Amperometric Determination of Metal Ions with Thio acids - Ga(III), In(III) and Tl(I) With 2-Mercaptopropanoic acid

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2-Mercaptopropanoic acid (RSH) has often been used as an analytical reagent for the amperometric determination of various transition metal ions because of its complexing properties [1-2]. The present work was undertaken with a view to examine it further.

EXPERIMENTAL

Stock solution of 2-mercaptopropanoic acid was prepared afresh daily and standardised using standard chloramin T solution [4]. $Ga_2(SO_4)_3$, $2In(NO_3)_3.9H_2O$ and Tl_2SO_4 were employed as source compounds for the respective metal species. Stock solutions of Ga(III) and In(III) were prepared in 0.1 M sulphuric and perchloric acids respectively and standardised amperometrically with thiomalic acid [3]. Thallium solutions were prepared by direct weighing of the source salts. Only analytical grade chemicals & doubly distilled water were used.

All titrations were performed at DME *vs* SCE using a manual polarograph (Toshniwal Model CLO2A). Agar agar salt bridge containing KCl was used with SCE. Purified nitrogen was used for deaeration. All titrations were carried out thrice.

RESULTS AND DISCUSSION

The organic acid is known to give a reversible 1 electron anodic wave in 0.1 M KCl [1] and 0.4 M $NaClO_4$ [5]. Similar wave was observed in 0.1M $NaClO_4$ and in 0.1 M K_2CO_3. The metals give cathodic waves. Different conditions and media have been studied. Conditions of successful titrations are presented in Table 1.

It is seen from the Table that the first break in case of Gallium titration has highly variable stoichiometry and hence not suitable for determinations. The second break was used for the determination. It is noteworthy that Ambulkar and Munshi have reported complexation of Ga with L through 1:2 and 1:3 stoichiometry [7]. The first break appears at higher ligand concentration range indicative of the presence of higher species.

In case of Indium, the lowest concentration determined is indicated as 1.15 ppm. Even more dilute solutions could be estimated with an error of $\pm$ 5.0 %. If thio acid was used as titrant, with the potential on the cathodic limiting current of indium, no reaction occured in KCl medium, but titration was possible in 0.1 M $NaClO_4$ medium. It is worth noting that M : L ratio here is as 2:1. It must

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Table 1

Titration Parameters - Different Metals & Media

Ligand: 2-Mercaptopropanoic acid (gives anodic wave)

Parameter	Gallium	Indium	Thallium
Titration Potential on the Anodic Wave of the Ligand			
Medium	0.1 M KCl	0.1 M KCl	0.1 M K_2CO_3
Limiting current Region of Ligand	0.0 to -0.2 V	0.0 to -0.2 V	-0.2 to -0.45 V
Cathodic Step of Metal	$E_{1/2}$ = -1.1 V Irreversible [6]	$E_{1/2}$ = -0.56 V [Ref 6]	Limiting region beyond -0.6 V
Titration Potl.	- 0.1 V	- 0.1 V	- 0.3 V
Titrant	Metal	Metal	Metal
Shape of Titration Curve	Reverse L shape (two breaks)	Reverse L shape (one break)	Reverse L shape (one break)
Stoichiometry	Variable at I bk M:L = 1:1 at II	M:L = 1:2	M:L = 1:2
Conc. Range (ppm)	1.74 to 348.60	1.15 to 575	20.43 to 1021.9
% Error	±3% or lower	±2%	±2%
Titration Potential on Cathodic Wave of Metal			
Medium	-	0.1 M $NaClO_4$	0.1 M K_2CO_3
Limiting current region of Ligand	-	0.0 to 0.1 V	
Titration Potential	-	-0.75 V	-1.2 V
Titrant	-	Ligand	Metal
Stoichiometry	-	M:L = 2:1	M:L = 1:2

be mentioned that potentiometric titration studies [8] have shown the presence of 1:1, 1:2 and 1:3 indium complexes with L. Under metal excess conditions, a possibility exists of a 2:1 cationic complex with RSH coordinating with two In(III) through deprotonated sulphydril and carboxyl group acting as bridge. These titrations enabled estimation of metal solutions more dilute than 1.15 ppm with accuracies higher than the titrations with metal solution. Mean error was ±2% and ±3% in case of 0.23 and 0.12 ppm respectively. In this medium anodic titrations gave variable results.

In case of thallium, both cathodic and anodic titrations could be carried out in 0.1 M K_2CO_3 medium. It may be recorded here that thallium reaction with the thio acid is not reported earlier.

Table 2

Limit of Concentration of Foreign ions wrt metal (in mM) in cell solutions

Foreign ion	Gallium	Indium in 0.1 M of KCl	$NaClO_4$	Thallium
Thiosulphate	1/10 times	1/10 times	t	equal
Tungstate	1/10 times	1/10 times	1/10 times	t
Acetate	10 times	t	t	t
Oxalate	equal	t	10 times	t
Al(III)	t	equal	t	5 times
Mn(II)	10 times	t	t	t
Co(II)	10 times	t	equal	1/10 times
Ni(II)	t	t	t	1/10 times
Zn(II)	10 times	t	t	1/10 times
Cr(III)	equal	1/15 times	10 times	equal
Fe(II)	1/10 times	1/10 times	interference	equal
Cd(II)	1/10 times	1/10. times	equal	1/10 times
Tl(I)	5 times	1/10 times	equal	-
Pb(II)	Interference	1/10 times	interference	1/10 times
V(V)	Interference	interference	1/15 times	1/10 times
Mo(VI)	10 times	1/15 times	t	equal
Ga(III)	-	Serious Interference		

Interference Studies

Tolerance Limits of a large number of foreign ions in all the above methods have been worked out. Nitrate, sulphate, chloride and magnesium do not interfere with the titration. Stannous, cupric, ferric and Mn(VII) interfere seriously. Other cases are included in Table 2.

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