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Thioglycolic Acid as an Amperometric Reagent for Trace Determination of Co(II) and Ni(II)

REKHA DEVI and S.P. KHATKAR*
Department of Chemistry, M.D.University, Rohtak-124 001, India
E-mail: s_khatkar@rediffmail.com

Amperometric determinations of Co(II) and Ni(II) have been carried out successfully with the help of thioglycolic acid (TGA) at d.m.e. in 0.1 M NH_3 + 0.1 M NH_4Cl supporting electrolyte. Metal species-TGA molar stoichiometric ratios of 1:1 for Ni(II) and 1:2 for Co(II) have been obtained using metal ions solutions as titrant (anodic titrations). Both methods seem to be the consequence of complexation reaction between the acid and the respective metal ions. Solutions as dilute as 5.86 ppm [Ni(II)] and 2.94 ppm [Co(II)] have been estimated with high degree of accuracy. Tolerance limits for foreign ions have also been worked out.

Key Words: Amperometry, Thioglycolic acid, Co(II), Ni(II).

INTRODUCTION

Amperometry being simple and low cost technique is employed for the quantitative determination of various metal ions in laboratories and chemical industries. It is also used in optimization and characterization of biosensors[1], in pharmaceutical formulations[2], micromolar determination of sulphur oxoanions[3], in binding assay for drug screening[4].

Many sulphur containing organic ligands have been used in amperometry for the trace determination of metal ions. Organic sulphur compounds containing –SH group are also known to give anodic wave at d.m.e.[5-10]. Thioglycolic acid (mercaptoacetic acid) formulated as $HSCH_2COOH$ and abbreviated as TGA in this report has often been used as a complexing agent[11-13] and an analytical reagent[14-17]. This acid has also been used in grafted onto silica gel[18], in preparation and characterization of glass embedding[19]. However its capacity to act as an amperometric reagent has by and large remained unexplored.

In recent years, owing to the growing awareness of environmental pollution and toxicity, the interest of researchers for the determination of cobalt and nickel has increased and various analytical technique such as atomic absorption spectrometry[20-22], direct voltammetric measurement[23], spectrophotometric detemination[24,25], flame atomic absorption spectrometry[26,27], batch absorption[28], flow injection chemiluminescence[29] have been exploited for the determination of these metal ions in different types of materials. Electro analytical methods like electrochemical Ni(II)-selective sensor[30], adsorptive stripping voltammetry[31], potentiometric membrane sensor[32] have also been employed. Electroanalytical technique can provide an interesting alternative to the traditional spectroscopic methods. These techniques offer two important advantages over the traditional technique. First of all, the cost of the instrumentation is relatively low and second, some of these technique are highly sensitive and selective.

The present work was undertaken with a view to develop new amperometric method using thioglycolic acid for the estimation of trace amount of Co(II) and Ni(II).

EXPERIMENTAL

All the titrations were performed at d.m.e. *vs.* S.C.E. using a Toshniwal manual polarograph. Agar-agar salt bridge containing KCl was used with S.C.E. Only analytical grade chemicals and doubly distilled water were used. $NiSO_4{\cdot}7H_2O$ and $CoSO_4{\cdot}7H_2O$ were used as source compound of Ni(II) and Co(II), respectively. Stock solutions of these compounds were standardized amperometrically[33].Titrations were accomplished in 10.0 mL of the solution in the cell using 0.1 M KCl as supporting electrolyte. The nitrogen gas was passed for 0.5 h in the beginning of the experiment. The gas was also passed for 3-5 min after every addition of titrant. This served the purpose of homogenizing the cell solution as well as deaerating the new aliquot of the liquid added. Limiting current corrected for dilution by the titrant was recorded as a function of the volume of titrant. Dilution correction was made with the help of the equation: $i_{corr.} = i_{obs.}(V+v)/V$, where $i_{corr.}$ is the corrected current, $i_{obs.}$ is the observed current, V is the volume of the solution taken initially and v is the volume of titrant added. The selected e.m.f. was kept constant throughout the titration. Null point was obtained graphically taking $i_{corr.}$ (along y-axis) *vs.* volume of titrant added along x-axis. TGA (mercaptoacetic acid) solution was prepared afresh daily and standardized. Amperometric estimation of each metal solution of any particular concentration was carried out at least thrice. Titration voltage (-0.20 volt) was selected in the anodic limiting region of TGA in case of both the metal ions and metal ion solutions were used as titrant in both cases.

RESULTS AND DISCUSSION

Determination of Ni(II)

Amperometric determination of Ni(II) was carried out in 0.1 M NH_3 + 0.1 M NH_4Cl supporting electrolyte medium with the help of thioglycolic acid (TGA). Ni has been reported[34,35] to give an irreversible, diffusion controlled wave in presence of 0.005 % gelatin in this medium with the limiting region stretching over the potential range of -1.00V through -1.80V; $E_{½}$ being -0.92V.

TGA has also been reported[36] to give a well defined one electron anodic wave in 1 M NH_3-0.2 M NH_4Cl medium. Similar wave was obtained in present studies in 0.1 M (NH_3-NH_4Cl) medium with the diffusion region stretching over the potential range of -0.00 V through -0.40 volt, $E_{½}$ being -0.56V. Anodic titrations were carried out at -0.20 volt which fell in the limiting region of TGA alone, using metal ion solution as titrant; no cathodic current of Ni(II) was present here. The amperometric curve obtained was of upside-down L-shape (Fig. 1). The null point corresponded to metal-ligand molar ratio of 1:1. The method enabled the estimation of Ni(II) in the concentration range of 293.46 ppm through 5.86 ppm. Maximum error (less than 2 %) was encountered in the case of the most diluted solution.

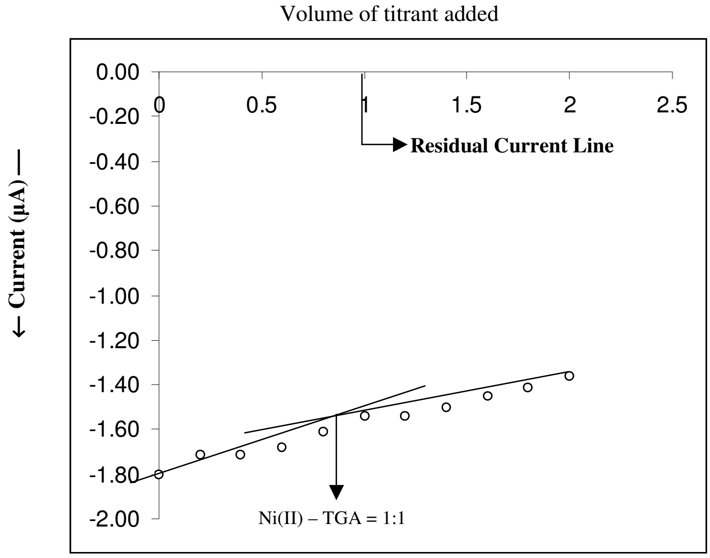

Fig. 1. Amperometric titration curve of Ni(II)-TGA system in 0.1 M NH_3 + 0.1 NH_4Cl medium
Titration voltage: -0.20 volt; Conc. of TGA: 0.50 mM; Conc. of Ni(II) in the titrant solution: 5.00 mM (293.46 ppm)

Determination of Co(II)

All the titrations were carried out in 0.1 M NH_3 + 0.1 M NH_4Cl medium. Co(II) is known[37] to give an irreversible, two electron cathodic wave in 0.1 M (NH_3-NH_4Cl) medium with the limiting region stretching over the potential range of -1.40 V through -1.80 V. The value of $E_{½}$ being -1.29 V. TGA also reported[36] to give a well defined one electron anodic wave in this medium with the limiting region stretching over the potential range of -0.00V through -0.40 volt, $E_{½}$ being -0.56V.

Anodic titrations were carried out at -0.20V. This voltage fell in the limiting region of TGA alone; no cathodic current of Co(II) was present here. The anodic current of TGA decreased linearly, finally yielding upside-down L-shaped titration curve of type shown in Fig. 2. The curve yielded a Co(II):TGA titrimetric molar ratio of 1:2. About 50 % current always remained unneutralized at the null point. Addition of aliquots of titrant produced dark brown colour.

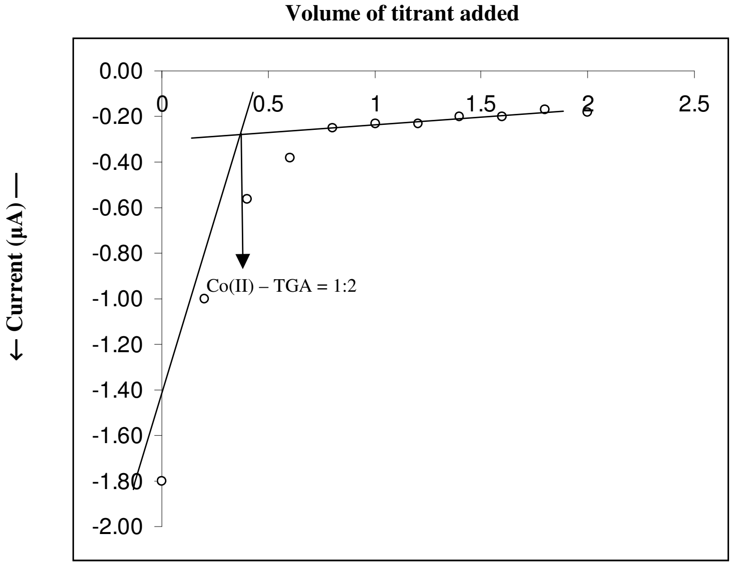

Fig. 2. Amperometric titration curve of Co(II)-TGA system in 0.1 M NH_3 + 0.1 M NH_4Cl medium
Titration voltage: -0.20 volt; Conc. of TGA: 0.50 mM; Conc. of Co(II) in the titrant solution: 5.00 mM (294.66 ppm)

Cathodic titrations were also carried out at -1.60 volt but cathodic current goes on increasing regularly. No any amperometric curve could be constructed. The method enabled the estimation of Co(II) in the concentration range 294.66 ppm through 2.94 ppm. Maximum error (less than 2 %) was encountered in the case of the most diluted solution only.

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 summed up in Table-1. Table-1 includes safe limits of foreign ions in the cell solution.

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		Foreign ions	Determination	
	Ni(II)	Co(II)		Ni(II)	Co(II)
Cl^-	A	A	Mn^{2+}	B	B
NO_3^-	A	A	Fe^{2+}	1/20	1/20
CH_3COO^-	1/10	Equal	Fe^{3+}	1/10	1/20
$S_2O_3^{2-}$	1/20	1/20	Co^{2+}	1/20	-
Ox^{2-}	A	A	Ni^{2+}	-	Equal
WO_4^{2-}	A	A	Cu^{2+}	B	B
Mg^{2+}	1/20	1/10	Zn^{2+}	5 times	Equal
Al^{3+}	Equal	1/10	Mo^{6+}	Equal	Equal
Mn^{7+}	B	B	Cd^{2+}	1/20	1/20
Cr^{3+}	1/10	Equal	Hg^{2+}	B	A
Cr^{6+}	1/20	1/20	V^{5+}	Equal	5 times

A = No interference even in the presence of 20 times excess of the foreign ion with respect to the metal species determined.
B = Serious interference even when foreign ion is 1/20th of metal ion concentration.

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