

2-Hydroxy, 4-n-Butoxy Acetophenone Oxime as a Reagent for Gravimetric and Spectrophotometric Determination of Copper(II)

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2-Hydroxy, 4-n-butoxy acetophenone oxime ($C_{12}H_{17}O_3N$) has been used for gravimetric estimation of Pd(II), Cu(II), and Ni(II) from their mixtures at pH values of 1.5, 3.5, 5.5 respectively. The reagent can also be used for extraction spectrophotometric determination of copper(II) in the pH range 6.0–10.0. The mole ratio, slope ratio and Job's method show the metal : ligand ratio in the complex to be 1 : 2 with a stability constant of 2.4×10^9 . The yellowish green complex formed and extracted in benzene layer obeys Beer's law up to 326.7 ppm. The optimum concentration range, the photometric sensitivity and molar absorptivity are found to be 197.2–326.7 ppm, $0.58 \mu\text{g}/\text{cm}^2$ and $108 \text{ L mole}^{-1} \text{ cm}^{-1}$ at 650 nm respectively. The complex is fairly stable for 24 h and 50°C ($\Delta G = -12.96 \text{ Kcal/mole}$).

INTRODUCTION

Some phenones and phenone oximes have been reported by various workers^{1–12} as reagents for determination of Cu(II) and such other cations. In an earlier publication¹³ 2-hydroxy, 4-n-butoxy acetophenone oxime (HBAO) has been reported as a photometric reagent for determination of Ni(II). In the present work the use of HBAO as a gravimetric and spectrophotometric reagent for Cu(II) has been described.

EXPERIMENTAL

All the chemicals used were of A.R./B.P. grade and recrystallized wherever necessary. Double distilled water was used throughout. A 0.1 M stock solution of Cu(II) was prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (G.R.) in double distilled water containing 2–3 drops of sulphuric acid. The amount of Cu(II) in the solution was determined iodometrically¹⁴ and also gravimetrically with salicylaldehyde¹⁴.

Preparation of 2-hydroxy, 4-n-butoxy acetophenone oxime (HBAO)

Resacetophenone was prepared from resorcinol by standard methods¹⁵. 2-Hydroxy, 4-n-butoxy acetophenone (HBA) was then prepared using resacetophenone, n-butyl bromide and anhydrous potassium carbonate in acetone¹⁶. The oxime¹⁷ of HBA was prepared by dissolving HBA in sufficient ethanol and adding to it an aqueous solution containing hydroxylamine hydrochloride and sodium acetate such that the amount of the three reagents were in the ratio 1 : 2 : 4 (w/w). The mixture was poured on crushed ice when the oxime separated as a white product. It was then recrystallized from ethanol in the form of colourless, needle-like crystals (m.p. $78 \pm 1^\circ\text{C}$). The reagent is easily soluble in solvents like

alcohol, acetone, chloroform, benzene, carbon tetrachloride, etc. The molecular weight of the compound, determined by Rast's cryoscopic method²⁶ was found to be 225 (calculated: 223). The elemental analysis of the oxime, showed its composition to be:

Elements	:	C	H	N
Found	:	64.98%	8.44%	6.50%
Calculated (for C ₁₂ H ₁₇ O ₃ N)	:	64.55%	7.68%	6.27%

Gravimetric procedure: An aliquot of 0.01 M solution of Cu(II) was treated with ammonium hydroxide solution till a sky blue precipitate formed. The precipitate was dissolved by adding just sufficient amount of acetic acid, diluted to about 100 mL with distilled water, warmed to 70–80°C on a water bath and its pH adjusted between 3.5–4.0 with acetic acid and sodium acetate buffer. 1% Solution of HBAO in ethanol was then added till precipitation was complete. The greenish white with yellowish tinge precipitates were digested on water bath at 80–90°C for about 1/2 h, filtered through a previously weighed sintered glass crucible (G-4), washed with hot water followed by warm 60% alcohol, dried at 110–120°C and weighed as Cu(C₁₂H₁₆O₃N)₂ (Gravimetric factor = 0.1251). Triplicate experiments were performed in each case and the mean values have been reported.

Spectrophotometric procedure: A series of buffer solution in the pH range 2.0–11.0 were prepared by adding hydrochloric acid or ammonia to a 0.2 M solution of sodium acetate. 25 mL of the buffer solution of known pH were taken in a separating funnel and a suitable aliquot (*e.g.*, 2.0 mL) of 0.01 M Cu(II) solution was added. The ionic strength of the solution was controlled by using the Cu(II) solution containing 0.1 M KCl. 20.0 mL of 0.02 M solution of HBAO in benzene were then added, the mixture was shaken vigorously for 2–3 minutes and the two layers were allowed to separate. The aqueous layer left after the first extraction did not give any qualitative test for Cu(II), *i.e.*, the extraction of Cu(II) was complete in a single extraction. The upper yellowish green layer was used for spectrophotometric measurements. The absorbance was recorded against the reagent blank prepared under similar conditions.

RESULTS AND DISCUSSION

Results are given in Fig. 1 and 2 and Tables 1–3.

Gravimetric determination of copper: To determine the feasibility of the reagent for gravimetric estimation of Cu(II), the metal was precipitated from solutions having pH values in the range 2.5–10.0. There was incomplete precipitation at pH 2.5 whereas between pH 3.0–10.0 copper could be quantitatively precipitated, the error being minimum ($\leq 0.1\%$) in the pH range 3.0–4.0 (Fig. 1) when attempts were made to determine copper from solutions (pH 3.5) containing different concentrations (6.35–47.66 mg) of Cu(II). Quantitative precipitation of the metal ion was possible in all the cases with the error of measurement ranging from 0.13–0.79% (Table-1).

Qualitative tests with the reagent also showed that copper could be detected as a greenish white with yellowish tinge precipitate at as low a concentration as

2.5 ppm. Below this concentration the solution became turbid and no precipitation could be observed.

To determine selectivity of the reagent, qualitative tests were carried out for precipitation of various metal ions in the pH range 1.0–10.0 using HBAO. The results (Table-2) shows that the reagent may be used for detection and determination of Pd^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , VO^{2+} , Ti^{4+} and Fe^{2+} . Ions like Al^{3+} , Cr^{3+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , Ca^{2+} , Ba^{2+} , Sr^{2+} , Mg^{2+} , Be^{2+} etc., failed to respond. Experiments were, therefore, carried out to determine (a) Pd^{2+} and Cu^{2+} , (b) Cu^{2+} and Ni^{2+} and (c) Pd^{2+} , Cu^{2+} and Ni^{2+} from their mixtures. From the results given in (Table-3) it may be generalised that with proper control of pH it is possible to determine palladium, copper and nickel from their mixtures. For example, palladium may be quantitatively precipitated as $\text{Pd}(\text{HBAO})_2$ complex in the pH range 1.0–2.0. From the filtrate copper can be precipitated by increasing the pH to 3.5–4.0 and finally nickel may be precipitated by further increasing the pH of the filtrate to 5.0–6.0. The error of measurement was found to range from 0.13–0.31% for copper, 0.16–0.20% for nickel and 0.31–0.56% for palladium depending upon the concentration of the metal ion taken, it being less in concentrated solutions.

Spectrophotometric determination of copper: Selection of pH and Wavelength: As the pH of the solution has a pronounced effect on the reaction between Cu(II) ion and HBAO, absorbance of the organic layer containing Cu(II)—HBAO complex extracted from the aqueous solution of different pH values was measured. From the results given in Fig. 1, it is evident that the maximum absorbance occurs in the pH range 6.0–10.0. A pH of 6.5 was selected for the present work.

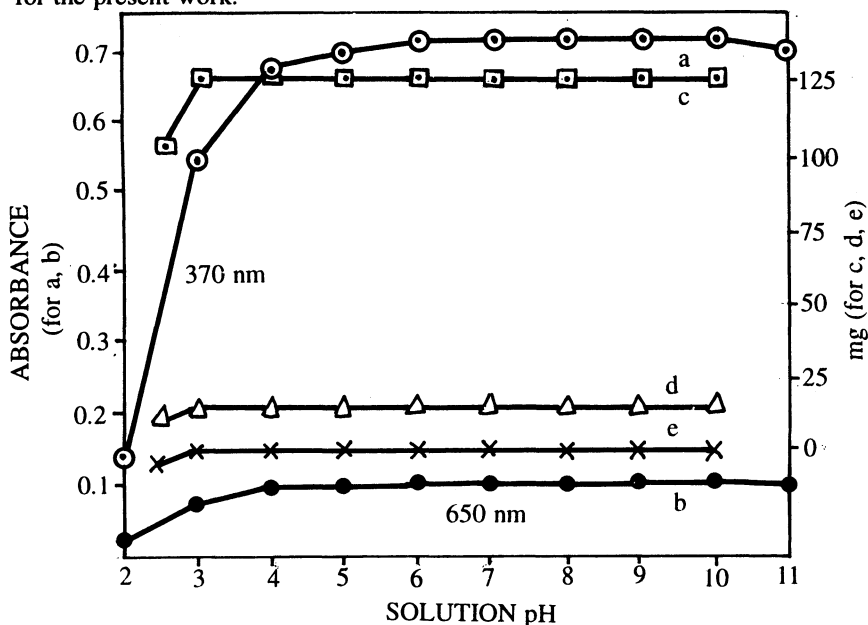


Fig. 1 Effect of pH on gravimetric and spectrophotometric determination of copper(II): (a) absorbance at 370 nm, (b) absorbance at 650 nm, (c) weight (mg) of Cu-HBAO complex, (d) weight (mg) of Cu(II) found, (e) error (mg)

TABLE-1
EFFECT OF Cu(II) CONCENTRATION ON GRAVIMETRIC ESTIMATION OF COPPER
AS Cu(II)—HBAO COMPLEX AT pH 3.5

Cu(II) taken (mg)	Cu—HBAO complex obtained (mg)	Cu(II) found (mg)	Error (mg)	Error (%)
6.35	51.1	6.40	0.05	0.79
15.89	127.3	15.92	0.03	0.19
31.77	254.3	31.82	0.05	0.16
47.66	381.6	47.72	0.06	0.13

TABLE-2
pH RANGE FOR PRECIPITATION OF VARIOUS METAL IONS BY HBAO

Metal ion	pH range	Colour of precipitate
Pd(II)	1.0–6.0	yellow
Cu(II)	3.0–10.0	greenish white with yellowish tinge
Ni(II)	4.5–10.0	green
Mn(II)	5.0–10.0	brown
Ti(IV)	1.5 2.5–6.5	(yellow coloured solution) golden yellow
Fe(III)	3.5–5.0 5.0	(violet coloured solution) reddish brown
Fe(II)	4.5–6.0	(violet coloured solution) violet

TABLE-3
SEPERATION AND ESTIMATION OF Pd(II), Cu(II) and Ni(II) FROM THEIR MIXTURES:
[pH FOR PRECIPITATION: Pd(II), 1.5; Cu(II), 3.5; Ni(II), 5.5]

Composition taken			Pd found (mg)	Cu found (mg)	Ni found (mg)
Pd (mg)	Cu (mg)	Ni (mg)	Error (%)	Error (%)	Error (%)
21.28	6.36	—	21.32 (0.19)	6.38 (0.31)	—
10.64	31.77	—	10.68 (0.38)	31.81 (0.13)	—
10.64	12.71	—	10.68 (0.38)	12.73 (0.19)	—
—	31.77	29.36	—	31.85 (0.25)	29.38 (0.12)
—	31.77	14.68	—	31.81 (0.13)	14.71 (0.23)
—	15.89	29.36	—	15.94 (0.31)	29.39 (0.10)
10.64	31.77	29.36	10.70 (0.56)	31.87 (0.31)	29.41 (0.17)
15.96	47.66	29.36	16.01 (0.31)	47.72 (0.13)	29.42 (0.20)
10.64	31.77	44.03	10.70 (0.56)	31.68 (0.28)	44.10 (0.16)

For the selection of the wavelength Vosburgh and Cooper's method¹⁸ was employed using 30.0 mL of aqueous solution (pH 6.5) containing Cu(II) and 15.0 mL of HBAO in benzene, the concentration of Cu(II) and HBAO being in the mole ratio 1:1, 1:2, 1:3 and 2:1. Absorbance measurements in the wavelength range 360–800 nm showed that only one complex was formed. The plots of absorbance vs wavelength show two maxima, a prominent one at 370 nm and a less prominent one at 650 nm. Of this the wavelength of 650 nm was selected

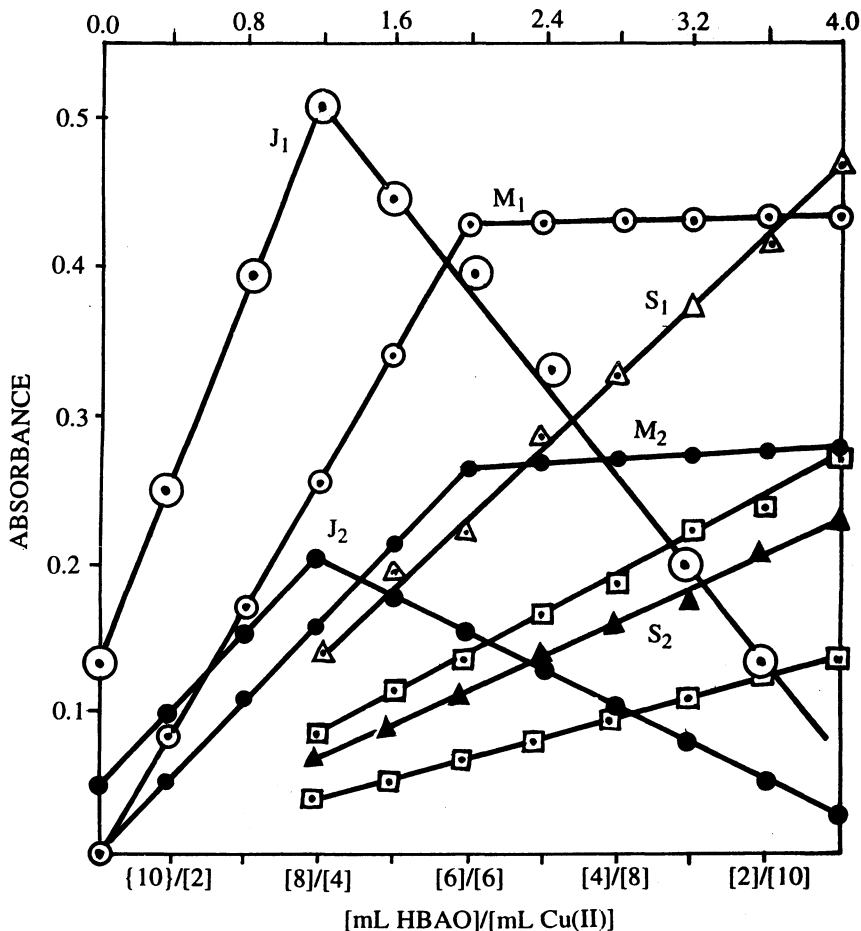


Fig. 2 Plots of Job's (J_1 , J_2), mole ratio method (m_1 , m_2) and slope ratio method (S_1 , S_2)

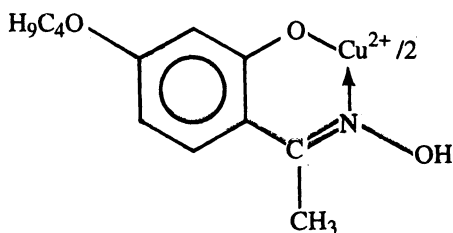
J_1	: 0.025 M Cu(II)	: 0.025 M HBAO
J_2, M_2	: 0.010 M Cu (II)	: 0.010 M HBAO
M_1	: 0.016 M Cu (II)	: 0.016 M HBAO
S_1	: 0.020 M Cu (II)	: 0.020 M HBAO
S_2	: 0.012 M Cu (II)	: 0.012 M HBAO

for spectrophotometric measurements because both the reagent as well as the metal ion do not absorb light at this wavelength.

Validity of Beer's law and optimum concentration range: The yellowish green Cu(II)—HBAO complex in benzene obeys Beer's law up to 326.7 μg copper per mL of organic layer. Beyond the concentration of 326.7 $\mu\text{g}/\text{mL}$ the solution becomes turbid and absorbance measurements become impossible. The optimum concentration range for the complex in organic layer as derived from the Ringbom plot¹⁹ is found to be 127.2–326.7 ppm. The molar absorptivity (ϵ) of the complex is 108 $\text{L mole}^{-1} \text{cm}^{-1}$. The photometric sensitivity as per Sandell's definition²⁰ is found to be 0.58 $\mu\text{g}/\text{cm}^2$ at 650 nm for an absorbance of 0.001.

Stoichiometry and stability constant of the complex: The stoichiometry of the Cu(II)—HBAO complex was studied by (i) Job's method of continuous variation²¹ (ii) Yoe and Jone's mole ratio method²² and (iii) Harvey and Manning's slope ratio method²³ (Fig. 2). All the three methods gave the metal : ligand ratio of 1:2. The gravimetric determination as well as the elemental analysis of the complex also confirmed this ratio. In the IR spectrum of the HBAO two bands are observed in the —OH stretch region, one at 3280 cm^{-1} due to 2-hydroxy group and the other at 2840 cm^{-1} due to the oximino group. In the IR spectrum of the Cu(II)—HBAO complex the first band at 3280 cm^{-1} disappeared while the second band shifted to 2820 cm^{-1} . This suggests that there is acid dissociation of the phenolic 2-hydroxy group followed by formation of Cu(II)—HBAO chelate thorough O⁻ of the phenolic group and N of the oximino group. A weak band at 650 nm in the spectrum of Cu(II)—HBAO complex could be assigned to ${}^2\text{B}_{1g} \leftarrow {}^2\text{A}_{1g}$ transition and a strong band at 370 nm could be assigned to charge transfer.

Based on the above data the copper complex with HBAO can be assigned the structure:



The stability constants of the Cu(II)—HBAO complex were calculated for different values of 'n' following equation²⁴:

$$k = \frac{x}{(a - mx)^m(b - nx)^n}$$

where, x = concentration of the complex, a = concentration of metal ion, b = concentration of the reagent and m and n are integers.

It has been found that the k values are nearly constant for n = 2 which confirms the formation of a 1:2 complex. The average value of the stability constant is

found to be 2.4×10^9 , while the free energy of formation (ΔG) calculated to be $-12.96 \text{ k cal mole}^{-1}$.

Effect of diverse ions: The influence of other ions on the determination of Cu(II) using HBAO has also been studied. A difference of more than 1.5 per cent in the absorbance value has been taken as interference. The tolerance limits for the various metal ions, expressed in ppm, at a copper(II) concentration of 127.1 ppm are:

5000 ppm of Na^+ , K^+ , NH_4^+ , Cl^- , Br^- , NO_3^- , SO_4^{2-} , CH_3COO^- , 2000 ppm of Ca^{2+} , Ba^{2+} , Sr^{2+} , Mg^{2+} , Al^{3+} , Zn^{2+} , Cd^{2+} , I^- , MoO_4^{2-} , citrate, tartrate, oxalate and Ni^{2+} , Co^{2+} , Mn^{2+} , Cr^{3+} , UO_2^{2+} , Pd^{2+} , Fe^{3+} , etc., were found to interfere considerably at a concentration of 100 ppm.

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