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NOTE

Thioglycolic 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 thioglycolic acid (TGA) at d.m.e. in 0.1 M NH_3 + 0.1 M NH_4Cl, 0.1 M Na_2CO_3 + 0.1 M $NaHCO_3$ and 0.1 M KCl medium, respectively. Metal ion solutions were used as titrant in all the cases (anodic titrations). Titrations of Hg(II) solutions using acid as titrant (cathodic titrations) were also carried out successfully. Metal species-TGA stoichiometry obtained was 1 : 2 in all the cases. Solutions as dilute as 6.539 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.

Key Words: Thioglycolic acid, Amperometric determination, Zn(II), Cd(II) and Hg(II).

Thioglycolic acid ($HSCH_2COOH$, TGA) has often been used as a complexing agent[1–3] and analytical reagent[4–7]. 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 of trace amount of Zn(II), Cd(II) and Hg(II).

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. $ZnSO_4 \cdot 7H_2O$, $(CH_3COO)_2Cd \cdot H_2O$ and $HgCl_2$ were used as source compounds for Zn(II), Cd(II) and Hg(II), respectively. TGA solution was prepared afresh daily and standardized. Amperometric determination of metal solution of any particular concentration was carried out at least thrice. Purified nitrogen was employed for deaeration. Titration potentials –0.20 and –0.15 V for Zn(II) and Cd(II) respectively were selected in the anodic limiting region of TGA and metal ion solutions were used as titrant. Titrations of Hg(II) could be carried out at –0.10 V in anodic region of the acid (anodic titrations) as well as at –0.60 V in the cathodic limiting region of the metal ion (cathodic titrations). Chloroform (5 mL) was 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 mercury and Hg(II)[8].

Determination of Zn(II): Amperometric determination of Zn(II) was carried out in 0.1 M NH_3 + 0.1 M NH_4Cl medium. TGA has been reported[9] to give a well defined one electron anodic wave in 0.2 M NH_4Cl-1 M NH_3 medium. Similar wave was obtainedin 0.1 M (NH_3-NH_4Cl) medium with the diffusion region spread over the potential range of –0.20–0.00 volt. Titrations with zinc solution (anodic titrations) were carried out at –0.20 volt. Zn(II) also gave its cathodic wave in this medium 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 326.95–6.539 ppm. Maximum error (less than 2%) was encountered in the case of the most dilute solution only.

Determination of Cd(II): Amperometric determination of Cd(II) was accomplished in 0.1 M Na_2CO_3 + 0.1 M $NaHCO_3$ medium. TGA gave a well defined anodic wave in this medium with the diffusion region spread over the potential range of –0.05 V through –0.30 V. Titration of TGA with the metal species solution (anodic titration) was carried out at –0.15 volt. This voltage fell in the limiting region of TGA 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) : TGA molar ratio of 1 : 2. The method enabled the estimation of Cd(II) solutions in the concentration range of 562.05–11.24 ppm. Maximum error (less than 2%) was encountered in the case of the most dilute solution only.

Determination of Hg(II): Amperometric determinations of Hg(II) were performed in 0.1 M KCl medium. Hg(II) has been reported[10] to give a cathodic wave starting from > 0.0 V in this medium. TGA also gave its one-electron anodic wave in this medium with the limiting region from –0.05 to 0.20 V, $E_{1/2}$ being –0.30 V. The characteristics of this wave remained unchanged in presence of chloroform. In fact, the height of the Hg(II) wave, in absence of chloroform, was found to decrease with time, obviously due to chemical interaction between Hg(II) and metallic mercury; this did not happen when mercury at the bottom was kept covered with chloroform. Both cathodic as well as anodic titrations were carried out at –0.60 V (in the limiting region of Hg(II) wave alone) and at –0.10 V (in the limiting region of both the waves), respectively. Gradual addition of the metal species into TGA solution during anodic titrations resulted in continuous linear increase in current on cathodic side right from the start. However, the slope changed at the null point and the break gave Hg(II)-TGA molar ratio of 1 : 2. This form of an amperometric curve suggested the possibility of the reaction product being reducible at d.m.e. The cathodic titrations were accomplished at –0.60 V using TGA solution as titrant. The titration resulted in L-shaped curve and the null point corresponded to the Hg(II)-TGA molar ratio of 1 : 2. No colour was produced in the cell solutions during the course of any of the above titrations. The new method enabled the estimation of Hg(II) in the concentration range of 1002.95–10.03 ppm with average inaccuracy of < 2%.

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, *viz*., 5.00, 1.00 and 0.50 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 given in 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 Ions	Determination of Zn(II)	Determination of Cd(II)	Determination of Hg(II)	
			Anodic titrations	Cathodic titrations
Cl^-	1/20	A	A	A
NO_3^-	A	A	A	A
CH_3COO^-	A	A	Equal	Equal
$S_2O_3^{2-}$	1/20	1/20	1/20	1/20
Ox^{2-}	A	A	A	A
WO_4^{2-}	A	A	A	A
Mg(II)	A	A	A	A
Al(III)	1/20	5 times	Equal	Equal
V(V)	Equal	Equal	a	a
Cr(III)	1/20	1/5	Equal	Equal
Cr(VI)	Equal	Equal	a	a
Mn(II)	A	1/20	A	A
Mn(VII)	a	a	a	a
Fe(II)	1/20	1/20	1/10	1/20
Fe(III)	1/10	1/10	1/10	1/10
Co(II)	a	a	Equal	Equal
Ni(II)	1/20	1/10	Equal	Equal
Cu(II)	a	a	a	a
Zn(II)	—	1/5	A	A
Mo(VI)	Equal	A	1/20	1/20
Cd(II)	1/20	—	1/20	1/20
Hg(II)	a	a	—	—

A = No interference even in the 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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