



2, 4-DIHYDROXY-5-BROMO HEXAPHENONE OXIME (DHBHPO) AS AN AMPEROMETRIC REAGENT FOR ANALYSIS OF COPPER(II) AND NICKEL(II)

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ABSTRACT

DHBHPO has been used as an analytical reagent for amperometric determination of copper and nickel. Cu(II) and Ni(II) forms colored complex with the reagent at pH 5.0 and 8.5 respectively. After studying the polarographic behavior of the metal ions and the reagent at dropping mercury electrode (DME), applied potential were fixed at - 0.4 v (Vs SCE) for copper(II) and - 1.5v (Vs SCE) for Nickel(II). The method was applied for the determination of copper and nickel in german silver alloy. Newly synthesized reagent was characterized using analytical techniques such as IR spectra, NMR and elemental analysis.

Key words: Amperometric determination, DHBHPO, Applied potential, Dropping mercury electrode (DME), Secondary calomel electrode (SCE), Supporting electrolyte.

INTRODUCTION

The formation of coordination compounds by organic reagents with metal ions has been extensively used in analytical chemistry. Most of the selective reagents employed have hydroxyl groups. o-hydroxy ketoximes (1-8) , oximes (9-10) has been used for gravimetric and spectrophotometric determination of several metal ions. A very few analytical reagents have been employed for the polarographic determinations. The amperometric method of determining the end point is an extension of polarographic analysis. Gallacetophenone phenylhydrazone(11) was used for amperometric determination of Bismuth. o-hydroxyacetophenone oxime (12,13) , 2,5-Dihydroxy acetophenone oxime (14) were used as an amperometric reagent for Cu(II), Ni(II) and Pd(II). 2-Hydroxy-1-acetophenone oxime(15) and 1-hydroxy-2-acetophenone oxime (16) have been successfully employed for the determination of copper and nickel in binary solution. In the present work, we synthesized a new reagent with a view to extend the use of o-hydroxy ketoximes for the amperometric determination of metal ions at DME. DHBHPO performed successfully for the simultaneous determination of copper and nickel in alloy.

METHODOLOGY

Analytical grade chemicals and doubly distilled water was used. Stock solution of copper(II) and nickel(II) were prepared freshly by dissolving copper sulphate and nickel sulphate, respectively. Solution of other ions was prepared from their salts in distilled water. Sodium acetate (0.5M) and acetic acid (0.5M) buffer of pH 5.0 acted as supporting electrolyte for estimation of copper(II) while ammonium chloride (0.5M) and ammonia (0.5M) buffer of pH 8.5 acted as supporting electrolyte for estimation of nickel(II). A 0.2% aqueous solution of gelatin was prepared freshly before use. Purified nitrogen gas was employed for deaeration. All the titrations were performed at DME Vs SCE using a systronic manual polarograph model no 1632 with inbuilt digital micro ameter. A systronic digital pH meter 335 was use to adjust pH. Perkin-Elmer 2400 Elemental Analyser, Bruker Avance II 400 NMR spectrometer and Simadzu FT-IR spectrophotometer were used to characterize the reagent.

Synthesis of the Reagent [DHBHPO]

DHBHPO was synthesized according to the method of H.Nogami (17), reaction between Resocinol (0.05M), Hexanoic acid (0.05M) and anhydrous zinc chloride gave 2,4-dihydroxyhexaphenone (DHHP) liquid ketone having density of 1.23 gm/mL. Bromination of above ketone (0.01 M) with bromine in acetic acid (0.01M) results in the formation of 2,4-dihydroxy-5-bromohexaphenone (DHBHP). The product was treated with sodium bisulphite to remove excess bromine. White solid separated, was recrystallized from ethanol. M.P. 121° C. This bromo ketone derivative (2 gm) further refluxed with NH₂OH.HCl (4 gm) in presence of sodium acetate (6 gm) for 4 hours forming the above reagent. Reagent was recrystallized after charcoal treatment from aqueous ethanol, M. P 148° C. A 0.02 M reagent solution was prepared in 95% ethanol just before used. Reagent is soluble in DMSO, DMF, CDCl₃ and absolute alcohol. It is insoluble in water, chloroform and carbon tetrachloride.

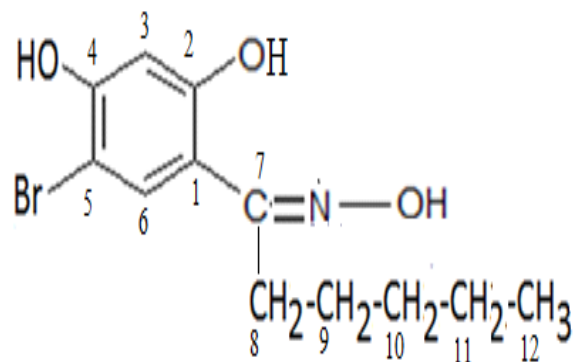
CHARACTERIZATION OF REAGENT :

Elemental analysis: Elemental analysis of the reagent shows that the percent elements found are in agreement with its molecular formula. The results are represented in Table 1.

FT-IR spectral studies: The IR spectrum of all reagents were taken by preparing pallet with KBr. The IR spectrum of DHBHPO shows strong band at 3475 cm⁻¹ which may be assigned to O-H stretching due to Phenolic -OH group and at 3363 cm⁻¹ due to -OH moiety of =N-OH group. Strong bands at 2854-2956 cm⁻¹, 1591 cm⁻¹, 1465 cm⁻¹ and 1492 cm⁻¹ may be assigned to aliphatic C-H stretching, aromatic C=C stretching, N-O stretching and C=N stretching respectively.

¹H and ¹³C NMR spectral studies of 2, 4-dihydroxy-5- bromo hexaphenone oxime DHBHPO:

The ¹H NMR and ¹³C NMR study for DHBHPO was carried out using CDCl₃ as solvent and TMS as reference. Assignment of signals to different protons and carbons are given in Table-2 and 3.



[2, 4-Dihydroxy-5-bromo hexaphenone oxime (DHBHPO)]

OBSERVATION

Determination of Cu(II) and Ni(II)

The polarographic behavior of DHBHPO, copper(II) and nickel (II) at DME was studied to arrive at the suitable voltage to be fixed for the amperometric determinations. 25 mL of acetate buffer (pH.5.0), 5 mL 0.02M reagent, 1.5 mL of 0.2% gelatin and 10 mL of alcohol were taken in titration cell and finally diluted to 50 mL. The solution was deoxygenated by bubbling nitrogen gas for 15 minutes. The drop time of the DME was adjusted to 3-4 seconds and the polarogram of the reagent was recorded. Experiment was repeated to record reagent polarogram at pH 8.5 using ammonia buffer. Similar procedure was followed to record polarogram for metal ions. 5 mL (0.01M) respective metal ion solution was used in place of reagent solution. Half wave potential was found to be -0.118V (Vs SCE) at pH 5.0 for Cu(II) (Figure 1) and -1.05V (Vs SCE) at pH 8.5 for Ni(II) (Figure 2). Half wave potential for the reagent DHBHPO was determined for both the pH and found -1.3V (Vs SCE) at pH 5.0 and -2.3V (Vs SCE) at pH 8.5. The titration were carried out by fixing the applied voltage -0.4V (Vs SCE) and -1.5V (Vs SCE) for Cu(II) and Ni(II) respectively.

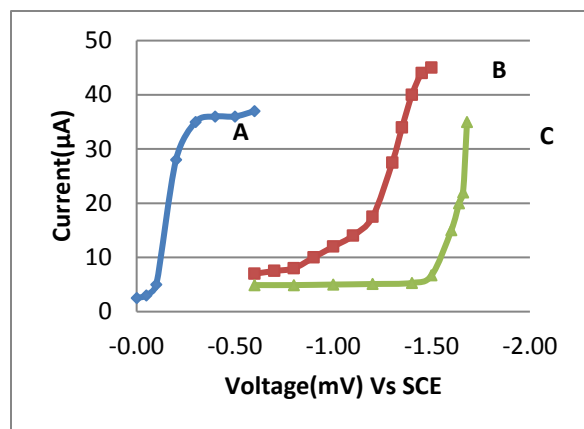


Figure 1: Polarograms of (A) Copper(II); (B) DHBHPO; (C) Supporting electrolyte (pH = 5.0, acetate buffer)

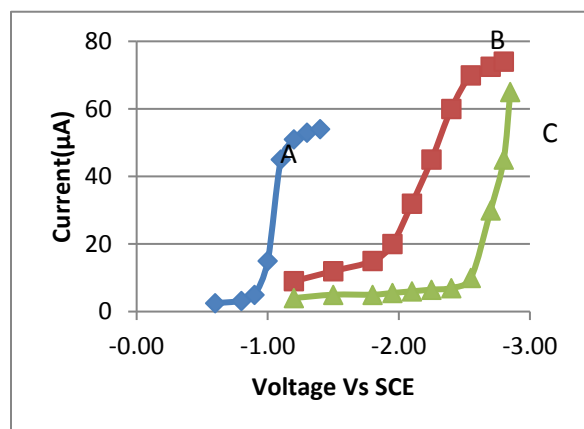


Figure 2: Polarograms of (A) Nickel(II); (B) DHBHPO; (C) Supporting electrolyte (pH = 8.5, ammonia buffer)

An aliquot of standard copper(II) solution (0.01 M, 0.6354 mg/mL) was transferred into the titration cell and above contents were added keeping the volume at 50 mL and pH 5.0. The voltage was fixed at -0.4V (Vs SCE) and the solution titrated against standard oxime solution (0.02 M). After the addition of the reagent from micro burette, nitrogen gas was passed into the solution to ensure thorough mixing and then corresponding current reading were noted. The current readings were corrected for dilution by the titrant was recorded as a function of the volume of the titrant. Dilution correction was made with the help of 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. Null point was obtained graphically taking i_{corr} along y-axis Vs volume

of titrant added along x-axis. An 'L' shaped curve was obtained. The procedure was repeated with known but different aliquots.

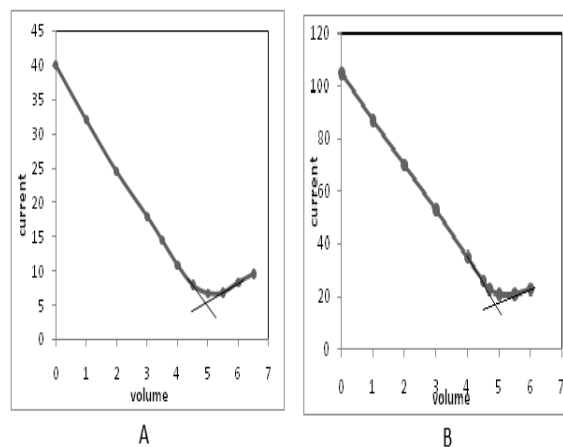


Figure 3: Amperometric titrations of (A) Cu(II) and (B) Ni(II) with DHBHPO

Similarly Nickel(II) solution (0.01M, 0.5869 mg/mL) was titrated at pH 8.5 and applied voltage -1.05V (Vs SCE). Results were calculated for the amount of copper and nickel from the graph (Figure 3: A and B). 1:2 (M:L) ratio found is in agreement with the ratio being established by the gravimetric procedure. The results of the determinations are given in Table 4.

Determination in presence of foreign ions

Study of interference of foreign ions in amperometric determination of copper(II) and nickel(II), was carried out. The interference due to foreign ions such as Iron(III), aluminum(III), arsenic(III), zinc(II), calcium(II) and lead(II) were studied as they are usually associated in ores, slags and alloys. Except Iron(III), the other metals did not interfere into the amperometric determination of copper(II) (3.177 mg copper), when they are present up to 25-30 fold excess. Interference due to Iron(III) was overcome by masking it with sodium fluoride. Iron(III), aluminium(III) and chromium(III) did not affect the current readings in the determination of nickel(II) (1.467 mg nickel), although they were precipitated as hydroxides. Palladium(II), zinc(II) and manganese(II) gave no precipitates with the reagent at 8.5 pH and hence did not interfere even when present 40-50 fold excess.

Trace amount of cobalt(II) (10 ppm) interfered in the determination.

Determination of Cu(II) and Ni(II) in german silver alloy

Copper(II) and nickel(II), have been accurately determined in german silver alloy at respective pH value. Percentage obtained agrees with the reported values within the experimental error.

The standard sample of german silver alloy, weighing 0.2860 gram was dissolved in nitric acid (1:1) by heating on sand bath. The excess acid was removed and mass dissolved in doubly distilled water and diluted to 250 mL. A 5 mL aliquot of the stock solution was pipette out into the polarographic cell. To this, ammonium chloride solution (20 mL, 0.5 M), 1.5 mL (0.2%) gelatin solution was added and pH adjusted to 5.0 with hydrochloric acid. Addition of ammonium chloride was preferred to an acetate buffer to maintain above pH in order to avoid addition of large amount of ammonium hydroxide required to raise the pH to 8.5 in subsequent nickel(II) determination. The amount of copper(II) was estimated by adopting the general procedure described earlier. The titration was continued until the current readings remained constant-equivalent point for copper obtained. Titration was stopped after addition of only a few increments of the reagent beyond equivalence point. Then the cell voltage was raised to -1.4 V (Vs SCE) and the pH of the solution was raised to 8.5 with ammonia buffer. Titration was continued until the equivalence point for nickel(II) is obtained. Results are shown in Table 5.

Weight of alloy: 0.2860 gm in 250 mL stock solution.

5 mL stock solution contains 5.720 mg german silver

For the set of three determination of German Silver alloy, the average %age found was 50.17% Cu(II) and 24.83% Ni(II). Standard deviation was 0.0125 % and 0.04 % for Cu(II) and Ni(II), respectively.

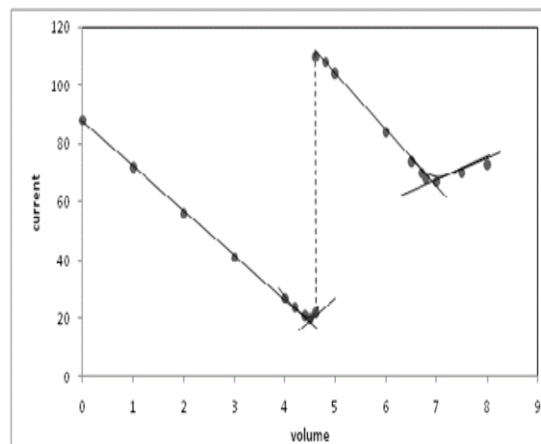


Figure 4: Simultaneous determination of copper(II) and nickel(II) from german silver alloy.

RESULTS AND DISCUSSION

The present amperometric method for simultaneous determination of Cu(II) and Ni(II) from german silver alloy, was found to be accurate and specific. The developed method is rapid and completes a single run in relatively short time.

CONCLUSION

The method enables rapid quantification and simultaneous analysis of both the metal from alloy without any interference of foreign ions. Therefore it can be concluded that the reported method could find practical application as rapid method for simultaneous determination of Cu(II) and Ni(II) ions in alloys and other mixture.

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Table-1: Elemental Analysis of the reagent

Reagent	% Found (Calculated)		
	Carbon	Hydrogen	Nitrogen
DHBHPO	47.73 % (47.68%)	5.25 % (5.30%)	4.52 % (4.63%)

Table-2: ¹H-NMR

Reagent	Alkyl group	Phenolic(-OH)	Oximino(-OH)	Aromatic Proton
DHBHPO	1.6475-0.800 ppm (multiplate)	12.9469 ppm (singlet)	6.0504 ppm (singlet)	7.9667-7.1911 ppm (multiplate)

Table-3: ¹³C-NMR

Assignment	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
Chemical shift(δ) in ppm	112.83	150.96	98.60	155.61	99.71	129.65	161.80	31.80	26.37	24.67	22.36	13.94

Table-4: Amperometric determination of copper(II) and nickel(II) with DHBHPO

Metal Ion	Taken (mg)	Found (mg)	Difference (mg)	Error (%)
Copper	3.177	3.165	- 0.012	- 0.38
	4.759	4.779	0.02	0.42
	6.354	6.367	0.013	0.21
Nickel	1.467	1.456	-0.012	-0.82
	2.935	2.917	-0.018	-0.61
	4.402	4.419	0.017	0.39

Table- 5: Simultaneous determination of Copper (II) and Nickel(II) in German Silver.

METAL	FOUND mg	% FOUND	% REPORTED	% ERROR
Copper	2.87	50.17	50.06	0.22
Nickel	1.42	24.83	25.0	-0.68