Determination of Ni(II) and Co(II) Spectrophotometricaly by using 2-[(2-Carboxy-4-nitrophenyl) azo]-4,5-diphenyl imidazole (CNPAI)

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Abstract

This work amid to determine of Ni(II) and Co(II) by using 2-[(2-Carboxy-4-nitrophenyl) azo]-4,5-diphenyl imidazole (CNPAI), maximum absorption of two complexes are 566nm and 592nm for Ni-CNPAI and Cd-CNPIA respectively while the maximum absorption of the ligand was 425nm.

Optimum condition were constructed, calibration curve was obeyed in the range (0.05-1.3) ppm for Ni and (0.1-8) ppm for Co ions, the linearity (R^2) was (0.9991), (0.9995), molar absorpitivty (ε) was 1.7448×10^4 L.mol^{-1}.cm^{-1}, 9.908×10^4 L.mol^{-1}.cm^{-1} for Ni(II) and Co(III) complex.

The stoichometry of metals to reagent were 1:2 for two complexes, Precision and accuracy of the analytical procedure for Ni(II) and Co(II) were R.S.D % (2.11 , 0.82)%, ($E_{rel.}$, R_e) % were (-3.1, 96.9) % and (-2.7, 97.3) %.

الخلاصة

يهدف البحث الـى تقدير النيكل والكوبلت الثنائيين بواسطة الكاشف (CNPAI) , وقد وجد ان الامتصـاص الاعظم للمعقدين كان عند الطول الموجي 566 نانوميتر للنيكل و 592 نانوميتر للكوبلت.

تم بنـاء منحنـي المعـايره لكـلا الايونين عند مـدى من التراكيز (1.5-0.05) جزء بـالمليون للنيكـل و (8-0.1) جزء بـالمليون بالنسبة للكوبلت اظهر كـلا المنحنيين خطية (R^2) قدرها (0.9991) و (0.9995) و قيمـة معامل امتصـاص مولاري هي 1.7448×10^4 و 9.908×10^4 للنيكل والكوبلت على التوالي.

تم تحديد نسبة الفلز الى الكاشف حيث وجد انها تساوي 2:1 لكلا المقدين كما تم تحديد دقة وضبط الطريقة التحليلية حيث وجد ان قيمـة الانحـراف القياسـي R.S.D% , (2.11 و 0.82)% ,امـا قيم الخطـأ النسبي($E_{rel.}$) و الاستعادية (R_e) فكانت (-3.1، 96.9) % و (-2.7، 97.3) % .

Introduction

Azo dyes, aromatic compound linked together by azo (–N=N–) chromophores, represent the largest class of dyes used in textiles, leather, plastics, cosmetics, and food industries [1].

Interest in azo dyes has been emphasized in the past few years because of the ability of these dyes to record optical information This ability comes from the *trans–cis* photoisomerization that modifies the molecular dipolar momentum and thus the refractive indexas well as the absorption of the material [2] . This class of compounds possess active (π-acidic) azo imine (—N=N—C=N—), function and efficient agents to stabilities low valent metal oxidation states , due to the presence of azo centered π*-molecular orbital, for this reason a number of these azo compounds were synthesized and their abilities as chelating ligands [3,4].

Azo dyes are used as analytical reagents and as a staining agents, there for azo-dyes with the heterocyclic diazo-component form coloured complexes with many metal ions in solution[1].Great number of the spectrophotometric methods based on these reactions were developed and used in analytical chemistry[5-7].

The determination of nickel is important due to its toxic nature , Nickel is also present at low concentrations in various foods of both animal and vegetable origin such as red meat, cotton seed, corn meal, saturated oils, chocolates, milk and milk products[8]. It is among the toxic metals of significance for environmental surveillance, food control, and occupational medicine, toxicology and hygiene and its toxicity can cause acute pneumonitis, dermatitis, asthma, disorders of central nervous system and cancer of nasal cavity and lungs[9]. Many analytical procedures have been proposed for nickel determination, such as spectrophotometry , flame atomic absorption spectrometry after preconcentration , inductively coupled plasma (ICP) atomic emission spectrometry following a preconcentration step , potentiometry using nickel-selective electrodes , and adsorptive cathodic stripping voltammetry (ACSV) [10] .

Cobalt is grayish lustrous metal. It is brittle and hard, Evidence indicates that minute quantities of cobalt may be detrimental to higher plant life, particularly in water and sand cultures. Cobalt toxicity is characterized by a chlorosis similar to that induced by lack of iron[11]. High sensitivity procedures for the determination of cobalt generally use graphite furnace atomic absorption spectrometry (GFAAS) after a pre concentration step, which usually involves the risk of sample contamination and analyte loss[12].

This work aimed to determine of Ni(II) and Co(II) by using using 2-[(2-Carboxy-4-nitrophenyl) azo]-4,5-diphenyl imidazole (CNPAI).

Experimental
Apparatus

A UV-Probe model (UV-1650) spectrophotometer (Schimadzu-Japan) and spectronic-21 model U.V-Visible single beam with 1 cm cells Bausch and Lomb (USA) was used for all absorbance measurements, pH measurements were made with Knick-Digital pH meter (England), Digital Balance, Sartorius, (BP 3015- Germany) and Water bath, Gesellschaft Fur Labortechnik (Germany) , FTIR 8400S Schimadzu (Japan) was used to get I.R spectrums and CHN elemental analyzer 1108 were used.

Reagents

All chemicals used were of analytical – grade reagent unless other wise stated, all solution were prepared using deionized water.

Synthesis of the reagent (CNPAI) [13]

2-[(2-Carboxy-4-nitrophenyl) azo]-4,5-diphenyl imidazole (CNPAI) was prepared[14] by dissolving (0.9100g, 5mmol) of 5-nitroanthranilic acid in 30 ml of water and 3 ml of concentrated hydrochloric acid.

The filtered solution was cooled to 0ºc, treated with 8 ml of aqueous (1 M) sodium nitrite drop wise, and stirred for 30 min.

A 4,5-diphenyl imidazole (1.1000g, 5mmol) was dissolved in 100 ml of pyridine, and 5 ml of 10% sodium hydroxide and 25 ml of 10% sodium carbonate were added, the diazonium solution prepared above was then added drop wise for coupling, after the mixture had been stirred for an hour at 5ºc, it was acidified with dilute hydrochloric acid to pH =5.

The precipitate was filtered off, and recrystallized twice from hot ethanol, and then dried in the oven at 60ºc for several hours, the yield was (54%) (2.2300g) of reddish brown powder (m.p = 112-114 ºc), with the formula $C_{22}H_{15}N_5O_4$ with the theoritcal value C= 63.92%, H= 3.63%, N= 16.94% while the element analysis gave the value of C= 63.58%, H= 3.45% and N= 16.78%.

Standard Ni & Co solutions

Solution of Ni(II) and Co(II) (100 ppm) were prepared by dissolving (0.0974 g) of $Ni(NO_3)_2.6H_2O$ and (0.1234g) of $Co(No_3)_2.6H_2O$ in 250 ml distilled water, working solution were prepared freshly by appropriate dilution of the stock solution.

CNPAI Solution

A solution of ($1x10^{-3}$ M) was prepared by dissolving (0.0413g) of pure reagent in 100 ml of absolute ethanol.

General procedure

Into a 10 ml calibrated flask, transfer (2 ml) of sample solution of Ni(II) or Cd(II) and (1 ml) of ethanolic reagent (CNPAI) solution and dilute to volume with deionized water the final concentration will be not more than 1 ppm for each ion and $1x10^{-4}$ M for the (CNPAI), mix well and after 5 minutes measure the absorbance at 566 nm for Ni(II) and 592 nm for Cd(II) at 10 °c in a 1 cm cell against a blank solution prepared in a similar way but without the presence of the ion under test.

Results & Discussion

Physical and chemical properties of CNPAI

The reagent is a reddish brown powder which is sparingly soluble in water. It has a good solubility in ethanol, methanol, acetone, chloroform and ether.

The color of the solution is red in alkaline medium, yellow in weakly and strong acidic solution.

Effect of pH

The effect of acidity on the absorbance value of the two complexes was investigated by changing the pH value of the solution and the results are shown in, figure (1).
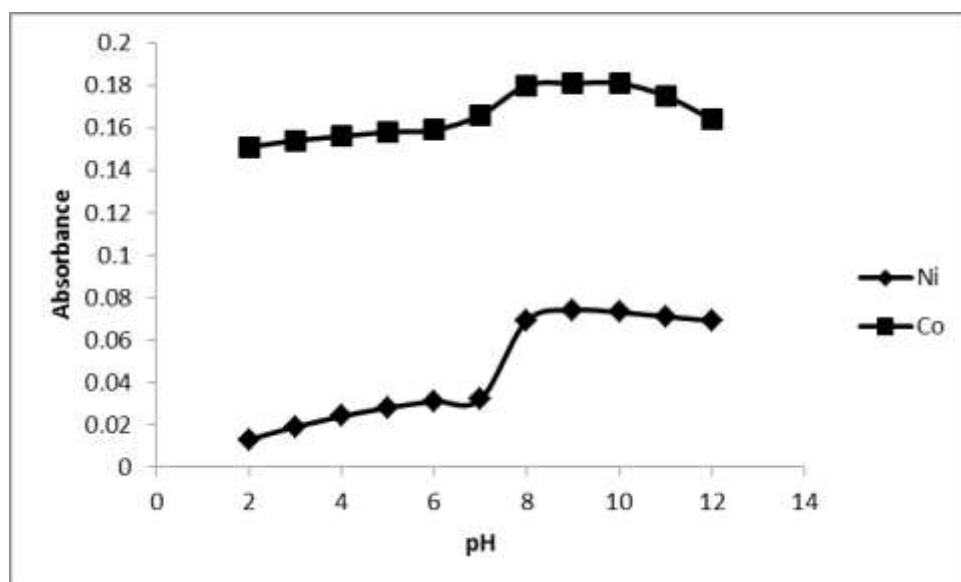

Fig.(1) Effect of pH on the absorbance of two complexes

From Figure (1) the best absorbance of Ni-CNPAI complex was in the pH range (8-10) and Co-CNPAI complex was in the pH range (9-11), pH (10) and (9) was obtained for Ni-CNPAI and Co-CNPAI complexes, higher these values the metal was precipitate as hydroxide.

Stability of the chromogenic system with the time

Stability of the two complexes with the time was studied in different periods , the results shown that the two complexes was stable with the time from 5 min. to 24 hours

Effect of temperature

The effect of temperature on the absorbance of Ni-CNPAI and Co-CNPAI was studied figure (2) show this effect
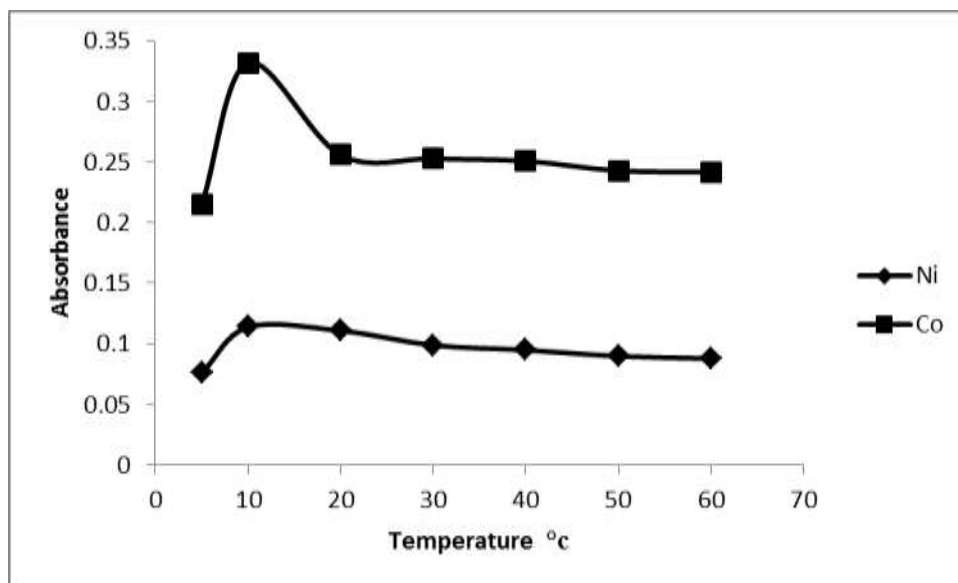

Fig.(2) Effect of temperature on the absorbance of two complexes.

The effect of temperature on the absorbance of two complexes was studied in the range (5-60) °c, figure (2) shown that the best temperature was (10 °c) for two complexes, the decreasing of absorbance value after this temperature was due to the dissociation of the complexes.

Composition of the complexes

The composition of the two complexes was determined by Job's[15] method of continuous variation and molar ratio[16] method the ratio between the metals to ligand was shown in figures (3-6).
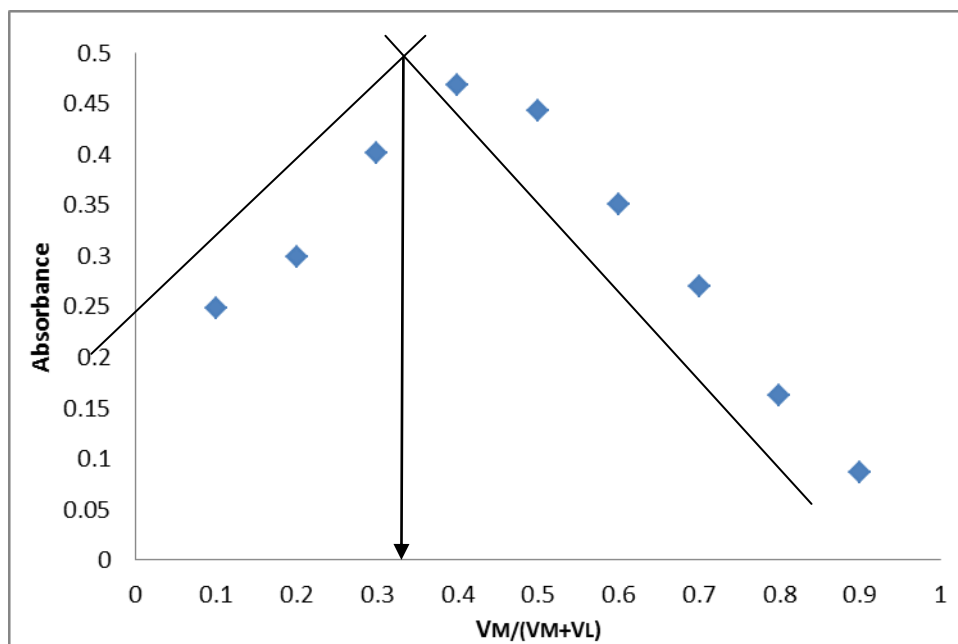
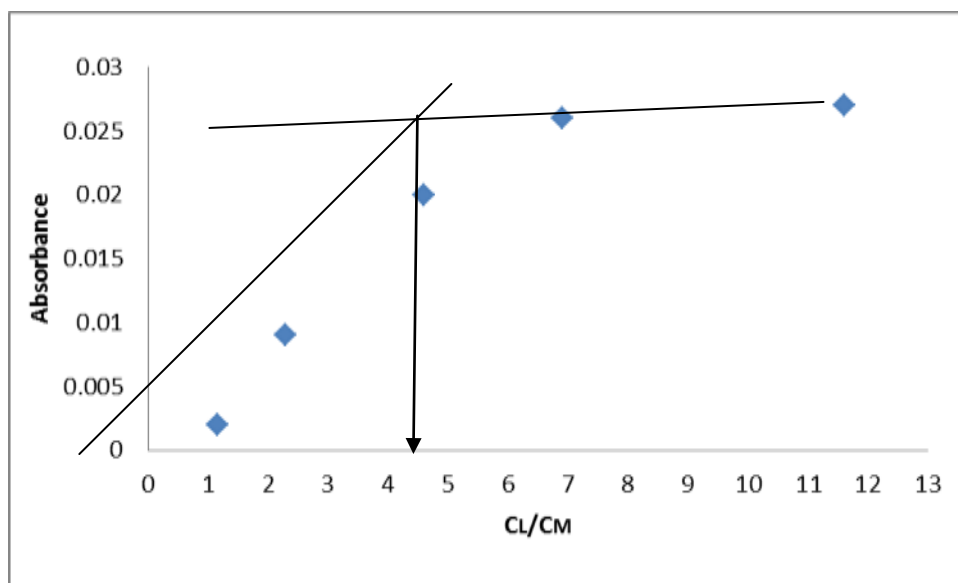

Fig.(3) continuous variation method for Ni-CNPAI

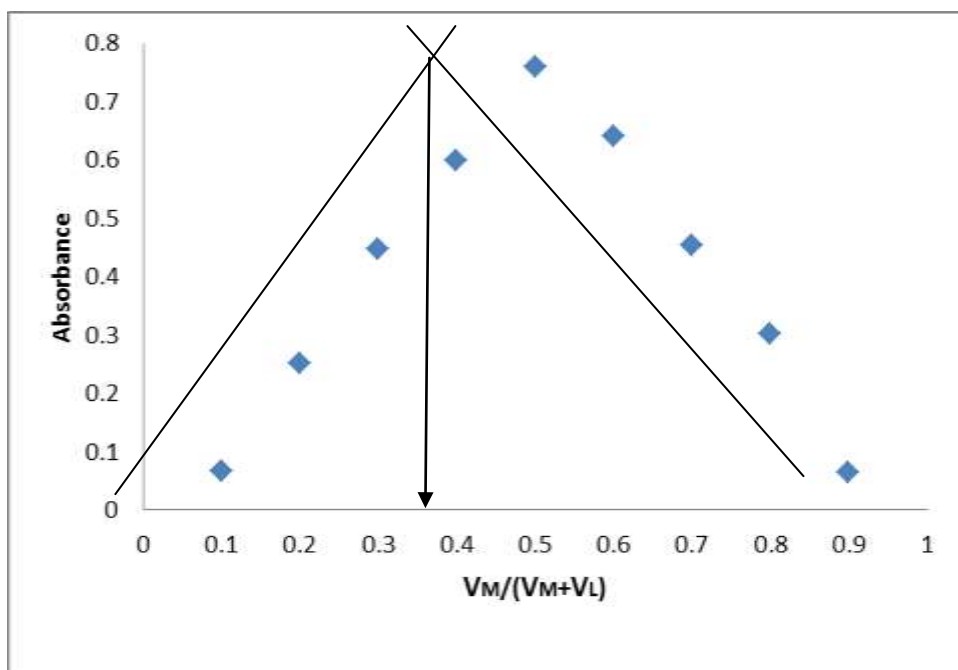Fig.(4) molar ratio method of Ni-CNPAI complex

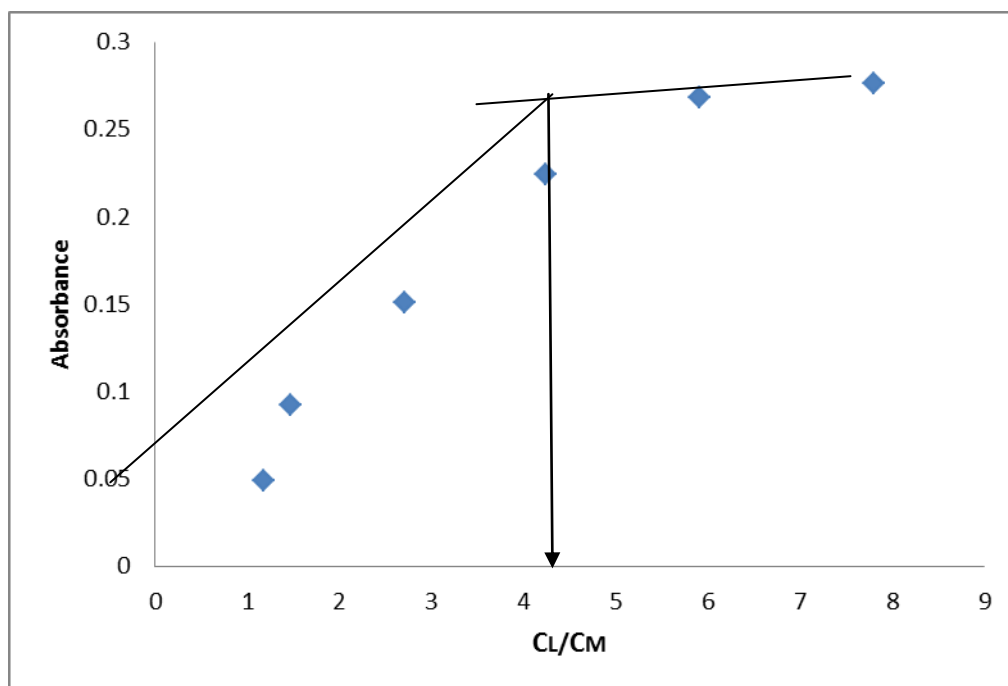Fig.(5) continuous variation method for Co-CNPAI complex

Fig.(6) molar ratio method for Co-CNPAI complex

From the results of continuous variation and molar ratio methods show in figures (3-6), the ratio between Ni(II) and Co(II) to CNPAI was (1:2), stability constant[17] ($K_{sta.}$) was (2.03×10^8 $L^2.mol^{-2}$), (4.94×10^8 $L^2.mol^{-2}$) for Ni-CNPAI and Co- CNPAI complexes, proposed composition of the two complexes was shown in figure (7).
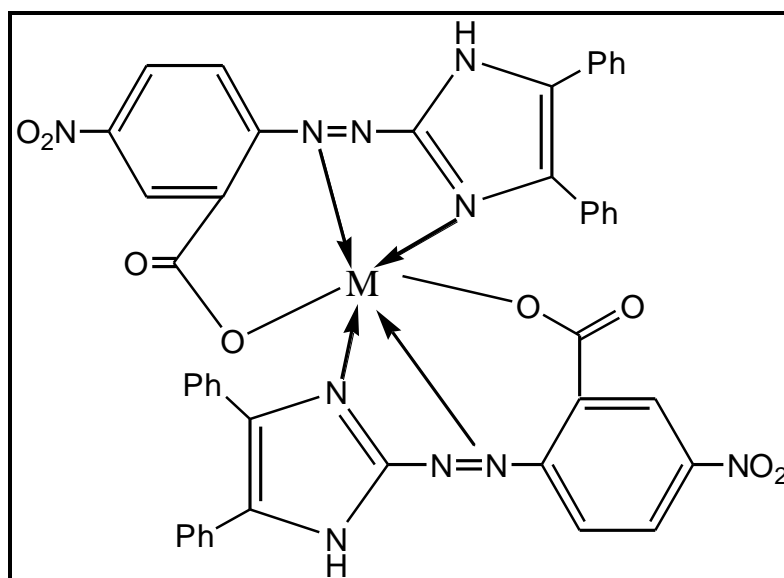
(M) is Ni(II) or Co(II)

Fig. (7) the proposed composition of the complex

Calibration curve

Calibration curve for Ni(II) and Co(II) complexes were obtained by following the proposed procedure under the optimum conditions.
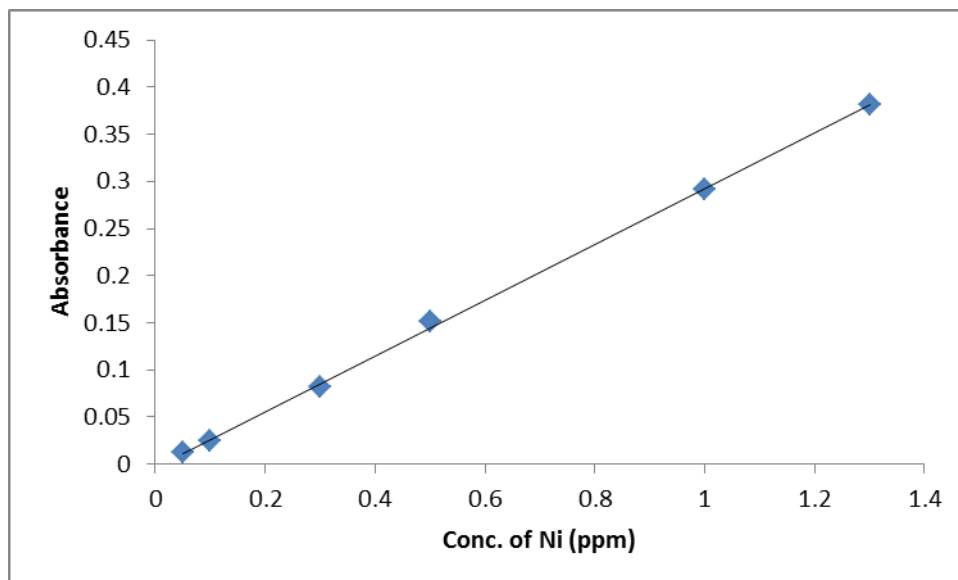The two calibration curve was shown in figures (8&9).

Figure (8) calibration curve of Ni(II).
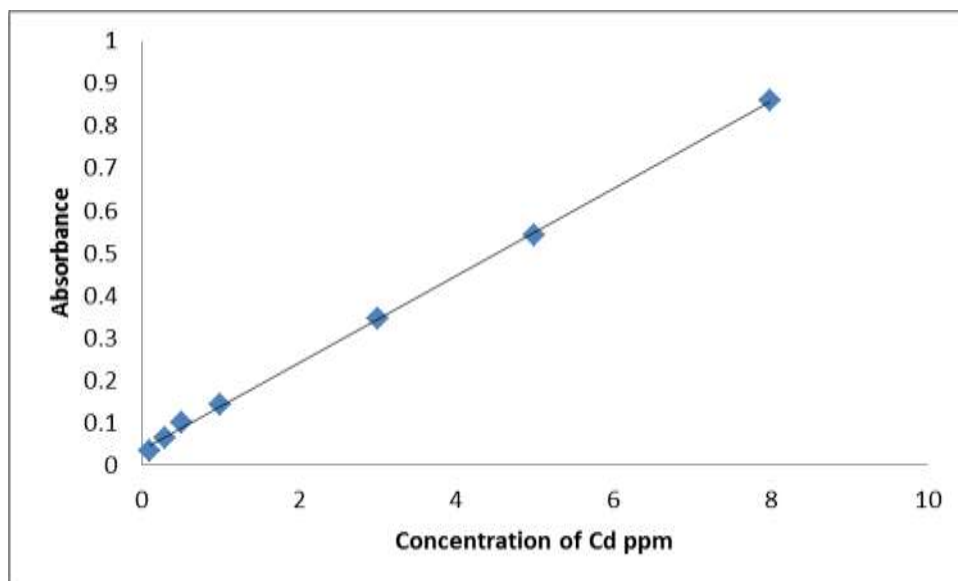
Figure (9) calibration curve of Co (II).

The results indicated that Beer's law was obeyed over the concentration range (0.05-1.3) ppm for Ni(II) and (0.1-8) ppm for Cd(II), linearity (R^2) for Ni(II) was (0.9991) and Cd(II) was (0.9995) respectively.
The molar absorption coefficient (ε) was 1.7448 x 10^4 L.mol^{-1}.cm^{-1},   9.908 x 10^4 L.mol^{-1}.cm^{-1} for Ni(II) and Co(III) complex
The detection limit was (0.02) ppm for Ni(II) and (0.04) ppm for Co(II).

The stoichometry of metals to reagent were 1:2 for two complexes, Precision and accuracy of the analytical procedure for Ni(II) and Co(II) were R.S.D % (2.11 , 0.82)%, ($E_{rel.}$, R_e) % were (-3.1, 96.9) % and (-2.7, 97.3) %.

Effect of Interferences ions
The effect of interferences ions on the selectivity of two complexes was studied by measuring the absorbance of each complex at optimum conditions in presence of different concentrations of foreign ions [18,19].
This effect was shown in table (1)
Table (1) effect of interference ions

Interference ions	Interference %	
3 ppm	Ni-(CNPAI)	Cd-(CNPAI)
Ni(II)	0.00	+9.74
Cd(II)	+7.61	0.00
Ag(I)	+2.52	+3.79
Ba(II)	+4.63	+2.93
Mn(II)	+11.27	+9.92
Co(II)	-5.05	+1.02
Sn(II)	1.30	-3.44
Pb(II)	+7.51	+4.88
Cu(II)	+8.68	+8.09
Bi(III)	+3.67	+1.12
Fe(III)	+6.76	+8.97

Table (1) show the effect of interference ions, the absorbance value varying by more than 5% from the expected value of two complexes[20], these ions are very interference with ions under studded so they must be mask by masking agents.

Effect of masking agents[21]
The effect of masking agents was studied to decrease the interference of the foreign ions and to increase the selectivity of the two complexes.
The effect of the masking agents on the absorbance of the complexes in presence of interferences ions was shown in tables (2 and 3).

Table (2) the effect of masking agents for Ni-CNPAI complex

	Ascorbic Acid	Tartaric Acid	Citric Acid	Oxalic Acid	NaF
Ni(II)	0.071	0.136	0.133	0.142	0.130
Cd(II)	0.044	0.137	0.221	0.140	0.124
Ag(I)	0.072	0.085	0.128	0.117	0.097
Ba(II)	0.172	0.129	0.120	0.091	0.120
Mn(II)	0.070	0.155	0.138	0.066	0.133
Co(II)	0.060	0.061	0.059	0.138	0.301
Sn(II)	0.131	0.122	0.102	0.121	0.128
Pb(II)	0.057	0.186	0.131	0.128	0.133
Cu(II)	0.097	0.159	0.130	0.118	0.185
Bi(III)	0.338	0.130	0.219	0.102	0.152
Fe(III)	0.055	0.069	0.217	0.144	0.077

Table (3) the effect of masking agents for Co-CNPAI complex

	Ascorbic Acid	Tartaric Acid	Citric Acid	Oxalic Acid	NaF
Co(II)	0.146	0.125	0.202	0.118	0.085
Cd(II)	0.121	0.123	0.139	0.180	0.134
Ag(I)	0.101	0.126	0.033	0.101	0.081
Ba(II)	0.142	0.109	0.200	0.088	0.084
Mn(II)	0.098	0.111	0.201	0.115	0.152
Ni(II)	0.144	0.033	0.141	0.279	0.113
Sn(II)	0.140	0.122	0.371	0.190	0.101
Pb(II)	0.140	0.197	0.248	0.155	0.150
Cu(II)	0.071	0.188	0.204	0.118	0.201
Bi(III)	0.110	0.221	0.230	0.114	0.139
Fe(III)	0.214	0.082	0.152	0.119	0.099

Table (2) shown the best masking agents for the Ni-CNPAI complex was ascorbic for (Ag, Mn and Co) ions, tartaric acid for (Cd, Ba, Sn and Bi) ions, citric acid for (Ag, Mn, Pb and Cu) ions, oxalic acid for (Cd, Co and Fe) ions, NaF for (Mn, Sn and Pb) ions.

Table (3) shown the best masking agents for the Co-CNPAI complex was ascorbic for (Ba, Ni and Pb) ions, tartaric acid for (Ag, Cd, and Sn) ions, citric acid for (Ba, Mn, and Cu) ions, oxalic acid for (Mn, Bi and Fe) ions, NaF for (Ag and Ba) ions.

U.V-Visible Spectrum

U.V-Visible spectrum was studied to determine the maximum absorption of the ligand (CNPAI) and two complexes (Ni-CNPAI) and (Co-CNPAI)

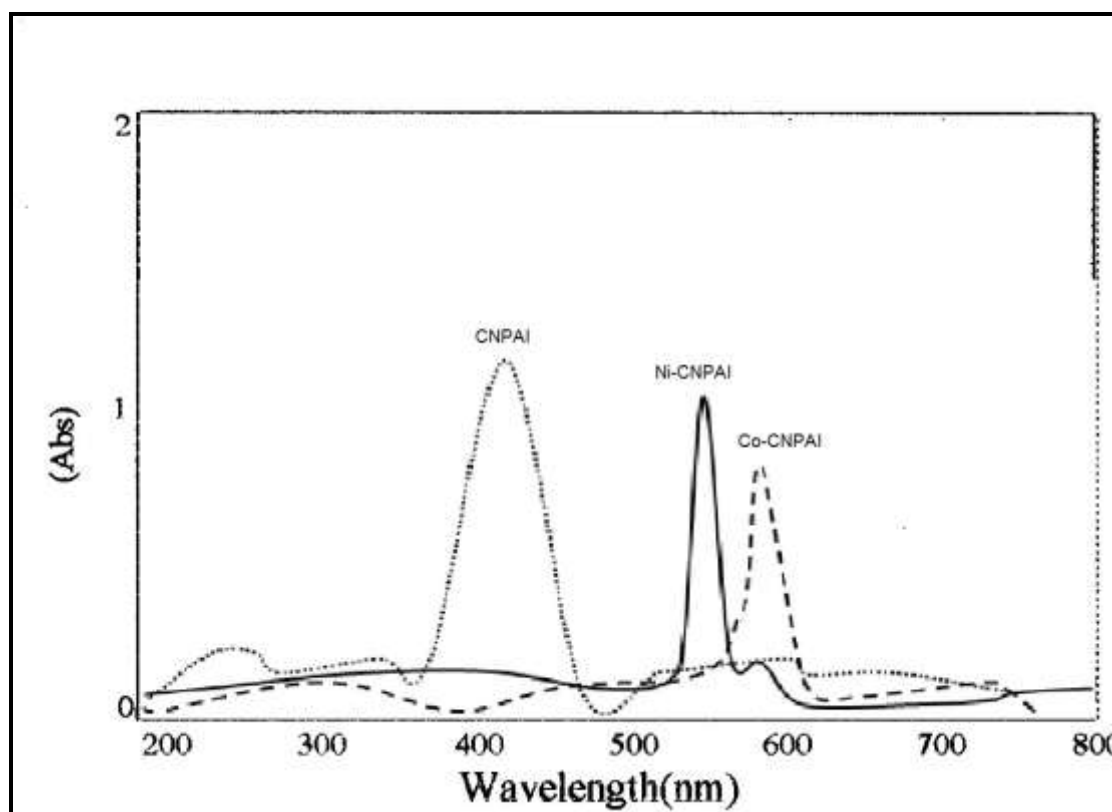The maximum absorption shown in figure (10)

fig.(10) U.V-Visible spectrum of the two complexes and the ligand.

U.V-Visible spectrum shown the maximum of absorption of the ligand (CNPAI) at 425 nm, Ni-CNPAI complex at 566 nm and Co-CNPAI complex at 592 nm, the red shift of maximum absorption of the complexes was a good evidence to the linkage between the metals under study and ligand.

FTIR spectrum

FTIR spectrum was studied to predict the main frequencies of functional groups in the ligand and complexes structures, figures (11) shown the FTIR spectrum of the ligand.
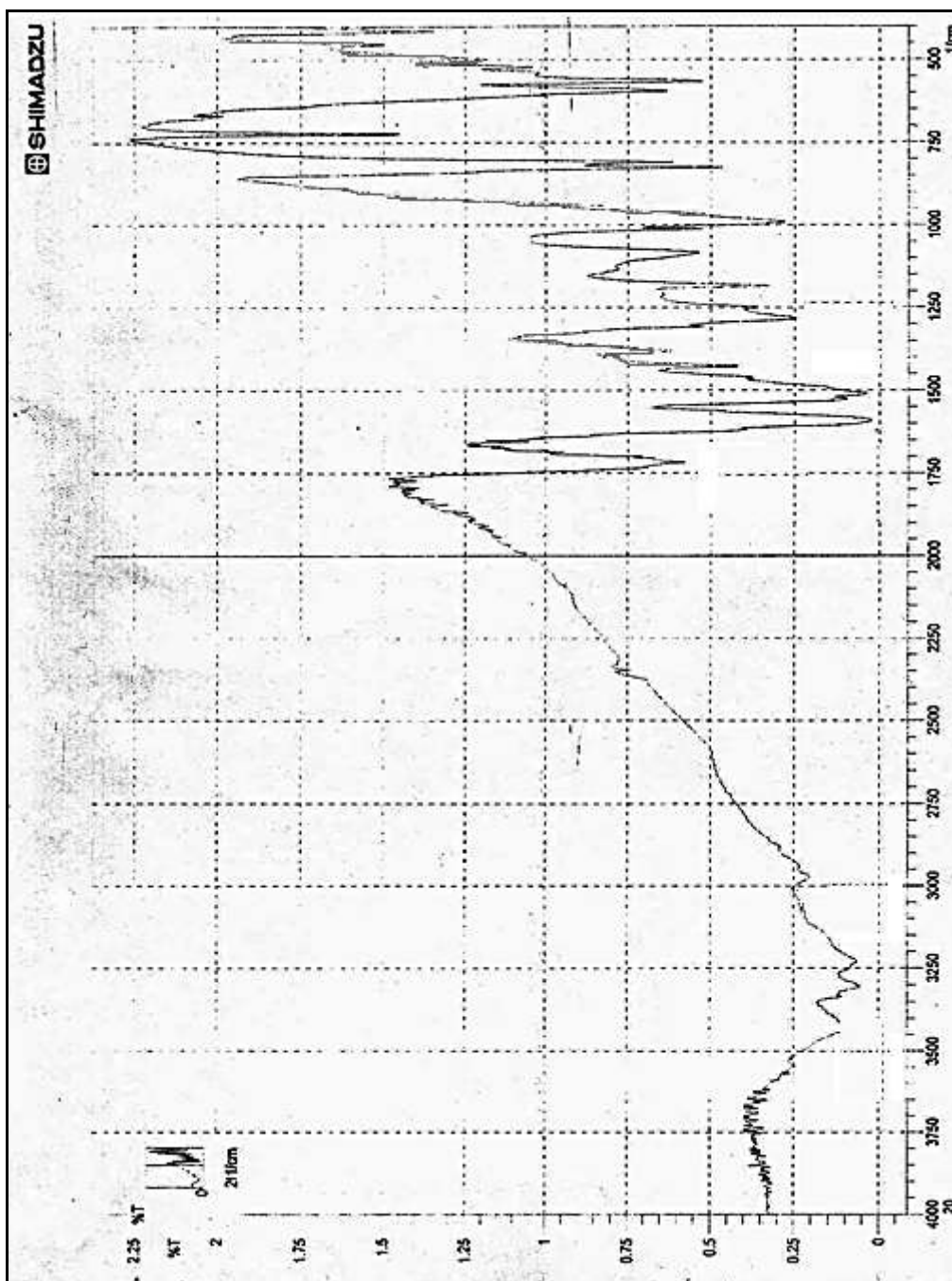

Figure (11) FTIR spectrum of the ligand (CNPAI).

FTIR spectrum of the ligand show many absorbance peaks of functional groups, these peaks shown in table (4).

Table (4) absorbance peaks of the ligand (CNPAI)

No	Frequency	Explanation
1	3450-3350 cm^{-1}	ν (N-H) of the imidazole ring [22]
2	3200 cm^{-1}	ν (C-H) aromatic
3	2980 cm^{-1}	ν (C-H) aliphatic
4	1690 cm^{-1}	ν (C=O) of carboxylic group
5	1590cm^{-1}	ν (C=N) of heterocyclic imidazole ring
6	1500 cm^{-1}	ν (N=N)[23, 24]
7	1460 cm^{-1}	ν (C=C) in benzene ring
8	1050-1400 cm^{-1}	ν (C-N=N-C)
9	1000 cm^{-1}	ν (C-N)[25].
10	690 & 760 cm^{-1}	The two mono substituted aromatic rings on the imidazole ring

FTIR studied of two complexes are undergo many dramatic change in the frequencies of many absorbance peaks these changes are a good evidences to formation of these complexes.

Table (5) show the change in the shape and frequencies of the peaks in the two complexes

Table (5) the frequencies of peaks in the two complexes

No	ν cm^{-1} Ni-CNPIA complex	ν cm^{-1} Co-CNPIA complex	Explanation
1	3445-3340	3445-3347	ν (N-H)
2	1640	1655	ν (C=O)
3	1574	1520	ν (C=N)
4	1417	1390	ν (N=N)
5	453	445	ν (M-O)
6	430	448	ν (M-N)

Table (5) shown the main change in the frequencies of some functional groups in two spectrum of complexes, these groups are a band at 3445-3340 cm^{-1} and 3445-3347 cm^{-1} this band remains in the same region in free ligand and in complex this is a good indicator for noninvolvement in coordination of the ligand to the metal ions, shift and reduce band in 1640 cm^{-1} , 1655cm^{-1} and 1574 cm^{-1}, 1520 cm^{-1} and 1417 cm^{-1} and 1390 cm^{-1} due to linkage of the ligand with the metals[26,27].
A new peaks at 453 cm^{-1}, 445 cm^{-1}, 430 cm^{-1} and 448 cm^{-1} these peaks back to (M-O) and (M-N) respectively[28,29], where M is Ni and Co.

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