



**Pelagia Research  
Library**

**Pelagia Research Library**

Der Chemica Sinica, 2010, 1 (3): 100-106



**Pelagia Research  
Library**

**ISSN: 0976-8505**

**CODEN (USA) CSHIA5**

## **2-Hydroxy-4-n-propoxy-5-bromoacetophenone (HnPBAO) oxime as a gravimetric reagent for Ni(II) and Cu(II) and spectrophotometric study of the complexes**

**Ambily P Nair, Christine Jeyaseelan\***

*Department of Chemistry, Amity Institute of Applied Sciences, Amity University, Noida, India*

---

### **ABSTRACT**

*2-Hydroxy-4-n-Propoxy-5-Bromoacetophenone oxime is a new analytical reagent, which was used for gravimetric estimation of Cu(II) and Ni(II) ions. In the pH range 3.0 to 6.0, this reagent gives a buff coloured precipitate with  $\text{Cu}^{2+}$  and Job's method and mole ratio method revealed that the stoichiometry of the complex is 1:2. Beer's law is obeyed upto 76.2 ppm of  $\text{Cu}^{2+}$ . The molar absorptivity at 420 nm was found to be  $1.638 \times 10^2 \text{ litre mol}^{-1} \text{ cm}^{-1}$  and the Sandell's sensitivity was found to be  $0.387 \mu\text{g of Cu(II)/cm}^2$ . The stability constant is found to be  $1.5 \times 10^9$ . Ni(II) gave a light green coloured precipitate in the pH range 8.0 – 10.0 and the stoichiometry of the complex was found to be 1:2. The molar absorptivity at 410 nm was found to be  $7.775 \times 10^2 \text{ litre mol}^{-1} \text{ cm}^{-1}$  and Sandell's sensitivity as  $0.0754 \mu\text{g of Ni(II)/cm}^2$ . The stability constant of the complex was found to be  $1.485 \times 10^9$ . Beer's law is obeyed upto 23.48 ppm. This reagent can be used for the determination of Cu(II) and Ni(II) in German silver alloy.*

**Key words:** Oxime, Analytical reagent, 2-Hydroxy-4-n-propoxy-5-bromoacetophenone oxime (HnPBAO)

---

### **INTRODUCTION**

A wide variety of reagents like oximes,[1,2] o-hydroxy ketooxime,[3] thiosemicarbazones,[4,5] chalcone oxime[6] etc. have been available which are used for gravimetric and spectrophotometric determination of various transition metal ions.

In the present work we report the use of 2-Hydroxy-4-n-propoxy-5-bromoacetophenone oxime (HnPBAO) as a gravimetric reagent for Ni(II) and Cu(II). The stoichiometry of the complexes can be confirmed by spectrophotometric methods and thus determining the stability of complexes.

## MATERIALS AND METHODS

All spectrophotometric measurement were done on a "Milton Roy"(Spectronic 20 D+) spectrophotometer and Shimadzu UV-160A UV-Visible spectrophotometer. All pH measurements were done on "Equiptronics" pH meter (Model-EQ-614) and the required pH was maintained using CH<sub>3</sub>COONa-CH<sub>3</sub>COOH, CH<sub>3</sub>COONa-HCl, NH<sub>3</sub>-NH<sub>4</sub>Cl or Borax-HCl buffer of suitable concentrations.

*Synthesis of HnPBAO:* Resacetophenone was prepared from resorcinol, acetic acid and anhydrous Zinc Chloride as reported earlier.[7] This was then treated with bromine in acetic acid and crystallized from ethanol to get 2,4 dihydroxy 5-bromoacetophenone. Further refluxing was done with n-propyl iodide and anhydrous potassium carbonate in acetone to obtain 2-Hydroxy-4-n-propoxy-5-bromoacetophenone which was dissolved in ethanol and the oxime prepared by the usual method, using hydroxylamine hydrochloride and sodium acetate. The oxime was recrystallized from ethanol. Light green crystals were obtained which gave a M.P of 172 °C.

The reagent solution of HnPBAO was prepared in ethanol for gravimetric study, whereas for spectrophotometric study the solution was prepared in DMF as the metal complex of this reagent was found to be insoluble in most of the common organic solvents.

### Gravimetric Determination of Cu(II)

A 0.05 M solution of the reagent in pure ethanol was used. Copper Sulphate solution (0.05 M, 10 ml) was taken in a clean beaker and diluted to about 100 ml with distilled water and the pH of the solution was adjusted to 3.0 to 4.0 using sodium acetate- hydrochloride acid buffer. The solution was warmed to 60°C and a little excess of HnPBAO was added (0.05 M, 22 ml). The buff precipitate was filtered through a previously weighed crucible (G4) and washed with warm water followed by 90% aq. ethanol to remove excess of reagent. The chelate was dried to a constant weight at 110 – 115 °C in hot air oven, cooled and weighed. The experiment was repeated at different pH of solution. It was also repeated with different aliquots, keeping optimum pH to evaluate its applicability. The results obtained are given in Table 1.

Table1- Result of gravimetric estimation of Cu(II) at pH 5.0, Cu(II)-HnPBAO

Weight of Cu(II) taken in mg	Weight of Cu(II) complex in mg	Weight of Cu(II) ion found in mg	Relative Error	
			mg	%
31.77	320.00	31.87	+0.10	+0.31
47.66	480.46	47.85	+0.19	+0.39
63.55	640.36	63.78	+0.23	+0.36

### Interference:

To study the effect of foreign ions on gravimetric determination of Cu(II), 8-10 mg of various cations were added to solution containing 31.77 mg Cu(II) at pH 4.0 and gravimetric estimations were done. It was observed that Mg(II), Ca(II), Ni(II), Sr(II), Zn(II), Ba(II), Cd(II), and Fe(II) donot interfere at this pH, but Pd(II), Co(II) and Fe(III) interfered seriously. Many common anions like chloride, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

### Gravimetric determination of Ni(II)

A 0.05 M solution of the reagent in pure ethanol was used. Nickel Sulphate solution (0.05 M, 10 ml) was taken in a clean beaker and diluted to about 100ml with distilled water and the pH of the solution was adjusted to 8.0 to 9.0 using ammonia-ammonium chloride buffer. The solution was warmed to 60 °C and a little excess of HnPBAO was added (0.05 M, 22 ml). A light green

precipitate was obtained which was digested on a water bath to 60°C. The precipitate was filtered through a previously weighed crucible (G4) and washed with warm water followed by 90% aq. ethanol to remove excess of reagent. The chelate was dried to a constant weight at 110 - 115°C in hot air oven, cooled and weighed. The experiment was repeated at different pH of solution. It was also repeated with different aliquots, keeping optimum pH to evaluate its applicability. The results obtained are given in Table 2.

**Table 2- Result of gravimetric estimation of Ni(II) at pH 9.0, Ni(II) –HnPBAO**

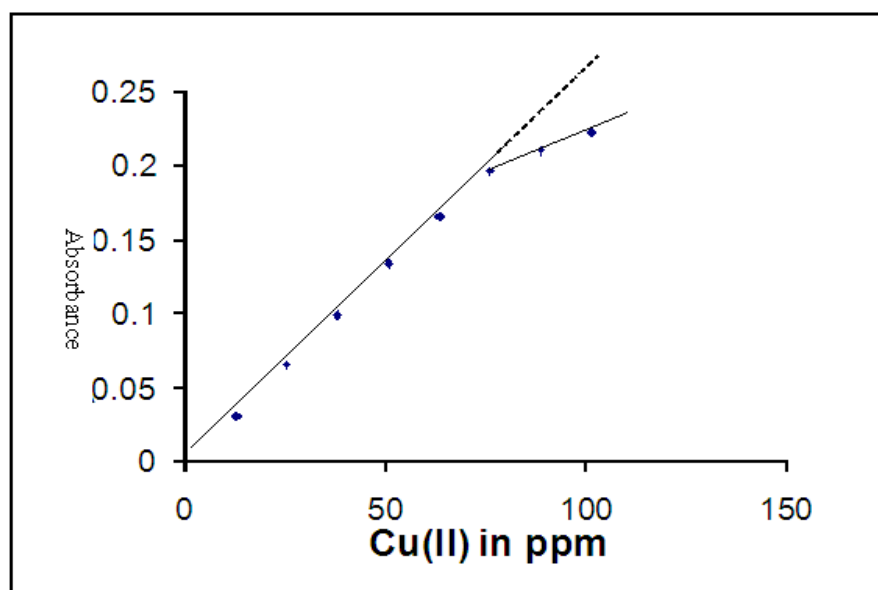
Weight of Ni(II) taken in mg	Weight of Ni(II) complex in mg	Weight of Ni(II) ion found in mg	Relative Error	
			mg	%
29.35	317.85	29.47	+0.12	+0.40
44.02	477.00	44.22	+0.20	+0.45
58.69	636.00	58.95	+0.26	+0.44

### Interference:

To study the effect of foreign ions on gravimetric determination of Ni(II), 8-10 mg of various cations were added to solution containing 29.35 mg Ni(II) at pH 9.0 and gravimetric estimations were done. It was observed that Mg(II), Ca(II), Sr(II), Zn(II), Ba(II), Cd(II), Pd(II), Al(III) and Fe(II) do not interfere at this pH, but Mn(II) and Co(II) interfered seriously. Many common anions like chloride, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

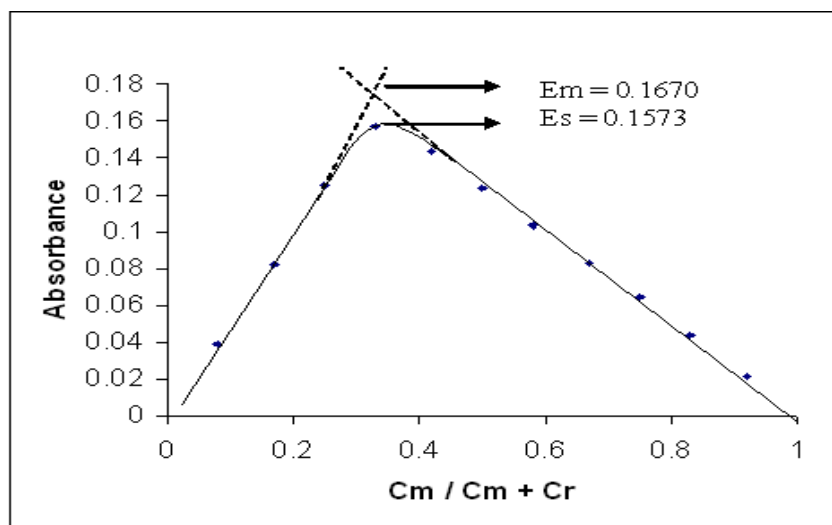
### Spectrophotometric study of Cu(II)-HnPBAO Complex:

A series of buffer solutions with pH value ranging from 4.0 – 7.0 were prepared using hydrochloric acid and sodium acetate and acetic acid-sodium acetate buffer. 6 ml of 0.01 M reagent solution was added to 1 ml of 0.05M of Cu(II) ion solution at varying pH. The final volume was adjusted to 25 ml using DMF. The spectra of the above solutions were recorded from 300 nm to 800 nm. It was found that the Cu(II)-HnPBAO complex showed a shoulder band at 420 nm and this was used as the wavelength of maximum absorbance for further studies. The absorbance was found to be maximum at pH 6.0 and hence this pH was used.

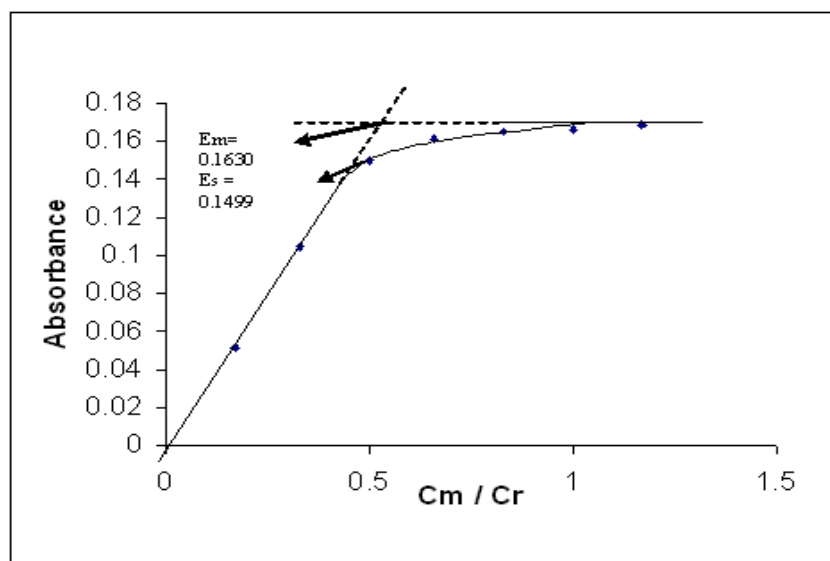


**Figure 1: Beer's Law Plot for Cu(II)- HnPBAO Complex**

Different aliquots of Cu(II) solution (0.05 M) were taken, 5 ml of buffer was added to maintain the pH at 6.0. The excess reagent (0.01 M, 6 ml) was added to get precipitate of the complex. The final volume of 25 ml was made up with DMF. The absorbance was measured at 420 nm. The absorbance was plotted against the concentration of Cu(II).



**Figure 2: Job's Method for Cu(II)-HnPBAO Complex**  
 Plot of Job's method of variation for determination of M:L ratio  
 0.005 M Cu(II), 0.01 M HnPBAO, pH = 6.0,  $\lambda = 420$  nm



**Figure 3: Mole-Ratio method for Cu(II)-HnPBAO Complex**  
 Plot of Yoe and Jones method for determination of M:L ratio  
 0.005 M Cu(II), 0.005 M HnPBAO, pH = 6.0,  $\lambda = 420$  nm

A straight line passing through the origin was obtained upto 76.2 ppm of Cu(II). The standard graph thus prepared is shown in Figure 1 and maybe used for determination of Cu(II) ion in unknown solution using HnPBAO. The molar absorptivity was calculated from the graph and it was found to be  $1.638 \times 10^2$  litre mol<sup>-1</sup> cm<sup>-1</sup> and Sandell's sensitivity was found to be 0.387  $\mu$ g of Cu(II) /cm<sup>2</sup>.

Jobs method[8] (Figure 2) and Yoe and Jones Mole Ratio method[9] (Figure 3) were used to determine the stoichiometry of the complex. It was found to be 1:2 (M:L) by both the methods.

This was in agreement with the stoichiometry found by gravimetry.

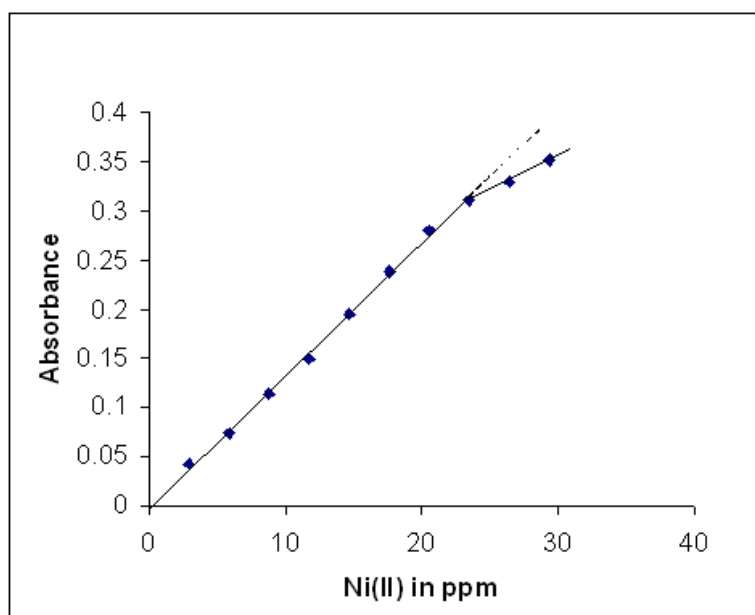
The Stability Constant was calculated using the formula  $K_s = (1-\alpha) / 4\alpha^3 C^2$  where  $\alpha = (E_m - E_s) / E_m$  ( $E_m$  is the maximum absorbance found from the graph and  $E_s$  is the absorbance at stoichiometric molar ratio of the metal to the reagent in the complex)

The average stability constant found from the two methods is  $1.5 \times 10^9$ .  $\Delta G^\circ$  for the complex formation at 25 °C is -12.59 kcal / mole.

#### **Spectrophotometric Study of Ni(II)-HnPBAO complex:**

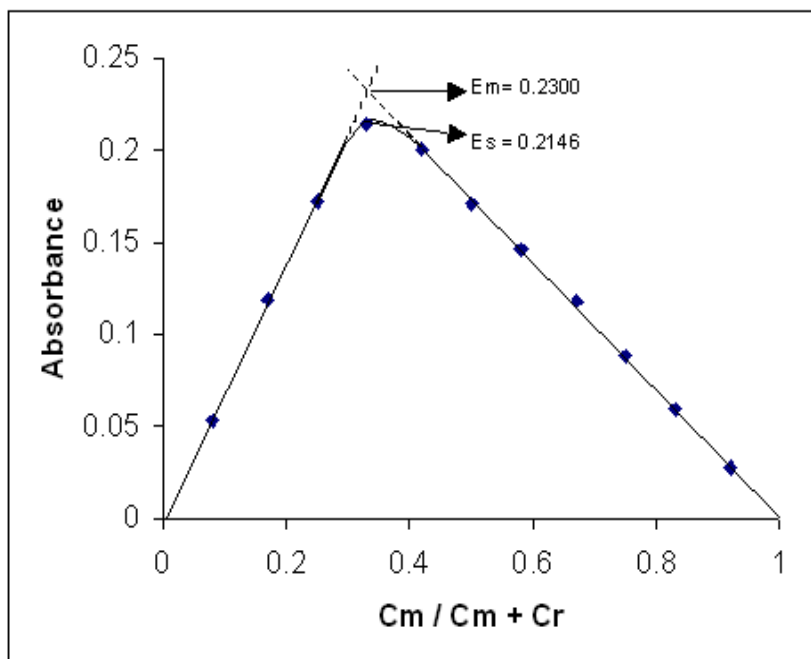
The studies were carried out in a similar manner as with Cu(II). The pH range of the buffer was varied from 8.0 – 10.0 prepared using ammonia-ammonium chloride buffer. The spectra of the above solutions were recorded from 350nm to 800nm. It was found that the Ni(II)-HnPBAO complex shows maximum absorption at 410nm. The pH for maximum complex formation is 9.0. The complex obeys Beer's Law upto 23.48 ppm (Figure 4)

The complex has a stoichiometry of 1:2 (M:L) as determined by Jobs method (Figure 5) and Yoe and Jones Mole Ratio method<sup>9</sup> (Figure 6). The molar absorptivity was calculated from the graph and it was found to be  $7.775 \times 10^2$  litre mol<sup>-1</sup> cm<sup>-1</sup> and Sandell's sensitivity was found to be 0.0754 µg of Ni(II)/cm<sup>2</sup>.

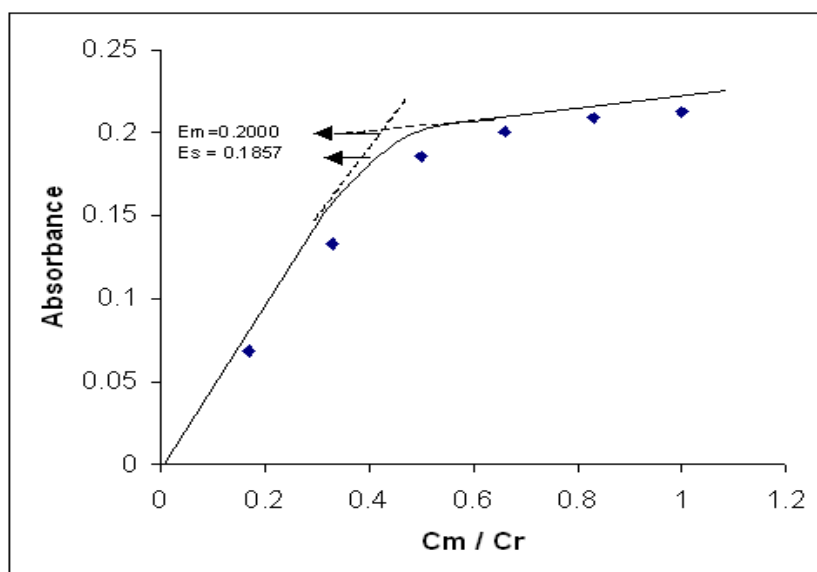


**Figure 4: Beer's Law Plot for Ni(II)- HnPBAO Complex**

The Stability constant found from the two methods is  $1.485 \times 10^9$ .  $\Delta G^\circ$  for the complex formation at 25 °C is -12.40 kcal / mole.



**Figure 5: Job's Method for Ni(II)-HnPBAO Complex**  
*Plot of Job's method of variation for determination of M:L ratio*  
*0.005 M Ni(II), 0.005 M HnPBAO, pH = 9.0,  $\lambda = 410$  nm*



**Figure 6: Mole-Ratio method for Ni(II)-HnPBAO Complex**  
*Plot of Yoe and Jone's method for determination of M:L ratio*  
*0.005 M Ni(II), 0.005 M HnPBAO, pH = 9.0,  $\lambda = 410$  nm*

#### **Analysis of German silver using HnPBAO:**

Exactly 460 mg of German silver was taken and dissolved in 50 ml of 1:1 nitric acid by heating on a sand bath. Excess nitric acid was removed by careful evaporation and the solution was diluted with distilled water.

10ml of aliquot was taken and Cu(II) was determined gravimetrically as per the procedure described above at pH 6.0 using sodium acetate- acetic acid buffer. The filtrate obtained after separating Cu(II) was concentrated by evaporation and the pH raised to 9.4 using ammonia-ammonium chloride buffer and Ni(II) was determined gravimetrically as described previously. The experiment was repeated thrice and the results obtained are given in Table 3.

**Table 3- Analysis of German silver**  
*Weight of German Silver sample = 460.0 mg*

S No		Extraction of Cu(II)	Extraction of Ni(II)
1.	Weight of Cu(II)-HnPBAO complex obtained	260.18 mg	95.09 mg
2.	Amount found in 10 ml	25.91 mg	8.81 mg
3.	Amount found in German Silver alloy	259.1 mg	88.1 mg
4.	Percentage found in German Silver alloy	56.32 %	19.16 %
5.	Percentage reported in alloy	56.0 %	19.0 %
6.	% error	+0.57	+0.84

### CONCLUSION

2-Hydroxy-4-n-Propoxy-5-Bromoacetophenone oxime (HnPBAO) is a suitable reagent for gravimetric as well as spectrophotometric determination of Cu(II) as well as Ni(II). Many anions and cations were not found to interfere.

### REFERENCES

- [1] K. K. Desai, B. D. Desai, *Asian J. Chem.*, **2001**, 13, 334.
- [2] S. K. Shingadia, K. K. Desai, *Oriental J Chem*, **2006**, 22(3), 703 .
- [3] K. Purohit, K. K. Desai, *Acta Ciencia Indica*, **2005**, 4, 329.
- [4] H. C. Gandhi, K. K. Desai, *Asian J Chem*, **2003**,15, 549.
- [5] M. S. Rao, N. B. L. Prasad, K. H. Reddy, *Indian J Chem*, **2006**, 45A, 1659.
- [6] M. J. Desai, P. G. Desai, A. G. Mehta, *Asian J Chem*, **1999**, 77, 519.
- [7] R. Robinson, R. C. Shah, *J Chem Soc*, **1934**, 1494.
- [8] P. Job, *Ann. Chem.*, **1938**, 115, 332.
- [9] J. H. Yoe, A L. Jones, *Ind. Eng. Chem. Anal. Ed.*, **1944**, 16, 111.