Microdetermination of Thallium and Indium Using Potassium Morpholine-4-Carbodithioate as an Amperometric Titrant

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Potassium morpholine-4-Carbodithioate has been utilized in the amperometric determination of thallium(I) and indium(III). These metal ions react quantitatively with this reagent in the pH range of 7.9-9.5 (tartrate buffer) for Tl(I) and 4.6-6.1 (acetate buffer) for In(III). Under these conditions, the reagent gives a well-defined diffusion controlled anodic wave while these metal ions are not reduced, thus L shaped curves are obtained. The determination of these metals can be carried out in the concentration range of 0.102-2.043 mg of Tl(I) and 0.115 - 1.722 mg of In(III) in 25 ml of the sample solution. Sample solutions containing 0.818 mg of Tl(I) and 0.918 mg of In(III) give standard deviations of 0.0052 and 0.0045 with relative standard deviations of 0.63% and 0.49% respectively. The method has been applied to the determination of these metals in synthetic samples

The analytical potential of potassium morpholine - 4-carbodithioate reagent was first explored by Beyer et al(1). A number of metal complexes with this compound were also synthesised and characterized by Macrotrigiano and coworkers(2) and Brown et.al(3). Spectrophotometric(4,5) and gravimetric(6-9) determination of some metal ions utilizing this reagent have also been reported. The polarographic studies and amperometric determination of a few metals have been reported by Rao and coworkers(10). In most of the amperometric procedures reported in the literature for the determination of thallium(11) and indium(12), the titrations have been carried out at a potential where the reagent is only oxidized and the metal ions present are not reduced. The control of pH further improves the selectivity of the method. The method has been applied to the determination of these metals in various synthetic samples.

EXPERIMENTAL

Reagents

Potassium morpholine -4-carbodithioate(MCDT) was prepared by the method of Macrotrigiano(2). Stock solution of MCDT was prepared by dissloving calculated amount in distilled water and standardized against a standard solution of mercuric nitrate using diphenylcarbozone as the internal indicator. Solutions of supporting electrolytes were prepared by dissloving A.R. grade potassium nitrate, ammonium tartrate and sodium acetate in distilled water. Stock solutions of the cations were prepared from their G.R. samples and standardized by known methods(13). Dilute solutions of ammonia, acetic acid and formic acid were used to adjust the pH.

Instruments

The titrations were performed by using a manual Toshniwal polarograph. An Elico pH meter was used for pH measurements.

Experimental Procedure

An aliquot of the metal solution was taken in a beaker. To this were added requisite amounts of ammonium tartrate and potassium nitrate for Tl(I) and sodium acetate-acetic acid in case of In(III) so as to have the concentration of 0.1 M of each in 25 ml of the final solution. The pH was adjusted in the desired range. Electrical connections were made and titration carried out at DME set to -0.2 V vs SCE. The solution was deaerated with a stream of N_2 gas before each current reading. Titrant solution (20 times stronger than the solution in the cell) is taken in a microburette. A 2 ml microburette was used to deliver the titrant in small increment. The mean deflection of the galvanometer was noted in each case.

RESULTS AND DISCUSSION

Morpholine-4-carbodithioate gives a well defined, diffusion controlled, reversible, one electron anodic wave(11) in the pH range 5.75 - 11.7 extending over a fairly wide span of potential, +0.2 V to -0.3 V vs SCE. The graph between diffusion current and concentration is linear upto 2.7 mM of this reagent in 25 ml of the solution in the cell. Preliminary observations revealed that under regulated conditions of pH and concentration of the base electrolyte, this reagent gave the formation of characteristic precipitates with Tl(I) and In(III)..

The applied potential -0.2 V vs SCE was selected for the titration of these cations where the metal ions were not reduced but the reagent was oxidized at the DME. The titrations, therfore, involved the measurement of the anodic current of the excess titrant only after the complete precipitation of the cation. The reverse L shaped curves were obtained by plotting current against volume of the titrant and the end point was located graphically.

EFFECT OF pH

Determination of Tl(I) and In(III) were carried out by the general procedure at various pH. The results were found to be accurate and reproducible over the pH range of 7.9 - 9.5 for Tl(I) and 4.6-6.1 for In(III).

EFFECT OF BASE ELECTROLYTE CONCENTRATION

Preliminary studies on base electrolytes for these determinations showed that 0.05 - 0.25 M each of potassium nitrate and ammonium tartrate for Tl(I) and sodium acetate-acetic acid for In(III) were found to be the most suitable one.

ACCURACY AND PRECISION

Tl(I) and In(III) could be accurately and conveniently determined over the concentration range (Table 1). Solutions containing 0.819 mg of thallium and 0.918 mg of indium gave standard deviations of 0.0052 and 0.0045 with relative standard deviations of 0.63% and 0.49% respectively.

TABLE 1

DETERMINATION OF THALLIUM AND INDIUM IN PURE SAMPLES
Applied Potential: -0.2 V, Indicator Electrode : DME
Reference Electrode = SCE for both Tl and In.

Titrant : Potassium Morpholine-4-Carbodithioate
Conc. is 5×10^{-3} M for Tl(I), and 3×10^{-2} M for In

Metal	Amount taken (mg)	Amount found (mg)	Error (%)
Thallium Supporting electolyte 0.1M KNO_3 + 0.1M Ammonium tartrate pH 8.7 (Tl) = 5 mM			
	0.102	0.103	0.97
	0.204	0.206	0.97
	0.406	0.409	0.74
	0.818	0.824	0.73
	1.635	1.645	0.63
	2.044	2.058	0.68
Indium Supporting electrolyte 0.1M sodium acetate, 0.1M acetic acid pH 5.10 (In) = 30 mM			
	0.115	0.115	0.86
	0.345	0.342	0.57
	0.575	0.572	0.52
	0.918	0.923	0.54
	1.148	1.153	0.54
	1.722	1.730	0.46

* Average of six determinations.

TABLE 2

DETERMINATION OF THALLIUM IN SYNTHETIC SAMPLES

S.No.	Amount of Tl taken (mg)	Foreign ions added (mg)	Amount of Tl found* (mg)	Error (%)	Remarks
1.	0.612	As = 0.75 Sb = 0.50 In = 0.50	0.616	0.65	--
2.	1.020	Sb = 0.50 Cu = 0.25 Co = 0.30	1.030	0.98	Cu(II) and Co(II) were masked with 5 ml of Sodium cyanide solution.
3.	1.530	As = 0.50 In = 0.25 Pb = 0.30	1.545	0.98	Pb(II) was masked with the addition of 5 ml of 5% sodium sulphate solution.

* Average of six replicate determinations.

INTERFERENCES

The interference on the determination of Tl(I) and In(II) by this method due to Mo(VI), Th(IV), U(VI), Rh(III), Ru(III), Pt(IV), As(III), Sb(III), W(VI), Ca(II), Ba(II), Mg(II), Mn(II), Al(III), Co(II), Ni(II), Cu(II), Pd(II), Cd(II), Ag(I), Hg(II) and Pb(II) was investigated in both cases. Most of these cations could be tolerated upto 5-6 hold in excess with the exception of the following: For Tl(I): Cu(II), Hg(II), Ag(I), Pd(II), Pb(II), Co(II), Ni(II) and Cd(II) interfered. Except Pb(II), all these could be masked by adding 5 ml of 5% solution of sodium cyanide while Pb(II) could be eliminated by adding sodium sulphate before titration. In case of indium determination; Ag(I), Hg(II), Pd(II), Cu(II), Cd(II), Pb(II) and Ni(II) were tolerated in equivalent amounts. Only Co(II), Zn(II) and Sb(III) interfered seriously. Co(II) and Zn(II) could be masked by adding 5 ml of 5% solution of sodium cyanide. Tl(I) and In(III) do not interfere in the determination of each other.

TABLE 3

DETERMINATION OF INDIUM IN SYNTHETIC SAMPLES

Sample No.	Amount of In taken (mg)	Foreign ions added (mg)	Amount of In found* (mg)	Error (%)	Remarks
1.	0.774	Cd = 0.35 Tl = 0.40 Zn = 0.25	0.768	0.77	Zn^{+2} was masked with 5ml of 5% sodium cyanide solution
2.	0.861	Tl = 0.60 Sn = 0.30 Pb = 0.80	0.870	1.04	---
3.	1.290	Pb = 1.20 Cd = 0.60 Tl = 0.40 Sn = 0.50	1.300	0.77	---

* Average of six determinations.

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