International Journal of Chemical Studies

P-ISSN 2349–8528
E-ISSN 2321–4902
IJCS 2015; 3(1): 27-29
© 2015 JEZS
Received: 25-04-2015
Accepted: 22-05-2015

Nagaraj P.
Department of Chemistry,
Dr. M.V.Shetty Institute of
Technology, Moodbidri,
Mangaluru-574225, Karnataka,
India.

Gopalakrishna Bhat N.
Department of Chemistry,
Srinivas Institute of Technology,
Valachil, Mangaluru – 574143,
Karnataka, India.

Chandrashekara K.G
Department of Chemistry,
Srinivas Institute of Technology,
Valachil, Mangaluru – 574143,
Karnataka, India.

Correspondence:
Nagaraj P.
Department of Chemistry,
Dr. M.V.Shetty Institute of
Technology, Moodbidri,
Mangaluru-574225, Karnataka,
India.

Indirect complexometric determination of Mercury(II) using L-Cystine as a selective masking agent

Nagaraj P., Gopalakrishna Bhat N., Chandrashekara K.G.

Abstract
A complexometric method for the determination of mercury in the presence of other metal ions based on the selective masking ability of L-Cystine towards mercury is described. Mercury(II) present in a given sample solution is complexed with a known excess of EDTA and surplus EDTA was titrated against lead nitrate solution at pH 5-6 using xylenol orange as the indicator. A known excess of 0.02M solution of L-Cystine is then added. The mixture is then shaken well and the EDTA released from Hg-EDTA complex was titrated against the standard lead nitrate solution. Reproducible and accurate results were obtained for 4.18–83.6 mg of mercury(II) with relative error ≤ 0.23 % and standard deviations ≤ 0.04 mg. The interference of various ions is studied. This method was applied to the determination of mercury(II) in its synthetic mixtures of ions, alloys and complexes.

Keywords: Complexometry, L-Cystine, Mercury(II) determination, Masking

1. Introduction

Mercury plays key role in chemical and biological processes. The methods used for the determination of mercury include, gravimetry, coulometry, neutron activation analysis, X–ray spectrometry, atomic absorption spectrometry, icp–optical emission spectrometry [1], mid–infrared spectroscopy [2], and spectrophotometry [3]. 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 prime importance. Keeping this in view, the study of the complexometric determination of mercury using some sulphur containing reagents, has been taken up for investigation. Normally mercury(II) cannot be accurately determined by direct EDTA titration, particularly in the presence of other metal ions [4] 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 like thiourea [5], thioglycolic acid [6], Glutathione [7], 2-mercaptoethanol [8], 2-thiozolinethiol [9], 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–cystine 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.

L- Cystine

Hg(II)- L-Cystine Complex

2. Materials and Method

2.1 Chemicals

All the reagents used were of analytical reagent grade or chemically pure grade. The stock solutions of mercury(II) chloride (supplied by Merck, India), 0.04M EDTA (Merck, India) and 0.02M lead nitrate (Merck, India) were prepared by dissolving requisite amounts of the compounds in minimum amount of distilled water, making up to the mark with distilled water and standardizing the solution by standard methods [10]. A 0.02M solution of L–Cystine (Merck, India) was prepared by dissolving in dilute hydrochloric acid and then diluted using deionised water. Solutions of various metal ions were prepared by dissolving calculated amounts of metal nitrate in distilled water. Xylenol orange indicator was made by mixing it with ground potassium nitrate crystals (1:100).

2.2 Procedure

To an aliquot of acidic solution containing 4.18–83.6 mg of mercury(II), excess of 0.04M EDTA was added and the solution was diluted with 25 mL of distilled water. The pH of the solution was adjusted to 5.0 to 6.0 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 0.02M solution of L–Cystine was added in the 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.

2.3 Analysis of dental amalgam sample

An accurately weighed alloy sample (0.1–0.2 g, supplied by Sri Ananthapadmanabha Dental Clinic, India) was dissolved in a minimum amount of concentrated nitric acid [11, 12] by slow heating on a water bath. The cooled solution was filtered, washed with distilled water and made up to the mark in 100 mL standard flask. Suitable aliquots were analysed for mercury content as described.

2.4 Analysis of mercury complexes

Mercury complexes with thiourea, thiocarbohydrazide and imidazolidine–2–thione were prepared and purified by the conventional methods [13, 14, 15]. 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 proposed procedure.

3. Results and discussion

3.1 Masking action of L–Cystine

L–Cystine [16] is readily available. It is a polydentate ligand with nitrogen, sulphur and oxygen as donor sites. Hg(II) bonds through sulphur of disulfide linkage, two oxygen atoms of two carbonyl groups and two nitrogen atoms of two ammine groups resulting in the formation of (1:1) stable complex [17]. The quantitative release of EDTA from Hg–ETDA complex by L–Cystine indicates that Hg – L–Cystine 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(II)–L–Cystine complex formed is soluble under the experimental conditions and the detection of the end point is very sharp.

3.2 Effect of L–cystine concentration

It was observed that for instantaneous and quantitative release of EDTA from the Hg(II)–EDTA complex, the amount of L–cystine required was in the molar ratio of 1:1 (M:L). For lower proportions of L–Cystine, the release of EDTA is found to be incomplete. However, it was noticed that the addition of excess of L–Cystine, as much as 10–fold excess over the required molar ratio doesnot have any adverse effect on the results obtained. In all subsequent determinations, the concentration of L–Cystine was maintained at slight excess over 1:1 (M:L) molar ratio.

3.3 Accuracy and precision

In order to check the accuracy and precision of the method, several determinations of mercury in the concentration range 4.18–83.6 mg were carried out under the optimized experimental conditions. The results in Table 1 show that the maximum relative error and the standard deviation of the method are ± 0.23 % and ≤ 0.04 mg respectively. From these results, it is reasonable to infer that the proposed method is precise and accurate.

Table 1: Determination of mercury in mercury(II) chloride solution (1.4183 g of $HgCl_2$ in 250 mL distilled water, i.e 0.02 M Solution)

Hg(II) Calculated (mg)	Hg(II)Found* (mg)	Standard deviation	Relative Error (%)
4.18	4.17	0.03	-0.23
8.36	8.35	0.02	-0.12
16.72	16.73	0.02	0.05
25.08	25.06	0.04	-0.07
33.44	33.42	0.01	-0.06
41.80	41.77	0.03	-0.07
62.70	62.66	0.04	-0.06
83.60	83.55	0.02	-0.06

* Average of Five determinations.

3.4 Effect of foreign ions

The presence of various foreign ions was examined for their possible interference in the determination of 16.72 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 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),Tl(III), Ce(III), Zr(IV), Sb(V), V(V), and As(V). Pd(II) shows severe interference in this method with positive error. The interference of Pd (II) is due to the release of EDTA from Pd–EDTA complex on the addition of L–Cystine and this can be obviated by using D L–methionine [3mL (1%)] for each 10 mg of Pd(II) [18]. D L–methionine is a sulphur containing proteinogenic amino acid. The coordination of the amino acid to Pd(II) through the carboxylate and amino groups in a square planar geometry [19, 20]. The presence of more than 5mg of Mn(II) causes some difficulty in the detection of end point, perhaps due to the low stability of its EDTA complex [21].

3.5 Applications

In order to explore the practical application of the proposed method, it was extended for the determination of mercury in its complexes, alloys and in synthetic mixture of ions. The experimental results of these analysis are presented in Tables 3, 4 and 5 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

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

* Average of four determinations

Mercury complexes of^{a}thiourea, ^{b}thiocarbohydrazide and ^{c}imidazolidine-2-thione

Table 3: Analysis of mercury(II) in solutions of mercury amalgam

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

* Average of four determinations.

Table 4: Analysis of mercury(II) in synthetic 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.

4. Conclusion

The masking agent L–Cystine does not form precipitate with mercury(II), the metal ion to be determined or the titrant (lead nitrate) under the experimental conditions. This facilitates the sharp end point without the need for addition of other chemicals. The investigated method is accurate, yet also simple and rapid as it does not require cooling or heating before or during the titration and does not require standardization of EDTA. The investigated method does not require the readjustment of pH after the addition of masking agent. The reproducible and accurate results in the analysis of complexes revealed that the investigated method can be suitable for the determination of mercury in its complexes and synthetic mixtures of ions. The main advantage of the investigated method when compared to other methods is, no interference from Cu(II), Tl(III) and Sn(IV). The investigated method is fairly selective for the rapid analysis of mercury in the presence of these ions.

5. Acknowledgement

The authors are grateful to the Srinivas Institute of Technology for providing the laboratory facilities.

6. References

1. Hellings J, Adeloju SB, Verheyen TV. Rapid determination of ultra-trace concentrations of mercury in plants and soils by cold vapour inductively coupled plasma-optical emission spectrometry. Microchem. J 2013; 111:62-66.
2. Sharon R, Jean-Philippe, Nicole Labbé, Jennifer A, Franklin, Amy Johnson. Detection of mercury and other metals in mercury contaminated soils using mid-infrared spectroscopy. Proceedings, International Academy of Ecology and Environmental Sciences (IAEES), 2012.
3. Hamza A, Bashammakhb AS, Al-Sibaai AA, Al-Saidi HM, El-Shahawi. Spectrophotometric determination of trace mercury (II) in dental-unit wastewater and fertilizer samples using the novel reagent 6-hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)-one and the dual-wavelength β-correction spectrophotometry. J. Hazard. Mater 2010; 178:287-292.
4. West TS. Complexometry with EDTA and related reagents, BDH Chemicals Limited, Poole, 1969, 105.
5. Singh RP. Selective complexometric determination of mercury using thiourea as masking agent Talanta 1969; 16(10):1447-1450.
6. Prakash Shetty, Nityananda Shetty A, Gadag RV. Complexometric determination of mercury(II) using thioglycollic acid as a selective masking reagent. *Rev. Roum. Chim.* 2000; 45(9):841- 843.
7. Prakash Shetty, Nityananda Shetty A. Rapid Complexometric Determination of Mercury(II) Using Glutathione as a Selective Demasking Reagent. Turk. J.Chem 2004; 28:573-578.
8. Rao MB, Narayana B. Complexometric determination of mercury(II) using 2-mercaptoethanol as an indirect agent, Chim. Acta Turc. 1993; 21:27-32.
9. Parameshwara P, Karthikeyan J, Nityananda Shetty A, Prakash Shetty. Quantitative Complexometric Determination of Mercury(II) in synthetic alloys and complexes using 2-thiazolinethiol as a masking agent. J. Iran. Chem. Soc 2006; 3(2):168-172.
10. Vogel AI. A Text Book of Quantitative Inorganic Analysis, 3rd Ed., Longmann Press, London, 1968.
11. Granath LE, Bladh E, Edlund J. Amalgam Specimen Technic. I. Studies on Comparable Specimens Controlled by Complexometric Titration of Mercury Content, J. Dent. Res 1967; 46(2):417-423.
12. Dulski TR. Trace Elemental Analysis of Metals: Methods and Techniques, 10th ed., Marcel Deckker, Inc: New York, 1999, 99.
13. Vogel AI. A Text Book of Quantitative Inorganic Analysis, 3rd Ed., Longmann, London, 1964, 487.
14. Gupta BK, Gupta DS, Dikshit SK, Agarwala U. Indian J. Chem. 1977; 15(A):624-626.
15. Allen CFH, Edens CO, Van Allan. Ethylene thiourea. Org. Syn. Coll. 1955; 3:394.
16. Chandrashekhara KG, Gopalakrishna Bhat N, Nagaraj P. Selective Complexometric Determination of Palladium by Using L-Cystine as Releasing Agent, Asian J. Chem 2015; 27(3):882-884.
17. Ali MM, Jesmin M, Salam SMA, Habib MR, Khanam JA. Mercury(II) Cystine complex as antineoplastic agent, Medical Journal of Islamic World Academy of Sciences. Medical Journal of Islamic World Academy of Sciences 2009; 17(2):81-86.
18. Rao MB, Narayana B. Selective complexometric determination of palladium(II) using DL-methionine as a selective masking agent. Analyst 1994; 119:2217-2219.
19. Pedro P. Corbi, Petr Melnikov, Antonio C.Massabni. Powder X-ray characterization of djenkolic acid. J. of Alloys and Compounds 2000; 308:153-157.
20. Pedro P Corbi, F lavia Cagnin, Lilian PB. Sabeh, Antonio C Massabni, Claudio M Costa-Neto. Synthesis, spectroscopic characterization and biological analysis of a new palladium(II) complex with methionine sulfoxide. Spectrochimica Acta Part A 2007; 66:1171-1174.
21. Raoot KN, Raoot S. Selective complexometric determination of palladium with thiosulphate as masking agent. Talanta 1986; 33(6):544-546.