

SHORT COMMUNICATION

Sodium dithionite as a selective demasking agent for the complexometric determination of thallium

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Abstract: Sodium dithionite is proposed as a new demasking agent for the rapid and selective complexometric determination of thallium(III). In the presence of diverse metal ions, thallium (III) was first complexed with excess EDTA and the surplus EDTA was then titrated with a standard zinc sulphate solution at pH 5–6 (hexamine buffer) using Xylenol Orange as the indicator. The EDTA equivalent to thallium was then released selectively with sodium dithionite and back titrated with a standard zinc sulphate solution as before. Reproducible and accurate results were obtained in the range 4–100 mg of thallium with a relative error of $\pm 27\%$ and a coefficient of variation ($n = 6$) of not more than 0.30%. The effects of various diverse ions were studied. The method was applied to the determination of thallium in its complexes and in alloys.

Keywords: complexometry, demasking agent, EDTA method, sodium dithionite, thallium.

INTRODUCTION

The alloys of thallium find extensive application in diverse fields because of their unique properties. Alloys of Pb and Tl have melting points above those of the constituent metals and are useful for applications as specialty fuses. The Hg–Tl alloy, which forms a eutectic at 8.7 wt.% of thallium, has a melting point of $-60\text{ }^{\circ}\text{C}$ and can be used as a substitute for mercury in switches and seals for equipment used in the polar region or the stratosphere. Tl–Sn–In alloys show super conductivity below the temperature of liquid air and a Tl–Sb–In alloy is used for optical recording materials.¹ Thallium is used in special glasses to improve the optical properties and increase the refractive index. Thallium compounds are mainly used as intermediates or catalysts in organic synthesis.² In spite of their known toxicity, compounds of thallium have been used in medicine. In view of this, the selective

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determination of thallium using a demasking technique gains considerable importance. The reported methods using demasking agents, such as thiosemicarbazide,³ 4-amino-5-mercapto-3-propyl-1,2,4-triazole,⁴ ethylene thiourea,⁵ are not rapid as they require heating for the quantitative release of EDTA from the Tl-EDTA complexes. The hydrazine sulphate method⁶ requires readjustment of the pH after the addition of excess reagent. 3-Mercapto-1,2-propanediol,⁷ hydroxylamine hydrochloride,⁸ 2-thiazoline-2-thiol⁹ and thioglycolic acid¹⁰ are also used as releasing agents for thallium(III). Some of these methods suffer from severe interference by several metal ions.

The present paper describes the use of sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) as a selective demasking agent for the decomposition of the Tl-EDTA complex at room temperature. The proposed method offers advantages of simplicity, rapidity and reasonable selectivity without the need for heating or readjustment of the pH.

EXPERIMENTAL

Reagents. All the chemicals used were of either Analytical-reagent grade or chemically pure grade. Steam distilled water was used throughout. A 1 % solution of sodium dithionite (Merck) was prepared in distilled water. The stock solution of thallium(III) nitrate was prepared from thallium(I) nitrate following a reported procedure¹¹ and standardized by the chromate method.¹² The zinc sulphate solution (0.02 M) was standardized by the oxinate method.¹² The EDTA solution (0.02 M) was prepared by dissolving the disodium salt of EDTA in distilled water. A freshly prepared 0.5 % aqueous solution of Xylenol Orange was used as the indicator.

Procedure. To an aliquot of solution containing 4–100 mg of thallium and varying amounts of diverse ions, a known excess of 0.02 M EDTA was added and diluted to about 100 ml with distilled water. The pH of the solution was adjusted to 5.0–6.0 by adding solid hexamine. A few drops of Xylenol Orange indicator were added. The surplus EDTA was back titrated with 0.02 M zinc sulphate solution. Then, a freshly prepared 1 % sodium dithionite solution was added in excess (1 ml for every 8 mg Tl) and the contents were swirled well. The released EDTA was then titrated with 0.02 M zinc sulphate solution as previously. The second titre value corresponds to the amount of thallium present in the aliquot.

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, thionalide were prepared and purified as per the reported procedures.^{13–15}

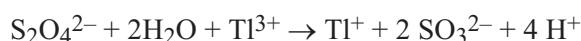
An accurately weighed sample (0.2–0.3 g) of the complex was carefully decomposed with aqua regia by evaporation to near dryness. The cooled residue was dissolved in the minimum volume of 2 M nitric acid and made up to mark in a 250 ml volumetric flask. Aliquots of 25 ml were analyzed for thallium by the recommended procedure.

RESULTS AND DISCUSSION

Mechanism of masking

Generally a metal ion which can exist in two different oxidation states differs in its tendency to complex with EDTA at different oxidation states. Thallium is one such metal, forming a stable complex with EDTA ($\log K = 22.5$) in its trivalent state,^{16,17} but showing 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 a ba-

sic medium (pH 8–9), with complete dissociation of the Tl(I)–EDTA complex occurring in an acidic medium.¹⁹ Therefore, the redox system Tl(III)–Tl(I) can be conveniently employed in an acidic medium for the complexometric determination of thallium. Being a good reducing agent, sodium dithionite effectively reduces Tl(III) to Tl(I) in an acidic medium.²⁰ The redox reaction can be represented as follows:



Sodium dithionite thus selectively decomposes the Tl–EDTA complex through reduction of Tl(III) to Tl(I) and EDTA is quantitatively released at room temperature. The +1 oxidation state of thallium in the reaction mixture was confirmed by the chromate test.

TABLE I. Determination of thallium in thallium (III)nitrate solutions

| Thallium/mg | | Coefficient of variation/% | Relative error/% |
|-------------|--------|----------------------------|------------------|
| Taken | Found* | | |
| 3.64 | 3.63 | 0.30 | – 0.27 |
| 7.28 | 7.29 | 0.28 | + 0.14 |
| 10.92 | 10.91 | 0.18 | – 0.09 |
| 18.20 | 18.19 | 0.20 | – 0.05 |
| 25.48 | 25.44 | 0.16 | – 0.16 |
| 36.40 | 36.44 | 0.12 | + 0.11 |
| 54.60 | 54.68 | 0.14 | + 0.15 |
| 72.80 | 72.74 | 0.10 | – 0.08 |
| 101.92 | 101.80 | 0.09 | – 0.12 |

*Average of 6 determinations

Effect of concentration of sodium dithionite

Investigation of solutions containing a constant amount of thallium(III) showed that the addition of sodium dithionite in a 1:1 (M:L) molar ratio was sufficient for the quantitative release of EDTA from the Tl–EDTA complex. Further, it was noticed that the addition of excess reagent had no adverse effect on the obtained results. In all the present determinations, the concentration of the reagent was maintained at a slight excess over the required molar ratio.

Precision and Accuracy

To assess the accuracy and precision of the method, Tl(III) at different concentration levels was determined as per the recommended procedure. The results presented in Table I indicate that the method functions well in the range 4–100 mg of thallium, with a maximum relative error of $\pm 0.27\%$ and coefficient of variation ($n = 6$) of less than 0.30%.

Effect of diverse ions

The effect of co-ions on the quantitative determination of thallium was studied by estimating 18.20 mg Tl(III) in presence of these ions. The tolerance limits found were 200 mg of Pb(II), Zn(II); 100 mg of Cd(II), Ni(II), Co(II), Bi(III); 60 mg of Tl(I), Al(III), Fe(III), Ti(IV), Mo(VI); 30 mg of Mn(II), Ce(III), V(V), As(V), Sb(V); 15 mg of Ir(III), Cr(III), Rh(III), Ru(III), Au(III), Pt(IV) and 200 mg of sulphate, nitrate, phosphate, chloride, fluoride, borate, acetate, tartarate, thiocyanate, citrate. However, the presence of metal ions such as Hg(II), Pd(II), Cu(II) and Sn(IV) interfere with the determination. This is perhaps due to the simultaneous release of EDTA from their respective EDTA complexes as well as from the Tl-EDTA complex, by the reagent. The interference of Hg(II) (up to 50 mg) and Pd(II) (30 mg) can be avoided by premasking them with ammonium thiocyanate (5 % NH₄SCN, 10–12 ml each). Fluoride (5% NH₄F, 6–10 ml) can be used for premasking Sn(IV) (50 mg).

TABLE II. Determination of thallium in complexes

| Complex | Thallium theoretically present/% | Thallium found* | |
|---|----------------------------------|-----------------------|--------------------|
| | | Complexometric method | Gravimetric method |
| Tl(C ₂ H ₂ N ₃ S) ^a | 67.12 | 67.00 | 66.94 |
| Tl(C ₃ H ₅ N ₄ S) ^b | 61.30 | 61.42 | 61.50 |
| Tl(C ₂ H ₂ N ₃ S ₂) ^c | 60.73 | 60.62 | 60.58 |
| Tl(C ₅ H ₉ N ₄ S) ^d | 56.52 | 56.38 | 56.44 |
| Tl(C ₁₁ H ₁₁ N ₄ S) ^e | 46.91 | 47.00 | 47.04 |
| Tl(C ₁₂ H ₁₀ ONS) ^f | 48.58 | 48.66 | 48.70 |

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

Applications of the method

In order to assess the analytical usefulness of the proposed method, it was used for the determination of thallium in its complexes with mercapto ligands. The observed complexometric results were compared with those obtained gravimetrically by the chromate method and were found to be in good agreement (Table II). A number of synthetic mixtures of thallium with mercury, bismuth, lead, cadmium, zinc, aluminium, nickel or iridium were prepared according to their alloy compositions. The thallium content of each was determined and the results are summarized in Table III.

TABLE III. Determination of thallium (III) in synthetic solutions

| Synthetic solutions | Composition/% | Thallium found*/% |
|----------------------|--------------------|-------------------|
| Tl + Hg [#] | 8.7 + 91.3 | 8.71 |
| Tl + Bi + Pb | 11.5 + 55.2 + 33.3 | 11.49 |
| Tl + Cd + Zn | 50.3 + 4.7 + 45.0 | 50.20 |

TABLE III. Continued

| Synthetic solutions | Composition/% | Thallium found [*] /% |
|------------------------|-------------------------------|--------------------------------|
| Tl + Pb + Zn + Al | 30.0 + 40.0 + 20.0 + 10.0 | 30.06 |
| Tl + Al + Ni + Zn + Ir | 5.6 + 55.0 + 35.0 + 2.4 + 2.0 | 5.59 |

^{*}Average of 3 determinations; [#] Premasked with ammonium thiocyanate

CONCLUSIONS

Sodium dithionite is a simple, cheap, water-soluble reagent, hence it can be readily used as a demasking agent. The method proposed is simple and rapid, as it requires no heating for the quantitative release of EDTA and works well in the range of 4–100 mg of thallium. The absence of any precipitate in the titration medium facilitates the detection of a sharp end point. The demasking agent used can tolerate the presence of a large number of metal ions and anions. Moreover, interfering metal ions, such as Hg(II), Pd(II) and Sn(IV), can be suitably premasked in the present method. Thus, the method is fairly selective for the rapid determination of thallium in its salts, complexes and alloys.

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ИЗВОД

НАТРИЈУМДИТИОНИТ КАО СЕЛЕКТИВАН ДЕМАСКИРАЈУЋИ АГЕНС ЗА КОМПЛЕКСОМЕТРИЈСКО ОДРЕЂИВАЊЕ ТАЛИЈУМА

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Натријумдितिонит се предлаже као нови демаскирајући агенс за брзо и селективно комплексометријско одређивање талијума(III). У присуству других металних јона талијум(III) је прво комплексиран вишком EDTA, а вишак EDTA затим титрисан стандардним раствором цинксулфата при рН 5–6 (хексамински пуфер) уз ксиленол-наранџасто као индикатор. Количина EDTA еквивалентна количини талијума је ослобођена селективно натријумдितिонитом и ретитрисана стандардним раствором цинксулфата као и претходно. Репродуктивни и тачни резултати, са релативном грешком од $\pm = 0,27$ и коефицијентом варијације ($n = 6$) не већим од 0,30 %, добијају се за количине талијума у опсегу 4–100 mg. Испитиван је утицај различитих других јона. Метода је примењивана за одређивање талијума у његовим комплексима и легурама.

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