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# Rapid Complexometric Determination of Mercury(II) Using Glutathione as a Selective Demasking Reagent

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A simple, rapid and selective complexometric method is proposed for the determination of mercury(II) in the presence of associated metal ions. Mercury(II) is first complexed with an excess of EDTA and the surplus EDTA is titrated against standard zinc sulphate solution at pH 5-6 using xylenol orange indicator. Glutathione is then added to displace EDTA from the Hg-EDTA complex quantitatively and the EDTA released is back titrated against a standard zinc sulphate solution as before. The method works well in the range 4 to 80 mg of mercury with a relative error of less than 0.30% and a coefficient of variation of not more than 0.38%. The effect of the presence of various diverse ions has been studied. The method is used for the determination of mercury(II) in its alloys and complexes.

**Key Words:** Complexometry, Demasking reagent, EDTA titration, Glutathione, Mercury determination.

## Introduction

The compounds of mercury are used extensively in insecticides, fungicides, and bactericides for agricultural and industrial purposes. Mercury forms useful amalgams with many metals. These amalgams find various applications in diverse fields such as Ag-Hg in dental fillings, Zn-Hg as a reducing agent in chemical synthesis and Cd-Hg in the Weston cadmium cell. The Hg-Tl alloy containing 8.7% Tl forms eutectic mixture freezing at –59 °C, and has been considered for applications in low temperature thermometers, switches, closures and seals. 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 normally not determined by direct EDTA titration, particularly in the presence of other ions[1]. Instead, mercury(II) and other metal ions are first complexed with EDTA, followed by the selective decomposition of the Hg-EDTA complex with suitable demasking reagents[1,2] and titration of the liberated EDTA. However, most of these methods suffer severe interference from many metal ions and some require

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heating for demasking the Hg-EDTA complex. 4-Amino-5-mercapto-3-propyl-1, 2, 4-triazole[3], thiocyanate [4], 2-imidazolidinethione[5], 2-mercaptoethanol [6], 3-mercapto-1,2-propanediol [7], acetylacetone[8], thioglycolic acid [9] and 2-mercapto propionyl glycine[10] are also used as demasking agents for Hg(II). Some of these reagents [3,5] require tedious and time-consuming procedures. In this paper, selective decomposition of the Hg-EDTA complex by the addition of glutathione at pH 5.0-6.0 at room temperature is described. The method, being accurate and reasonably selective, is simple and rapid as it does not require heating.

## Experimental

**Chemicals:** Analytical grade chemicals were used. Steam distilled water was used throughout for dilution purposes. A stock solution of mercury(II) (0.02 M) was prepared by dissolving mercury(II) nitrate (supplied by Merck) in distilled water and standardised gravimetrically by the ethylene diamine method [11]. EDTA solution (0.04 M) was prepared by dissolving the disodium salt of EDTA (Merck) in distilled water. Zinc sulphate solution (0.02 M) was standardized by the oxinate method [11]. A 1% solution of glutathione (Merck) was prepared in distilled water. A freshly prepared 0.5% aqueous solution of xylenol orange was used as indicator.

**Procedure:** To an aliquot of stock solution containing 4-80 mg of mercury and varying amounts of foreign metal ions, an excess of 0.04 M EDTA solution was added. The solution was diluted to about 100 mL with distilled water and the pH was adjusted to 5.0-6.0 with solid hexamine. A few drops of xylenol orange indicator were added and surplus EDTA was titrated with 0.02 M zinc sulphate solution to a sharp end point. To this, a freshly prepared solution of glutathione (1%) was added in required amounts (2 ml for each milligram of Hg) and the contents were mixed well. The EDTA released was then titrated with 0.02 M zinc sulphate solution as before. The second titre value corresponds to the amount of mercury present in the aliquot.

**Analysis of alloy samples:** An accurately weighed alloy sample (0.1-0.2 g) was dissolved in a minimum amount of concentrated $HNO_3$by slow heating on a water bath. The cooled solution was made up to the mark in a 100 mL standard flask. Suitable aliquots were analysed for mercury content as described.

**Analysis of mercury complexes:** Mercury(II) complexes with some sulphur-donor ligands were prepared and purified as per the reported methods [12–14]. A known weight (0.1-0.2 g) of the complex was carefully decomposed with aquaregia by evaporation to near dryness. The residue was then cooled, dissolved in distilled water and made up to the mark in a 100 mL standard flask. Aliquots of the made up solution were used for the determination of mercury.

## Results and Discussion

In the proposed method glutathione (GSH) selectively demasks mercury from the Hg-EDTA complex and releases EDTA quantitatively at room temperature. The demasked mercury then forms a highly soluble complex with GSH. It has been reported that GSH forms a stable 1:2 (M:L) complex with Hg(II)[15]. The stability constant ($\log K = 40.96$) [15] of $Hg(SG)_2$ being very large compared to that of the Hg-EDTA complex ($\log K = 21.50$), it is reasonable to expect that GSH can readily displace EDTA from the Hg-EDTA complex.

The addition of GSH in the molar ratio of 1:2 (M:L) was found to be sufficient for the instantaneous and quantitative release of EDTA from the Hg-EDTA complex. 2 mL of 1% solution of glutathione was

required for each milligram of mercury. Further more, it was noted that the addition of excess reagent had no adverse effect on the results obtained.

**Precision and Accuracy:** To assess the precision and accuracy of the proposed method, determinations of Hg(II) at different concentration levels were carried out under the experimental conditions. The results obtained (Table 1) are reproducible and accurate in the concentration range 4 to 80mg of Hg(II), with a relative error and coefficient of variation of not more than 0.30% and 0.38% respectively.

**Table 1.** Determination of mercury in mercury(II) nitrate solution.

| Hg, mg | | Coefficient of | Relative |
|---|---|---|---|
| Taken | Found * | variation, % | error, % |
| 4.02 | 4.03 | 0.38 | +0.25 |
| 8.04 | 8.02 | 0.32 | -0.25 |
| 12.06 | 12.04 | 0.26 | -0.17 |
| 20.10 | 20.06 | 0.21 | -0.20 |
| 28.14 | 28.19 | 0.12 | +0.18 |
| 40.20 | 40.16 | 0.15 | -0.10 |
| 60.30 | 60.40 | 0.13 | +0.17 |
| 80.40 | 80.58 | 0.14 | +0.22 |

* Mean of 6 determinations.

**Effect of foreign ions:** The presence of various foreign ions was examined for their possible interference in the determination of 20.10 mg of Hg(II). Of the various cations and anions tested individually in the estimation of Hg(II), no interference was observed in the presence of following ions: 200 mg of Zn(II), Pb(II), nitrate, phosphate, sulphate, acetate, borate, citrate, oxalate and tartarate; 180 mg of chloride and fluoride ; 60 mg of Ni(II), Co(II), Cd(II) and Bi(III) ; 40 mg of Al(III), Fe(III), Ti(IV) and Mo(VI) ; 20 mg of Ag(I), Mn(II), Ce(III), Zr(IV), Sb(V), V(V) and As(V) ; and 10 mg of Ru(III), Rh(III), Au(III), Cr(III) and Pt(IV). Metal ions such as Cu(II), Pd(II), Tl(III) and Sn(IV) show severe interference, giving positive errors. This is due to the simultaneous release of EDTA from their respective EDTA complexes by the reagent. However, the interference of Pd(II) (up to 20 mg), Tl(III) (40 mg) and Sn(IV) (25 mg) can be avoided by premasking these ions with L-histidine (3% $C_6H_9N_3O_2$, 10-12 mL), hydrazine sulphate (5% $H_4N_2H_2SO_4$, 6-8 mL) and sodium fluoride (5% NaF, 3-5 mL) respectively.

# Applications

The method was applied to the determination of mercury in alloy samples. The results shown in Table 2 are in good agreement with those obtained gravimetrically by the ethylene diamine method [11].The method was also used for the analysis of mercury complexes. The results are summarised in Table 3. It is evident from these results that the method can be conveniently employed for the rapid analysis of such samples.

# Conclusions

The proposed method is simple and rapid as it requires no heating. Reproducible and accurate results are obtained in the determination of 4-80 mg of mercury. The demasking reagent used forms no precipitate either with Hg(II) or with titrant under the experimental conditions. This facilitates the detection of a

sharp end point. The method tolerates the presence of a number of metal ions and anions and is useful for the rapid analysis of complexes and alloy samples of mercury with a fair degree of accuracy.

**Table 2.** Determination of mercury in alloy samples.

| Alloy | Hg Present*, % | Hg Found**, % | Relative error, % |
|---|---|---|---|
| Hg-Ag | 69.60 | 69.42 | -0.26 |
| Hg-Zn | 41.20 | 41.32 | +0.29 |
| Hg-Cd | 78.50 | 78.65 | +0.19 |

* Gravimetrically determined by the ethylene diamine method.
** Mean of 3 determinations.

**Table 3.** Determination of mercury in complexes.

| Complexes | Hg calculated, % | Hg found*, % | Relative error,% |
|---|---|---|---|
| $Hg(CH_4N_2S)_2Cl$ [a] | 47.28 | 47.14 | -0.30 |
| $Hg(CH_6N_4S)_2Cl_2$ [b] | 41.46 | 41.36 | -0.24 |
| $Hg(C_2H_2N_3S)_2$ [c] | 49.55 | 49.40 | -0.30 |
| $Hg(C_3H_5N_4S)_2$ [d] | 43.71 | 43.82 | +0.25 |
| $Hg(C_5H_9N_4S)_2$ [e] | 38.95 | 38.82 | -0.33 |
| $Hg(C_{12}H_{10}ONS)_2$ [f] | 31.70 | 31.80 | +0.32 |
| $Hg[Zn(CNS)_4]$ | 40.26 | 40.38 | +0.30 |

*Mean of 3 determinations.
Mercury complex with thiourea [a], thiocarbohydrazide [b], 1,2,4-triazole- 3(5)-thiol [c], 4-amino-5-mercapto-3-methyl-1,2,4-triazole [d], 4-amino–5-mercapto-3-propyl- 1,2,4-triazole [e] and thionalide [f].

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