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Indirect complexometric determination of thallium(III) in its alloys and complexes using thiomalic acid as a selective releasing agent

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A simple and selective complexometric method for the determination of thallium in presence of other metal ions is proposed on the basis of selective masking ability of thiomalic acid 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 lead nitrate solution at pH 5-6, using xylenol orange as the indicator. A 0.6% aqueous solution of thiomalic acid is then added to displace EDTA from the Tl(III)-EDTA complex. The released EDTA is titrated with standard lead nitrate solution. Reproducible and accurate results are obtained for 3-92 mg of Tl(III) with relative error less than $\pm 0.17\%$ and coefficient of variation not more than 0.36%. The interference of various ions is studied. This method is used for the analysis of thallium in its synthetic alloy mixtures and also in complexes.

Keywords: Thallium(III), Thiomalic acid, Masking agent, Complexometric titration

IPC Code(s): C01G15/00, C01B6/06

Thallium alloys and its complexes find various applications in diverse fields such as photo-electric cells, insoluble anodes, corrosion inhibitors, bearings and fungicides. Considering these excellent and extensive applications of thallium alloys and its complexes, a reliable and rapid method often becomes 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, accurate, selective and rapid methods 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 along with the associated ions 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 thiopyrene³, thiosemicarbazide⁴, hydrazine sulphate⁵, 2-mercapto-ethanol⁶, thiocarbohydrazide⁷, ascorbic acid⁸, DL-

cysteine⁹, 3-mercapto-1,2-propanediol¹⁰, ethylene thiourea¹¹, sodium sulphite¹², 2-thiazoline-2-thiol¹³, hydroxylamine hydrochloride¹⁴, semicarbazide hydrochloride¹⁵, thiosulphate¹⁶, thiourea¹⁷, cysteamine hydrochloride¹⁸, thioglycolic acid¹⁹, oxalic acid²⁰ etc. have been used as selective releasing agents in the complexometric determination of Tl(III). Some of these methods either require heating or readjustment of pH for the quantitative release of EDTA from Tl-EDTA complex. A comparison of the reported method with the presently proposed method is given in the Table 1.

The present investigation describes, thiomalic acid as a selective releasing agent in the complexometric determination of thallium(III). The effects of foreign ions have been studied and application of the method in the determination of thallium in its complexes and synthetic mixture of ions has been reported.

Experimental Procedure

All reagents used were of analytical or chemically pure grade. A thallium nitrate solution was prepared as per the reported procedure²¹. A known weight of thallos nitrate was dissolved in minimum amount of water, oxidized to Tl(III) by alkaline bromine,

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 sulphite	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
Thiosulphate	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
Thiomalic acid	Hg(II), Pd(II) and Sn(IV). For Hg(II) and Sn(IV) interference obviated by using acetyl acetone and sodium fluoride respectively.	Proposed reagent

separated and purified by precipitation as $Tl(OH)_3$. It was then dissolved in 2 N HCl, made up to the mark with distilled water and standardized by the chromate method²². EDTA solution (~0.04 M) (sodium salt) and lead nitrate solution (0.02 M) were prepared by dissolving a requisite amount of water, making up to the mark with distilled water and standardizing by the standard methods²². Freshly prepared (0.5%) aqueous solutions of xylenol orange (indicator) and (0.6%) thiomalic acid (masking agent) were prepared by dissolving the requisite amount of reagent in distilled water. Solutions of various metal ions were prepared by dissolving calculated amounts of the metal chlorides/nitrates/sulphates in distilled water or with suitable acids and then making up to a known volume.

Method

To an aliquot of the solution containing 3-92 mg of thallium solution and varying amounts of diverse metal ions taken in a 250 mL conical flask, an excess of 0.04 M EDTA solution was added. The solution was diluted with 20 mL of distilled water. The pH of the solution was adjusted to 5-6 by adding solid hexamine. The uncomplexed EDTA was back-titrated with standard lead nitrate solution to the sharp colour change of xylenol orange indicator from yellow to

red. A 0.6% aqueous solution of thiomalic acid was added (just above 1:3 molar ratio M:L), shaken well and allowed to stand for 1-2 min. The released EDTA was back-titrated with standard lead nitrate 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 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 3 mL of 2 N HNO_3 , and made up to 250 mL with distilled water. Aliquots of the made up solution were used for titration as per the proposed method using thiomalic acid as the masking agent.

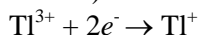
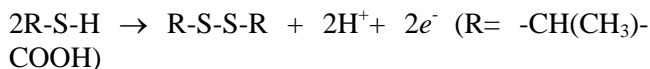
Results and Discussion

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 one such element, which forms a stable complex with EDTA in its trivalent state²⁵, but shows little tendency for complexation with EDTA in its monovalent state²⁶. Even if thallium (I) forms complex with EDTA it may do so only in the basic medium (pH 8-9) and complete decomposition of Tl(I)-EDTA complex takes place in the acidic medium²⁷. 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, thiomalic acid effectively reduces Tl(III) to Tl(I) by a 2-electron change process²⁸. The redox reaction can be represented as follows



Thiomalic acid thus 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, thiomalic acid forms a stable and soluble complex with Tl(I) so formed. This explanation accounts for the actual consumption of three moles of thiomalic acid per mole of thallium for the quantitative release of EDTA. The +1 oxidation state of thallium in its complex was confirmed by spot test²⁹. A red precipitate was formed when a solution of the complex in dilute hydrochloric acid was treated

with a drop each of bismuth nitrate solution and sodium iodide solution.

Effect of thiomalic acid concentration

Preliminary experimental results showed that addition of thiomalic acid in 1:3 molar ratio (M:L) was sufficient for the quantitative release of EDTA from Tl(III)-EDTA complex at room temperature. However, no adverse effects on the results were observed even on adding 20-fold excess of the reagent. In all the subsequent determinations, the concentration of the reagent was maintained at slightly excess above the required molar ratio.

Accuracy and precision

In order to study the accuracy and precision of the method, determinations of thallium in the concentration range of 3-92 mg 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 $\pm 0.17\%$ and coefficient of variation not more than 0.36%. From these results, it is reasonable to infer that the proposed method is precise and accurate.

Effect of foreign ions

In order to ascertain the possible interference of the diverse ions, thallium determination was carried out with an aliquot containing 18.65 mg of Tl(III) in the presence of various metal ions and anions. No interference was observed for the ions at the amounts shown in mg: Pb(II) (250), Zn(II) (220), Ba(II) (100), Co(II) (30), Ni(II), Cd(II) (25), Mn(II) (5), La(III), Y(III), Ce(III) (100), Rh(III) (25), Au(III) (15),

Table 2—Precision and accuracy in the determination of thallium(III) (n=6)

Thallium(III), mg		Relative error (%)	Standard deviation (mg)	Coefficient of variation (%)
Taken	Found			
3.73	3.73	+0.00	0.01	0.27
7.46	7.45	-0.13	0.02	0.27
11.19	11.21	+0.17	0.04	0.36
14.92	14.93	+0.07	0.04	0.27
18.65	18.65	+0.00	0.04	0.21
22.38	22.36	-0.08	0.04	0.18
29.84	29.88	+0.13	0.07	0.24
37.30	37.34	+0.10	0.05	0.13
55.95	56.02	-0.12	0.04	0.07
74.60	74.65	+0.06	0.12	0.16
92.25	92.18	-0.08	0.14	0.15

(n=number of average determination)

Table 3—Analysis of thallium complexes (n=3)

Complex	Thallium(III) calculated (%)	Thallium(III) found (%)	Relative error (%)
Tl(C ₄ H ₇ N ₄ S) ^a	58.83	58.72	-0.19
Tl(C ₃ H ₅ N ₄ S) ^b	61.37	61.45	+0.13
Tl(C ₅ H ₉ N ₄ S) ^c	56.55	56.50	-0.08
Tl(C ₂ H ₂ N ₃ S ₂) ^d	60.73	60.87	+0.23

^aThallium complex with 4-amino-5-mercapto-3-ethyl-1,2,4-triazole

^bThallium complex with 4-amino-5-mercapto-3-methyl-1,2,4-triazole.

^cThallium complex with 4-amino-5-mercapto-n-propyl-1,2,4-triazole

^dThallium complex with 5-amino-2-mercapto-1,3,4-thiadiazole.

Table 4—Determination of thallium(III) in synthetic mixtures of metal ions(n=5)

Mixture	Composition (mg)	Thallium(III) found (mg)	Relative error (%)
Tl + Zn + Co	18.0+57.8+24.2	18.03	+0.16
Tl + Pb + Zn	15.7+50.5+33.8	15.68	-0.13
Tl + Zn + Cd	10.9+62.9+26.2	10.92	+0.18
Tl + Pb + Co	19.8+51.5+28.7	19.83	+0.15
Tl + Pb + Cd	13.8+53.0+33.2	13.77	-0.22
Tl + Ni + Cd + Co	14.7+26.3+26.3+32.7	14.68	-0.14

Fe(III), Al(III), Ru(III) (5), Pt(IV), Se(IV) (50), Sb(III) (35), W(VI) (60), U(VI) (5), chloride, citrate (90), sulphate, tartarate (200), borate (180). Metal ions such as Pd(II), Hg(II), Cr(III) and Sn(IV) as its chloride show severe interference giving positive errors. This is due to the release of EDTA from their respective complexes by the reagent. However, the interference of Sn(IV) (up to 5 mg) and Hg(II) (10 mg) can be avoided by premasking these ions with sodium fluoride (sat. solution of NaF, 10 mL) and acetyl acetone (5 mL, 98%) respectively. The interference of Cr(III) is due to the deep purple colour of its EDTA complex, which makes the detection of the end point rather difficult.

Application

In order to explore the utility of the proposed method, quantitative analysis of complexes and synthetic mixtures of thallium were carried out. The results of analysis of such samples are given in Tables 3 and 4. From these results, it can be concluded that the proposed method can be conveniently employed for rapid analysis of such samples.

Conclusions

The 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 a 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

- 1 Amar M M, Pribil R & Tawakkol M S, *Egypt J Pharm Sci*, 17 (1978) 21.
- 2 Kaluba F Ya & Platunova N B, *Zh Anal Khim*, 28 (1973) 1009.
- 3 Tanaka T L, *Yakugaku Zasshi*, 93 (1973) 252.
- 4 Narayana B & Gajendragad M R, *J Indian Chem Soc*, 64 (1987) 620.
- 5 Nityananda Shetty A, Gadag R V & Gajendragad M R, *Indian J Chem*, 27A (1988) 82.
- 6 Muralidhara Rao B & Narayana B, *Acta Indica Chem*, 18(2) (1992) 193.
- 7 Narayana B, Lucos Jose P, Karunakaran V & Gajendragad M R, *Asian J Chem*, 5(1) (1993) 115.
- 8 Muralidhara Rao B & Narayana B, *Turk J Chem*, 17(2) (1993) 138.
- 9 Narayana B, Abraham Joesph & Praveen Chandra N H, *Acta Indica Chem*, 19(2) (1993) 48.
- 10 Prakash Shetty, Nityananda Shetty A, Khader A M A & Gadag R V, *Indian J Chem Technol*, 1 (1994) 129.
- 11 Abraham Joesph & Narayana B, *Asian J Chem*, 6(2) (1994) 233.

- 12 Raghavan Nambiar C H, Narayana B, Muralidhara Rao B & Biju Mathew, *Analyst*, 120(6) (1995) 1843.
- 13 Vasundhara B R, Nityananda Shetty A & Gadag R V, *Bull Pure Appl Sci*, 14C (1995) 1.
- 14 Muralidhara Rao B & Narayana B, *Ann Chim (Rome)*, 85(1-2) (1995) 105.
- 15 Biju Mathew, Narayana B, Muralidhara Rao B, Raghavan Nambiar H & Ramachandra B, *Mikro Chim Acta*, 122(3-4) (1996) 295.
- 16 Abraham Joesph, Biju Mathew & Narayana B, *Microchem J*, 53(2) (1996) 175.
- 17 Raghavan Nambiar C H, Narayana B, Muralidhara Rao B & Biju Mathew, *J Indian Chem Soc*, 75(4) (1998) 265.
- 18 Abraham Joseph, Narayana B & Subramanya Bhat K, *J Indian Chem Soc*, 76(10) (1999) 511.
- 19 Prakash shetty, Nityananda Shetty A & Gadag R V, *Indian J Chem Technol*, 7 (2000) 227.
- 20 Gopalakrishna Bhat N, Narayana B & Sreekumar N V, *Ann Chim (Rome)*, 92 (2002) 139.
- 21 Agarwal R C & Srivastava A K, *Indian J Chem*, 35A (1996) 359.
- 22 Vogel A I, *A Text Book of Quantitative Inorganic Analysis*, 3rd edn (Longmann London), 1978, 549.
- 23 Gadag R V & Gajendragad M R, *Indian J Chem*, 16A (1978) 703.
- 24 Gupta B K, Gupta D S, Dikshit S K & Agarwal U, *Indian J Chem*, 15A (1977) 624.
- 25 Saito K & Jerry H, *J Chem Soc*, (1956) 4701.
- 26 Pribil R, *Talanta*, 14 (1967) 613.
- 27 Ioan Al Crisan & Maria Paniti Bolyai, *Ser Chem*, 12 (1967) 39.
- 28 Verma K K & Rawat R, *Chem Anal (Warsaw)*, 25 (1980) 729.
- 29 Van Nieuwenburg C J & Gillis J, *Reagents for Quantitative Inorganic Analysis* (Elesvier, Amsterdam), 1948, 160.