

# Direct Spectrophotometric Determination of Ni (II) Using Esomeprazole

B. Ranganath<sup>1</sup>, V. Saleem Basha<sup>1</sup>, M. R. Jayapal<sup>2</sup>, P. Venkata Ramana<sup>1</sup>

<sup>1</sup>Department of Chemistry, Sri Krishnadevaraya University, Anantapuramu, India

<sup>2</sup>Department of Chemistry, NEC College, Guntur, India

## Email address:

mrjayapal007@gmail.com (M. R. Jayapal)

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**Abstract:** Esomeprazole is a new chromogenic reagent used for the determination of nickel (II) by direct spectrophotometric method. Esomeprazole forms a greenish yellow coloured complex with nickel (II) at pH 5. The method obeys Beer's law over  $0.139 - 1.394 \mu\text{g mL}^{-1}$ , Sandell's sensitivity is  $0.0029 \text{ mg/cm}^2$  and molar absorptivity value ( $\epsilon = 2.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). The method is useful for determination of nickel in groundnut seeds and sesame seeds was determined by the following procedure.

**Keywords:** Esomeprazole, Nickel (II), Spectrophotometry, Groundnut Seeds, Sesame Seeds

## 1. Introduction

Nickel is a silvery-white, hard, malleable, and ductile metal. It is of the iron group and it takes on a high polish. It is a fairly good conductor of heat and electricity. In its familiar compounds, nickel is bivalent although it assumes other valences. It also forms a number of complex compounds. Most nickel compounds are blue or green. Nickel dissolves slowly in dilute acids but, like iron, becomes passive when treated with nitric acid. Finely divided nickel adsorbs hydrogen.

The major use of nickel is in the preparation of alloys. Nickel alloys are characterized by strength, ductility, and resistance to corrosion and heat. About 65% of the nickel consumed in the western world is used to make stainless steel, whose composition can vary but is typically iron with around 18% chromium and 8% nickel. 12% of all the nickel consumed goes into super alloys. The remaining 23% of consumption is divided between alloy steels, rechargeable batteries, catalysts and other chemicals, coinage, foundry products, and plating.

Although nickel complexes in +3 oxidation state are known, it usually occurs in +2 state. It is one of the important alloying element for steel and cast iron. These alloys are used in ship building, jet turbines, magnets, heating elements, electrodes, electronic, electroplating, inks, varnishes, pigments and ceramics. Because of its permanence in air and its innerness to oxidation, it is used in coins, for plating iron, brass, etc. It is equally important as a catalyst in the hydrogenation of oils.

The possibility that nickel may be an essential micro nutrient [1-3] for plants arose from ureases which is a nickel metalloenzyme. Nickel is biologically important, being an essential trace element in human diet. Nickel bound to ribonucleic acid, has a special affinity for bone and skin and plays an important role in pigmentation. It has been reported that normal human plasma contains 0.012-0.085 ppm of nickel (II). Nickel is abundant in lithosphere and biosphere so that natural deficiency does not occur. This may be the reason why nickel was not found to be essential for many years. Nickel is proved essential trace element for several organisms, it is an environmental carcinogen. It is very toxic to most plants and moderately toxic to mammals. A view of this there is a necessity for the development of methods for the determination of nickel (II) at micro levels.

Several spectrophotometric methods for determining Ni(II) based on organic reagents containing sulphur as a ligand atom are known. Among them thiosemicarbazones are the most important. Though a good number of thiosemicarbazones were prepared, their potentiality for the photometric determination of Ni(II) has not been explored much.

Bendito et al [4] reported the use of biacetylmonoximethiosemicarbazone (BAMOT) for the spectrophotometric determination of nickel. Cano Pavon et al [5] found that in comparison with BAMOT, biacetylmonoxime -4-phenyl-3-thiosemicarbazone (BAMOPT) has enhanced sensitivity in the photometric

determination of nickel. Khasnis *et al* [6] observed that quinoline-2-aldehyde thiosemicarbazone was more selective than the corresponding reagent, picolinaldehydethiosemicarbazone in the extraction photometric determination of Ni(II). SankeGowda *et al* [7] studied the colour reaction between Ni(II) and p-anisaldehydethiosemicarbazonespectrophotometrically. They also analyzed alloys and minerals by applying the reaction. Subbarami Reddy *et al* [8] employed salicylaldehydethiosemicarbazone for the direct and extraction spectrophotometric determination of Ni(II).

Gomez Ariza *et al* [9] developed a method for the direct and extraction spectrophotometric determination of nickel using picolinaldehyde-4-phenyl-3-thiosemicarbazone. They also applied the method to determine nickel and cobalt in mixtures. Hussain Reddy *et al* [10] studied 1,3-cyclohexanedionebithiosemicarbazone for the photometric determination of nickel in the pH range 8.5 to 10.0. This procedure was applied to determine nickel in alloy steels. Bhahamande *et al* [11] employed dipyrityldglyoxalthiosemicarbazone for the extraction photometric determination of nickel. Phenanthroquinonemonothiosemicarbazone was used as analytical reagent for the photometric determination of nickel by Sinha *et al* [12]. They determined nickel in bright way 'G' wire. Salim *et al* [13] studied 5,5-dimethyl-1,2,3-cyclohexane trione 1,2-dioxime 3-thiosemicarbazone as a reagent for the sprctrophotometric determination of nickel.

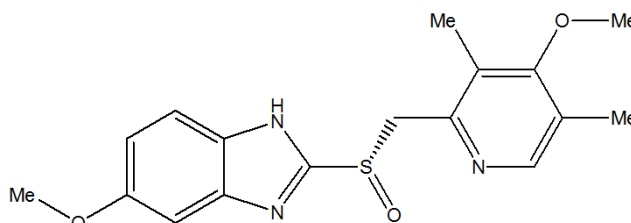
Youngwen Liu *et al* [14] developed a method for solid-phase spectrophotometric determination of nickel in water and vegetable samples at sub- $\mu\text{g/l}$  level with O-carboxylphenyldiazoaminoazobenzene loaded XAD-4. adsorbed resin phase spectrophotometric determination of nickel was developed by LI R *et al* [15]. Surfactant extraction-spectrophotometric determination of nickel(II) in the samples of a high salinity was developed by Tagashira shoji *et al*. [16]. Tagashira shoji *et al* [17] developed a method for micellar extraction and spectrophotometric determination of Ni(II) as the dodecylxanthato complex in a solution of the anionic surfactant sodium dodecylsulfate. Spectrophotometric determination of nickel using a new chromogenic reagent in plant leaves was developed by Suresh Kumar *et al* [18]. Studies on solid phase extraction and spectrophotometric determination of nickel in waters and biological samples was reported by Qiufin Hu *et al*[19]. Direct spctrophotometric determination of Ni(II) using 5-Bromo-2-hydroxy-3-methoxybenzaldehyde-4-hydroxybenz oichydrazone by Saritha *et al* [20]. Direct spectrophotometric determination of Ni(II) with 1-Nitroso-2-Napthol in Aqua phase by G.A.shar and G.A.Soomro *et al* [21]. Direct determination of nickel with p-methoxyphenylazo-bis-acetoxime by Rehanakhanam, Rekhadashora *et al* [22]. Spectrophotometric determination of Ni(II) using 1-(2-pyridylazo)-2-naphtal by V.N.VarazinKharkiv *et al* [23].

## 2. Experimental

Reagent:

Esomeprazole solution:

Esomeprazole is 5-metoxy-2-[[[(4-methoxy-3, 5-dimethyl-2-pyridinyl) methyl] sulfinyl]-1H-benzimidazole. It is white crystalline powder freely soluble in water and its molecular formula is  $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$ . (M.Wt:345.11). The structure of esomeprazole is given in Fig. 1.



**Fig. 1.** 1(S)-5-methoxy-2-[[[(4-methoxy-3, 5-dimethyl-2-pyridinyl)sulfinyl]-1H benzimidazole (ESOMEPRAZOLE)

Esomeprazole was characterized by IR,  $^1\text{H}$ -NMR and Mass spectral data.

IR (KBr)  $\nu_{\text{max}}$ : 3346, 3168, 2961, 2928, 2683, 1657, 1597, 1449, 1255, 1218, 1092, 876, 710  $\text{cm}^{-1}$

$^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 500 MHz) : $\delta$  2.20 (s, 3H,  $\text{CH}_3$ ), 2.22 (s, 3H,  $\text{CH}_3$ ), 3.73 (s, 3H,  $\text{OCH}_3$ ), 3.88 (s, 3H,  $\text{OCH}_3$ ), 4.60 (d, 1H), 4.77(d, 1H), 6.97, 6.99 (m, 2H, Ar-H), 7.65 (m, 1H, Ar-H), 8.25 (s, 1H, Pyridine ring), 9.57 (s, 1H, NH) ppm.

MS  $m/z$ : found 345.11  $[\text{M}^+]$ ; calcd. 345. Anal  $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$ .

0.01M stock solution of Ni(II) was prepared by dissolving requisite amount of nickel ammonium sulphate in distilled water and standardized gravimetrically[24]. The working solutions were prepared by diluting the stock solutions with distilled water.

Buffer solution of pH 5.0 was prepared by mixing 0.2M sodium acetate and 0.2M acetic acid in suitable proportion and the pH was adjusted by a pH meter.

Instrument:

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

Procedure:

To 5 ml of buffer solution (pH 5.0), 0.5 ml of ESMPZL ( $1 \times 10^{-2}\text{M}$ ) in DMF, 1.5 ml of DMF taken in each of a set of 10 ml volumetric flasks, varying amounts of Ni(II) were added and diluted to 10 ml in a volumetric flask with distilled water. The absorbance of these solutions was measured at 405 nm against reagent blank and plotted against the mount of nickel. A straight line is obtained which corresponded to the equation  $A_{405} = 0.34215C + 0.00051$ . (C is the amount of nickel in  $\mu\text{g/ml}$ ).

### 3. Results and Discussion

#### 3.1. Absorption Spectra of the Metal Complex and the Reagent Blank

The absorption spectra for the greenish yellow coloured Ni (II)-ESMPZL solution and almost colourless ESMPZL solution in pH 5.0 buffer solutions were recorded in the wavelength region 340–540 nm using the established procedure and presented in fig.2. The Ni (II) complex has an absorption maximum at 405 nm where the reagent blank has negligible absorbance. Therefore, 405 nm was chosen as the analytical wavelength to carry out the determination of the metal ion.

#### 3.2. Effect of pH on the Absorbance of the Complex

The absorbance measurements made for the experimental solution at different pH values employing the general procedure confirmed the formation of Ni (II)-ESMPZL greenish yellow coloured complex with maximum and constant absorbance in the pH region 4.0 – 7.0 (Fig.3). Further studies, therefore were carried out at pH 5.0.

#### 3.3. Effect of Reagent Concentration on the Absorbance

The effect of variation in the concentration of ESMPZL on the colour intensity of the metal complex was studied as indicated in procedure and the results are presented in table.2. From the table.1, it can be observed that a minimum of 15 fold excess of reagent is necessary to obtain maximum sensitivity for the coloured reaction between nickel and ESMPZL.

Table 1. Effect of ESMPZL concentration.

Ni (II) : ESMPZL	Absorbance
1 : 5	0.339
1 : 10	0.383
1 : 15	0.491
1 : 20	0.486
1 : 25	0.481
1 : 30	0.470

[Ni (II)] =  $2 \times 10^{-5}$  M  
pH = 5.0  
 $\lambda_{\text{max}}$  = 405 nm  
[Triton X-100] = 0.2%

#### 3.4. Effect of Surfactant

In order to improve the sensitivity of the proposed method, the effect of various surfactants on the colour intensity of the gallium complex solution was studied using the developed procedure and the corresponding results are presented in table.2.

Table 2. Effect of different surfactants on the absorbance of Ni(II)-ESMPZL complex.

Surfactant	Type	Absorbance
None	-	0.409
Triton X-100	Neutral	0.491
Cetylpyridinium chloride	Cationic	0.425
Sodium dodecyl sulphate	Anionic	0.432

[Ni(II)] =  $1.39 \mu\text{g mL}^{-1}$ ; [Surfactant] = 0.2%;  $\lambda$  = 405nm.

Of all the surfactants studied, the neutral surfactant triton X-100 was found to enhance the colour intensity of the metal complex more than the other surfactants. Hence, triton X-100 was used in the analysis of Ni (II).

#### 3.5. Effect of Concentration of Triton X-100

To evaluate the minimum amount of surfactant required to obtain maximum sensitivity, the effect of variable concentrations of triton X-100 on the absorbance was studied and observed that 0.2% by volume of the surfactant gives maximum absorbance for a given metal ion concentration (Table.3). Presence of excess of surfactant has no effect on the absorbance.

Table 3. Effect of Triton X-100 concentration.

Volume of Triton X-100 (ml)	Absorbance
0.5	0.438
1.0	0.452
1.5	0.465
2.0	0.492
2.5	0.490
3.0	0.489

[Ni(II)] =  $2 \times 10^{-5}$  M  
[ESMPZL] =  $2.873 \times 10^{-4}$  M  
pH = 5.0  
[Triton X-100] = 1%  
 $\lambda_{\text{max}}$  = 405 nm

#### 3.6. Determination of Nickel

Variable amounts of Ni (II) in the range  $0.13 - 1.40 \mu\text{g mL}^{-1}$ , taken in different 10 ml volumetric flasks, were treated with optimum amounts of ESMPZL solution and a buffer solution of pH 5.0 as described in 3.iv.e. The absorbance of the resultant solutions was measured at 405 nm and plotted against the amount of Ni (II). A straight line with a slope of 0.3574 passing through the absorbance values was obtained as shown in fig.1. This shows that Beer's law is obeyed in the concentration range  $0.139 - 1.394 \mu\text{g mL}^{-1}$  of Ni (II). The sensitivity of the proposed method has been derived from its molar absorptivity value ( $\epsilon = 2.5 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$ ). The other parameters such as detection limit, correlation coefficient, relative standard deviation confirm the best suitability of the proposed method for the determination of Ni (II). All the derived analytical results are presented in table.5.

#### 3.7. Effect of Foreign Ions

The effect of various anions and cations normally associated with Ni (II) on the absorbance of the experimental solution was studied by adopting the procedure. The tolerance limit of the tested foreign ions, which bring about a change in the absorbance by  $\pm 2\%$  were calculated and presented in table.4.

Among anions, except EDTA and oxalate, all other tested ions were tolerable in more than 200 fold excess. EDTA and oxalate were tolerable in 40 fold and 20 fold excess respectively. Of the tested cations, majority of them did not interfere even when present in more than 50 fold excess. Zr(IV)

(40 fold), Hg(II) (30 fold), Tl(III) (17 fold), U(VI) (10 fold), Bi(III), Co(II), Cr(VI) (9 fold), Mo(VI) and Ag(I) (7 fold), Sn(II) (6 fold) were tolerable. Ions like Cu (II), Pd (II), Fe (II) and Al (III).

### 3.8. Stoichiometry and Stability Constant

The stoichiometry of Ni(II) – ESMPZL complex solution was determined by Job's continuous variation method, mole ratio method and slope ratio method using already described general procedures and obtained as 2 : 3 (Metal : Ligand). The formation constant of the soluble complex was calculated from the results obtained in Job's method as  $2.39 \times 10^{19}$ .

**Table 4.** Tolerance limits of foreign ions Amount of Ni (II) taken = 0.697  $\mu\text{g mL}^{-1}$  pH = 5.0.

Foreign ion	Tolerance limit ( $\mu\text{g mL}^{-1}$ )	Foreign ion	Tolerance limit ( $\mu\text{g mL}^{-1}$ )
Bromide	1700	Na(I)	1725
Carbonate	1600	Mg(II)	1700
Thiosulphate	1600	Ca(II)	1680
Sulphate	1160	K(I)	1490
Iodide	1020	Sr(II)	1310
Thiourea	800	Ba(II)	1240
Nitrate	710	La(III)	420
Phosphate	710	Y(III)	360
Tartrate	650	Te(IV)	350
Thiocyanate	390	W(VI)	340
Citrate	200	Cd(II)	310
Fluoride	180	Mn(II)	300
Chloride	160	Se(IV)	240
EDTA	40	Zn(II)	40
Oxalate	20	Ce(IV)	40
		Pb(II)	40
		Ir(III)	40
		Ti(IV)	35
		Zr(IV)	30
		Hg(II)	20
		Au(III)	20
		Tl(III)	10
		U(VI)	7
		Bi(III)	6
		Co(II)	6
		Cr(VI)	6
		Mo(VI)	5
		Ag(I)	5
		Sn(II)	4
		Ga(III)	2
		Cu(II)	0.9
		Pd(II)	0.4
		Fe (II)	0.2
		Al	0.2

## 4. Applications

The present method is applied for the determination of Ni(II) in groundnut seeds and sesame seeds. (Table.5) The data shows that the results obtained by proposed method for groundnut seeds and sesame seeds are in good agreement with those obtained by the AAS method. The groundnut seeds and

sesame seeds brought into solution by the procedure given below. The amount of nickel present in groundnut seeds and sesame seeds was determined by the following procedure.

## 5. Procedure

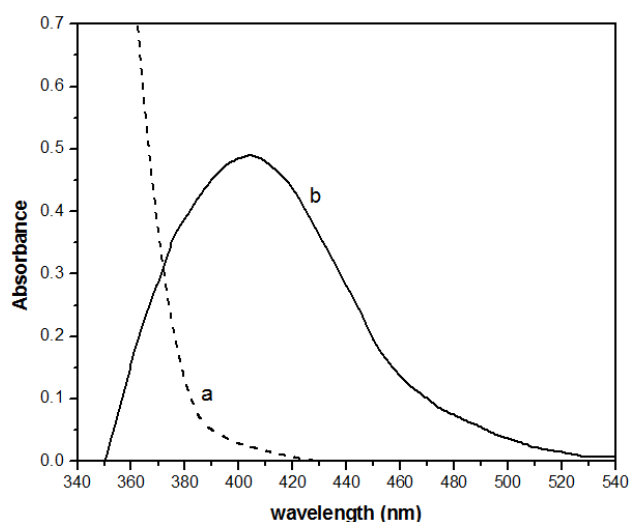
50 g of biological material was heated in a 500 ml conical flask with 40 ml of conc.  $\text{HNO}_3$  on a steam bath and shaken vigorously until a fine emulsion was formed. The heating was continued with the gradual addition of 6 per cent  $\text{H}_2\text{O}_2$  (40ml). The aqueous phase was then transferred to the beaker. The extraction was repeated twice with further addition of 20 ml of concentrated nitric acid and 20 ml of 6 percent  $\text{H}_2\text{O}_2$ . The combined extracts were evaporated to dryness. The residue was dissolved in minimum amount of dil. HCL and it is transferred into a 50-ml standard flask quantitatively. The contents were diluted to the mark with distilled water.

## 6. Present Method

A known aliquot of the sample solution was taken in a 25 ml standard flask containing 10 ml of buffer solution. Then 2 ml of  $2.873 \times 10^{-4} \text{M}$  of the reagent solution was added. The contents were made up to the mark with distilled water. The absorption of the complex was measured at 405 nm against respective reagent blank solution. The absorbance values were referred to the predetermined calibration plot to compute the unknown amount of the metal ion.

**Table 5.** Present preparation method of Ni Ni(II) ( $\mu\text{g/ml}$ ) by AAS method 2 ml  $2.873 \times 10^{-4} \text{M}$

Sample	Amount of Ni(II) ( $\mu\text{g/ml}$ )		Error(%)
	Present method	AAS method	
Groundnut seeds	1.189	1.205	-1.33%
Sesame seeds	1.261	1.273	-0.94%



\* Average of five determinations

**Fig. 2.** Absorption spectra of (a) ESMPZL vs buffer blank; (b) Ni (II) – ESMPZL vs reagent blank.

$$[\text{Ni (II)}] = 2 \times 10^{-5} \text{ M}, [\text{ESMPZL}] = 2.873 \times 10^{-4} \text{ M}$$

pH= 5.0, [Triton X-100] = 0.2%.

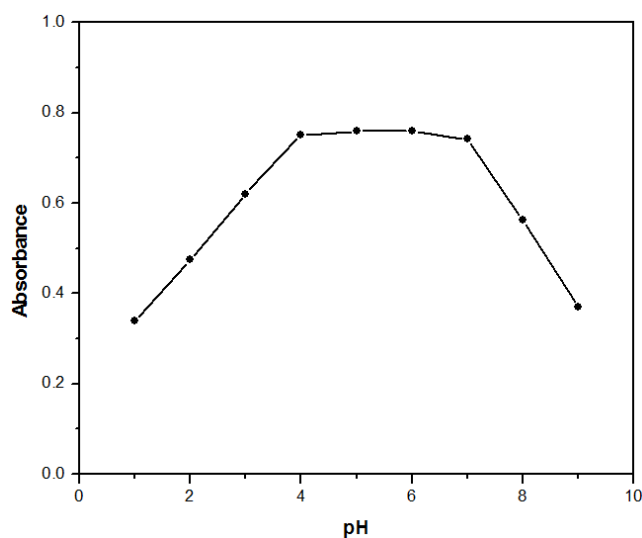


Fig. 3. Effect of pH on the absorbance of Ni (II) – ESMPZL system.

[Ni (II)] =  $4 \times 10^{-5}$  M, [ESMPZL] =  $6 \times 10^{-4}$  M, Wavelength = 405 nm  
[Triton X-100] = 0.2%.

## 7. Conclusion

The proposed method is simple, accurate, sensitive, do not involve extraction or heating and do not use surfactants. The method can be easily applied for the determination of nickel (II) in groundnut seeds and sesame seeds.

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