

Determination of Mercury Using 4-Amino-3-Mercapto-1,2,4-Triazine (4H)-5-One as an Indirect Masking Reagent

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A selective complexometric determination of mercury is proposed, 4-amino-3-mercapto-1,2,4-triazine (4H)-5-one being used as masking agent. Mercury(II) is first complexed with a known excess of EDTA and the surplus EDTA is back titrated (pH 5.0-6.0, hexamine) with lead nitrate solution using xylenol orange as indicator. 4-Amino-3-mercapto 1,2,4-triazine (4H)-5-one in acetone-water mixture is then added to displace EDTA from the Hg-EDTA complex and the released EDTA is titrated with lead nitrate solution. Reproducible and accurate results are obtained in the range 5-72 mg of mercury. The interference of various cations has been studied. The method also works for the analysis of mercury in its complexes.

INTRODUCTION

Pribil and Korbl¹ reported the determination of Hg(II) by complexation with EDTA in presence of associated cations followed by selective decomposition of the Hg-EDTA complex with another masking agent such as thiosemicarbazide and titration of the liberated EDTA. In this method Cu(II) interferes severely. Ueno² suggested the use of potassium iodide as a masking agent in alkaline medium for estimating Hg(II) in the presence of Cu(II). In the method he suggested many ions are reported to be interfering. Singh³ described the determination of Hg(II) in presence of various cations with thiourea as masking agent. In this method the interference of copper was avoided by controlling the pH at 5.5 and cooling the solution to below 15°C. Good results are obtainable in presence of Cu(II) with thiourea as masking agent provided it is only in slight excess over the stoichiometric proportions. This condition is rather difficult to ensure in the case of unknown concentrations of mercury. Chickerrur and Venugopalam⁴ suggested a method for the determination of Hg(II) in presence of Ca²⁺ by masking Ca²⁺ with ammonium fluoride. The method of selective determination of Hg(II) followed by Vasilikiotis and Apostolopoulou⁵ using N-allyl thiourea is also not convenient because it involves heating to ensure complete decomposition of the Hg-EDTA complex. Besides the method involves precipitation of Hg(II) as HgS. The method of estimation of Hg(II) using thiocyanate⁶ as replacing reagent however found to be reliable besides being convenient.

The paper now reported highlights the merits of 4-amino-3-mercapto-1,2,4-triazine (4H)-5-one (AMT) as a selective masking agent for the determination of Hg(II) by complexometric titration with EDTA.

EXPERIMENTAL

Reagents

4-Amino-3-mercapto-1,2,4-triazine (4H)-5-one (AMT).

Synthesized using the reported procedure in the literature⁷ (M. pt. 148°C)⁸. Used as a 0.5% solution in acetone-water (50 : 50) mixture.

Mercuric nitrate solution

Prepared from the analytical grade sample and standardised by the ethylene diamine method⁹.

Lead nitrate solution : 0.02M

Prepared from AR grade sample and standardised by chromate method⁹.

EDTA solution, approx. 0.02M

Prepared by dissolving a good quality of disodium salt of EDTA in distilled water.

Xylenol orange indicator

0.5% aqueous solution.

Procedure

To an aliquot of the acidic solution (containing 5.72 mg) of Hg(II), a known excess of 0.02M EDTA solution is added and the mixture diluted to about 100 ml, followed by 5 drops of xylenol orange indicator. The pH of the solution is adjusted to between 5.0–6.0 by adding hexamine. The excess of EDTA is back titrated against the standard lead nitrate solution to the sharp colour change of the xylenol orange indicator. To this is then added excess (one fold excess over the molar ratio of 1 : 2 of 4-amino-3-mercapto-1,2,4-triazine (4H)-5-one solution in acetone-water mixture, the contents mixed well and allowed to stand for 3–5 minutes. The liberated EDTA is titrated against the lead nitrate solution. The second titre value is equivalent to Hg(II) present in the aliquot. The results are presented in Table 1.

Interference Studies

Interference of a number of metal ions *i.e.*, rare-earth metal ions and anions is studied in the determination of mercury by this method. Cations

TABLE I
RELIABILITY OF MERCURY (II) DETERMINATION IN
ITS SOLUTION

Mercury (II) taken (mg)	Mercury (II) found (mg)	Standard deviation	Recovery* %
4.82	4.82	0.02	100.41
12.05	12.02	0.02	99.75
24.10	24.09	0.02	99.96
36.15	36.27	0.03	100.33
48.20	48.30	0.02	100.21
60.25	60.12	0.02	99.78
72.30	72.42	0.02	100.17

*Average of 3 determinations.

such as Sn(IV), Pd(II) and Tl(III) are found to interfere rather severely. But the interference can be avoided by using suitable secondary masking agents. The results of analysis of Hg(II) (24.10 mg) in an aliquot are presented in Table 2.

TABLE 2
DETERMINATION OF MERCURY IN PRESENCE OF
DIVERSE METAL ION

(Mercury present in the solution = 24.10 mg)

Diverse ion	Level of conc. (mg)	Amount of* found (mg)	Mean	Recovery %
Cu(II)	6	24.17	24.17	100.29
	60	24.17		
Ni(II)	12	24.17	24.13	100.12
	30	24.09		
Co(II)	12	24.09	24.07	99.88
	30	24.05		
Zn(II)	10	24.01	24.07	99.88
	50	24.13		
Cd(II)	32	24.13	24.15	100.21
	80	24.17		

TABLE 2 (Contd.)

Diverse ion	Level of conc. (mg)	Amount of* found (mg)	Mean	Recovery %
Mn(II)	25	24.13	24.11	100.04
	5	24.09		
Pd(II)	1	24.13	24.15	100.21
	5	24.17		
Tl(III)	2	24.09	24.05	99.79
	10	24.01		
Al(III)	5	24.05	24.09	99.96
	50	24.13		
La(III)	14	24.13	24.17	100.29
	70	24.21		
Ce(III)	14	24.09	24.11	190.04
	70	24.13		
V(IV)	5	24.13	24.11	100.04
	10	29.09		
Ti(IV)	10	24.01	24.05	99.79
	25	24.09		
Zr(IV)	10	24.01	24.03	99.71
	25	24.05		
Sn(IV)	5	24.01	24.05	99.79
	10	24.09		
Chloride	50	24.09	24.11	100.04
	100	24.13		
Citrate	50	24.13	24.09	99.96
	100	24.05		
Tartarate	50	24.09	24.07	99.88
	100	24.05		
Phosphate	50	24.05	24.07	99.88
	100	24.09		
Acetate	50	24.09	24.09	99.96
	100	24.09		
Fluoride	50	24.17	24.09	99.96
	100	24.01		

*Average of 3 determinations.

Analysis of mercury complexes

A number of mercury(II) complexes with some sulphur containing ligands are prepared by the conventional methods and their purity checked from elemental analysis. About 0.1–0.2g of the complex was decomposed by evaporation to near dryness with aqua regia. The residue was then cooled, dissolved in water and made up to 100 ml. Aliquots of 10 ml are used for titration by the recommended procedure. The results are presented in Table 3.

TABLE 3
ANALYSIS OF MERCURY COMPLEXES

Complex	Mercury found %	Mercury present %
$\text{Hg}(\text{C}_3\text{H}_5\text{N}_4\text{S})_2^a$	43.51	43.36
$\text{Hg}(\text{C}_3\text{H}_6\text{N}_2\text{S})_2^b$	42.26	42.18
$\text{Hg}(\text{C}_4\text{H}_8\text{N}_2\text{S}_2)\text{Cl}_2^c$	39.75	39.84
$\text{Hg}(\text{C}_{10}\text{H}_{11}\text{N}_4\text{OS})_2^d$	29.85	29.91
$\text{Hg}(\text{C}_9\text{H}_7\text{N}_4\text{OS})_2^e$	31.45	31.31

a. Mercury complex of 4-amino-5-mercapto-3-methyl-1,2,4-triazole.

b. Mercury complex of imidazolidine-2-thione.

c. Mercury complex of 1,3,4,6-tetrahydropyrimidine-2-thione.

d. Mercury complex of 3-(*o*-tolylloxymethyl)-4-amino-5-mercapto-1,2,4-triazole,

e. Mercury complex of 4-amino-5-oxo-3-thioxo-2,3,4,6-tetrahydro-1,2,4-triazine.

RESULTS AND DISCUSSION

The fact that AMT displaces EDTA quantitatively from the Hg-EDTA complex indicates that Hg-AMT complex is more stable than Hg-EDTA complex. EDTA in the complex is released quantitatively and instantaneously at room temperature itself. The Hg-AMT complex is highly soluble in that medium. Thus the absence of any precipitate in the reaction mixture facilitates sharp end point. A minimum one-fold excess of the reagent over the molar ratio of 1 : 2 is however required for the complete release of the complexed EDTA. It is worthwhile to note that copper(II) can be tolerated even beyond three-fold excess without resorting to cooling below room temperature, unlike in some methods reported earlier. However no satisfactory results are obtained in the presence of Sn(IV), Pd(II), and Tl(III). But the interference in these cases can be

avoided by using secondary masking agents like fluoride for Sn(IV), dimethylglyoxime for Pd(II) and hydrazine sulphate for Tl(III).

Merits

The speciality of the reagent is that it does not form any precipitate with either Hg(II) the metal ion to be estimated or Pb(II) the titrant under the experimental conditions. This enables determination of sharp end point without the need for addition of the chemicals. The method works well in the range 5-72 mg of Hg.

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