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Analytical Cupferron : A Micro-Analytical Reagent for Electrometric Estimation of Dysprosium & Terbium



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Abstract

Cupferron, an ammonium salt of N Nitrosophynyl hydroxylamine [$C_6H_5 N(NO)ONH_4$] has been used as a reagent for the amperometric titration of Dy^{3+} and Tb^{3+} in very dilute solution using dropping mercury electrode. Hydrochloric acid ($pH = 2.75 \pm 0.02$) has been used as supporting electrolyte for the study of polarographic behaviour of cupferron. Cupferron gives a well defined cathodic wave in hydrochloric acid. The half wave potential varies with pH. The height of the diffusion current is proportional to the concentration of cupferron. The plateau potential of polarogram for cupferron, i.e. - 1.20 V Vs SCE was applied. These titrations revealed cupferron to metal ratio of 1:1. Titrations are not hampered by the presence of a fairly large amount of divers ion i.e. Li^+ , Na^+ , K^+ , Mg^{++} , Zn^{++} , Al^{+++} , Cl^- , Br^- , I^- , No_3^- , SO_4^{--} , NO_2^- , CH_3COO^- and ClO_4^- ions. The results of amperometric titrations of Dy^{3+} and Tb^{3+} with cupferron on a d.m.e. at $pH = 2.75$ are reported in the present note. Observation table and graph revealed that the cupferron have been successfully used to determination of micro-and ultra-micro- quantities of Dy^{3+} and Tb^{3+} ion with an error of less than $\pm 0.70\%$. Statistical data proved relevance of the above method.

Keyword: Cupferron/D.M.E./Micro Titration/Divers ions/Tolerance limit.

Introduction

CUPFERRON, an ammonium salt of N-Nitrosophynyl hydroxylamine [$C_6H_5 N(NO)ONH_4$] was introduced as a precipitant for Cu^{2+} and Fe^{3+} . The reagent has been successfully used in the determination of metals, such as those belonging to Titanium family¹. Kolthoff and Liberti² have amperometrically titrated Cu^{2+} ion with cupferron using d.m.e. as an indicator electrode. The amperometric titration of Yttrium and some other rare earths using a rotating platinum anode and stationary platinum cathode in an ammonia cal acetate medium of pH 3.5 to 6, has been reported by Vasilenko³. The use of cupferron in the amperometric titrimetry of various other ions e.g. Fe^{3+} , Tl^{3+} , Sn^{4+} , Pr^{3+} and Nd^{3+} has been discussed in literature. No account, however, is available in literature on the use of cupferron as a reagent for amperometric titration of Dy^{3+} and Tb^{3+} on a d.m.e.

The results of amperometric titrations of Dy^{3+} and Tb^{3+} with cupferron on a d.m.e. at $pH = 2.75 \pm 0.02$ are reported in the present paper.

Experimental

Cupferron (B.D.H.) was purified⁴ by recrystallisation from ethanol. The dried crystals were stored in dark over ammonium carbonate. A fresh solution of this reagent was prepared in air free distilled water before use and the solution was standardised by amperometric titration method⁵⁻⁶. Dy^{3+} and Tb^{3+} solutions were prepared by dissolving a calculated amount of dysprosium oxide (Kotch Light) & Terbium Chloride (B.D.H.) respectively in the required volume of double distilled water. The solutions were standardised by conventional titrimetric method⁷.

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Hydrochloric acid (pH = 2.75) was used as a supporting electrolyte for the study of the polarographic behaviour of cupferron and purified nitrogen gas was passed through the solutions before recording the polarograms. An automatic polarographic set up with multiflex galvanometer (sens = 8.10×10^{-9} amp/div) was used for measurement of current. The d.m.e. used in conjunction with S.C.E. had the characteristics $m = 2.45$ mg/sec, $t = 2.5$ sec/drop and $h = 41$ cm.

For titrations, number of solutions containing calculated amounts of Dy^{3+} and Tb^{3+} (0.005 mM to 0.05 mM) were prepared. The pH of these solutions was adjusted at 2.75 with hydrochloric acid. Titrations of these solutions were carried out at an applied voltage of - 1.20 volts (Vs S.C.E.) using an H-type cell with d.m.e. as an indicator electrode and S.C.E. as reference electrode⁸

Result and Discussion

Cupferron gives a well defined cathodic wave in hydrochloric acid⁹. The half wave potential varies with pH. The height of the diffusion current is proportional to the concentration of cupferron. The plateau potential of the polarogram for cupferron, i.e. - 1.20 V. (Vs S.C.E.) (at which Dy^{3+} or Tb^{3+} do not give any diffusion current) was applied. The metal ion solution in dil. HCl (pH = 2.75) was taken in a titration cell and the solution was titrated against cupferron (pH = 2.75). After each addition of an aliquot of the titrant the galvanometer reading was noted. On plotting galvanometer reading against the titrant volume a reversed L shaped curve was observed (Fig. 1). The end point has been located graphically as the point of intersection of the two straight lines. This estimates the metal to cupferron ratio of 1:1 (Tables 1 and 2). The literature, however, records 1:3 stoichiometric ratio of metal (Dy^{3+} or Tb^{3+}) to cupferron. The observed 1:1 ratio may be attributed to the relatively low pH value of the test solution¹⁰⁻¹¹.

Similar results were observed by choosing metal as titrant and the rare earth as titrate under the identical experimental conditions. In this case an L shaped curve was observed.

The data in Tables 1 and 2 clearly indicate that the method is successfully applicable for the estimation of micro and ultra-micro for the estimation of micro and ultra-micro quantities of the metal ions under study with an error of less than $\pm 0.70\%$.

Effect of Diverse ions

Concentrated solutions of the diverse ions used were prepared. For interference studies, known amount of diverse ion was added to a definite of metal ion and the pH was adjusted to 2.75 using dil. HCl solution. The solution was titrated against cupferron amperometrically as described above. Titrations are not in any way hampered by the presence of different amount of the diverse ions (Table 3). Moreover, a fairly large amount of the ions Cl^- , I^- , NO_3^- , NO_2^- , SO_4^{2-} , CH_3COO^- is tolerated. However, neither of these two rare earths could be estimated in presence of the each other. It is also found that Cu^{2+} , Fe^{3+} , MnO_4^- , Ti^{4+} , Pi^{3+} and Nd^{3+} , even in small amount, interfere seriously.

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Table - 1

Amperometric Determination Of Dy^{3+} With Cupferron Ph = 2.75 \pm 0.02

Amount of Dy^{3+} taken (m.M)	Amount of Cupferron cpmsused (m.M)	Mole ratio M : L	% Error
0.005	0.005	1:1	-
0.010	0.010	1:1	-
0.015	0.0149	1.0.993	-0.70
0.020	0.020	1:1	-
0.025	0.0249	1:0.996	-0.40
0.030	0.0298	1:0.993	-0.70
0.040	0.0401	1:1.0025	+0.25
0.050	0.050	1:1	-

Table - 2

Amperometric Determination Of Tb^{3+} With Cupferron pH = 2.75 \pm 0.02

Amount of Tb^{3+} taken (m.M)	Amount of Cupferron cpmsused (m.M)	Mole ratio M : L	% Error
0.005	0.00503	1:1.0060	+0.60
0.010	0.010	1:1	-
0.015	0.01492	1:0.9946	-0.54
0.020	0.0201	1:0.9950	-0.50
0.025	0.025	1:1	-
0.030	0.0302	1:0.0067	+0.67
0.040	0.040	1:1	-
0.050	0.0502	1:1.004	+0.40

Table - 3

Effect of Diverse Ions on the Amperometric
Determination of Dy³⁺ and Tb³⁺ Metal taken :
Dy³⁺ = 0.01 mM (1.3891 mg), Tb³⁺ = 0.01 mM
(1.4012 mg)

Diverse ion Added	Dy ³⁺ found (mg.)	% Error	Tb ³⁺ found (mg.)	%Error
K+(130mg)	1.3920	+0.20	1.3937	-0.53
Na+(115mg)	1.3781	-0.79	1.4086	+0.53
Al ₂ +(67 mg)	1.3854	-0.26	1.3929	-0.59
Mg ₂ + (60mg)	1.3782	-0.78	1.4106	+0.67
Li+ (35mg)	1.4015	+0.89	1.3950	-0.44
Zn ₂ +(16mg)	1.3804	-0.62	1.4185	+1.28
Cr ₂ + (7mg)	1.4058	+1.20	1.3951	-1.15

Figures within parenthesis indicate the maximum amount of foreign ion which do not interfere under the experimental condition.

