Complexometric determination of thallium(III) using sodium metabisulphite as a selective releasing agent

Article *in* Revue Roumaine de Chimie · February 2006

CITATION
1

READS
86

2 authors:

Prakash Shetty
Manipal Academy of Higher Education
198 PUBLICATIONS **975** CITATIONS
SEE PROFILE

Nityananda Shetty
National Institute of Technology Karnataka
91 PUBLICATIONS **830** CITATIONS
SEE PROFILE

Revue Roumaine de Chimie, **2006**, *51*(2), 123–126

COMPLEXOMETRIC DETERMINATION OF THALLIUM(III) USING SODIUM METABISULPHITE AS A SELECTIVE RELEASING AGENT

Prakash SHETTY [a] and A. Nityananda SHETTY [b]

[a] Department of Chemistry, Manipal Institute of Technology, Manipal-576104. Karnataka, INDIA. [E-mail: prakash.shetty@mit.manipal.edu]
[b] Department of Chemistry, National Institute of Technology, Karnataka, Surathkal-574157. INDIA.

Received September 30, 2003

A selective complexometric method is described for the determination of Tl(III) using sodium metabisulphite as releasing agent. Thallium(III) and associated metal ions are complexed with excess EDTA and the surplus EDTA is back titrated at pH 5-6 (hexamine or acetic acid-acetate buffer) with standard zinc sulphate solution using xylenol orange as indicator. The addition of sodium metabisulphite displaces the EDTA selectively from the Tl-EDTA complex. The released EDTA, equivalent to Tl(III) present, is titrated with standard zinc sulphate solution. The results obtained are reproducible and accurate in the range 4-100 mg of thallium with relative error less than 0.30% and coefficient of variation not exceeding 0.40%. The proposed method is employed in the determination of thallium in its salts, complexes and synthetic mixture of metal ions.

INTRODUCTION

Some of the alloys of thallium have found applications as a result of their unique properties. Tl-Hg alloy containing 8.7% Tl forms an eutectic mixture freezing at -59^0C, and has been considered for applications in low temperature thermometers, switches, closures and seals. Alloys of thallium are also used in good quality bearings, having a very high resistance to corrosion and low coefficient of friction. The Tl-Sn-In alloys show super conductivity below the temperature of liquid air. In spite of their known toxicity, compounds of thallium have been used in medicine. Thallium compounds are mainly used as intermediates or catalysts in organic synthesis.[1] Thallium compounds also find applications in preparing optical glasses on account of their high refractive indices. In the light of various applications of thallium and its compounds in diverse fields, there is a growing need for a simple and rapid analytical method for its determination. A search in the literature discloses that a number of sulphur-nitrogen donor ligands such as thiosemicarbazide,[2] 4-amino-5-mercapto-3-propyl-1,2,4-triazole,[3] hydrazine sulphate,[4] 2-mercaptoethanol,[5] ethylene thiourea,[6] 3-mercapto-1,2-propanediol,[7] hydroxylamine hydrochloride,[8] 2-thiozoline-2-thiol,[9] thioglycollic acid,[10] have been used as releasing agents in the complexometric determination of thallium(III). Some of these methods either require heating[2,3,6] or readjustment[4] of pH for the quantitative release of EDTA from the Tl-EDTA complex. Many of these methods suffer severe interference from several metal ions. This paper describes the application and advantages of sodium metabisulphite ($Na_2S_2O_5$) as a selective releasing agent in the complexometric determination of thallium(III).

EXPERIMENTAL

Reagents. Analytical-reagent grade chemicals were used. Steam distilled water was used for dilution purposes. Sodium metabisulphite (1%) was prepared in distilled water. Standard thallium(III) nitrate solution was prepared from thallium(I) nitrate (supplied by Merck) by following the reported procedure[11]and standardized by the chromate method.[12] Zinc sulphate solution (0.02M) was standardized gravimetrically by the oxinate method.[12] The stock solution of EDTA (0.04M) was prepared by dissolving the disodium salt of EDTA in distilled water. Xylenol orange indicator was used as 0.5% solution in distilled water.

Procedure. An excess of 0.04M EDTA solution was added to an aliquot containing 4-100 mg of thallium(III) and associated metal ions, followed by few drops of xylenol orange indicator. The solution was diluted to about 100 mL with distilled water and the pH was adjusted to 5.0-6.0 by addition of solid hexamine or acetic acid–acetate buffer. The surplus EDTA was back titrated against 0.02M zinc sulphate solution till the color changed from yellow to red. Then it was treated with a 1% sodium metabisulphite solution (1 mL for every 8 mg of Tl) and swirled well. The released EDTA was then titrated against 0.02M zinc sulphate solution as before. The second titre value is equivalent to the thallium present in the aliquot.

Analysis of thallium complexes. Thallium(I) complexes with some sulphur-donor ligands were prepared and purified as per the reported methods.[13,14,15] An accurately weighed sample of the complex was carefully decomposed with *aqua regia* by slow evaporation to near dryness. The residue was then cooled, dissolved in a minimum volume of 2N HNO_3 and made up to a known volume with distilled water. Suitable aliquots of solutions were analyzed for thallium as per the procedure described.

RESULTS AND DISCUSSION

Mechanism of demasking

Thallium forms a stable complex with EDTA (log K=22.5) in its trivalent state,[16,17] but shows little tendency for complexation with EDTA in its monovalent state.[18] Even if Tl(I) forms a complex with EDTA, it may do so only in basic medium (pH 8-9), but complete dissociation of the Tl-EDTA complex takes place in acidic medium.[19] Therefore, the redox system Tl(III)-Tl(I) can be conveniently employed in acidic medium for its complexometric determination. Sodium metabisulphite is a good reducing agent.[20] So, it effectively reduces Tl(III)-Tl(I) in the acidic medium. The reagent thus selectively decomposes the Tl(III)-EDTA complex through reduction of Tl(III) to Tl(I) and releases EDTA quantitatively at room temperature itself. The +1 oxidation state of thallium in the solution was confirmed also by the chromate test. The absence of any precipitate in the titration medium favours the detection of a sharp end point.

Effect of reagent concentration

It was found that the addition of sodium metabisulphite in 1:1(M:L) molar ratio was sufficient for the instantaneous and quantitative release of EDTA from the Tl-EDTA complex at room temperature. However, no adverse effects were observed even on adding excess reagent. In all our determinations, the concentration of the reagent was maintained slightly above the required molar ratio.

Accuracy and precision of the method

In order to check the accuracy and precision of the method, determinations of thallium were carried out under optimized experimental conditions. The results presented in Table 1 indicate that the method is accurate besides being precise.

Table 1

Determination of thallium in thallium(III)nitrate solution

Thallium, mg		Recovery, (%)	Coefficient of Variation, (%)
Taken	Found *		
3.68	3.68	100.00	0.40
7.36	7.37	100.14	0.34
11.04	11.02	99.82	0.36
14.72	14.68	99.73	0.24
18.40	18.41	100.05	0.18
25.76	25.72	99.84	0.20
36.80	36.86	100.16	0.14
55.20	55.24	100.07	0.08
73.60	73.68	100.11	0.12
103.04	103.20	100.16	0.10

* Mean of six determinations.

Effect of diverse ions

The effect of presence of various diverse ions on the accuracy and precision of the method was studied by estimating 18.40 mg of thallium(III) in the presence of these ions. The presence of the following ions did not interfere with in the concentration range studied. 200 mg of Pb(II), Zn(II), Tl(I); 100 mg of Cu(II),Cd(II), Co(II), Ni(II), Bi(III); 60 mg of Ag(I), Fe(III), Al(III), Ti(IV), Mo(VI); 40 mg of Mn(II), Ce(III), Zr(IV), As(V), V(V), Sb(V); 20 mg of Au(III), Cr(III), Ru(III), Rh(III), Pt(IV); 200 mg of sulphate, chloride, fluoride nitrate, phosphate, acetate, borate and tartarate. However, metal ions like Hg(II), Pd(II) and Sn(IV) show severe interference. This is presumably due to the release of EDTA from their respective EDTA complexes by the reagent. The interference of Hg(II) (up to 40 mg), Pd(II) (20 mg) and Sn(IV) (40 mg) however, may be avoided by premasking them with potassium thiocyanate, L-histidine and ammonium fluoride respectively.

Applications of the method

In order to explore the utility of the proposed method, it was employed in the analysis of thallium complexes and synthetic mixtures of metal ions with composition of alloy samples. The results pertaining to the analysis of some such samples are presented in Tables 2 and 3. From these results, it can be concluded that the method can be conveniently employed for the rapid analysis of such samples.

Table 2

Determination of thallium in complexes

Complex	Thallium (%)		Relative
	Present	Found*	Error, (%)
$Tl(C_2H_2N_3S)$ [a]	67.12	66.96	-0.24
$Tl(C_2H_2N_3S_2)$ [b]	60.73	60.55	-0.30
$Tl(C_{11}H_{11}N_4S)$ [c]	46.91	47.05	+0.30
$Tl(C_3H_5N_4S)$ [d]	61.30	61.14	-0.26
$Tl(C_5H_9N_4S)$ [e]	56.52	56.65	+0.23
$Tl(C_{12}H_{10}ONS)$ [f]	48.58	48.44	-0.29

*Mean of three determinations.
Thallium complex with 1,2,4-triazole-3(5)-thiol[a]; 5-amino-2-mercapto-1,3,4-thiadiazole[b]; 4-benzylidene-3-ethyl-5-mercapto-1,2,4-triazole[c]; 4-amino-5-mercapto-3-methyl-1,2,4-triazole[d]; 4-amino-5-mercapto-3-propyl-1,2,4-triazole[e]; thionalide[f].

Table 3

Determination of thallium in synthetic mixtures of metal ions

Mixture	Composition (%)	Thallium * Found,(%)	Relative Error, (%)
Tl + Hg#	8.7 + 91.3	8.71	+0.11
Tl + Pb + Bi	11.5 + 33.3 + 55.2	11.53	+0.26
Tl + Cu + Cd	30.0 + 20.0 + 50.0	29.92	-0.27
Tl + Bi + Pb + Cd	18.9 + 39.3 +30.8 +11.0	18.85	-0.26
Tl + Bi + Cd + Sn**	24.6 +40.5 +14.5 + 20.4	24.68	+0.32

* Mean of three determinations.
# Hg(II) premasked with potassium thiocyanate.
** Sn(IV) premasked with ammonium fluoride.

CONCLUSIONS

The proposed method is simple and rapid besides being accurate. It does not require any heating for the quantitative displacement of EDTA from the Tl-EDTA complex. Sodium metabisulphite is a cheap, readily available and water soluble reagent, so that it can be used conveniently as demasking reagent. The absence of any precipitate in the titration medium facilitates the detection of the sharp end point. The tolerance of several metal ions in the method makes it suitable for the rapid analysis of complexes and alloys of thallium.

ACKNOWLEDGEMENT. The authors are thankful to MAHE (Deemed University) Manipal for the grant of project seed money.

REFERENCES

1. P. Singh, M. D. Rausch and T. E. Bitter Wolf, *J. Organomet. Chem*., **1988**, *352*, 273.
2. B. Narayana and M. R. Gajendragad, *J. Indian Chem. Soc.*, **1987**, *64*,620.
3. A. Nityananda Shetty, R. V. Gadag and M. R. Gajendragad, *Talanta*, **1988**, *35***,** 721.
4. A. Nityananda Shetty, R. V, Gadag and M. R. Gajendragad, *Indain J. Chem*., **1998**, *27*, 82.
5. B. M. Rao and B. Narayana, *Acta Cienc. Indica Chem*., **1993**, *18*,193.
6. Abraham Joseph and B. Narayana, *Asian J. Chem*., **1994**, *6*, 233.
7. Prakash Shetty, A. M. A. Khader, A. Nityananda Shetty and R. V. Gadag, *Indian J. Chem. Technol*., **1994**, *1*, 129.
8. B. M. Rao and B. Narayana, *Ann. Chim*., **1995**, *85*, 105.
9. B. R. Vasundhara, A. Nityananda Shetty and R. V. Gadag, *Bull. Pure Appl. Sci*., **1995**, *14*, 1.
10. Prakash Shetty, A. Nityananda Shetty and R. V. Gadag, *Indian J. Chem. Technol*., **2000**, *7*, 227.
11. R. C. Agarwal and A. K. Srivastava, *Indian J. Chem*., **1966**, *4*, 359.
12. A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", 3rd edn., p. 549 & 128. Longman, Lodon, 1964.
13. B. K. Gupta, D. S. Gupta, S. K. Dikshit and U. Agarwala, *Indian J. Chem*., **1977**, *15*, 624.
14. R.V. Gadag and M. R. Gajendragad, *Indian J. Chem*., **1978**, *16*, 703.
15. R. V. Gadag and M. R. Gajendragad, *Curr. Sci*., **1979**, *48*, 839.
16. K. Saito and H. Jerry, *J. Chem. Soc*., **1956**, 4701.
17. R. G. Pearson, *J. Am. Chem. Soc*., **1963**, *83*, 3533.
18. R. Pribil, *Talanta*, **1967**, *14*, 613.
19. I. A. Crisan and M. Paniti Bolyai, *Ser. Chem*., **1967**, *12*, 39.
20. J. Litt, *Metal Finish,* **1971**, *52*, 61.