Solvent Extraction and Spectrophotometric Determination of Nickel (II) using 2 – Hydroxy 1- Naphthaldehyde Thiosemicarbazone (HNT) as an Analytical Reagent

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ABSTRACT

2 – hydroxy 1- naphthaldehyde thiosemicarbazone (HNT) is synthesized in laboratory and characterized by NMR, IR and elemental analysis for its purity. This reagent forms a yellowish green coloured complex with Ni (II) which can be quantitatively extracted into ethyl acetate at pH 7. Complex in ethyl acetate shows an intense absorption peak 430 nm. It is observed that Beer's law is obeyed in the range of 10μg to 100μg of metal solution. It gives linear and reproducible graph under appropriate conditions, the complex having a molar absorptivity of 0.275 x 10 ^{6}L mol^{-1} cm^{-1}, Sandell's sensitivity calculated was found to be 0.275 x 10^2 μg cm^{-2}·Nature of the extracted complex, determined by Job's continuous variation method, Slope ratio method and Mole ratio method shows that the composition of Ni (II): HNT is 1:1. Interference by various ions is studied and masking agents used where required. The proposed method has been applied for the determination of Ni (II) in various samples. The results of the analysis are found to be comparable with those obtained by standard method.

KEYWORDS: *Nickel (II); solvent extraction-spectrophotometric determination; 2 – hydroxy 1- naphthaldehyde thiosemicarbazone (HNT)*

1. INTRODUCTION

Its most important ore minerals are laterites, including limonite and garnierite, and pentlandite. The bulk of the nickel mined comes from two types of ore deposits. The first are laterites where the principal ore minerals are nickeliferous limonite: (Fe, Ni)O(OH) and garnierite (a hydrous nickel silicate): $(Ni, Mg)_3Si_2O_5(OH)$. The second are magmatic sulfide deposits where the principal ore mineral is pentlandite: $(Ni, Fe)_9S_8$.

The metal is corrosion-resistant, finding many uses in the manufacture of coins, magnets and common household utensils, as a catalyst for hydrogenation, and in a variety of other applications. Nickel is chiefly valuable for the alloys it forms, especially many superalloys, and particularly stainless steel and its chief use is in the nickel steels and nickel cast irons, of which there are many varieties.

Nickel is also used as a binder in the cemented tungsten carbide or hardmetal industry. Nickel is used in many industrial and consumer products, including rechargeable batteries, electric guitar strings and special alloys. It is also used for plating and as a green tint in glass. It is used in coins, for plating metals such as iron and brass, for chemical apparatus, and in certain alloys such as German silver.

It is also widely used in many other alloys, such as nickel brasses and bronzes, and alloys with copper, chromium, aluminium, lead, cobalt, silver, and gold ·Nickel is also used in fire assay as a collector of platinum group elements.Nickel foam or nickel mesh is used in gas diffusion electrodes for alkaline fuel cells·

Enzymes of certain life-forms contain nickel as an active center making the metal essential for them. Nickel plays numerous roles in the biology of microorganisms and plants.

2. MATERIALS AND METHODOLOGY:

The stock solution of the nickel was prepared by dissolving weighed quantity of nickel sulphate in double distilled water containing dilute sulphuric acid and diluted to the desired volume by double distilled water. An aliquot of this solution was used for gravimetric determination of nickel by dimethyl glyoxime method.

All the measurements of absorption spectra were made on one cm silica cells or 1 cm glass cells and the spectrophotometer used was Shimatzu UV 2100 and for p^H measurements an Elico 120 model p^H meter of Electronic Instruments Co. Ltd. was used. For calibration appropriate buffer solutions were used.

2.1. Reagent preparation :
In the present method, we report here the synthesis of 2-Hydroxy 1-naphthaldehyde thiosemicarbazone and its application for extractive separation of ions by spectrophotometric method.

Preparation of 2-Hydroxy 1-naphthaldehyde thiosemicarbazone:
Hydrazine Carbothioamide, 2-[(2-hydroxy-1- =naphthalenyl) methylene]

2-Hydroxy 1-naphthaldehyde (0.5 m mol) and thiosemicarbazide (0.5 m mol) were added to a dry 250 ml round bottom flask. The mixture dissolved in 10 ml of anhydrous methyl alcohol. The mixture was refluxed for 3 hours on a water bath with stirring. The solvent was removed in vacuo, and resulting solid of 2-hydroxy 1-naphthaldehyde thiosemicarbazone was rinsed with sufficient amount of water and recrystallised. The product was solid and yellow in colour. The melting point recorded was 245^0C.

The yellow colour of 2-hydroxy-1-naphthaldehyde thiosemicarbazone in the alkaline range was studied by the spectrophotometric method.

Reaction:

2-hydroxy 1-naphthaldehyde + Thiosemicarbazide

Reflux for 3.hrs

2-hydroxy 1-naphthaldehyde thiosemicarbazone
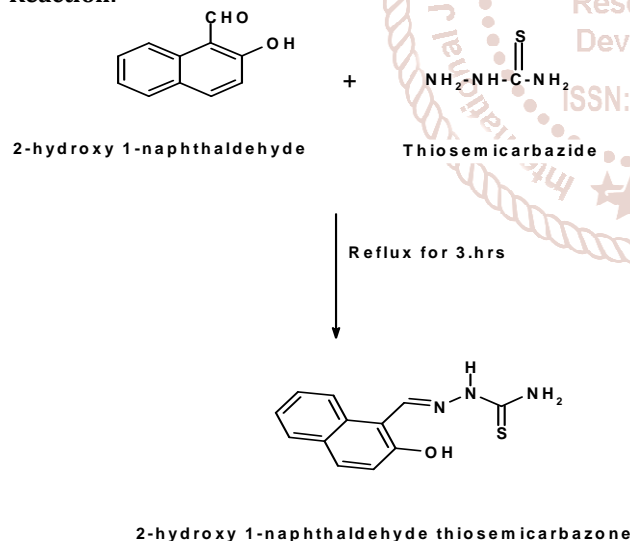
2.2. Proposed Analytical method
A working solution was obtained by diluting stock Ni(II) solution. 1 ml of aqueous solution of Ni(II) [containing 100 µg Ni (II)] was taken in a separating funnel. The pH was adjusted using buffer (pH 7). To this 0.5 mL of 0.01 % reagent in dimethyl formamide was added. Total volume of aqueous solution was made to 10 ml. The yellow coloured complex formed was extracted into 10 ml of ethyl acetate by shaking for 1 min. The phases were separated and absorbance of the organic layer was measured at 430.0 nm using a reagent blank.

3. RESULTS AND DISCUSSION
3.1. Extraction as a function of pH
The extraction was found to be quantitative between pH 6.5 and 7.5. Hence pH 7.0 was selected for further studies (**Fig. 1**).
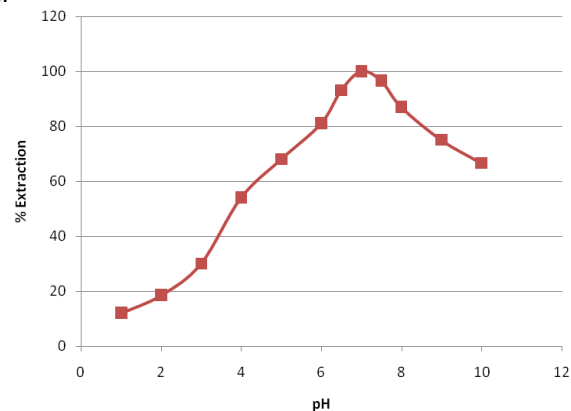

Fig. 1 EFFECT OF pH ON EXTRACTION OF Ni(II) : HNT

3.2. Absorption spectrum :
The absorption spectrum of Ni(II) : 2-Hydroxy 1-Naphthaldehyde Thiosemicarbazone in Ethyl Acetate (B) shows the maximum absorption at 430 nm and the absorption due to the reagent(A) at this wavelength is nearly negligible (Fig. 2).
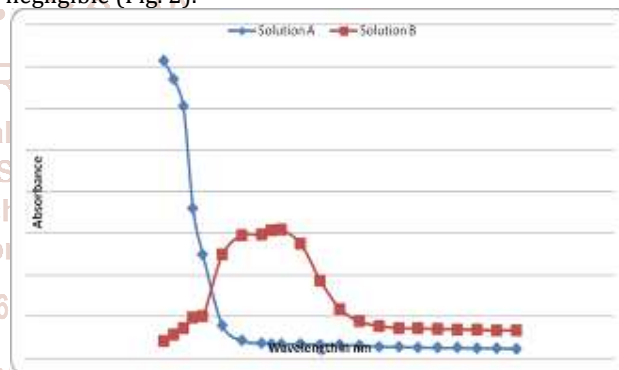

Fig. .2 ABSORPTION SPECTRUM OF Ni (II) : HNT

3.3. Selection of solvents:
Many organic solvents were employed to determine the most suitable solvent for the extraction of Ni(II) with HNT. The organic solvents can be arranged in the order of their extraction efficiency as follows,

Ethyl Acetate > Chloroform > n-Butanol > Benzene > Toluene > Ethyl Methyl Ketone > CarbonTetrachloride = n-Hexane Ethyl Acetate was chosen as the solvent as it gave clean and quick separation.

3.4. Reagent concentration
Variation in concentration of reagent shows that 1.0 ml of 0.01 % of 2-Hydroxy 1-Naphthaldehyde Thiosemicarbazone of in dimethyl formamide solution is sufficient for full colour development and extraction of 100 µg of Ni (II).

3.5. Effect of equilibration time
Equilibration time from 30 seconds to 60 minutes was studied and it was found that 30 seconds are sufficient for the quantitative extraction of Ni (II).

3.6. Stability of the complex with time
The extracted complex is found to be stable up to 48.0 hours.

3.7. The Calibration Plot

The calibration plot of the absorbance against concentration of the Ni (II) gives linear reproducible graph in the concentration range of 10µg to 100 µg (**Fig.3**) indicating that the Beer's law is obeyed in this range .The Molar Absorptivity and Sandell's Sensitivity was calculated to be 0.275×10^6 L mol^{-1} cm^{-1} and 0.275×10^2 µg cm^{-2} .
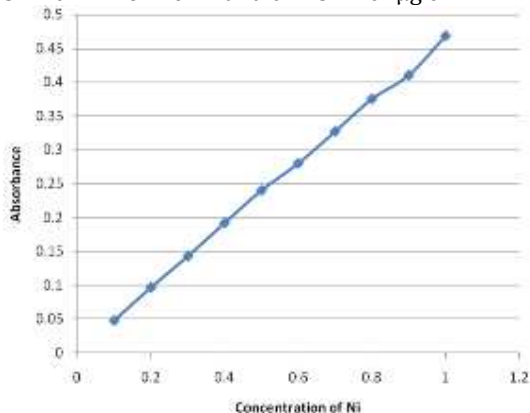

Fig. 3 CALIBRATION PLOT OF Ni (II): HNT COMPLEX

3.8. Composition of extracted species

The composition of the extracted complex was studied by Job's continuous variation Method, **(Fig. 4)**, Mole ratio method, and Slope ratio method, **(Fig. 5)**. On the basis of results of these studies, it can be concluded that the composition of Ni(II): HNT complex is 1:1.
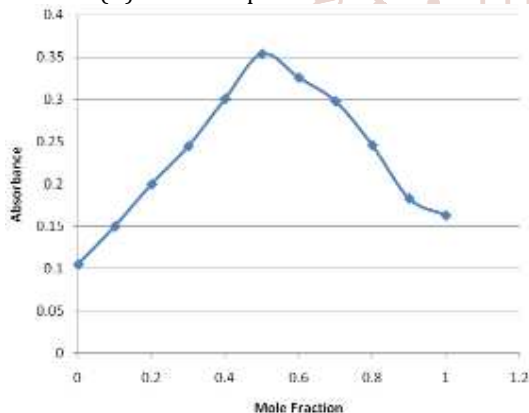

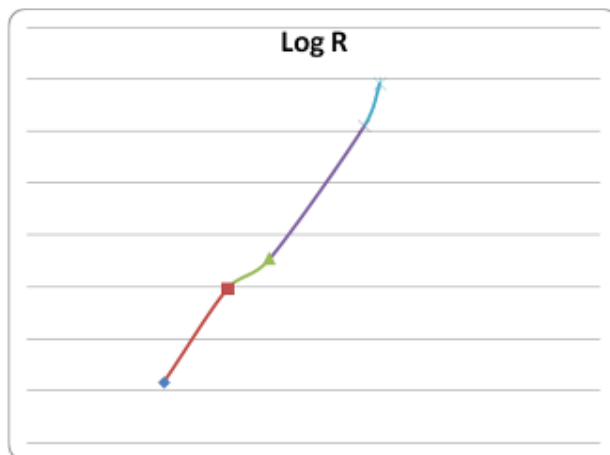**Fig.4 JOB'S CONTINUOUS VARIATION METHOD Ni (II): HNT**

Fig.5 SLOPE RATIO PLOT FOR THE Ni (II): HNT

3.9. Effect of diverse ions

The tolerance limits of the interfering species were established for 100 µg of nickel. The ions which show interference in the spectrophotometric determination of nickel were masked using appropriate masking agents. **(Table 1)**

Table 1 MASKING AGENTS REQUIRED TO SUPPRESS THE INTERFERENCE OF FOREIGN IONS

Sr.No.	Interfering ion	Masking agents added
1.	Fe (II)	Thiourea
2.	Pd (II)	Thiourea
3.	Cyanide	Boiling with HNO_3 and formaldehyde
4.	EDTA	Sodium molybdate
5.	Citrate	Sodium molybdate
6.	Tartarate	Sodium molybdate

3.10. Precision and Accuracy of the method

The precision and accuracy of the spectrophotometric method was studied by analyzing five solutions each containing 100 µg of nickel. The standard deviation and confidence limits were calculated accordingly **(Table 2)**.

Table 2

Sr. No.	Absorbance	Amount of Ni(II) in µg	Mean X	Deviation from mean $D=\mid x_i - x^{..}\mid$	$D^2= (x_i - x^{..})^2$
1)	0.449	100		0.22	0.0484
2)	0.501	99.5		0.28	0.0784
3)	0.500	99.9	99.78	0.12	0.0144
4)	0.501	99.5		0.28	0.0784
5)	0.449	100		0.22	0.0484

Standard deviation: 0.258
Confidence limit: 99.78 ± 0.465

4. APPLICATIONS:

The present method was applied to various samples for the determination of nickel and results obtained in good agreement with the results obtained by standard method.

1. Synthetic mixture

Synthetic mixture of the nickel with copper, zinc and cobalt were prepared and analyzed by 2-Hydroxy 1-naphthaldehyde thiosemicarbazone.

2. Determination of Nickel in Nickel alloy and stainless Steel

0.1 -0.2g of the alloy sample was dissolved in 10.0ml aqua regia. The solution was then evaporated to dryness and the residue was treated with 6.0N HCl and diluted to 50ml. The working solution was prepared by 10-times dilution of stock solution. An aliquot of this solution was used for the extraction and spectroscopic determination of Ni (II) by the present method.(Table 3)

Table 3 DETERMINATION OF NICKEL USING HNT FROM REAL SAMPLES

From commercial samples	Samples	Amount in mg	
		% Present method	% Standard method
1)	Cupronickel alloys	64.8	65.0
2)	Magnesium alloys	51.0	43.0
From synthetic Mixtures	Sample type	Ni(II) found (ppm)	
		Present Method	Standard Method
1)	Ni(5)+Fe(5)	4.89	4-97
2)	Cu(5)+Ni(5)	4.89	4.91
3)	Ni(5)+Zn(5)	3.95	3.97

5. CONCLUSION:

The results obtained show that the newly synthesized 2-Hydroxy 1-Naphthaldehyde Thiosemicarbazone in Ethyl Acetate can be effectively for quantitative extraction of Ni(II) from aqueous medium. The proposed method is quick and required less amount of organic solvent. The equilibrium time required is very less and the complex is stable for 48 hours. The results show good agreement with the standard method. The method is very precise .The method can be applied for estimation of the Ni (II) in pharmaceutical samples as well as alloys.

6. ACKNOWLEDGEMENT:

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