



## Extraction and spectrophotometric determination of nickel in water, alloys and edible oil samples

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**Abstract:** An extraction-spectrophotometric method has been developed for determination of nickel using N'-(2-hydroxybenzylidene)-3-(4-o-tolylpiperazin-1-yl) propanehydrazide (HTP) as the new extractant. The reagent reacts with nickel (II) at pH = 9.0 and form a 1:1 yellow color complex, which is extracted into chloroform solvent. The complex showed maximum absorption wavelength at 382 nm. Beer's law is obeyed in the concentration range of 1.17-12.91  $\mu\text{g}\cdot\text{mL}^{-1}$  with apparent molar absorptivity ( $0.72 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and Sandell's sensitivity ( $0.008 \mu\text{g}/\text{cm}^2/0.001$  absorbance units). The tolerance limit of various foreign ions was investigated. The developed method was successfully applied for the determination of Nickel (II) in real water samples, alloy samples and Edible oil samples.

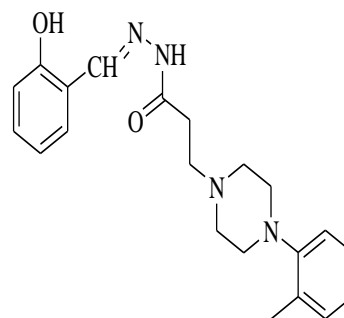
**Key words:** Spectrophotometry; Nickel (II)-HTP complex and different samples

### INTRODUCTION

Nickel is widely used in electroplating, the manufacture of Ni-Cd batteries, rods for arc welding, pigments of paints, ceramic, surgical and dental prostheses, magnetic tapes and computer components and nickel catalysts. Nickel enters waters from dissolution of industrial processes and waste disposal [1]. Nickel was thought to be essential for plants and some domestic animals [2], but not considered to be a metal of biological importance until 1975, when Zerner discovered that urease was a nickel enzyme [3]. Nickel is essential constituent in plant urease. Jack beans and soybeans generally contain high concentration of nickel [1]. Compared with other transition metals, nickel is moderately toxic element, and still at low concentration produces a general toxic effect on the human organism, causing nasopharynx and lung diseases, malignant tumors and dermatological disease [4]. Nickel-containing sewage is harmful after ingress into water. This fact explained the importance of the monitoring of nickel concentration in natural and waste water samples. Flame and graphite furnace atomic absorption spectrometry and spectrophotometric methods provides accurate and rapid determination of nickel in natural and waste waters [5]. However, very frequently a direct determination cannot be applied due to low concentration of analyte or matrix interferences.

The most widely used techniques for the separation and pre concentration of nickel are liquid-liquid extraction [6], precipitation [7], and chelating resin [8]. The large distribution ratios attainable in some solvent extraction systems allow the analytes determination at trace levels. An advantage of solvent extraction is that both separation and pre concentration which are often required; can be obtained in the same step [9]. Historically the first instance of chemical analysis of metal ions was combination of liquid extraction and spectrophotometric methods, in which the analysis was performed on the extracting phase. Nevertheless, the solvent extraction of nickel is still an important process and is used in several plants to recover and separate nickel from wastewaters [10, 11]. Many classical ligands such as dimethylglyoxime, dithizone, and sodium-diethyldithiocarbamate are known as an extractant

for extraction/spectrophotometric determination of nickel and other various extractive spectrophotometric methods have been reported [12-14]. In this work the capability of N'-(2-hydroxybenzylidene)-3-(4-o-tolylpiperazin-1-yl) propanehydrazide (HTP) (Figure 1) for the extraction and spectrophotometric determination of nickel is investigated. The influences of analytical parameters including extraction solvent, pH and reagent amounts, etc. on the complex formation were studied. The developed method is simple, selective and free from interference of other ions.



N'-(2-hydroxybenzylidene)-3-(4-o-tolylpiperazin-1-yl) propanehydrazide (HTP)  
Figure 1: Chemical structure of ligand

### MATERIALS AND METHODS

#### Apparatus

All spectral and absorbance measurements were carried out on a Shimadzu UV-Visible 1601 spectrophotometer (Shimadzu Corporation, Japan) with 1 cm matched quartz cells. The pH of buffer solutions was monitored by using Systronic digital pH meter (India). An electronic micro balance (Sartorius MC 5, Germany) and Afcost electronic balance (Mumbai, India) were used for weighing the solid materials.

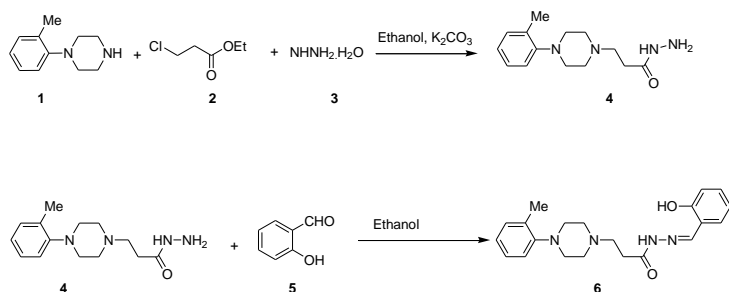
#### Procedure for preparation of N'-(2-hydroxybenzylidene)-3-(4-o-tolylpiperazin-1-yl) propanehydrazide (HTP)

A mixture of Tolylpiperzine (1) (3.52 gms, 0.02 mol), ethyl 3-chloropropanoate (2) (2.72 gms, 0.02mol) and

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Hydrazene hydrate (**3**) (1.96gms, 0.04 mol) was taken into ethanol in presence of potassium carbonate for 6 hours at reflux temperature. After completion of the reaction, as monitored by TLC, the reaction mass was cooled to room temperature and filtered. The ethanol layer was distilled off by using vacuum to get 3-(4-O-tolylpiperzin-1-yl) propane hydrazide (**4**). The crude product of recrystallized from ethanol. A mixture of **4** (2.62, 0.01) and 2-hydroxybenzaldehyde (1.22 gms, 0.01 mol) in Ethanol was refluxed for 4 hrs. After completion of the reaction, as monitored by TLC, the reaction mass was cooled to room temperature and filtered. The ethanol layer was distilled off by using vacuum to get N'-(2-hydroxybenzylidene)-3-(4-o-tolylpiperazin-1-yl) propanehydrazide. The crude product of recrystallized from ethanol. Yield: 2.80 gms, (76.5%). The main intermediate, 3-(4-O-tolylpiperzin-1-yl) propane hydrazide (**4**) and final product, N'-(2-hydroxybenzylidene)-3-(4-o-tolylpiperazin-1-yl) propanehydrazide are characterized by elemental and spectral analysis. The complete reaction mechanism is depicted in scheme.1



Scheme 1

### Reagents and standards

All reagents used were of analytical reagent grade. Stock solution of nickel (II) ( $1 \times 10^{-2}$  M) was prepared by dissolving 0.2377 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (AR GSC) in double distilled water and made up to the mark in a 100 mL volumetric flask. A few drops of diluted hydrochloric acid were added to avoid hydrolysis before dilution of stock solution. The resulting solution was standardized gravimetrically [15]. From this stock solution; ( $1 \times 10^{-3}$  M) nickel (II) was prepared. 1.0 M Hydrochloric acid and 1.0M sodium acetate (pH 0.5-3.0), 0.2 M of sodium acetate and 0.2 M acetic acid (pH 4.0-7.0) and 2.0 M ammonium chloride 2.0 M ammonium hydroxide (7.0-10.0) buffer solutions were prepared in distilled water. Suitable portions of these solutions are mixed to get the desired pH.

### Procedure for the Determination of Nickel (II)

Into a series of 100 mL separating funnels, aliquots (0.2-2.2 mL) of  $1 \times 10^{-3}$  M Nickel (II) solution were taken. To each funnel, 2.0 mL of buffer (pH 9.0) and 1.0 mL of HTP reagent ( $1 \times 10^{-2}$  M) solution were added. The final volume of aqueous phase was adjusted up to 10 ml with double distilled water. The contents were mixed and equilibrated with 10 ml Chloroform for 60 sec. The two phases were allowed to separate and organic phase was collected in 10 ml flask after passing through anhydrous sodium sulphate to remove water droplets. The absorbance of extract was measured against at a 382 nm against a corresponding reagent blank prepared similarly.

## RESULTS AND DISCUSSIONS

N'-(2-hydroxybenzylidene)-3-(4-o-tolylpiperazin-1-yl) propanehydrazide (HTP) gave yellow colored water insoluble complex with Ni (II) in basic buffer (pH 7.0-10.0) medium. This complex was quantitatively extracted in chloroform solvent. This color reaction was investigated in detail and developed extractive spectrophotometric method for the determination of Ni (II) in non-aqueous medium. The Ni (II) – HTP complex formed in aqueous phase is transferred quickly into chloroform giving a maximum and constant absorbance for the variation of equilibration time from 10 to 150 sec.

### Optimization of reaction conditions

In order to optimize the conditions for proposed spectrophotometric methods, the effect of experimental variables was studied by altering each variable in turn while keeping the others constant.

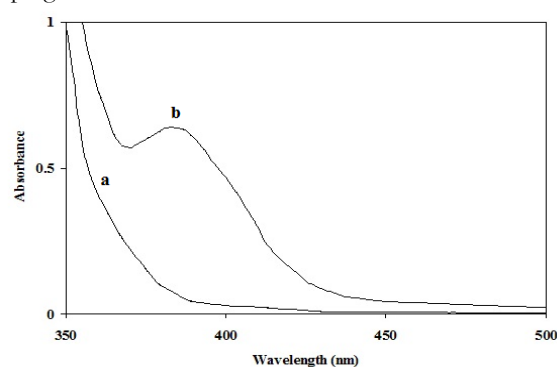


Figure 2: Absorption spectra

a) HTP ( $1 \times 10^{-3}$  M) against chloroform

b)  $1 \times 10^{-4}$  M Ni (II)-HTP complex against reagent blank.

### Effect of solvents on the Extraction of Ni (II)-HTP Complex

Solvents such as isoamylalcohol, chloroform, dichloromethane, n-hexanol, xylene, carbon tetrachloride, cyclohexane, and methyliso-butylketone were examined as extractants in the following study. In series of 100 ml separate funnels, 2 mL ammonia buffer (pH: 9.0), 1.0 ml of  $1 \times 10^{-3}$  M Ni (II) and 1.0 mL of  $1 \times 10^{-2}$  M reagent (HTP) solution were taken in each separating funnel. The final volume of aqueous phase was adjusted up to 10 ml with double distilled water. The complex formed in aqueous phase was transferred quantitatively (100%) into isoamylalcohol, chloroform, dichloromethane, n-hexanol, xylene, carbon tetrachloride, cyclohexane, and methyliso-butylketone through single extraction with equal volumes of solvent. The two phases were allowed to separate and organic phase was collected in 10 ml flask after passing through anhydrous sodium sulphate to remove water droplets.

As per the results reported in Table 1, the maximum constant absorbance was observed in chloroform solvent. Hence chloroform is found to be a suitable solvent for the effective extraction of Ni (II)- HTP complex. Hence, chloroform was chosen for all further studies.

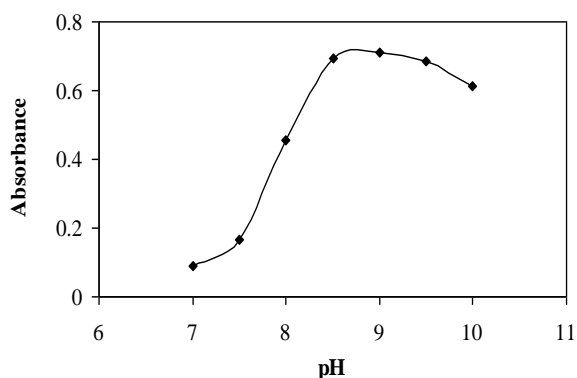
**Table 1:** Effect of solvents on the extraction of Ni (II)-HTP complex.

Solvent	Absorbance
Isoamylalcohol	0.421
Chloroform	0.716
Dichloromethane	0.673
n-hexanol	0.544
Xylene	0.398
Carbon tetrachloride	0.641
Cyclohexane	0.473
Methyliso-butyl ketone	0.554

[Ni(II)] =  $1 \times 10^{-4}$  M  
 pH = 9.0  
 $\lambda_{\max}$  = 382 nm

### Effect of pH

The effect of pH on the system was examined in terms of absorbance of complex in organic phase. Complex is not formed in acidic conditions. Based on the preliminary studies, the Ni (II) - HTP complex is formed in basic conditions. The optimum pH range for the maximum absorbance has been studied.

**Figure 3:** Effect of pH on absorbance [Ni (II)- HTP system]

[Ni(II)] =  $1 \times 10^{-4}$  M  
 [HTP] =  $1 \times 10^{-3}$  M  
 $\lambda_{\max}$  = 382 nm

From **Figure 3** it is suggested that, in neutral medium Ni (II) does not give any color with reagent. The complex begins to form at approximately pH 7.5, the maximum absorbance reached at pH 9.0. Hence pH 9.0 has been selected for further studies.

### Effect of reagent concentration on the absorbance of reaction mixture

The effect of reagent (HTP) concentration on the absorbance of the complex was investigated at pH=9.0 by using  $1 \times 10^{-4}$  M Nickel (II) solution. The concentration of HTP was varied from 0.0001 M to 0.001 M. It is found that a 10-fold excess of the reagent concentration was selected as color developing reagent for determination of nickel (II) in the proposed method.

### Characteristics of the complex

Job's method of continuous variation [16] was conducted to find out stoichiometry of the reaction and stability constant of complex. Keeping the total volume constant, equimolar solutions of nickel (II) and HTP were taken in different volume ratios in 10 mL volumetric flasks. The general experimental procedure was followed and a graph was plotted between the absorbance and mole

fraction of the metal. The plot (**Figure. 4**) reveals stoichiometry between metal and ligand is 1:1 ratio. The following equation has been used for calculation of stability constant.

$$K = \frac{[ML]}{[M] \times [L]}$$

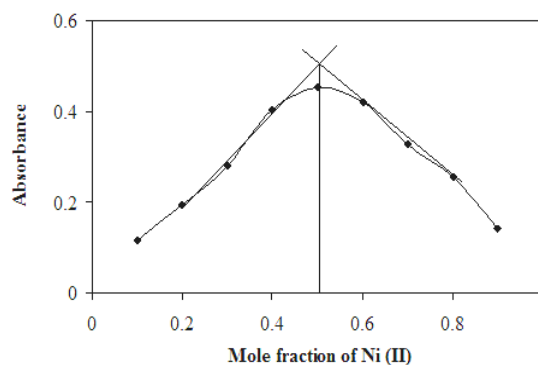
$$K = \frac{[A_2 / A_1]}{[1 - A_2 / A_1] \times [C_L - C_M \times A_2 / A_1]}$$

Where,  $A_1$  = absorbance at break point,  $A_2$  = actual absorbance,

$C_M$  = concentration of metal and

$C_L$  = concentration of ligand

The absorbance value of the Ni (II)- HTP complex was measured at different intervals of time at 382 nm to ascertain the time stability of the color of the complex. It was observed that the formed complex was stable for 8 h and stability constant of complex is  $2.048 \times 10^6$

**Figure 4:** Job's method of continuous variation [Ni (II)] = [HTP] =  $1 \times 10^{-3}$  M;  $\lambda_{\max}$  = 382 nm; pH = 9.0.

### Effect of interference ions

The tolerance limit of foreign ions on the absorbance of the color reaction was studied with a view to examine the applicability of the method for the determination of Nickel (II) in the presence of foreign ions were studied by measuring the absorbance of the reaction mixture containing  $5.869 \mu\text{g mL}^{-1}$  Ni (II) in the presence of different amount of foreign ions. An error  $\pm 2$  in the absorbance value was considered. The results are presented in **Table 2**.

**Table 2** Effect metal ions on the determination of  $5.869 (\mu\text{g mL}^{-1})$  Ni (II)

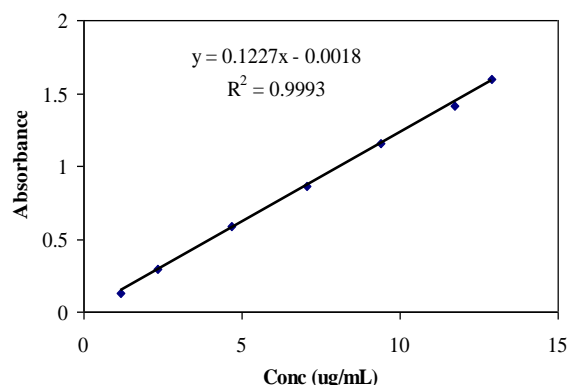
Metal ion	Tolerance limit ( $\mu\text{g mL}^{-1}$ )	Metal ion	Tolerance limit ( $\mu\text{g mL}^{-1}$ )
Iodide	930	$\text{Mg}^{+2}$	48
Tetraborate	775	$\text{Sn}^{+2}$	65
Citrate	680	$\text{Bi}^{+2}$	42
Thiourea	892	$\text{Se}^{+4}$	54
Tartrate	534	$\text{Fe}^{+2}$	41
Thiosulphate	225	$\text{Mo}^{+6}$	32
Oxalate	356	$\text{Pd}^{+2}$	66
Chloride	128	$\text{Zn}^{+2}$	27
Fluoride	115	$\text{Cd}^{+2}$	19
Phosphate	720	$\text{Mn}^{+2}$	38
$\text{Ba}^{+2}$	28	$\text{Cu}^{+2}$	12
$\text{Fe}^{+3}$	34	$\text{Co}^{+2}$	35

\*masked by Thiourea ( $250 \mu\text{g mL}^{-1}$ )

It can be seen from the table that large number of common ions did not interfere in the proposed method.

### Validation

Under the optimized experimental conditions, a linear relation was obtained between absorbance and concentration of nickel (II) in the proposed method. Regression analysis for the results was carried out using least-square method (Figure 5). Beer's law plots were linear with good correlation coefficients as shown Table 3. The limits of detection (LOD) and limits of quantification (LOQ) were determined [17] using the formula:  $LOD$  or  $LOQ = kS_a/b$ , where  $k = 3.3$  for LOD and 10 for LOQ,  $S_a$  is the standard deviation of the intercept, and  $b$  is the slope



**Figure 5:** Absorbance Vs. Amount of Ni (II) in  $\mu\text{g mL}^{-1}$

[HTP] =  $1 \times 10^{-3}$  M  
 $\lambda_{\text{max}}$  = 382 nm  
 pH = 9.0

**Table 3:** Optical and regression characteristics of the proposed method

Parameter	Proposed method
$\lambda_{\text{max}}$ (nm)	382
Beers law limit ( $\mu\text{g mL}^{-1}$ )	1.1738-12.9118
Molar absorptivity (L./mol. cm)	$0.7208 \times 10^4$
Sandell's sensitivity ( $\mu\text{g cm}^{-2}$ )	0.008
Regression equation ( $Y = a + bC$ )	
Slope (b)	0.1227
Intercept (a)	-0.0018
Regression coefficient ( $r^2$ )	0.9993
Standard deviation of slope ( $S_b$ )	$11 \times 10^{-3}$
Standard deviation of intercept ( $S_a$ )	0.0014
Detection limit LOD ( $\mu\text{g mL}^{-1}$ )	0.32
Quantification limit LOQ ( $\mu\text{g mL}^{-1}$ )	0.97

In order to determine the accuracy and precision of the proposed method, solutions containing three different concentrations of nickel were prepared and analyzed in six determinations. The relative standard deviation as precision and percentage relative error (RE%) as accuracy of the suggested methods was calculated. The analytical results for accuracy and precision as shown in Table 4 reveal that the proposed methods have good repeatability.

**Table 4:** Precision and accuracy of the proposed method

Ni (II) taken ( $\mu\text{g mL}^{-1}$ )	Ni (II) found $\pm$ SD ( $\mu\text{g mL}^{-1}$ )	% RSD	% RE
2.3476	$2.3401 \pm 0.043$	1.83	-0.32
9.3904	$9.3912 \pm 0.098$	1.04	0.01
12.9118	$12.9198 \pm 0.123$	0.95	0.06

### Applications

To confirm the usefulness of the developed extractive spectrophotometric method, it was applied to the determination of nickel in water samples, alloys and Edible oils.

#### Determination of Ni (II) in water samples

Different water samples (river water and Tap water) were collected from various places in and around Warangal, A.P., India. The samples (150 mL) were stored at 0-5°C in metal free polyethylene bottles. Water samples were filtered through what man filter paper no. 41 and clean solution was collected into 250 mL beaker. The contents were diluted up to the mark with double distilled water. 15 mL of this solution was further diluted to get working solution for determination of Ni (II) as described in above procedure. A known amount of nickel standard solution spiked to sample and determined its recovery. The results are presented in the Table 5 (a).

#### Determination of Nickel (II) alloys

The present method was also applied for the determination of nickel (II) content in standard alloy samples such as Low alloy steel (BCS 251) and Nickel base super alloy (IN 718). A total of 0.1 g of each oven-dried (110°C) alloy sample was dissolved in 15 ml of Aqua-regia. The solution was heated to near dryness and nitrate was expelled from the residue using 5ml of concentrated hydrochloric acid. The residue was dissolved in double-distilled water and made up to 100 ml. Suitable aliquot of these solutions were taken for nickel determination. The results are presented in the Table 5 (b).

#### Determination of Nickel (II) in Edible oil

Oil sample solutions were prepared following the procedure given in the literature. 50 g of the sample was digested in 40 ml of conc  $\text{HNO}_3$ , heated on a water bath shaken vigorously until fine emulsion was formed. The heating was continued with the gradual addition of 40 ml of 6% Hydrogen peroxide. The aqueous phase was then transferred into the beaker with help of separating funnel. The extraction was repeated thrice with further addition of 20 ml of Conc  $\text{HNO}_3$  and 20 ml of 6% hydrogen peroxide. The extraction were evaporated to dryness. The residue was dissolved in minimum amount of 1M HCl and transferred into a 50 ml volumetric flask and diluted to the mark with distilled water. The suitable aliquots of the sample were analyzed by the proposed method. The results are presented in the Table 5 (c).

**Table 5 (a):** Determination of nickel (II) in water samples

S.No	Sample	Nickel (II) $\mu\text{g mL}^{-1}$		Recovery (%)
		Amount added	Amount found	
1	Waddepally Lake (Kazipet, Warangal Dt)	-	4.73	-
		6.0	10.65	98.7
2	Tap water	-	1.47	-
		6.0	7.44	99.5



**Table 5 (b):** Determination of nickel (II) in alloys

S.No	Sample	Composition	% Nickel (II)		%RE
			Certified	Calculated	
1	Low alloy steel (BCS 251)	Ni: 5.15, Mo:0.185, Mn: 0.165, Co: 0.007, <sup>b</sup> Cu, 0.090	5.15	5.17	0.4
2	Nickel base super alloy (IN 718).	Ni: 54.9, Cr: 18, Mo: 3, Fe: 19, Co: 5.1.	54.9	54.2	1.27

**Table 5 (c):** Determination of nickel (II) in Edible oils

S. No	Sample	Nickel (II) $\mu\text{g mL}^{-1}$		%RE
		AAS Method	Present method	
1	Sun flower oil	0.66	0.63	-3.03
2	Groundnut oil (Hydrogenated)	0.42	0.41	-2.38

## CONCLUSIONS

In the present investigation, N<sup>1</sup>-(2-hydroxybenzylidene)-3-(4-o-tolylpiperazin-1-yl) propanehydrazide (**HTP**) has been used in the extractive spectrophotometric determination of nickel (II). The color reaction between Ni (II) and **HTP** is almost instantaneous and the absorbances of complex remain constant for 8 hrs. The reagent was found to be selective and freedom from interferences. The results from the present developed method clearly demonstrate the usefulness of **HTP** as an extracting agent for the determination of nickel (II) in environmental matrices such as water samples, standard alloys and edible oils.

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