

Indirect complexometric determination of thallium(III) using thioglycolic acid as masking agent

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A simple and selective complexometric method for the determination of thallium(III) is proposed by using thioglycolic acid as a masking agent. In the presence of diverse metal ions thallium(III) is complexed with excess EDTA and the surplus EDTA is back titrated (pH 5 - 6, hexamine) with standard zinc sulphate solution using xylenol orange indicator. A freshly prepared 1% aqueous solution of thioglycolic acid is then added to displace EDTA from Tl(III)-EDTA complex and the released EDTA is titrated with standard zinc sulphate solution. The results for the determination of 4 - 87 mg of thallium are obtained with a relative error of 0.3% and coefficient of variation 0.46%. The effect of diverse ions are studied. The method is applied to the determination of thallium in its complexes and synthetic mixtures.

Recently, complexometric titrations, particularly those involving masking and demasking technique are receiving considerable attention since they provide simple, rapid and accurate methods for the determination of the desired metal ion in the presence of associated metal ions. A search in the literature discloses that a number of sulphur - nitrogen donor ligands such as thiosemicarbazide¹, hydrazine sulphate², 4-amino-5-mercapto-3-propyl-1,2,4-triazole³, 2-mercaptoethanol⁴, ascorbic acid⁵, ethylene thiourea⁶, 3-mercapto-1,2-propanediol⁷, hydroxylamine hydrochloride⁸, 2-thiazoline-2-thiol⁹ have been used as selective releasing agents in the complexometric determination of thallium(III). Some of these methods either require heating or readjustment of pH for the quantitative release of EDTA from Tl-EDTA complex. In this paper, the application of thioglycolic acid as a selective releasing agent in the indirect complexometric determination of thallium(III) has been reported.

Experimental Procedure

All chemicals used were of either AR or chemically pure grade. An aqueous 1% solution (v/v) of thioglycolic acid (TGH_2) was used. Thallous nitrate solution was prepared from thallic nitrate by following the reported procedure¹⁰ and standardised by chromate method¹¹. Zinc sulphate solution was prepared in distilled water and standardised gravimetrically as zinc oxinate¹¹. EDTA solution ($\sim 0.04 M$)

was prepared by dissolving disodium salt of EDTA in distilled water. A freshly prepared 0.5% aqueous solution of xylenol orange indicator was used.

To an aliquot of thallium solution associated with varying amounts of diverse metal ions taken in a 250 mL conical flask, an excess of EDTA solution was added. The solution was diluted with 25 mL of distilled water, followed by the addition of solid hexamine to adjust the pH between 5 and 6. The surplus EDTA was back titrated with standard zinc sulphate solution using xylenol orange as indicator to a sharp colour change from yellow to red. To this a freshly prepared 1% solution of TGH_2 was added in required quantities. The contents were mixed well and allowed to stand for 5 min to ensure complete release of

Table 1—Precision and accuracy in the determination of thallium(III)

Thallium, mg		Recovery (%)	Coefficient of variation (%)
Taken	Found*		
3.48	3.48	100.00	0.46
6.97	6.95	99.71	0.46
10.45	10.46	100.09	0.31
17.42	17.41	99.94	0.29
24.38	24.39	100.04	0.13
34.83	34.84	100.03	0.17
52.25	52.21	99.92	0.08
69.67	69.66	99.98	0.09
87.08	87.23	100.17	0.07

*Average of six determinations

EDTA. The liberated EDTA was then back titrated with the same standard zinc sulphate solution to the same end-point as before. The second titre value corresponds to the thallium content in the aliquot.

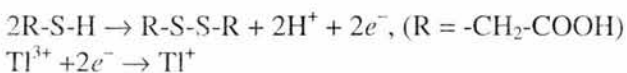
Analysis of thallium complexes—Thallium(I) complexes with 5-amino-2-mercapto-1,3,4-thiadiazole, 4-amino-5-mercapto-3-methyl-1,2,4-triazole, 4-amino-5-mercapto-3-propyl-1,2,4-triazole-3(5)-thiol were prepared and purified as per the reported methods^{12,13}. About 0.3 g of the complex was carefully decomposed with aquaregia by slow evaporation to near dryness. The residue was then cooled, dissolved in minimum volume of 2N HNO₃ and made up to 250 mL with distilled water. Aliquots of the made up solutions were used for performing titrations as per the proposed procedure.

Results and Discussion

Effect of reagent concentration—Preliminary experimental results showed that addition of TGH₂ 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 excess reagent. In all our subsequent determinations the concentration of the reagent was maintained at slightly excess above the required molar ratio.

Mechanism of demasking—Generally a metal ion, which can exist in two different oxidation states, differs in its tendency to form complex with EDTA at different oxidation states. Thallium is one such element, which forms a stable complex with EDTA (log $K = 22.5$) in its trivalent state¹⁴, but shows little tendency for complexation with EDTA in its monovalent state¹⁵. Even if Tl(I) forms a complex with EDTA, it may do so only in the basic medium (pH 8-9), but complete dissociation of Tl(I)-EDTA complex takes place in acidic medium¹⁶. Therefore, the redox system Tl(III) - Tl(I) can be conveniently employed in acidic medium for its complexometric determination by demasking technique.

Being a good reducing agent, TGH₂ effectively reduces Tl(III) to Tl(I) by a 2-electron change process¹⁷. The redox reaction can be represented as follows:



TGH₂ thus selectively demasks thallium from Tl(III)-EDTA complex through a change in the ox-

Table 2—Analysis of thallium complexes ($n=3$)

Complex	Tl calculated (%)	Tl found (%)	Relative error (%)
Tl(C ₂ H ₂ N ₃ S ₂)*	60.73	60.60	-0.21
Tl(C ₃ H ₅ N ₄ S) [#]	61.30	61.04	-0.42
Tl(C ₅ H ₉ N ₄ S) [§]	56.52	56.35	-0.30
Tl(C ₂ H ₂ N ₃ S) [¶]	67.12	66.81	-0.46

*Thallium complex of 5-amino-2-mercapto-1,3,4-thiadiazole

[#]Thallium complex of 4-amino-5-mercapto-3-methyl-1,2,4-triazole

[§]Thallium complex of 4-amino-5-mercapto-3-propyl-1,2,4-triazole

[¶]Thallium complex of 1,2,4-triazole-3(5)-thiol.

Table 3—Determination of thallium(III) in synthetic mixture of metal ions ($n=3$)

Mixture	Composition (%)	Thallium found (%)	Relative error (%)
Tl(III)+Hg(II)*	8.7+91.3	8.65	-0.57
Tl(III)+Bi(III)+Pb(II)	11.5+55.2+33.3	11.52	+0.17
Tl(III)+Zn(II)+Cd(II)	14.8+59.6+25.6	14.88	+0.54
Tl(III)+Zn(II)+Al(III)	19.9+57.2+22.9	19.97	+0.35
Tl(III)+Cd(II)+Pb(II)+Bi(III)	8.9+11.0+35.8+44.3	8.85	-0.56
Tl(III)+Pd(II) [#]	60.0+40.0	60.10	+0.37
Tl(III)+Sn(IV) [§]	40.5+59.5	40.45	-0.12

*Hg(II) is premasked with thiocyanate

[#]Pd(II) is premasked with L-histidine

[§]Sn(IV) is premasked with fluoride

idation state of thallium (reduction) and thereby releases EDTA quantitatively. Besides changing the oxidation state of thallium, TGH₂ forms a stable complex with Tl(I) so formed. This explanation accounts for the actual consumption of 3 moles of TGH₂ per mole of thallium for quantitative release of EDTA. The +1 oxidation state of thallium in its complex was confirmed by spot test¹⁸. 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.

Precision and accuracy—In order to check the accuracy and precision of the method, determinations of thallium in the concentration range of 3 - 80 mg were carried out under optimised experimental conditions. These results are presented in Table 1. The results show that the maximum mean error and coefficient of variation ($n=6$) of the method are 0.3 % and 0.46 % respectively. From these results, it is reasonable to

infer that the proposed method is precise and accurate.

Effect of diverse ions—In order to ascertain the possible interference of the diverse ions, thallium determination was carried out with an aliquot containing 17.42 mg of thallium(III) in the presence of various metal ions and anions. No interference was observed for the following ions at the amounts shown in mg: Pb(II), Zn(II) (200); Bi(III) (120); Cd(II) (100); Co(II) (90); Ni(II) (80); Mo(VI), Ti(IV) (70); Fe(III) (66); Al(III) (54); Mn(II) (10); chloride (150); sulphate, nitrate, citrate, oxalate, acetate, borate, fluoride (200).

However, Pd(II), Hg(II), Sn(IV), Cu(II) and Cr(III) interfere severely. The interference of Pd(II), Hg(II), Sn(IV) and Cu(II) is presumably due to the release of EDTA from their respective EDTA complexes by the reagent. This interference from the first three can be avoided by premasking these metal ions with suitable secondary masking agents, such as L-histidine for 33 mg of Pd(II); thiocyanate for 50 mg of Hg(II); and fluoride for 40 mg of Sn(IV). The interference of Cr(III) is due to the deep purple colour of Cr-EDTA complex which causes the detection of the end-point rather difficult.

Applications

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 some such samples are given in Tables 2 and 3. From these results it can be concluded that the proposed method can be conveniently employed for rapid analysis of such samples.

Conclusion

The method is simple and rapid as it does not require any heating for the quantitative release of

EDTA from Tl(III)-EDTA complex. The reagent does not form precipitate either with Tl(III) or with the titrant under the experimental conditions. This facilitates the detection of a sharp end point. The proposed method can be used for the rapid analysis of complexes and alloys of thallium.

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