

A Simple and Rapid Complexometric Determination of Thallium(III) using Mercaptoethane as Demasking Agent

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ABSTRACT

A simple, rapid and selective complexometric method is proposed for the determination of thallium(III), using mercaptoethane(EtSH) as demasking agent. The sample solution containing Tl(III) is first complexed with excess EDTA and the surplus EDTA is removed by titration at pH 5–6 with zinc sulphate solution using xylenol orange as indicator. EtSH solution is then added to displace EDTA selectively from Tl-EDTA complex. Thallium is determined indirectly by titration of released EDTA with zinc sulphate solution. Reproducible and accurate results are obtained in the concentration range 4–80 mg of thallium with a relative error $\leq \pm 0.6\%$ and relative standard deviation $\leq 0.7\%$. The method is successfully applied to the determination of Tl(III) in its synthetic alloy compositions and complexes, and waste-water samples.

KEY WORDS

Complexometric determination, thallium, demasking agent, mercaptoethane.

1. Introduction

Thallium is a rare element in the earth's crust. Both the element and its compounds are extremely toxic.^{1,2} In spite of their known toxicity, compounds of thallium have been used in diverse fields. Thallium is widely used in pesticides, medicines and in the manufacture of optical glasses with high refractive indices. Thallium bromide and thallium iodide are used in photosensitive diodes and infrared detectors. Some of the alloys of thallium have found wide applications due to their unique properties. Tl-Hg alloy containing 8.7% thallium forms a eutectic mixture freezing at -59°C , and has been considered for applications in low temperature thermometer, switches, closures and seals. Alloys of lead and thallium have melting points above the constituent metals and are useful for applications in specialty fuses. Alloys of thallium are also used in good quality bearings, having a very high resistance to corrosion and low coefficient of friction. Thallium-antimony-indium alloys are used for optical recording materials.³ Thallium compounds are mainly used as intermediates or catalysts in organic synthesis.⁴ Because of the toxic nature of thallium and its widespread industrial applications, there is a growing need for a simple, rapid and accurate analytical method for the determination of thallium in various samples. Keeping this in view, the study of complexometric determination of thallium using mercaptoethane as demasking agent, has been taken up for investigation.

Some of sulphur-nitrogen donor ligands such as thiosemicarbazide,⁵ 4-amino-5-mercapto-3-propyl-1,2,4-triazole,⁶ hydrazine sulphate,⁷ ascorbic acid,⁸ ethylene thiourea,⁹ 3-mercapto-1,2-propanediol,¹⁰ hydroxylamine hydrochloride,¹¹ 2-thiozoline-2-thiol,¹² thioglycolic acid,¹³ sodium metabisulphite,¹⁴ have been reported so far as demasking agents for the complexometric determination of Tl(III). Many of these reported methods either require heating^{5,6,9} or readjustment of pH after the addition of excess reagent.⁷ Several common metal ions show interference in many of these reported methods.^{5,6,12} This paper

reports the demasking property of mercaptoethane and its application to the determination of thallium(III) in various samples. The proposed method does not require heating or readjustment of pH or very expensive facilities.

2. Experimental

2.1. Reagents

Analytical-reagent grade chemicals were used.

Thallium(III)nitrate solution: the stock solution was prepared from thallium(I) nitrate (Merck) by following the reported procedure¹⁵ and standardized gravimetrically by chromate method.¹⁶

Zinc sulphate solution (0.02 M): prepared by dissolving a known amount of zinc sulphate (Merck) in distilled water and standardized gravimetrically by oxinate method.¹⁶

EDTA solution (0.02 M): prepared by dissolving disodium salt of EDTA in distilled water and making up to a known volume.

Mercaptoethane (1%): A freshly prepared aqueous solution of the reagent was used.

Solutions of diverse ions: solutions of various cations and anions were prepared by dissolving calculated amount of appropriate salts in distilled water or in suitable diluted acids and making up to a known volume.

Xylenol orange indicator (0.5%): a freshly prepared solution of xylenol orange in distilled water was used.

2.2. Procedure

To a solution containing 4–80 mg of thallium(III) and varying amounts of diverse metal ions taken in a 250 mL conical flask, an excess of 0.02 M EDTA solution was added. The solution was diluted to about 100 mL with distilled water followed by the addition of solid hexamine to adjust the pH between 5 and 6. The surplus EDTA was titrated with 0.02 M zinc sulphate solution using xylenol orange as indicator to a sharp colour change from yellow to red. To this an excess of 1% EtSH solution was added.

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Table 1 Determination of thallium in thallium(III)nitrate solution.

Thallium /mg		R.S.D. /% (n = 6)	Relative error /%
Taken	Found*		
3.60	3.59	0.28	-0.28
7.20	7.19	0.42	-0.14
10.80	10.82	0.37	0.18
14.40	14.41	0.28	0.07
18.00	17.95	0.17	-0.28
28.80	28.76	0.21	-0.14
36.00	36.07	0.11	0.19
54.00	53.91	0.11	-0.17
79.20	79.03	0.13	-0.22

* Average of six determinations.
R.S.D., relative standard deviation.

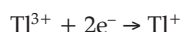
The liberated EDTA was then titrated with 0.02 M zinc sulphate solution as before. The second titre volume corresponds to the thallium content present in the aliquot taken.

3. Results and Discussion

3.1. Mechanism of Demasking

Generally a metal, which can exist in two different oxidation states, differ in its tendency to form a stable complex with EDTA. Thallium is one such metal. It forms a stable complex with EDTA ($\log K = 22.5$) in its trivalent state,^{17,18} but shows little tendency for complexation with EDTA in its monovalent state.¹⁹ Even if Tl(I) forms a complex with EDTA, it may do so only in basic medium (pH 8–9), but complete dissociation of Tl(I)-EDTA complex takes place in acidic medium.²⁰ Therefore, the redox system Tl(III)–Tl(I) can be conveniently employed in acidic medium for its complexometric determination.

Like many mercapto compounds, mercaptoethane is a good reducing agent. The reagent selectively displaces EDTA from Tl-EDTA complex through reduction of Tl(III) to Tl(I) for which one electron change per thiol group occurs.²¹ The redox reaction can be represented as follows:



Besides changing the oxidation state of thallium, EtSH forms a soluble and stable 1:1 complex with Tl(I) so formed.²² This was confirmed by the absence of free Tl(I) ions in the solution as indicated by the spot-test for Tl(I).

3.2. Effect of Reagent Concentration

Experimental results showed that addition of EtSH in 1:6 molar ratio (M:L) was sufficient for the quantitative and instantaneous displacement of EDTA from Tl-EDTA complex at room temperature. Addition of a large excess of the reagent did not cause any adverse effect in the determination.

3.3. Accuracy and Precision of the Method

In order to check the accuracy and precision of the proposed method, determinations of thallium in thallium(III)nitrate solution, thallium complexes, alloy samples and waste-water samples were carried out by following the procedure described. The results (Tables 1, 3, 4 and 5) show that reproducible and accurate determination of thallium in the concentration range 4–80 mg is possible with a relative error $\leq \pm 0.6\%$ and relative standard deviation $\leq 0.7\%$.

Table 2 Determination of thallium in presence of diverse metal ions. (Thallium taken in solution = 18.00 mg).

Diverse ion	Diverse ion taken /mg	Thallium found * /mg	Relative error /%
Ag(I)	20	17.91	-0.50
Tl(I)	150	18.10	0.55
Mg(II)	200	18.07	0.39
Ca(II)	200	18.08	0.44
Pb(II)	200	17.97	-0.17
Zn(II)	200	17.97	-0.17
Cd(II)	100	17.89	-0.61
Ni(II)	90	18.08	0.44
Mn(II)	20	18.10	0.55
Co(II)	100	18.07	0.39
Hg(II) †	50	18.10	0.55
Pd(II) †	30	17.91	-0.50
Fe(II)	50	18.12	0.67
Ce(III)	30	17.94	-0.33
Cr(III)	10	18.12	0.67
Al(III)	50	17.91	-0.50
Fe(III)	55	18.10	0.55
Bi(III)	120	18.12	0.67
Au(III)	40	17.94	-0.33
In(III)	50	18.08	0.44
Ru(III)	10	17.89	-0.61
Rh(III)	10	18.10	0.55
Ti(IV)	80	18.09	0.50
Zr(IV)	25	17.90	-0.56
Sb(IV)	35	18.10	0.55
Th(IV)	40	18.07	0.39
Pt(IV)	10	18.08	0.44
Sn(IV) ‡	40	18.10	0.55
V(IV)	30	17.91	-0.50
Mo(VI)	100	18.09	0.50
U(VI)	30	18.10	0.55
Chloride	140	18.07	0.39
Sulphate	180	18.04	+0.22
Nitrate	170	17.91	-0.50
Tartarate	230	18.05	0.28
Citrate	200	18.10	0.55
Acetate	240	17.94	-0.33
Borate	200	17.95	-0.28
Fluoride	240	18.08	0.44

* Average of five determinations.

† Premasked with thiocyanate.

‡ Premasked with fluoride.

3.4. Effect of Foreign Ions

In order to evaluate the suitability of the proposed method for the quantitative determination of thallium(III), the effect of various ions which often accompany Tl(III), was studied by adding different amounts of diverse ions to a solution containing 18.00 mg of thallium. The tolerance levels of the various diverse ions studied are summarized in Table 2. An error of less than $\pm 1\%$ in the recovery was considered to be tolerable. The metal ions such as Ag(I), Tl(I), Mg(II), Ca(II), Pb(II), Zn(II), Cd(II), Ni(II), Mn(II), Co(II), Fe(II), Ce(III), Cr(III), Al(III), Fe(III), Bi(III), Au(III), In(III), Ru(III), Rh(III), Ti(IV), Zr(IV), Sb(IV), Th(IV), Pt(IV), V(IV), Mo(VI), U(VI) and anions like chloride, sulphate, nitrate, tartarate, citrate, acetate, borate, fluoride, do not show any interference in the determination of Tl(III). However the metal ions like, Pd(II), Hg(II), Sn(IV) and Cu(II) were found to interfere causing positive errors. This is presumably due to the simultaneous release of EDTA from their respective EDTA complexes by EtSH. The interference of Pd(II) (up to 30 mg) and

Table 3 Determination of thallium in complexes.

Complex	Thallium present /%	Present method			Reference method ²⁶		
		Thallium found /%	R.S.D. /% (n = 3)	Relative error /%	Thallium found /%	R.S.D. /% (n = 3)	Relative error /%
Tl(C ₂ H ₂ N ₃ S) ^a	67.12	66.80	0.48	-0.48	66.86	0.50	-0.39
Tl(C ₃ H ₃ N ₄ S) ^b	61.30	60.99	0.50	-0.50	60.92	0.45	-0.62
Tl(C ₂ H ₂ N ₃ S ₂) ^c	60.73	60.47	0.30	-0.43	60.56	0.40	-0.28
Tl(C ₃ H ₉ N ₄ S) ^d	56.52	56.41	0.32	-0.20	56.32	0.30	-0.35
Tl(C ₁₁ H ₁₁ N ₄ S) ^e	46.91	47.08	0.45	0.36	47.14	0.38	0.50

^a Thallium complex of 1, 2, 4-triazole-3(5)-thiol.^b Thallium complex of 4-amino-5-mercapto-3-methyl-1, 2, 4-triazole.^c Thallium complex of 5-amino-2-mercapto-1, 3, 4-thiadiazole.^d Thallium complex of 4-amino-5-mercapto-3-propyl-1, 2, 4-triazole.^e Thallium complex of 4-benzylidene-3-ethyl-5-mercapto-1, 2, 4-triazole.**Table 4** Determination of thallium in synthetic mixtures with alloy composition.

Mixture	Composition /%	Present method			Reference method ²⁶		
		Thallium found /%	R.S.D. /% (n = 3)	Relative error /%	Thallium found /%	R.S.D. /% (n = 3)	Relative error /%
Tl + Hg *	8.7 + 91.3	8.74	0.50	0.46	8.75	0.56	0.57
Tl + Sb + In	20 + 40 + 40	19.88	0.56	-0.60	19.90	0.62	-0.50
Tl + Pb + Cd + Ag	51 + 24 + 20 + 5	51.3	0.50	0.59	51.2	0.56	0.39
Tl + Bi + Pb + Cd	7 + 52 + 34 + 7	7.04	0.70	0.57	6.97	0.62	-0.43
Tl + Pb + Zn + Al	30 + 40 + 20 + 10	30.12	0.28	0.40	30.08	0.40	0.27

* Premasked with thiocyanate.

Hg(II) (50 mg) can be obviated by the addition of ammonium thiocyanate (5% NH₄SCN, 10 mL each) prior to EDTA complexation as masking agent. Interference by Sn(IV) can be avoided by premasking with ammonium fluoride (5% NH₄F, 10 mL) prior to EDTA complexation.

3.5. Analytical Applications of the Method

In order to explore the utility of the proposed method, quantitative analysis of thallium complexes, synthetic mixtures of thallium with alloy compositions and water samples containing thallium were carried out.

3.5.1. Determination of Thallium in Complexes

Thallium(I) complexes with 1,2,4-triazole-3(5)-thiol, 4-amino-5-mercapto-3-methyl-1,2,4-triazole, 5-amino-2-mercapto-1,3,4-thiadiazole, 4-amino-5-mercapto-3-propyl-1,2,4-triazole, 4-benzylidene-3-ethyl-5-mercapto-1,2,4-triazole were prepared and purified by per the reported methods.²³⁻²⁵ An accurately weighed sample of the complex (0.2–0.3 g) was decomposed with aqua regia by slow evaporation to near dryness. The cooled residue was then dissolved in minimum volume of 2N HNO₃ and diluted to 250 mL in a standard flask. Suitable aliquots were analysed for thallium as per the procedure described. To confirm the results obtained by this method, measurements of the Tl(III) contents in the complex samples were carried out by a reported spectrophotometric method.²⁶ The results of analysis shown in Table 3 indicate that there is no significant difference between the results obtained by the proposed method and the reference method.

3.5.2. Determination of Thallium in Alloys

Various synthetic mixtures of thallium with silver, mercury, bismuth, lead, cadmium, zinc, aluminium, antimony or indium

were prepared according to their alloy compositions. The thallium content in these mixtures was determined by following the present method and also by a reported spectrophotometric method.²⁶ The results obtained by the present method are in close agreement with those obtained by the reference method (Table 4). The obtained results indicate that the present method would be effective for the analysis of alloy samples of similar complexity.

3.5.3. Determination of Thallium in Waste-water Samples

The proposed method was also applied to the determination of thallium in synthetic waste-water samples containing Tl(III) and other common metal ions that usually accompany thallium in natural water samples. The waste-water samples (100 mL) each containing 20 mg of Ca(II), Mg(II), Zn(II), Cd(II), Pb(II), Al(III), Mn(II), Fe(III), Ni(II) and different amounts of Tl(III) (say, 5, 10, 15 and 20 mg) were prepared in the laboratory. Suitable aliquots of these samples were analysed for thallium(III) by following the procedure described. The result obtained by the present method was cross-checked by a reported spectrophotometric method.²⁶ The data obtained (Table 5) indicate that there is no much significant difference between the amount of thallium added and those obtained by the proposed method or reference method. This test was conducted to confirm the usefulness of the proposed method in the determination of thallium(III) in environmental water samples.

3.6. Comparison with Other Demasking Agents

The proposed demasking agent, mercaptoethane, is compared with other reported reagents for the complexometric determination of thallium(III) (Table 6). The main advantage of the proposed method is its fair selectivity with no requirement of heating or readjustment of pH.

Table 5 Determination of thallium in waste-water samples.

Thallium added /mg	Present method			Reference method ²⁶		
	Thallium found /mg	R.S.D. /%(n = 5)	Relative error /%	Thallium found /mg	R.S.D. /%(n = 5)	Relative error /%
5	5.03	0.70	0.60	5.02	0.78	0.40
10	10.05	0.62	0.50	9.96	0.54	-0.40
15	15.08	0.56	0.53	15.04	0.56	0.40
20	20.12	0.50	0.60	20.10	0.54	0.50

Table 6 Comparison of demasking agents for the complexometric determination of thallium(III).

Demasking agent	Interference	Comments	Ref.
Thiosemicarbazide	Cu(II), Hg(II), Fe(II), Pd(II), Sn(II), Al(III), Bi(III), Cr(III)	Requires heating	5
4-Amino-5-mercapto-3-propyl-1,2,4-triazole	Pd(II), Hg(II), Bi(III), Cr(III), Sn(IV)	Requires heating	6
Hydrazine sulphate	Pd(II), Mn(II), Sn(II), Ga(III), In(III), Cr(III), Al(III), Sn(IV)	Requires readjustment of pH	7
Ascorbic acid	Ag(I), Hg(II), Sn(IV)	–	8
Ethylene thiourea	Ag(I), Hg(II), Sn(IV)	Requires heating	9
3-Mercapto-1,2-propane diol	Hg(II), Cu(II), Pd(II), Cr(III), Sn(IV)	–	10
Hydroxylamine hydrochloride	Ag(I), Hg(II), Pd(II), Au(III), Sb(IV), Sn(IV)	–	11
2-Thiazoline-2-thiol	Cu(II), Hg(II), Pd(II), Al(III), Fe(III), Cr(III), Ce(IV), Sn(IV)	–	12
Thioglycolic acid	Hg(II), Cu(II), Pd(II), Cr(III), Sn(IV)	–	13
Sodium metabisulphite	Hg(II), Pd(II), Sn(IV)	–	14
Mercaptoethane	Hg(II), Pd(II), Cu(II), Sn(IV). The interference due to these ions [except Cu(II)] can be avoided by premasking them	Requires neither heating nor readjustment of pH	Proposed reagent

4. Conclusion

The simplicity, rapidity and reasonable selectivity of analytical procedures make the technique very attractive for a wide range of applications. The proposed method does not require heating, readjustment of pH and also standardization of EDTA. The demasking agent, mercaptoethane does not form many precipitates either with Tl(III) or the titrant, under the experimental conditions. This facilitates the detection of a sharp end point. The lack of adverse effect of many foreign ions on the accuracy and precision of the method reveals that the method may be suitable for the determination of thallium in its alloys, complexes and also in water samples.

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