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**Research Article**

# Second order derivative visible spectrophotometric determination of Ni(II) using 5-bromo-2-hydroxy-3-methoxybenzaldehyde-p-hydroxybenzoic hydrazone

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## Abstract

A second order derivative spectrophotometric method has been developed for the determination of Ni(II) using 5-bromo-2-hydroxy-3-methoxybenzaldehyde-p-hydroxybenzoic hydrazone (5-BHMBHBH ). Ni(II)  reacts with 5-BHMBHBH in acidic pH4.0-8.0 to give a green colored complex. The complex has an absorption maximum at440 nm. The second order derivative spectrum of the complex shows a peak at 475nm, a valley at 447 nm and zero points at404.5 nm and 462.4 nm. The valley and peak amplitudes are found to vary linearly with the concentration of Ni (II) at pH 6.0. A five fold excess of the reagent is sufficient to produce maximum amplitudes either at 475 or 447 nm.  Linear plots are obtained between the amount of Ni(II) and the amplitude either at 475 or 447 nm. They obey the equations $A_{475}$= 22.5476 C + 0.002 and $A_{447}$=32.260 C +  0.046. Beers law is obeyed in the range   0.18–2.93 µg $mL^{-1}$ both at 475 and 447 nm. The correlation coefficients are 0.99996 at 475 nm and 0.99995 at 447 nm. The standard deviation for eleven determinations is 0.0734 at 475 nm and 0.0957 at 447nm . The effect of various diverse ions on the derivative amplitude is studied.The method is accurate, sensitive and precise. The method has been successfully applied for the determination of Ni (II) in alloys, vegetable oil and leaf samples.

 **Key words:** Ni (II), 5-BHMBHBH, Second order derivative spectrophotometry ,alloys, vegetable oil, leaf samples.

## INTRODUCTION

Nickel was discovered by Axcel Fredrik Cronstedt in 1751 in Sweden. The name originated from the German word " Kupferni, Ckel" meaning Devil's Copper or St Nicholas's (old Nick's) copper. Though the usual oxidation state of nickel is +2, the +3 state is stabilized in its complexes. Nickel is an alloying element present in steel and cast iron and these are used in ship building, jet turbines, magnets, heating elements, electrodes, electronic devices, electroplating industry, preparation of inks and varnishes as well as in pigments and ceramics. Nickel is used in coins, in iron plating, brass, etc, being resistant to aerial oxidation. It is also used as a catalyst in the hydrogenation of oils. Nickel is essential micro nutrient[1-3]  for plants, which was identified from urease, a nickel metalloenzyme. Nickel is an essential trace element in human diet, when bound to ribonucleic acid has a special

affinity for bone and skin and plays crucial role in pigmentation. Reports indicate that nickel (II) is present in human plasma in quantities of about 0.012-0.085 ppm. Lithosphere and biosphere contains nickel abundantly, being the reason why nickel was not found to be essential for many years, so that its natural deficiency doesn't happen. Nickel is also an essential trace element for several organisms. Nickel is an environmental carcinogen and toxic to most plant and mammals. These indicate that there is a need for the development of methods for trace level estimation of nickel (II).

Several instrumental techniques have been employed for the determination of nickel(II), of which UV –visible spectrophotometry is preferred because of its low cost, rapidity and easy handling. Several classes[4] of organic reagents were used for the spectrophotometric determination of nickel(II).

Of these some spectrophotometric reagents which were used for the determination of nickel (II) have been reported[5], some of which suffer from low sensitivity or interference from foreign ions or involve extraction.

Singh etal[6] have reviewed the potentialities of hydrazones as analytical spectrophotometric reagents. Several hydrazones[7-9] have been reported for spectrophotometric estimation of nickel(II). They lack sensitivity or involve interference from foreign ions or use surfactants for enhancing sensitivity.

Derivative spectrophotometry(DS) is an analytical technique of great utility for extracting both qualitative and quantitative information from spectral curves composed of unresolved bands. DS enhances the resolution of spectral bands allowing the detection and location of the wavelength of poorly resolved components of complex spectra and reducing the effect of spectral background interferences. Because of these characteristics, the process of isolation of active components, usually require in qualitative and quantitative spectrophotometric procedures, applied in the analysis of complex system is completely avoided. The simplicity, relatively quick and easy realization, increased selectivity and sensitivity in the analysis of minor components are the important reasons, why the interest in DS is constantly growing for practical application. DS have been used in pharmaceutical analysis , environmental analysis and finger print analysis of proteins but few data have been published on the determination of inorganic ions [10].

In view of the importance of DS and paucity of DS methods for the determination of Ni(II) , the author reports a sensitive , highly selective and accurate second order derivative spectrophotometric method for the determination of Ni(II) in alloy steel , vegetable oil and plant extracts.

**Materials and Methods :**
*Reagents*
The reagent 5 - Bromo - 2- hydroxyl - 3 - methoxy benzaldehyde - P - hydroxy benzoic hydrazone was synthesized in our laboratory by condensing 5 - Bromo - 2 - hydroxy-3-methoxy benzaldehyde and P-hydroxy benzoic hydrazide in methonal using a general procedure[11]. A 0.01 M solution in dimethyl formamide is used in the present studies.

A 0.01M stock solution of Ni (II) was prepared by dissolving requisite amount of nickel ammonium sulphatein distilled water and standardized gravimetrically[12].Working solutions were prepared daily by diluting the stock solutions to an appropriate volume .

For the preparation of buffer solutions , 1M HCl and 1 M sodium acetate ( pH 1 to 3) and 0.2 M acetic acid and 0.2 M sodium acetate ( pH 3.2 to 7.0 ) were used.

*Instruments*
The absorbance and pH measurements were made on a Perkin Elmer ( LAMDA 25 ) UV – Visible spectrophotometer ( Model UV-160 A) controlled by a computer fitted with 1 cm path length quartz cells and Elico digital pH meter (Model LI 613 ) respectively.

*Procedure*
To each of a set of different 10 ml standard flask , 5 ml of buffer solution (pH 4.0 ), various volumes of $4 \times 10^{-4}$ M Ni (II) solution, 1.5 ml of dimethyl formamide and 0.5 ml of 5-bromo-2-hydroxy-3-methoxybenzaldehyde-P-hydroxybenzoic hydrazone $(1 \times 10^{-2}$ M ) in DMF were added and made upto the mark with distilled water. The second order derivative spectra were recorded in the wavelength region 360-600 nm. The derivative peak height and the valley height were measured by peak-zero and valley –zero method at 475 and 447 nm respectively. The peak amplitude was plotted against the amount of Ni(II) at 475 nm and the valley amplitude at 447 nm was plotted against the amount of Ni(II) to obtain calibration curves at 475 and 474 nm. The plots are linear and follow the equations $A_{475} = 22.5476 C + 0.002$ and $A_{447} = 32.260 C + 0.046$.

**RESULT AND DISCUSSION**
*Second order derivative spectra*
Ni (II) reacts with 5-BHMBHBH to form a green colored complex in acidic pH.The second order derivative spectrum of Ni(II)-5-BHMBHBH was recorded in the wavelength region 360-600 nm at pH 6.0 against the reagent blank and is shown in Fig . 1 .The spectrum shows a peak at 475 nm, a valley at 447 nm and zero points at 404.5 nm and above 462.4 nm.

*pH effect*
It is observed that a green colored complex is formed between Ni (II) and 5-BHMBHBH in the pH range 2.0-9.0 . The study of effect of pH on color intensity of the reaction mixture showed that the color intensity is maximum in the pH range 4.0-7.0. Analytical studies were carried out at pH 6.0 as the interference due to foreign ions is at a minimum at this pH.

*Effect of 5-BHMBHBH concentration*
The studies revealed that a 5 fold molar excess of 5-BHMBHBH is essential for maximum and constant

color development. Excess of the reagent has no effect on the derivative amplitude of the complex.

### Color and stability of the complex
The color reaction between Ni (II) and 5-BHMBHBH  was instantaneous at room temperature .The amplitude of the complex was found to constant for more than 60 hours.

### Order of addition of reactants
It is observed that the color intensity of the complex solution is independent of the order of addition of the reactants. However, the reagent was addedafter the addition of DMF to avoid precipitate formation.

### Applicability of Beers law
The Beers law range along with regression characteristics, precision and accuracy of  the proposed second order derivative method  for  the determination of Ni (II) are given in table-1.The data in table-1 indicate that  the method is highly sensitive , accurate and precise.

### Effect of foreign ions
The effect of  various  diverse ions  on the determination of Ni (II)  was studied to find  out the tolerance  levels of  these diverse ions  in the present method . The tolerance limit of  a foreign ion was taken   as the amount of that ion that caused  an error in  the  amplitude  value by $\pm$ 2 % .The data  are presented in  table- 2. The data in table-2 indicate that many metal ions and anions do not interfere in the determination of Ni(II). 15 excess of Cu(II) is masked with thiourea. 10 fold excess of Co(II) and 30 fold excess of Fe(III) are masked using thiocyanate and phosphate respectively.

### Applications
The second order derivative spectrophotometric method developed for the determination of nickel(II) is applied for its determination in alloy steel sample, vegetable oil and leaf samples.

### Determination of nickel in alloysteel samples
1gm of the alloy sample was dissolved in a mixture of 2ml of concentrated hydrochloric acid and 10ml of  concentrated nitric acid. The solution was evaporated to a small volume. 5ml of 1:1 sulfuric acid was added and the solution was evaporated to dryness. The residue left over was extracted with 15ml of water and the solution was diluted to 100ml with double distilled water. This serves as the stock solution. The stock solution was appropriately diluted and analyzed by the general procedure. The results are given in table-3.

### Preparation of plant samples:
Freshly collected samples were cleaned and dried for one hour in open air protecting from mineral contamination. The dry samples were finely powdered in a mortar. The powdered material was brought in to solution by wet ashing method according to the procedures given in the literature. The suitable aliquots of the above sample were analyzed by the general procedure and the results are presented in table -4.

### Preparation of vegetable oil:
Hydrogenated edible groundnut(100g) was dried in a hot air oven at $100^0C$ and subsequently dissolved in 20ml mixture of 1:2:5 of $H_2SO_4$ :$H_3PO_4$ :$HNO_3$. The contents were heated until sulphurous acid fumes were evolved and the volume was reduced to about 5ml. A small quantity of distilled water was added and filtered into a 100ml volumetric flask and made up to the mark with distilled water.

A known aliquot of the above sample is analysed by the general procedure.  The results are presented in table-5.

### CONCLUSIONS
The second order derivative spectrophotometic method developed for the determination of Ni (II) using 5-BHMBHBH   is highly selective, sensitive, accurate and precise. It is highly suitable for the determination of Ni(II) in alloy and environmental samples.The method is more sensitive than the direct spectrophotometric method reported by Saritha etal [13].
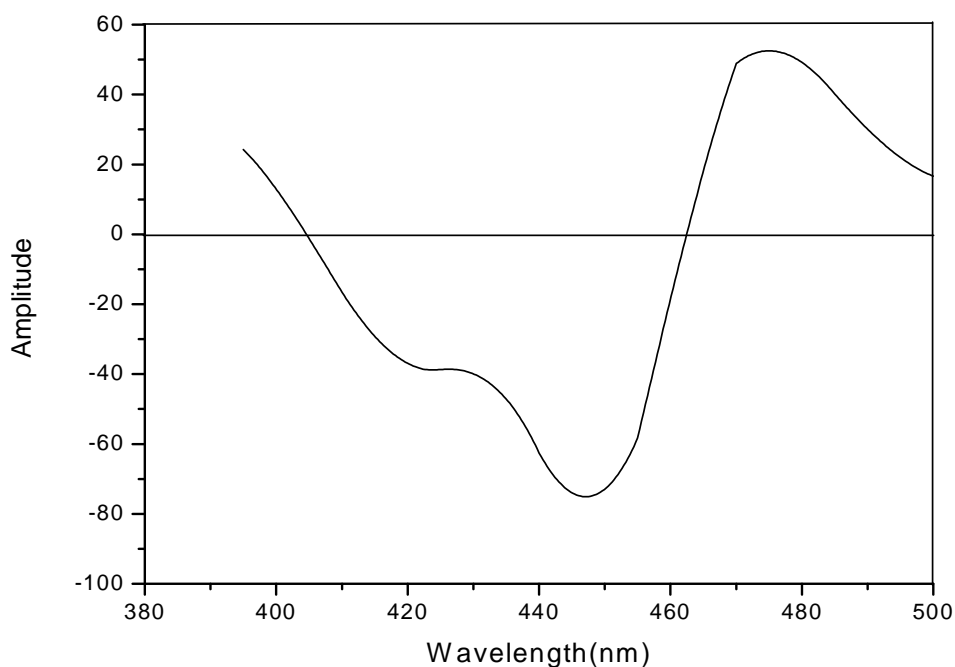
**Fig.1**
**Second derivative spectrum ofNi(II) -5-BHMBHBH**
**Vs   reagent blank;     [ Ni(II)] = 4.0  x10$^{-5}$M**
**[5- BHMBHBH]  = 5.0 x 10$^{-3}$M ;     pH   = 6.0**

**Table 1**
**Regression characteristics, precision and accuracy of the**
**proposed method for Ni(II)**

| Parameter | Peak | Valley |
|---|---|---|
| Analytical wavelength (nm) | 475 | 447 |
| Beer's law limits (µg mL$^{-1}$) | 0.18-2.93 | 0.18-2.93 |
| Limits of detection (µg mL$^{-1}$) | 0.097 | 0.008 |
| Regression equation  ( y = a + b x ) | | |
| Slope (b) | 22.547 | 32.260 |
| Intercept (a) | 0.002 | 0.095 |
| Correlation coefficient (γ) | 0.99995 | 0.99996 |
| Standard deviation (Sd) | 0.0734 | 0.0957 |

**Table 2**
**Tolerance limit of foreign ions.**
**Amount of Ni (II) = 1.76 μg mL$^{-1}$ pH = 6.0; λ =475**

| Ion | Tolerance Limit (μg mL$^{-1}$) | Ion | Tolerance Limit(μg mL$^{-1}$) |
|---|---|---|---|
| Thiosulphate | 2360 | Cd (II) | 333 |
| Ascorbate | 1320 | Mo (VI) | 11 |
| Iodide | 1220 | Hg (II) | 130 |
| Sulphate | 950 | Zn (II) | 120 |
| Carbonate | 595 | Pb (II) | 66 |
| Chloride | 528 | Mn (II) | 65 |
| Nitrate | 425 | Ce (IV) | 58 |
| Bromide | 455 | V (V) | 54 |
| Thiocyanate | 444 | Se (IV) | 38 |
| Phosphate | 110 | Tl (III) | 35 |
| EDTA | Interferes | W (VI) | 46 |
| Citrate | 105 | Al (III) | 42 |
| Tartarate | 92 | Cr (VI) | 11 |
| Thiourea | 202 | Ti (IV) | 40 |
| Oxalate | 104 | Th (IV) | 9 |
| Fluoride | 192 | U (VI) | 18 |
| DMG | Interferes | Fe (III)[a] | 80 |
| | | Co (II)[b] | 18 |
| | | Cu (II)[c] | 24 |

a: Masked with phosphate; b: Masked with thiocyanate; c: Masked with thiourea

**Table 3**
**Determination Ni (II) in alloy and steel samples**

| Sample | Composition (%) | | Error (%) |
|---|---|---|---|
| | Certified | Found | |
| Copper-Nickel alloy[a] | 31.20 | 31.39 | +0.60 |
| NTPC ball bearing[b] | 10.00 | 9.88 | -1.2 |

\* Average of seven determinations
Composition (%)
    a)    Cu 67%: Ni 31.2%:Fe 0.0835%:Mn 0.08%: Si 0.29%:
    b)    Ni 10%: Fe 65%: Cr 15%: Cu 4.5%: Mn 2%:

**Table -4.**
**Determination of Ni (II) in the vegetable oil and leaf samples**

| Sample | Amounnt of Ni(II) (µg/ml) | | Relative error (%) |
|---|---|---|---|
| | Present method* | AAS method | |
| Groundnut oil | 0.532 | 0.534 | 0.37 |
| Sunflower oil | 0.651 | 0.660 | 1.38 |
| Eucalyptus leaves | 1.055 | 1.066 | 1.03 |
| Mangiferaindica leaves | 2.168 | 2.160 | -0.37 |

* Average of seven determinations.

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