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Complexometric Determination Of Thallium(III) By Using "Mixed Masking" Method

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ABSTRACT

A simple and selective complexometric method for the determination of thallium in presence of other metal ions is proposed based on the selective masking ability of thiouracil towards thallium(III). Thallium present in a given sample solution is first complexed with a known excess of EDTA and the surplus EDTA is titrated with standard lead nitrate solution at pH 5-6(hexamine) using xylenol orange as the indicator. A 1 % aqueous solution of thiouracil is then added to displace EDTA from the Tl(III)-EDTA complex. The released EDTA is titrated with standard lead nitrate solution. Reproducible and accurate results are obtained for 3mg to 95mg of Tl (III) with relative error less than ± 0.26% and coefficient of variation not more than 0.35%. The interference of various ions are studied. This method is used for the analysis of thallium in its synthetic alloy mixtures and also in complexes.

KEYWORDS

Thallium determination;
Mixed masking method;
Thiouracil;
EDTA titrations.

INTRODUCTION

Thallium alloys and its complexes find various applications in diverse fields such as photo-electric cells, insoluble anodes, corrosion inhibitors, bearings and fungicides. Considering these excellent and extensive applications of thallium alloys and its complexes, a reliable and rapid method is often essential for the determination of thallium in a single stage.

Owing to poor selectivity, earlier complexometric methods[1, 2] for thallium could not be used for the determination in its alloys. Complexometric titrations particularly those involving masking and demasking technique are of considerable importance as they provide simple, accurate, selective and rapid methods for the determination of a specific desired metal ion in the presence of associated metal ions. In the determination of thallium by this technique, it is first

complexed with EDTA along with the associated ions followed by selective decomposition of Tl-EDTA complex with the suitable masking agent. The released EDTA is back titrated with suitable titrant. Literature survey shows that a number of sulphur-nitrogen donor ligands such as thiopyrene[3], thiosemicarbazide[4], hydrazine sulphate[5], 2-mercapto ethanol[6], thiocarbohydrazide[7], ascorbic acid[8], DL-cysteine[9], 3-mercapto-1,2-propanediol[10], ethylene thiourea[11], sodium sulfite[12], 2-thiazoline-2-thiol[13], hydroxylamine hydrochloride[14], semicarbazide hydrochloride[15], thiosulfate[16], thiourea[17], cysteamine hydrochloride[18], thioglycolic acid[19], oxalic acid[20], ethanethiol[21] etc. have been used as selective releasing agents in the complexometric determination of Tl(III). Some of these methods either require heating or readjustment of pH for the quantitative release of EDTA from Tl-EDTA complex. The proposed method when compared with other recently reported method (TABLE 1), shows that there is no interference from most of the metal ions including copper. Moreover, the interference of metal ions such as Hg(II), Pd(II) and Sn(IV) can also be obviated by using the suitable secondary masking agent.

The present investigation describes, thiouracil as a selective releasing agent in the complexometric determination of thallium(III). The effects of foreign ions have been studied and application of the method in the determination of thallium in its complexes and synthetic mixture of ions has been reported.

EXPERIMENTAL

Reagents

All reagents used were of analytical or chemically pure grade.Thallium(III) chloride solution -Prepared by following the reported procedure[22]. A known weight of thallous nitrate was dissolved in minimum amount of water, oxidized to Tl(III) by alkaline bromine, separated and purified by precipitation as $Tl(OH)_3$. It was then dissolved in 2N HCl, made up to the mark with distilled water and standardized by the chromate method[23].

Lead nitrate solution (0.02M) - Prepared by dissolving a known amount of lead nitrate in water and standardized gravimetrically by the chromate method[23].

EDTA solution (~0.04M)- Prepared by dissolving the disodium salt of EDTA in distilled water.

Xylenol orange indicator - A freshly prepared 0.5% aqueous solution of the indicator was used.

Thiouracil solution-Used as a freshly prepared 1% aqueous solution

Preparation of Foreign ions - Solutions of various metal ions were prepared by dissolving the appropriate metal salts in water or suitable acids.

Procedure

To an aliquot of the solution containing 3-95 mg of thallium solution and varying amounts of diverse metal ions taken in a 250mL conical flask, an excess of 0.04M EDTA solution was added. The solution was diluted with 20mL of distilled water. The pH of the solution was adjusted to 5-6 by adding solid hexamine. The uncomplexed EDTA was back titrated with standard lead nitrate solution to the sharp color change of xylenol orange indicator from yellow to red. A 1% aqueous solution of thiouracil was added (just above 1:10 molar ratio M: L), shaken well and allowed to stand for 1-2 minutes. The released EDTA was back titrated with standard lead nitrate solution to the same end point as before. The second titre value is equivalent to the thallium content present in the aliquot.

Analysis of Thallium Complexes

A number of thallium(I) complexes with 5-amino-2-mercapto-1,3,4-thiadiazole, 4-amino-5-mercapto-3-methyl-1,2,4-triazole, 4-amino-3-ethyl-5-mercapto -1,2,4-triazole, 4-amino-5-mercapto-3-n-propyl-1,2,4-triazole were prepared and purified as per the reported methods[24,25]. A known weight of the complex was decomposed by evaporation to near dryness with aqua-regia. The residue was then cooled, dissolved in 3mL of 2N HNO_3, and made up to 250mL with distilled water. Aliquots of the made up solution were used for titration as per the proposed method using thiouracil as the masking agent.

RESULTS AND DISCUSSIONS

Mechanism of demasking by using mixed mask-

Full Paper

ing method. Among the many possible mechanisms of demasking metal-EDTA complexes, the one involving a change in the oxidation state of the metal seems to be more plausible in the proposed method ("Mixed" masking, reduction followed by complexation). Generally, a metal, which can exist in two different oxidation states, differs in its tendency to form a stable complex with EDTA at different oxidation states. Thallium is one such element, which forms a stable complex with EDTA in its trivalent state[26], but shows little tendency for complexation with EDTA in its monovalent state[27]. Even if thallium (I) forms complex with EDTA it may do so only in the basic medium (pH 8-9) and complete decomposition of Tl(I)-EDTA complex takes place in the acidic medium[28]. Therefore, the redox behavior of Tl(III)-Tl(I) can be conveniently employed in acidic medium for its complexometric determination by "mixed" masking method.

Being a good reducing agent, thiouracil effectively reduces Tl(III) to Tl(I) by a 2-electron change process[29]. The redox reaction can be represented as follows

$$2R\text{-}S\text{-}H \rightarrow R\text{-}S\text{-}S\text{-}R + 2H^+ + 2e^- \quad (R = C_4H_3N_2O\text{-})$$

$$Tl^{3+} + 2e^- \rightarrow Tl^+$$

Thiouracil act as a monodentate ligand, selectively demasks thallium from Tl(III)-EDTA complex through a change in the oxidation state of thallium (reduction) and thereby releases EDTA quantitatively. Besides changing the oxidation state of thallium, thiouracil forms a stable and soluble complex with Tl(I). The +1 oxidation state of thallium in its complex was confirmed by spot test[30]. A red precipitate was formed when a solution of the complex in dilute hydrochloric acid was treated with a drop each of bismuth nitrate solution and sodium iodide solution.

Effect of reagent concentration

Preliminary experimental results showed that addition of thiouracil in 1:10 molar ratio (M:L) was found to be sufficient for the quantitative release of EDTA from Tl(III)-EDTA complex at room temperature. However, no adverse effects on the results were observed even on adding 20 fold excess of the reagent. In all our subsequent determinations the concentration of the reagent was maintained at slightly excess above the required molar ratio.

Accuracy and precision

In order to study the accuracy and precision of the method, determinations of thallium in the concentration range of 3-95 mg were carried out under optimized experimental conditions. These results are presented in TABLE-1. The results show that the maximum relative error does not exceed ±0.26% and coefficient of variation not more than 0.35 %. From these results, it is reasonable to infer that the proposed method is precise and accurate.

Effect of foreign ions

In order to ascertain the possible interference of

TABLE 1: Comparison of the reported reagents with the proposed reagent

Reagent	Conditions	Remarks	References
Ethylene thiourea	pH 5-6(hexamine) Xylenol orange as the indicator	Ag(I), Hg(II) and Sn(IV)	11
Sodium sulfite	pH 5-6(hexamine) Xylenol orange as the indicator	Hg(II), Pd(II) and Sn(IV)	12
2-Thiazoline-2-thiol	pH 5-6(hexamine) Xylenol orange as the indicator	Hg(II), Pd(II), Cu(II), Fe(III), Al(III) V(III), Cr(III), Ce(IV) and Sn(IV),	13
Hydroxylamine hydrochloride	pH 5-6(hexamine) Xylenol orange as the indicator	Ag(I), Hg(II), Pd(II), Au(III), Sb(IV) and Sn(IV)	14
Thiosulfate	pH 5-6(hexamine) Xylenol orange as the indicator-	Pd(II), Hg(II), Au(III), Zr(III) and Sn(IV)	16
Thiourea	pH 5-6(hexamine) Xylenol orange as the indicator	Cu(II), Pd(II), Hg(II), Zr(III) and Sn(IV)	17
Cysteamine hydrochloride	pH 5-6(hexamine) Xylenol orange as the indicator	Cu(II), Pd(II) and Sn(IV)	18
Thioglycolic acid	pH 5-6(hexamine) Xylenol orange as the indicator	Pd(II), Hg(II), Cu(II), Cr(III) and Sn(IV)	19
Oxalic acid	pH 5-6(hexamine) Xylenol orange as the indicator	Pd (II), Hg (II), Cr (III) and Sn(IV)	20
Ethane thiol	pH 5-6(hexamine) Xylenol orange as the indicator	Pd (II), Hg (II), Cr (III) and Sn(IV	21
Thiouracil	pH 5-6(hexamine) Xylenol orange as the indicator	Pd (II), Hg (II), Cr (III) and Sn(IV	Proposed reagent

TABLE 2: Precision and accuracy in the determination of Tl(III)

Thallium, mg		Relative error (%)	Standard deviation	Coefficient of variation (%)
Taken	Found (*)			
3.82	3.83	+0.26	0.01	0.26
7.64	7.65	+0.13	0.02	0.26
11.46	11.44	-0.17	0.04	0.35
15.28	15.30	+0.13	0.04	0.26
19.10	19.11	+0.05	0.02	0.10
22.92	22.88	-0.17	0.06	0.26
30.56	30.53	-0.09	0.06	0.19
38.20	38.17	-0.08	0.05	0.13
57.30	57.39	+0.16	0.11	0.19
76.40	76.51	+0.14	0.13	0.17
95.50	95.38	-0.13	0.15	0.15

(*)Average of six determinations

the diverse ions, thallium determination was carried out with an aliquot containing 18.65mg of Tl(III) in the presence of various metal ions and anions. The non interfering ions are listed in TABLE 3. However, Pd(II), Hg(II), and Sn(IV) interfere severely. The interference of these ions are due to the release of EDTA from their EDTA complexes on the addition of the reagent. However the interference of Pd(II)(up to 10 mg), Hg(II) (up to 20 mg) and Sn(IV) (5mg) can be avoided by premasking these ions with L-histidine (5%,15-20ml), acetyl acetone (5ml) and sodium fluoride (saturated solution of NaF, 10ml) respectively.

APPLICATION

In order to explore the utility of the proposed method, quantitative analysis of complexes and synthetic mixtures of thallium were carried out. The results of analysis of such samples are given in TABLES 2 & 3. From these results it can be concluded that the proposed method can be conveniently employed for rapid analysis of such samples.

CONCLUSIONS

The method is simple and rapid, does not require any heating for the quantitative release of EDTA

TABLE 3: Determination of 18.65 mg of thallium (III) in the presence of diverse metal ions

Metal ions	Quantity added (mg)	Thallium found* (mg)	Relative error (%)
Pb(II)	250	18.65	0.00
Zn(II)	200	18.65	0.00
Co(II)	100	18.63	-0.11
Cd(II)	80	18.64	-0.05
Ba(II)	80	18.66	+0.05
Cu(II)	50	18.65	0.00
Mn(II)	25	18.63	-0.11
Hg(II)♦	20	18.65	0.00
NiII)	05	18.66	+0.05
Pd(II)θ	10	18.66	+0.05
La(III)	100	18.65	0.00
Y(III)	80	18.64	-0.05
Al(III)	30	18.63	-0.11
As(III)	20	18.62	-0.16
Rh(III)	20	18.63	-0.11
Ce(III)	10	18.65	0.00
Bi(III)	10	18.64	-0.05
Ru(III)	05	18.62	-0.16
Se(IV)	30	18.64	-0.05
Pt(IV)	30	18.65	0.00
Sn(IV)♠	05	18.66	+0.05
W(VI)	30	18.65	0.00
U(VI)	15	18.64	-0.05
Citrate	200	18.65	0.00
Sulphate	200	18.64	-0.05
Acetate	150	18.67	+0.11
Phosphate	140	18.63	-0.11
Oxalate	150	18.64	-0.05
Borate	120	18.67	+0.11
Tartarate	100	18.65	0.00
Chloride	50	18.66	+0.05

*Average of 4 determinations
♦Premasked with Acetyl acetone
θPremasked with Histidine
♠Premasked with sodium flouride

TABLE 4: Analysis of thallium complexes

Complexes	Thallium calculated (%)	Thallium found (*) (%)	Relative error (%)
$Tl(C_4H_7N_4S)$(a)	58.83	58.70	-0.22
$Tl(C_3H_5N_4S)$(b)	61.37	61.45	+0.13
$Tl(C_5H_9N_4S)$(c)	56.55	56.43	-0.21
$Tl(C_2H_2N_3S_2)$(d)	60.73	60.84	+0.18

(*)Average of four determinations
(a)Thallium complex with 4-amino-5-mercapto-3-ethyl-1,2,4-triazole
(b)Thallium complex with 4-amino-5-mercapto-3-methyl-1,2,4-triazole.
(c)Thallium complex with 4-amino-5-mercapto-3-n-propyl-1,2,4-triazole
(d)Thallium complex with 5-amino-2-mercapto-1,3,4-thiadiazole.

Full Paper

TABLE 5: Determination of thallium in synthetic mixtures

Mixtures	Composition (%)	Tl found (*) (%)	Relative Error (%)
Tl + Zn + Ba	17.5 + 45.8 + 36.7	17.47	-0.17
Tl + Pb + Ba	13.7 + 50.3 + 36.0	13.72	+0.15
Tl + Zn + Pb	12.0 + 37.7 + 50.3	12.02	+0.16
Tl + Pb + Cd	16.0 + 50.4 + 33.6	15.98	-0.12
Tl +Zn + Cd	16.0 + 42.0 + 42.0	16.04	+0.25
Tl + Pb + Co	14.8 + 54.2 +31.0	14.81	+0.07
Tl + Zn + Co	17.5 + 55.0 + 27.5	17.46	-0.23

(*)Average of four determinations

from Tl(III)-EDTA complex. The reagent does not form any precipitate either with Tl(III) or with the titrant under the experimental conditions. This facilitates the detection of sharp end point. The proposed method can be conveniently used for the rapid analysis of complexes and alloys of thallium.

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