Indirect complexometric determination of mercury(II) using 3-acetyl-2-thiohydantoin as a selective masking agent

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

[a]Department of Chemistry, Sathyabama University, Chennai 600 119, India

[b]Department of Chemistry, National Institute of Technology Karnataka, Surathkal,

Srinivasnagar 575 025, India

Email: nityashreya@rediffmail.com

A complexometric method for the determination of mercury(II) in presence of other metal ions is described based on the selective masking action of 3-acetyl-2-thiohydantoin 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 standard lead nitrate solution at pH 5-6 (hexamine buffer) using xylenol orange as the indicator. A 0.5% solution of 3-acetyl-2-thiohydantoin is then added to displace EDTA from the Hg(II)-EDTA complex. The released EDTA is estimated. Reproducible and accurate results are obtained for 3.96 - 80 mg of mercury(II) with relative error less than $\pm$ 0.25% and coefficient of variation not more than 0.38%. The effects of various ions were studied. The method is used for the analysis of mercury in its synthetic mixtures of ions and in complexes.

Keywords: Mercury(II), 3-Acetyl-2-thiohydantoin, Complexometric titration

Mercury plays an important role in chemical and biological processes. Mercury is quantitatively estimated by reducing the mercuric salt to mercury, by electrolysis[1]. The metal is then separated by distillation and weighed. The methods used for the determination of mercury include, gravimetry, coulometry, neutron activation analysis, X-ray spectrometry, atomic absorption spectrometry and spectrophotometry. Most of these methods are disadvantageous in terms of cost and need extreme care during the operation. Hence, the accurate determination of mercury using simple and rapid method is of great importance. Keeping this in view, the study of the complexometric determination of mercury using some sulphur containing organic reagents, has been taken up for investigation.

Normally mercury(II) can not be accurately determined by direct EDTA titration, particularly in the presence of other metal ions[2] as EDTA is an unselective complexing agent which forms stable complexes with most of the metal ions. Hence the 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. A number of compounds have been tried as masking agents for mercury determination. An account of some complexometric methods[3-20] using various masking agents for the determination of mercury is presented in Table 1.

The present investigation describes, the use of 3-acetyl-2-thiohydantoin ($C_5H_6N_2O_2S$) as a masking agent for the quantitative determination of mercury(II). The main advantage of the proposed method when compared with recent reported methods is that, there is no interference from Cu(II), Tl(III) and Sn(IV). The effect of foreign ions are studied and the application of the method in the analysis of synthetic mixtures of ions and mercury complexes are reported in this paper.

Experimental Procedure

Materials

All reagents used were of analytical or chemically pure grade. The stock solutions of mercury(II) chloride, EDTA (~0.04 M) and lead nitrate (0.02 M) were prepared by dissolving requisite amounts of the compounds in minimum amount of water, making up to the mark with distilled water and standardizing the

Table 1 – Masking agents used in mercury(II) estimations

Reagents	Range (mg)	pH	Accuracy & precision	Remarks	Ref.
Thiourea	1-50	5 – 6 (Hexamine)	R.E ≤ ± 1 %	Cu(II), Al(III) and Mg(II) interfere	3
N-allylthiourea	1-50	5 – 6 (Hexamine)	R.E ≤ ± 0.5 % C.V ≤ 0.5 %	Involves heating and precipitation of HgS occurs	4
Thiosemicarbazide	1-100	5 – 6 (Utropine)	R.E ≤ ± 1 %	Cu(II) and Fe(III) interfere	5
Potassium iodide	0-50	5 – 6 (Hexamine)	R.E ≤ ± 1 %	Cu(II), Ni(II), Co(II) and ferrocyanide ions interfere	6
Sodium nitrite	3-50	5 – 6 (Hexamine)	R.E ≤ ± 0.5 % C.V ≤ 0.5 %	Pd(II) and Sn(IV) interfere.	7
3-Mercapto-1,2-propanediol	3-75	5 – 6 (Hexamine)	R.E ≤ ± 0.41% C.V ≤ 0.43 %	Pd(II), Tl(III), Bi(III), Cr(III) and Sn(IV) interfere.	8
Sodium thiosulphate	3-78	5 – 6 (Hexamine)	R.E ≤ ± 0.5 % C.V ≤ 0.5 %	Pd(II), Tl(III) and Sn(IV) interfere.	9
1,10-Phenanthroline	3-80	5 – 6 (Hexamine)	R.E ≤ ± 0.5 % C.V ≤ 0.5 %	Cd(II), Cu(II), Pd(II) and Tl(III) interfere.	10
DL-Cystein	3-120	5 – 6 (Hexamine)	R.E ≤ ± 0.5 % C.V ≤ 0.5 %	Pd(II), Cu(II) and Tl(III) interfere	11
Cysteamine hydrochloride	4-125	5 – 6 (Hexamine)	R.E ≤ ± 0.4 % S.D ≤ 0.04 mg	Cu(II), Mn(II), Fe(III), Au(III) and Tl(III) interfere.	12
Thioglycolic acid	5-84	5 – 6 (Hexamine)	R.E ≤ ± 0.21 % C.V ≤ 0.34 %	Pd(II), Cu(II), Tl(III) and Sn(IV) interfere.	13
2-Mercaptopropionyl glycine	4-85	5 – 6 (Hexamine)	R.E ≤ ± 0. 26 % C.V ≤ 0. 42 %	Pd(II), Tl(III) and Sn(IV) interfere.	14
Guanidine nitrate	2-160	5 – 6 (Hexamine)	R.E ≤ ± 0.30 % S.D ≤ 0.26 mg	Au(III) and Sn(IV) interfere.	15
Potassium bromide	8-250	5 – 6 (Hexamine)	R.E ≤ ± 0.28% S.D ≤ 0.5 mg.	No interference from Cu(II), Pd(II) and Tl(III).	16
Glutathione	4-80	5 – 6 (Hexamine)	R.E ≤ ± 0.30 % C.V ≤ 0.38 %	Pd(II), Cu(II), Tl(III) and Sn(IV) interfere.	17
Sodium metabisulfite	4-100	5 – 6 (Hexamine)	R.E ≤ ± 0.26 % C.V ≤ ± 0.40 %	Pd(II), Tl(III) and Sn(IV) interfere.	18
1-Propanethiol	4-85	5 – 6 (Hexamine)	R.E ≤ ± 0.23 % C.V ≤ 0.41 %	Pd(II), Cu(II), Tl(III) and Sn(IV) interfere.	19
2-Thiazolinethiol	4-78	5 – 6 (Hexamine)	R.E ≤ ± 0.25 % C.V ≤ 0.28 %	Pd(II), Tl(III) and Sn(IV) interfere.	20
3-Acetyl-2-thiohydantoin	3.9-80	5 – 6 (Hexamine)	R.E ≤ ± 0.25 % C.V ≤ 0.28 %	Pd(II) interfere.	Proposed method

solution by the standard methods[21]. Freshly prepared (0.5%) aqueous solutions of xylenol orange (indicator) was used. The masking agent 3-acetyl-2-thiohydantoin was prepared and purified by the reported method[22]. The purity of the sample was checked by the elemental analysis. The reagent was used as a 0.5% solution in acetone. 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 3.96-80.0 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 lead nitrate solution to a sharp colour change of xylenol orange from yellow to red. To this, a freshly prepared 0.5% solution of 3-acetyl-2-thiohydantoin 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 lead nitrate 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[23-27]. 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 3-acetyl-2-thiohydantoin

3-Acetyl-2-thiohydantoin (ATH) is a polydentate ligand with nitrogen, sulphur and oxygen as donor sites. Thus it may act as bidentate or poly dentate ligand, if required. According to hard soft acid base theory (HSAB)[28,29] soft mercury(II) forms strong bonds through soft sulphur of mercapto group. Therefore, it is reasonable to expect the bonding of Hg(II) with deprotonated sulphur of thiol group and oxygen of carbonyl group, which results in the formation of a stable chelate. The quantitative release of EDTA from Hg-EDTA complex by ATH indicates that $Hg(ATH)_2$ chelate is more stable than Hg-EDTA complex under the conditions employed[30]. The release of EDTA is quantitative and instantaneous at room temperature itself. The $Hg(ATH)_2$ complex formed is soluble under the experimental conditions and the detection of the end point is very sharp.

Effect of ATH concentration

It was observed that for instantaneous and quantitative release of EDTA from the Hg(II)-EDTA complex, the amount of ATH required was in the molar ratio of 1:2(M:L). For lower proportions of ATH, the release of EDTA is found to be incomplete. However, it was noticed that the addition of excess of ATH, as much as 10-fold excess over the required molar ratio does not have any adverse effect on the results obtained. In all subsequent determinations, the concentration of ATH 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, determination of mercury in the concentration range 3.96-80 mg were carried out under the optimized experimental conditions. The results show that the maximum relative error and coefficient of variation (n=6) of the method are ±0.25% and ±0.38% 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 19.80 mg of Hg(II) in the presence of different metal ions. No interference was observed for the following ions at the amounts in mg shown: Na(I) (50), K(I) (50), Mg(II) (100), Pb(II) (70), Zn(II) (60), Cu(II) (40), Co(II) (55), Ni(II) (48), Mn(II) (4), Cd(II) (50), Fe(III) (28), Al(III) (25), Bi(III) (100), Ce(III) (36), Ti(III) (24), Ir(III) (32), Tl(III) (60), Rh(III) (30), Ru(III) (40), Au(III) (5), Pt(IV) (50), Sn(IV) (45), Zr(IV) (50), Se(IV) (100), U(VI) (50), acetate(100), chloride(100), sulphate (100), oxalate(100), tartarate (100), phosphate(100). Metal ions like Pd(II) and Cr(III) show interference in this method with positive error. The interference of Pd(II) is due to the release of EDTA from the Pd-EDTA complex on the addition of ATH. 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. The presence of more than 5 mg of Mn(II) causes some difficulty in the detection of the end point, perhaps due to the low stability of its EDTA complex[31].

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 ions. The experimental results of these analyses are presented in Tables 2 and 3 respectively. It is evident from these results that the method can be conveniently employed in the analysis of mercury in its complexes and synthetic mixtures of ions with a fair degree of accuracy.

Table 2 – Analysis of mercury(II) complexes (n=4)

Complex	Hg(II) calculated (%)	Hg(II) found (%)	Relative error (%)
$Hg(CH_4N_2S)Cl_2$[a]	57.69	57.60	-0.15
$Hg(CH_4N_2S)_2Cl_2$[b]	47.34	47.31	-0.06
$[Cu(en)_2][HgI_4]$[c]	50.05	49.93	-0.23
$Hg(CH_6N_4S)_2Cl_2$[d]	41.46	41.31	-0.36

Mercury complexes of [a,b]thiourea, [c]ethylene-diamine, [d]thiocarbohydrazide.

Table 3 – Analysis of mercury(II) in synthetic mixtures of ions
(n=4)

Mixture	Hg(II) present (%)	Hg(II) found (%)	Relative error (%)
Hg(II) + Zn(II) + Cu(II)	19.84 + 50.10 + 30.06	19.80	-0.20
Hg(II) + Zn(II) + Ni(II)	12.40 + 43.80 + 43.80	12.38	-0.16
Hg(II) + Al(III) + Co(III)	22.40 + 20.60 + 57.00	22.33	-0.31
Hg(II) + Cu(II) + Co(II) + Bi(III)	18.00 + 18.30 + 27.30 + 26.40	18.00	0.00
Hg(II) + Ni(II) + Zn(II) + Cd(II)	19.80 + 20.00 + 30.00 + 30.20	19.78	-0.10

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 and the main advantage of the method when compared to other method is, no interference from Cu(II), Tl(III) and Sn(IV). The method is fairly selective for the rapid analysis of mercury in the presence of these ions.

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