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Complexometric Determination of Tl(III) Using Thiocarbohydrazide as a Replacing Reagent

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A simple and selective complexometric method using masking and demasking techniques is proposed for the determination of thallium(III). In presence of diverse metal ions thallium(III) is complexed with a known excess of EDTA and the uncomplexed EDTA is back titrated (pH, 5-6, hexamine) with lead nitrate solution, using xylenol orange as indicator. Thiocarbohydrazide (TCH) solution in water is then added and the liberated EDTA from the Tl-EDTA complex is titrated against lead solution. Reproducible and accurate results are obtained in the concentration range 2-61 mg of thallium with relative error of $<0.05\%$ and standard deviation of <0.04.

INTRODUCTION

Of late, complexometric titrations, particularly those involving masking and demasking techniques are receiving considerable attention in analysis. This is because they provide more selective, accurate and rapid methods for the determination of the desired metal ion in the presence of associated metal ions. Survey of literature reveals that although reagents like $Na_2S_2O_3$[1], ascorbic acid[2], diethylene-triammine-N, N, N′, N″, N″-penta acetic acid[3] etc. have been used for the direct complexometric titration of Tl(III). Complexometric determination of Tl(III) using the demasking and masking technique is seldom tried. Thiopyrin[4], thiosemicarbazide[5] and hydrazin sulphate[6] are such reagents used in complexometric titration of Tl(III). Complexometric determination of Tl(III) using thiocarbohydrazide as a replacing reagent is therefore attempted with success and the results reported hereunder.

EXPERIMENTAL

Thiocarbohydrazide was prepared by the reported method[7] and used as 0.5% solution in water with a few drops of perchloric acid. Thallic nitrate solution was prepared from thallous nitrate (AR) following the reported procedure[8] and standardised by chromate method[9]. A 0.02M lead nitrate solution was prepared from an analytical grade sample and standardised by chromate method[9]. EDTA solution (0.04M) was prepared by dissolving the disodium salt of EDTA in distilled water. A 0.05% aqueous solution of xylenol orange indicator was prepared.

Procedure

To an aliquot of acidic solution of the sample containing 2–61 mg of Tl(III), an excess of 0.04M EDTA solution was added. The solution was diluted to 80–100 ml with distilled water followed by solid hexamine (pH 5.0–6.0) and xylenol orange indicator. The excess EDTA was titrated against standard lead nitrate solution to a sharp colour change of xylenol orange indicator from yellow to pink. A 0.5% solution of thiocarbohydrazide in water was then added and the released EDTA titrated against the lead nitrate solution as before. The second titre value corresponds to thallium present in the aliquot (Table 1).

TABLE 1

PRECISION AND ACCURACY IN THE DETERMINATION OF THALLIUM(III)

Tl taken (mg)	Tl found (mg)	Standard deviation	Recovery* %
2.04	2.03	0.03	99.51
5.10	5.08	0.02	99.61
10.20	10.16	0.02	99.61
15.30	15.35	0.03	100.33
20.40	20.41	0.02	100.05
25.50	25.42	0.02	99.69
30.60	30.63	0.04	100.10
40.80	40.70	0.01	99.75
51.00	51.18	0.03	100.35
61.20	61.06	0.04	99.77

*Average of five determinations.

Effect of Foreign Ions

The effect of co-ions (cations and anions) on the accuracy and precision of the method for Tl(III) determination was studied by estimating 10.20 mg of Tl(III) in presence of each of these cations. The results relating to non-interfering cations are summarised in Table 2. It may be noted that cations like Cu(II), Pd(II), Hg(II), Bi(III), Sn(IV) and Zr(IV) severely interfere. Consequently Tl(III) cannot be estimated by this method in presence of these ions.

TABLE 2

DETERMINATION OF THALLIUM IN PRESENCE OF DIVERSE METAL IONS AND ANIONS

(Thallium present in solution = 10.20 mg)

Metal ion or anion	Level of conc. (mg)	Thallium* found (mg)	Mean	Recovery (%)
Zn(II)	5	10.27	10.21	100.10
	50	10.14		
Cd(II)	32	10.14	10.18	99.80
	80	10.22		
Co(II)	6	10.27	10.23	100.29
	30	10.18		
Ni(II)	6	10.22	10.18	99.80
	30	10.14		
Mn(II)	2.5	10.14	10.16	99.61
	5	10.18		
Fe(III)	6	10.31	10.23	100.29
	30	10.14		
Al(III)	25	10.10	10.14	99.41
	50	10.18		
Ce(III)	14	10.10	10.19	99.90
	28	10.27		
La(III)	14	10.22	10.22	100.20
	28	10.22		
Ru(III)	4	10.14	10.16	99.61
	8	10.18		
Rh(III)	4	10.22	10.22	100.20
	8	10.22		
Au(III)	4	10.18	10.20	100.00
	8	10.22		
Cr(III)	5	10.18	10.16	100.61
	10	10.14		
V(IV)	10	10.10	10.19	99.91
	25	10.27		

TABLE 2 (contd.)

Metal ion or anion	Level of conc. (mg)	Tallium* found (mg)	Mean	Recovery (%)
Ti(IV)	10	10.31	10.25	100.49
	25	18.18		
Fluoride	75	10.10	10.16	99.61
	150	10.22		
Phosphate	75	10.27	10.21	100.10
	150	10.14		
Acetate	75	10.18	10.23	100.29
	150	10.27		
Oxalate	75	10.27	10.25	100.49
	150	10.23		
Tartarate	75	10.14	10.18	99.80
	150	10.22		
Citrate	75	10.18	10.18	99.80
	150	10.18		
Borate	75	10.22	10.25	100.49
	150	10.27		

*Average value of three determinations.

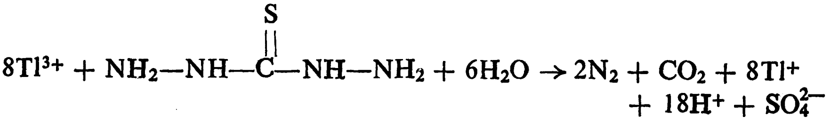
Analysis of Thallium Complexes

Thallium(I) complexes were prepared from some sulphur donor ligands by conventional methods and their purity was checked from elemental analysis. The complex (0.1–0.2g) was decomposed by evaporation to near dryness with aqua regia. The residence was then cooled, dissolved in 2N-HNO_3 (3 ml) and made up to 100 ml with distilled water. Aliquots of 10 ml were used for titration as per the proposed procedure.

RESULTS AND DISCUSSION

The fact that TCH displaces EDTA quantitatively from the Tl-EDTA complex indicates that the Tl-TCH complex is more stable than the Tl-EDTA complex. The reaction takes place quantitatively and rapidly at room temperature. The absence of a precipitate in the reaction mixture favours sharpness of the end-point. Slight excess of the reagent, TCH is required over the molar ratio of 1 : 1 for the complete release of EDTA, but a larger excess has no adverse effect. A high concentration of chloride and sulphate should be avoided, since they may tend to form a precipitate with the titrant.

In the acidic medium as employed in the present work, effective reduction of Tl(III) to Tl(I) takes place by a 16-electron change. The reactions involved are likely to be



$$8Tl^{3+} + NH_2{-}NH{-}\overset{\overset{\displaystyle S}{||}}{C}{-}NH{-}NH_2 + 6H_2O \rightarrow 2N_2 + CO_2 + 8Tl^{+} + 18H^{+} + SO_4^{2-}$$

and the SO_4^{2-} formed is identified by testing with barium chloride solution. Besides changing the oxidation state of thallium, thiocarbohydrazide complexes with the Tl(I) so formed and releases the previously complexed EDTA quantitatively. The +1 oxidation state of thallium was further confirmed by spot test technique.

TABLE 3

ANALYSIS OF THALLIUM COMPLEXES

Complex	Tl present %	Tl found %
$Tl(C_3H_5N_4S)$[a]	61.30	61.35
$Tl(C_{10}H_{11}N_4OS)$[b]	46.51	46.59
$Tl(C_{11}H_{11}N_4S)$[c]	46.97	47.01
$Tl(C_2H_2N_3S_2)$[d]	60.73	60.61
$Tl(C_3H_3N_4OS)$[e]	58.83	58.91

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-triazine (4H)-5-one.

Application

The usefulness of the proposed method lies in the fact that it can be successfully applied for the determination of thallium in its complexes with sulphur containing ligands and also in the mixture of salts of Tl(II) (Table 4). It can also be used for the determination of the composition of alloys containing Tl.

TABLE 4

DETERMINATION OF THALLIUM IN ARTIFICIAL MIXTURES
(Thallium present in solution = 20.40)

Metal ions	Quantity added (mg)	Tl found* (mg)	Recovery (%)
Zn + Co	10 + 30	20.49	100.44
Zn + Ni	10 + 30	20.45	100.26
Zn + Cd	10 + 32	20.45	100.26
Zn + Al	10 + 10	20.41	100.05
Zn + Ce	10 + 28	20.38	99.90

*Average of four determinations.

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