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NOTE

Ethanethioic Acid as a Reagent for Trace Determination of Zn(II), Cd(II) and Hg(II)

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Amperometric determination of Zn(II), Cd(II) and Hg(II) was carried out with the help of ethanethioic acid (ETA) at d.m.e. in 0.1 M K_2SO_4, 0.1 M NH_3 + 1.0 M NH_4Cl and 0.1 M $HClO_4$ medium respectively. Metal ions solutions were used as titrant (anodic titrations) in all the cases. Metal species-ETA stoichiometry was 1 : 2 for each metal. Solutions as dilute as 6.54 ppm (Zn), 11.24 ppm (Cd) and 10.03 ppm (Hg) were estimated with high degree of accuracy. Tolerance limit for foreign ions has also been worked out.

Ethanethioic acid (thioacetic acid-ETA) has sometimes been used as a ligand for complexing with metals[1-3] and numerous biological applications of the acid and its salts have been reported[4]. However, its capacity to act as an analytical reagent has by and large remained unexplored. The present work was undertaken with a view to unravel this aspect of ETA and unique amperometric methods have been evolved for estimating small amounts of Zn(II), Cd(II) and Hg(II).

EXPERIMENTAL

All the titrations were performed at d.m.e. *vs.* s.c.e. using a Toshniwal manual polarograph. Analytical grade chemicals and doubly distilled water were used. ETA solution was prepared afresh daily and was used as such. Amperometric determination of metal solution of any particular concentration was carried out at least thrice. Purified nitrogen was employed for deaeration. Titration potential (–0.05 V) was selected in the anodic limiting region of ETA in case of Cd(II) and metal ion solution was employed as titrant. In case of Zn(II), titrations were carried out in the anodic limiting region of ETA at –0.10 V and metal ion solution was used as titrant. Determination of Hg(II) could be carried out in the cathodic limiting region of the metal ion at –0.50 V using metal ion solution as titrant. 5 mL of chloroform were added to the cell solution each time while determining Hg(II) right in the beginning so that the metallic mercury falling from the capillary and accumulating at the bottom of the cell always remained covered with this organic layer. This precluded any significant interaction between the mercury and Hg(II)[5].

Determination of Zn(II):

Amperometric determination of Zn(II) was carried out in 0.1 M K_2SO_4 medium. ETA gave a well defined, diffusion controlled, one electron anodic wave

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in this medium, with the diffusion region spread over the potential range of 0.00 V through –0.15 V, $E_{1/2}$ being –0.24 V. Titrations with zinc solution (anodic titrations) were carried out at –0.10 V. Zn(II) also gave its cathodic wave in this medium, $E_{1/2}$ being –1.09 V, but its cathodic current was nil at the titration potential. The titration resulted in upside-down L-shaped amperometric curve. The null point corresponded to metal-ligand molar ratio of 1 : 2. The method enabled the estimation of Zn(II) in the concentration range of 362.9 ppm through 6.54 ppm. Maximum error (less than 2%) was encountered in the case of most dilute solutions only. Also noteworthy is the fact that the 1 : 2 ratio being reported here is the same as reported by Nyholm and Hollebone[6] on the basis of solid phase studies.

Determination of Cd(II)

Amperometric determination of Cd(II) was accomplished in 0.1 M NH_3 + 1.0 M NH_4Cl medium. Cd(II) has been reported[7] to give a reduction wave in 0.5 M NH_3—NH_4Cl medium. A similar wave was observed by the authors in their medium with the limiting region stretched from –0.80 V through –1.80 V. Titration of ETA with the metal species solution (anodic titration) was carried out at –0.05 V. This voltage fell in the limiting region of ETA alone; no cathodic current of Cd(II) was present here. The titration resulted in upside-down L-shaped amperometric curve and the null point corresponded to Cd(II) : ETA molar ratio of 1 : 2. The method enabled the estimation of Cd(II) solutions in the concentration range of 562.02 ppm through 11.24 ppm. Maximum error (less than 2%) was encountered in the case of most dilute solutions only.

Determination of Hg(II)

Amperometric determination of Hg(II) was carried out in 0.1 M $HClO_4$ medium. Anodic titrations [using Hg(II) solution as titrant] were performed at –0.50 V which fell in the limiting region of Hg(II) alone. The titrations resulted in continuous linear increase in current on cathodic side right from the beginning. However, the slope changed at the null point and the break gave amperometric titrimetric Hg(II)-ETA molar ratio of 1 : 2. The new method enabled the estimation of Hg(II) solution in the concentration range of 1002.95 ppm through 10.03 ppm with average inaccuracy of less than 2%.

No colour was produced in the cell solutions during the course of any of the above titrations. Also, more than 50% of initial current always remained unneutralized at the null point indicating the formation of weak complexes.

Checking of interference of foreign ions and selectivity

Study of interference of foreign ions in the new-titrimetric methods was carried out for three concentrations of each metal species: 5.0 mM, 1.0 mM and 0.5 mM. A large number of foreign ions were quite well tolerated. Such foreign species

did not interfere even when present together in the cell solution. The data have been summed up Table-1.

TABLE–1
SAFE LIMIT OF THE CONCENTRATION OF FOREIGN IONS IN THE CELL SOLUTION WITH RESPECT TO THE CONCENTRATION OF THE METAL SPECIES

Foreign ion	Detn. of Zn (II)	Detn. of Cd(II)	Detn. of Hg(II)
SO_4^{2-}	A	A	A
NO_3^-	A	A	A
CH_3COO^-	A	A	A
$S_2O_3^{2-}$	equal	a	a
SCN^-	a	A	A
Ox^{2-}	A	A	A
WO_4^{2-}	A	A	10t
Mg(II)	A	A	A
Al(III)	A	A	A
V(V)	1/10	a	a
Cr(III)	1/10	equal	A
Cr(VI)	a	equal	A
Mn(II)	a	1/10	A
Mn(VII)	a	a	a
Fe(II)	a	a	a
Fe(III)	a	a	a
Co(II)	a	a	10t
Ni(II)	1/10	a	A
Cu(II)	a	1/10	a
Zn(II)	–	A	A
Mo(VI)	1/10	a	1/10
Cd(II)	a	–	1/10
Hg(II)	a	a	–

A = No interference even in presence of 20 times excess of the foreign ion with respect to the metal species determined.

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

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