

ORIGINAL RESEARCH ARTICLE

A SENSING BEHAVIOR SYNERGISTIC LIQUID-LIQUID EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF NICKEL (II) BY USING 1-(2',4'-DINITRO AMINOPHENYL)-4,4,6-TRIMETHYL-1,4-DIHYDROPYRIMIDINE-2-THIOL: ANALYSIS OF FOUNDRY AND NICKEL ELECTROPLATING WASTE WATER**Ganesh S. Kamble^{1,2*}, Sunil S. Joshi³, Mansing A. Anuse^{2*}**

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ABSTRACT:

We report the sensing behavior liquid-liquid extraction of nickel (II) which have been selectively determined from contaminated water samples by simple Uv-visible spectrophotometer. The method is based on synergistic extraction of nickel (II) by 1-(2',4'-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol, [2',4'-dinitro APTPT] with pyridine. Nickel (II) reacts with 2',4'-dinitro APTPT and forms a green coloured complex at pH 9.2. Also, the Ni(II) ion were detected through naked-eye with the ligand. The absorbance of coloured complex was measured at 660 nm and coloured complex is stable for more than 48 h even in the presence of other competing ions. The system obeyed Beer's law in the concentration range of 5 to 50 $\mu\text{g mL}^{-1}$ of nickel (II) and optimum range evaluated by Ringbom's plot method is 10 to 40 $\mu\text{g mL}^{-1}$ with an excellent linearity and a correlation coefficient of 0.999. The molar absorptivity and Sandell's sensitivity of the extractive species were found to be $1.64 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $0.0585 \mu\text{g cm}^{-2}$ in presence of pyridine, and $7.4 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $0.78 \mu\text{g cm}^{-2}$ in absence of pyridine, respectively. The composition of nickel (II)-2',4'-dinitro APTPT-pyridine was established by slope ratio method, mole ratio method and Job's method of continuous variation. It was found that Metal:Ligand:Synergent (M:L:Sy) ratio is 1:2:2. To assess precision and accuracy of the developed method, determinations were carried out at $n = 5$. The relative standard deviation of all measurements does not exceed 0.16 %. Excellent selectivity was found toward Ni(II) ion due to a specific complex formation between Ni(II) ion and organic ligand. In the extraction of Ni(II), several affecting

factors, including the solution pH, ligand concentration, equilibrium time, initial Ni(II) ion concentration, foreign ions were investigated and applicability of the method checked by the analysis of synthetic mixtures and alloys. The developed method is successfully used for determination of nickel (II) from waste water effluents from foundry region and nickel plating industry (Kolhapur city). Results obtained by the developed method also confirmed by AAS. We claimed from this study that Ni(II) could be successfully determined by the spectrophotometric method developed in the current work. The present work is obviously much simpler than the conventional comprising multistep processes.

KEYWORDS: Nickel (II); Synergistic extraction; 2',4'-dinitro APTPT; Pyridine; Spectrophotometry

ABBREVIATIONS:

2',4'-dinitro APTPT	1-(2',4'-dinitro aminophenyl)-4,4,6-trimethyl-1,4- dihydropyrimidine-2-thiol
DMG	Dimethylglyoxime
PAR	4-(2-Pyridylazo) resorcinol
Py	Pyridine
Sy	Synergent

INTRODUCTION:

Nickel is moderately abundant (99 ppm) and it is used in large quantities in wide varieties of alloys both ferrous and nonferrous. Meteoritic iron-nickel was raw material for the swords of many ancient warriors [1]. Nickel is an important element for use in the food industry as a catalyst in hydrogenation of oils. Due to its high strength and resistance to corrosion in many media [2]. It is used in nickel plating and also in the manufacture of alloys along with iron, copper, aluminium, chromium, zinc, and molybdenum. Very strong permanent magnets are made from 'Alnico' steel. Monel metal is very resistant to corrosion and is used in apparatus to handle F₂ and other corrosive fluorides. Nickel improves both the strength of steel and its highly resistance to corrosion. Because of its high melting point (1453 °C) it is used in the manufacture of some food processing vessels and many other pieces of equipment. Nickel is an important element of the enzyme urease and as such is considered to be essential to plants and some domestic animals. The determination of trace amounts of nickel is important

in biological sciences, environmental analytical chemistry, metallurgy and industry [3]. On the other hand, due to the industrial facilities, heavy metal contents in environmental samples increase unfavorably. US EPA has classified nickel as one of the 13 priority metal pollutants for its widespread use [4]. Compared with other transition metals, nickel is a moderately toxic element. However, it is known that inhalation of nickel and its compounds can lead to serious problems including cancer of the respiratory system [5]. Moreover, nickel toxicity can cause a skin disorder known as nickel-eczema [6], cancer of nasal cavity and lungs, dermatitis, asthma, acute pneumonitis and disorders of central nervous system.

Considering its toxicity and owing to its involvement in some essential metabolic processes [7], it has become necessary to develop the procedures with high selectivity for determination of nickel content from waste effluents. Among the various instrumental techniques available for the determination of nickel (II). Some of these methods comprise ion selective electrode [8,9], voltammetry

[10,11], polarography [12], atomic fluorescence [13], X-ray fluorescence [14]. But spectrophotometry is preferred as a versatile technique due to its low cost and easy experimental procedures. The successful application of such procedures mainly relies on the stability of the coloured complex that usually formed between the analyte metal ions and organic complexing agent.

The aim of this work is to develop a very simple, selective and low cost procedure and is to study the synergistic effect of 1-(2',4'-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol, [2',4'-dinitro APTPT] with pyridine on the extraction of nickel (II) into chloroform, and to apply this extraction system to the determination of the mentioned analytes, using spectrophotometer and reliability of the method is confirmed by AAS. The effects of 2',4'-dinitro APTPT and pyridine on the percent extraction of the metal complexes were studied and the optimum extraction conditions were investigated. Furthermore, this method has been applied successfully for the analysis of nickel (II) in synthetic mixtures and alloys. The proposed method, when compared with other spectrophotometric methods, was found to be satisfactorily selective (Table 1) [15-35]. The present results from spectrophotometry have been compared with those obtained through the AAS. It also offers advantages like reliability and reproducibility in addition to its simplicity, instant colour development and less interferences.

EXPERIMENTAL:

Apparatus:

The absorbance measurements of the reagent and its nickel (II) complexes were measured with a UV-Vis digital spectrophotometer model Systronic 106 (300 -800 nm) using 1 cm quartz cell. For measurement of the pH values, Elico digital pH meter model LI-120 was used.

All glass vessels were cleaned by $K_2Cr_2O_7$ solution and followed by washing carried out with soap water and rinsed with distilled water before to use.

Preparation of reagents and standard nickel (ii) solution:

A stock solution of nickel (1 mg mL^{-1}) was prepared $NiSO_4 \cdot 6H_2O$ (Merck, Darmstadt, Germany) and standardized by a known method [36]. More diluted standard solutions ($10 \text{ to } 100 \text{ } \mu\text{g mL}^{-1}$) were freshly prepared by appropriately diluting the stock nickel (II) solution with water immediately before use.

All other solvents and chemicals were of analytical reagent. Different interfering ions were prepared by dissolving weighed quantities of their salts in water or dilute HCl [37]. Synthetic mixtures containing nickel (II) were prepared by combining with commonly associated metal ions in definite composition [38]. Double distilled, de-ionized water was used throughout the experiments.

Synthesis of chromogenic ligand, 2',4'-dinitro APTPT:

1-(2',4'-Dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol, [2',4'-dinitro APTPT] was synthesized and recrystallized as reported by R. A. Mathes [39]. The synthesis was carried out in two steps. In the first step, 2-methyl-2-isothiocyanato-4-pentanone was prepared by mixing of mesityl oxide with ammonium thiocyanate in presence of sulphuric acid in water for 15 min. While in the second step, the 2-methyl-2-isothiocyanato-4-pentanone was condensed with 2,4-dinitro phenyl hydrazine in 50 mL ethanol. The mixture was refluxed for 50 min, and cooled. The crystalline product was precipitated. It was recrystallised from glacial acetic acid, washed with water and air dried and finally characterized. A 0.02 M stock solution of 2',4'-dinitro APTPT was prepared by dissolving 0.324 g in a 50 cm^3 of chloroform.

Recommended procedure:

An aliquot of the sample containing 300 μg nickel (II) was transferred into a 125 mL separatory funnel before that pH was adjusted to 9.5 with dilute hydrochloric acid and sodium hydroxide and made volume to 25 mL with water. The whole solution was thoroughly mixed with 5.0 mL of a 0.02 mol L^{-1} 2',4'-dinitro APTPT and 5.0 mL of 0.5 mol L^{-1} pyridine in

chloroform and equilibrated for 10 min. The organic layer having green colour was allowed to separate and dried over anhydrous sodium sulphate. The green colour organic layer was transferred to a 10.0 mL of standard volumetric flask and made upto the mark with chloroform. The absorbance of the green coloured complex was measured at 660 nm against respective reagent blank prepared in similar manner. Percentage extraction (% E) and metal distribution ratio (D) were calculated according to Eqs. (1) and (2), respectively.

$$\%E = \frac{[\text{Ni}^{2+}]_{\text{org.}}}{[\text{Ni}^{2+}]_{\text{aq., init.}}} \times 100$$

..... (1)

$$D = \frac{[\text{Ni}^{2+}]_{\text{org.}}}{[\text{Ni}^{2+}]_{\text{aq.}}}$$

..... (2)

where, $[\text{Ni}^{2+}]_{\text{aq., init.}}$ are represents the initial concentration of metal ion in the aqueous phase. $[\text{Ni}^{2+}]_{\text{aq.}}$ and $[\text{Ni}^{2+}]_{\text{org.}}$ the total concentrations of metal ion in the aqueous and organic phases after equilibrium, respectively.

RESULTS AND DISCUSSION:

Spectral characteristics:

Nickel (II) reacts with 2',4'-dinitro APTPT at pH 9.2 into chloroform and forms a green coloured ternary complex in presence of pyridine as an auxiliary ligand. The ratio of the ternary complex showed 1:2:2 (M:L:Sy). The maximum absorption of coloured complex was 660 nm in chloroform, and was stable for a more than 48 h. The optimum conditions for the effective extraction of nickel (II) were established by studying the effect of pH, ligand concentration, pyridine concentration, choice of solvent, equilibrium time and interference of various diverse ions. The optimized conditions and spectral characteristic properties are shown in Table 2.

Absorption spectra:

Preliminary studies of extraction of nickel (II) with 2',4'-dinitro APTPT in presence of pyridine have indicated that, the formation of green colored complex at room temperature. The absorption spectra of reagent and its nickel (II) complex were studied over the wavelength range 300-800 nm and

shown in Fig. 1. The spectrum of reagent versus solvent as a blank and spectrum of nickel (II) complex against reagent blank showed at 660 nm and 415 nm, respectively. It was clearly seen that, on the subsequent work the developed spectrophotometric technique is sensitive for the determination of nickel (II).

Effect of pH:

The pH plays very important role in the spectrophotometric determination of nickel (II). Because in the optimized pH range hydroxo complex of metal species are stable and enhances the complex colour. Therefore we have studied the effect pH on the developed colour complex of nickel (II)-2',4'-dinitro APTPT-pyridine by varying the pH of nickel (II) solution in the range from 1 to 14. The results are shown in Fig. 2, where it was clearly found that, the optimal pH range for the reaction of nickel (II) with 2',4'-dinitro APTPT is 8.7-9.8 in the presence and absence of pyridine. However, in the presence of 5.0 mL of 0.5 mol L⁻¹ pyridine, there was enhancement of absorbance but in absence of pyridine absorbance was decreased in the same pH range. Thus, in the subsequent work, to ensure complete colour formation the aqueous solution was adjusted at pH 8.7-9.8. On the other hand, in the aqueous solution of pH ≤ 8.5, the absorbance of the coloured complex was found low and in the aqueous solution of pH ≥ 10.0, the absorbance of the produced coloured complex decreased drastically. Hence, for further studies, the central value of this range pH 9.2 was recommended.

Effect of solvent:

In the extraction of nickel (II), solvent plays as an very important role in solvation of nickel (II) species with ligand. For this purposes the influence of various organic solvents were examined for the effective extraction of nickel (II) with 2',4'-dinitro APTPT complex in presence of 5 cm³ of 0.5 mol L⁻¹ pyridine. The results are shown in Table 3. It was observed that, the percentage extraction (%E) values increased in the order of kerosene (6.14), < n-butanol (7.48) < amyl acetate (9.59) < amyl alcohol (22.07) <

toluene (26.48) < xylene (58.15) < methyl-iso-butylketone (62.57) < 1, 2-dichloroethane (84.26) < carbon tetrachloride (93.28) < chloroform (99.99). In the light of these findings, chloroform was selected for further extraction studies.

Effect of a chromogenic ligand concentration (2',4'-dinitro APTPT):

The effect of ligand concentration on the formation of complex species of nickel (II) was studied at pH 9.2. Different molar concentrations (0.01 to 0.04 mol L⁻¹) of 2', 4'-dinitro APTPT in chloroform were added into a fixed nickel (II) ion concentration (30 µg mL⁻¹) and absorbances were measured according to the standard procedure. It was observed that, 3.5 mL of 0.02 mol L⁻¹ reagent was necessary for full and constant color development in the presence of 5.0 mL of 0.5 mol L⁻¹ pyridine. The absorbance of the organic phase was measured at 660 nm and against reagent blank. In absence of pyridine, absorbance was lowered. However, in order to ensure the complete complexation 5.0 mL of 0.02 mol L⁻¹ reagent was recommended. A further excess of 2',4'-dinitro APTPT has no adverse effect on the sensitivity and absorbance of nickel (II)- 2',4'-dinitro APTPT-pyridine complex.

Effect of equilibrium time:

It is often necessitated to investigate the trace amounts of metal ions with high efficiency in a minimum time. The results indicated that, the optimum shaking time of 7 min was determined by varying the shaking time from 0.5 to 20 min in absence and presence of pyridine. It was found that, the color formation was instantaneous and absorbance remained constant for more than an hour. Prolonged shaking has no adverse effect on the extraction of nickel (II) in presence of pyridine. Hence, shaking time of 10 min was chosen for in all further studies.

Effect of pyridine concentration:

Synergistic effect also plays an very important role in the extraction of metal ions.

Herewith, dilute pyridine is used as synergist for extraction of nickel (II). Pyridine shows the synergistic effects by the formation of an adduct with nickel (II) species. The effect of pyridine concentration was studied from 0 to 5.0 mL of 0.5 mol L⁻¹ to obtain the maximum and constant color development. It was observed that color of nickel (II) complex into chloroform increases with the pyridine concentration and remains constant from 3.0 mL of 0.5 mol L⁻¹ pyridine. Therefore 5.0 mL of 0.5 mol L⁻¹ pyridine was used for further extraction.

Effect of color stability of complex:

Synergistic effect of pyridine over the extraction of nickel (II) also helps to enhance the colour stability of complex. The color stability of nickel (II) with ligand was studied at room temp by measuring the absorbance at regular time intervals. The absorbance of the nickel (II)-2',4'-dinitro APTPT-pyridine complex in chloroform was stable for more than 20 h. But in absence of pyridine complex was stable for 10 h. Herewith, synergistic effect proved the colour stability of the complex.

Analytical performance: Validity of Beer's law and sensitivity:

At the optimized reaction conditions of the nickel (II) with 2',4'-dinitro APTPT in the pH 9.2. The developed method obeyed Beer's law over the concentration range of 5 to 50 µg mL⁻¹ of nickel (II) as evaluated by Ringbom's plot method [40] was 10 to 40 µg mL⁻¹. Molar absorptivity was 1.64 x 10³ dm³ mol⁻¹ cm⁻¹ in presence of pyridine and 7.4 x 10² in absence of pyridine were calculated by Beer's plot. The sensitivity of the method defined by Sandell was 0.0585 µg cm⁻² in presence of pyridine while 0.78 µg cm⁻² in absence of pyridine. The standard deviation calculated from ten determinations on a solution containing 30 µg mL⁻¹ of nickel (II) is 0.018 and relative standard deviation of the method is 0.16%. These results indicate that the method has good level of precision and hence was found suitable for the routine analysis of the nickel (II) in water samples. The precision and accuracy data of the method is

shown in Table 2. The data given in Table 2 revealed that, the developed method is simple, reliable, less toxic and free from interference ions compared to the reported methods.

Stoichiometry of the complex:

The synergistic extraction of nickel (II) by mixtures of an acidic chelating extractant and synergent has been investigated. In order to apply this kind of extraction system for the separation of nickel (II) from environmental samples. The extraction properties of nickel (II) have been evaluated at pH 9.2.

The probable composition of extracted species was ascertained by plotting graphs of $\log D_{[Ni(II)]}$ against $\log C_{[2',4'\text{-dinitro APTPT}]}$ at fixed pyridine concentration (0.5 mol L^{-1}) (Fig. 3). The plots were

linear having the slopes 1.9 and 2.0 at pH 8.0 and 10.2, respectively. Also plots of $\log D_{[Ni(II)]}$ against $\log C_{[pyridine]}$ at fixed 2',4'-dinitro APTPT concentration (0.02 mol L^{-1}) (Fig. 4) were linear with slopes of 1.7 and 1.8 at pH 8.0 and 10.2, respectively. The probable composition of extracted species was calculated to be 1:2:2 (Metal:Thiol:Pyridine). The composition was also verified by Mole ratio (Fig. 5) and Job's method of continuous variation (Fig. 6).

Nickel (II) reacts with 2',4'-dinitro APTPT in the presence of auxiliary ligand pyridine, giving an uncharged chelate which is distributed between two phases according to the following equations No. (3), (4) and (5). The probable partition equilibrium of the Ni(II)-2',4'-dinitro APTPT complex with and without the pyridine between water and chloroform may be expressed as follow.



and the equilibrium constant can be expressed as,

$$\beta_{1,2} = \frac{[Ni(R-S)_2(H_2O)_2]_{org.} [H_2O]_{aq.}^4}{[Ni(H_2O)_6]^{2+}_{aq.} [R-SH]_{org.}^2}$$

The Ni(II)-2',4'-dinitro APTPT complex reacts with pyridine to give 1:2:2 (Nickel:Thiol:Pyridine) ternary complex.



which is defined by an equilibrium constant,

$$\beta_{1,2,3} = \frac{[Ni(R-S)_2(Py)_2]_{org.} [H_2O]_{aq.}^2}{[Ni(R-S)_2(H_2O)_2]_{org.} [Py]_{org.}}$$

Thus, overall extraction mechanism may be expressed as,



Therefore, extraction constant is given by,

$$K_{ex} = \frac{[Ni(R-S)_2(Py)_2]_{org.} [H_2O]_{aq.}^6}{[Ni(H_2O)_6]^{2+}_{aq.} [R-SH]_{org.}^2 [Py]_{org.}}$$

Then distribution ratio is given by,

$$D_{1,2,2} = \frac{[\text{Ni}(\text{R-S})_2(\text{H}_2\text{O})_2]_{\text{org.}} + [\text{Ni}(\text{R-S})_2(\text{Py})_2]_{\text{org.}}}{[\text{Ni}(\text{H}_2\text{O})_6]_{\text{aq.}}^{2+}}$$

$$= \beta_{1,2} [\text{R-SH}]_{\text{org.}}^2 [\text{H}_2\text{O}]_{\text{aq.}}^4 + \beta_{1,2,3} [\text{Py}]_{\text{org.}}^2 [\text{H}_2\text{O}]_{\text{aq.}}^2$$

Where, R - S H is 2',4'-dinitro APTPT and Py is pyridine.

On the basis of above reactions and data of composition of extracted species confirmed that, the coloured species is most likely fit with the valencies of

Study of diverse ions:

The determination of nickel (II) ion at concentration $30 \mu\text{g mL}^{-1}$ in the presence relatively high excess of some diverse ions relevant to industrial effluent was critically investigated by the developed procedure. The effect of foreign ions on the determination of nickel (II) was investigated by adding the known amount of diverse ion to a standard nickel (II) solution and by comparing the final absorbance with the standard. The results showed in Table 4. The results revealed that the presence of large amounts of foreign ions did not cause any significant change in the corrected absorbance of the nickel (II) complex. The tolerance level of the interfering ions and selectivity of this method was improved to acceptable limit $99 \pm 2\%$ by using suitable masking agents.

APPLICATIONS:

Separation of nickel (II) from associated metals:

The developed method was used for separation and determination of nickel (II) from associated metal ions containing Au(III), Bi(III), Cu(II), Co(II), Sb(III), Ru(III), Ir(III), Ag(I), Hg(II), Zn(II), Cd(II), and Fe(III). At pH 9.2, nickel (II) separated from these metal ions by its extraction with 5 cm^3 of 0.02 mol L^{-1} 2',4'-dinitro APTPT and 5 cm^3 of 0.5 mol L^{-1} pyridine in chloroform. Under these conditions metal ions remain quantitatively found in the aqueous phase. Therefore, for determination of metal ions from the aqueous phase, it was evaporated to moist

nickel (II), ligand and synergent. Based on this investigation the structure is recommended for the complex is shown in Fig. 7.

dryness by treating with 5 cm^3 conc. HNO_3 followed by HCl. Then the residue was dissolved in water and diluted to appropriate volume and determined by standard methods [39, 41-43]. The organic phase containing nickel (II)-2',4'-dinitro APTPT-pyridine complex was estimated spectrophotometrically at 660 nm against reagent blank. Some of the metal ions were strongly interfered with nickel (II) such as Cu(II), Hg(II), Co(II), and Cd(II)

Copper(II), Hg(II), Co(II), and Cd(II) were interferred with nickel (II) and co-extracted which affects on the colour stability of nickel (II) complex. Therefore, separation of these metal ions can be achieved by use of masking agent. Copper(II), Co(II) and Cd(II) masked by each of 1 mg of thiosulphate while Hg(II) was masked by 50 mg of sulphate, under these conditions the added metal ions remained in the aqueous phase quantitatively and were subsequently demasked by evaporation to moist dryness by treating with 2 cm^3 of conc. HClO_4 . The residue was dissolved in water, diluted to appropriate volume and metal ions were determined by standard methods (Table 5) [38, 39, 44, 45, 46]. The absorbance of nickel (II)-2',4'-dinitro APTPT-pyridine complex from organic phase was measured at 660 nm against reagent blank.

Determination of nickel (II) in a synthetic mixtures:

For validation of proposed analytical method, we have prepared the several synthetic

mixtures containing 30 $\mu\text{g mL}^{-1}$ of nickel (II) and known amount of different composition of metal ions were added followed by suitable masking agents. The recommended general spectrophotometric procedure used for analysis of nickel (II). The results were obtained in good agreement with the amount added (Table 6).

Determination of nickel (II) from alloys:

Analytical applicability of proposed method was also confirmed by analysis of standard alloys such as Monel metal (Shubh Chemi Incorporate, Mumbai), Gun metal (Kamini Industries, India), Brass (Shubh Chemi Incorporate, Mumbai), Nickel-Silver (ITA Laboratory, Mumbai), Cast iron (33b) and Nickel-Base alloy (Nimonic 901). About 0.1 g of each alloy was dissolved in 5.0 mL of *aqua-regia* and were heated almost to dryness. The allowed residue was filtered to remove silica and metastannic acid if present. The filtrate was diluted with water to 100.0 mL in a standard volumetric flask. An aliquot of nickel (II) content solutions are taken and was determined by recommended general procedure. The results mentioned in Table 7 and revealed good and perfect agreement with AAS.

Analysis of nickel (II) from foundry waste effluents:

The developed method used for investigation of nickel (II) from foundry waste effluents from Kolhapur city. Toady, Kolhapur city (Maharashtra State, India) is new born city for various industries and now well known for foundry industries since last 20 years. Day by day, foundry industries are going to increases in Kolhapur region. Therefore, environmental have affected by the foundry industries because in such foudrys for removal of adhering sand, scale and decomposition products high pressure streams of water are used against the castings. During the washings of castings eliminates the black waters which are extremely diilicult to filter and clarify. Therefore such foundry effluents are directly discharges into the fresh water. An object of the present invention is to determine the

trace nickel (II) from the foundry waste water in an efficient but simple manner.

The water samples were collected from various foundry region of Kolhapur city as mentioned in Table 8. Each sample (100.0 mL) was evaporated almost to dryness and treated with 5.0 mL concentrated nitric acid. The residue was boiled with 50.0 mL of water and filtered through Whatmann filter paper No. 1. The filtrate was diluted to required volume with water. An aliquot of nickel (II) solution was analyzed by the proposed method. The accuracy of the results obtained by proposed method were confirmed directly with AAS method.

Analysis of nickel (II) from electroless nickel plating waste water:

A wider variety of industrial parts were coated by electroless nikel (EN) plating techniques provides a large benefits towards the corrosion protection. The plating were crried out by chemical bath deposition techniques. Large amount of waste water discharges in to the environment fresh water. Therefore, the environment protection point of view, it is essential to develop an effective technique for determination of nickel (II) from electroless nickel plating (EN) waste water. In order to determine a nickel (II) from the electroless nickel plating waste water, the spectrophotometric method was carried out using a chromogenic reagent.

As mentioned in Table 9, the water samples were collected from various places of Gokul Shirgaon, MIDC, Kolhapur (Maharashtra State, India) and aliquot of nickel (II) solution was prepared and analyzed by same as above mentioned in topic 4.4.

CONCLUSION:

The method described the spectrophotometric determination of nickel (II) by using 2',4'-Dinitro APTPT as a metallochromic ligand. The developed method proved its sensitivity and selectivity towards the nickel (II). The developed method is simple, reproducible, rapid and reliable. Moreover, the method has advantages of less interference ions. Thus, it can acts as alternative

approach to the widely used instrumental techniques for determination of nickel (II) from natural waters. Due to following important features of the proposed method, it had been used for an analysis of nickel (II) from the industrial effluents as well as natural waters. (i) low ligand concentration; (ii) the recommended

extraction procedure is a single stage; (iii) 2',4'-dinitro APTPT forms complex with nickel (II) in weak acidic medium; (iv) pyridine used as a synergent; (v) stoichiometry of extracted species is 1:2:2 (M:L:Py); (vi) the ternary complex is stable for more than 48 h.

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Table 1. Comparison of the present method with other spectrophotometric methods for the determination of nickel (II)

Reagent	λ_{\max} nm	Acidity / pH	Beer's law validity range, ppm	Molar absorptivity Lit mol ⁻¹ cm ⁻¹ ϵ	M:L ^a	Remarks	Ref. No.
i) 2-[2-(6-Methyl benzothiazolyl)azo]-5-(N-methyl-N-sulphomethyl)amino- benzoic acid	642	pH 5.6	0-7	$\epsilon = 8.81 \times 10^4$ $s = 0.6 \times 10^{-3}$	1:2	<ul style="list-style-type: none"> Most foreign ions do not interfere 	15
ii) 2-[2-(6-Methyl benzothiazolyl)azo]-5-(N-ethyl-N-sulphomethyl) aminobenzoic acid	620		0-6	$\epsilon = 8.82 \times 10^4$ $s = 0.7 \times 10^{-3}$		<ul style="list-style-type: none"> Good selectivity 	
iii) 2-[2-(6-Methyl benzothiazolyl)azo]-5-(N-ethyl-N-carboxymethyl)aminobenzoic acid	625		0-12	$\epsilon = 1.03 \times 10^5$ $s = 0.5 \times 10^{-3}$		<ul style="list-style-type: none"> Absorbance was measured after 5 min 	
2-[2-(3,5-Dibromo- pyridyl)azo]-5-dimethylamino benzoic acid	618	pH 6.0	0.04-0.4	$\epsilon = 1.50 \times 10^5$	1:2	<ul style="list-style-type: none"> Cu(II), Co(II), Fe(III), Pd(II), V(II) seriously interfered Absorbance was stable for 24 h 	16
4-(2-Benzo-thiazolylazo) salicylic acid	525	pH 7.0	0.59-7.08	$\epsilon = 0.6 \times 10^4$ $s = 2.824 \times 10^{-9}$	1:1	<ul style="list-style-type: none"> Fe(III), F⁻, HPO₄²⁻ interfered seriously 	17
2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol	520 and 560	pH 5.5	0-15	$\epsilon = 1.26 \times 10^5$	1:2	<ul style="list-style-type: none"> Absorbance was measured after 30 min Absorbance was stable for 24 h 	18
2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol	547	pH 2.5	0.4-72	$\epsilon = 1.0 \times 10^5$	-	<ul style="list-style-type: none"> Equilibrium time 20 min Absorbance measured at 457 nm and 526 nm 	19
2-(2-Thiazolylazo)- <i>p</i> -cresol	pH 5.7	580	20-70	$\epsilon = 2.6 \times 10^4$	-	<ul style="list-style-type: none"> Equilibrium time 10 min Absorbance was stable for 24 h 	20
1-(1,2,4-Triazolyl-3-azo)-2 naphthol	pH 5.0	523	0.2-2.8	$\epsilon = 3.7 \times 10^4$	-	<ul style="list-style-type: none"> Cd(II), Co(II), Cu(II), Fe(III), Hg(II), La(III), V(IV) were interfered 	21
1-(2-Thiazolylazo) 2-naphthol	pH 8.0	621	0.05-1.05	$s = 0.012$	-	<ul style="list-style-type: none"> Simultaneously determined Co(II) and Cu(II) with nickel (II) 	22
<i>p</i> -Acetyl aresenazo	pH 6.0	630	0-0.8	$\epsilon = 6.5 \times 10^4$	1:2	<ul style="list-style-type: none"> Absorbance was stable for 48 h Maximum absorbance measured after 1 min 	23
Benzothiazolyldiazoaminoazobenzene	pH 9.4	550	0-0.7	$\epsilon = 1.96 \times 10^5$	-	<ul style="list-style-type: none"> <i>p</i>-Octyl polyethylene glycol 	24

							phenyl ether was used as a emulsifier	
							<ul style="list-style-type: none"> Equilibrium time 50 min 	
5,17-Bis(quinolyl-8-azo)-25,26,27,28-tetrahydroxycalix [4]arene	pH 10.7	580	1.7×10^{-7} – 5.1×10^{-6}	$\epsilon = 1.28 \times 10^5$	1:1		<ul style="list-style-type: none"> Highly sensitive Absorbance was stable for 3 h 	25
5-(6-Methoxy-2-benzothiazole azo)-8-aminoquinolene	pH 10	623	0-0.32	$\epsilon = 1.28 \times 10^5$	1:3		<ul style="list-style-type: none"> CTAB was used as a surfactant Absorbance was measured after 20 min 	26
Ammonium 2-amino-1-cyclohexene-1-dithiocarboate	pH 3.0-8.0	535	0-4.0	$\epsilon = 2.8 \times 10^4$	1:2		<ul style="list-style-type: none"> Higher pH range Low interference of ions 	27
2-Hydroxy-1-naphthaldoxime	pH 5.8	410	5-50	$\epsilon = 8.1 \times 10^3$	1:2		<ul style="list-style-type: none"> Equilibrium time 10 min 	28
N-ethyl-3-carbazolecarboxy- aldehyde-3-thiosemicarbazone	pH 6	400	1.2-5.6	$\epsilon = 1.114 \times 10^4$ $s = 5.29 \times 10^{-3}$	-		<ul style="list-style-type: none"> Absorbance was stable for 72 h Less interfered 	29
1-Phenyl-1,2-propanedione-2-oxime thiosemicarbazone	pH 3-4	395	0.42-3.76	$\epsilon = 1.01 \times 10^4$ $s = 5.0 \times 10^{-3}$	1:2		<ul style="list-style-type: none"> Absorbance was stable for 12 h 	30
2,2'-Dihydroxybenzophenone thiosemicarbazone	pH 7.8	385	5-40	$\epsilon = 15.4 \times 10^3$	-		<ul style="list-style-type: none"> Absorbance was stable for 24 h 	31
2-Pyridinecarbaldehyde 3,5-dinitro-2-pyridylhydrazone	pH 4.5	484	0-6	$\epsilon = 1.0 \times 10^5$	1:2		<ul style="list-style-type: none"> Equilibrium time 7 min 	32
2-Benzoyl pyridine-2-pyridyl hydrazone	pH 8.3	375, 385	0-1.5	$\epsilon = 5.04 \times 10^4$	-		<ul style="list-style-type: none"> Extraction method was free from interference ions Synergistic effect caused by thiocyanate ion 	33
2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol	pH 5.25	530 and 562	10-200	$\epsilon = 1.10 \times 10^5$	1:2		<ul style="list-style-type: none"> Triton X-100 was used as a surfactant Absorbance was measured after 50 min Absorbance was stable for 24 h 	34
2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol	pH 4.5	530 and 560	0-0.40	$\epsilon = 1.22 \times 10^4$ at 530 and $\epsilon = 8.20 \times 10^4$ at 560 nm	-		<ul style="list-style-type: none"> Tergitol NPX was used as a surfactant Absorbance was measured after 50 min Absorbance was stable for 6 h 	35

Table 2. Spectral characteristics and precision data of nickel (II)-2',4'-dinitro APTPT-pyridine complex

Optical characteristics and precision	Parameters
Solvent	Chloroform
λ_{\max} (nm)	660
pH range	8.7-9.7
2',4'-dinitro APTPT concentration	5 mL (0.02 mol L ⁻¹)
Pyridine concentration	5 mL (0.5 mol L ⁻¹)
Equilibrium time (min)	10
Stability (h)	> 48
Beer's law range ($\mu\text{g mL}^{-1}$)	5-50
Ringbom optimum conc. range ($\mu\text{g mL}^{-1}$)	10-40
With pyridine	
Molar absorptivity (lit mol ⁻¹ cm ⁻¹)	1.67×10^3
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.058
Without pyridine	
Molar absorptivity (lit mol ⁻¹ cm ⁻¹)	7.4×10^2
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.78
Relative standard deviation*, (%)	0.16
Range of error	± 0.2
Mean recovery	99.8 ± 0.06
Stoichiometry of the extracted complex	1:2:2

*Average of five determinations

Table 3. Effect of solvent on extractability of nickel (II)-2',4'-dinitro APTPT-pyridine complex

Solvent	Dielectric constant	λ_{\max} , nm	Absorbance	% Extraction
Kerosene	1.80	460	0.032	6.14
<i>n</i> -Butanol	11.20	465	0.039	7.48
Amyl acetate	17.10	460	0.050	9.59
Amyl alcohol	2.30	450	0.115	22.07
Toluene	2.38	415	0.138	26.48
Xylene	5.00	425	0.303	58.15
Methyl isobutylketone	13.11	445	0.326	62.57
1,2-Dichloroethane	2.24	425	0.439	84.26
Carbon tetrachloride	4.40	435	0.486	93.28
Chloroform	10.50	460	0.512	99.99

Table 4. Study of diverse ions for the determination of 30 µg mL⁻¹ nickel (II) with 2',4'-dinitro APTPT at 660 nm (relative error ±2%)

Ions added as	Tolerance limit, mg
Fluoride, bromide, nitrate, nitrite, tartarate, malonate, oxalate,	100
Mg(II), Ca(II), Te(IV), sulphate, thiourea, salicylate	50
Ir(III), Tl(III), Se(IV), acetate, succinate	25
Mo(VI), Al(III), Zn(II), Ga(III), Sr(II), Nb(V)	15
Mn(II) ^c , Bi(III), W(VI), Sn(II), Cd(II) ^a , Hg(II) ^b , Pd(II), citrate	10
In(III), Cr(VI) ^d , Cr(III), Sn(IV), Co(II) ^a , Mn(VII) ^a , ascorbate	5
Y(III), Th(IV), Fe(II), Pb(II), Pt(IV), Ti(III), Gd(III), Cu(II) ^a	3
Sb(III), Au(III), Ag(I), Ru(III), Fe(III), thiocyanate, thiosulphate	1
U(VI), Zr(IV), Os(VIII), Rh(III)	0.500
Iodide, EDTA	None

^a = Masked by 1mg Thiosulphate ^b = Masked by 50 mg Sulphate

^c = Masked by 100 mg Fluoride ^d = Masked by 10 mg Citrate

Table 5. Separation of nickel (II) from associated metal ions

Metal ion	Amount taken, µg	Average % Recovery*	R.S.D. %	Chromogenic ligand	Reference number
Ni(II)	300	99.8	0.15		
Hg(II) ^b	100	99.9	0.07	PAR	38
Ni(II)	300	99.5	0.49		
Zn(II)	100	98.4	1.11	PAR	38
Ni(II)	300	99.8	0.22		
Cd(II) ^a	100	99.5	1.23	PAR	38
Ni(II)	300	99.9	0.27		
Bi(III)	100	99.7	0.11	Ascorbic acid + KI	39
Ni(II)	300	99.8	0.20		
Sb(III)	250	98.8	1.32	Ascorbic acid + KI	39
Ni(II)	300	99.9	0.06		
Fe(III)	50	98.6	1.39	Thiocyanate	39
Ni(II)	300	99.7	0.23		
Ir(III)	150	99.6	0.41	HBr + SnCl ₂	39
Ni(II)	300	99.8	0.09		
Au(III)	1000	99.9	0.17	2',4'-Dinitro APTPT	41
Ni(II)	300	99.7	0.30		
Ru(III)	200	99.6	0.42	Thiourea	43
Ni(II)	300	99.9	0.10		
Cu(II) ^a	500	99.8	0.05	2',4'-Dinitro APTPT	44
Ni(II)	300	99.9	0.24		
Co(II) ^a	100	99.8	0.15	2',4'-Dinitro APTPT	45
Ni(II)	300	99.9	0.15		
Ag(I)	50	99.7	0.26	2',4'-Dinitro APTPT	46

* = Average of five determinations ^a = Masked by 1mg Thiosulphate ^b = Masked by 50mg Sulphate

Table 6. Determination of nickel (II) from ternary synthetic mixtures

Composition (μg)	Average Recovery*, %	R.S.D., %
Ni(II), 300; Cu(II) ^a , 300; Co(II) ^a , 100	99.9	0.09
Ni(II), 300; Fe(III), 50; Mn(II), 100	99.9	0.12
Ni(II), 300; Cu(II) ^a , 300; Zn(II), 100	99.8	0.09
Ni(II), 300; Ag(I), 50; Au(III), 100	99.7	0.18
Ni(II), 300; Pd(II), 100; Au(III), 100	99.8	0.13
Ni(II), 300; Pd(II), 100; Ir(III), 200	99.9	0.15
Ni(II), 300; Mn(II), 100; Mo(VI), 100	99.8	0.09
Ni(II), 300; Cd(II) ^a , 100; Pb(II), 100	99.8	0.09
Ni(II), 300; Hg(II) ^b , 100; Bi(III), 100	99.9	0.09
Ni(II), 300; Sn(II), 300; Pb(II), 100	99.9	0.17
Ni(II), 300; Ag(I), 100; Cd(II) ^a , 100	99.9	0.10
Ni(II), 300; Au(III), 100; Hg(II) ^b , 100	99.9	0.09

* Average of five determinations

^a = Masked by 1mg Thiosulphate^b = Masked by 50 mg Sulphate

Table 7. Determination of nickel (II) from alloys

Composition of Alloy, %	Certified values of Ni(II), %	Amount of Ni(II) found*, %		Confidence limit $\alpha = 0.95$	R.S.D., %
		AAS method	Proposed method		
Monel Metal (Shubh Chemi Incorporate, Mumbai) Cu ^a , 80.1; Mn ^b , 13.50; Fe, 0.68	4.65	4.64	4.63	0.04	0.22
Gun Metal (Kamini Industries supplied standards, India) Cu ^a , 65; Fe, 0.5; Sn, 1; Pb, 20, Zn, 30	0.3	0.3	0.29	0.13	0.08
Brass (Shubh Chemi Incorporate, Mumbai) Zn, 41.90; Fe, 0.78; Mn ^b , 0.55; Al, 0.51	0.3	0.3	0.28	0.21	0.15
Nickel-Silver (ITA, Laboratory, India) Cu ^a , 54.6; Pb, 0.13; Sn, 0.05; Mn ^b , 0.21	17.4	17.2	17.2	0.08	0.03
Cast Iron alloy 33b Si, 2; Mn ^b , 0.5; Cr, 0.5; Mo, 0.5	2.0	2.0	1.92	0.06	0.15
Nickel-Base alloy 387 BCS (Nimonic 901) Cr ^c , 12.46; Co ^a , 21; Ti, 2.95; Al, 0.24; Mo, 5.83; Mn ^b , 0.08; Fe, 36; Cu, 0.032	41.9	41.8	41.76	0.11	0.09

* = Average of five determinations ^a = Masked by 1mg Thiosulphate^b = Masked by 100 mg Fluoride ^c = Masked by 10 mg Citrate

Table 8. Analysis of nickel (II) from foundry waste water effluents

Foundry waste effluent water	Amount of Ni(II) found* mg		Confidence limit $\alpha = 0.95$	R.S.D., %
	L ⁻¹			
	Proposed method	AAS method		
Gokhale College, Kolhapur ^a	7.4	7.3	0.03	0.002
Udyamnagar, Kolhapur ^a	9.8	9.7	0.21	0.016
Near Panchanganga River ^a	12.5	12.4	0.11	0.004
Rankala Lake ^b	4.6	4.5	0.06	0.012
Rankala Lake ^b	4.4	4.4	0.08	0.031
MIDC-Kagal ^c	14.8	14.9	0.11	0.028

* Average of five determinations

^a Jayanti Nala (River), Kolhapur City, Maharashtra, India.

^b Rankala Lake, Kolhapur City, Maharashtra, India.

^c Waste effluent water from MIDC-Kagal, Kolhapur, Maharashtra, India.

Table 9. Analysis of nickel (II) from electroless nickel plating waste water

Electroless nickel plating waste water	Amount of Ni(II) found* mg		Confidence limit $\alpha = 0.95$	R.S.D., %
	L ⁻¹			
	Proposed method	AAS method		
Waste water Sample 1 ^a	4.1	4.3	0.02	0.014
Waste water sample 2 ^a	4.8	4.7	0.02	0.006
Waste water sample 3 ^b	5.9	5.8	0.13	0.011
Waste water sample 4 ^b	6.3	6.5	0.05	0.018

* Average of five determinations

^a Gokulshirgaon, MIDC, Kolhapur, Maharashtra, India.

^b Shirolu MIDC, Kolhapur, Maharashtra, India.

Figures:

Fig. 1. (A) Absorption spectra of 2',4'-dinitro APTPT Vs. Chloroform blank

(B) Absorption spectra of Ni(II)-2',4'-dinitro APTPT-pyridine complex Vs. 2',4'-dinitro APTPT blank

Ni(II) = 30 $\mu\text{g mL}^{-1}$, pH = 9.2, 2',4'-Dinitro APTPT = 5 cm^3 of 0.02 mol L^{-1} , Pyridine = 5 cm^3 of 0.5 mol L^{-1} , Solvent = Chloroform, Equilibrium Time = 10 min, Wavelength = 300 to 800 nm.

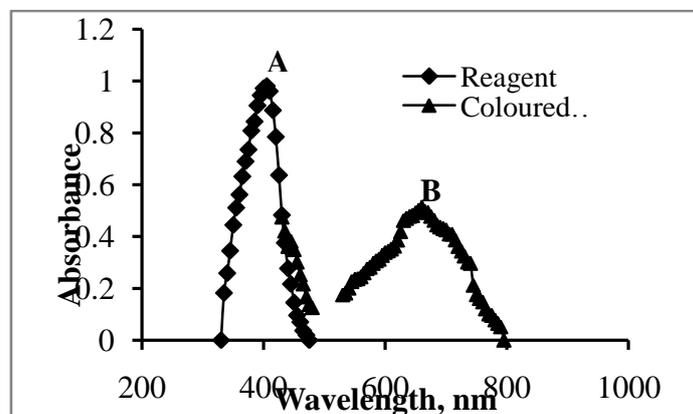


Fig. 2. Effect of pH on the extraction of

(A) Ni(II)-2',4'-dinitro APTPT-pyridine complex

(B) Ni(II)-2',4'-dinitro APTPT complex

Ni(II) = 30 $\mu\text{g mL}^{-1}$, pH = 1-14, 2',4'-Dinitro APTPT = 5 cm^3 of 0.02 mol L^{-1} , Pyridine = 5 cm^3 of 0.5 mol L^{-1} , Solvent = Chloroform, Equilibrium Time = 10 min

$\lambda_{\text{max}} = 660 \text{ nm}$.

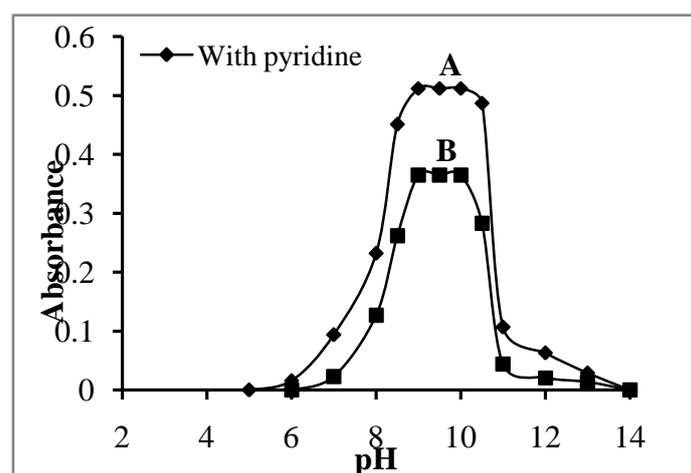
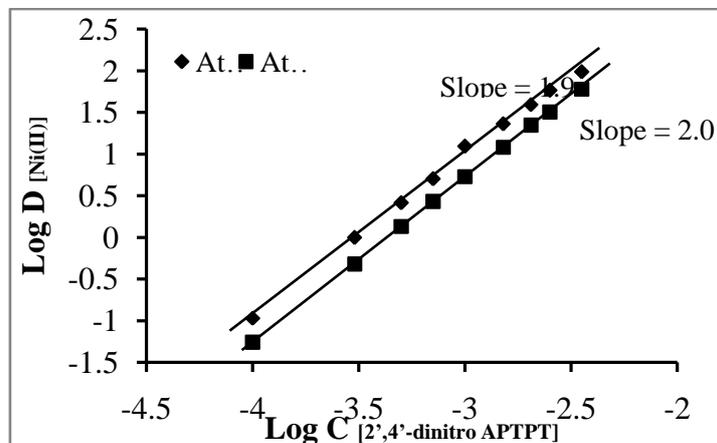


Fig. 3. Slope ratio method: With fixed pyridine concentration

Log D_[Ni(II)] – Log C_[2',4'-dinitro APTPT] plot for determination of composition of extracted species in chloroform

Ni(II) = 30 µg mL⁻¹, pH = 8.0 and 10.2, 2',4'-Dinitro APTPT = 0.1 to 3.5 cm³ of 0.02 mol L⁻¹ Pyridine = 5 cm³ of 0.5 mol L⁻¹, Solvent = Chloroform, Equilibrium Time = 10 min, λ_{max} = 660 nm.

**Fig. 4. Slope ratio method: With fixed 2',4'-dinitro APTPT concentration:**

Log D_[Ni(II)] – Log C_[Pyridine] plot for determination of composition of extracted species in chloroform

Ni(II) = 30 µg mL⁻¹, pH = 8.0 and 10.2, 2',4'-Dinitro APTPT = 5 cm³ of 0.02 mol L⁻¹ Pyridine = 0.1 to 3.5 cm³ of 0.5 mol L⁻¹, Solvent = Chloroform, Equilibrium Time = 10 min, λ_{max} = 660 nm.

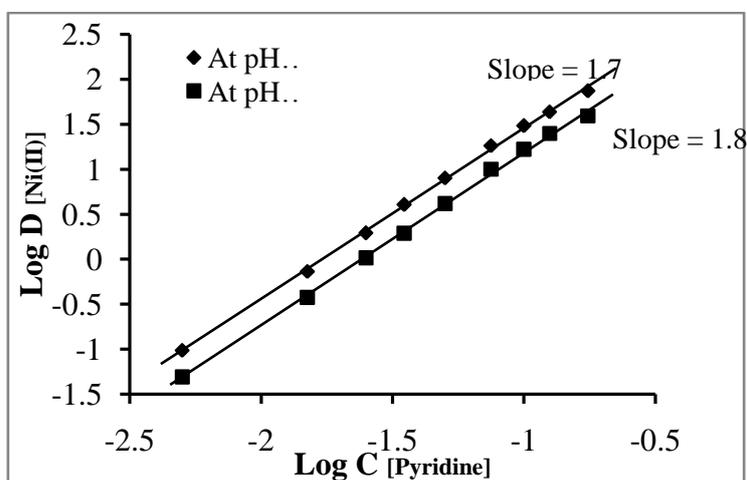


Fig. 5. Mole ratio method for determination of composition of complex Ni(II)-2',4'-dinitro APTPT-pyridine complex

Ni(II) = 0.2 to 1.8 cm³ of 50 μg mL⁻¹, pH = 9.2, 2',4'-Dinitro APTPT = 1.0 cm³ of 8.518 x 10⁻³ mol L⁻¹, Equilibrium Time = 10 min, Pyridine = 5.0 cm³ of 8.518 x 10⁻³ mol L⁻¹, Solvent = Chloroform, λ_{max} = 660 nm.

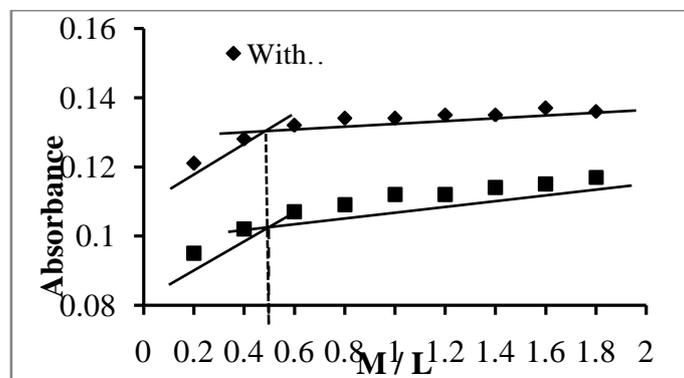


Fig. 6. Job's plot for continuous variation method for Ni(II)-2',4'-dinitro APTPT-pyridine complex

Ni(II) = 0.2 to 1.8 cm³ of 50 μg mL⁻¹, pH = 9.2, Pyridine = 5.0 cm³ of 8.518 x 10⁻³ mol L⁻¹, Equilibrium Time = 10 min, 2',4'-Dinitro APTPT = 0.2 to 1.8 cm³ of 8.518 x 10⁻³ mol L⁻¹, Solvent = Chloroform, λ_{max} = 660 nm.

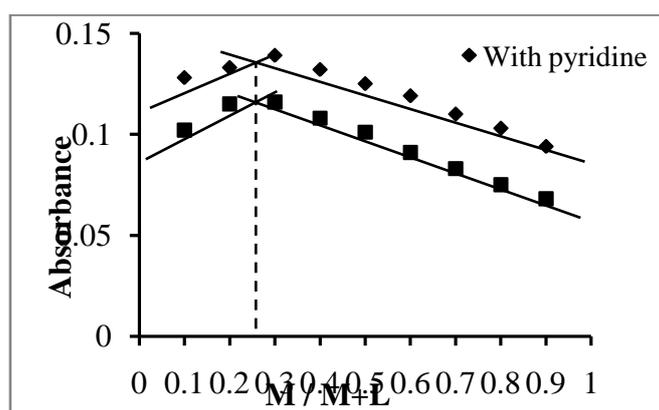


Fig. 7. Structure of Ni(II)- 2',4'-dinitro APTPT-pyridine complex

