Mater. Environ. Sci. 5 (4) (2014) 1188-1199 *Reddy*
ISSN : 2028-2508
CODEN: JMESCN

Extractive direct and derivative spectrophotometric determination of Nickel (II) in Medicinal leaves, Soil, and Alloy samples by using Pyridoxal-3-thiosemicarbazone (PDT)

D. Nagarjuna Reddy
Department of Chemistry, Analytical division, College of Natural and Computational Sciences, Mekelle University, Mekelle, Ethiopia. P.O Box-231.

Received 2 Jan 2014, Revised 4 May 2014, Accepted 4 May 2014
**Corresponding author. Email: dndnrchem@gmail.com*

Abstract
Nickel(II) reacts with 3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carbaldehyde thiosemicarbazone or Pyridoxal-3-thiosemicarbazone (PDT) and forms a yellow colored complex, which was extracted into isobutanol from sodium acetate and acetic acid buffer at pH 6.0. The absorbance value of the Ni(II)–PDT complex was measured at different intervals of time at 430 nm, to ascertain the time stability of the complex. The extraction of the complex into the solvent was instantaneous and stable for more than 5hrs. The system obeyed Beer's law in the concentration range of 0.35-3.53 µg/ml of nickel(II), with an excellent linearity and a correlation coefficient of 0.999. The molar absorptivity and Sandell's sensitivity of the extracted species were found to be 1.6×10^4 L mol^{-1} cm^{-1} and 3.6×10^{-3} µg/cm^2 at 430 nm, respectively. Hence, a detailed study of the extraction of nickel(II) with PDT has been undertaken with a view to developing a rapid sensitive extractive direct and derivative spectrophotometric method for the determination of nickel(II) when present alone or in the presence of diverse ions which are usually associated with nickel(II) in medicinal leaves, soil and leafy vegetable oils. Various standard alloy samples (CM 247 LC, IN 718, BCS 233, 266, 253 and 251) have been tested for the determination of nickel for the purpose of validation of the present method. The results of the proposed method are comparable with those from atomic absorption spectrometry and were found to be in good agreement.

Key words: Nickel(II); Extractive spectrophotometry; pyridoxal-3-thiosemicarbazone; AAS

1. Introduction
Nickel is present in small amounts in soils, plants and animal tissues. The main source of nickel comes from the hydrogenation of oils, iron factories, from the combustion of coal, diesel and residual oils, tobacco smoke, chemicals and catalysts [1]. It is used in nickel plating and also in the manufacture of alloys along with iron, copper, aluminum, chromium, zinc and molybdenum. Nickel containing steels are highly resistant to corrosion. Because of its high melting point (1453°C), nickel is also used in the production of heat-resistant steels and cast iron. Nickel-plated steels are used in the manufacture of some food processing vessels and many other pieces of equipment. Nickel(II) is present in small amounts in most soils, plants and animal tissues. The interest in the determination of nickel has grown considerably in recent years, owing to its involvement in some essential metabolic processes [2]. Nickel is relatively non-toxic and does not cause any serious human health hazard, despite the fact that acid foods take up nickel during cooking. The nickel deposited in the human body from nickel vessels is not readily absorbed and causes no detectable hazard. However, a high incidence of respiratory tract neoplasia among workers in nickel refineries and carcinogenic properties of this metal have been reported [1]. Thiosemicarbazones have a wide range of applications in medicine and agriculture. Owing to the ability of these reagents to form intense colored complexes with various metal ions [3-5] they are widely employed in spectrophotometric and extractive spectrophotometric analysis, atomic absorption spectrometry and solid–liquid separation. The nickel(II)–thiosemicarbazone complexes have intense colors and high molar absorptivities when compared with the analogous thiosemicarbazone complexes. A literature survey indicated that only a few

thiosemicarbazones [6-25] have been explored for the extractive spectrophotometric determination of nickel(II) and Pyridoxal-3-thiosemicarbazone (PDT) has so far not been used as an analytical reagent for the extraction of nickel(II). In the present work, PDT has been examined in order to evaluate its usefulness as an extractive spectrophotometric reagent for nickel(II). Further, this method has been applied successfully for the analysis of nickel(II) in environmental matrices like soil and industrial effluents. For the determination of nickel at micro levels there are several frequently adopted methods using analytical techniques such as AAS, ICP–OES, ICP–AES, ICP–MS, X-ray fluorescence spectroscopy, spectrophotometry, spectrofluorometry and other such techniques. Among these, the spectrophotometric methods are preferred as they are cheaper and easier to handle and have comparable sensitivity. The present method when compared with other existing spectrophotometric methods is found to be more sensitive and selective.

2. Materials and Methods

2.1. Instrumentation

A Perkin-Elmer lambda 25 UV–VIS spectrophotometer with a 1.0 cm quartz cell was used for absorbance studies. An Elico LI-120 digital pH meter was used for pH adjustment. A Perkin–Elmer 2380 atomic absorption spectrometer was used for the comparison of results.

2.2. Reagents and Samples

Pyridoxal amounting 0.5 g was dissolved in 25.0 ml ethanol and mixed in a flask containing 1.5 g 3-thiosemicarbazide dissolved in 25.0 ml of a 1:1 ethanol–water mixture. The resulting reaction mixture was refluxed in a water bath for 30 min. It was allowed to stand at room temperature until pale yellow crystals were formed [26]. The crystals were separated and recrystallized from ethanol (Scheme 1).

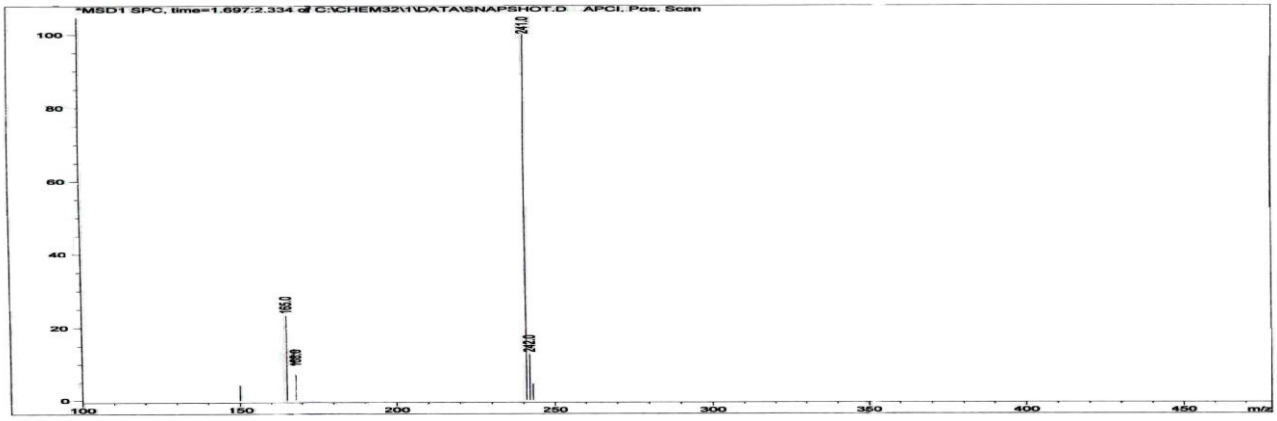
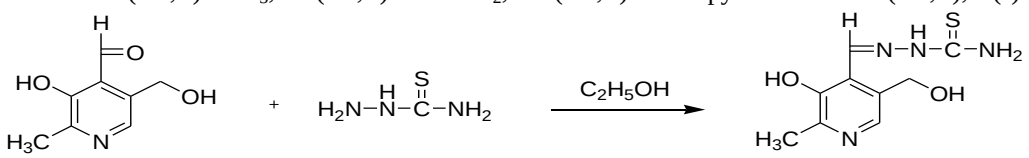


Figure 1: Mass spectrum of Pyridoxal-3-thiosemicarbazone.

The molecular formula and molecular weight of PDT are $C_9H_{12}N_4O_2S$ and 240, respectively; it is shown in the figure.1. The compound was characterized by IR and ^{1}H-NMR spectral data is shown in the figure 2 and 3 respectively. Infra red spectrum of PDT shows bands at 3450(s), (3288(s), 3239(s), 3043(m), 1577(s), 1537(s), 1497(s), 1364(w), 1147(m), 832(s) and 681(s)cm^{-1} corresponding to ν(C-OH), ν(N–H) (asymmetric and symmetric), ν(C–H)aromatic stretch, ν(C=N)stretching(Schiff base), ν(C–H) aromatic ring, ν(C–H)of pyridine ring, ν(N–H) stretch(primary amide), ν(C=S), ν(C–H)-oop bend (aromatic) and ν(C–C)-oop bend aromatic ring vibrations. ^{1}H-NMRspectrum of PDT ($CDCl_3$+DMSO–d_6) showed signals at 2.15 (3H, s) –CH_3, 2.6(2H, s) C=C-CH_2, 7.7 (1H, s) due to pyridine and 5.4 (1H, s), C(s)-OH.



Pyridoxal 3-thiosemicarbazide Pyridoxal-3-thiosemicarbazide

Scheme-1 synthesis of pyridoxal-3-thiosemicarbazone (PDT)

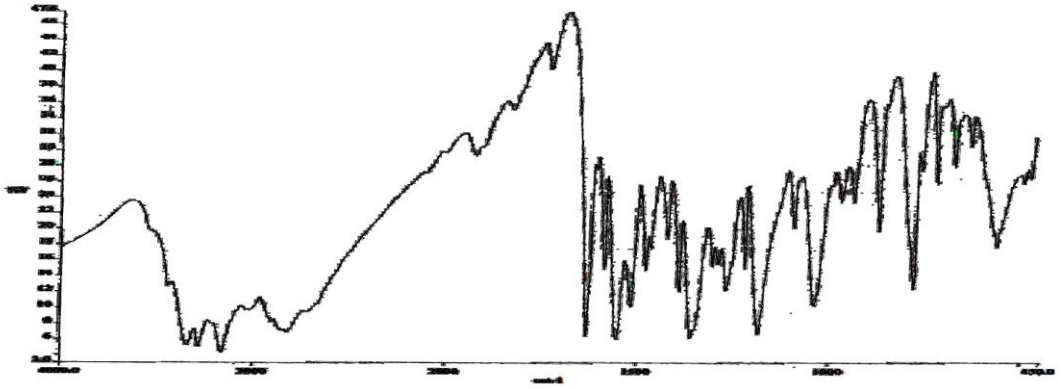


Figure 2: Infrared spectral data of Pyridoxal-3-thiosemicarbazone.

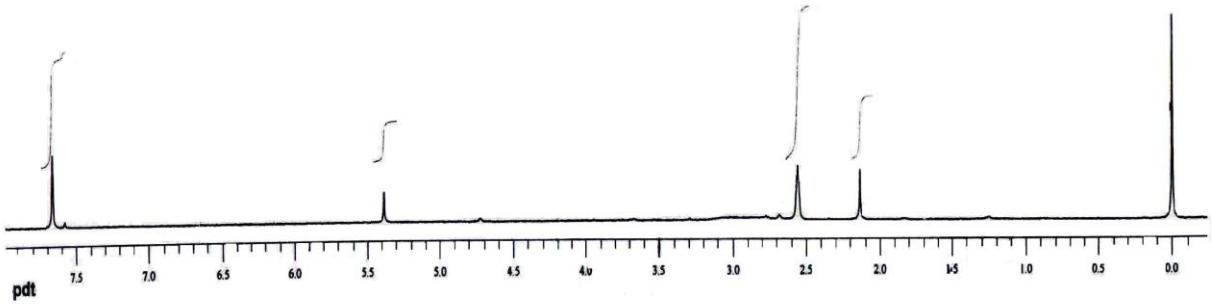


Figure-3: ^{1}H-NMR Spectrum of Pyridoxal-3-thiosemicarbazone

2.3. Preparation of Standard Solution of Nickel(II)

A total of 6.73 g of ammonium nickel sulfate hexahydrate [$(NH4)_2Ni(SO4)_26H_2O$)] was weighed, dissolved in double-distilled water containing a few drops of concentrated sulfuric acid and made up to one liter. The stock solution was then standardized gravimetrically using dimethylglyoxime[27]. The required dilute solutions of nickel(II) were prepared by diluting the stock solution with double-distilled water. All reagents used were of analytical reagent grade unless otherwise stated.

2.3.1. Buffer Solutions

1.0 M Hydrochloric acid and 1M sodium acetate (pH 0.5-3.0), 0.2 M of NaOAc and 0.2 M AcOH (pH 4.0-7.0) and 2.0 M NH_4Cl - 2.0 M NH_4OH (7.0-10.0) buffer solutions were prepared in distilled water. Suitable portions of these solutions are mixed to get the desired pH.

2.3.2. Analytical Procedure for Medicinal leaves and soil samples.

The samples of medicinal leaves and soil were dried in open air to prevent them from mineral concentration. The dried sample was pulverized to a convenient size in a mortar for the purpose of analysis. Ten grams of the powdered medicinal leaves/soil or 10mL of industrial effluent,10mL nitric acid and 1mL of sulphuric acid were transferred into a 100 mL standard flask. A pre cleaned glass funnel was inserted and heated on a hot plate at approximately 290°C until nitrogen oxide fumes just give off. The digestion was repeated with three heating steps after the final addition of nitric acid until the nitrogen oxide fumes and the sulphite have disappeared. The flask was cooled for about 2min and the funnel was rinsed with a small volume of deionizer double-distilled water in the flask and the contents were transferred into a 25mL calibrated flask and made up to the mark with deionizer double-distilled water. The concentration of nickel was determined by the general procedure described.

2.3.3. Analytical Procedure for Standard Alloy Samples

A total of 0.1 g of each oven-dried (110°C) alloy sample was dissolved in 15 ml of aquaregia. The solution was heated to near dryness and nitrate was expelled from the residue, using 5ml of concentrated hydrochloric acid. Each residue was extracted into double-distilled water, separately, and made up to 100 ml.

2.3.4. General Procedure

To an aliquot of a working standard solution containing 0.1–10 µg ml^{-1} nickel(II) were added pH 6.0 buffer (3 ml), 1 x 10^{-3}M reagent solution (1 ml) and a salting-out agent, 0.1 M magnesium sulfate (1 ml). The mixture was shaken two times with 10 ml portions of isobutanol each time for 1 min and allowed to stand for a few minutes. The two organic phases were collected into a 25.0 ml volumetric flask and made up to the mark with isobutanol. The absorbance's of all the organic phases were measured at 430nm against the reagent blank.

3. Results and Discussion

3.1. Absorption Spectra of The Reagent and Ni(II)–PDT Complex

An aliquot of 1.0 ml of 4 x 10^{-5}M nickel(II) solution was transferred into a 25ml separating funnel and to it; 3.0 ml of buffer (pH 6.0) and 1.0 ml of 4 x10^{-4} M PDT solutions were added. The absorption spectrum of the reagent solution against the solvent blank, and the absorption spectrum of the solution containing nickel(II) complex against the reagent blank is given in Figure 4. From the spectra, it is clear that the Ni(II)–PDT complex and the reagent have maximum absorbance at 430 and 390 nm, respectively. The reagent has a minimum absorbance at the maximum absorbance of the complex and does not interfere in the determination of nickel(II). Hence, further absorbance measurements of the complex were carried out at 430 nm.

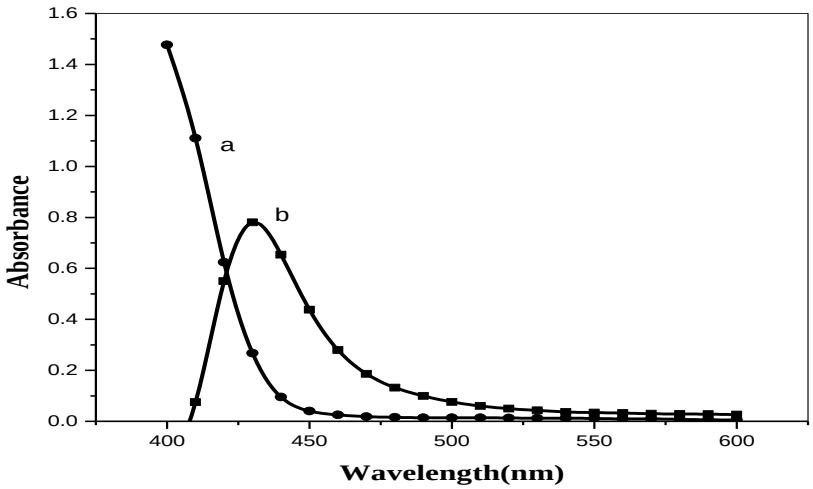


Figure 4: Absorption Spectra of a. PDT Vs Water blank, b. Ni(II) –PDT Vs PDT, Ni(II): 1.0 ml of 4 x10^{-5} M, PDT: 1.0 ml of 4 x10^{-4} M, pH:6.0, λmax 430 nm.

3.2. Effect of pH on The Extraction of Ni(II)–PDT complex

A preliminary study showed that the formation of Ni(II)–PDT complex was affected by the hydrogen ion concentration. The optimum pH range for the absorbance was determined by using buffers such as potassium chloride–hydrochloric acid (pH 1.0–2.5), sodium formate–formic acid (pH 2.6–3.5), sodium acetate–acetic acid (pH 3.6–6.9) and ammonium chloride–ammonium hydroxide (pH 7.0–11.0). In each case, a mixture containing 1.0 ml of 4 x10^{-5}M nickel(II) solution, 3.0 ml of the suitable buffer and 1.0 ml of 4 x10^{-4} M of PDT solution were taken into a 25ml separating funnel and the volume of the aqueous phase adjusted to 10.0 ml with double distilled water. The absorbance's of all the organic extracts was measured at 430 nm using their respective reagent blanks. A graph between pH and absorbance is given in Figure 5. This indicates that the complex shows constant and maximum absorbance in the pH range 5.0—7.0. Hence, pH 6.0 is chosen for all further studies.

3.3. Effect of Reagent Concentration on The Absorbance of Ni(II)–PDT complex

The effect of reagent concentration on the formation of the Ni(II)–PDT complex was studied using 1.0 ml of 4x10^{-5} M metal ion solution, 3.0ml of pH 6.0 buffer and 1.0 ml of PDT solution containing different concentrations ranging from 4 x 10^{-4} M to 12.03 x10^{-4} M. The total volumes of the aqueous phases were brought

up to 10.0 ml with double-distilled water. The aqueous phases were shaken separately with 10.0 ml of isobutanol, and the organic phases were collected into 25 ml standard flasks. The organic phases were made up with isobutanol to the mark and the absorbances of these phases were measured at 430nm, against their corresponding reagent blanks it is shown in the table.1. This study has revealed that a ten-fold molar excess of the PDT to that of nickel is necessary for maximum extraction of the metal ion. Hence, a tenfold molar excess of the reagent was maintained for maximum extraction of nickel(II).

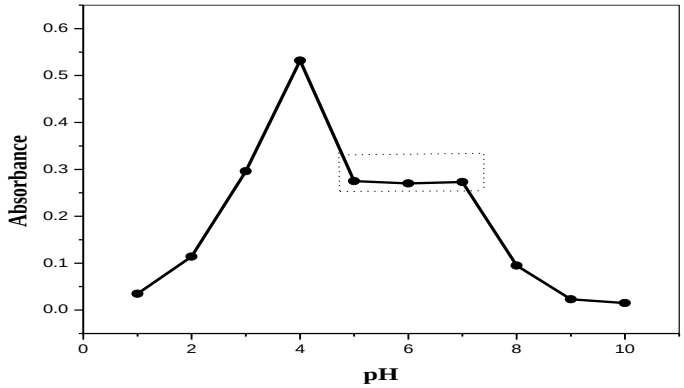


Figure 5: Effect of pH on the absorbance of Ni(II) –PDT complex, Ni(II): 1.0 ml of 4 x10^{-5} M, PDT: 1.0 ml of 4 x10^{-4} M, λmax 430 nm.

Table 1: Effect of regeant concentration on the absorbance of Ni(II)-PDT complex: M= Metal and L= Ligand

M:L	1:05	1:10	1:15	1:20	1:25	1:30
Absorbance	0.585	0.654	0.668	0.662	0.663	0.661

3.4. Effect of solvents on the extraction of Ni(II)–PDT complex

Solvents such as isoamylalcohol, n-amylalcohol, n-butanol, isobutanol, n-hexanol, benzene, xylene, chloroform, carbon tetrachloride, cyclohexane, cyclohexanol and methylisobutylketone were examined as extractants. As per the results reported in Table 2, isobutanol was found to be a suitable solvent for the effective extraction of Ni(II)–PDT complex. Hence, isobutanol was chosen for all further studies.

Table 2: Effect of solvents on the extraction of Ni(II)-PDT complex

Solvent	**Absorbance**
n-Amyl alcohol	0.731
Isoamyl alcohol	0.672
Benzene	0.613
n-Butanol	0.693
Isobutanol	0.801
n-hexanol	0.615
Xylene	0.754
Chloroform	0.732
Cyclohexanane	0.681
Cyclohexanol	0.785
Carbon tetrachloride	0.793
Methyl isobutyl ketone	0.641

Ni(II): 1.0 ml of 4x10^{-5} M; PDT: 1.0 ml of 4x10^{-4} M; pH: 6.0; λmax: 430 nm.

3.5. Effect of Salting-out Agents on The Extraction of Ni(II)–PDT complex

Various salting-out agents, such as magnesium sulfate, magnesium nitrate, lithium acetate, lithium sulfate, lithium nitrate and ammonium sulfate were employed to enhance the metal complex extraction into organic

solvent in a single step. After the studies, it was observed that the presence of 0.1 M magnesium nitrate solution enhanced the extraction. The presence of nickel(II) in the aqueous phase after extraction was tested gravimetrically by using dimethylglyoxime. It was found that with magnesium nitrate as a salting-out agent, the complex was extracted quantitatively into isobutanol.

3.6. Time Stability of the Color Reaction

The absorbance value of the Ni(II)–PDT complex was measured at different intervals of time at 430 nm to ascertain the time stability of the color of the complex shown in Figure. 6. It was observed that the color remained constant for more than 5 h. Physico-chemical and analytical properties of nickel (II) complex of PDT are summarized in Table 3.

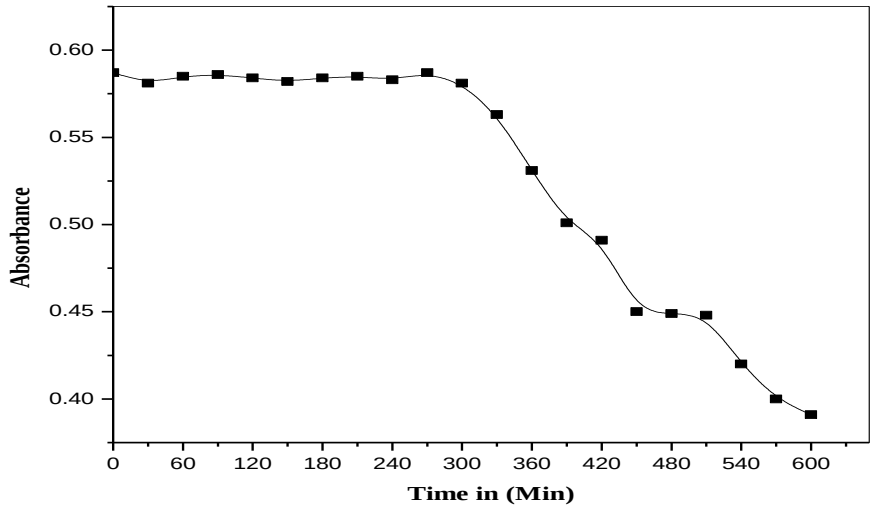


Figure 6: Time stability of the Ni(II)-PDT complex; Ni(II):4 x 10^{-5}M; PDT: 4 x 10^{-4}M; pH:6.0; λmax=430nm.

3.7. Applicability of Beer's law to the Ni(II)–PDT complex system

Known aliquots of 10.0 ml solutions containing constant volumes of 3.0 ml of buffer (pH 6.0), 1.0 ml of 4x10^{-4} M PDT, 1.0 ml of 0.1M magnesium nitrate solution and varying amounts of nickel(II) ranging from 0.1–10.0 µg ml^{-1} were prepared. Each solution was shaken with 10.0 ml of isobutanol for 2 min and then allowed to settle. The organic phases were collected in different 25.0 ml standard flasks and then made up to the mark with isobutanol. The absorbance's of all the organic phases were measured at 430nm, against their corresponding reagent blanks. From the experimental data, it was found that the complex system obeys Beer's law in the concentration range 0.35 – 3.53µg ml^{-1} of nickel (II). The straight line obeys the equation A_{430} = 0.2724 C - 0.0101is shown in the Figure.7. The molar absorptivity and Sandal's sensitivity of the method are 1.6 x 10^4 L mol^{-1} cm^{-1} and 3.6 x 10^{-3} µg cm^{-2} of Ni (II) respectively. The specific absorptivity of the system is found to be 0.284 ml g^{-1} cm^{-1}. The standard deviation in the determination of 2.12 µg ml^{-1} of Ni (II) is 0.003 for ten determinations. The relative standard deviation and the mean absorbance are 0.64 percent and 0.572 ± 0.0013 respectively.

3.8. Determination of The Composition of Ni(II)–PDT complex

The composition of the Ni(II) complex with PDT was studied using Job's method of continuous variation, and the mole ratio method[27]. Extractive spectrophotometric investigation of the metal complex was conducted to obtain the composition of the complex. The composition of the complex was established by Job's method of continuous variation is shown in the Figure.8. Equimolar solutions of nickel(II) and PDT (2x10^{-4} M) were prepared. The metal and reagent solutions were mixed in different proportions, keeping the total volume constant at 1.0 ml. To each solution, 3.0 ml of buffer (pH 6.0) solution and 1.0 ml of 0.1M magnesium nitration solution

as salting-out agent were added and the volumes of the aqueous phases brought to 10.0 ml with double-distilled water. Each of the aqueous phases was shaken with 10.0 ml of isobutanol for 2 min and allowed to settle. The organic phase was collected into a 25.0 ml standard flask and made up to the mark with isobutanol. The absorbance values of the organic phases were recorded at 430 nm, against their respective reagent blanks. From the above experimental results, it is evident that one mole of nickel(II) reacts with two mole of PDT, showing the composition of the complex to be 1:2. This composition was verified using the molar ratio method is shown in the Figure.9. From jobs continuous variation method the stability constant of the complex found to be 1.74 x 10^{11}.

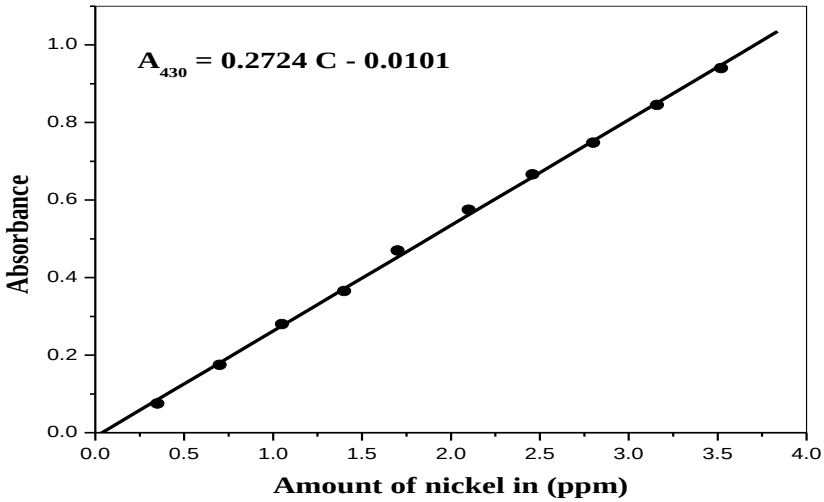


Figure.7. Zero order calibration plot for the Ni(II)-PDT system; Ni(II): 0.35-3.53 ppm; PDT: 6x10^{-6}M,; pH:6.0; max:430nm.

Table 3: Physico – Chemical and Analytical characteristics of Ni-$(PDT)_2$ complex

S.No	Characteristics	Results
1	λ_{max} (nm)	430
2	pH - range (optimum)	5.0-7.0
3	Mean absorbance	0.549 ± 0.0013
4	Mole of reagent required per mole of metal ion for full color developed	10
5	Time stability of the complex (in hrs)	5
6	Beer's law validity range (µg/ml)	0.35-3.53
7	Molar absorptivity (L mol^{-1} cm^{-1})	1.6 x 10^4
8	Specific absorptivity (ml g^{-1} cm^{-1})	0.284
9	Sandell's sensitivity (µg/cm^2)	0.0036
10	Composition of complex as obtained Jobs and molar ratio methods (M:L)	1 : 2
11	Stability constant of the complex	1.74 x 10^{11}
12	Standard deviation in the determination of 1.174 µg/ml of Ni (II) for ten determinations	0.0038
13	Relative standard deviation (RSD)%	1.7
14	Y intercept	-0.010
15	Angular coefficient (m)	0.273
16	Correlation coefficient (ν)	0.999
17	Diction limit	0.021
18	Determination limit	0.061

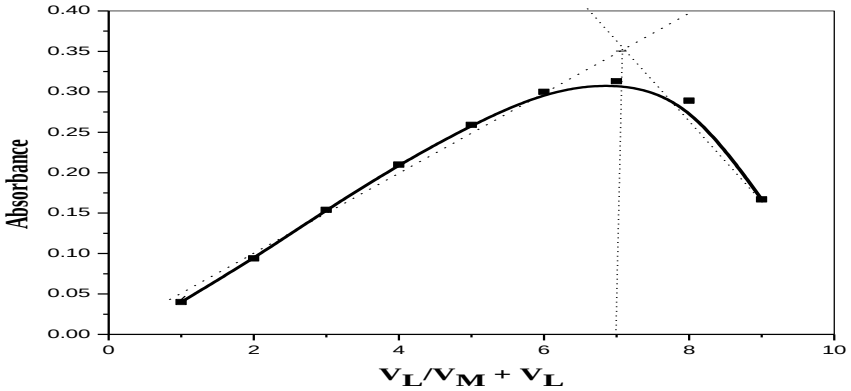


Figure.8. Jobs continues variation method of Ni(II)-PDT complex; Ni(II): $2x10^{-4}$M; PDT:2×10^{-4} M; pH:6.0; λmax:430nm.

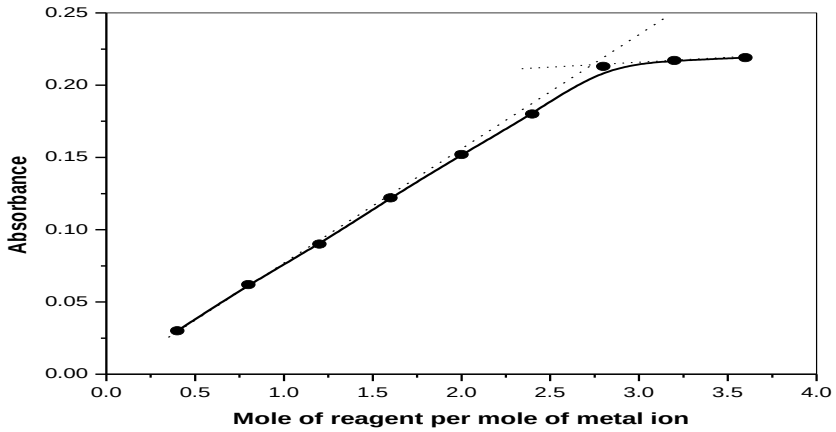


Figure. 9: Mole ratio method of Ni(II)-PDT Complex: Ni(II): $2x10^{-4}$M; PDT:2×10^{-4} M; pH:6.0; λmax:430nm.

3.9. Effect of Foreign Ions on The Extraction of Ni(II)–PDT complex

Known amounts of salts of various cations and anions were added to a fixed amount of nickel(II) in order to study the effect of interference of these ions on the extraction and determination of nickel(II), using the analytical procedure described in the Experimental section. An error of 72% in the absorbance reading was considered to be tolerable. Cations like Aluminum(III), Uranium(VI), Indium(III) and Iron(II) do not interfere, even when present up to 4000 µg. Manganese(II), Tungsten(VI), Barium(II) and Magnesium(VI) do not have any effect up to 2500 µg, whereas Zinc(II), Lead(II), Selenium(IV), Cerium(IV), Copper(II) and Palladium(II) interfere seriously with the extraction of Nickel(II). Anions like Fluoride, Chloride, Bromide, Tartrate, Thiosulphate and oxalate do not interfere when present up to 4000 µg or more. Thiocynate, Thiourea and Phosphate interfere seriously, whereas EDTA masks Nickel(II) completely due to the higher stability of the Ni(II)–EDTA complex. Sulfate, Acetate and Citrate do not interfere when present up to 2000 µg. The interference of Zinc(II), Lead(II) Selenium(IV), Cerium(IV), Copper(II), Cadmium(II) and Palladium(II) can be eliminated by using 1.0 ml of 0.5% Thiosulphate solution.

It also offers advantages like reliability and reproducibility in addition to its simplicity, instant color development and low interference. PDT is cheap, stable at high temperatures, and easy to dispense and store. The reagent PDT was more stable when complexed with Ni(II) and the color of the complex was stable for more than 5h. PDT extracts nickel selectively when associated with the following metal ions: Al(III), U(VI), In(III), Fe(II), Mn(II), W(VI), Ba(II), Mg(VI), Fluoride, Chloride, Bromide, Tartrate, Thiosulphate and Oxalate. PDT is a stable reagent for extractive determination of nickel(II).

3.10. Derivative method

A sensitive second order derivative spectrophotometric method was developed for the determination of nickel(II). For the second derivative spectra the derivative amplitudes at 478 nm (valley) and at 526 nm (peak) were proportional to the concentration of nickel (II) is shown in the Figure.10. The derivative amplitudes were measured different concentration of nickel (II) and plotted against the amount of Ni (II). The derivative peak height was measured by the peak zero method at 478 and 526nm. The peak height was plotted against the amount of Ni(II) to obtain the calibration plot.

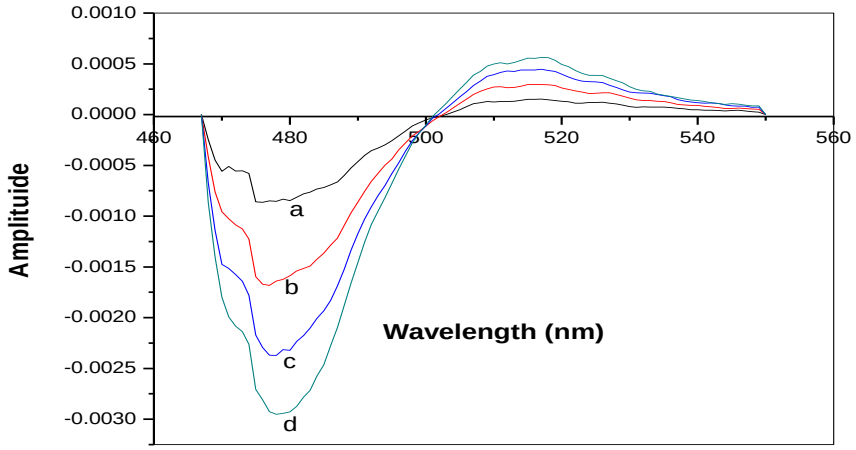


Figure. 10. Second order derivative spectrum of Ni(II)-PDT Complex; Nickel(II), ppm ; a. 0.704; b.1.408; c. 2.112; d. 2.816; PDT: 4 x 10^{-4} M; pH: 6.0.

The calibration graph (Figure.11) follows straight line equation, y=mc + b; where c is the concentration of the solution, y is measured the absorbance or peak height and m and b are constants. By substituting the corresponding experimental data substituted in the above equation, the calibration equations were calculated as A_{430} = 0.2724 C - 0.0101 for zero order data and A_{478} = 0.0012C + 0.0001 and A_{526} 0.00013C + 0.0003 for second derivate data, which give the best straight lines. The plots were linear and obeyed beers law in the range 0.24 to 2.45 µg/ml at 478 nm and 0.24 to 2.67 µg/ml at 526 nm. In the second order derivative method the angular coefficient (m) of the linear plot was found to be 0.244 and 0.343 at 478 and 526 nm respectively. The correlation coefficient (γ) is calculated as 0.997 and 0.999 at 478 and 526 nm respectively.

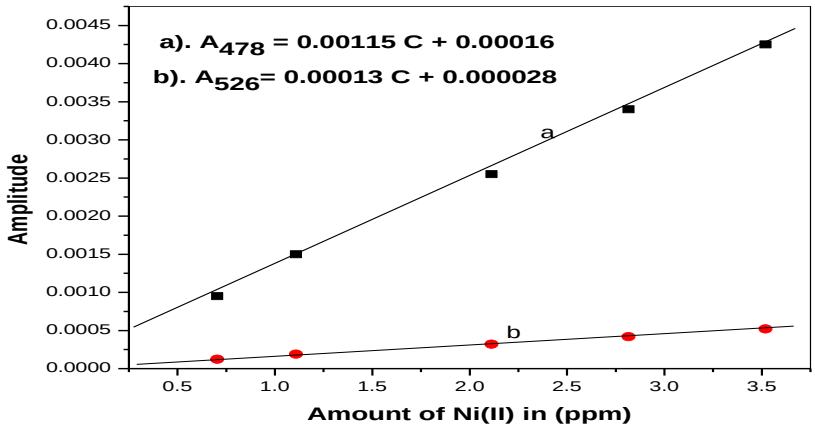


Figure.11. Second derivative amplitude *Vs* amount of Ni(II) µg/ml; PDT: 4 x 10^{-4} M; pH: 6.0.

3.11. Applications of the developed method

The developed extractive spectrophotometric method for nickel(II) has been successfully applied for its determination in medicinal leaves, soil, vegetable oils and standard alloy samples.

3.11.1. Determination of nickel(II) in Medicinal leaves

Medicinal leave samples were collected from around Kadapa, AP and India. Each aliquot was analyzed for nickel(II) by the general procedure which was given in the experimental section. nickel(II) present in medicinal samples was determined from the calibrated plot (Beer's law plot) using PDT and the results checked by atomic absorption spectrometry Table 4.

Table 4: Determination of nickel(II)in medicinal leaves[a]

Name of the sample	Amountofnickel(II)[b] found, mg/mL		Standard deviation		Relative standard deviation (%)	
	AAS Method	Present Method	AAS Method	Present Method	AAS Method	Present Method
Datura stramonium	10.00	09.80	0.0590	0.1097	0.59	1.12
Rhinacanthus nasutus	15.00	14.80	0.0915	0.1332	0.61	0.90
Phllanthus reticulatus	11.00	10.60	0.0594	0.1303	0.54	1.23
Ocimum gratissimum	14.50	14.40	0.1102	0.1944	0.76	1.35
Tylophora indica.Merr	09.00	08.90	0.0801	0.0765	0.89	0.86
Nicotiana tabacum.	10.00	09.40	0.0570	0.0864	0.57	0.92
Tribulus terrestris	14.00	13.86	0.0938	0.1815	0.67	1.31
Ocimum basilicum	08.00	07.70	0.0552	0.0677	0.69	0.88
Boswellia SerrataRoxb	08.50	08.30	0.0723	0.0780	0.89	0.94
Nyctanthes arbor-tristis	20.00	19.60	0.0685	0.2450	0.34	1.25

[a]No statistically significant differences were found between Ni(II) concentrations measured by the AAS method and the present method.
[b]Average of four determinations

3.11.2. Determination of nickel(II) in soil samples

Soil samples were collected from around Kadapa, AP, and India. Each aliquot was analyzed for nickel(II) by the general procedure which was given in the experimental section. Nickel(II) present in soil samples was determined from the calibrated plot (Beer's law plot) using PDT and the results checked by atomic absorption spectrometry Table 5

.**Table 5:** Determination of nickel(II) in soil samples.

Name of the area	Amount of nickel(II)[a] found (µg ml^{-1})		SD	RSD (%)
	AAS Method	Present Method		
Rayachoty	24.0	23.7	0.227	0.96
Pamidi	23.0	22.8	0.225	0.99
Madhanapalli	20.0	19.8	0.194	0.98
Narpala	20.0	19.5	0.175	0.90
Vempalli	20.0	19.6	0.180	0.92
Dhadithota	21.0	20.7	0.184	0.89
Penuconda	20.0	19.3	0.231	1.20
S.V. Puram	19.0	18.6	0.167	0.90
Dharmavaram	19.0	18.2	0.145	0.80
Madhavaram	22.0	21.9	0.219	1.00
Reddyvari palli	22.0	21.8	0.239	1.10
Gooty	23.0	22.9	0.286	1.25

[a]Average of five determinations

3.11.3. Determination of nickel(II) in Standard Alloy Samples

The present method was also applied for the determination of nickel(II) content in standard alloy samples such as nickel base super alloys (CM 247 LC and IN 718), alloy steels (BCS 233 and 266) and low alloy steels (BCS 253 and 251). An appropriate aliquot of each solution was analyzed for nickel(II) employing the recommended procedure given in Materials and methods, using PDT, and the obtained results were checked by direct atomic absorption spectrometry as shown in Table 6.

Table 6: Determination of nickel(II) in standard alloy and certified reference materials[a]

Alloy Sample	Composition (%)	Amount of nickel(II)[b] found (µg ml^{-1})		Standard Deviation		RSD(%)	
		AAS Method	Present Method	AAS Method	Present Method	AAS Method	Present Method
Nickel base super alloy (CM 247 LC)	Ni, 61.91;Cr,8.1; Mo, 0.5 ; Al,5.6;Ta, 3.2; Zr,0.015;C, 0.06; [c]Co, 9.0;W, 9.5; Ti,0.7; Hf, 1.4; B, 0.025	61.90	61.88	0.4147	0.6002	0.67	0.97
Nickel base super alloy (IN 718)	Ni, 54.9; Cr,18; Mo, 3; [c]Fe, 19; [c]Co, 5.1	54.88	54.86	0.2963	0.5211	0.54	0.95
Alloy steel (BCS 233)	Ni, 11.22; [c]Co, 23.4; Sn, 7.95; Mn,0.235; [c]Cu,5.09	11.20	11.18	0.0829	0.1095	0.74	0.98
Alloy steel (BCS 266)	Ni, 1.33; Al,7.95; [c]Co, 23.4;[c]Cu, 3.33	13.28	13.26	0.0916	0.1193	0.67	0.90
Low alloy steel (BCS 253)	Ni, 2.92; Mo,0.94; Cr, 0.34; V,0.220; [c]Cu, 0.495	2.90	2.89	0.0267	0.0300	0.92	1.04
Low alloy steel (BCS 251)	Ni, 5.15; Mo,0.185; Mn, 0.165; [c]Co, 0.007; [c]Cu, 0.090	5.13	5.12	0.0446	0.0501	0.87	0.98

aNo statistically significant differences were found between Ni(II) concentrations measured by AAS method and the present method
[b]Average of four determinations. [c]Masked with EDTA.

Conclusions

Few thiosemicarbazones are used in the extractive spectrophotometric determination of nickel(II). In the present investigation, the authors introduced a new reagent, Pyridoxal-3-thiosemicarbazone (PDT) to the field of extractive spectrophotometric determination of nickel(II). The reagent was found to be sensitive when compared to earlier reported reagents. The selectivity of the reagent was further improved by the use of proper masking agents to suppress the interference of diverse metal ions. The results from the newly developed method clearly demonstrate the usefulness of PDT as an extracting agent for the determination of nickel(II) in environmental matrices and standard alloy samples.

Acknowledgments-I am highly grateful thanks to G. Ramachandra Reddy, A. Babul Reddy and P. Hari Babu for extending their financial support to provide me the AAS results from University Grants Commission, New Delhi under the special assistance programme in the form of meritorious research fellowship. My sincere thanks to Sri Krishnadevaraya University for conducting this research programme.

References

1. Sharma, B.K., "Environmental Chemistry". Meerut, Goel Publishing House, (1997).
2. Judith, T. Z., Peter, T. and Thomas, T., "Immunotoxicology of Environment Occupational Metals", School of Medicine, New York, (1998).
3. Reddy, K. H., and Reddy, D.V., *Quart. Chem. Rev.* 1 (1985) 47–98.
4. Garg, B.S. and Jain, V.K., Journal *of Microchem*, 38 (1988) 144–169.
5. Singh, R.B. and Ishii, H., *Crit . Rev. Anal. Chem*. 22 (1991) 381–409.
6. Salinas, F., Sanchez, J. C. J., and Lemus, J. L., *Bull. Soc. Chim*. Belg. 95 (1986) 293–294.
7. Asuero, A.G., *journal of Microchem.* 28 (1983) 198–202.
8. Reddy, K.G., Prakash, ., K. M. M. S., Reddy K. H., Reddy, D.V., *Acta Cienc. Indica (Ser.) Chem.* 10 (1984) 175–177.

9. Singh S.K., Kamini, M., and Sindhwani, S. K., *J. Chin. Chem. Soc. (Taipei)*, 29 (1982) 131–134.
10. Reddy A. V., and Reddy, Y.K., *Talanta.* 33 (1986) 617–619.
11. Jadhav V. A. and Kulkarni, M. U., *J. Indian Chem. Soc*. 69 (1992) 287–288.
12. Desai V. K., and Desai, K. K., *Orient J. Chem.* 12 (1996) 203–205.
13. Kumar A. P., Reddy, P. R., and Reddy, V. K., *Ind jour of Chem.* 46A (2007) 1625-1629.
14. Attah L. E., *Global journal of Pure and Applied Science.* 15 (2009) 357-363
15. Patel K. N., Parikb, K. S., and Rashmin, Pate, M.l, *Orbital Elec. J. Chem*. 2 (2010) 341-346.
16. Asuero A.G., and Ganzalez, B.M., *Microchem. J.* 25 (1980) 14.
17. Atalay T., and Akgemci, E.G., *Turk. J. Chem.* 22 (1998) 123.
18. Ramachandraiah C., Kumar, J.R.., Reddy, K.J., Narayana, S.L., and Reddy, A.V., *J. Environ. Manag*., 88 (2008) 729.
19. Rao G.P.C., Seshaiah, K., Rao, Y.K., Wang, M.C., *J. Agric. Food Chem*. 54 (2006) 2868.
20. Kumar A.P., Reddy, P.R., Reddy, V.K., *J. Autom. Methods Manag. Chem.*, 48 (2007) 768.
21. Konstantinovic S.S., Radovanovic, B.C., . Todorovic, Z. B., and Ilic, S.B., *J. Serb. Chem. Soc.*, 72 (2007) 975.
22. Lokhande, R.S., Pawar R.N., and Sharma, M.R., *Asian J. Chem.*, 16 (2004) 1225.
23. Reddy K.H., Prasad, N.B.L., and Reddy, T.S., *Talanta*, 59 (2003) 425.
24. Sarma L.S., Kumar, J.R., Reddy, K.J., Triveni, T., and Reddy, A.V., *J. Trace Elem. Med. Biol.*, 22 (2008) 285.
25. Bansal A.K., and Nagar, M., *J. Indian Chem. Soc.*, 83, (2007) 731.
26. Cristofol E., Sanchez Rojas, F., and Pavon, J. M. C., *Talanta*. 38 (1991) 445–448.
27. Vogel A. I., "A Text Book of Quantitative Inorganic Analysis", Longman, Green, London, (1961).