

NOTE**Complexometric Determination of Thallium(III) Using Bromide as Masking Agent and Silver(I) as Demasking Agent**

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Thallium(III) ions (4-40 mg) in presence of co-ions are treated with excess of bromide (0.05 M) and followed by excess of EDTA (0.02 M). The surplus EDTA is titrated with zinc sulphate solution using xylenol orange as an indicator at pH 5-6 (hexamine). Bromide complex of thallium(III) is then demasked using silver nitrate solution. Thallium(III) free from bromide ion is then titrated with EDTA to the end point violet to yellow. Reproducible and accurate results are obtainable with relative errors $\leq 0.5\%$ and standard deviations ≤ 0.05 mg.

Key Words: Thallium(III), Complexometry, EDTA, Bromide, Masking.

Thallium compounds are highly toxic, but are commonly used as fungicides and in medicine for skin diseases. Thallium has significant use in electronic components such as the activated sodium iodide crystals in photomultiplier tubes. Thallium oxysulphide is used in light sensitive cells as photosensitive agent. It also forms useful alloys with Pb, Ti, Zn, Pd, Pt, U, Cd, Ce, Co, La, Sn, W, Hg, Bi, Au, Ag, *etc.* The selective determination of Tl(III) using direct EDTA titration reported in literature by using several indicators like methyl violet¹, 1-(2-pyridylazo)naphthol², 1-(2-pyridylazo)-resorcinol², 4-(2-pyridylazo)resorcinol³, 4-(2-thiazolylazo)resorcinol³, xylenol orange⁴, sulpho-salicylic acid⁴ and methylene blue⁵. The selective determination of Tl(III) is also successful by indirect complexometric method using several reducing agents that also act as complexing agents such as sulphite³, thiopyrine⁶ thiosemicarbazide⁷, hydrazine sulphate⁸, 4-amino-5-mercapto-3-propyl-1,2,4-triazole (AMPT)⁹, 2-mercaptoethanol¹⁰ 3-mercapto-1,2-propane-diol¹¹, hydroxylamine hydrochloride¹². The methods⁶⁻¹¹ have some experimental difficulties such as being tedious and time consuming, preparation for AMPT, 2-mercaptoethanol and 3-mercapto-1,2-propane-diol are less selective and unpleasant to use. Heating required using thiosemicarbazide, pH changes take place on adding excess hydrazine sulphate and hydroxylamine hydrochloride.

All reagents used were of analytical reagent grade. Thallous nitrate solution was prepared from thallium nitrate trihydrate and standardized by the chromate method¹³. Zinc sulphate solution (0.02 M) was prepared in distilled water. EDTA solution (0.02 M) was prepared by dissolving the disodium salt of EDTA in distilled water and standardized by zinc sulphate solution. Aqueous solution of xylenol orange

0.05 % (m/v) indicator, sodium bromide (*ca.* 0.05 M) and silver nitrate (*ca.* 0.05 M) was used.

Procedure: An aliquot of acidic solution containing 4-40 mg of thallic nitrate solution in presence of co-ions are masked with excess of bromide above the molar ratio 1:6 followed by excess of EDTA. Surplus EDTA is titrated against zinc sulphate solution using xylenol orange indicator at pH 5-6 (10 ± 2 g hexamine). Bromide complex of Tl(III) is then demasked using silver nitrate solution. Free Tl(III) is then titrated against standardized EDTA to the end point violet to yellow.

Analysis of thallium in thallium complexes: Thallium(I) complexes were prepared from various sulphur donor ligands by conventional methods and their purity was confirmed by elemental analysis. About 0.2-0.3 g of the complex was decomposed with aqua regia. The residue was then cooled, dissolved in dilute nitric acid and made upto 100 mL with distilled water. Aliquots of 10 mL were used for titration as described in method proposed. Results of analysis of Tl in thallium complex of 4-amino-5-mercapto-3-methyl-1,2,4-triazole is shown in Table-1.

TABLE-1
ANALYSIS OF THALLIUM COMPLEXES (n = 5)

Complex	Thallium (%)		Relative error (%)
	Present	Found	
Tl(C ₃ H ₅ N ₄ S)	61.30	61.20	-0.16

Tl(C₃H₅N₄S) = Thallium complex of 4-amino-5-mercapto-3-methyl-1,2,4-triazole.

Thallium(III) forms 1:6 stable soluble complex with bromide with stability constant¹⁴, $\log \beta = 31.6$. Thallium(III) forms instantaneously stable 1:1 complex¹⁵ with EDTA having stability constant¹⁶, $\log \beta = 22.5$ yielding a conditional stability constant of 16.6. 25 mL of *ca.* 0.05 M sodium bromide is necessary for masking 40 mg of Tl(III) present in the aliquot. At pH 5-6 all diverse metal ions complexed with EDTA. Excess of Ag(I) or AgBr precipitate do not effect the titration.

The determination of Tl(III) (4-40 mg) in thallic nitrate solution (Table-2) shows that the accurate and consistently reproducible results are obtainable within a permissible relative error of ± 0.5 %, standard deviation ≤ 0.05 mg and coefficient of variation ≤ 0.73 %. A good agreement of the experimental values with the expected ones suggest an effective masking and demasking by Br⁻ and Ag⁺, respectively for 4-40 mg range of Tl(III).

The method is simple and rapid, as it does not require heating and adjustment of pH. The effects of foreign ions were studied using 10.20 mg of Tl(III). The presence of following ions did not interfere (≤ 0.3 % error) at the amount shown: 100 mg of Ag(I), Tl(I), Zn(II), Pb(II), Co(II), Ni(II), Cu(II), Fe(II), Pd(II), Hg(II), Ba(II), Mg(II), Al(III) or Bi(III); 50 mg of Ce(III), La(III), Cr(III), Fe(III) or Sc(III); 25 mg of V(IV), Ti(IV), Sn(IV), Zr(IV), Pt(IV) or U(VI). The lack of effect of foreign ions on the accuracy and precision of the method reveals that the method may be suitable for the determination of thallium in its alloys.

TABLE-2
DETERMINATION OF Tl(III) IN THALLIC NITRATE SOLUTION (n = 5)

Tl(III) (mg)		Standard deviation (mg)	Relative error (%)	Coefficient of variation (%)
Taken	Found			
4.08	4.10	0.03	+0.49	0.73
8.16	8.18	0.03	+0.25	0.37
10.20	10.25	0.04	+0.49	0.39
20.40	20.38	0.03	-0.10	0.15
24.48	24.42	0.05	-0.25	0.20
32.64	32.57	0.05	-0.21	0.15
40.80	40.72	0.05	-0.20	0.12

Conclusion

Fast methods such as atomic adsorption spectroscopy can not be used for the analysis of Tl(III) in the mixture of Tl(I) and Tl(III). The analysis of Tl(III) in presence of Tl(I) is possible by the proposed method without prior separation.

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