

THIOACETAMIDE AS A RELEASING AGENT FOR THE COMPLEXOMETRIC DETERMINATION OF THALLIUM(III) IN ITS SYNTHETIC ALLOYS AND COMPLEXES

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A simple and selective complexometric method for the determination of thallium is proposed, based on the masking ability of thioacetamide towards thallium(III). Thallium present in a given sample solution is first complexed with a known excess of EDTA and the surplus EDTA is titrated with standard zinc sulphate solution at pH 5-6 (hexamine buffer) using xylenol orange as the indicator. A 0.8% aqueous solution of thioacetamide is then added to displace EDTA from the Tl(III)-EDTA complex. The released EDTA is titrated with standard zinc sulphate solution as before. Reproducible and accurate results are obtained for 0.018 - 0.371 mol L⁻¹ (3.79mg - 75.91mg) of Tl(III) with relative error less than $\pm 0.43\%$ and coefficient of variation not more than 0.26%. The interference of various ions was studied and the method was used for the analysis of thallium in its synthetic alloy mixtures and also in complexes.

INTRODUCTION

Thallium alloys and its complexes find various applications in diverse fields such as photo-electric cells, insoluble anodes, corrosion inhibitors and fungicides. Considering these excellent and extensive applications of thallium alloys and its complexes, a reliable and rapid method is often essential for the determination of thallium in a single stage.

Owing to poor selectivity, earlier complexometric methods,^{1,2} for thallium could not be used for the determination in its alloys. Complexometric titrations, particularly those involving masking and demasking technique are of considerable importance as they provide simple and rapid method for the determination of a specific desired metal ion in the presence of associated metal ions. In the determination of thallium by this technique, it is first complexed with EDTA followed by selective decomposition of Tl-EDTA complex with the suitable masking agent. The released EDTA is back titrated with suitable titrant. Literature survey shows that a number of sulphur-nitrogen donor

ligands such as thiopyrene,³ thiosemicarbazide,⁴ hydrazine sulphate,⁵ 2-mercapto ethanol,⁶ thiocarbohydrazide,⁷ ascorbic acid,⁸ DL-cysteine,⁹ 3-mercapto-1,2-propanediol,¹⁰ ethylene thiourea,¹¹ sodium sulfite,¹² 2-thiazoline-2-thiol,¹³ hydroxylamine hydrochloride,¹⁴ semicarbazide hydrochloride,¹⁵ thiosulfate,¹⁶ thiourea,¹⁷ cysteamine hydrochloride,¹⁸ thioglycolic acid,¹⁹ oxalic acid,²⁰ etc. have been used as selective masking agents in the complexometric determination of Tl(III). Some of these methods either require heating or re-adjustment of pH for the quantitative release of EDTA from Tl-EDTA complex. In many of the methods, Cu(II) interferes and other ions show interference in other methods. A comparison of the reported method with the presently proposed method is given in the Table 1.

The present investigation describes, the use of thioacetamide as a masking agent for the selective and quantitative determination of thallium(III). The effects of foreign ions are studied and application of the method in the analysis of mixture of ions and thallium complexes is also reported in this paper.

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Table 1

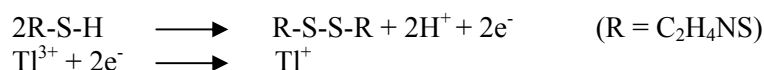
Comparison of the reported reagents with the proposed reagent

Reagent	Interfering ions	Reference
Thiosemicarbazide	Hg(II), Cu(II), Fe(II), Pd(II), Sn(II), Cr(III), Bi(III) and Al(III)	4
Hydrazine sulphate	Cr(III), Mn(II), Sn(IV), Pd(II), Ga(III), In(III) and Al(III)	5
2-mercaptoethanol	Pd(II), Hg(II), Cu(II), Cr(III) and Sn(IV)	6
Thiocarbohydrazide	Cu(II), Pd(II), Hg(II), Bi(III), Zr(III) and Sn(IV)	7
Ascorbic acid	Ag(I), Cu(II), Hg(II), Pb(II), Au(III), Sb(IV) and Sn(IV)	8
DL-Cysteine	Cu(II), Pd(II) and Hg(II)	9
3-Mercapto-1,2-propanediol	Pd(II), Hg(II) Cu(II) Cr(III) and Sn(IV)	10
Ethylene thiourea	Ag(I), Hg(II) and Sn(IV)	11
Sodium sulfite	Hg(II), Pd(II) and Sn(IV)	12
2-Thiazoline-2-thiol	Hg(II), Pd(II), Cu(II), Fe(III), Al(III) V(III), Cr(III), Ce(IV) and Sn(IV),	13
Hydroxylamine hydrochloride	Ag(I), Hg(II), Pd(II), Au(III), Sb(IV) and Sn(IV)	14
Thiosulfate	Pd(II), Hg(II), Au(III), Zr(III) and Sn(IV)	16
Thiourea	Cu(II), Pd(II), Hg(II), Zr(III) and Sn(IV)	17
Cysteamine hydrochloride	Cu(II), Pd(II) and Sn(IV)	18
Thioglycolic acid	Pd(II), Hg(II) Cu(II) Cr(III) and Sn(IV)	19
Thioacetamide	Hg(II), Pd(II) and Sn(IV). For Hg(II) interference obviated by using acetyl acetone.	Proposed reagent

RESULTS AND DISCUSSION

Mechanism of demasking

Generally, a metal, which can exist in two different oxidation states, differs in its tendency to form a stable complex with EDTA at different oxidation states. Thallium is such an element, which forms a stable complex with EDTA ($\log K=22.5$) in its trivalent state,²⁵ but shows little tendency for complexation with EDTA in its monovalent state.²⁶ Even if thallium (I) forms a



Thus, thioacetamide selectively demasks thallium from Tl(III)-EDTA complex through a change in the oxidation state of thallium (reduction) and thereby releases EDTA quantitatively. Besides changing the oxidation state of thallium, Thioacetamide (TA) acts as a monodentate ligand and can form a 1:1 complex with Thallium(I).²⁹ According to hard soft acid base theory^{30, 31} soft Thallium(I) forms strong bond through soft sulphur of mercapto group. It leads to the formation of a stable and soluble complex with Tl(I). The +1 oxidation state of thallium in its complex was confirmed by spot test.³² A red precipitate was formed when a solution of the complex in dilute hydrochloric acid was treated with one drop of bismuth nitrate solution and sodium iodide solution.

complex with EDTA it behaves like this only in basic medium (pH 8-9) and complete decomposition of Tl(I)-EDTA complex takes place in acidic medium.²⁷ Therefore, the redox behaviour of Tl(III)-Tl(I) can be conveniently employed in acidic medium for its complexometric determination by demasking technique.

Being a good reducing agent, thioacetamide effectively reduces Tl(III) to Tl(I) by a 2-electron change process.²⁸ The redox reaction can be represented as follows

Effect of reagent concentration

It was observed that for instantaneous and quantitative release of EDTA from the Tl(III)-EDTA complex, the amount of thioacetamide required was in the molar ratio of 1:2(M:L). However, no adverse effects on the results were observed even on adding 10 fold excess over the required quantity of the reagent. In all our subsequent determinations the concentration of the reagent was maintained slightly above the required molar ratio.

Accuracy and precision

In order to check the accuracy and precision of the method, determinations of thallium in the

concentration range of 0.018 - 0.371 mol L⁻¹ (3.79 – 75.91mg) were carried out under optimized experimental conditions. These results are presented in Table 2. The results show that the maximum

relative error does not exceed $\pm 0.43\%$ and the coefficient of variation not more than $\pm 0.26\%$. From these results, it is reasonable to infer that the proposed method is precise and accurate.

Table 2

Precision and accuracy in the determination of thallium(III) (n=6)

Thallium, mg		Relative error (%)	Standard deviation	Coefficient of variation (%)
Taken	Found			
3.79	3.79	0.00	0.01	0.26
7.59	7.60	+0.13	0.02	0.26
11.38	11.40	+0.17	0.03	0.26
18.97	18.97	0.00	0.04	0.21
37.95	37.92	-0.07	0.04	0.10
56.93	56.98	+0.08	0.04	0.07
75.91	75.94	+0.03	0.03	0.03

(n- Number of average determination)

Effect of foreign ions

In order to ascertain the possible interference of the diverse ions, thallium determination was carried out with an aliquot containing 11.55mg of Tl(III) in the presence of various metal ions and anions. The non interfering ions having minimum error with maximum precision are listed in Table 3. However, Pd(II), Hg(II), Cr(III) and Sn(IV) show interference. The interference of Pd(II), Hg(II) and

Sn(IV) is due to the release of EDTA from their EDTA complexes on the addition of the reagent. The interference of Cr(III) is mainly due to the deep purple color of its EDTA complex, which makes the detection of the end point rather difficult. However, the interference of Hg(II) can be avoided by pre-masking the metal ions with acetyl acetone as a secondary masking agent.

Table 3

Determination of 11.55mg of Tl(III) in the presence of foreign ions (n=4)

Metal ions	Quantity added (mg)	Thallium found (mg)	Relative error (%)
Mg(II)	15	11.54	-0.08
Mn(II)	30	11.58	+0.26
Co(II)	75	11.58	+0.26
Ni(II)	100	11.54	-0.08
Cu(II)	75	11.54	-0.08
Zn(II)	200	11.54	-0.08
Cd(II)	15	11.50	-0.43
Pb(II)	200	11.54	-0.08
Fe(II)	15	11.58	+0.26
La(II)	150	11.54	-0.08
Hg(II)*	10	11.58	+0.26
Y(III)	150	11.54	-0.08
Ir(III)	75	11.54	-0.08
Al(III)	75	11.54	-0.08
Bi(III)	5	11.58	+0.26
Rh(III)	100	11.55	0.00
Ru(III)	5	11.54	-0.08
Au(III)	2	11.50	-0.43
As(III)	100	11.54	-0.08
Sb(IV)	25	11.54	-0.08
Pt(IV)	50	11.54	-0.08
Se(IV)	150	11.58	+0.26
U(VI)	50	11.54	-0.08
W(VI)	150	11.54	-0.08

Table 3 (continues)

Table 3 (continued)

Cl ⁻	150	11.54	-0.08
CH ₃ COO ⁻	100	11.54	-0.08
Phosphate	50	11.50	-0.43
Citrate	150	11.54	-0.08
Tartarate	150	11.54	-0.08
Acetate	80	11.58	+0.26
Borate	50	11.54	-0.08
Sulphate	150	11.54	-0.08
Oxalate	100	11.54	-0.08

*Pre-masked using Acetyl acetone(5mL).

Application

In order to explore the utility of the proposed method, it was extended for the determination of thallium in its complexes and in synthetic mixture of

metal ions. The analytical reports of such samples are given in Tables 4 and 5. It is evident from these results that the method can be conveniently employed in the analysis of thallium in its complexes and alloys with a fair degree of accuracy.

Table 4

Analysis of thallium complexes (n=4)

Complex	Thallium calculated (%)	Thallium found (%)	Relative error (%)
Tl(C ₄ H ₇ N ₄ S) ^a	58.83	58.76	-0.12
Tl(C ₃ H ₅ N ₄ S) ^b	61.37	61.25	-0.19
Tl(C ₅ H ₉ N ₄ S) ^c	56.55	56.53	-0.03
Tl(C ₂ H ₂ N ₃ S ₂) ^d	60.73	60.70	-0.04

Thallium complexes of ^a4-amino-5-mercapto-3-ethyl-1,2,4-triazole, ^b4-amino-5-mercapto-3-methyl-1,2,4-triazole, ^c4-amino-5-mercapto-n-propyl-1,2,4-triazole, ^d5-amino-2-mercapto-1,3,4-thiadiazole.

Table 5

Determination of thallium in synthetic mixtures of metal ions (n=4)

Mixture	Composition (%)	Thallium found (%)	Relative error (%)
Tl(III) + Pb(II)	12.61 + 87.39	12.62	+0.08
Tl(III) + Co(II)	23.46 + 76.54	23.48	+0.08
Tl(III) + La(III)	24.73 + 75.27	24.73	0.00
Tl(III) + Pt(VI)	11.96 + 88.04	11.96	0.00
Tl(III) + Pb(II) + Sb(III)	23.46 + 15.32 + 61.22	23.43	-0.12
Tl(III) + W(VI) + Pb(II)	11.37 + 29.55 + 59.08	11.38	+0.08

EXPERIMENTAL PART

Reagents

All reagents used were of analytical or chemically pure grade. A Thallium nitrate solution was prepared as per the reported procedure.²¹ A known weight of thallos nitrate (Supplied by Merck, India) was dissolved in minimum amount of water, oxidized to Tl(III) by alkaline bromine, separated and purified by precipitation as Tl(OH)₃. It was then dissolved in 2M HCl, made up to the mark with distilled water and standardized by the chromate method and thionalide method.²² Zinc sulphate (Supplied by Merck, India) solution (0.02M) was prepared from an analytical reagent grade sample, and was standardized gravimetrically by the oxinate method and quinaldinate method.²² EDTA (Supplied by Merck, India) solution (~0.04M) was prepared by dissolving the di-sodium salt of EDTA in distilled water. A Freshly prepared 0.5% aqueous solution of the Xylenol orange (Supplied by Merck,

India) indicator was used. Thioacetamide (Supplied by Spectrochem, India) was used as a 0.8% solution in distilled water. Solutions of various metal ions were prepared by dissolving the appropriate metal salts in distilled water or with suitable acids.

Procedure

To an aliquot of the solution containing 0.018 - 0.371 mol L⁻¹ (3.79 - 75.91 mg) of thallium solution and varying amounts of diverse metal ions taken in a 250 mL conical flask, an excess of 0.04M EDTA solution was added. The solution was diluted with 20 mL of distilled water. The pH of the solution was adjusted to between 5-6 by adding solid hexamine. Excess EDTA was back titrated with standard zinc sulphate solution taken in a burette (Capacity 5mL, Sensitivity 0.02mL) to the sharp color change of xylenol orange indicator from yellow to red. A 0.8% aqueous solution of thioacetamide was added (just above 1:2 molar ratio M: L), shaken well and allowed to stand for two minutes. The released EDTA was back titrated

with standard zinc sulphate solution to the same end point as before. The second titre value is equivalent to the thallium content present in the aliquot.

Analysis of Thallium complexes

A number of thallium(I) complexes with 5-amino-2-mercapto-1,3,4-thiadiazole, 4-amino-5-mercapto-3-methyl-1,2,4-triazole, 4-amino-3-ethyl-5-mercapto-1,2,4-triazole, 4-amino-5-mercapto-3-n-propyl-1,2,4-triazole were prepared and purified as per the reported methods.^{23,24} A known weight of the complex was decomposed by evaporation to near dryness with aqua-regia. The residue was then cooled, dissolved in 3mL of 2M HNO₃, and made up to 250mL with distilled water. Aliquots of the made up solution were used for titration as per the proposed method using thioacetamide as a masking agent.

CONCLUSION

The proposed method is simple and rapid, as it does not require any adjustment of pH after the addition of the reagent or heating for the quantitative release of EDTA from Tl(III)-EDTA complex. The absence of any precipitate either with Tl(III) or with the titrant under the experimental condition facilitates easy detection of sharp end point. Since many metal ions do not show interference, the proposed method is fairly selective for the rapid analysis of thallium in the presence of these ions.

REFERENCES

- M. M. Amar, R. Pribil and M. S. Tawakkol, *Egypt J. Pharm. Sci.*, **1978**, *17*, 21; *Chem. Abstr.* **1979**, *90*, 13228.
- F. Ya. Kaluba and N.B. Platonova, *Zh. Anal. Khim.*, **1973**, *28*, 1009; *Chem. Abstr.* **1973**, *79*, 73253.
- T. L. Tanaka, *Yakugaku Zasshi*, **1973**, *93*, 252; *Chem. Abstr.* **1973**, *78*, 131678.
- B. Narayana and M. R. Gajendragad, *J. Indian Chem. Soc.*, **1987**, *64*, 620.
- A. Nityananda Shetty, R.V. Gadag and M.R. Gajendragad, *Indian J. Chem.*, **1988**, *27A*, 82.
- B. Muralidhara Rao and B. Narayana, *Acta Cienica Indica*, **1993**, *18C*, 193.
- B. Narayana, P. Lucos Jose, V. Karunakaran and M.R. Gajendragad, *Asian J. Chem.* **1993**, *5*, 115.
- B. Muralidhara Rao and B. Narayana, *Turk. J. Chem.*, **1993**, *17(2)*, 138.
- B. Narayana, Abraham Joesph and N. H. Praveen Chandra, *Acta Indica Chem.*, **1993**, *19*, 48.
- Prakash Shetty, A. Nityananda Shetty, A. M. A. Khader and R. V. Gadag, *Indian J. Chem. Tech.*, **1994**, *1*, 129.
- Abraham Joseph and B. Narayana, *Asian J. Chem.*, **1994**, *6*, 233.
- C. H. Raghavan Nambiar, B. Narayana, B. Muralidhara Rao and Biju Mathew, *Analyst*, **1995**, *120*, 1843.
- B. R. Vasundhara, A. Nityananda Shetty and R. V. Gadag, *Bull of Pure and Applied Sciences*, **1995**, *14C*, 1.
- B. Muralidhara Rao and B. Narayana, *Ann. Chim., (Rome)* **1995**, *85*, 105.
- Biju mathew, B. Narayana, B. Muralidhara Rao, H. Raghavan Nambiar, and B. Ramachandra, *Mikro Chim Acta*, **1996**, *122*, 295.
- A. Joesph, Biju Mathew and B. Narayana, *J. Indian Chem. Soc.*, **1996**, *73*, 633.
- C. H. Raghavan Nambiar, B. Narayana, B. Muralidhara Rao and Biju Mathew, *J. Indian Chem. Soc.*, **1998**, *75*, 265.
- Abraham Joseph, B. Narayana and K. Subramanya Bhat, *J. Indian Chem. Soc.*, **1999**, *76*, 511.
- Prakash Shetty, A. Nityananda Shetty and R. V. Gadag, *Indian J. of Chem. Tech.*, **2000**, *7*, 227.
- N. Gopalakrishna Bhat, B. Narayana and N.V. Sreekumar, *Annali-di-chimica (Rome)*, **2002**, *92*, 139.
- R. C. Agarwal and A. K. Srivastava, *Indian J. Chem.*, **1996**, *4*, 359.
- A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", 3rd ed., Longmann, London, 1968, p. 549, 390.
- R. V. Gadag and M. R. Gajendragad, *Indian J. Chem.*, **1978**, *16(A)*, 703.
- B.K. Gupta, D.S. Gupta, S.K. Dikshit and U. Agarwal, *Indian J. Chem.*, **1977**, *15A*, 624.
- K. Saito and H. Jerry, *J. Chem. Soc.*, **1956**, *47*, 01.
- R. Pribil, *Talanta*, **1967**, *14*, 613.
- Ioan Al Crisan and Maria Paniti Bolyai, *Ser. Chem.*, **1967**, *12*, 39.
- K. K. Verma and R. Rawat, *Chem. Anal (Warsaw)*, **1980**, *25*, 729.
- J. Andre, O. D. Herman and M. A. Herman, *Trans. Met. Chem.*, **1978**, *3*, 144.
- R. G. Pearson, *Chem. Engg. News*, **1965**, *43*, 90.
- R. G. Pearson, *Chem. Britt.*, **1967**, *3*, 103.
- C. J. Van Nieuwenburg and J. Gillis, "Reagents for Quantitative Inorganic Analysis"; 1st Ed, Elsevier, Amsterdam, 1948, p. 160.