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Original Research Article

A Highly Selective Complexometric Determination of Mercury (II) Using *L*-Tyrosine as a Masking Agent

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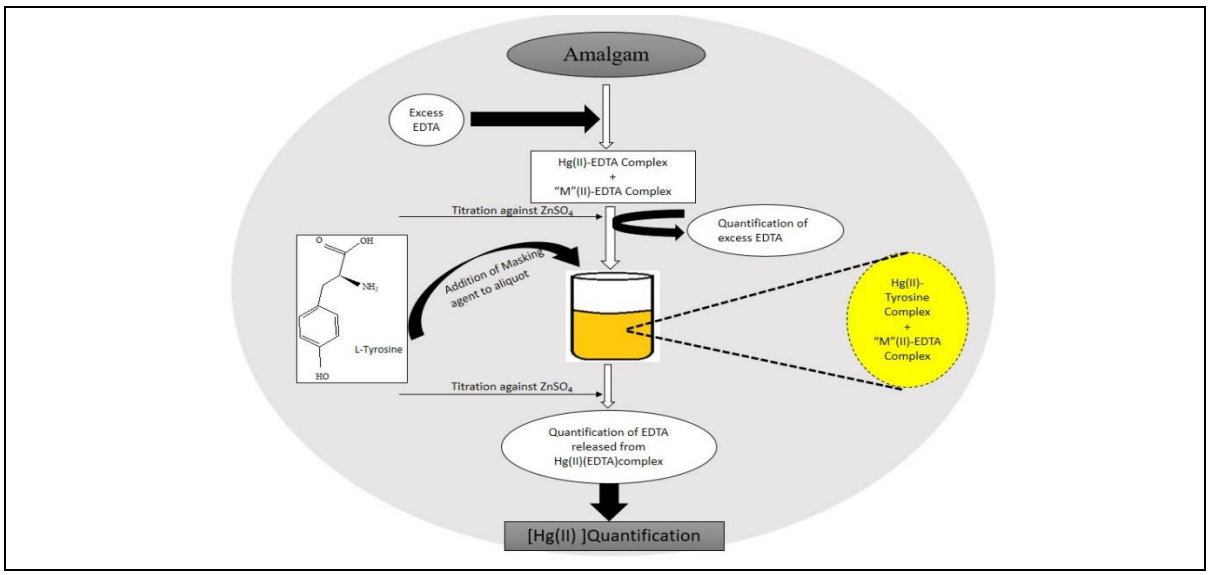
ABSTRACT

Determination of mercury in the existence of various other metal ions, a transparent speedy and accurate complexometric method is described, depending on the selective masking ability of *L*-Tyrosine towards Hg (II). Along with other associated metal ions, Hg (II) present in a given sample solution is first complexed with an surplus of EDTA and the leftover EDTA is titrated with Zinc sulfate solution in the presence of xylenol orange as an indicator at pH 5.0-6.0.A known excess of 0.02M *L*-Tyrosine solution is then added to discharge the EDTA from Hg (II)-EDTA complex and then it is mixed well. The displaced EDTA is again titrated with a Zinc sulfate solution. The method goes well in the range 4-80 mg of mercury (II) with the relative error ±0.4 and standard deviation ≤0.05 mg. The issue of the existence of various metal ions on the exactitude of the results has been studied. And the method can be applied for the determination of Mercury in alloys, in its synthetic mixtures of ions and its complexes.

GRAPHICAL ABSTRACT



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Introduction

Mercury metal naturally is a heavy, silvery-white liquid. Compared to other metals, it is a poor conductor of heat, but a fair conductor of electricity [1].

Mercury does not react with most of the acids, such as dilute sulfuric acid, although oxidizing acids such as concentrated sulfuric acid and nitric acid or aqua regia dissolve it to give sulfate, nitrate, and chloride. Like silver, mercury reacts with atmospheric hydrogen sulfide. Mercury reacts with solid sulfur flakes, which are used in mercury spill kits to absorb mercury (spill kits also use activated carbon and powdered zinc) [2].

Except for Iron, Mercury dissolves many metals such as gold and silver to form amalgams. Except for manganese, copper and zinc, several other first-row transition metals are also resistant in forming amalgams [3,4]. Sodium amalgam is a common reducing agent that is used in organic synthesis and is also used in high-pressure sodium lamps.

In chemical and biological processes Mercury plays an important key role.

Mercury is used in a variety of applications and its compounds are used as fungicides and pesticides. The amalgams find varied applications in diverse fields, such as Sn-Hg in the silvering of mirrors, Ag-Hg in dental fillings, Na-Hg as a reducing agent and Cd-Hg in Weston cadmium cell. The Hg-Tl alloy which forms a eutectic at 8.7% (by weight) of thallium, having a melting point of -60 °C, can be used in switches and seals for equipment used in the polar region or in the stratosphere. Often, a simple, speedy and an accurate analytical method for the determination of mercury content in the samples is required in most of these applications [5].

The various methods which are used for the determination of mercury include gravimetry, coulometry, neutron activation analysis, X-ray spectrometry, atomic absorption spectrometry, icp–optical emission spectrometry [6], mid-infrared spectroscopy [7], and spectrophotometry [8]. Most of these methods are disadvantageous in terms of cost and need and extreme care is required during the operation. Hence, the accurate determination of mercury using a simple and rapid method is of prime importance. Keeping this in view, the study of the complexometric determination of mercury using some sulfur-containing reagents has been taken up for investigation. As EDTA is an unselective complexing agent which forms stable complexes with most of the metal ions, mercury (II) cannot be accurately determined by direct EDTA titration, particularly in the existence of other metal ions [9]. Hence the usual practice is to use masking agent to complex only mercury (II) in the existence of other metal ions, by decomposing Hg (II)-EDTA complex. The released EDTA is titrated against the standard metal ion solution. A number of compounds like 3-Acetyl-2-thiohydantoin [10], 2-thiobarbituric acid [11], ethane thiol [12], thiomalic acid [13], 2-mercaptoethanol [14], 2-thiozolinethiol [15], *L*-cystine [16], have been tried as masking agents for mercury determination. However, most of these methods suffer severe interference from many metal ions and some require heating for demasking the Hg-EDTA complex. In this paper, selective decomposition of the Hg (II)–EDTA complex by the addition of *L*–tyrosine 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

Materials

All analytical reagent grade chemicals were used of. A stock solution of Hg (II) was prepared by dissolving a known amount of

Mercuric nitrate solution in Millipore water. The solution was standardized by the standard methods [17]. The titrant, Zinc sulphate solution (0.02M) was prepared by dissolving the fixed amount of Zinc sulphate crystals in Millipore water. 0.02 M *L*-Tyrosine was prepared by dissolving *L*-tyrosine in a small quantity of 2 M HCl solution. 0.02 EDTA solution was prepared by solubilising the required amount of disodium salt of ethylene diammine tetra acetic acid (EDTA) in Millipore water. Xylenol orange indicator was made by mixing it with potassium nitrate crystals in the ratio 1:100.

Standard procedure

To a solution containing 4-80 mg of mercury (II) in the existence of other metal ions taken in a 250 mL conical flask, an exuberance of 0.02 MEDTA was added, then the concentration of the solution was decreased by adding 60-70 mL of Millipore water. Solid hexamine was added to fix the pH to 5.0-6.0. Then the remaining EDTA in the conical flask was titrated against 0.02 M Zinc sulphate solution using Xylenol Orange as an indicator. The colour change was from yellow to orange. To the same solution, 0.02 M *L*-Tyrosine was added in the required quantity and shaken well. The EDTA which was liberated from the Hg-EDTA complex on adding *L*-Tyrosine was titrated against 0.02 M Zinc sulphate solution. The new titre value corresponds to the mercury (II) content in the aliquot.

Analysis of dental amalgam sample

An alloy sample was weighed accurately (0.1–0.2 g, supplied by multispecialty dental & implant centre, India). It was dissolved by slow heating on a water bath using a minimum amount of concentrated nitric acid [18,19]. After cooling, the solution was filtered, washed with Millipore water and made up to the mark in 100 mL standard flask. Shaken well for uniform concentration. Using suitable aliquots, analysis of mercury content was done as described.

Analysis of mercury complexes

Complexes of mercury with thiourea, thiocarbohydrazide, and imidazolidine–2–thione were prepared and purification was done by the conventional methods [20-22]. A known weight of the complex was carefully decomposed with aqua–regia by evaporation to dryness. After cooling, the residue was then dissolved in Millipore water and made up to the mark in 100 mL standard flask and shaken well. Aliquots of this solution were used for the estimation as described.

Results and Discussion

Masking property of L-Tyrosine

L-Tyrosine contains nitrogen and oxygen as donor sites and it's a polydentate ligand. It has been reported that *L*-Tyrosine forms a strong complex with Hg (II). The stability constant of Hg-EDTA is found to be lesser than the stability constant of Hg-*L*-Tyrosine complex. The stability constant of Hg-EDTA is 21.7 [23], which is less than the stability constant of the Hg-*L*-Tyrosine complex [24]. The liberation of EDTA quantitatively from Hg (II)-EDTA complex by *L*-Tyrosine at lab temperature again confirms that the Hg-EDTA complex is less stable than Hg (II)-*L*-Tyrosine complex under the experimental conditions employed.

Effect of L-Tyrosine concentration

To find the exact amount of *L*-Tyrosine required for the quantitative liberation of Hg (II) from the Hg-EDTA complex, titrations were carried out by taking 8mg of Hg (II) and varying amounts of *L*-Tyrosine was added. From the plot of the volume of reagent added versus the volume of Hg (II) recovered, it is clear that to release 8mg of Hg (II) from Hg-

EDTA complex 2.5 mL of 0.02 M *L*-Tyrosine was required. Inclusion of an excess of the reagent over the requisite amount has no adverse effect on the experimental results as shown in Figure 1.

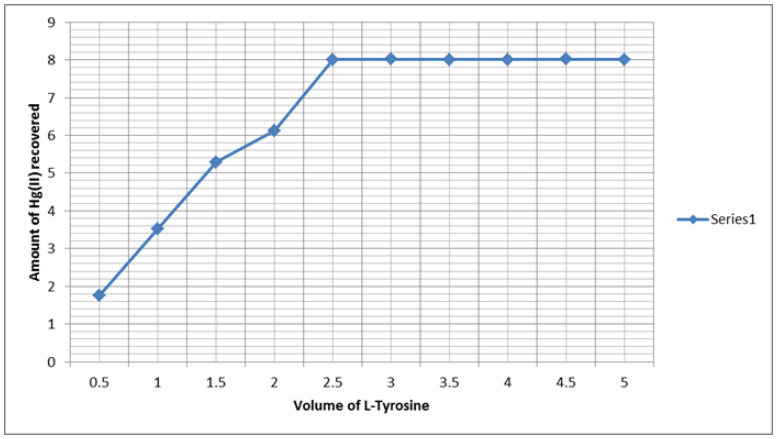

Figure 1. Effect of *L*-Tyrosine concentration

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

Hg (II) calculated (mg)	Hg (II) found (mg)	Standard deviation	Relative error (%)
4.01	4.03	0.01	0.40
8.02	8.01	0.01	-0.14
12.03	12.02	0.01	-0.10
14.04	15.98	0.02	-0.35
20.06	20.02	0.03	-0.16
24.07	24.06	0.02	-0.04
28.08	28.06	0.01	-0.04
32.09	32.12	0.04	0.09
36.10	35.99	0.01	-0.29
40.12	40.08	0.05	-0.09
52.16	52.14	0.01	-0.03
64.19	64.16	0.01	-0.04
72.22	72.21	0.01	-0.01
80.25	80.24	0.01	-0.01

*Average of 5 determinations

Reliability of the proposed method

To evaluate the precision and accuracy of the recommended method, the estimation of mercury at different concentration levels were carried out under optimized experimental conditions. Reproducible and accurate results were achieved in the range 4-80mg of mercury with relative error ±0.4% and the standard deviation not exceeding 0.05 (Table1).

Effect of varied ions

The study of possible interference due to various metal ions in the determination of 16.048 mg of Hg (II) was done using recommended procedure. The results obtained are as follows, no interference was observed in the presence of following ions: 200 mg of Pb(II), Zn(II), acetate, chloride, sulphate, oxalate, tartarate and phosphate; 50 mg of Ni(II), Bi(III), Cd(II) Co(II), Sn(IV); 30 mg of Al(III), Fe(III), Ti(III) and Mo(VI), 20 mg of Ag(I), Cu(II), Ce(III), Zr(IV), V(V), and As(V).

Analytical applications of the method

Table 2. Analysis of mercury (II) in complexes

Complex	Hg (II) Calculated (%)	Hg (II) Found* (%)	Relative error (%)
Hg $(CH_4N_2S)_2Cl_2$ [a]	47.29	47.28	-0.02
Hg $(CH_6N_4S)_2Cl_2$ [b]	41.41	41.29	-0.28
Hg $(C_3H_6N_2S)_2Cl_2$ [c]	42.11	42.08	-0.07

Complexes of mercury (II) with [a] Thiourea
[b] Thiocarbahydrazide
[c] Imidazolidine-2-thione
*Average of four determinations

Table 3. Analysis of mercury (II) in amalgam

Alloy	Composition (%)	Hg (II) Found* (%)	Relative error (%)
Hg +Ag + Sn + Cu + trace metals	50 + 22.32 + 14 + 8 + 5.68	49.94	0.001

*Average of four determinations

Table 4. Analysis of mercury (II) in mixtures of ions

Mixture	Composition (%)	Hg (II) Found* (%)	Relative error (%)
Hg(II) + Zn(II) +Pb(II)	15.40 + 70.50 + 14.10	15.42	+0.13
Hg(II) + Zn(II) + Cu(II)	19.84 + 50.10 + 30.06	19.79	-0.25
Hg(II) + Zn(II) + Ni(II) + Co(II)	19.50 + 35.80 + 17.90 + 26.80	19.48	-0.10
Hg(II) + Cu(II) + Co(II) + Bi(III)	16.00 + 30.30 + 27.30 + 26.40	16.00	0.00

*Average of four determinations

Conclusion

The proposed method does not require heating, reconstruction of pH and any extraction. It is simple rapid and reliable. Tyrosine does not form any precipitate with the metal ion which is to be determined and the titrant. This method is suitable for the determination of mercury (II), in amalgam, complexes and in mixtures. The most advantage of this method is that there is no interference from most of the metal ions and this method is selective in the determination of mercury in the existence of other metal ions.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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