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Amperometric Trace Determination of Arsenic with 2-Mercapto and 3-Mercaptopropanoic Acids

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Amperometric determination of trace amounts of As(III) and As(V) is reported with the help of 2-mercaptopropanoic acid (RSH) and 3-mercaptopropanoic acid (MPSH) at d.m.e. 0.5 M NH_3 + 0.5 M NH_4Clmedium has been employed for As(III) while determination of As(V) with RSH has been carried out in 0.5 M K_2CO_3 and that with MPSH in 0.1 M K_2SO_4 medium. Titration potentials have been selected in the limiting region of the anodic wave of organic acids and metal ion solutions used as titrants. M : L titrimetric molar ratio has been found to be 1 : 1 for both the metal species. Complexation of metal ions has been proposed as the basis of the new amperometric methods. Solutions as dilute as 7.5 ppm have been estimated with high degree of accuracy. Tolerance limits for foreign ions have also been worked out.

INTRODUCTION

2-Mercaptopropanoic acid (RSH)[1–5] and 3-mercaptopropanoic acid (MPSH)[6–9] have often been used as complexing agents and sometimes as analytical reagents[6,10] for determination of metal ions. In fact, these ligands have been exploited earlier also for the amperometric determination of a large number of metal ions in this laboratory[10–14]. The present work was undertaken with a view to probe their utility for the amperometric determination of As(III) and As(V) also in traces at d.m.e.

EXPERIMENTAL

Only analytical grade chemicals and doubly distilled water were used. All the titrations were perfomed at d.m.e. (versus SCE) employing a manual polarograph (Toshniwal, India, Model CL02A). $NaAsO_2$ and $Na_2HAsO_4 \cdot 7H_2O$ were used as source compounds of As(III) and As(V) respectively. As(III) was standardized volumetrically[14] and As(V) amperometrically.[15] RSH and MPSH solutions were prepared afresh daily and standardized.[16] Amperometric determination of metal ion solution of any particular concentration was carried out atleast thrice. Purified nitrogen was employed for deaeration. Titration potentials were selected in the limiting region of the anodic wave of the organic acids.

RESULTS AND DISCUSSION

Both RSH and MPSH are known to undergo reversible, one-electron oxidation at d.m.e. in certain supporting electrolytes.[10,17–19] Similar anodic waves were obtained in our media too. As(V) did not undergo reduction in any of the media employed while As(III) gave an ill-defined cathodic wave in 0.5 M NH_3 + 0.5 M NH_4Cl medium though no reduction current was present at the titration potential. Arsenic solutions were used as titrant. Amperometric curves of upside-down L-shape were obtained in both the cases and the null point always corresponded to M : L ratio of 1 : 1. Approximately 50% anodic current remained unneutralized in each case. Concentration of arsenic solutions taken for the present study ranged from 374.6 ppm through 7.5 ppm with the standard deviation in case of the most dilute solution being a meagre 0.052. Other important details of the amperometic processes developed have been included in Table-1.

TABLE-1
TITRATION CONDITIONS FOR THE AMPEROMETRIC DETERMINATION OF ARSENIC

Metal	Medium	Anodic limiting region of the ligand wave (–E)	Titration poential (–E)
		PART A—LIGAND: RSH	
As(V)	0.5 M K_2CO_3	0.10–0.50	0.30
As(III)	0.5 M NH_3 + 0.5 M NH_4Cl	0.20–0.45	0.30
		PART B—LIGAND: MPSH	
As(V)	0.1 M K_2SO_4	0.00–0.20	0.10
As(III)	0.5 M NH_3 + 0.5 M NH_4Cl	0.20–0.45	0.30

No colour change was observed during titrations though complexation of the two metal species with the organic reagents seems to be the fundamental basis of the new titrimetric processes.

Checking of interference of foreign ions and selectivity

Study of interference of foreign ions in the new amperometric methods was carried out for three concentrations of each metal species *viz.* 374.6 ppm, 74.9 ppm and 37.5 ppm. Table-2 includes safe limits of foreign ions in the cell solution. Non-interfering species did not interfere even when present simultaneously in this solution.

TABLE-2
SAFE LIMIT OF THE CONCENTRATION OF FOREIGN IONS IN THE CELL SOLUTION WITH RESPECT TO THE CONCENTRATION OF THE METAL SPECIES (IN MOLAR TERM)

Metal ion	As(III)		As(V)	
Medium	0.5 M NH_3	0.5 M NH_4Cl	0.1 M K_2SO_4	0.5 M K_2CO_3
Ligand	MPSH	RSH	MPSH	RSH
Foreign ion				
Mg(II)	a	a	a	a
Cr(III)	1/10	1/10	1/10	Equal
$S_2O_3^{2-}$	b	b	b	b
Al(III)	a	a	a	a
Tl(I)	Equal	Equal	Equal	Equal
V(V)	b	b	b	b
Mn(VII)	b	b	b	b
Mn(II)	a	a	a	a
Co(II)	a	a	a	a
Fe(II)	1/10	1/10	1/10	equal
Fe(III)	b	b	b	b
Ni(II)	a	a	a	a
Cd(II)	1/10	1/10	1/10	1/10
Cu(II)	b	b	b	b
Zn(II)	a	a	a	a
Pb(II)	1/10	1/10	1/10	1/10
As(V)	a	a	—	—
As(III)	—	—	a	a
Mo(VI)	b	b	b	b
WO_4^{2-}	a	a	a	a
F^-	a	a	a	a
Ga(III)	b	b	b	b
CH_3COO^-	a	a	a	a
In(III)	b	b	b	b
NO_3^-	a	a	a	a
Sn(II)	a	a	a	a
SO_4^{2-}	a	a	a	a

a = No interference even when concentration in cell solution is 20 times that of the metal ion in the titrant solution.

b = Serious interference even when concentration is 1/20 of the metal ion.

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