Determination of Ni^{2+} and Zn^{2+} by using a
new ligan 2-[(2-Benzimidazolyl) azo]-4-methoxyphenol

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Abstract

A new ligand 2-[(2-Benzimidazolyl) azo]-4-methoxyphenol (BIAMP), is used for the determination of Ni^{2+} and Zn^{2+}, the wavelengths of maximum absorption of complexes are (549 nm) and (600 nm) for Ni-BIAMP,   Zn-BIAMP.

After optimum condition like pH (10), (10),temperature (30 ºc),   (40 ºc) for Ni^{2+}, Zn^{2+}, Beer's law was obeyed in the range (0.03-2), (0.03-1.3) ppm, detection limit was (0.0002), (0.0015) ppm, linearity (R^2) was (0.9995), (0.9996), correlation factor (r) was (0.9997), (0.9998), molar absorbitivty (ε) was 2.04x 10^4 L.mol^{-1}.cm^{-1}, 1.03 x 10^4 L.mol^{-1}.cm$^-$ for Ni^{2+}, Zn^{2+}.

The stoichometry of metal to ligand were (1:2) of complexes, Precision and accuracy of the analytical procedure was R.S.D % (0.30, 1.75) % and E$_{rel.}$% and R$_e$ % were (-1.45, -2.03) %, (98.55, 97.97) % for Ni, Zn.   The interferences of ions were study and masked by using suitable masking agents.

الخلاصة

استعمل الكاشف الجديد (2-BIAMP)   (Benzimidazolyl) azo]-4-methoxyphenol) (لتقدير النيكل (II) والزنك (II) ، وجد ان اعلى امتصاص للمعقدين كان عند الطول الموجي (549 nm) و (600 nm) لكل من النيكل و الزنك ، حددت الظروف المثلى لتكوين المعقدين من داله حامضية (10) و (10) ودرجة حرارة (30) و (40) مئوية، تم بناء منحني المعايره عند مدى من التراكيز تراوحت بين (2ppm-0.03) و (0.03-1.3 ppm) لكل من النيكل والزنك.

وجد ان حد الكشف لهذه الطريقة هو (0.0002 ppm) و (0.0015 ppm) وبخطية (R^2) مساويه الى (0.9995) و (0.9996)(وقيمة معامل الارتباط (0.9997) و (0.9998) ، اما قيمة معامل الامتصاص المولاري هي 2.04x 10^4 L.mol^{-1}.cm^{-1} و 1.03 x 10^4 L.mol^{-1}.cm^{-1} لكل من النيكل والزنك على التوالي.

تم تحديد نسبة الفلز الى الكاشف حيث وجد انها تساوي (2:1) لكلا المعقدين كما تم تحديد دقة وضبط الطريقة التحليلية حيث وجدان قيمة 0.30 (%R.S.D%) و (1.75 %) اما E$_{rel}$ بلغت (1.45- %) و (2.03- %) اما R$_e$ (98.55 %) و (97.97 %)) لكل من النيكل والزنك على التوالي ، كما درس تاثير الايونات المتداخلة وحجبت باستخدام عوامل الحجب المناسبة.

Introduction

Industrial Ni^{2+} is encountered in the proximity of other as a macro component or a micro component, Ni^{2+} is to be found in arsenates, silicates, sulfides and phosphates together with iron, cobalt, copper, chrome and zinc, Ni^{2+} is used in industry as such or under the form of alloys like Monel   (a trademark used for an alloy of nikel, copper, iron and manganese), germane silver (Cu, Zn and Ni^{2+}), nichrome (Ni and Cr) and special brass (Ni, Cu and Zn)[1].

A great variety of methods for determination of Ni^{2+} have been reported.[2-5] Method for Ni^{2+} determination by potentiometric titrations, which make used of different metallic electrodes and different titration, are also reported[6].

Potentiometric determination of Ni^{2+} in brass allowys, involving the selective extraction of Ni^{2+} as dimethylglyoximate, followed by the latter's determination by the potentiometric titration of EDTA excess with cadmium nitrate[7].

Zn is an essential element in the nutrition of animals, human beings and plants[8,9]. However, zinc can be toxic when exposures exceed physiological needs, zinc is present in food, soil and water, there are many methods for zinc determination such as spectrophotometry[10-12].

Atomic absorption spectrometry[13,14], inductivity coupled plasma atomicemission spectroscopy[15]. Flow-injection analysis can improre procedures such as high analytical throughput, precision, accuracy, low ligands and sample consumption[16,17].

In this paper a new spectrophotometric method was proposed for determination of low concentration of Ni^{2+} and Zn^{2+} by using a new organic ligand.

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.

Ligands

Synthesis of 2-[(2-Benzimidazolyl) azo]-4-methoxyphenol (BIAMP)

The azo ligand (BIAMP) was prepared as described below:

A diazonium solution was prepared by dissolving (2.66 g, 20 mmol) of 2-amino-benzoimidazole in (30 ml) of water and (8 ml) of concentrated hydrochloric acid. The filtered solution was cooled to (0 ºc), treated with (30 ml) of aqueous (1 M) sodium nitrite drpwise, and stirred for (30 min.), the resulting diazonium chloride solution was added dropwise with cooling to a solution of 4-methoxyphenol (3.60 g, 20 mmol) dissolved in (100 ml) alkaline ethanol. After leaving overnight in the refrigerator, the mixture was neutralized with dilute hydrochloric acid until (pH=6).

The solid product was filtered off, washed with cold distilled water until a negative chloride reaction with silver nitrate was obtained. Then it was recrystallized twice from hot ethanol and dried in a desiccators over anhydrous calcium chloride the yield was (59 %) (3.16 g) of red crystallizes which was malted at (235 ºc), the structural of this ligand as shown below.

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Standard Solutions

A solution of Ni^{2+} (20 ppm) was prepared by dissolving (0.0075 g) of NiCl$_2$.6H$_2$O in 50 ml distilled water

A solution of Zn^{2+} (20 ppm) was prepared by dissolving (0.0020 g) of ZnCl$_2$ in 50 ml distilled water.

Working solution was prepared freshly by appropriate dilution of the stock solution.

2-[(2-Benzimidazolyl)azo]-4-methoxyphenol (BIAMP) solution

A solution of (1x10^{-2} M) was prepared by dissolving (0.0670g) of pure ligand in 25 ml of absolute ethanol.

General procedure

Into a 5 ml calibrated flask, transfer (1 ml) of sample solution containing not more than 0.3 ppm of Ni^{2+}, 0.4 ppm of Zn^{2+} ions and   (1 ml) of 1x10^{-4} M ethanolic ligand (BIAMP) solution dilute to volume with deionized water, mix well and after 10 minutes measure the absorbance at 549 nm for Ni^{2+}, 600 nm for Zn^{2+} 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 BIAMP

The ligand is a 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 brown in alkaline medium, yellow in weakly and strong acidic solution.

Effect of pH

The effect of pH on the absorbance value of the complexes was investigated by changing the pH value of the solution and the results are shown in, figures (1, 2).
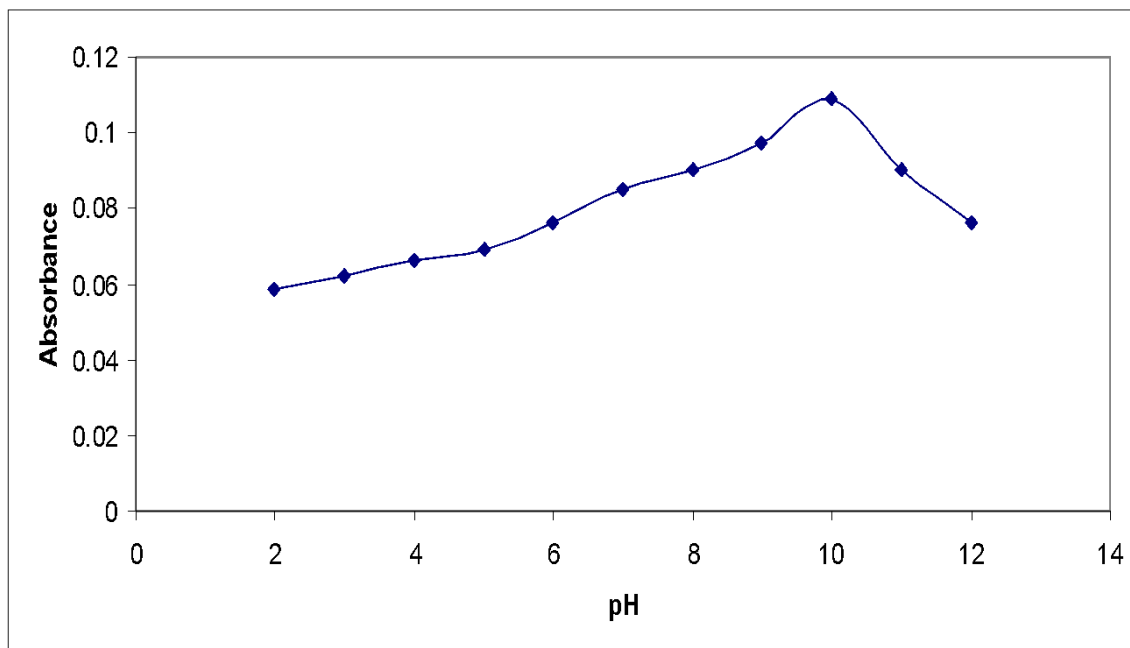
Fig.(1) Effect of pH on the absorbance of Ni-BIAMP complex .
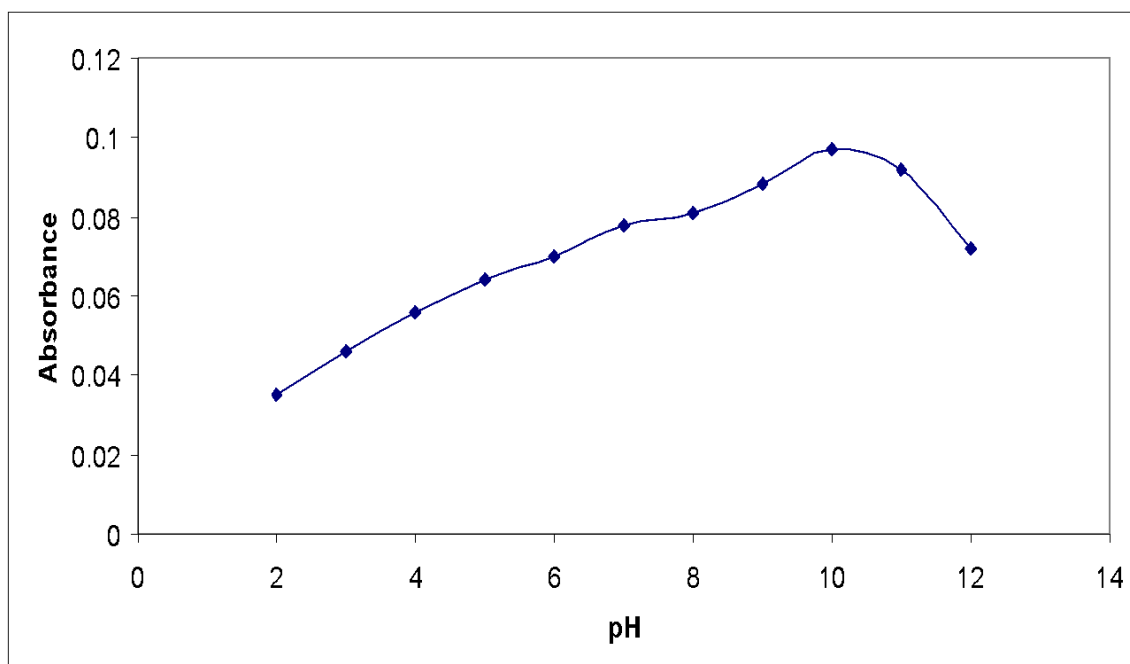

Fig.(2) Effect of pH on the absorbance of Zn-BIAMP complex.

From figures (1, 2) the best pH value of Ni-BIAMP complex is in the range (9-11) and pH (10) was adopted as optimum while for Zn-BIAMP complex is in the range (9.5-10.5) and the pH (10) was adopted.

Stability of complexes with the time
Stability of the tow complexes with the time was studied, the color of the tow complex system reaches it's maximum value of absorbance from (5) min. and remain stable for about (24) hours.

Effect of temperature

The effect of temperature on the absorbance of the complexes Ni-BIAMP, Zn-BIAMP was studied figures (3, 4) show this effect.
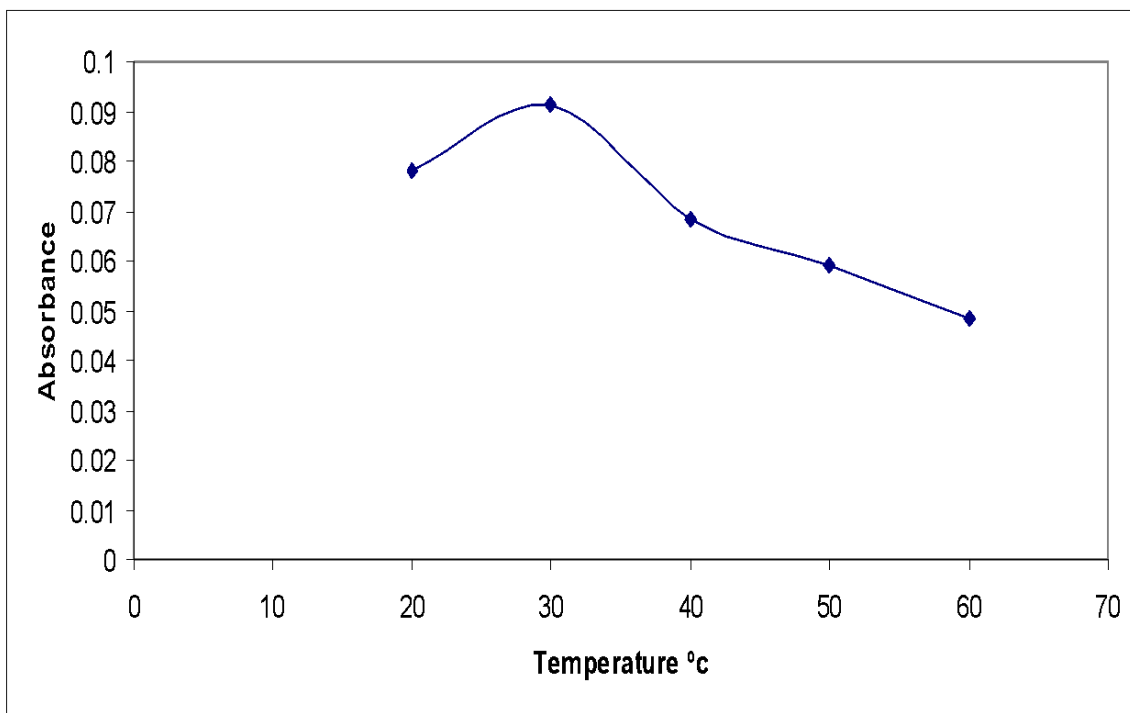

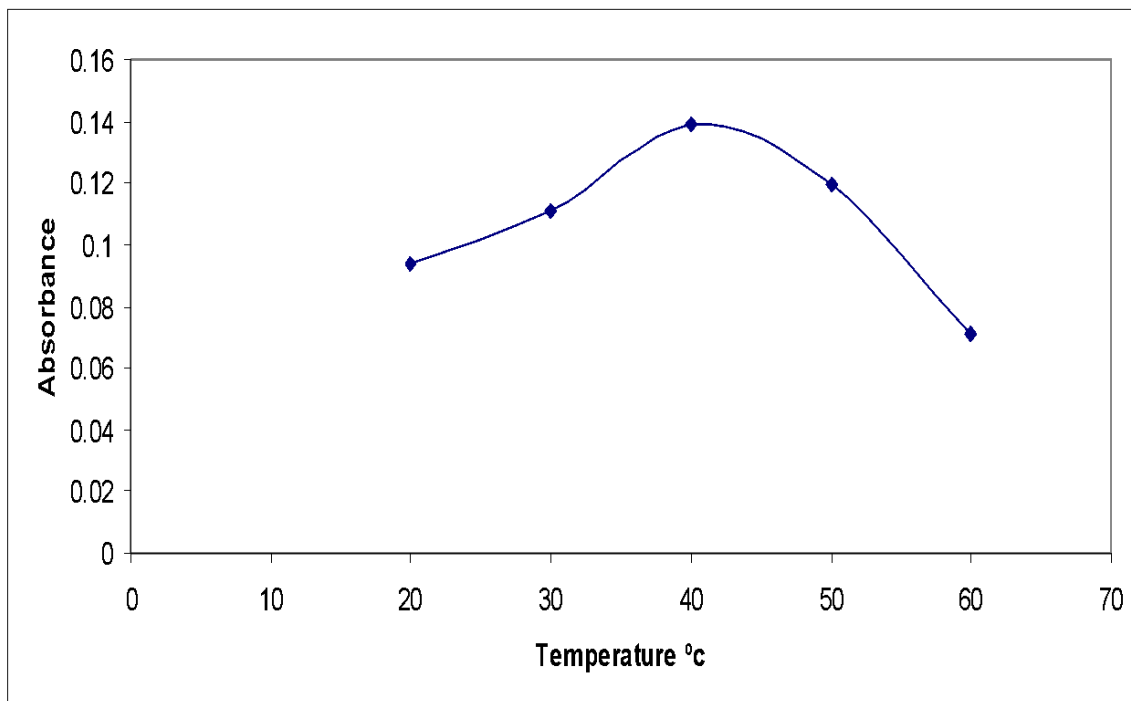Fig.(3) Effect of temperature on the absorbance of Ni-BIAMP complex.

Fig.(4) Effect of temperature on the absorbance of Zn-BIAMP complex.

The effect of temperature on the absorbance of tow complexes was studied in the range (20-60) ºc, the maximum absorption was obtained at 30 ºc, 40 ºc for Ni, Zn, the decrease in absorbance value may be is due to the dissociation of the complex.

Composition of the complexes

The composition of the two complexes was determined by Job's[18] method of continuous variation and molar ratio[19] methods, the composition of tow complexes were shown in figures (5-8).
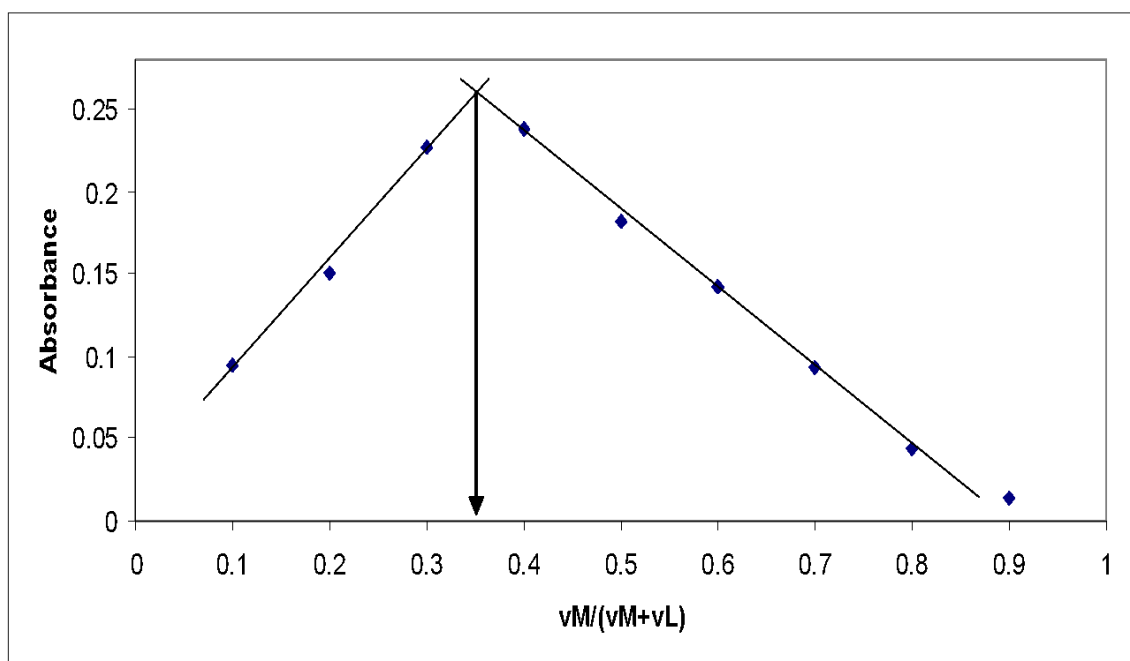

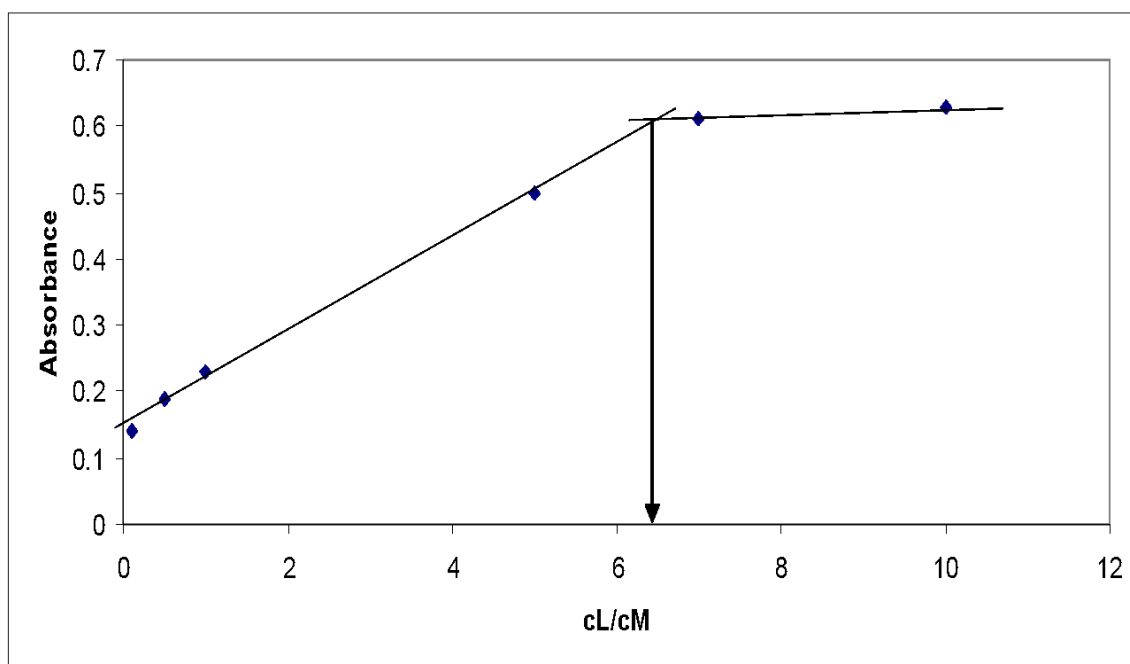Fig.(5) continuous variation method for Ni-BIAMP complex at optimum conditions.

Fig.(6) molar ratio method for Ni-BIAMP complex at optimum condition.
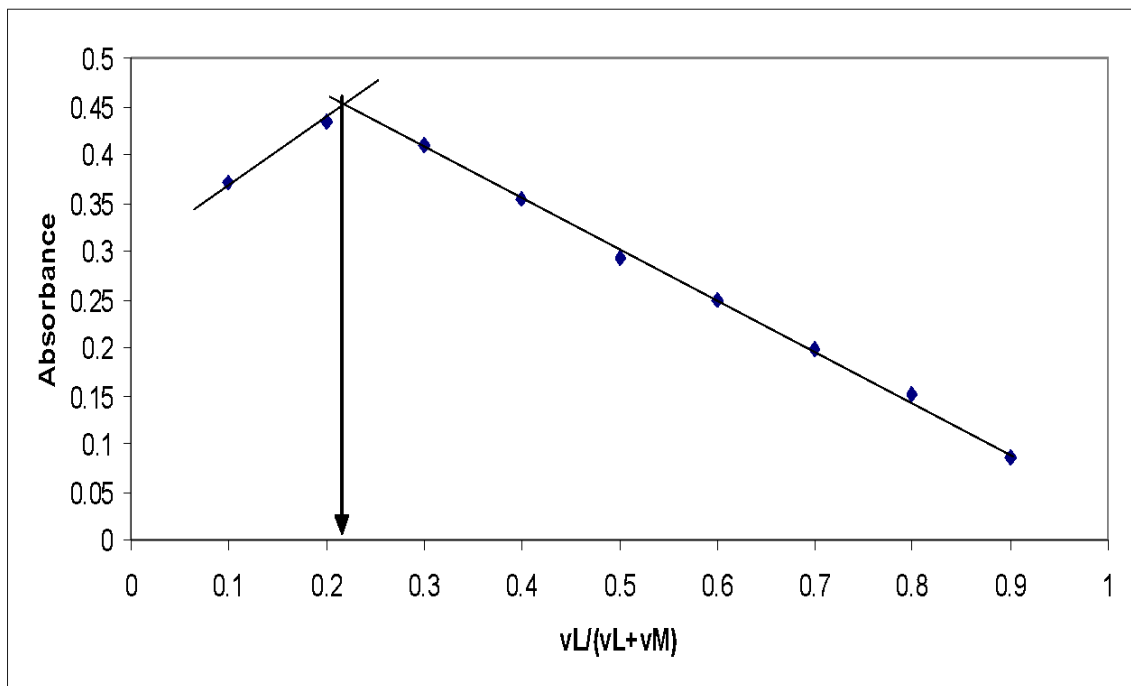
Fig.(7) continuous variation method for Zn-BIAMP complex at optimum conditions.
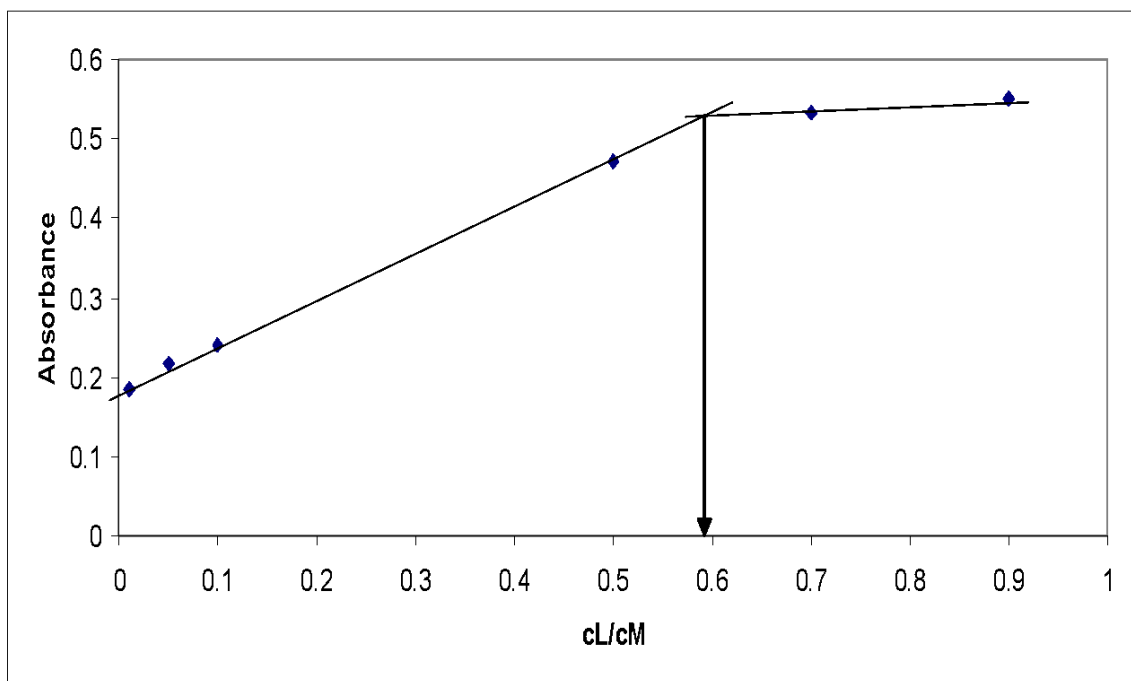

Fig.(8) molar ratio method for Zn-BIAMP complex at optimum conditions.

From the results of continuous variation and molar ratio methods show in figures (5-8), the ratio between Ni, Zn to BIAMP is (1:2), and the stability constant[20] $(K_{sta.})$ was $(2.39 \times 10^6 \ L^2.mol^{-2})$, $(9.70 \times 10^5 \ L^2.mol^{-2})$ for Ni-BIAMP, Zn-BIAMP complexes, figures (9, 10) shown the proposed composition of the complexes.

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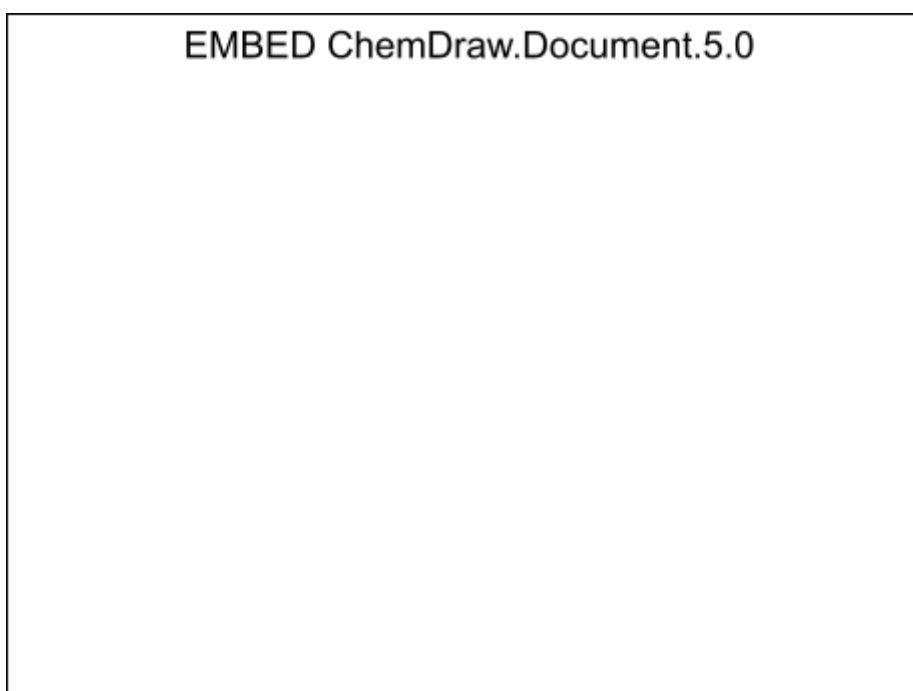Fig. (9) the composition of Ni-BIAMP complex

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Fig. (10) the composition of Zn-BIAMP complex

Beer's low

Calibration curve for tow complexes were obtained by following the proposed procedure under the optimum conditions, figures (11, 12).
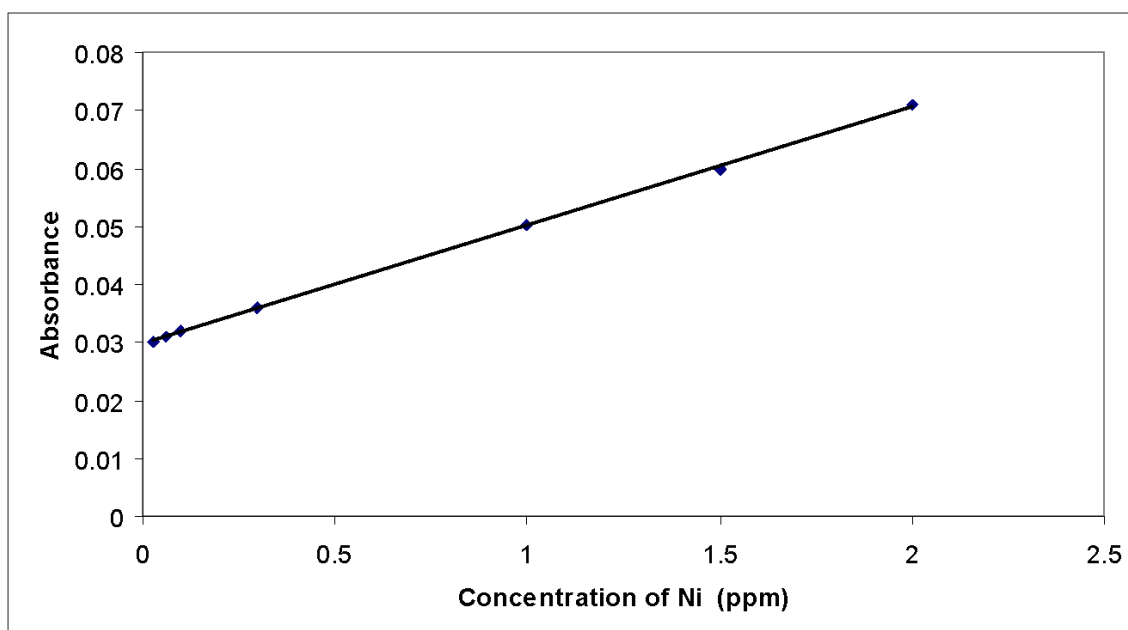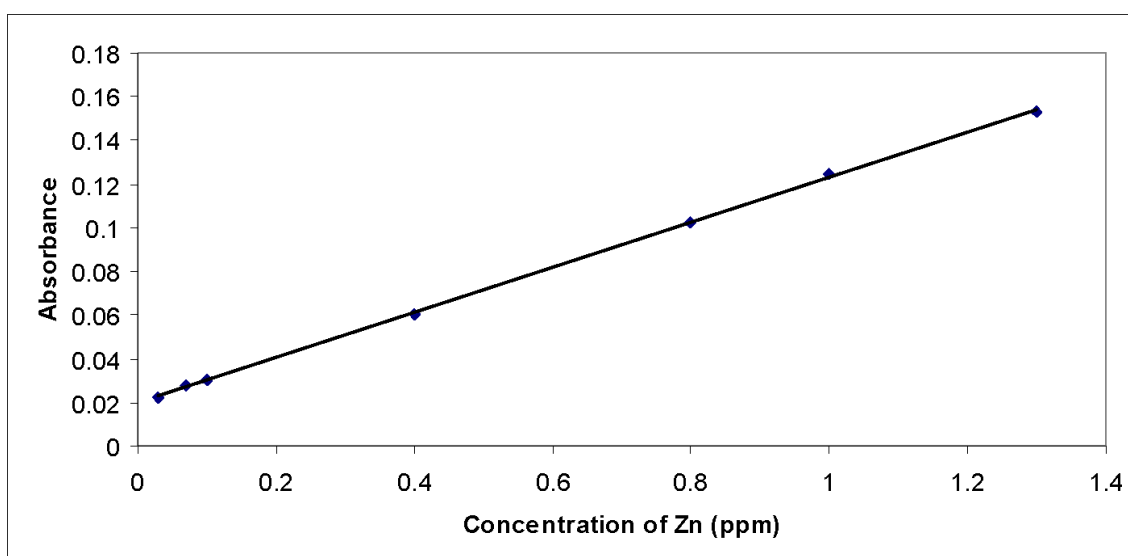

Fig (11) calibration curve of Ni $^{2+}$ ion.

Figure (12) calibration curve of Zn^{2+} ion.

Beer's law was obeyed in the range (0.03-2), (0.03-1.3) ppm, detection limit was (0.0002), (0.0015) ppm, linearity (R^2) was (0.9995), (0.9996), correlation factor (r) was (0.9997), (0.9998), molar absorbitivty (ε) was 2.04x 10^4 L.mol^{-1}.cm^{-1}, 1.03 x 10^4 L.mol^{-1}.cm^{-1} , Sandell's sensitivity were 2.84x10^{-4} , 6.29 x10^{-5} for Ni^{2+}, Zn^{2+}.
Precision and accuracy of the analytical procedure was R.S.D % (0.30, 1.75) % and E$_{rel.}$% and R$_e$ % were (-1.45, -2.03) %, (98.55, 97.97) % for Ni, Zn.

Effect of interference ions[21,22]

The selectivity of Ni-BIAMP, Zn-BIAMP complexes were tested by measuring the absorbance of complex of 1 ppm of Ni^{2+}, 1 ppm Zn^{2+} at optimum conditions in presence of different foreign ions of 5 ppm concentration which are able to form complexes with (BIAMP).

The extent of reaction of these ions is shown in table (1)

Table (1) effect of interference ions

Interference ions 5 ppm		
Ni^{2+}	-------	+4.41
Zn^{2+}	+3.87	-------
Sn^{2+}	+3.95	+2.77
Mn^{2+}	+4.54	+3.86
Fe^{2+}	+1.12	+5.92
Co^{2+}	+6.23	+4.01
Cu^{2+}	+7.18	+7.33
Cd^{2+}	+3.08	+8.36
Pb^{2+}	+1.44	+2.42
Al^{3+}	+2.22	+1.31

Table (1) shown that ions (Co^{+2} and Cu^{+2}) were the absorbance value varying by more than 5% from the expected value for Ni^{2+} complex and (Cu^{+2} and Cd^{+2}) ions for Zn^2.

Effect of masking agents[23]

The effect of masking agents was studied to increase the selectivity of complexes; this effect is shown in table (2).

Table (2) the effect of masking agents

	Complex without any addition	Tartaric acid	Oxalic acid	Citric acid	Ascorbic acid	KCN	NaF
Ni-BIAMP	0.070	0.071	0.030	0.017	0.030	0.040	0.016
Zn-BIAMP	0.042	0.040	0.064	0.015	0.022	0.041	0.039

Table (2) shown the best masking agent for Ni-BIAMP complex was Tartaric acid, for Zn-BIAMP were Tartaric acid and KCN, other masking agents are less effect comparatively.

Absorption spectra

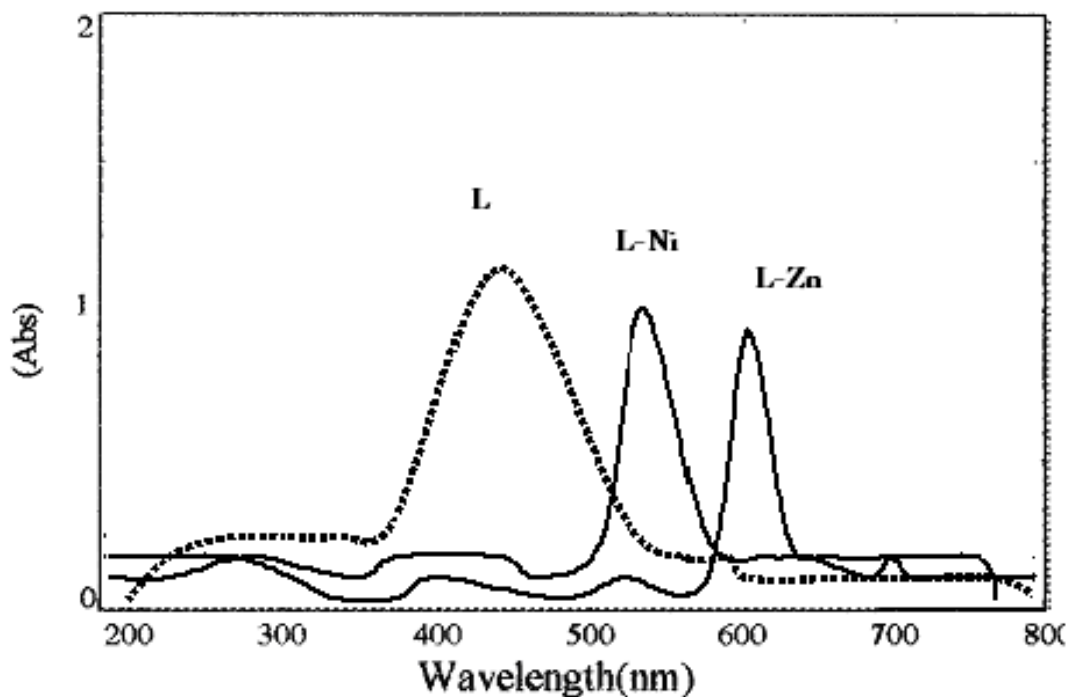The absorption spectra of the two complexes and the ligand are shown in figure (13) under optimum conditions

fig.(13) absorption spectra of the two complexes and the ligand.

Absorption spectra show that the λ_{max} absorption of the ligand (BIAMP) at 449 nm, , Ni-BIAMP complex at 549 nm and Zn-BIAMP complex at 600 nm, this a new λ_{max} mean red shift in λ_{max} of complexes.

FTIR spectrum of (BIAMP) ligand

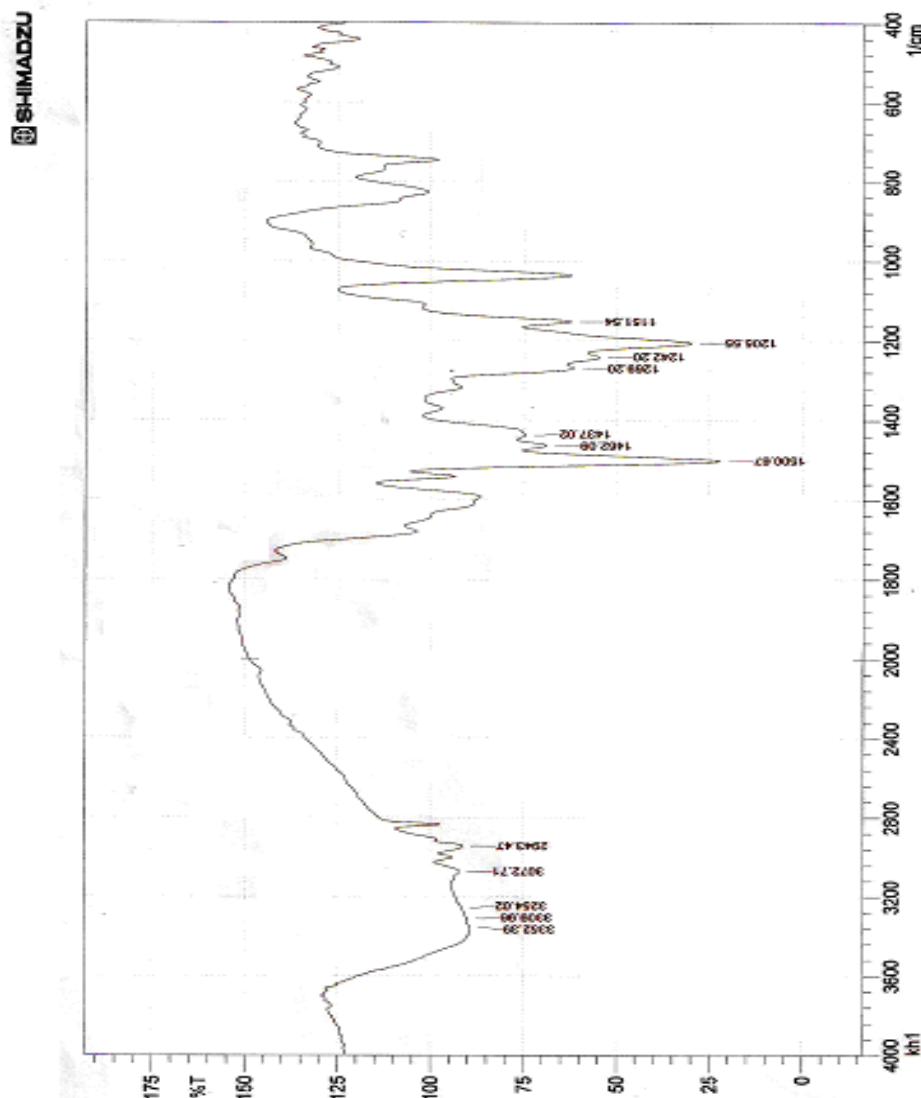FTIR spectrum of (BIAMP) ligand shown in figure (14)

fig.(14) FTIR spectrum of (BIAMP) ligand

The infrared spectrum show in figure (14) give an evidence for the formation of the ligand BIAMP, table (3) show the main absorbance peaks

Table (3) main absorbance peaks

Value cm^{-1}	Conclusion
3352	Hydrogen bond between H atom in –OH group and N in N=N
3254	N-H stretching in amidazol ring
3072	C-H aromatic stretching
2943	C-H aliphatic stretching

| 1610 | C=N stretching of amidazol ring that is fusion with benzene ring |
| 1500 | N=N stretching |

FTIR spectrum of (BIAMP-Ni) complex
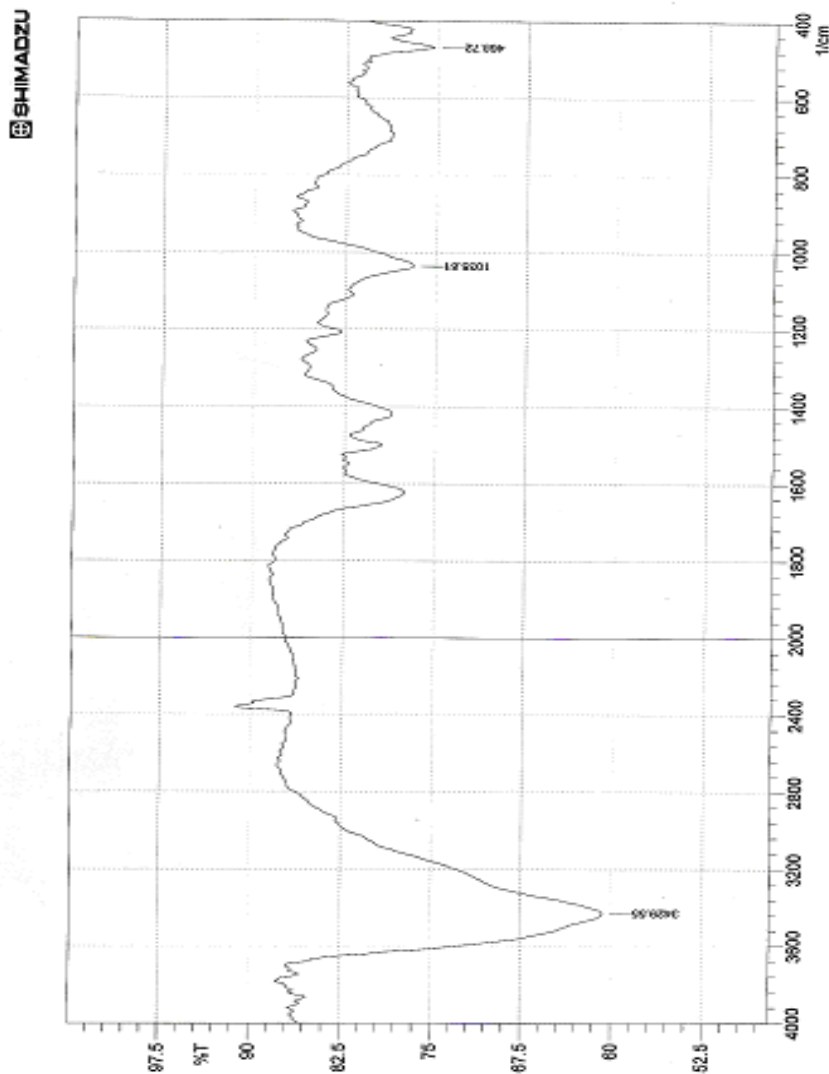FTIR spectrum of (BIAMPI-Ni) complex shown in figure (15)

fig.(15) FTIR spectrum of (BIAMP-Ni) complex

FTIR spectrum of (BIAMP-Zn) complex

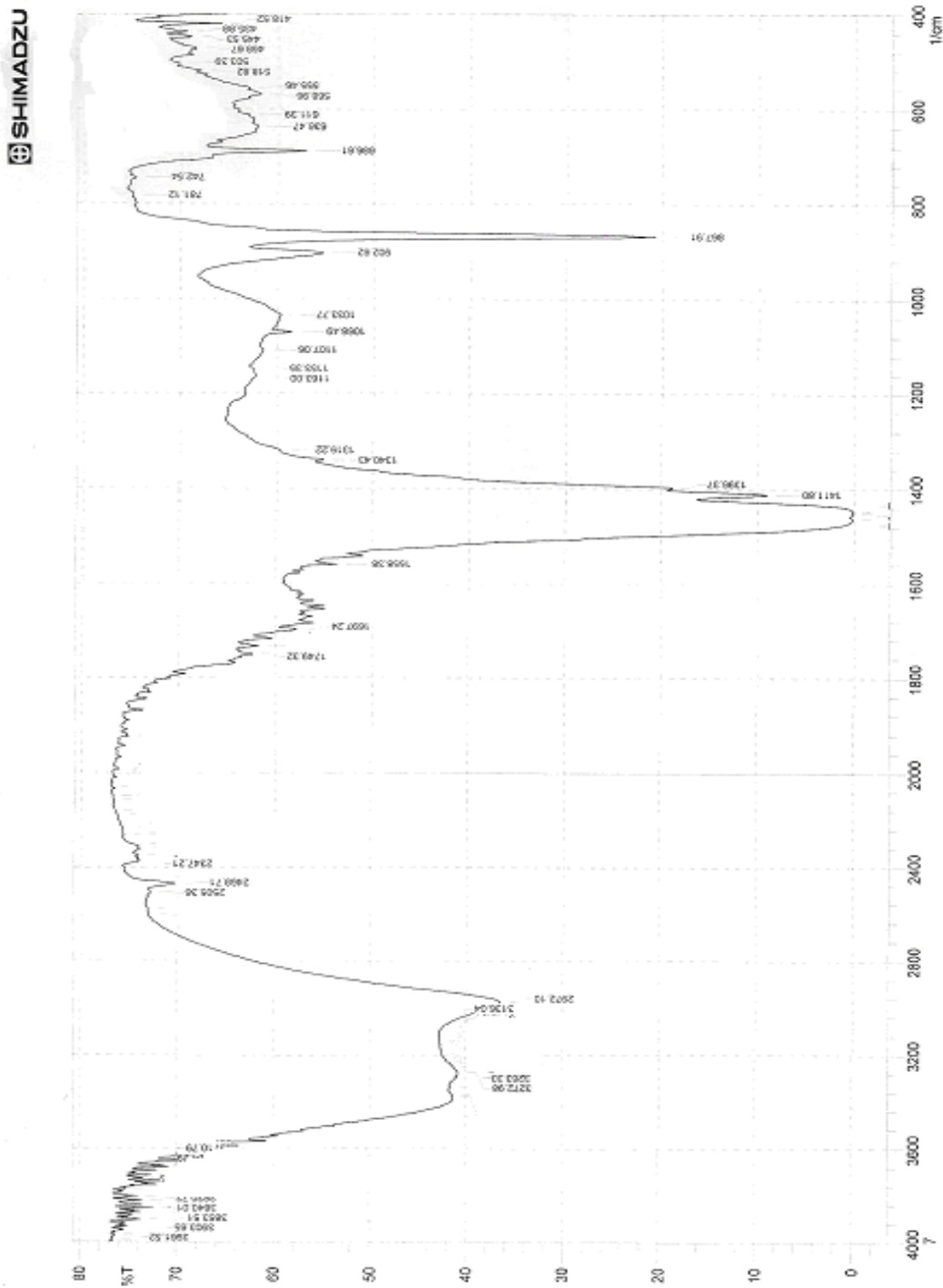FTIR spectrum of (BIAMPI-Zn) complex shown in figure (16)

fig.(16) FTIR spectrum of (BIAMP-Zn) complex

The comparison between spectra of the ligand with those of the coordination complexes have revealed certain characteristic differences, these difference was shown in figures (15 and 16).

From figure (15and 16) all metal complexes show that (BIAMP) behaves as monobasic tridentate ligand, coordinating via (C=N, N=N and phenolic OH) groups with displacement of hydrogen atoms from the latter.

The absence of broad band at 3429 cm⁻¹ in (Ni-BIAMP) complex spectrum and at 3272-3377 cm⁻¹ in (Zn-BIAMP) complex spectrum indicate the deprotonation of phenolic oxygen and cleavage of the hydrogen bond with the involvement of the oxygen in bonding[24,25].

The spectra of the BIAMP ligand figure (14) shown a single strong absorption bands at (1610 cm⁻¹) due to (C=N) stretching of imidazol ring, this band was reduced and shift to (1520 cm⁻¹) and (1480 cm⁻¹) in (Ni-BIAMP) and (Zn-BIAMP) complex spectrums, these shift suggest the linkage of metal ion with nitrogen of imidazol ring[26,27]. A (N=N) band at (1500 cm⁻¹) in BIAMP ligand figure (14) was shifted to (1415 cm⁻¹) and (1411 cm⁻¹) in figures (15 and 16) this shift could contributed to the metal-azo linkage[28].

A new bands appeared in (418-468 cm⁻¹) and (418-445 cm⁻¹) in the spectrum of the complexes that does not appeared in BIAMP spectrum, this may be back to the (M-O), (M-N) stretching for (Ni-BIAMP) and (Zn-BIAMP) [29,30].

Applications

This method was applied to determine Ni²⁺ and Zn²⁺ standard solutions, the results show in table (4)

Table (4) the results of standard method

Ion	True Value	Experimental Value
Ni²⁺	0.9 ppm	0.901 ppm
Zn²⁺	0.8	0.749 ppm

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