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NOTE

Amperometric Determination of Nickel(II), Copper(II), Zinc(II) and Cadmium(II) using 3-Phenyl Rhodanine

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3-Phenyl rhodanine is employed as amperometric reagent for the trace determination of metals such as Ni(II), Cd(II), Cu(II) and Zn(II) in 30% dimethyl formamide-aqueous Britton Robinson buffer at pH 5.80, 5.68, 5.11 and 5.01 respectively with $\mu = 0.1$ M (KCl) and fresh 0.001% gelatin. Titration potential has been selected in the limiting region of the cathodic wave of the present metals. The titrations were performed using 3-phenyl rhodanine as titrant. L-shaped curve is obtained. The statistical analysis of the observed data reveals high accuracy and precision.

Key words: **Amperometric, Determination, Ni, Cu, Zn, Cd, 3-Phenyl rhodanine.**

p-Dimethylaminobenzylidene rhodanine has been known to be a sensitive reagent for Cu, Ag and Hg[1]. Rhodanine (4- thiazolidene-2-thione) is a well known metal complexing agent. Rhodanine is polarographically active and shows anodic wave at dropping mercury electrode[2] .The present paper deals with the applicability of rhodanine derivative, *i.e.*, 3-phenyl rhodanine as an amperometric titrant for the estimation of small amount of Ni(II), Cu(II), Zn(II) and Cd(II).

3-Phenyl rhodanine has been prepared as reported in literature[3, 4]. Electrochemical behaviour of 3-phenyl rhodanine has been investigated in 0.1 M KCl, fresh 0.001% in gelatin and 30% dimethyl formamide-Britton Robinson buffer at pH 5.5 ± 0.02. Polarograms were recorded after removal of oxygen by passing a stream of purified nitrogen gas for 15 min. Well defined cathodic waves were obtained for 3-phenyl rhodanine with Ep-0.25 V *vs.* SCE. A manually operated polarograph with Tinsley potentiometer and multiflex galvanometer (sens. 8.10×10^{-9} A/div.) was used. Dropping mercury electrode (d.m.e.) with capillary

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characteristics of $m^{2/3}t^{1/6} = 2.214$ $mg^{2/3}$ $s^{1/2}$ at 40 cm effective height of mercury column was used as an indicator electrode. A calomel electrode was used as reference electrode. pH was measured on an Elico LI 120 pH-meter. Double distilled mercury was used throughout. The test solution was deaerated by bubbling purified nitrogen gas before titration for 10 min. All titrations were performed at room temperature. All the chemicals used were of extra pure grade. Stock solutions of the metals (0.01 M) were prepared in double-distilled water and standardized[5]. Fresh solution 3-phenyl rhodanine was prepared in dimethylformamide. Titrations of the titled metals were performed in 30% dimethylformamide-Britton Robinson buffer.

For amperometric estimations of title metals experimental sets of the solution containing different but known amounts of metal ions (conc. 0.2–1.4 mg) were prepared in 30% dimethylformamide-Britton Robinson buffer and 0.001% gelatin (= 0.1 M KCl). Solution of the reagent was prepared in dimethylformamide. Titrations were performed at the plateau potential of cathodic wave of metal ions, *viz*, 1.3 V, 0.9 V. 0.5 V and –1.3 V *vs.* SCE at pH 5.80, 5.68, 5.11 and 5.01 for Ni(II), Cd(II), Cu(II) and Zn(II), respectively. Titrations were carried out by usual method by passing purified nitrogen gas prior to the addition of titrant from microburette. The current was noted on multiflex galvanometer. On plotting $[(V + v)/V] \times i$ against volume of titrant, L-shaped curves were observed. The results are shown in Table-1. The end point indicated M : L ratio 1 : 1 for Cu and Zn and M : L ratio 1 : 2 for Ni and Cd. Optimum concentration range for detection of metal ions was found to be 0.3 mg with ±0.81% error.

TABLE-1
AMPEROMETRIC DETERMINATION OF Cu(II), Zn(II), Cd(II) AND Ni(II) WITH 3-PHENYL RHODANINE

Plateau potential: Cu(II) = –0.5, Zn(II) = –1.3, Cd(II) = –0.9, Ni(II) = –1.3 V *vs.* SCE; supporting electrolyte: BR buffer; Ionic stringth (μ): 0.1 (KCl); pH: 5.11, 5.01, 5.68, 5.80 ± 0.02, repectively; Temp: 27°C

S. No.	Amount of Cu(II)		Error (%)	Amount of Zn(II)		Error (%)	Amount of Cu(II)		Error (%)	Amount of Zn(II)		Error (%)
	Taken (mg)	Found (mg)		Taken (mg)	Found (mg)		Taken (mg)	Found (mg)		Taken (mg)	Found (mg)	
1.	0.2612	0.2636	+0.91	0.2961	0.2938	–0.77	0.3357	0.3388	+0.92	0.2714	0.2695	–0.70
2.	0.5339	0.5308	–0.58	0.4244	0.4219	–0.58	0.5166	0.5136	–0.58	0.4838	0.4870	+0.66
3.	0.7497	0.7538	+0.54	0.6738	0.6781	+0.63	0.6007	0.6035	+0.46	0.6492	0.6451	–0.63
4.	0.8505	0.8536	+0.36	0.7901	0.7868	–0.41	0.8952	0.8911	–0.45	0.7552	0.7515	–0.48
5.	1.0332	1.0306	–0.25	0.8555	0.8581	+0.30	1.0668	1.0703	+0.32	0.8750	0.8782	+0.36
6.	1.2285	1.2312	+0.21	1.1754	1.1728	–0.22	1.3476	1.3448	–0.20	1.0148	1.0129	–0.19

Ultramicro and micro quantities of Cu(II), Zn(II), Ni(II) and Cd(II) were determined by the proposed procedure using 3-phenyl rhodanine. The amount of metal ions in the concentration range 1.0×10^{-4} to 1×10^{-3} was detected with less than ±1% error, with minimum detection limit of 0.3 mg. The values of standard deviation and coefficient of variance are with respect to minimum detection limit. The statistical treatment of the observed data, *i.e.*, coefficient of variation (1.02, 0.83, 0.79, 0.70 for Cu(II), Zn(II), Cd(II) and Ni(II)) indicates that the developed procedure is simple, sensitive and fairly selective for estimation of title metal ions.

Amperometric titrations were not hampered by the presence of Li^+, Na^+, K^+, Cl^-, SO_4^{2-}, NO_3^- and CH_3COO^-. However, Bi^{3+}, Cd^{2+} and Mn^{2+} interfered seriously even if present in minute quantities ($\mu = 0.1$ M) and buffer of suitable pH. Britton-Robinson buffer was prepared[6] from glacial acetic acid, boric acid, phosphoric acid and sodium hydroxide.

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