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Spectrophotometric Determination of Ni^{+2} by 3- ((2- Hydroxyphenyl)imino)indolin- 2- one

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Abstract: 3- ((2- Hydroxyphenyl) imino) indolin- 2- one was prepared by reacting isatin with 2- aminophenol(HIAP),The reagent was characterized by IR, H ^{1}NMR spectrum, This reagent with a nickel complex forms a violet color (1: 2) at pH = 9.0, λ_{max} =575nm and room temperature using sodium tetraborate buffer solution, The molar absorptivity 1.43 $\times 10^{+4}$ L mol^{-1} cm^{-1} and Sandell's sensitivity value is 0.03800 µg cm^{-2} and The Beer's law is obeyed in the range 0.50- 5.28 µg mL^{-1} of nickel (II) and the Calibration curve equation y = 0.0663x + 0.0749, R² = 0.9988.

Keywords: Ni^{+2}, 3- ((2- hydroxyphenyl) imino) indolin- 2- one, Spectrophotometric Determination

التقدير الطيفي لـ Ni^{+2} بواسطة 3- (2- هيدروكسي فنيل) إيمينو إندولين 2- ون

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المستخلص: تم تحضير 3- ((2- هيدروكسي فينيل) إيمينو) إندولين- 2 ون عن طريق تفاعل الايزاتين مع 2- أمينوفينول (HIAP)، تم تشخيص الكاشف بواسطة أطياف ,^{1}NMR ،IR H يشكل هذا الكاشف مع أيونات النيكل معقد بنفسجي اللون 2: 1 عند الرقم الهيدروجيني pH=9.0، 575 λ_{max} = نانومتر وبدرجة حرارة الغرفة باستخدام محلول منظم رباعي بورات الصوديوم، الامتصاصية المولارية 1.43 × 10^{+4} لتر مول- ^{1} سم- ^{1} وقيمة حساسية ساندل هي 0.03800 ميكروغرام سم- ^{2} ويتم الامتثال لقانون بير في حدود 0.50- 5.28 ميكروغرام. مل$^{-1}$ من النيكل (II) ومعادلة المنحنى العياري y = 0.0663x + 0.0749. ومعامل الارتباط R² = 0.9988

الكلمات المفتاحية: نيكل ((II)، 3- (2- هيدروكسي فينيل) إيمينو) إندولين- 2 ون، التقدير الطيفي.

1. Introduction

Many different organic compounds have been used as spectrophotometric reagents for the determination of nickel (II) in aqueous solutions [1], This metal is used in the manufacture of alloys, and refractory products and is present in small quantities most types of soils, plants and tissues[2]. It is a rather toxic ingredient. Inhaling nickel and its compounds leads to serious diseases such as lung and throat cancer.[3] Nickel can enter water from industrial processes, so it is important developing sensitive methods for determination nickel in water samples [4],Spectruml measurement methods have been used because of its multiple features such as simplicity, speed, low costs and wide application. [5- 7], and table (1) shows some of the reagents for determining nickel by spectroscopic methods

Table (1) some of the reagents for determining nickel by spectroscopic methods

The reagent	ε(L mol^{-1} cm^{-1})	Wavelength/nm	Ref
the chromogenic reagent (dopa- semiquinone)	9.3×10^3	590	8
(E)- N1- (2- hydroxy- 5- nitrobenzylidene) isonicotinoylhydrazone	5.1×10^4	480	9
2- (4- fluoro benzylideneamino) benzenethiol	6.3×10^4	520	9
(L- dopasemiquinone)	2.4×10^3	591	10
5- methyl- 2- acetylfuran- 4- methyl- 3- thiosemicarbazone	1.87×10^4	361	11
dimethylglyoximate on naphthalene	3.2×10^3	375	12

In this paper a new organic reagent (3- ((2- Hydroxyphenyl)imino)indolin- 2- one) was prepared and used to determine nickel by spectroscopy by forming a complex [HIAP- Ni^{+2}].

2. Experimental

2.1 Apparatus

A spectrophotometer Optizen UV- VIS containing 7 cells 1 cm glass was used to measure absorbance, The FT- IR spectrum (4000- 500 cm- 1) was recorded in a FTIR spectrophotometer (Jasco- 300E) and the H1NMR spectrum was recorded using a spectrophotometer H1NMR. A Martini Mi- 180 digital pH meter equipped with a glass calomel electrode was used for the pH and pH- adjusting measurements, respectively.

2.2 Reagents

All the raw in the preparation of the organic reagents and Complex in this paper are from Sigma- Aldrich and Merck company, and are characterized by the high- purity analytical type, isatin, 2- amino- phenol, nickel nitrate and table (2) shows some of the materials used in the study.

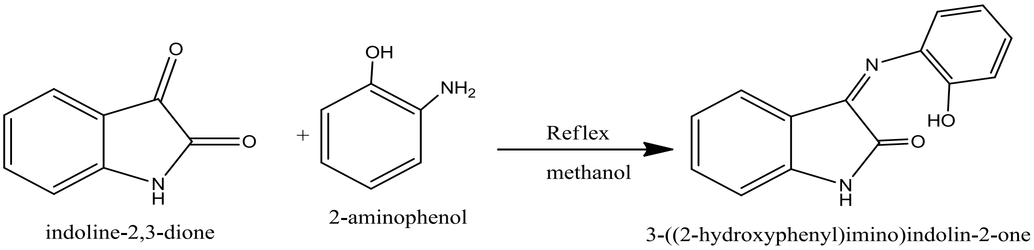
Table (2) some of the materials used in the study.

The compound	M_w (g/mol)	Chemical Formula	Company
Isatin	147.13	$C_8H_5NO_2$	AL- DARSH
2- amino phenol	109.05	C_6H_7NO	Sigma- Aldrich
$Ni(NO_3)_2.6H_2O$	290.81	$N_2O_6Ni,6H_2O$	Merck

3. General procedure

3.1 Preparation of the ligand:

The Schiff Base ligand HIAP was prepared by reacting equimolar amounts of o- aminophenol (0.02 mol; 2.18 g) and isatin (0.02 mol; 2.94 g) in 150 ml absolute methanol. The reaction mixture was refluxed on a steam bath for 4 hours. The excess of solvent was partially evaporated and the brownish mass product was precipitated by cooling and filtered off, washed with methanol and dried over P_4O_{10} in vacuo at room temperature[13]



The HIAP solution (1,5 x10^{-3})M was prepared in DMF, Nickel nitrate (II)solution (1,5 x10^{-3})M was prepared in distilled water and The buffer solution with pH = 9 was prepared by taking 100 ml of a borax solution of a concentration of 0.025 M and adding 1.8 ml of 0.1 M NaOH and diluted to 200 ml with distilled water.

3.2 Preparation of the Complex:

A volume of 2.0 ml of HIAP (1,5 x 10^{-3}) mol/L, 1.0 ml of nickel nitrate (II) (1,5 x 10- 3) mol/L and 1 ml of buffer solution pH = 9.0 were added to 25 ml standard vial. The volume was completed to 25 mL with distilled water. The absorbance was measured for each solution at 575 nm

4. Results and Discussion

4.1 The IR spectrum of free ligand were recorded in range 400- 4000 nm with a (Jasco- 300E) spectrophotometer

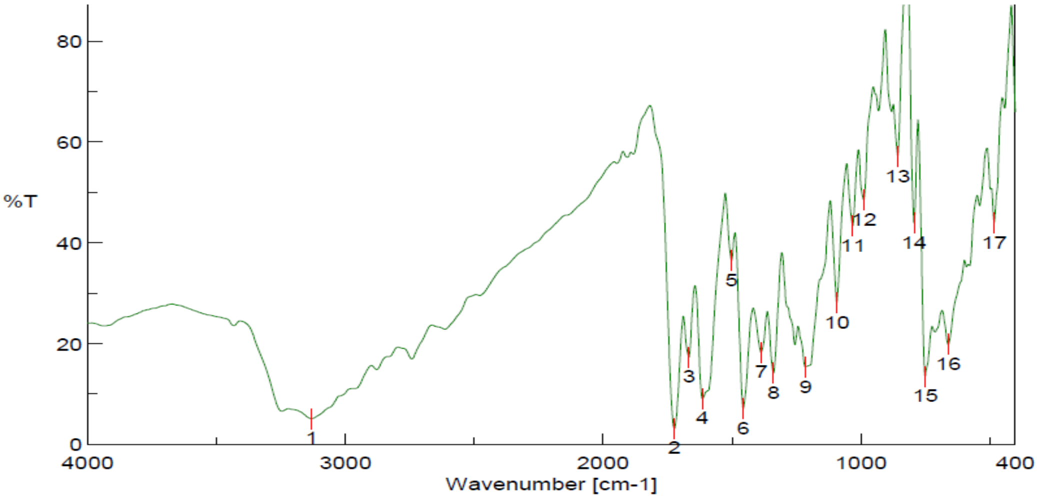


Fig (1) The IR spectrum of free ligand[HIAP]

The three strong bands appearing at 3130, 1667 and 1723 cm- 1 in the ligand spectrum may be assigned to stretching vibration modes ʋN- H, ʋC=N and ʋC=O, respectively.

4.2 The H 1NMR spectrum of free ligand

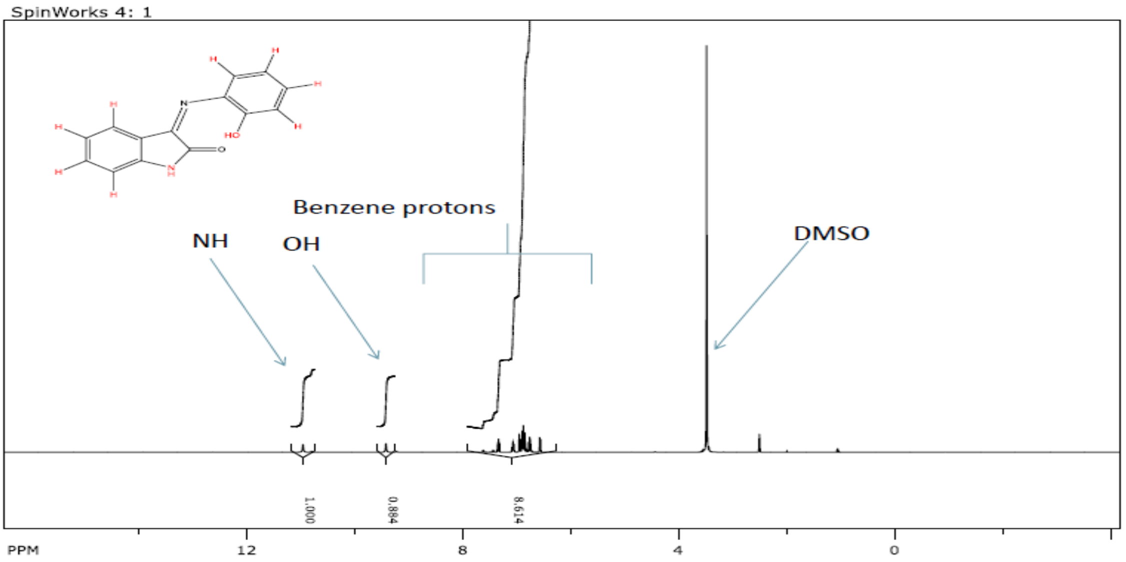


Fig (2) The H ^{1}NMR spectrum of [HIAP]

Signals from 6.4- 6.9 (cm, 4H, aryl- aminophenol protons), 7.3- 7.8 (cm, 4H, aryl Isatin moiety protons), 9.3 (s, 1H, phenol OH to aminophenol), 10.9(s, 1H, Isatin NH)

4.3 Absorption spectrum

Under the optimal experimental conditions, the absorption spectrum of nickel (II)- HIAP complex was scanned with UV- visible spectrophotometer. The absorption maximum of nickel (II)- HIAP complex gave an absorption peak at 575 nm. Hence, the wavelength for maximum absorption was fixed at 575 nm for all the subsequent studies as illustrated in Fig.3

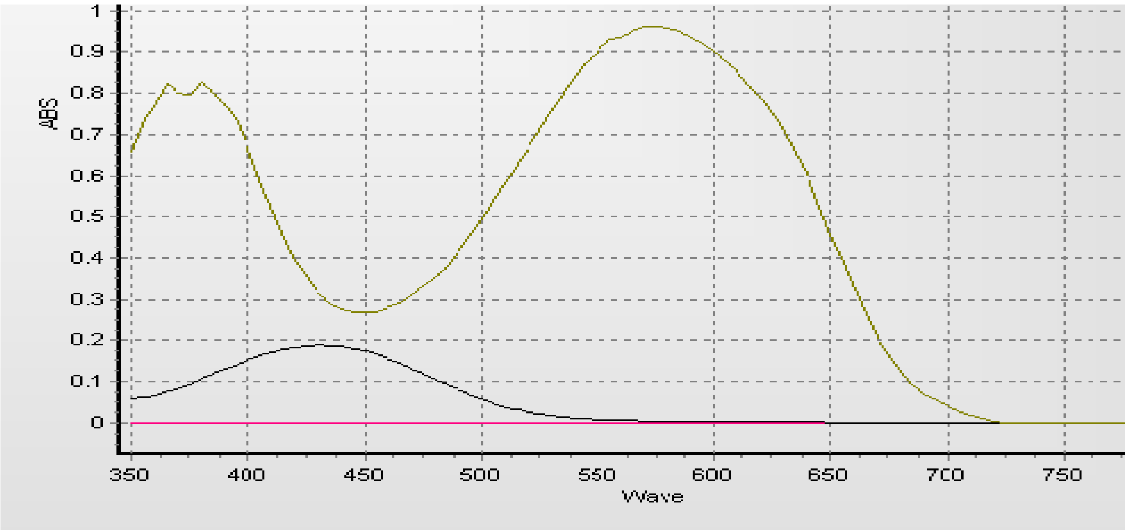


Fig (3) Absorption spectrum of Ni (II) – HIAP complex.

4.4.Effect pH:

A maximum and constant absorbance was obtained in the pH range of 8.5- 9.5 using HCl and NaOH 0.1M.Therefore, all subsequent studies were carried out at 9.0 using 1.0 ml of sodium tetraborate buffer solution.

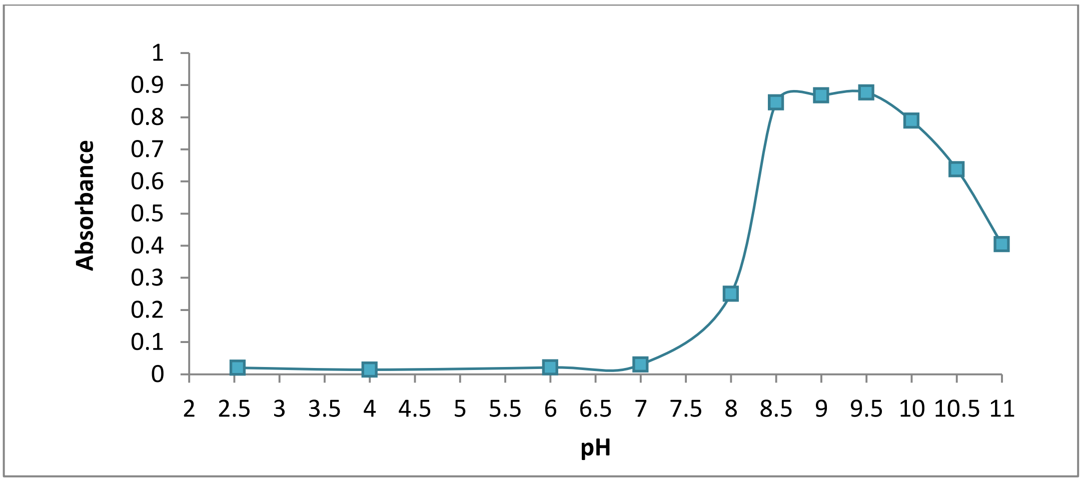


Fig. (4) Effect of pH on the change in the absorbance of Ni(II)- HIAP complex, λ_{max}=575 nm $C_{[L]}$=12. 10^{-5} M, $C_{[Ni+2]}$= 6.10^{-5}M, L=1.0cm.

5. Composition of the Complex

5.1 Job's method of continuous variation

A Series of solutions of varying mole fractions of Ni (II) and HIAP were prepared keeping the total volume constant,the absorbance of each solution was measured at 575 nm. A graph was plotted between absorption and mole fraction of the ligand and from the graph it is observed that one mole of nickel chelates with 2 moles of HIAP indicating that the composition of the complex as 1:2 in Ni–HIAP complex.

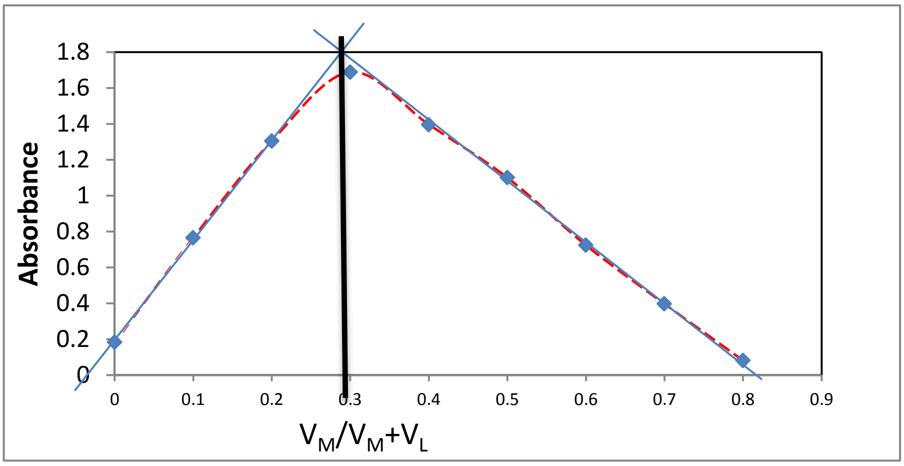


Fig. (5). Curved the continuous variation of a complex solution ligand with nickel ions,,λ_{max}=575 nm, pH =9 $C_{[L]}$=12. 10^{-5} M, $C_{[Ni+2]}$= 6.10^{-5}, L=1.0cm

The molar composition of the complex (M:L) (1:2).

5.2 The Mole- Ratio Method

A series of [HIAP- Ni + 2] complex solutions were prepared under optimal conditions containing increasing concentrations of the reagent within a specified range while maintaining a constant nickel concentration in each solution. Distilled water was extended in 25 mℓ flasks and the absorbance of each solution was measured at a wavelength. The maximum absorption using a comparative solution prepared in the same way except for the metal. The absorbance changes of the complex were drawn as a function of the molecular ratio of the detector, resulting in a straight line refracting at the molar ratio of 2, which corresponds to the following binding ratio: (2: 1) for the [HIAP- Ni^{+2}]complex as shown in Figure 6

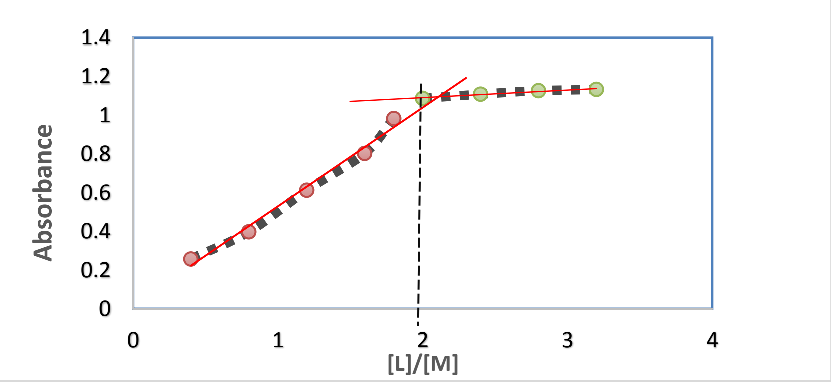


Fig. (6). Curved the mole- ratio of a complex solution ligand with nickel ions,,λ_{max}=575 nm,pH =9 $C_{[L]}$=12. 10^{-5} M, $C_{[Ni+2]}$= 6.10^{-5}, L=1.0cm

6. Formula and proposed form of the prepared complex:

The two methods of molar ratio and continuous changes were used to achieve the ratio (metal: ligand) required to prepare the complex. For both methods, the required ratio is (1: 2):

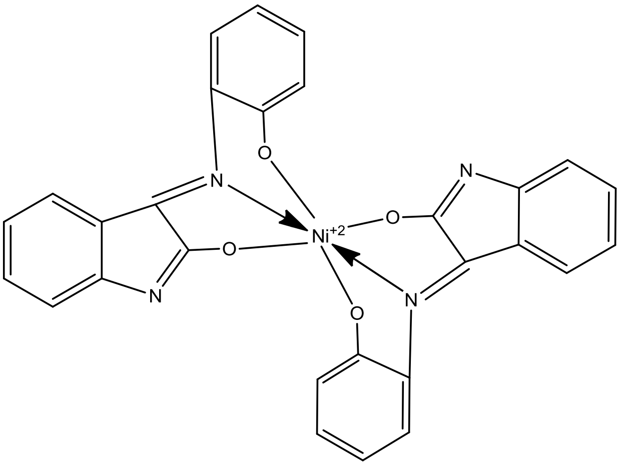


Fig (7) The proposed structural formula of the complex

7. Calculation Stability Constant for Metal Complex:

Three solutions were prepared with different concentrations and the stability of the complex was studied relative to time. A decrease in the absorption of the least concentrated solution was observed, while stability was observed at the top Concentration.

Table (3): Concentrations Complexes used in the study: 1.022 x10^{-4}, 1.042 x10^{-4}, 1.042 x10^{-4} mol/L

Time (min)	5	10	20	30	40	50	60
Abs Complex 1	1.471	1.432	1.396	1.250	1.081	0.912	0.873
Abs Complex 2	1.500	1.500	1.500	1.486	1.312	1.077	0.913
Abs Complex 3	1.500	1.500	1.500	1.500	1.500	1.500	1.500

$C_{[L]}$=18. 10^{-5} mol/L, $C_{[Ni+2]}$= 9.10^{-5} mol/L, $C_{[L]}$=36. 10^{-5}mol/L, $C_{[Ni+2]}$= 18.10^{-5}mol/L, $C_{[L]}$=72. 10^{-5}mol/L, $C_{[Ni+2]}$= 36.10^{-5} mol/L. respectively

8. Calibration curve:

To perform a quantitative nickel determination using a HIAP reagent in order to find the linear field of nickel concentration that is subject to Beer's Law(0.50- 5.28), a series of complex solutions of nickel concentration were prepared within the range1.74- 14 µg/mL and contain a fixed concentration of the reagent 28.56 µg/mL with 1 ml of buffer solution at PH = 9 The correlation coefficient was from 0.9988, and this indicates a good linearity of the standard curve, according to the curve equation $y = 0.0663x + 0.0749$, as shown in the fig.8.

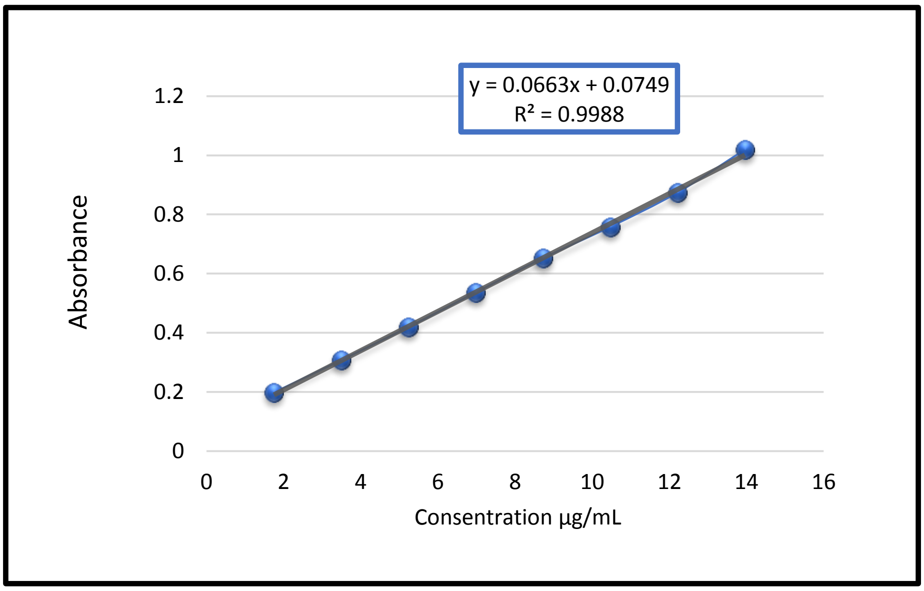


Fig (8) Calibration curve

9. Calculation The apparent molar absorptivity and Sandell's sensitivity:

The apparent molar absorptivity was $1.43 \times 10^{+4}$ L mol^{-1}cm^{-1} whereas the Sandell's sensitivity was Calculated of the relationship:[14]

$$Ss\ (\mu g.cm^{-2}) = c_{min}.F_W.l.10^3$$

$$C_{min} = .A_{min}/\varepsilon.l$$

$A_{min} = 0.01$, C_{min} (mol/L)= 6.94734×10^{-8} mol/L, F_W=547.09 g/mol, $\varepsilon = 1.43 \times 10^{+4}$,. $l = 1cm$

$$S_s = 0.03800\ \mu g.\ cm^{-2}$$

10. APPLICATION:

- The proposed method was tested on nickel samples prepared in the laboratory from nickel nitrate salts (Ni $(NO_3)_2.6H_2O$) and gave the following results and Table 4 show the Statistical treatment to determine the nickel[15].

Table (4) show the Statistical treatment to determine the nickel in salt (Ni $(NO_3)_2.6H_2O$)

Ni(µg/ mL)	$\bar{x}$	S	RSD	C (µg/mL)- Ni^{+2} (Found)	C (µg/mL)- Ni^{+2} (Taken)	Percentage Recovery R%	Error%
1.761	0.6534	0.0001733	0.0003	1.761240241	1.760939	100.01	0.03
2.641	0.9474	0.0002653	0.0003	2.656321712	2.64140917	100.56	1.49

- Important analytical parameters of Ni (II) and HIAP are incorporated in Table 5.

Table (5): the analytical parameters of [Ni^{+2}- HIAP]

Characteristics	Results
Name	[3- ((2- hydroxyphenyl) imino) indolin- 2- one- Ni (II)]
λ max (nm)	575
Color	Violet
pH	9.0
Composition of complex (M:L) obtained in Job's and mole ratio method	1:2
Molar absorptivity (L/mol.cm)	$1.40 \times 10^{+4}$
Stability constant of complex obtained in Job's and mole ratio method	7.914 ± 0.03
Sandell's sensitivity µg. cm^{-2}	0.03800
Beer's law validity range µg/ mL	0.50- 5.28
correlation coefficient	0.9988
Calibration curve equation	$y = 0.0663x + 0.0749$

11. Conclusions

Thus, in this study, a new reagent was prepared for the determination of nickel, (II) by spectroscopy. The currently developed method is direct, simple, fast, sensitive, accurate and selective without the need for heating or extraction.

References:

- Barreto, W. J., Barreto, S. R. G., Scarminio, I. S., Ishikawa, D. N., Soares, M. D. F., & Proença, M. V. B. D.. Determination of Ni (II) in metal alloys by spectrophotometry UV- Vis using dopasemiquinone. *Química Nova*, (2010) *33*(1), 109- 113.

- Barreto, W. J., Barreto, S. R. G., Scarminio, I. S., Ishikawa, D. N., Soares, M. D. F., & Proença, M. V. B. D. Determination of Ni (II) in metal alloys by spectrophotometry UV- Vis using dopasemiquinone. Química Nova, (2010), 33(1), 109- 113.
- Barreto, W. J., Magosso, H. A., Soares, M. F., Silveira, B. M. O., Scarminio, I. S., Ishikawa, D. N., & Barreto, S. R. G. DETERMINATION OF NI (II) IN ALLOYS USING A NEW REAGENT DERIVED FROM L-DOPA. Eclética Química Journal, (2018),36(3), 15- 20.
- Barreto, W. J., Magosso, H. A., Soares, M. F., Silveira, B. M. O., Scarminio, I. S., Ishikawa, D. N., & Barreto, S. R. G. DETERMINATION OF NI (II) IN ALLOYS USING A NEW REAGENT DERIVED FROM L-DOPA. Eclética Química Journal, (2011). 36(3), 15- 20.
- Fakhari, A. R., Khorrami, A. R., & Naeimi, H. Synthesis and analytical application of a novel tetradentate N2O2 Schiff base as a chromogenic reagent for determination of nickel in some natural food samples. Talanta, (2005),66(4), 813- 817.
- GOYAT, G., MALIK, A., GARG, S., & VERMA, K. K., SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES ON SOME COMPLEXES OF TELLURIUM (IV) WITH SCHIFF BASE DERIVED FROM ISATIN AND 2- AMINOPHENOL. INT J CHEM SCI, (2016), 14(3), 1498- 510.
- GÜRAY, T. Bir Hidroksiazo Bileşiği Kullanılarak Gerçek Örneklerde Nikelin Eser Miktarlarının Spektrofotometrik Tayini. Süleyman Demirel Üniversitesi Fen Bilimleri Enstitüsü Dergisi, (2019),23(3), 673- 678.
- Kumar, B. N., Kanchi, S., Sabela, M. I., Bisetty, K., & Jyothi, N. V. V.,Spectrophotometric determination of nickel (II) in waters and soils: Novel chelating agents and their biological applications supported by DFT method. Karbala International Journal of Modern Science, (2016), 2(4), 239- 250.
- Long G.L.,Winefordner J.D., Limit of Detection a Closer Look at the IUPAC Definition.,Analytical Chemical Acta, 1983,55(7)712- 716.
- Muthuselvi, R. Determination of nickel (II) by spectrophotometry in micellar media. *Pharm Anal Chem*, (2017),*3*(3).
- Patnaik, P. Dean's analytical chemistry handbook. (2004). McGraw- Hill Education.
- Sabermahani, F., Saeidi, M., & Sharifzade, V. Removal of nickel (II) and palladium (II) from surface waters. Bulletin of the Chemical Society of Ethiopia, (2013), 27(1), 15- 23.
- Satake, M. Spectrophotometric determination of nickel by adsorption of nickel dimethylglyoximate on naphthalene, (1979).
- Weldeabzgi, A., Reddy, D. N., & Mekonnen, K. N.,Spectrophotometric determination of nickel (II) in soil and standard alloy samples using 5- methyl- 2- acetylfuran- 4- methyl- 3- thiosemicarbazone (5-MAFMT). Communications in soil science and plant analysis, (2017), 48(4), 439- 448.
- Z. Marczenko, Spectrophotometric Determination of Elements, Horwood, Chichester, 1976.