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THE ANALYTICAL CHEMISTRY OF THALLIUM

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CONTENTS

Introduction 479

1. Classification of methods for the determination of thallium 479
2. Analytical reactions of thallium(I) 480
   A. Precipitation 480
   B. Oxidation 481
   C. Reduction to the metal 482
   D. Complex formation 482
3. Analytical reactions of thallium(III) 482
   A. Complex formation 482
   B. Reduction 484

INTRODUCTION

The ever increasing use of rare elements in various technical fields in recent years, and advances in metallurgy, have caused increasing interest in the analysis of such elements as thallium.

The existence of two comparatively stable states (univalent and trivalent) has resulted in a larger number of analytical methods for thallium than for indium and gallium, its analogues. These methods are based on the precipitation of univalent thallium (less often of trivalent thallium), on the oxidation of Tl^+ to Tl^{3+} and the reduction of Tl^{3+} to Tl^+. The Tl^+ and Tl^{3+} ions differ markedly in many of their properties. For example Tl^{3+} shows a pronounced tendency to form complexes, whereas Tl^+ shows practically none. The various complexes which recent studies have revealed, make possible more selective and sensitive analytical methods. A comparatively large number of methods of detection and determination of thallium have been published, but neither the handbook of Fresenius and Jander[1], nor Anderson's survey[2], completely cover the modern methods of analysis of this element.

This review systematises the analytical reactions of uni- and trivalent thallium published in recent years.

1. CLASSIFICATION OF METHODS FOR THE DETERMINATION OF THALLIUM

Detection. Thallium can be detected spectroscopically by a flame test, and by the characteristic formation of crystalline precipitates on addition of potassium iodide, chloroplatinate, chromate[3], thiosulphate[4], iodobismuthate[5], uric acid[6], and picrolonic acid[7], to solutions containing Tl^+, and by the appearance of a characteristic colour when trivalent thallium is treated with benzidine (or *o*-toluidine). The instantaneous oxidation of benzidine by Tl(III) produced from Tl(I) by reaction with Pt(IV), has been suggested as a spot test[8]. A photoluminescent detection of thallium has been described; this is based on the ability of hydrated Tl^+ to luminesce on introduction into the lattice of alkali-metal halides[9]. As little as 0.00012 μg Tl, at a limiting concentration of $1:10^7$, can be detected. The method has been applied to ores and minerals[10]. Reactions accompanied by fluorescence provide the basis for other methods of detection[11,12].

Methods for the determination of thallium. The most accurate methods for determining substantial quantities of thallium are gravimetric, principally involving precipitation as (1) the chromate, Tl_2CrO_4, (2) the iodide, TlI, (3) the thionalidate, $C_{12}H_{10}ONSTl$, (4) the mercaptobenzothiazolate, $C_7H_4NS_2Tl$, (5) the hydroxyquinolinate, $(C_9H_6ON)_3Tl$, (6) the hexamminecobalt(III) hexachlorothallate $[Co(NH_3)_6][TlCl_6]$, (7) the tetraphenylarsonium tetrachlorothallate $[(C_6H_5)_4As][TlCl_4]$, and (8) the diantipyrinylmethane tetrabromothallate, $C_{23}H_{24}O_2N_4.HTlBr_4$.

Of greater practical value are the titrimetric methods in which Tl(I) is oxidised by solutions of $KMnO_4$, $KBrO_3$, KIO_3, KIO_4, or the iodine, liberated when Tl(III) reacts with KI, is reduced with thiosulphate. Potentiometric methods are widely employed, using platinum spirals or discs as electrodes. Determinations of end-points amperometrically or conductimetrically find only slight application, though the former could be developed. A few papers describe coulometric methods based on the oxidation of Tl(I) with electrolytically generated substances such as free halogens or ferricyanide.

In industry thallium is frequently determined polarographically, after extraction from solution

The most important of the spectrophotometric and photometric methods involve precipitation of complex chlorides (or more seldom bromides), TlX_4^-, with large cations of various triphenylmethane dyes. The compounds formed are extracted with solvents such as benzene or toluene, and the optical density of the extracts measured; the dyes themselves remain in aqueous solution. The commonest dyes employed are methyl violet, rhodamine B, brilliant green, and certain other basic dyes.

Spectroscopic methods for determining thallium are most sensitive and widespread in analytical practice. Thallium can be detected by introducing a powder containing it into an oxy-acetylene flame: by the appearance of a green line at 5360.46 Å, 10^{-3}–5.10^{-4}% of thallium can be detected[13]. Spectroscopic methods have been described for determining thallium in zinc[14,15], in cadmium[16,17,18], in lead-zinc ores and the products of their processing[19], in lead[20,21], in soil[22], in pyrite[23], in zinc blende[24], and in ores and minerals[25]. The application of this method in forensic medicine is also described[26].

Traces of thallium may be determined by an activation method[27,28].

The separation of thallium from accompanying elements and its concentration. Extraction of thallium dithizonate at pH 10 from solution containing cyanide and citrate, permits the separation of this element from many others which form stable cyanide and citrate complexes. Extraction with diethyl ether from solutions 4M in HCl or 1M in HBr is most important: in the first instance Fe, Ga, Hg, Sb, Au, and Mo are extracted besides Tl; in the second, a more selective separation is achieved; only Hg, Sb, and Au accompany Tl. Subsequent separation from these elements is effected chemically: Hg and Au are plated out on copper (Sb is only partially removed). Antimony is removed by coprecipitation of small quantities of thallium with ferric hydroxide in the presence of excess alkali[29], or by means of the SBS cation exchanger in the presence of citric, tartaric, or oxalic acids[30], separation from the other elements being also accomplished.

The separation of thallium from many elements, including Hg, Ag, Cu, Cd, Zn, etc., by precipitation as $TlClO_4 . 4CS(NH_2)_2$, has been described.

A good method of concentration and simultaneous separation from accompanying elements consists in coprecipitation with silver iodide,[31,32], with manganese(IV) hydroxide[33], with ferric hydroxide[33a,33b], or with the precipitate formed by *p*-dimethylaminoazobenzene and the sodium salt of *p*-dimethylaminoazobenzene-*p*-sulphonic acid[34]. The mechanism has been studied of the coprecipitation of thallium sulphide with the sulphides of metals of the "H_2S group" in analysis[35,36,37], and with zinc sulphide[37a]. Also coprecipitation with calcium phosphate[38], barium and lead chromates[39], lead sulphate[40], and cuprous and mercurous iodides[40a], have been studied.

2. ANALYTICAL REACTIONS OF THALLIUM (I)

The Tl^+ ion shows some resemblance to Group I cations, Pb^{2+}, Hg_2^{2+}, and Ag^+ ("HCl group" in analysis), and also to the alkali-metal ions K^+, Rb^+, and Cs^+. This dual nature is ascribable to its ionic radius (1.49 Å, cf. K^+ 1.33 Å, Rb^+ 1.49 Å, Cs^+ 1.65 Å) and the value of the electrostatic function z^2/r (Tl^+ 0.67, K^+ 0.75, Rb^+ 0.67, Cs^+ 0.61), the latter indicating a tendency to form typically ionic compounds. Thus Tl^+ forms sparingly soluble compounds with the same anions as the larger alkali-metal cations, and is precipitated by $[Co(NO_2)_6]^{3-}$, $[PtCl_6]^{2-}$, $[BiI_4]^-$, or $[BiI_5]^{2-}$, and $H_4[P(Mo_2O_7)_6]^{3-}$.

On the other hand Tl^+ resembles Ag^+, in that it forms bonds which are largely or completely covalent (characterised by Yatsimirskii[41], in terms of the difference between the ionisation potential of the atom and the heat of hydration of its ion). Thus relatively small ions such as Cl^-, Br^-, and I^-, with easily polarised electron clouds, combine with Tl^+ to give compounds of low solubility, due to the sharp increase in lattice energy brought about by the introduction of covalent links in the crystal. Hence Tl^+ reacts with ions and molecules which tend to form covalent links, such as mercaptobenzothiazole, thionalide, dithizon, thiourea, and Reinecke salt. Thus, many precipitation reactions are known for Tl^+, but few are selective.

A. Precipitation

Precipitation as the chromate. Crookes[42,43,44] observed in 1861, when he discovered thallium, that the addition of K_2CrO_4 to alkaline solutions of Tl^+ gave a yellow precipitate practically insoluble in water. Browning and Hutchings[45] first described the gravimetric determination of thallium as Tl_2CrO_4, without indicating the solution for washing the precipitate. Moser and Brukl[46] determined the solubility of Tl_2CrO_4 in water, alcohol, and solutions of NH_3 and K_2CrO_4. At 20° the solubilities were 8.15×10^{-5} mole/litre in water and 1.14×10^{-5} mole/litre in 96% alcohol: from these results they worked out the following gravimetric method: an ammoniacal solution of Tl^+ is brought to the boil and K_2CrO_4 is added with stirring till there is a 2% excess (the concentration of NH_3 is unspecified). After standing 12 h the precipitate is washed by decantation with 1% K_2CrO_4 solution, then with 50% alcohol till the washings are colourless, and is dried at 120°. Mach and Lepper[47] used 1.25% solutions of NH_3 and K_2CrO_4. Bodner and Terenyi[48] carried out a parallel determination with $KMnO_4$ to verify the precipitation method. Bashilova[49] verified that the optimum concentrations of NH_3 and K_2CrO_4 were 1%. The possible temperature range for drying was found to be 97°–745° by thermogravimetry[50].

Thallium can be determined by the chromate method in the presence of Be, Al, Fe, Cr, Zn, Cd, Ni, Co, Ag, Hg, Cu, if the latter are converted to suitable complexes[46]. The Tl^+ ion mixed with Tl^{3+} can be determined in aqueous $HClO_4$ solution. Another method of precipitation of Tl^+ employs Na_2CrO_4, NaCN, ethanol, and a slight excess of ammonia[51,52]. If the solution contains Fe^{3+} besides Tl^+ and Tl^{3+}, then the alkaline $Fe(CN)_6^{3-}$ oxidises the Tl^+ to Tl^{3+}, and the estimation of Tl^+ is impossible. Forchheimer and Epple[53] suggested the separation of Tl^+ from other ions by precipitation from a 1M $HClO_4$ solution with Na_2CrO_4 solution: Tl^+ is said to be precipitated quantitatively as chromate and dichromate. The precipitate is washed with 1 M NH_3 and 1 M NaCN containing 1 g of Na_2CrO_4 per 150 ml, and weighed as Tl_2CrO_4.

Halide ions, Bi, Pb, Mn, Th, Zr, Ti, Ce, Ga, Sn, and reducing ions interfere with the chromate method. The small selectivity of the method and the high conversion factor to thallium (0.77895) limit its use in analysis. An easier method involves the iodometric back-titration of an excess of added chromate[54]. Amperometric titration of Tl^+ by K_2CrO_4 is possible using a dropping mercury electrode at -0.6 to -0.7 V and Complexone III (EDTA tetrasodium salt) to mask interfering ions[55].

Precipitation as dichromate. Bashilova suggests[56,57] a method of precipitation of Tl^+ from acid or neutral solution by means of excess chromium trioxide. The crystalline precipitate of $Tl_2Cr_2O_7$ (large crystals) is allowed to stand for two hours before filtration and drying at 110°–130°. Fewer ions interfere than in the precipitation as Tl_2CrO_4.

Precipitation as iodide. Though less sensitive than the chromate method, precipitation by KI solution is widely used. Thallous iodide forms a greenish-yellow or orange-yellow finely crystalline precipitate which becomes straw-yellow on standing. The solubility of TlI (2.4×10^{-4} mole/litre) is ten times that of Tl_2CrO_4 (2.41×10^{-5} mole per litre).

The gravimetric estimation of TlI was first elaborated by Lepper[58]. The acetate solution of Tl^+ is warmed to 80°–90°, 4% KI solution is added, the precipitate is cooled, filtered in a crucible, washed with a solution containing 1% KI and 1% CH_3COOH, followed by 80% acetone, and then dried at 120°–130°. The conversion factor to thallium (0.6170) is more favourable than for Tl_2CrO_4. The possible drying range is 70°–473°.[50] The iodide method is recommended for mineral analysis[59,60]. It is sufficiently selective if Complexone III is added to the acetate solution to mask the ions of Pb, Cu, Fe, Bi, etc.[61]. It is used to estimate Tl in metallic lead: if Pb^{2+} is bound with ammonium acetate the limit of detection is 0.4% Tl.[62] Tl^+ may be titrated with standard KI solution using bromophenol blue as adsorption indicator[63,64]. Thallium can be determined by treatment of precipitated TlI with zinc and concentrated HCl, titrating I^- with standard KIO_3 solution[65]. Amperometric[66] and radiometric[67] titrations of Tl^+ with KI solution are possible.

Precipitation with Reinecke salt. A recent method for thallium estimation involves precipitation from acid, neutral, or weakly basic solution with Reinecke salt, $NH_4[Cr(SCN)_4(NH_3)_2]$.[68,69,70] The solubility of the thallium derivative of the salt at 18° was found to be 8.7×10^{-6} mole/litre (using Tl^{204}),[71] and 5.3×10^{-5} mole/litre (by weighing the residue from evaporation of a saturated solution)[72]. The precipitate can be titrated in aqueous HCl in the presence of benzene with KIO_3 solution till the pink colour in benzene disappears; not less than 0.2 mg of Tl in 25 ml may be determined in this way[73]. Alkali, alkaline-earth and "sulphide group" (in analysis) cations do not interfere with the determination. This method is preferable to those described previously (smaller solubility and conversion factor to Tl).

Precipitation as iodate. Rao[74] describes the precipitation of $TlIO_3$, but as the solubility is 1.85×10^{-3} mole/litre, the method has little use.

Precipitation as cobaltinitrite. This method[75] gives a precipitate whose composition is independent of Tl concentration and corresponds to $Tl_3[Co(NO_2)_6]$.[76] Prolonged action of the reagent leads to a change in composition of the precipitate, introducing some $Tl_2Na[Co(NO_2)_6]$. The solubility of $Tl_3[Co(NO_2)_6]$ determined using Co^{60} and Cs^{134}, was 8×10^{-5} mole/litre at 20°.[77] In the presence of silver, thallium forms a precipitate of $Tl_2Ag[Co(NO_2)_6]$ which is easily soluble in aqueous-acetone NH_4SCN solution; the Co^{2+} in solution is then equivalent in quantity to the thallium and is titrated with Complexone III solution till the blue of the cobalt thiocyanate disappear[78].

Precipitation as mixed ferrocyanides. Thallium resembles Rb^+ and Cs^+ in forming mixed ferrocyanides. Tananaev and Glushkova showed[79] that thallium forms sparingly soluble ferrocyanides with magnesium, calcium, and strontium, of composition $Tl_2M[Fe(CN)_6]$, as well as $Tl_2Cu_3[Fe(CN)_6]_2$, $Tl_4Ni_4[Fe(CN)_6]_3$, $TlLa[Fe(CN)_6].4H_2O$, $TlCe[Fe(CN)_6].3H_2O$, $Tl_2(UO_2)_3[Fe(CN)_6]_2$, and $Tl_4(UO_2)_4[Fe(CN)_6]_3$. Ssuspensions of copper, nickel, and uranyl ferrocyanides can evidently be used to remove traces of thallium. Potentiometric titrations with $K_4Fe(CN)_6$ in the presence of calcium ions with an electrode reversible with respect to the ferri–ferrocyanide system[80] and conductimetirc titrations[81], have been suggested.

Precipitation as sulphide. This is inaccurate because the precipitate tends to adsorb other materials and to oxidise in air. Small quantities of thallium, however, can be titrated radiometrically, using a solution of Na_2S containing S^{35},[82] or photometrically[83].

Other inorganic precipitations. The reaction of Tl^+ with $Na_2S_2O_4$[84,85] has been used to determine Tl nephelometrically. Conductimetric titrations of Tl^+ with KSeCN[86] and KSCN[87] are also possible.

Precipitation with organic reagents. The use of organic reagents enables Tl^+ to be determined with greater sensitivity, and occasionally with greater selectivity. Thallium tetraphenylboron has a solubility of 6×10^{-7} mole/litre (found radiometrically)[88], and the sensitivity of the precipitation is 9 μg Tl/ml. Wendlandt[89] elaborated a gravimetric method using sodium tetraphenylboron; the precipitate is dried at 100°–105°; Tl^+ is also titrated conductimetrically using this reagent[90]. Radiometric titration has been applied to various technical products[91].

Most characteristic of Tl^+ are precipitations with reagents containing -SH and >C=S groups. Precipitation with mercaptobenzothiazole[92], or thionalide[93,94], in alkaline tartrate–cyanide solution permits the separation of Tl^+ from all major impurity elements. The microgravimetric determination with thionalide is performed as follows: 0.5 ml of 10% CH_3COONa, 0.25 ml of 20% KCN, and 0.5 ml of 2*N* NaOH are added, and then, to the solution at 80°, containing 3–6 mg Tl^+, are added 25–35 ml of thionalide in acetone. The precipitate is dried at 110°.

Sodium diethyldithiocarbamate and other dithiocarbamates[95-98] form sparingly soluble internal complexes with Tl^+. Dithizon forms a compound with Tl^+, with a dissociation constant $K = 4.35 \times 10^{-6}$,[99] which is stable enough for its use in the quantitative extraction of Tl^+ from elements which interfere with its spectrophotometric determination[100-102].

Other precipitations use 3-mercapto-4-hydroxytoluene[103], the β-semicarbazones of isatin and *N*-benzylisatin[104], the thioderivative of salicylaldehyde[105], 8-mercaptoquinoline[106], thioacetamide[107], *o*-mercaptoacetamido-*p*-nitrophenol[108], and *p*-(mercaptoacetamido)acetanilide[109].

B. Oxidation

The normal redox potential of the couple Tl^{3+}/Tl^+ is 1.222 V in *N* H_2SO_4.[110] The thallous ion reduces silicomolybdic acid to the blue form, and can thus be determined photometrically in solutions of 0.7–0.4 mg Tl^+/10 ml.[60]

In acid solution containing sufficient Cl^- to complex Tl^{3+} firmly, Tl^+ reduces $KMnO_4$ to Mn^{2+},[111-113] and in alkaline medium to MnO_2 or to K_2MnO_4 in the presence of $BaCl_2$.[114,115]. Thallous ion is used to back-titrate the excess $KMnO_4$ after oxidation of H_2O_2 and hydrazine[116], and in the course of the estimation of Pb^{2+}, Se^{4+}, Te^{4+}, and Cr^{3+}.[117] Salts of Tl^+ selectively reduce MnO_4^- in the presence of $Cr_2O_7^{2-}$;[118] Tl^+ can be titrated with $KMnO_4$ in the presence of KBr and the indicators victoria ruby-red, acid black 10B, methyl orange, and indigocarmine[119].

Desmukh[120] suggested iodine in alkaline solution as an oxidant of Tl^+, excess iodine being titrated with thiosulphate. He also used selenious acid which was reduced by Tl^+ to elementary selenium[121].

The thallous ion in 28–37% HCl solution reduces IO_4^- [122] and $K_7Cu(IO_6)_2$ [123] to ICl.

It also reduces other oxygen containing oxidants such as KIO_3 and $KBrO_3$: Tl^+ can be titrated with KIO_3 in the presence of KI, [124] and of HCl. [125] The following titrations of Tl^+ have been described: with chloramine-T in HCl solution with indigosulphonic acid as indicator [125]; with Ce^{4+} and ferroin; [126] and with vanadate in the presence of ICl as catalyst [127]. Potentiometric titration with $KBrO_3$ in acid solution can be carried out in the presence of Na_2HPO_4 which complexes Fe^{3+}. [128]

In alkaline solution Tl^+ is titrated potentiometrically with $K_3Fe(CN)_6$. [129,130] Tl^+ is oxidised with chlorine or bromine water [131] (excess chlorine is removed by boiling, and excess bromine by reaction with phenol or sulphosalicyclic acid), and with potassium or ammonium persulphate in solutions containing about 1 M free H_2SO_4.

Thallous ion has been titrated coulometrically with $Fe(CN)_6^{3-}$, [130] Cl_2 or Br, [131] generated electrolytically, the end-point being found potentiometrically or amperometrically.

The Tl^+ ion is oxidised at a rotating platinum electrode [132,133], at which half-wave potentials become more positive with lower pH values.

The Tl^+ ion is quantitatively deposited as Tl_2O_3 by electrolytic oxidation under defined conditions, but the method lacks sufficient accuracy [134]. Thallium separates quantitatively at the anode from ammoniacal NH_4NO_3 solution if the solution contains Cu^{2+} as a depolariser preventing deposition of thallium at the cathode [135]. Thallium separates from metallic cadmium by electrolysis in ammoniacal solution at 2 V potential and 0.2–0.4 A current [136]. Internal electrolysis with a Pb/PbO_2 cathode in sulphuric acid at pH 1.5, causes thallium to separate quantitatively as Tl_2O_3, even in the presence of 100-fold excess of Ag, Cd, or Zn. [137]

C. Reduction to the Metal

Polarographic reduction at a dropping mercury electrode. The half-wave potentials depend relatively little on the nature of the supporting electrolyte in the reduction of Tl^+ to the metal [138]. The Tl^+ ion has featured in many studies of the influence of ionic strength on the magnitude of diffusion current [139], and in the determination of diffusion coefficients in solutions of various electrolytes [140]. Recently the polarographic constants of thallium (I_d, $E_{\frac{1}{2}}$, D) have been published for various non-aqueous media: ethylene glycol [141], ethylenediamine [142], formamide [143], mixtures of formamide and acetamide [144], aqueous-alcoholic solutions of indifferent electrolytes [145], absolute ethanol [146], and aqueous dioxan [147].

Aqueous solutions are widely employed for the polarography of thallium, used successfully in the determination of thallium in highly purified zinc [148], and in lead [149], cadmium [150,151,152], indium [153], and zinc salts in the presence of tin [154].

Electrolytic reduction at other electrodes. Thallium is deposited at a cathode as a weakly adhering mass which is easily oxidised in air [134]: it is deposited at a mercury cathode from a solution containing nitric and benzoic acids [155]. The results obtained are somewhat high; the maximum error of 6.25% is probably due to oxidation of the thallium. Electrolytic deposition of Tl^{204} from $Tl^{204}ClO_4$ solution has been described [156].

D. Complex Formation

The Tl^+ ion, like Ag^+, forms rather unstable complexes with halide ions, which have been studied spectrophotometrically [157] and their solubilities have been determined. The former study showed the existence in solution of undissociated molecules TlCl and TlBr, and that on addition of excess halide ions new absorption peaks appear nearer the infra-red region, due to TlX_2^-, TlX_3^{2-}, TlX_4^{3-}. Determinations of thallium based on the TlCl peak at 245 mμ (in the presence of lead and bismuth) [158], and the fluorescence of $TlCl_3^{2-}$ at 2537 Å, [159] have been described. Kuo-Hao Hu and Scott [160] measured the solubility of TlCl in solutions of alkali-metal chlorides and showed that the $TlCl_2^-$ ion exists and has a dissociation constant of 0.68; they confirmed their results spectrophotometrically [161]. Dissociation constants derived from solubility measurements have been obtained for $TlBr_2^-$, $TlBr_3^{2-}$, [162] TlI_2^-, TlI_3^{2-}, and TlI_4^{3-}. [163]

Thiocyanate complexes, still less stable than the halide complexes, have been studied potentiometrically and from their solubility [164,165]. Thiosulphate complexes have been studied [166]; the dissociation constants of the compounds $Na[Tl(S_2O_3)]$ and $K[Tl(S_2O_3)]$ have been found to be of the order of 10^{-2}. [167] The existence of $Na[Tl(S_2O_3)]$ has been shown polarographically: it has a pK of 1.91. [168]

Complex formation with Tl^+ has been proved for histamine [169], pyrophosphate [170], and citrate [171].

Typical of Tl^+ are the thiourea complexes which may be precipitated with heavy anions such as perchlorate, picrate, and tetrathiocyanatodiamminechromate(III) (from the Reinecke salt) [172]. The presence of Tl^+ is reliably detected by the formation of needle-shaped crystals of $\{Tl[SC(NH_2)_2]_4\}ClO_4$, [173] which also allows the quantitative separation of Tl from impurity elements [174].

The Tl^+ ion complexes with ethylenediaminetetracetic acid only at high pH values [175], making determination difficult by this means. Spectrophotometric titration with a solution of the tetrasodium salt of EDTA (Complexone III) at pH 10 and 222 mμ has been described [176]. The considerable instability of these thallium complexes is shown by the results of high-frequency titrations of equivalent quantities of Tl^+ and the acid with NaOH solution [177]. The dissociation-constant exponents (pK's) of Tl^+ complexes with nitrilotriacetic and ethylenediaminetetraacetic acid at 25° are 3.44 (μ = 1.4) and 5.81 (μ = 1.0), where μ is the ionic strength [178].

3. ANALYTICAL REACTIONS OF THALLIUM (III)

The thallium(III) ion shows pronounced oxidative properties and a tendency to complex with both inorganic and organic ligands. The stability of trivalent ion complexes decreases in the series Tl > Bi > Sb > Fe > Cr > Al. [179]

A. Complex Formation

Hydroxo complexes. Trivalent thallium gives the sparingly soluble hydroxide by hydrolysis even in acid solution. The light-absorption maximum for $Tl(ClO_4)_3$ solution increases as the $HClO_4$ concentration decreases, due to $Tl(OH)^{2+}$ and $Tl(OH)_2^+$ formation, only mononuclear complexes being formed [180]. The pK for the first step of the

hydrolysis is 0.2; [181] at acid strengths from 0.5 to 2.0 M the basic $Tl(OH)^{2+}$ ion is absent from solution. Biedermann [182], in a potentiometric study of the hydrolysis, found

$$K_1 = \frac{[Tl(OH)^{2+}][H^-]}{[Tl^{3+}]} = 7.3\times10^{-2} \text{ and } K_2 = \frac{[Tl(OH)_2^+][H^+]^2}{[Tl^{3+}]} = 2.3\times10^{-3}.$$

The solubility product of $Tl(OH)_3$ at 25° has been reported as $10^{-43.6}$, [181] $10^{-43.8}$, [183] and $10^{-45\pm0.2}$. [184]

Starik [185], studying the state of thallium at a concentration 10^{-4} M in sulphate solutions at various pH values, showed that although at pH 3 trivalent thallium was completely colloidal, it was almost instantaneously coagulated, from which he concluded that thallium hydroxide does not form a stable positively charged colloid. Coagulation ceases at pH 7, above which a fairly stable negatively charged colloid is formed. Thallium may be determined spectrophotometrically [186] as $Tl(OH)_3$ stabilised by the addition of gelatine.

Thallic salts may be used as acid-base titration indicators on account of their easy hydrolysis [187] – for example the Tl^{3+}/Tl^+ system in the presence of KI. [188]

Nitrato complexes. The redox potential for the Tl^{3+}/Tl^+ system is lower in nitric acid than in perchloric acid solution of the same concentration; in 1 M $HClO_4$ the potential is 1.260 V, [183] in 1 M HNO_3, 1.230 V. [189] More recent studies on the rate of exchange between $Tl^{204}ClO_4$ and $Tl(ClO_4)_3$ in the presence of NO_3^- (more rapid exchange) indicate complex formation of Tl^{3+} with NO_3^-. [52] Peshanski [190] found the equilibrium constant to be 1.5 at 18° and μ = 3.5 by a spectrophotometric method. Burns and Whiteker [191] showed that as μ varied from 0.57 to 3.0, the equilibrium constant changed from 8.3 to 2.0.

Sulphato complexes. The lowering of the redox potential of Tl^{3+}/Tl^+ in sulphuric acid solution [192] indicates complex formation of Tl^{3+} with SO_4^{2-} comparable to that with NO_3^-, but the sulphato complexes have been little studied. The magnitude of the solubility product can, however, be found from measurements of hydrolysis in sulphuric acid solution. The values 10^{-38}, [185] and 10^{-37}, [193] are higher than those found from hydrolysis in perchlorate solutions, which confirms the complexing of Tl^{3+} by SO_4^{2-}.

Cyano complexes. The increase in the rate of isotopic exchange in the Tl^+–Tl^{3+} system in the presence of CN^- indicates the formation of $Tl(CN)^{2+}$, $Tl(CN)_2^+$, and $Tl(CN)_3$. [194]

Halogeno complexes. Most fully studied are the chloro and bromo complexes, first demonstrated by the redox measurements of Spenser and Abegg [195] on Tl^{3+}/Tl^+ in the presence of halide ions, and confirmed by Hughes and Garner [196]. Recently chloro complexes have been studied by isotopic exchange between $TlClO_4$ and $Tl(ClO_4)_3$. [197] Benoit [181] found potentiometrically at 25° and μ = 0.1–0.2 pK values (dissociation constant exponents) for the following complexes: $TlCl^{2+}$ (pK_1 = 8.1), $TlCl_2^+$ (pK_2 = 5.5) $TlCl_3$ (pK_3 = 2.2), $TlCl_4^-$ (pK_4 = 2.6), $TlBr^{2+}$ (pK_1 = 9.7), $TlBr_2^+$ (pK_2 = 6.9), $TlBr_3$ (pK_3 = 4.6), and $TlBr_4^-$ (pK_4 = 2.7). Peshanski and Valladas-Dubois found the following values for chloro complexes: pK_1 = 6.25, pK_2 = 5.15, pK_3 = 3.10, pK_4 = 2.5, pK_5 = 1.80 (for $TlCl_5^{2-}$); and for the bromo complexes: pK_1 = 8.9, pK_2 = 7.5, pK_3 = 5.7, pK_4 = 4.0, pK_5 = 3.1 (for $TlBr_5^{2-}$), and pK_6 = 2.4 (for $TlBr_6^{3-}$). [157,198] The Tl^{3+}–I^- system is complicated by simultaneous complex formation and oxidation-reduction [198a]. Iodination of TlI in methanol and dioxan gives TlI_3 together with its complexes with dioxan [199].

Sharpe has shown that in aqueous solutions containing KI and TlI_3, TlI_4^- is formed [200], which has been confirmed spectrophotometrically for solutions of I^- and Tl^{3+} in various molar ratios [201]. The pK of TlI_4^- is 32.15. [202]

Halogeno complexes have considerable stability and are widely used in the estimation of thallium: they may be precipitated by organic and inorganic cations of high molecular weight or extracted by organic solvents from complex mixtures.

Of the acid complexes of $HTlCl_4$, but not H_2TlCl_5, is extracted by diethyl ether from solutions containing HCl; [203] by this means thallium is estimated in lead [204], in toxic materials [205], in urine and hair [206], and in certain other cases [207]. Thallium may be separated from all elements except Au and Hg by paper chromatography of its chloro complexes in butanol saturated with 1 N HCl. [208,209,210].

The extraction of thallium from solutions containing HBr was introduced by Wada and Ischii [211], has been studied repeatedly by many workers [212,213,214], and has been employed to estimate thallium in tin–cadmium alloys [215], and in ores and process products of non-ferrous metals [151]. The extraction of thallium from solutions containing HI has been studied but not applied [212,213,214].

Meyer [216] and Renz [217] describe the precipitation of chloro thallium complexes with various organic nitrogenous bases. Bivalent metal chlorides have been used similarly [218]. Thallium may be determined gravimetrically by precipitation as $[(C_6H_5)_4As][TlCl_4]$, though MnO_4^-, IO_4^-, ClO_4^-, SCN^-, NO_3^-, I^-, Br^-, and ReO_4^- interfere [219]. $(C_6H_5)_4AsCl$ and $(C_6H_5)_4SbCl$ are used as precipitants [220]. A finely crystalline precipitate, $[Co(NH_3)_6]TlCl_6$, insoluble in HCl, ethanol, and ether, is formed from $[Co(NH_3)_6]Cl_3$ and a solution containing Tl^{3+} and excess Cl^-. This is used to determine thallium gravimetrically in pure salts and lead alloys [221], and radiometrically using Tl^{204} or Co^{60}. [222,223]. Other complex cation precipitates include $[Co(en)_3][TlCl_6]$, $[Co(en)_2Cl_2][TlCl_4]$, and $[Co(en)_2(NO_2)_2]H_2[TlCl_6]$. [224]

Precipitations involving bromide instead of chloride ions are distinctly more sensitive. The detection of Tl^{3+} as a finely crystalline bromo complex with urotropine and acridine has been described [225]. Sandri [226] used $HTlBr_4$ to detect pyridine, α-picoline, quinoline, urotropine, choline, betaine, caffeine, theobromine, theophylline, and nicotinamide. Busev and Tiptsova [227] studied precipitation of complex bromides with derivatives of pyrazolone, and determined Tl^{3+} gravimetrically using diantipyrinylmethane [227,227a] and spectrophotometrically using the same reagent and diantipyrinylpropylmethane [227b].

Complex iodothallates may be employed analytically, for example thallium may be detected by precipitation as the iodothallates of cocaine, strychnine, codeine, pilocarpine, atropine [228], quinoline [229], pyridine [225], and caesium [230].

The colourless chloro and bromo complexes of thallium precipitated with certain cationic dyestuffs may be extracted by non-polar organic solvents, and the thallium can be estimated by spectrophotometric measurement of the dye-

stuff extract; methyl violet (crystal violet) is commonly used[231-238]. The molar extinction coefficient of the extract of the complex is 48000 at 570 mμ and 64000 at 620 mμ; [234] the optimum acidity is 1 *N* HCl according to Gur'ev, and 0.08–0.2 *N* HCl according to Shchemeleva; excess oxidising agents destroy the dye and should be excluded. Beer's law is obeyed for concentrations of Tl^{3+} from 0.2 to 2.5 μg/ml. [231]

Trivalent thallium is estimated as $TlCl_4^-$ or $TlBr_4^-$ complexes with Rhodamine B; [239,240] the molar extinction coefficient is 87000 at 560 mμ, and the extract fluoresces at 580 mμ. Brilliant green gives a maximum optical density with solutions 0.08–0.16 *N* in HBr, the molar extinction coefficient being 70000. [241-243] Tetramethyldiaminodiphenylantipyrinylcarbinol is used as a precipitant for $TlCl_4^-$; [244] the molar extinction coefficient is 68000 at 638 mμ, Beer's law being obeyed for Tl^{3+} concentrations from 0.1 to 2.0 μg/ml. Certain other dyes have been employed[245]. All spectrophotometric methods based on this principle require previous separation of thallium from Au, Hg, and Sb.

Acetato complexes of thallium are quite stable. Moeller and King showed that in the presence of excess sodium acetate at pH 4.5 Tl^{3+} can be separated from Fe^{3+} as an acetato complex[246]. Toropova found the dissociation constants of $Tl(CH_3COO)_2^+$ and $Tl(CH_3COO)_3$ to be 3.1×10^{-12} and 5.6×10^{-16}, by measuring the redox potential of Tl^{3+}/Tl^+ in the presence of acetate ions[247]. Oxalic acid reduces Tl^{3+} to Tl^+. [247]

Tartrato complexes. The stability of tartrato complexes of thallium(III) relative to those of gallium, indium, and aluminium has been studied[248].

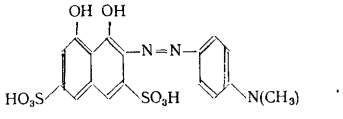
Complexes with amines. 2,2'-Dipyridyl yields $[Tl(dp)_2](NO_3)_3$, $[Tl(dp)_3](NO_3)_3$, and $[Tl(dp)_2](ClO_4)_3$. The dissociation constant of $[Tl(dp)_3]^{3+}$ was found potentiometrically to be $5 \pm 2.5 \times 10^{-26}$. [249] Mixed complexes have been obtained from halide ions and ammonia[250], ethylenediamine, 2,2'-dipyridyl and *o*-phenanthroline[251].

Ethylenediaminetetraacetic acid complexes. Like all trivalent metals, thallium forms an acid-stable compound with Complexone III, which is used for the amperometric titration of thallium at pH 1.0–1.2, in which Tl^{3+} is reduced at a rotating platinum electrode[252]. Flaschka determined thallium by means of EDTA tetrasodium salt, the thallium derivative being more stable in alkali than that of magnesium[253]. Trivalent thallium can be titrated directly against 1-(2-pyridylazo)-napththol with xylenol orange as indicator[254]. In indirect determinations the excess EDTA tetrasodium salt may be back-titrated with zinc salts and benzidine-ferrocyanide as indicator[255], thorium salts and alizarin S [176], ferric salts and sulphosalicylic acid[256], vanadium salts and diphenylcarbazide or diphenylcarbazone[257], cobalt salts and thiocyanate[258]; zinc salts are used for the potentiometric titration of the excess Complexone using a mercury test electrode[259].

Complexes with 8-hydroxyquinoline and its derivatives. Thallic ion precipitates quantitatively with 8-hydroxyquinoline; the precipitate is dried at 120° and weighed as a monohydrate[260,261]. The absorption curve of the chloroform solution shows a maximum at 400–402 mμ, with a molar extinction coefficient of 6790; 1.2–5 μg Tl/ml may thus be determined, though the solution decomposes on ultra-violet irradiation[261]. The solubility product of the 8-hydroxyquinoline complex is 4×10^{-33}. [262] Thallium is precipitated by dibromohydroxyquinoline[260], 2-methyl-8-hydroxyquinoline and 5-nitroso-8-hydroxyquinoline[263]. The 8-hydroxyquinoline[264] and 5-methyl-8-hydroxyquinoline[265] derivatives have been studied thermogravimetrically.

Complexes with various dithiocarbamates. Thallium(III) precipitates quantitatively with diethyldithiocarbamate[95]; the complex is extracted with CCl_4, the extract having an absorption maximum at 426 mμ with a molar extinction coefficient of 1330. Moderate quantities of thallium (600 μg/25 ml) may thus be determined spectrophotometrically: Tl^{3+} is also precipitated by other disubstituted dithiocarbamates[98,266]. The Tl^{3+} ion can be radiometrically titrated with sodium 5-methylpyrazoline-1-dithiocarboxylate[266]. Successive radiometric titration of Tl(III)-In(III) and Tl(III)-Zn(II) can be carried out with 3-methyl-5-phenylpyrazoline-1-carboxylic acid.

Complexes with other organic reagents. Various internal xanthate complexes have been obtained $[Tl(ROCS_2)_3]$ where R = methyl, ethyl, isopropyl, n-butyl, s-hexyl [267]. Certain chromotropic azo-dyes have been studied as reagents for Tl^{3+}, the most sensitive being



with which 0.05 μg Tl(III)/ml can be detected[268]. Evidence exists for thallium complexes with nitrosophenylhydroxylamine and 1-nitrosonaphthylhydroxylamine[269].

B. Reduction

When Tl^{3+} is reduced with KI, the iodine liberated is titrated with thiosulphate[270,271]. Photometric determination of a starch–iodine complex may also be employed[272,273]. The semimicro-determination of Tl^{3+} is carried out by titration in H_2SO_4 with standard KI and a starch indicator[201].

Thallium(III) is determined by photometric measurement of the colour produced by oxidation of certain organic compounds with thallium(III). Thus thallium(III) with *p*-phenetidine at pH 3.1 [274] and with pyramidon gives a reddish-violet colour with an absorption band between 350 and 540 mμ; the solutions obtained obey Beer's law for thallium concentrations between 0.05 and 5 mg per 50 ml, Pb, Bi, Zn, and Cd not interfering[275]. At concentrations up to 0.5 mg/ml Fe(III), Zn, Cd, As, and Cu do not interfere with the determination based on the violet colour obtained with *p*-aminophenol sulphate[276]. With benzidine thallium(III) gives a blue colour, the stability of which depends on the pH of the solution[277]. Electrochemical reduction has been little studied. Smith and Nelson[278] studied the effect of thallium(III) on a dropping mercury electrode in chloride solutions; Hughes and Husch[279] studied the effect in perchlorate solutions, but their results are seldom applied due to the proximity of the redox potential of Tl^{3+} and the anodic-dissolution potential of mercury. Reduction on platinum is of greater analytical use; Songina observed the reversible redox wave for the Tl^{3+}–Tl^+ system using a rotating platinum electrode[280].

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A considerable number of methods for the determination of thallium are based on Tl^{+}, principally involving its precipitation. Insufficient attention has so far been paid to analyses based on reactions of Tl^{3+}. Such reactions, particularly those involving complex formation, are very promising for the development of new methods which may overcome some of the existing inadequacies in the estimation of thallium. Research into thallium(III) complexes should lead to analytical methods satisfying present requirements as regards simplicity, speed, precision, selectivity, and sensitivity.

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