

2-Hydroxy-4-n-butoxyacetophenone Oxime as an Extraction Photometric and Gravimetric Reagent for Simultaneous Determination of Nickel and Copper[#]

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Various phenones and phenone oximes have been reported in literature as reagents for gravimetric as well as spectrophotometric determination of nickel and copper. In earlier communications¹ 2-hydroxy-4-n-butoxy-acetophenone oxime (HBAO), -propio-phenone oxime (HBPO) and -butyrophenone oxime (HBBO) have been reported as gravimetric and extraction spectrophotometric reagents for Ni^{II}. In the present work the use of HBAO for simultaneous spectrophotometric determination of nickel and copper from their mixtures as well as a standard alloy sample has been reported.

Results and Discussion

The results are given in Tables 1-2. Maximum absorbance was observed in the pH range 8.0-10.5

for Ni^{II} and 6.0-10.0 for Cu^{II} in benzene layer. A pH of 9.0 was selected for Ni^{II} and 6.5 for Cu^{II} complex.

The method of Vosburgh and Cooper² was employed to determine the nature of the complex formed and extracted in the organic layer. Absorbance study showed the formation of only one complex with both the metal ions. The Ni^{II}-HBAO complex showed maxima at 380 and 600 nm while the Cu^{II}-HBAO complex showed at 370 and 650 nm. The wavelengths of 600 and 650 nm were selected for Ni^{II} and Cu^{II} complexes respectively. For full colour development at least 2.5-fold excess of the reagent was necessary in both the cases.

The Job's method³, as well as the mole-ratio⁴

TABLE 1-SPECTROPHOTOMETRIC SIMULTANEOUS DETERMINATION OF Cu AND Ni

Sample no	Composition Taken (μg)		Composition Found (μg)		% Error	
	Cu	Ni	Cu	Ni	Cu	Ni
1	317.7	2642.0	316.5	2657.4	-0.39	0.58
2	635.5	2348.4	639.1	2360.8	0.58	0.53
3	953.2	2054.9	961.8	2064.2	0.90	0.45
4	1270.9	1761.3	1265.6	1769.5	-0.42	0.46
5	1588.6	1467.8	1578.4	1478.9	-0.64	0.76
6	1906.4	1174.2	1907.2	1163.9	0.04	-0.88
7	2224.1	880.7	2233.5	879.7	0.42	-0.11
8	2541.8	587.1	2527.5	591.0	-0.56	0.67
9	2859.5	293.6	2845.6	292.3	-0.49	-0.43
Cu/Ni alloy (%)	1754.0 (68.12)	781.5 (30.35)	1747.8 (67.88)	779.4 (30.27)	(-0.35)	(-0.27)

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TABLE 2—SEPARATION AND GRAVIMETRIC DETERMINATION OF Cu^{II} AND Ni^{II} FROM THEIR MIXTURES

Composition Taken		Cu-HBAO	Cu	Error	Ni-HBAO	Ni	Error
Cu	Ni	obtained	Found		obtained	Found	
mg	mg	mg	(mg)	(%)	(mg)	(mg)	(%)
31.77	29.36	254.6	31.85	0.25	251.8	29.39	0.10
31.77	14.68	254.3	31.81	0.13	126.0	14.70	0.14
15.89	29.36	127.4	15.94	0.31	251.7	29.37	0.03
31.77 ^a	29.36 ^a	255.3	31.94	0.53	251.7	29.37	0.03
47.66 ^a	29.36 ^a	382.0	47.79	0.27	250.8	29.27	-0.31
31.77 ^a	44.03 ^a	255.3	31.94	0.54	377.7	44.08	0.11

^aContained in addition 10.64–15.96 mg of Pd^{II} also which was precipitated out at pH 1.5.

and slope-ratio⁵ methods showed the stoichiometry (M : L) of the complex to be 1 : 2 for both the complexes. The gravimetric determination as well as the elemental analysis of the complexes also confirmed this ratio. In the ir spectra of the metal-HBAO complexes, the ligand band at 3280 cm^{-1} (OH) disappeared, while the ligand band at 2840 cm^{-1} (oximino) shifted on complexation (to 2880

and 650 nm respectively. The composition of each mixture was determined following the equations⁶,

$$A_{600} = \epsilon_{\text{Ni},600} b C_{\text{Ni}} + \epsilon_{\text{Cu},600} b C_{\text{Cu}}$$

$$A_{650} = \epsilon_{\text{Ni},650} b C_{\text{Ni}} + \epsilon_{\text{Cu},650} b C_{\text{Cu}}$$

where A_{600} and A_{650} are the absorbances of the mixture at 600 and 650 nm respectively, b is the cell width (1 cm) and C_{Ni} and C_{Cu} are the concentrations of Ni and Cu respectively in the mixture. The molar absorptivities of the two complexes at 600 and 650 nm, obtained from the Beer's law plots, were found to be $\epsilon_{\text{Ni},600} = 120$, $\epsilon_{\text{Ni},650} = 65$; $\epsilon_{\text{Cu},600} = 80$, $\epsilon_{\text{Cu},650} = 108\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$. The results are given in Table 1.

To test the validity of the method, nickel and copper were also determined from a standard copper-nickel alloy (B.C.S; 180/2). In addition to nickel and copper, the alloy also contained 0.68% Fe and 0.75% Mn. The alloy sample (0.103 g) was dissolved in concentrated nitric acid, evaporated to dryness and the mass dissolved in distilled water to make 100 ml. Three measurements, each with 2.5 ml of the aqueous solution of the alloy gave on analysis the percentages of Ni and Cu (Table 1). Thus it is evident that both the metal ions could be simultaneously determined spectrophotometrically using HBAO with the error of measurement $< \pm 1\%$.

An attempt was also made to determine the feasibility of the reagent as a precipitant for gravimetric determination of the two cations individually and also from their mixtures. It was found that Ni^{II} could be quantitatively precipitated as a green complex by adding an ethanolic solution of HBAO to the aqueous solution in the pH range 5.0–10.0, while Cu^{II} could be quantitatively

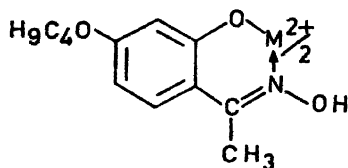


Fig. 1

cm^{-1} in case of Ni and to 2820 cm^{-1} in the case of Cu). This suggests chelation through O⁻ of the phenolic group and N of the oximino group (Fig. 1).

The Ni^{II} and Cu^{II} complexes follow Beer's law upto 294 and 327 $\mu\text{g ml}^{-1}$ with molar absorptivity of 130 and $108\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ respectively. The stability constants of the complexes were found to be 3.1×10^7 for Ni^{II} and 2.4×10^9 for Cu^{II} , i.e. the copper complex is more stable than the nickel complex.

As the absorbances of the two complexes are additive, an attempt was made to determine the two metal ions simultaneously from their mixtures. Synthetic mixtures containing from 2.642–294 $\mu\text{g Ni}^{\text{II}}$ and 318–2186 $\mu\text{g Cu}^{\text{II}}$ were taken, the pH of the solution was adjusted to 9.0, both the complexes were extracted in the benzene layer containing HBAO and the absorbance was measured at 600

precipitated as a greenish white complex in the pH range 3.0–10.0. To determine Ni^{II} and Cu^{II} from their mixture, pH of the aqueous solution was first adjusted to 3.5. Copper was then precipitated by adding 1% ethanolic solution of HBAO in slight excess to the hot (70–80°) aqueous solution. The Cu^{II} -HBAO complex was filtered, washed, dried and weighed as $\text{Cu}(\text{C}_{12}\text{H}_{16}\text{O}_3\text{N})_2$. The filtrate containing Ni^{II} was then concentrated and the pH increased to 5.5 when Ni^{II} precipitated out. The results (Table 2) show that Ni^{II} and Cu^{II} could be gravimetrically estimated from their mixtures with an error of $\pm 0.6\%$. From a set of six determinations from solutions containing 29.36 mg of Ni^{II} and 31.77 mg of Cu^{II} the standard deviations for Ni^{II} and Cu^{II} were found to be 0.057 and 0.054 respectively.

It may be concluded that HBAO can be used as an extraction spectrophotometric reagent for simultaneous estimation of Ni^{II} and Cu^{II} from their mixtures containing as low as 294 μg of Ni^{II} and 320 μg of Cu^{II} with an error not exceeding $\pm 1\%$. By proper control of pH, the reagent can also be used for sequential gravimetric determination of Ni^{II} and Cu^{II} from their mixture.

Experimental

Stock solutions were prepared by dissolving $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water acidified with a few drops of acid. Ni^{II} and Cu^{II} were determined following standard procedures⁷.

An Elico LI 120 pH meter and a Systronics 118 spectrophotometer were used.

HBAO was prepared following the reported method¹. It was crystallised from ethanol as colourless needles, m.p. $78 \pm 1^\circ$ (Found : C, 64.98; H, 8.44; N, 6.50. $\text{C}_{12}\text{H}_{17}\text{O}_3\text{N}$ calcd. for : C, 64.55; H, 7.68; N, 6.27%). The reagent was found insoluble in water but soluble in alcohol, acetone, chloroform, carbon tetrachloride and benzene.

Preparation of M^{II} -HBAO complex and selection of the solvent : When alcoholic solution of HBAO was added to 0.005 M aqueous solution of the

metal ion, green and greenish white precipitates were obtained with Ni^{II} and Cu^{II} respectively. The precipitates were insoluble in ethanol or methanol but soluble in nonpolar organic solvents. As the solubility of copper complex was more in benzene than in carbon tetrachloride, benzene was selected for the extraction and spectrophotometric studies.

A series of buffer solutions in the pH range 2.0–11.0 were prepared by adding HCl or NaOH to 0.2 M sodium acetate. To the buffer solution (25 ml) of known pH, suitable aliquot (e.g. 2.0 ml) of 0.01 M $\text{Ni}^{\text{II}}/\text{Cu}^{\text{II}}$ solution was added. The ionic strength of the solution was maintained at about 0.01 M using KCl. As the complex was soluble in organic solvents it was formed and extracted directly in the nonaqueous medium by adding 0.002 M HBAO (20 ml) in benzene to the aqueous solution and shaking the mixture for 2–3 min. The aqueous layer left after the first extraction did not give any qualitative test for Ni^{II} or Cu^{II} , i.e. the extraction was complete in a single extraction. The upper benzene layer was used for spectrophotometric measurements against the reagent blank.

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