Asian Journal of Chemistry Vol. 6, No. 2 (1994), 233–236

Complexometric Determination of Thallium(III) using Ethylene Thiourea as a Replacing Reagent

ABRAHAM JOSEPH and B. NARAYANA*
Department of Studies in Chemistry
Mangalore University, Mangalagangothri-574 199, India

A simple and selective complexometric method is proposed for the determination of thallium(III). Thallium(III) with associated diverse metal ions, is first complexed by adding a known excess of EDTA and the surplus EDTA is back-titrated at pH 5.0–6.0 (hexamine) with lead nitrate using xylenol orange as indicator. Ethylene thiourea solution (ETU in water) (1%) is added to displace EDTA from the Tl–EDTA complex. The released EDTA is then titrated with the lead nitrate solution. The interference of many commonly associated metal ions and diverse anions were also studied.

INTRODUCTION

Tanka[1] reported the determination of thallium(III) by complexation with EDTA in presence of associated cations, followed by selective decomposition of Tl-EDTA complex with masking agent thiopyrin, and titration of the EDTA liberated. Literature revealed that hydrazine sulphate[2] and 3-*n*-propyl-4-amino-5-mercapto triazole[3] were effective for the selective replacement of EDTA from the Tl-EDTA complex. Narayana *et al.* suggested that thiosemicarbazide[4] and thiocarbohydrazide[5] as effective masking agents for thallium(III). Mercaptoethanol[6] have also been found to be reliable and convenient as replacing reagent. This paper describes the merits of ethylene thiourea (ETU) as selective releasing agent for the indirect chelatometric determination of thallium(III) by EDTA titration.

EXPERIMENTAL

Ethylene thiourea (ETU) was synthesised as reported in literature[7] and used as 1% solution in water. Thallium(III) nitrate solution was prepared by the reported method[8] and standardised by the chromate method.[9] 0.02 M solution of lead nitrate is prepared and standardised by the chromate method.[9] 0.04 M solution of EDTA was prepared by dissolving the disodium salt in distilled water. 0.5% of Xylenol orange indicator solution was prepared in water.

Procedure

To an aliquot of acidic solution (containing 3–43 mg of Tl(III)), an excess of 0.04 M EDTA is added and the mixture is diluted with water. The pH is adjusted to 5.0–6.0 by adding hexamine, a few drops of xylenol orange indicator are added and the excess EDTA is back-titrated with the standard lead nitrate solution. About 3–10 ml of ethylene thiourea in water is added and the mixture is heated to

40–45°C on a water bath for 2–5 minutes. (1.2 ml of 1% solution of ETU is required to release 1 mg of Tl from Tl-EDTA complex). The liberated EDTA is titrated at room temperature with lead nitrate solution to the sharp colour change of the xylenol orange indicator from yellow to red. This second volume of titrant is equivalent to the Tl(III) present in the aliquot taken. The results are given in Table 1.

TABLE 1
DETERMINATION OF THALLIUM(III) IN ISOLATION

Thallium taken (mg)	Thallium* found (mg)	Standard deviation	Percentage recovery
3.60	3.60	0.02	100.00
7.20	7.21	0.03	100.13
10.81	10.82	0.05	100.09
14.41	14.42	0.04	100.06
18.00	17.95	0.03	99.72
21.61	21.60	0.03	99.95
25.21	25.20	0.02	99.96
32.41	32.40	0.02	99.97
43.22	43.20	0.04	99.95

*Average value of five determinations.

Analysis of Thallium Complexes

Few thallium(I) complexes with some sulphur containing ligands were prepared by conventional methods and their purity was checked by elemental analysis. About 0.1–0.2 gm of complex was decomposed by evaporation to near dryness with aqua regia. The residue was then cooled, dissolved in 3 ml of 2N HNO_3 and made up to 100 ml with distilled water. From this 10 ml were used for titration as per recommended procedure. The results are reported in Table 2.

TABLE 2
ANALYSIS OF THALLIUM COMPLEXES

Complex	Tl present (mg)	Tl found*	Relative standard deviation (%)
$Tl(C_3H_5N_4OS)$[a]	30.65	30.69	0.03
$Tl(C_{10}H_{11}N_4OS)$[b]	23.26	23.35	0.04
$Tl(C_{10}H_{11}N_4S)$[c]	23.48	23.54	0.05
$Tl(C_2H_2N_3S_2)$[d]	30.37	30.32	0.05
$Tl(C_3H_3N_4OS)$[e]	29.42	29.47	0.03
$Tl(C_3H_9N_4S)$[f]	28.26	28.19	0.04

*Average value of six determinations

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

[b]Thallium complex of 3-(*o*-tolyloxymethyl)-4-amino-5-mercapto-1,2,4-triazole.

[c]Thallium complex of 4-benzylidene-3-ethyl-5-mercapto-1,2,4-triazole

[d]Thallium complex of 5-amino-2-mercapto-1,3,4-thiodiazole.

[e]Thallium complex of 4-amino-3-mercapto-1,2,4-triazin(4H)-5-one.

[f]Thallium complex of 4-amino-5-mercapto-3-*n*-propyl-1,2,4-triazole.

RESULTS AND DISCUSSION

The results of determination of thallium(III) from its solution (Table 1) and from the complexes (Table 2) show that accurate and reproducible values are obtainable with a relative error of ± 0.4%. No interference in the determination of 5.84 mg of thallium was observed when any of the following ions were present in the amounts stated in the brackets: Zn, chloride, flouride, sulphate, borate, tartrate, acetate, oxalate (200 mg); Fe(III), Co(II), Ni(II) (30 mg); Cd (64 mg); Mn(II) (12 mg); Al(III), Cu(III) (25 mg); V(IV) (10 mg); Zr(IV) and Sn(IV) interferes severely. The method is extended to the determination of Tl(III) in some artificial alloy solutions. Accurate and reproducible results were obtained (Table 3).

TABLE 3
DETERMINATION OF THALLIUM(III) IN ARTIFICIAL ALLOY SOLUTIONS

Metal ions	Percentage composition	Tl present percentage	Tl found[a] percentage	Percentage recovery
Pb : Tl	80 : 20	20.00	20.00	100.00
Hg : Tl	91.3 : 8.7	8.70	8.72*	100.22
Pb : Sn : Tl	70 : 20 : 10	10.00	10.04†	100.40
Pb : Sb : Tl : Sn	72 : 15 : 8 : 5	8.00	7.98†	99.75
Au : Ag : Tl	30 : 30 : 40	40.00	40.05*	100.13

[a]Average of three determinations
*Hg and Ag were masked by KSCN
†Sn masked by adding NaF.

The fact that ETU displaces EDTA quantitatively from the Tl-EDTA complex indicates that the Tl-ETU complex is more stable than the Tl-EDTA complex. At room temperature it will take some 7–15 minutes to release EDTA from the Tl-EDTA complex. The reaction takes place quantitatively. A larger excess of the reagent (ETU) does not have any adverse effect on the results of the determination.

Conclusion

A special feature of the reagent is that it does not form any precipitate with either Tl(III) or Pb(II) under the experimental conditions, and as a result sharp end-point is obtained without the need for the addition of other chemicals. The method works well up to 43 mg of thallium.

The main advantage of the proposed method is that numerous metal ions can be present without inference and hence suitable for the determination of Tl in alloys. The method does not involve extraction of the Tl-EDTA complex and can be carried out in a single step with a slight heating of the solution.

REFERENCES

1. T. Tanaka, *Yakugaku Tasshi*, **93**, 252 (1973).
2. A.N. Shetty, R.V. Gadag and M.R. Gajendragad, *Indian J. Chem.*, **27A**, 82 (1988).
3. _____, *Talanta*, **35**, 721 (1987).
4. B. Narayana and M.R. Gajendragad, *J. Indian Chem. Soc.*, **64**, 620 (1987).
5. B. Narayana, P. Lucose Jose, V. Karunakaran and M.R. Gajendragad, *Asian J. Chem.*, **5**, 115 (1993).
6. Muraleedhara Rao and B. Narayana, *Acta Ciencia Indica*, **15** (1983).
7. C.F.H. Allen, C.O. Edens and J. van Allen, *Org. Syn. Coll.*, **3**, 394.
8. R.C. Agarwal and A.K. Srivastava, *Indian J. Chem.*, **4**, 359 (1966).
9. A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, 4th Ed., ELBS Longmans, London, pp. 444, 482 (1978).

(*Received*: 31 July 1992; *Accepted*: 29 May 1993) AJC–636