried out under the optimized experimental conditions. These results are presented in Table 1. The results show that the maximum relative error and coefficient of variation (n=6) of the method are ±0.46 and ±0.34%, respectively. From these results, it is reasonable to infer that the proposed method is precise and accurate.

Effect of foreign ions

The effect of various cations and anions on the quantitative determination of Hg(II) was studied by estimating 21.94 mg of Hg(II) in the presence of dif-

Table 1—Precision and accuracy in the determination of mercury(II)

Mercury, mg		Relative error (%)	Standard deviation (mg)	Coefficient of variation (%)
Taken	Found			
4.38	4.36	-0.46	0.01	0.34
8.76	8.78	+0.23	0.01	0.17
13.14	13.16	+0.15	0.02	0.16
21.90	21.90	+0.00	0.01	0.05
35.04	35.11	+0.19	0.02	0.05
43.80	43.86	+0.14	0.02	0.05
65.70	65.73	+0.05	0.02	0.03
87.60	87.64	+0.04	0.01	0.02

Table 2—Analysis of mercury complexes (n=3)

Complex	Hg calculated (%)	Hg found (%)	Relative error (%)
$Hg(CH_4N_2S)Cl_2$[a]	57.69	58.01	+0.55
$Hg(CH_4N_2S)_2Cl_2$[b]	47.34	47.54	+0.42
$Zn[Hg(SCN)_4]$[c]	40.27	39.96	-0.77
$Hg(C_2H_2N_3S)_2$[d]	50.05	49.88	-0.34
$Hg(CH_6N_4S)_2Cl_2$[e]	41.46	41.34	-0.29

[a]Mercury-thiourea complex; [b]Mercury-dithiourea complex; [c]Mercury-thiocyanate complex; [d]Mercury-1,2,4-triazole-3(5)-thiol complex; [e]Mercury-thiocarbohydrazide complex

Table 3—Determination of mercury(II) in synthetic mixtures of metal ions (n=3)

Mixture	Composition (%)	Hg found (%)	Relative error (%)
Hg + Zn	80.0 + 20.0	79.91	-0.11
Hg + Mg	62.0 + 38.0	62.17	+0.27
Hg + Ni	55.0 + 45.0	54.94	-0.11
Hg+Ni+Mg	50.0 + 25.0 + 25.0	49.98	-0.04
Hg+Cd+Mn	43.0 + 32.0 + 25.0	42.92	-0.19
Hg+Co +Al	35.0 + 40.0 + 25.0	35.02	+0.06

ferent metal ions. No interference was observed for the following ions at the amounts in mg shown: Na(I) (50), K(50), Mg(II) (100), Pb(II) (150), Zn(II) (150), Co(II) (75), Ni(II) (75), Mn(II) (30), Cd(II) (75), Fe(III) (20), Al(III) (50), Bi(III) (10), Ce(III) (100), Ti(III) (75), Rh(III) (30), Ru(III) (5), Au(III) (5), Pt(IV) (50), Se(IV) (100), U(VI) (100), acetate(100), chloride(100), sulphate (100), oxalate(100), tartarate (100), phosphate(100). Metal ions like Pd(II), Cu(II), Tl(III), Cr(III) and Sn(IV) interfere severely. The interference of Pd(II), Cu(II), Tl(III) and Sn(IV) is due to the release of EDTA from their M-EDTA complexes on the addition of 2-MPA. The interference of Cr(III) is due to the deep purple colour of its EDTA complex, which makes the detection of the end point rather difficult.

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 mixture of metal ions. The experimental results of these analyses are presented in Tables 2 & 3, 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.

Conclusion

The proposed method is simple, as it does not require any adjustment of pH 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 show interference, the method is fairly selective for the rapid analysis of mercury in the presence of these ions.

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