Preparation, Characterization, Analytical and Thermodynamic Studies of Complex of Ni(II) with Antipyriyl azo-1-nitrozo-2-naphthol as a Complexing Reagent

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Abstract: A new, simple, sensitive and rapid spectrophotometric method is proposed for the determination of trace amount of nickle(II). The method is based on the formation of a 2:1 complex with 3-(4'- antipyriyl azo) 1- nitroso-2-naphthol (APANN) as a new reagent is developed. The complex has a maximum absorption at 469 nm and ε_{max} of 0.6×10^5 L. mol^{-1} cm^{-1}. A linear correlation ($0.1 - 1.8$ µg. mL^{-1}) was found between absorbance at λ_{max} and concentration. The accuracy and reproducibility of the determination method for various known amounts of nickle (II) were tested. The results obtained are both precise (RSD was better than 0.11%) and accurate (relative error was better than 0.97%). The effect of diverse ions on the determination of nickle(II) to investigate the selectivity of the method were also studied. The stability constant of the product was 0.1×10^7 L. mol^{-1}. The proposed method was successfully applied to the analysis of synthetic mixtures and raw milk without any preliminary concentration or separation, The apparent thermodynamic parameters were estimated and the obtained results concluded that. The thermodynamic Parameters like ΔG°, ΔH° and ΔS° have been calculated from the effect of temperature on reaction process,its found from these process is Endothermic and spontaneous.

Keywords: Nickle(II) determination, Spectrophotometry, Antipyriyl-azo-1-nitroso-2-naphthol, Thermodynamics analysis

Introduction

Azo dyes constitute the largest and most versatile class of synthetic dyes used in the textile, pharmaceutical, food and cosmetics industries. These dyes are characterized by the presence of one or more azo bonds (–N=N–). These are prepared by azo coupling between a diazonium compound and aniline, phenol or other aromatic compound[1].

Nickel occurs naturally and abundantly in the Earth's crust. The alloys containing nickel are widely used to make coins, jewelry, and stainless steel. However, this metal can be toxic to humans and animals. In humans, nickel toxicity typically presents itself via allergic reactions. Usually, these reactions occur after prolonged skin contact with nickel alloys. People are also exposed to the metal by eating food, drinking water or breathing air that contains small amounts of nickel. Thus, the determination of quantities of nickel in some matrices, such as

water, plants, animals, and soils can provide important information for the control of food and water, and environmental monitoring[2,3]. At present, several techniques such as ions chromatography[4], liquid-liquid extraction with atomic absorption spectrometry[5], atomic fluorescence spectrometry[6], X-ray fluorescence spectrometry[7,8] and inductively coupled plasma atomic emission spectrometry[9], show good sensitivity but is limited because of expensive instrumentation and high cost for routine analysis. In this study, we wish to report this reagent as a selective reagent in spectrophotometric determination of micro amounts of nickle(II).

Experimental

The reagent was prepared by coupling 1-nitroso-2-naphthol with diazotate 4-amino antipyrine in alkaline alcoholic solution. A diazonium solution was prepared by taking 1 g of 4-amino antipyrine in 25 mL of ethanol and concentrated hydrochloric acid with 5 mL of distilled water and adding sodium nitrite solution drop wise at (0-5 ^{0}C). 1.2 g of 1-nitroso-2-naphthol was dissolved in 25 mL of ethanol and 30 mL of 4.0 M from sodium hydroxide were added at (0-5 ^{0}C) .The mixture was left to stand over night. The precipitate was filtered off and recrystallized from ethanol[10].

Preparation of Nickle(II) complex

The complex was prepared by direct reaction between nickel chloride hexahydrate and the appropriate ligand (APANN) in 1:2 mole ratio, using aqueous ethanol as solvent. The formed precipitate was filtered off, washed with warm ethanol, then dried in a vacuum desiccator.

Apparatus

Spectrophotometric measurement were made with Shimadzu UV – visible – 1700 double beam spectrophotometer using 1.00 cm glass cells. Vibrational spectra were recorded on Test scan Shimadzu FT-IR 8000 series. Measurements of pH were made using an Hanna, HI9811-5 pH – meter equipped with a glass - saturated calomel combined electrode Melting points of both ligand and complex were obtained with an electrothermal melting point apparatus. Conductivity was measured in DMSO (10^{-3}) solution with an Alpha digital conductivity model-800. Elemantal analysis (C.H.N) were carried out with a EuroEA Elemental Analyser.

Reagents

All chemicals used were of analytical grades Nickle(II) stock solution (100 μgmL^{-1})

This solution was prepared by dissolving 0.081 g of nickel chloride hexahydrate in 200 mL of distilled water, working standard of Ni(II) solutions were prepared by simple dilution of the appropriate volume of the standard Ni(II) solution (100 $\mu g\, mL^{-1}$) with distilled water.

3 –(4$^'$- Antipyriyl azo)1-Nitroso-2-naphthol (1 mM)

0.0969 g of reagent was dissolved in 250 mL of ethanol.

Foreign ion solutions (10 μgmL^{-1})

All the solutions were prepared by dissolving an appropriate amount of the compound in distilled water in a volumetric flask.

General procedure

An aliquot of sample containing 1-20 μg of Ni(II) was transfer into a series of 10 mL standard flask. 2 mL of 1 Mm of APANN was added and pH was adjusted to 9. The complexes formed were solubilized in water and diluted up to 10 mL in a standard flask. The absorbance of the resulting solution was measured at the respective absorption maxima against a reagent blank prepared under similar condition.

Results and Discussion

Properties of (APANN) and its metal chelate

APANN is a tridentate with coordination of azo group nitrogen, hydroxyl group and carbonyl group; it has the following structure Scheme 1:
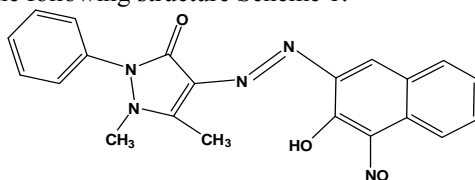
Scheme 1. Structure of APANN

Owing to the large conjugated system, the compound showed excellent chelating ability to form inner metal chelates. APANN and its metal chelates can be easily solubilized in an aqueous solution .Elemental analyses were carried out on the resulting compound (C% calc. 65.11; found 64.46, H% calc.4.42; found 4.15, N% calc.18.08; found 17.99)[10]. (m.p) 201 C^0.

Spectra

The result of this work indicated that the reaction of Ni(II) with APANN at pH yield highly soluble product which can be utilized as a suitable assay procedure for Ni(II). This product has a maximum absorption at 469 nm Figure 1 was adopted in all subsequent experiments.

The effect of various parameters on the absorbance intensity of the formed products were studied and the reaction conditions were optimized. The electronic absorption of APANN and its complex in ethanol have been recorded in the wavelength range (200 – 800) nm Figure 1. The electronic absorption of complex showed a red shift for ($\pi - \pi^*$) electronic transition band. [Ni (L)] shows one broad in visible region at (15000-26000) cm^{-1} refer to($^3A_{2g}(F) \rightarrow T_{2g}(F)[v_1]$, $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)[v_2]$, $^3A_{2g}(F) \rightarrow T_{1g}(P)[v_3]$) that is in accordance with octahedral geometry of Ni metal ion[11,12].

Effect of pH

The pH of metal complex solutions was adjusted using dilute solutions (0.05 M) NaOH and (0.05 M) HCl and the effect on absorbance was studied Figure 2. The absorbance of the complex was maximum and constant in the pH range given in Table 1.
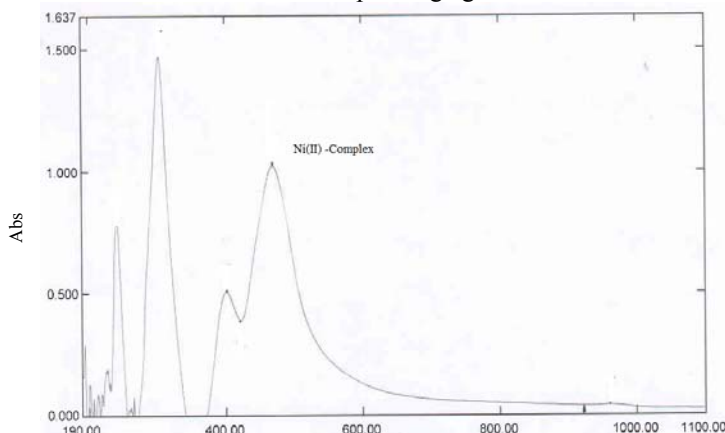

Figure 1. Absorption spectra of [Ni(II) + APANN] treated as described under procedure and against a reagent blank
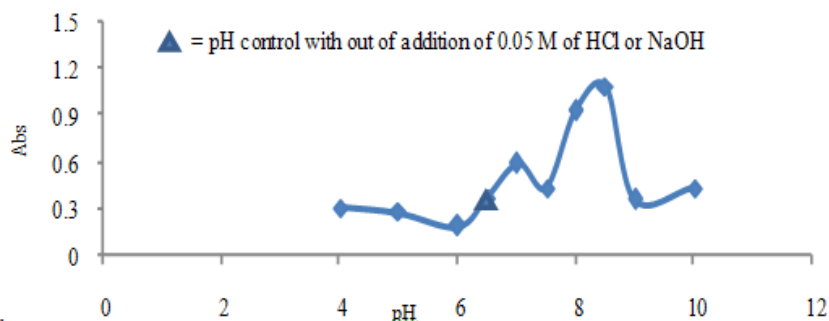
Figure 2. Effect of pH

Table 1. Analytical characteristics of Ni(II) – complex

Characteristic	Ni(II) – complex
Absorption maximum, nm	469
Beer's law range, ppm	0.1-1.18
pH range	8-9
Sandell's sensitivity, $\mu g \cdot cm^{-2}$	0.00107
Molar absorptivity, L. $mol^{-1} \cdot cm^{-1}$	0.6×10^5
Stability constant, K_{st} (L. mol^{-1})	0.1×10^7
Melting point for reagent	199-201 C^0
Melting point for Ni(II) – complex	256-258 C^0

Effect of (APANN) concentration

When various concentrations of of 3 –(4'- antipyriyl azo) 1-nitroso-2-naphthol was added to afixed concentration of Ni(II), 2.5 mL of 1 mM (APANN) solution was sufficient to develop the colour to its full intensity and gave minimum blank value, above 2.5 mL, theabsorbance of the blank value was increased causing a decrease in the absorbance of the sample. Therefore, 2.5 mL of 1 mM of 3-(4'- antipyriyl azo) 1-nitroso-2-naphthol was used in all subsequent experiments (Figure 3).
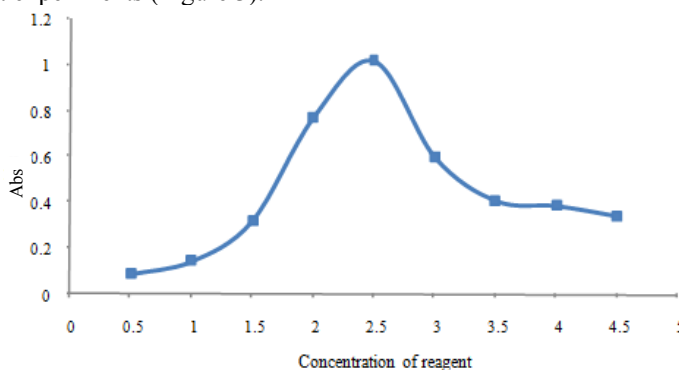

Figure 3. Effect of (APANN) concentration

Effect of reaction time

The colour intensity reached a maximum after the Ni(II) has been reached immediately with APANN and became stable after one minute, therefore one minute development time was selected as optimum in the general procedure. The colour obtained was stable for a least 24 hours (Figure 4).
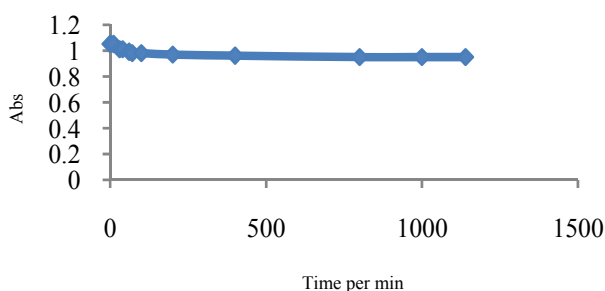
Figure 4. Effect of time on complex of Ni[APANN]$_2$

Effect of temperature

The effect of temperature on the colour intensity of the product was studied. In practice, the same absorbance was obtained when the colour was developed at room temperature (15-35) C$^{\circ}$, but when the volumetric flask were placed in a water – bath at (40-70) C$^{\circ}$ a loss in colour intensity and stability were observed , therefore it is recommended that the colour reaction should be carried out at room temperature for complex Figure 5.
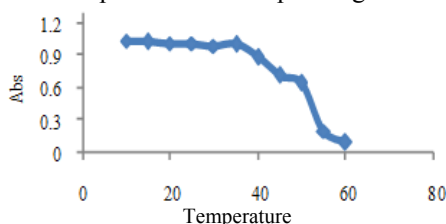

Figure 5. Effect of temperatures on complex Ni[APANN]$_2$

Calibration graph

The calibration equation for (0.1-1.8 µg mL^{-1}) Ni(II) is: Y = 0.9627X + 0.023(R^2 = 0.9912).

Since the coloured complex is stable for 24 h, the method can be applied to large series of samples. The molar absorptivity and sandell' sensitivity are given in Table 1.

Composition of the complex

The composition of complex was studied in the excess of reagent solution by the mole-ratio and Job s˙ methods Figure 6,7. A break at a 1:2 (M:L) mole ratio suggested the formation of complex where M= Ni(II) and L= APANN under the given condition.
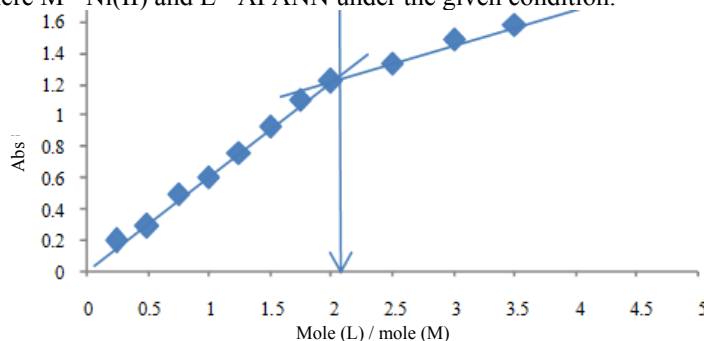

Figure 6. Mole-ratio method for Ni[APANN]$_2$ complex
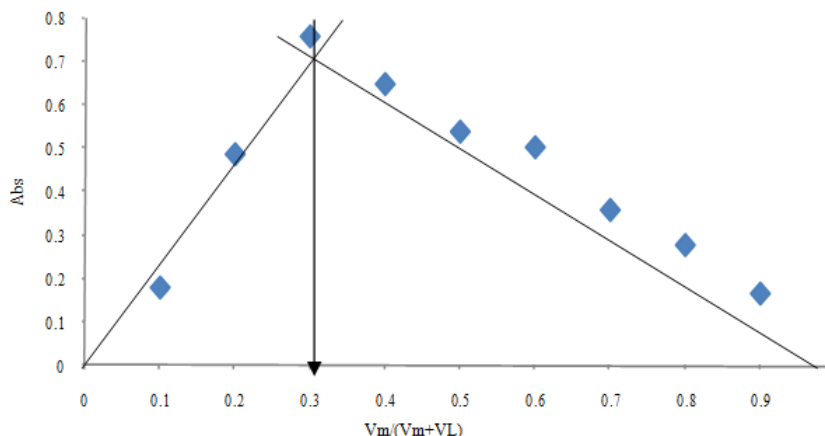
Figure 7. Job s` method for Ni[APANN]$_2$ complex

Thermodynamics analysis

The thermodynamic functions, ΔH^o, ΔG^o and ΔS^o can be estimated using equilibrium constant charging with temperature. The free energy change of the reaction is given by the following equation[13,14].

$$\Delta G^o = -R\,T\,\ln k_{st} \tag{1}$$
$$\ln k_{st} = A - \Delta H/RT \tag{2}$$
$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{3}$$

Where K_{st} is the The equilibrium constant for various complexes solution at different temperature. The equation (2) was used to calculate the ΔH^o, by plotting against $1/T$. Table (2) and Figure (8) showed a linear relationship and the slope represent $(-\Delta H^o/R)$ where R is the gas constant (8.314 JK^{-1}. $mole^{-1}$) and ΔH^o ads were calculated. The ΔG^o, ΔS^o and ΔH^o values at different temperature were given in Table 3.

Table 2. The values of the reciprocal of temperature and $\ln k_{st}$

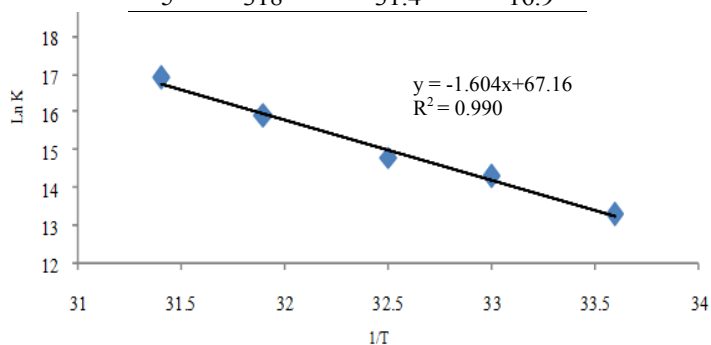| No.	$T(K_{st})$	$1/T \times 10^4$	$\ln K_{st}$
1	298	33.6	13.288
2	303	33	14.3
3	308	32.5	14.8
4	313	31.9	15.9
5	318	31.4	16.9

Figure 8. Plot of ($\ln k_{st.}$) against ($1/T \times 10^4$) the reciprocal of temperature

Table 3. Show the thermodynamic functions of the reaction process

No.	T, K	ΔH^o K J . mole $^{-1}$	ΔG^o x 10^{-3} K J. mole $^{-1}$	ΔS^o J.mole $^{-1}$. K $^{-1}$
1	298		-32.9219	+ 110.5209
2	303		-36.0237	+118.9341
3	308	+13.342	-37.8985	+123.0904
4	313		-41.3763	+ 132.2353
5	318		-44.6811	+140.5486

As seen in Table 3, the negative values of ΔG^o confirm the feasibility of the process and the spontaneous nature of process, The positive values of ΔH^o indicate the endothermic nature of the process while the positive ΔS^o corresponds to increase disorder of the system increase.

Conductivity measurements

The solubility of the complex in dimethyl sulfoxide and ethanol permitted of the molar conductivity of 10^{-3} M solution at 25 °C and by comparison, the electrolytic nature forcomplex. The low values of the molar conductance data listed in (Table 4) indicate that the complex is non electrolyte[15].

Table 4. Conductivity values of complex

Complex	Molar conductivity, S. mole^{-1} .cm^2 DMSO	Molar conductivity, S mole^{-1}. cm^2 Ethanol
Ni (APANN)	11.3	15.7

FT-IR of reagent and its complex

The FT.IR of the free ligand and its metal chelate were carried out in the (400-4000) cm^{-1} Range. The IR bands of the (APANN) and its Ni(II) complex with their probable assignment are given in Table 4. The IR spectrum of ligand shows a broad band at 3425 cm^{-1}, which can be attributed to the naphtholic OH group. However, the υ(N=N) stretching band in the free ligand is observed[10] at 1535 cm^{-1}. This band is shifted to lower with low intensity at 1492 cm^{-1} frequency value upon complexation suggesting chelation via the (M-N)[16]. The IR spectrum of the ligand revealed a sharp band at 1650 cm^{-1} due to υ(C=O) of pyrazole azo[10]. This band is shifted to higher with low intensity at 1676 cm^{-1} frequency value upon complexation[17]. The bonding of oxygen to the metal ion is provided by the occurrence of band at 455 cm^{-1} as the result of υ(M-O)[18,19].

Table 5. Selected FT-IR data of (APAP) and it's complex with Ni(II)

Compound	υ (OH)	υ (C=N)	υ (C-H) arom.	υ (N=N)	υ (C=C)	υ (C=O)	υ (M-O)	υ (M-N)
HL	3425 m	1697 s	3062 m	1535 m	1627 s	1650 s	_	_
[I (L)]	3411 m	-	3062 m	1492 m	1669 s	1676 s	455 w	414 w

S: sharp; m: medium; w: weak

On the basis of the FT.IR, stoichiometric and elemental analysis molar conductivity data the structure of complex can be suggested as in Scheme 3.

Applications

Determination of Nickle(II) in practical samples

To determine the accuracy and precision of the method, Nickle(II) was determined at two different concentrations. The results are shown in Table 6 indicate that satisfactory precision and accuracy could be attained with proposed method.

Table 6. Determination of Ni(II) in synthetic samples

Amount taken of Ni(II) p.p.m	Recovery%	RSD%
1	99.03	0.11
0.5	99.81	0.22

[Ni(APAN)₂].XH₂O
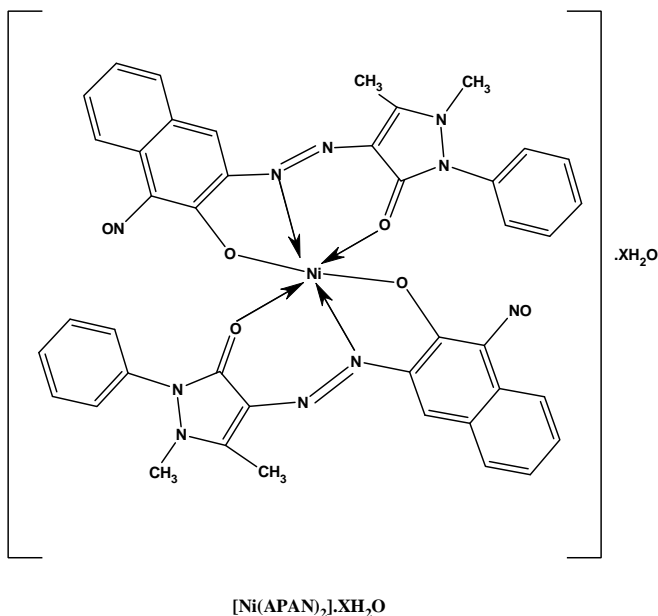
Scheme 2. The suggested structural formula of Ni(II) -complex

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