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# 2-Hydroxy-4-Isobutoxy Acetophenone Oxime as an Analytical reagent for Nickel

**Dr. J. R. Shukla**
Associate Professor (Principal), Chemistry Department, Shri C.N.P.F Arts & D.N.Science College, Dabhoi, Gujarat, India

## ABSTRACT

2-Hydroxy-4-isobutoxy acetophenone oxime(HIBAO) has been used for the spectrophotometric determination for Ni(II) at pH range 8 to 9 in chloroform medium. Job's method for continuous variation, Yoe and Jones' mole ratio method, the slope ratio method show metal ligand ratio in complex to be 1:2. The stability constant of the complex is found to be 6.31 $X10^7$. The green coloured complex obeys Beer's law in the concentration range 29.35 to 234.77 ppm for Ni(II) ion, while the optimum concentration range from Ringbom plot is found to be 58.69 to 234.77ppm. The photometric sensitivity and molar absorptivity at the 600nm are found to be 0.448µg/$cm^2$ and 131 l $mol^{-1}cm^{-1}$ respectively. The standard free energy of formation of complex is -10.82 kcal/mole at 30$^o$C. The complex is stable for one week. The reagent has also been found to give quite satisfactory results for Ni(II) present in alloy like brass, Nicrome and synthetic mixtures. The antimicrobial Activity of HIBAO and Ni-HIBAO complex have also been checked.

**Keywords:** Acetophenone Oxime, HIBAO, HIBA, UV/VIS

## I. INTRODUCTION

Various o-hydroxy phenones, phenone oximes, phenyl hydrozones, chalknoneoximes, etc, have been used as an analytical reagent for the spectrophotometric and gravimetric determination of Nickel and other transition metal ions1-5. In the present work the use of 2-hydroxy-4-isobutoxy acetophenone oxime (HIBAO) as photometric reagent for Ni(II) has been described.

## II. METHODS AND MATERIAL

A 0.1M stock solution of Ni(II) has been prepared by dissolving Nickel Chloraid (A.R) in distilled water containing few drops of glacial acetic acid. The amount of Ni(II) in this solution was determined following standard procedures[6].

**Preparation of 2-hydroxy-4-isobutoxy acetophenone oxime (HIBAO):**

Resacetophenone was prepared from resorcinol by standard methods[7]. 2-hydroxy-4-isobutoxyacetophenone (HIBA) has been prepared by refluxing resacetophenone and isobutyl bromide in suitable solvent for 4 hrs. 2-hydroxy-4-isobutoxyacetophenoneoxime(HIBAO)[8] has been prepared by refluxing HIBA with hydroxyl amine hydrochloride in the presence of sodium acetate in ethanol medium for 4 hrs. The reagent when recrystallized from ethanol was obtained in the colourless, needle like crystals (m.p. 102$^o$C ± 1$^o$C ), with M.W 223.40 (calcd. for $C_{12}H_{17}NO_3$ = 223.27). The reagent is insoluble in water but soluble in alcohol, acetone benzene chloroform, carbon tetrachloride, etc. The elemental analysis and spectral analysis of the compound its structure has been confirmed.

**Preparation of Ni(II)-HIBAO complex and selection of solvent** : When an alcoholic solution of HIBAO was added to 0.01 M aqueous metal ion solution, green precipitates of complex were obtained in the pH range 6.0 - 9.5. The complex was found to be insoluble in polar solvents like water, methanol or ethanol but soluble in non-polar solvents like chloroform, benzene, $CCl_4$ etc. As Ni-HIBAO complex was more soluble in chloroform, it was selected as a solvent for extractive spectrophotometric determination of Ni(II).

**Apparatus :** Spectrophotometric measurements were made with a Systronics UV/VIS spectrophotometer (model-118) using 10mm glass cells. All pH measurements were made with Systronic pH meter (model-324).

## III. RESULTS AND DISCUSSION

Results are given in Fig. I-IV and Table I-II.

**Optimum pH and Selection of Wavelength :** The pH of the solution has pronounced effect on the reaction between Ni(II) and HIBAO and the stability of the complex. On the other hand the absorbance is dependant upon the wavelength used. Both the parameters were therefore controlled to give maximum absorbance. Absorbance measurements of the reagent in chloroform show maxima at 240nm, 268nm and 301nm with negligible absorbance beyond 390nm. The absorbance measurements of Ni(II)-HIBAO complex show a maxima at 390nm and 600nm. As the interference due to the reagent appeared to be negligible a wavelength of 600 nm was selected for the present work.

**Table I** : Stability Constant of Ni(II) –HIBAO Complex at $30^oC$

| Method employed | Em | Es | α | K (n=1) |
|---|---|---|---|---|
| **Mole ratio method** | | | | |
| Set-I | 0.327 | 0.300 | 0.08257 | $6.35 \times 10^7$ |
| Set-II | 0.389 | 0.360 | 0.07455 | $6.20 \times 10^7$ |
| **Job's Method** | | | | |
| Set-I | 0.260 | 0.235 | 0.09615 | $6.35 \times 10^7$ |
| Set-II | 0.521 | 0.489 | 0.06142 | $6.33 \times 10^7$ |
| **Mean K Stab** | | | | **$6.31 \times 10^7$** |

**Table II**: Analysis of Nickel in various samples

| Sample | "Ni" taken | | Absorbance | "Ni" found | | Relative error(%) |
|---|---|---|---|---|---|---|
| | µg | % | | µg | % | |
| Nichrome | 963.2 | 60.20 | 0.210 | 938.5 | 60.33 | 0.21 |
| | | | 0.218 | 974.2 | | |
| | | | 0.220 | 983.2 | | |
| | | | Avg. | 965.3 | | |
| Synthetic mixture No. 1 | 586.9 | - | 0.121 | 546.3 | - | 0.78 |
| | | | 0.133 | 600.5 | | |
| | | | 0.139 | 627.6 | | |
| | | | Avg. | 591.5 | | |
| Synthetic mixture No. 2 | 1173.8 | - | 0.246 | 1110.6 | - | 1.67 |
| | | | 0.276 | 1246.1 | | |
| | | | 0.271 | 1223.5 | | |
| | | | Avg. | 1193.4 | | |
| Synthetic mixture No. 3 | 880.4 | - | 0.190 | 849.1 | - | 1.69 |
| | | | 0.188 | 840.2 | | |
| | | | 0.203 | 907.2 | | |
| | | | Avg. | 865.5 | | |

To determine the optimum pH for complex formation series of buffer solutions with pH values ranging from 6.0 to 9.5 were prepared. To above buffer solutions, 2.0 ml of 0.01 M Ni(II) solution and 10 ml 0.01 HIBAO solution in chloroform were added. After shaking the mixture for two minutes, the green coloured complex was extracted. The absorbance of organic layer containing complex was measured at 600nm against a blank. From the results given in Fig. I, it may be generalized that maximum absorbance takes place at pH range 8.0 to 9.0. Hence a pH of 8.5 and wavelength of 600nm have been selected for the present work.

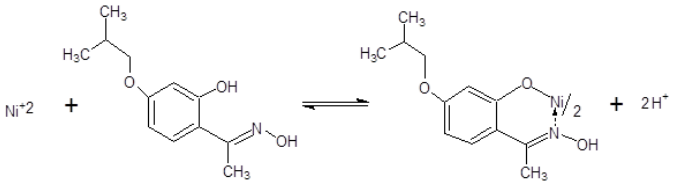
**Reproducibility :** Absorbance measurements of a set of ten solution prepared in a similar way and containing the same concentrations of all the reagents show that the reproducibility of measurements are quite good with a standard deviation of ± 5.608 Units, i.e., 0.48%.

**Effect of time and temperature :** To determine the effect of time and temperature on the intensity of colour and the stability of the Ni(II)- HIBAO complex, absorbance was measured at room temperature (30°C) at regular intervals of time up to two week and also at temperatures of 30°C to 55°C. The results show that complex is stable (± 2% deviation) for one weeks and up to 45°C.

**Stoichiometry and Stability Constant of the Complex** : The method of Vosbourgh and Cooper[9] showed that one complex is formed. To determine the stoichiometry of complex, Yoe and Jones mole ratio method[10] the slope ratio method[11] and Job's method of continuous variation[12] were employed (Fig. II-IV). All the three methods show a 1:2 metal:ligand ratio in the complex.

The value of the stability constants calculated from the job's method as well as from the mole ratio method are given in Table-I. From the table the average value of stability constant may be taken as $6.31 \times 10^7$. The standard free energy of formation of the complex, $\Delta G^o$, is -10.82 kcal/mole at 30°C.

The IR spectra of reagent and complex revealed that the –OH (stretch) band of 3393cm$^{-1}$ for the reagent disappears when the complex is formed i.e., the complex formation takes place through the N of oximino group and O- of the 2-hydroxy group. Based on above data the Ni(II)-HIBAO complex can be assigned the following structure.



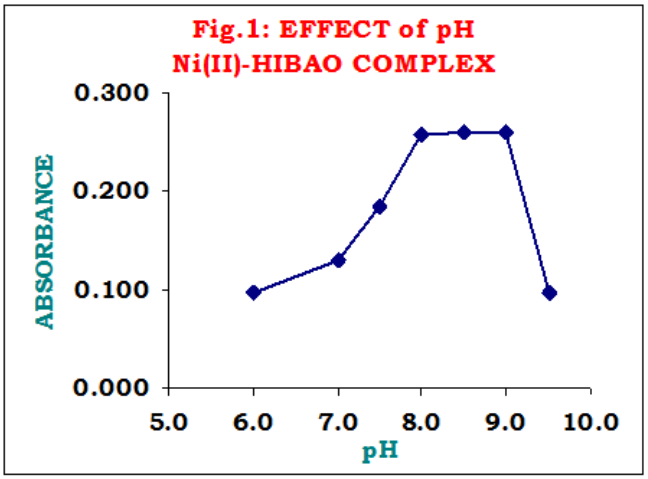




**Figure : I** : Effect of pH

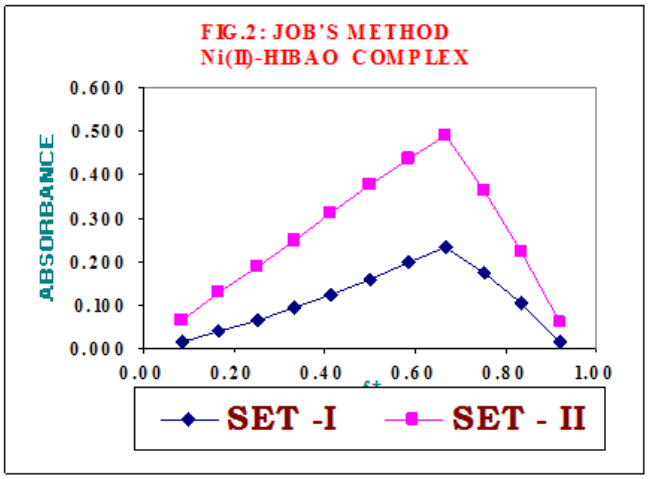



**Figure : II** : Job's method of continuous variation
**Set-I** : 0.01 M Ni(II) and 0.01 M HIBAO
**Set-II** : 0.01 M Ni(II) and 0.02 M HIBAO

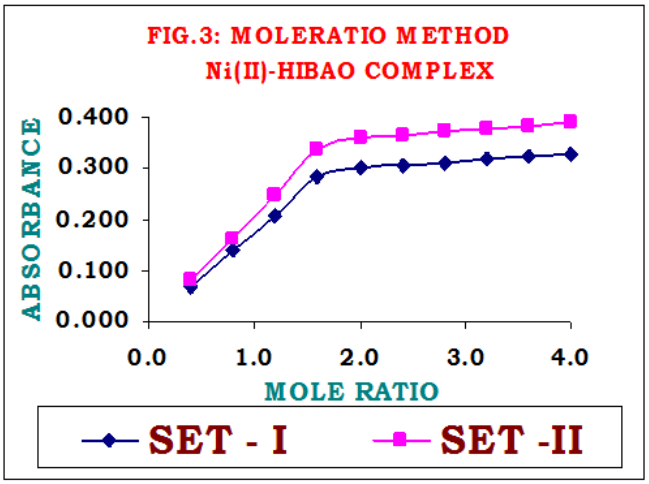



**Figure : III** :Yoe and Jones mole ratio method

**Set-I :**0.005M Ni(II) and 0.010M HIBAO,
**Set-II :**0.0025M Ni(II) and 0.0050M HIBAO

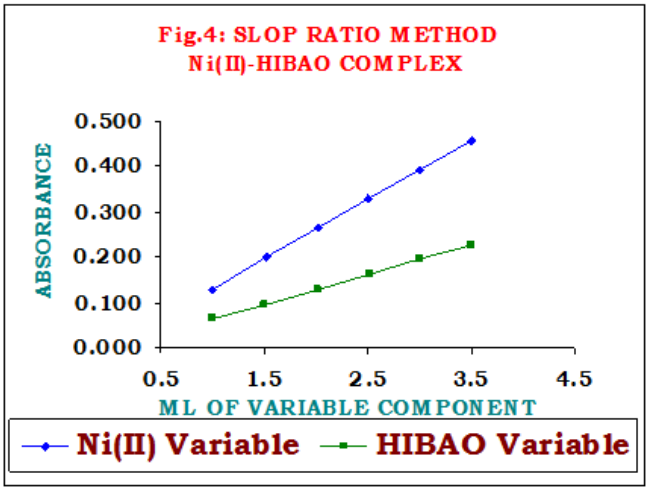



**Figure IV :** Slope ratio method.

10 ml 0.01 M HIBAO ; 0.01 Ni(II) (variable)
10 ml 0.01 M Ni(II) ; 0.01 M HIBAO (variable)

**Conformity to Beer's law and the optimum concentration range**

Beer's law is obeyed between the range 29.35 to 234.77ppm of Ni(II). At higher concentrations negative deviations occur. The optimum concentration range for determination of Ni(II) in solution, as deduced from the Ringbom plot[13], is found to be 58.69 to 234.77ppm. The molar absorptivity (ε) of the complex is 131 $mol^{-1}cm^{-1}$ and the photometric sensitivity as per Sendell's definition[14] is found to be 0.448µg/$cm^2$ at 600nm.

**Effect of diverse ions**

The interference due to the presence of other ions on the determination Nickel ions as Ni(II)-HIBAO complex has also been studied. A difference of more than ± 2 % in the absorbance value has been considered as interference. According to this criterion, the tolerance limits of various ions, expressed in µg, for a solution containing 586.92 µg (Ni(II)) are as follows.

up to 100000 µg : $Na^+$, $K^+$, $NH_4^+$, $Br^-$, $NO_3^-$ , $SO_4^{-2}$, $CH_3COO^-$

up to 10000 µg : $Ca^{+2}$, $Ba^{+2}$,$Sr^{+2}$,$Mg^{+2}$, $Al^{+3}$, $Zn^{+2}$,$Cd^{+2}$, $S_2O_3^-$

$V^{+5}$, $MoO_4^-$, citrate, tartrate, oxalate

up to 1000 µg : $Cr^{+3}$, $UO_2^{+2}$, $Pd^{+2}$

up to 100 µg : $Cu^{+2}$, $Co^{+2}$, $Mn^{+2}$, $Fe^{+3}$

up to 10 µg : EDTA

**Determination of Nickel from various samples**

To determine the usefulness of the reagent in estimation of Nickel from various samples containing Nickel were taken and estimated by HIBAO. For this purpose, the alloy samples containing Nickel metal were dissolved in 1:1 nitric acid by heating on a sand bath. The resulting solution was made up to 250 ml with distilled water in a volumetric flask. The synthetic mixtures containing Nickel metal were also taken for analysis. Aliquot of this sample solution was pipeted out and its spectrophotomatic determation was carried out by the proposed method. The result are given in Table-II.

**Antimicrobial Activity**

HIBAO and Ni-HIBAO were screened for their antibacterial activity against Gram positive bacteria i.e. *Bacillus subtilis* and Gram negative bacteria i.e. *Psudomonas aeruginosa* using Cup-plate agar diffusion method. The Fungi *Aspergillus niger* was used for antifungal activity of above compound using Cup-plate agar diffusion method. HIBAO exhibit good antibacterial activity and excellent antifungal activity with respect to standard drugs while the Ni-HIBAO complex found quit good antibacterial and antifungal activity.

## IV. ACKNOWLEDGEMENTS

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