2-Hydroxy 4-*n*-Butoxy Butyrophenone Oxime as an Analytical Regent for Nickel.

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In the present work, the authors describe 2-hydroxy, 4-*n*-butoxy butyrophenone oxime as a gravimetric and photometric reagent for nickel.

INTRODUCTION

Several organic compounds with phenolic protogenic group and a suitably placed electron pair donating functional atom like nitrogen, oxygen or sulphur are found to interact with metal ions giving precipitation or coloration due to complex formation. Thus various phenones, phenone hydrazones and phenone oximes as well as chalcone oximes have been reported as gravimetric and spectrophotometric reagents for nickel. In earlier communications[1-2], 2-hydroxy, 4-*n*-butoxy acetophenone oxime and 2-hydroxy, 4-*n*-butoxy propiophenone oxime have been described as gravimetric and/or spectrophotometric reagents for Ni(II). In the present work 2-hydroxy, 4-*n*-butoxy butyrophenone oxime (HBBO) has been reported as a gravimetric and extraction photometric reagent for nickel.

EXPERIMENTAL

Instruments: Spectrophotometric measurements were made with a Systronics UV/VIS Spectrophotometer, model-118. All pH measurements were made with an Elico digital pH meter, model LI-120.

Reagent: 2-Hydroxy, 4-*n*-butoxy butyrophenone (HBB) was prepared from resbutyrophenone following the method of Eijkmann et al.[3], using *n*-butyl bromide and anhydrous potassium carbonate in acetone. When crystallized from ethanol colourless, needlelike crystals with m.p. 37 ± 1°C were obtained. The oxime of HBB was prepared by the sodium acetate method. On crystalization from alcohol pure HBBO in the form of colourless needles with m.p. of 64 ± 1°C was obtained. The reagent is soluble in solvents like alcohol, acetone, benzene, carbon tetrachloride, etc. The molecular weight of HBBO was found by Rast's cryoscopic method to be 251.32 (Calcd: 250.80). The elemental analysis of the oxime showed its composition to be: C, 66.55%; H, 8.30%; N, 5.34%; (Calcd: C, 66.93%; H, 8.32%; N, 5.38%).

Stock solution: Stock solution of $NiCl_2 \cdot 6H_2O$ (0.5M) was prepared by dissolving the pure salt in double distilled water and employed after standerdization[4] with EDTA and DMG.

Gravimetric Procedure: An aliquot of 0.05M solution of Ni(II) was diluted to 100 ml with distilled water, warmed to about 70–80°C on a water bath and 20% solution of sodium acetate was added dropwise to bring the pH between 5.0 and 6.0 1% solution of HBBO in ethanol was then added till precipitation was complete. The light green precipitates were digested on watherbath at 80–90°C for about 30 min and filtered through a previously weiged sintered glass crucible (G–4), washed with hot water followed by warm 60% alcohol, dried at 110–120°C and weighed as $Ni(C_{13}H_{18}O_3N)_2$ [gravimetric factor= 0.1050]. Tripli- cate experiments were performed in each case and the mean values have been reported.

Spectrophotometric Procedure: The precipitates of Ni(II)-HBBO complex were insoluble in absolute ethanol or methanol and partially soluble in isobutyl alcohol. However, they were soluble in nonpolar solvents like benzene, chloroform, carbon tetrachloride, etc. The complex was, therefore, directly extracted in carbon tetrachloride layer. For this purpose a suitable aliquot of Ni(II) solution was added to 20.0 ml of sodium acetate buffer of pH 8.0. The ionic strength of the solution was maintained at 0.1M by addition of KCl. Ni(II) was then extracted from the aqueous layer by equilibrating the solution with 10.0 ml of carbon tetrachloride containing a fixed concentration of HBBO. The extraction was found to be complete in a single operation. The absorbance of the organic layer was recorded against the reagent blank prepared under similar conditions.

RESULTS AND DISCUSSION

Results are given in Fig. 1–2 and Table 1–4.

Gravimetric determination of nickel: To determine the feasibility of the regent for gravimetric esimation of Ni(II), the metal ion was precipitated from solutions having pH values in the range 4.0–10.0. There was incomplete precipitation at pH 4.5 whereas between pH 5.0–10.0 nickel could be quantitatively precipitated, the error being minimum ($\leq 0.1\%$) in the pH range 5.0–6.0 (Fig. 1). When attempts were made to determine nickel from solutions (pH = 5.5) containing different
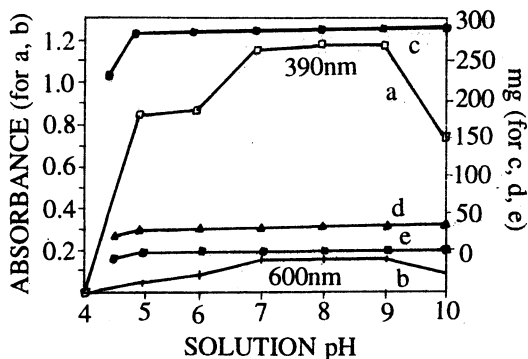

Fig. 1 Effect of pH on gravimetric and spectrophotometic determination of nickel.
    (a) Absorbance at 390 nm.   (b) Absorbance at 600 nm.
    (c) mg of Ni-HBBO complex.   (d) mg of nickel found.
    (e) Error (mg).

concentrations (7.34–44.03 mg) of Ni(II) quantitative precipitation of the metal ion was possible in all the cases with error of measurement ranging from 0.03% to 0.41% (Table 1).

Table 1
EFFECT OF Ni(II) CONCENTRATION ON GRAVIMETRIC ESTIMATION OF NICKEL AS Ni(ii)-HBBO COMPLEX AT pH = 5.5

Nickel taken (mg)	Ni-HBBO complex obtained (mg)	Nickel found (mg)	Error (mg)	Error (mg)
7.34	70.3	7.38	0.04	0.58
14.68	139.9	14.69	0.01	0.09
29.36	279.5	29.35	−0.01	−0.02
44.03	419.5	44.04	0.01	0.03

Qualitative tests with the reagent also showed that nickel could be detected as a green precipitate at as low a concentration as 2 ppm. Below this concentration the solution became turbid and no precipitation could be observed.

To determine the selectivity of the reagent, qualitative tests were carried out for precipitation of various metal ions in the pH range 1.0–10.0 using HBBO. The results (Table 2) show that the reagent may be used for detection and

TABLE 2
pH RANGE FOR PRECIPITATION OF VARIOUS METAL IONS BY HBBO.

Metal ion	pH range	Colour of precipitate
Pd(II)	1.0 to 6.0	Yellow
Cu(II)	3.0 to 10.0	Greenish white
Mn(II)	5.0 to 10.0	Brown
Ti(II)	1.5	Yellow coloured solution
	2.5 to 6.5	Golden yellow
Fe(III)	3.5 to 5.0	Violet coloured solution
	5.0	Reddish brown (probably due to hydrolysis)
Fe(II)	4.5 to 6.0	Violet coloured solution
	7.0 to 8.5	Violet

determination of Pd^{2+}, Cu^{2+}, Mn^{2+}, Co^{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 Ni^{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 nickel, copper and palladium from their mixtures, *e.g.*, palladium may be quantitatively precipitated as $Pd(HBBO)_2$ complex in the pH range 1.0–2.0. From the filtrate, copper may 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 measurment was found to range from 0.05–0.43% for nickel,

0.17–0.54% for copper and 0.02–0.47% for palladium depending upon the concentration of the metal ion taken, it being less in concentrated solutions.

Spectrophotometric deremination of nickel

Selection of pH and wavelength: As the pH of the solution has a pronounced effect on the reaction between Ni(II) ion and HBBO absorbance of the organic layer containing Ni(II)-HBBO 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 7.0–9.0. A pH of 8.0 was selected for the present work.

For the selection of the wavelength Vosburgh and Cooper's method was using 30.0 ml of the aqueous solution (pH = 8.0) containing Ni(II) and 10.0 ml of HBBO in carbon tetrachloride, the concentration of Ni(II) and HBBO being in the mole ratio 1 : 1, 1 : 2, 1 : 3 and 2 : 1. Absorbance measurements in the wavelength range 360–700 nm showed that only one complex was formed. The plots of absorbance *vs* wave length show two maxima, a prominent one at 390 nm and a less prominent one at 600 nm. Of this the wavelength of 600 nm was selected for spectrophotometric measurements because neither the reagent nor the metal ion show any absorbance at this wavelength.

Validity of Beer's law and optimum concentration range: The green Ni(II)-HBBO complex in carbon tetrachloride obeys Beer's law up to 264 µg nickel per ml of the organic layer. Beyond this concentration the absorbance plot shows a negative deviation from linearity. The optimum concentratioin range for the complex in organic layer as derived from the Ringbom plot is found to be 117–264 ppm. The average molar absorptivity (ε) of the complex obtained from the absorbance data of ten different concentrations is found to be 150 l mol^{-1} cm^{-1} at 600 nm. The value at 390 nm is found to be 1170 l mol^{-1} cm^{-1}. The photometric sensitivity as per Sandell's definition is 0.39 µg/cm^2 at 600 nm.

Stoichiometry and stability constant of the complex: The stoichiometry of the Ni(II)-HBBO complex was studied by (i) Job's method of continuous varia-tion[5] (ii) Yoe and Jone's mole ratio method[6] and (iii) Harvey and Manning's slope ratio method[7] (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 HBBO two bands are observed in the –OH stretch region, one at 3285 cm^{-1} due to the 2-hydroxy group and the other at 2840 cm^{-1} due to the oximino group. In the IR spectrum of Ni(II)-HBBO complex the first band at 3285 cm^{-1} disappeared while the second band shifted to 2880 cm^{-1}. This suggests that there is acid dissociation of the phenolic 2-hydroxy group followed by the formation of Ni(II)-HBBO chelate through O^- of the phenolic group and N of the oximino group. A weak band at 600 nm in the spectrum of Ni(II)-HBBO complex could be assigned to $^1B_{1g} \leftarrow {}^1A_{1g}$ transition and a strong band at 390 nm could be assigned to charge transfer.

TABLE 3

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 complex obtained (mg)	Pd found (mg)	Cu complex obtained (mg)	Cu found (mg)	Ni complex obtained (mg)	Ni found (mg)
Pd (mg)	Cu (mg)	Ni (mg)						
21.28	—	5.87	123.8	21.24	—	—	55.4	5.84
10.64	—	11.74	60.6	10.62	—	—	111.1	11.66
10.64	—	29.36	60.7	10.65	—	—	280.2	29.43
—	31.77	29.36	—	—	282.5	31.81	279.6	29.36
—	31.77	14.68	—	—	282.5	31.81	139.9	14.70
—	15.89	29.36	—	—	140.9	15.86	280.0	29.40
10.64	31.77	29.36	60.9	10.68	283.3	31.90	279.7	29.37
15.96	47.66	29.36	91.3	16.01	424.2	47.70	279.0	29.30
10.64	31.77	44.03	60.8	10.66	282.6	31.93	419.7	44.10

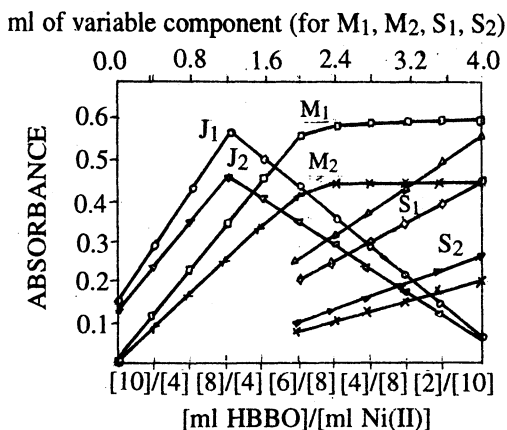ml of variable component (for M_1, M_2, S_1, S_2)

Fig. 2 Plots of Job's method of continuous variation (J_1, J_2); Mole ratio method (M_1, M_2) and slope ratio method (S_1, S_2) for determination of M : L ratio.
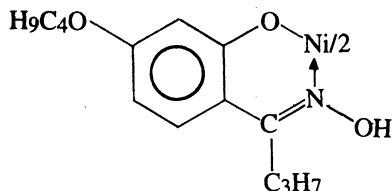
J_1, S_1 : 0.05M Ni(II); 0.01M HBBO

J_2, S_2 : 0.008M Ni(II); 0.008M HBBO

M_1 : 0.004M Ni(II); 0.016M HBBO

M_2 : 0.003M Ni(II); 0.012M HBBO

Based on the above data the nickel complex with HBBO can be assigned the structure:

The stability constants of the complex for different values on 'n' were calculated from the data of mole ratio method. From the values given in Table 4 it is evident 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 may be taken as 5.4×10^8, the value of ΔG being -10.1 K.cal. $mole^{-1}$.

Effect of diverse ions: To determine the effect of diverse ions on the estimation of Ni(II) using HBBO, 1174.2 µg of Ni(II) were taken and various amounts of different ions were added. The final volume of the aqueous buffered layer was 35.0 ml. Nickel from this solution was estimated spectrophotometrically. A difference of more than $\pm$ 1.5% in the absorbance value has been taken as an interference. The tolerance limits for the various ions, are as follows:

Na^+, K^+, NH_4^+, Cl^-, Br^-, NO_3^-, SO_4^{2-}, CH_3COO^-, (100000 µg); Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, Cd^{2+}, I^-, $S_2O_3^{2-}$, MoO_4^{2-}, citrate, tartate, oxalate, (10000 µg); Cu^{2+}, Co^{2+}, Mn^{2+}, Cr^{3+}, UO_2^{2+}, Pd^{2+}, Fe^{3+}, Fe^{2+}, (1000 µg) were found to interfere considerably.

TABLE 4

STABILITY CONSTANTS FOR Ni(II)-HBBO COMPLEX FROM THE DATA OF MOLE RATIO METHOD.

Mole Ratio [HBBO] [Ni(II)]	Stability Constant for Different Values of "n"				Mean k
	Set I		Set II		
	$n = 1$	$n = 2$	$n = 1$	$n = 2$	
0.4	2.85E + 02	5.34E + 07	3.68E + 02	5.24E + 07	
0.8	3.81E + 02	5.54E + 07	4.94E + 02	5.44E + 07	
1.2	5.57E + 02	5.39E + 07	7.15E + 02	5.25E + 07	
1.6	9.97E + 02	5.17E + 07	1.26E + 03	5.50E + 07	
2.0	3.38E + 03	5.32E + 07	3.67E + 03	5.44E + 07	
Average		5.35E + 07		5.37E + 07	5.36E + 07

ACKNOWLEDGEMENT

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