

## Complexometric Titration of Thallium(III) using Hydrazine Sulphate as Demasking Agent

ANITYANANDA SHETTY & R V GADAG

Department of Chemistry, Karnataka Regional Engg. College,  
Surathkal, Sririvasnagar 574 157

and

M R GAJENDRAGAD\*

Department of Chemistry, Mangalore University,  
Mangalagangothri 574 199

Received 12 January 1987; revised and accepted 20 April 1987

A simple and selective complexometric method is proposed for the determination of thallium(III) using hydrazine sulphate as demasking agent. In the presence of diverse metal ions, thallium(III) is complexed with excess EDTA and the EDTA is back titrated ( $pH$  5-6, hexamine) with zinc sulphate solution, using xylenol orange as indicator. Hydrazine sulphate solution is then added, the mixture shaken well and allowed to stand for 2-3 min to release EDTA from the Tl-EDTA complex. The EDTA so released is titrated with standard zinc sulphate solution. Reproducible and accurate results are obtained in the range 4-80 mg of thallium with relative error  $\pm 0.3\%$  and coefficient of variation ( $n = 6$ ) not more than 0.42%.

The reduction of thallium(III) by hydrazine sulphate in the presence of EDTA and other complexons has been studied by spectrophotometric and kinetic methods<sup>1,2</sup>. The redox reaction was used for the estimation of Tl(III) by potentiometric method<sup>3</sup>, hydrazine sulphate being used as a reducing agent. Tl(III) has been also used for the determination of reductants like hydrazine sulphate by EDTA titrations<sup>4</sup> and by iodate methods<sup>5</sup>. However, no reference is found in literature about complexometric determination of Tl(III) using hydrazine sulphate as a demasking agent. The present note describes the determination of Tl(III) in its salts and alloys using hydrazine sulphate as a reducing and demasking agent. The distinct advantage of the proposed method is that the release of EDTA is instantaneous and quantitative at room temperature itself and the method requires no heating unlike the triazole method.

Hydrazine sulphate (1%) solution was prepared from AR grade hydrazine sulphate by dissolving the crystals in deionised water.

Thallic chloride solution was prepared from AR grade thallic nitrate as follows. A known weight of thallic nitrate was dissolved in water, oxidized to Tl(III) by alkaline bromine, purified by precipitation

as  $Tl(OH)_3$ , dissolved in 2 N HCl, made up to known volume<sup>6</sup> and standardised by the chromate method<sup>7</sup>.

Zinc sulphate solution (0.02 M) was prepared from AR grade zinc sulphate crystals and standardised by gravimetric method<sup>7</sup>.

EDTA solution ( $\sim 0.04$  M) was prepared by dissolving the disodium salt in deionised water.

An aqueous solution of xylenol orange indicator (0.5%) was used in the present study.

### Procedure

An aliquot of the stock solution containing 4-80 mg of Tl was treated with excess of EDTA solution. The solution was diluted with 20 ml of distilled water, followed by the addition of solid hexamine to adjust the  $pH$  to 5-6. The EDTA was titrated against the standard zinc sulphate solution to the sharp colour change of xylenol orange to pink. 1% aqueous solution of hydrazine sulphate (1 ml for every 4 mg of Tl) was then added, the reaction mixture shaken well, allowed to stand for 2-3 min and the released EDTA was titrated against the standard zinc sulphate solution as before. The second titre value corresponds to the thallium in the aliquot taken.

### Analysis of thallium complexes

A number of Tl(I) complexes with some sulphur donor ligands were prepared by the reported method<sup>8,9</sup>, and their purities checked by their elemental analyses. About 0.3 g of complex was decomposed by evaporation to nearly dryness with aqua regia. The residue was then cooled, dissolved in 3 ml of 2 N HCl, volume made up to 250 ml with deionised water. Aliquots of 25 ml were used for titration as per the recommended procedure.

### Effect of excess of hydrazine sulphate

Preliminary experiments showed that addition of hydrazine sulphate in 1:2 molar ratio [hydrazine sulphate:Tl(III)] was sufficient for the quantitative release of EDTA from the Tl-EDTA complex. However, no adverse effects were noticed on adding excess of the reagent. Even a ten-fold excess of the reagent did not affect the results. In order to ensure complete reduction of Tl(III) to Tl(I), we kept hydrazine sulphate:Tl(III) ratio as 2:1; the Tl(I) ion formed as a result of reduction was masked by the excess of the hydrazine sulphate.

To check the accuracy and precision of the method, determination of thallium was carried out under

Table 1—Precision and Accuracy in the Determination of Thallium(III)

Tl(mg)		Recovery* (%)	Coeff. of variation (%)
Taken	Found		
4.08	4.08	100.00	0.39
8.16	8.14	99.76	0.42
12.24	12.27	100.25	0.03
16.32	16.31	99.94	0.11
20.40	20.40	100.00	0.08
32.64	32.59	99.85	0.15
40.80	40.78	99.95	0.14
61.20	61.26	100.10	0.22
81.60	81.66	100.07	0.12

\*Average of six readings.

Table 2—Determination of Thallium in Presence of Diverse Metal Ions

(Thallium present in solution = 20.40 mg)

Metal ions	Quantity added (mg)	Tolerance (mg)	Tl found (mg)	Recovery* (%)
Pb(II)	30	200	20.34	99.71
Cu(II)	20	160	20.37	99.85
Ni(II)	25	80	20.41	100.05
Cd(II)	20	100	20.44	100.20
Co(II)	40	180	20.42	100.10
Bi(III)	26	205	20.41	100.05
Fe(III)	10	80	20.42	100.10
Hg(II)	15	100	20.39	99.95
Al(III)	20	100	20.39	99.95

\*Average of five readings

optimised conditions. The results presented in Table 1 indicate that the method is accurate besides being precise.

#### Effect of foreign ions

The effect of diverse metal ions present as co-ions in the solution on the accuracy and precision of the method for determination of Tl(III) was examined by estimating 20 mg of Tl(III) in the presence of cations like Pb(II), Cu(II), Ni(II), Cd(II), Co(II), Bi(III), Fe(III) and Hg(II). These ions did not interfere in the determination. Al(III) interfered at room temperature as its complexation with EDTA is kinetically slow. However, its interference could be avoided by heating the mixture to 80°C just before the back titration. But cations like Cr(III), Mn(II), Sn(II), Sn(IV), Pd(II), Ga(III) and In(III) interfered. The results relating to non-interfering cations are summarised in Table 2.

#### Application

In order to confirm the utility of the proposed method, it was used for the determination of

Table 3—Determination of Thallium in Artificial Mixtures

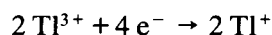
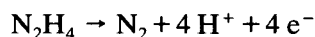
Metal ions	Quantity added (%)	Thallium† present (%)	Thallium* found (%)
Pb + Bi	33.3 + 55.2	11.5	11.51
Pb + Bi + Cd	35.8 + 44.3 + 11.0	8.9	8.89
Hg	59.5	40.5	40.56

\*Average of 3 readings; †By difference.

thallium in its complexes with mercapto ligands and also in mixtures of thallium(III). Tl(III) complex with 4-amino-5-mercapto-3-methyl-1,2,4-triazole (Found: Tl, 61.38%, Calc. 61.27%). Tl(III) complex with 4-benzylidene-3-ethyl-5-mercapto-1,2,4-triazole (Found: Tl, 46.82%, Calc. 46.97%). Tl(III) complex with 5-amino-2-mercapto-1,3,4-thiadiazole (Found: Tl, 60.89%, Calc. 60.73%). Tl(III) complex with 4-amino-3,5-dimercapto-1,2,4-triazole (Found: Tl, 58.01%, Calc. 58.13%). The method was also used for determining the compositions of alloys containing thallium. The results are summarised in Table 3.

#### Mechanism of demasking

Of the many possible mechanisms of demasking metal-EDTA complexes, the one involving change in the oxidation state of the metal seems to be the most plausible. Thallium forms a stable complex with EDTA in its trivalent state<sup>10</sup> (log *K*, 22.5), but shows little tendency for complexation in monovalent state<sup>11</sup>. Even if Tl(I) forms a complex with EDTA, it may do so only in basic medium (pH 8-9), but complete decomposition of Tl(I)-EDTA complex takes place in acidic medium (pH 5-6)<sup>12</sup>. Therefore, the redox system Tl(I)-Tl(III) can be conveniently employed in the acidic medium for its complexometric determination. Hydrazine sulphate is a powerful reducing agent in both acidic and basic media and is also a good complexing reagent. In the acidic medium, as employed in the present work, effective reduction of Tl(III) to Tl(I) takes place by a 4 electron process. The reaction involved can be represented as follows:



Hydrazine sulphate thus selectively demasks Tl(III)-EDTA complex through reduction of Tl(III) to Tl(I) and releases EDTA quantitatively and instantaneously at room temperature itself. Besides changing the oxidation state of thallium, hydrazine

sulphate forms stable complex with the Tl(I) so formed. This is indicated by the fact that chloride and chromate tests with the solution are negative.

The authors are thankful to Prof. B S Basavarajiah and Prof. T Ramachandran, Principals and Prof. S B Akki, Head of the Chemistry Department, Karnataka Regional Engineering College, for providing laboratory facilities.

#### References

- 1 Vekshin U V, Pechurova N I, Spitsyn V I, *Zh neorg Khim*, **21** (1976) 972.
- 2 Vekshin U V, Pechurova N I, Spitsyn V I, *Zh neorg Khim*, **22** (1977) 3044.
- 3 Prague Busev A I, *Anal chim Acta*, **27** (1962) 493.
- 4 Szekers Kelinek A, *Chem Anal*, **55** (1966) 77.
- 5 Verma Krishna K & Rawat Rameshwar, *Chem Anal (Warsaw)*, **25** (1980) 729.
- 6 Agarwal R C & Srivastava A K, *Indian J Chem*, **4** (1966) 359.
- 7 Vogel A I, *A text book of quantitative inorganic analysis*, 4th Edn (Longmans, London), 1978, 482 & 488.
- 8 Gadag R V & Gajendragad M R, *Indian J Chem*, **16A** (1978) 703.
- 9 Gadag R V & Gajendragad M R, *Curr Sci*, **48** (1979) 839.
- 10 Saito K & Jerry H, *J chem Soc*, (1976) 4701.
- 11 Prabil R, *Talanta*, **14** (1967) 613.
- 12 Ioan Al Crisan & Maria Paniti-Bolyai, *Ser Chem*, **12** (1967) 39.