

NOTE**Amperometric Trace Determination of As(III), As(V) and Pb(II) with Thioglycolic Acid**

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Amperometric trace determination of As(III), As(V) and Pb(II) is reported with the help of thioglycolic acid at d.m.e. 0.1 M NH_3 + 0.1 M NH_4Cl medium has been employed for As(III), 0.1 M KCl for As(V) and acetate buffer of pH = 4.99 is used for Pb(II). Titration potential has been selected in the limiting region of the anodic wave of thioglycolic acid and metal ion solutions are used as titrant. M : L titrimetric ratios have been found to be 1 : 1 for As(III) and 1 : 2 for As(V) as well as for Pb(II). Solutions as dilute as 18.73 for As(III), 7.49 for As(V) and 20.72 ppm for Pb(II) have been estimated with high degree of accuracy. Interferences of different foreign ions have also been worked out.

Key Words: Amperometric determination, As(III), As(V), Pb(II), Thioglycolic acid.

Thioglycolic acid (TGA) formulated as $\text{HS-CH}_2\text{-COOH}$ has often been used as a complexing agent and analytical reagent¹⁻⁶. However, its capacity to act as an amperometric reagent has by and large remained unexplored. The present work was undertaken with a view to unravel this aspect of the acid and new amperometric methods have been evolved for estimation to trace amount of As(III), As(V) and Pb(II).

All the titrations were performed at d.m.e. vs. S.C.E. employing a manual polarograph (Toshniwal India, Model CLO2A). Only analytical grade chemicals and doubly distilled water were used. Sodium arsenite (NaAsO_2), sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) and lead acetate ($\text{CH}_3\text{COO}_2\text{Pb} \cdot 3\text{H}_2\text{O}$) were used as source compounds for As(III), As(V) and Pb(II) respectively.

Determination of As(III) and As(V): Thioglycolic acid is known to give a reversible one electron anodic wave in 0.2 F NH_4Cl , 1 F NH_3 media⁷ having $E_{1/2} = -0.56$ V similar wave was obtained in 0.1M NH_3 + 0.1M NH_4Cl medium with $E_{1/2} = -0.51$ V.

Arsenic solutions were used as titrant and titrations were carried out selecting -0.20 V for As(III) and -0.10 V for As(V) in the limiting region of the anodic

wave of TGA. Amperometric curves of upside down L-shape were obtained in both cases and null point corresponded to M : L ratio of 1 : 1 for As(III) and 1 : 2 for As(V). Concentration ranges of arsenic solutions taken for various titrations were from 374.6–18.73 ppm for As(III) and 374.6–7.49 ppm for As(V). No colour change was observed during titrations. Details of the amperometric results have been given in Table-1. Maximum error ($\pm 2\%$) was encountered in the case of most dilute solution of arsenic only.

TABLE-1
AMPEROMETRIC ESTIMATION OF As(III) AND As(V)

Metal	Medium	Anodic limiting region of the ligand wave (-E)	Titration potential (V)	Concentration range of metal ion (ppm)
As(III)	0.1 M NH ₃ + 0.1 M NH ₃ Cl	0.10–0.30	-0.20	374.6–18.73
As(V)	0.1 M KCl	0.0–0.20	-0.10	374.6–7.49

Determination of Pb(II)

Thioglycolic acid gives one electron anodic wave in 0.2 F HOAc, 0.2 F NaOAc medium⁷, $E_{1/2} = -0.26$ V. Similar wave was also obtained in acetate buffer of pH = 4.99 with $E_{1/2} = -0.26$ V. Amperometric titrations have been carried out keeping the potential fixed at -0.10 V in the anodic limiting region of TGA and Pb(II) solutions were used as titrant.

Amperometric curves of upside-down L-shape were obtained and the null point always corresponded to metal to ligand stoichiometry of 1 : 2. The new method enabled the estimation of Pb(II) in the concentration range of 1036–20.72 ppm. No colour change was observed during the titrations. Maximum error ($\pm 2\%$) was encountered in the case of most dilute solution of lead only.

TABLE-2
AMPEROMETRIC ESTIMATION OF Pb(II)

Metal	Medium	Anodic limiting region of the ligand wave (-E)	Titration potential (V)	Concentration range of metal ion (ppm)
Pb(II)	Acetate buffer of pH = 4.99	0.05–0.20	-0.10	10.36–20.72

Checking of Interference of Foreign Ion and Selectivity

Study of interference of foreign ions in the new amperometric methods developed was carried out for three concentrations of each metal species 5.0, 1.0 and 0.5 mL. A large number of foreign ions were quite well tolerated. Such foreign ions did not interfere even when present together in the cell solution. The results have been summed up in Table-3.

TABLE-3
SAFE LIMIT OF THE CONCENTRATION OF FOREIGN IONS IN THE CELL SOLUTION WITH RESPECT TO THE CONCENTRATION OF THE METAL SPECIES

Foreign ions	Determination of As(III)	Determination of As(V)	Determination of Pb(II)
Mg(II)	Equal	a	a
Cr(III)	Equal	Equal	1/20
Cr(VI)	Equal	b	b
S ₂ O ₃ ²⁻	1/20	b	1/20
Al(III)	Equal	Equal	Equal
Co(II)	b	b	5 times
V(V)	1/20	b	b
Mn(II)	b	a	a
Mn(VII)	b	b	b
Fe(II)	1/5	1/10	1/5
Fe(III)	1/20	1/20	1/20
Ni(II)	1/20	a	Equal
Cd(II)	1/20	a	1/20
Zn(II)	1/5	a	1/5
As(III)	—	1	10 times
As(V)	—	1/10	a
Mo(VI)	b	b	Equal
WO ₄ ²⁻	a	a	a
CH ₃ COO ⁻	a	10 times	1/20
NO ₃ ⁻	a	a	a
Ox ²⁻	a	a	a
Cu(II)	b	b	b
Hg(II)	b	b	b

a = No interference even when concentration in cell solution is 20 times in excess to that of the metal ions in the titrant solution

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

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