Determination of Co^{2+} and Ni^{2+} by using 2-[(6-Methoxy-2-Benzothiazolyl) azo]-4-methoxyphenol

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Abstract

A 2-[(6-Methoxy-2-Benzothiazolyl)azo]-4-methoxyphenol (MBTAMP) ligand was used to determine Co^{2+} and Ni^{2+}, the chelating complexes of these ions with (MBTAMP) ligand were also prepared using mole ratio and continues variation methods, metal to reagent were (1:2) for two complexes. The complexes were identify by using UV-Vis spectrophotometry and (FTIR) spectra.

The wavelengths of maximum absorption of two complexes are (512 nm) and (605 nm) for Co-MBTAMP and Ni-MBTAMP respectively.

The optimum condition of pH and temperature were studied, the molar absorbitivty (ε) was $3.84x\ 10^4$ $L.mol^{-1}.cm^{-1}$, $3.9\ x\ 10^4$ $L.mol^{-1}.cm^{-1}$ for Co^{2+} and Ni^{2+}, detection limit was (0.0002), (0.0010) ppm,

The interferences of ions, and suitable masking agents for two complexes was studied.

الخلاصة

تضمن البحث تقدير الكوبلت (II) والنيكل (II) باستعمال الكاشف ٢-[(٦-ميثوكسي-٢-بنزوثايزول) ازو]-٤-ميثوكسي فينول، حضرت معقدات كليتية جديدة لليكاند مع ايوني الكوبلت والنيكل ، وعينت صيغها باستخدام طريقة النسب المولية وطريقة التغيرات المستمرة.

تم تحديد نسبة الفلز الى الكاشف حيث وجد انها تساوي (٢:١) لكلا المعقدين وشخصت المعقدات بالطرق الطيفية (,UV-Vis FTIR).

وجد ان اعلى امتصاص للمعقدين كان عند الطول الموجي (512 nm) و (605 nm) لكل من الكوبلت والنيكل، حددت الظروف المثلى لتكوين المعقدين من داله حامضية ودرجة حرارة .

وجد ان قيمة معامل الامتصاص المولاري هي $3.84x10^4$ $L.mol^{-1}.cm^{-1}$ و $3.9x10^4$ $L.mol^{-1}.cm^{-1}$ لكل من الكوبلت والنيكل على التوالي وان حد الكشف لهذه الطريقة هو (0.0002 ppm) و (0.0010 ppm) كما درس تاثير الايونات المتداخلة وحجبت باستخدام عوامل الحجب المناسبة.

Introduction

Thiazolylazo dyes have attracted much attention as they are sensitive chromogenic reagents in addition to being interesting complexing agents, and have been used as reagents for spectrophotometric and extraction photometric determinations of many metal ions[1]. These compounds are easily prepared as, compared with the analogous 2-aminopyridines, no special conditions are required for the diazotisation of 8-aminothiazole and its derivatives[2,3]. The diazotisation reaction occurs readily in concentrated solutions of hydrochloric, phosphoric and sulphuric acids, or in **a** mixture of dimethylformamide and sulphuric acid[4-7]. The diazotate formed is so reactive that it has to be coupled with the phenol in cold acidic solution, which often results in the immediate production of the dye in a crystalline state[8,9].

The geochemistry of cobalt has combined complexities of the possible biochemical substitution of Co with Zn or Cd and the influence of the chemical speciation of each on the biological availability to phytoplankton[10-12]. The chemical speciation of metals in seawater is believed to be of fundamental importance in determining metal bioavailability to phytoplankton[13]. Nickel in nature is mainly

available in the form of ores like magnesium nickel silicate of variable composition, now days nickel becomes an important element, not only for industry, but also for biological systems, nickel is used in ceramic industry and also used in batteries which are in convincing to the environment, nickel is relatively non toxic element, the high concentration of the nickel does show serious health hazards, several analytical techniques have been monitored for the determination of trace level nickel(II), it is includes atomic absorption spectrometry[14-17], inductive coupled plasma emission[18-20] and X-Fluorences spectrometry[21,22] were reviewed. A few reagents are available for the spectrophotometric determination of nickel(II)[23,24] while several technique, such as ion chromatography[25], X-Ray fluorescence spectrometry[26], graphite furnace atomic absorption spectrometry[27] have been applied for the simultaneous determination of cobalt ion in different samples.

In this paper a new spectrophotometric method was used for determination of cobalt and nickel.

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.

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

Synthesis of 2-[(6-Methoxy-2-Benzothiazolyl)azo]-4-methoxyphenol (MBTAMP)
The azo ligand (MBTAMP) was prepared as described in the literature[28].

A diazonium solution was prepared by dissolving (3.60 g, 20 mmol) of 2-amino-6-methoxybenzothiazole 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 desiccator over anhydrous calcium chloride the yield was (59 %) (3.72 g) of red crystallizes which was malted at (103 ºc), the structural of this ligand as shown below.

2-[(6-Methoxy-2-Benzothiazolyl) azo]-4-methoxyphenol
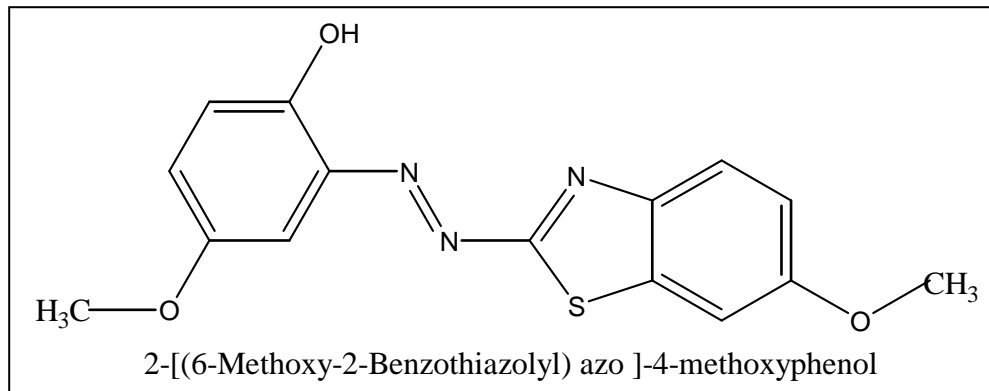
Standard Solutions

Co^{2+} and Ni^{2+} solutions (20 ppm) was prepared by dissolving an appropriate amount of $Co(NO_3)_2.6H_2O$ and $NiCl_2.6H_2O$ in 50 ml distilled water.

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

2-[(6-Methoxy-2-Benzothiazolyl)azo]-4-methoxyphenol (MBTAMP) solution

A solution of ($1x10^{-2}$ M) was prepared by dissolving appropriate amount of pure reagent in 25 ml of absolute ethanol.

General procedure

Into a 5 ml calibrated flask, transfer (1 ml) of sample solution containing not more than 0.5 ppm of Co^{2+} and 0.8 ppm of Ni^{+2} ions and (1 ml) of $1x10^{-4}$ M ethanolic reagent (MBTAMP) solution dilute to volume with deionized water, mix well and after 10 minutes; the absorbance was measured at 512 nm for Co^{2+} and 605 nm for Ni^{+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 MBTAMP

The reagent 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

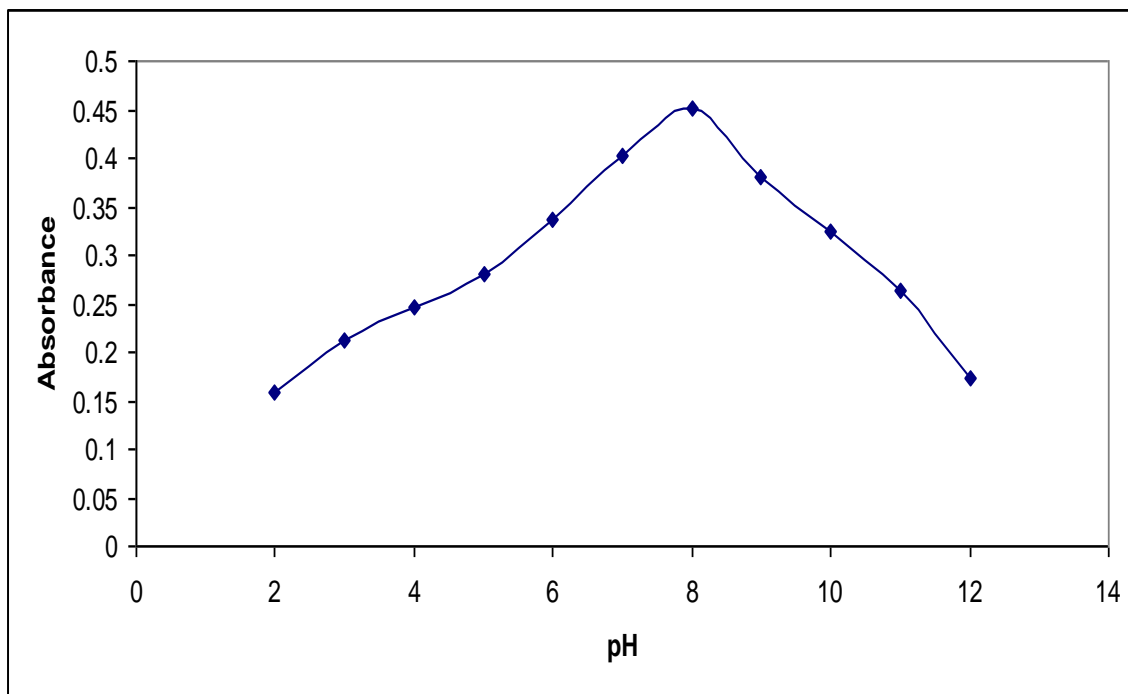The relation ship between the absorbance value and the pH value was drown in figure (1 & 2).

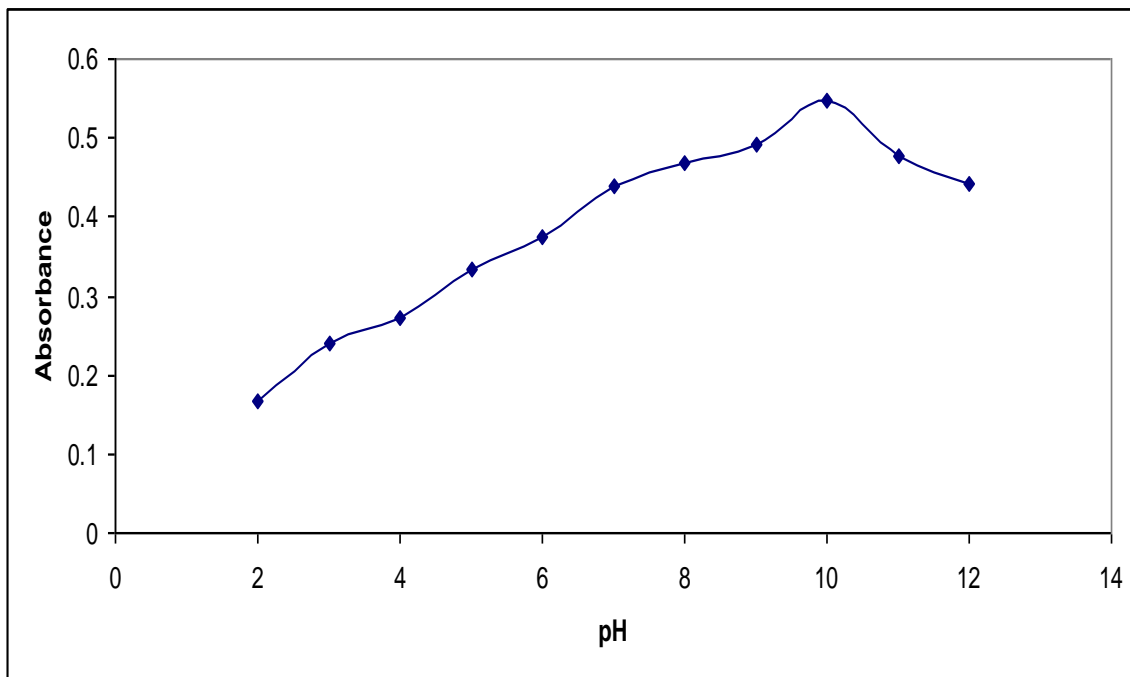Fig.(1) Effect of pH on the absorbance of Co-MBTAMP complex .

Fig.(2) Effect of pH on the absorbance of Ni-MBTAMP complex.

From figures (1&2) the range of optimum pH value for Co-MBTAMP was (7.8-8.3) while for the Ni-MBTAMP was (9.7-10.2).
Below pH (7.8) and (9.7) for Co-MBTAMP and Ni-MBTAMP complexes the decrease of absorbance value was due to the linkage between acidic proton's with non bonding ion-pair of (N) atom in thiazol ring and formation the ozolium cation, this cation lead to decrease the activity of the ligand to combine with metals, higher than pH (8.3) and (10.2); the absorbance value was decrease due to competitive of hydroxyl anion and formation of metal's hydroxide $Co(OH)_2$, $Ni(OH)_2$.

Stability of complexes with the time
Stability of the two complexes with the time was studied, the color of the two 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 two complexes Co-MBTAMP and Ni-MBTAMP was studied in the range (20-70) ºc figures (3&4) show this effect.
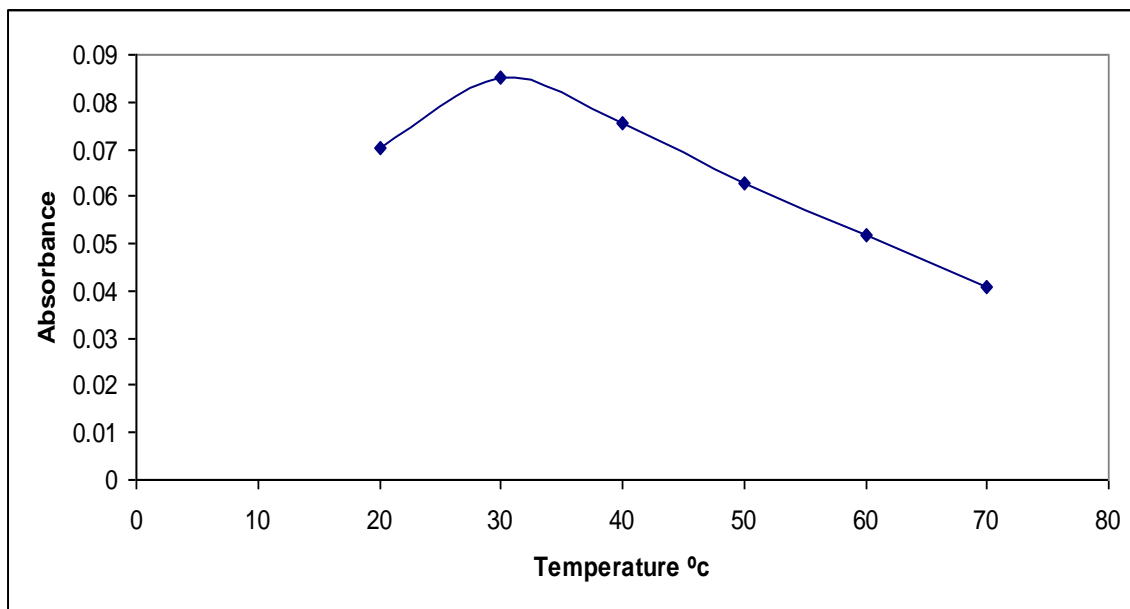
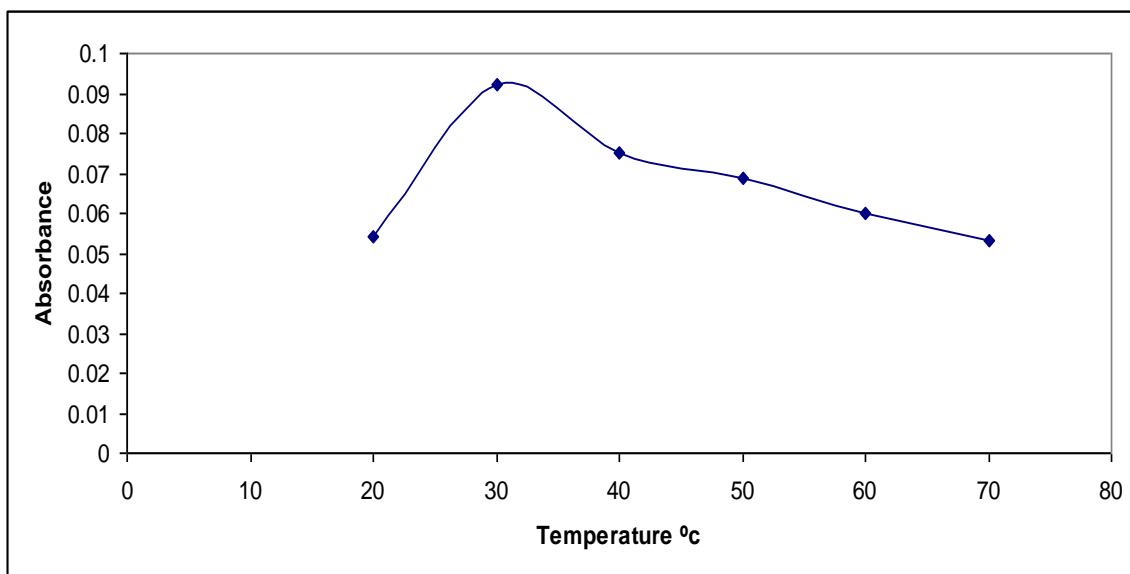Fig.(3) Effect of temperature on the absorbance of Co-MBTAMP complex.

Fig.(4) Effect of temperature on the absorbance of Ni-MBTAMP complex.

The effect of temperature on the absorbance of two complexes was studied in the range (20-70) ºc, the maximum absorption was obtained at 30 ºc and for Co-MBTAMP and 30 ºc Ni-MBTAMP, 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[29] method of continuous variation and molar ratio[30] methods, the composition of two complexes were shown in figures (5-8).
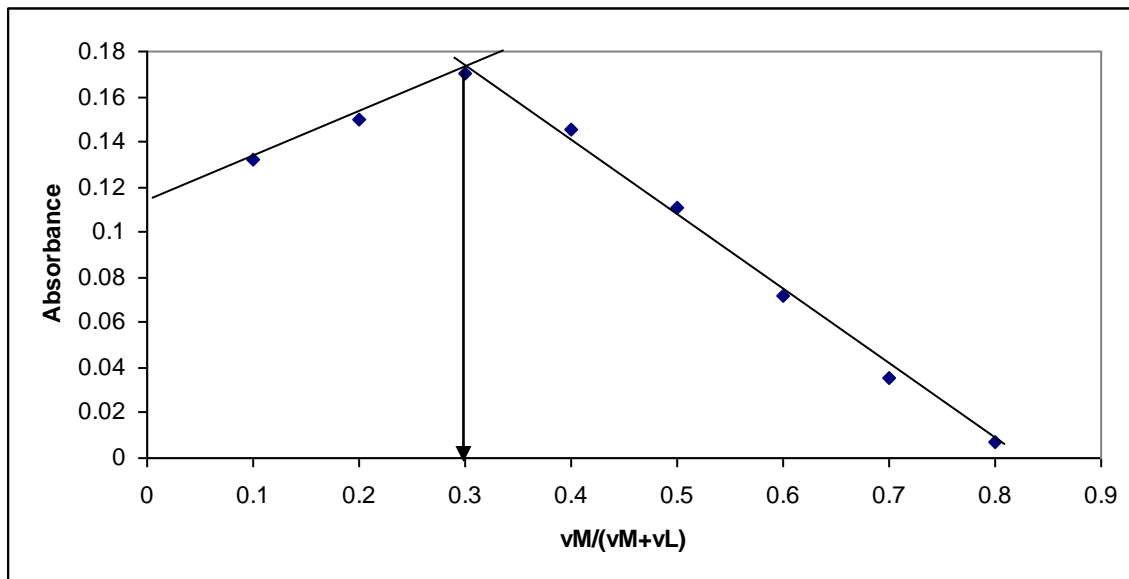

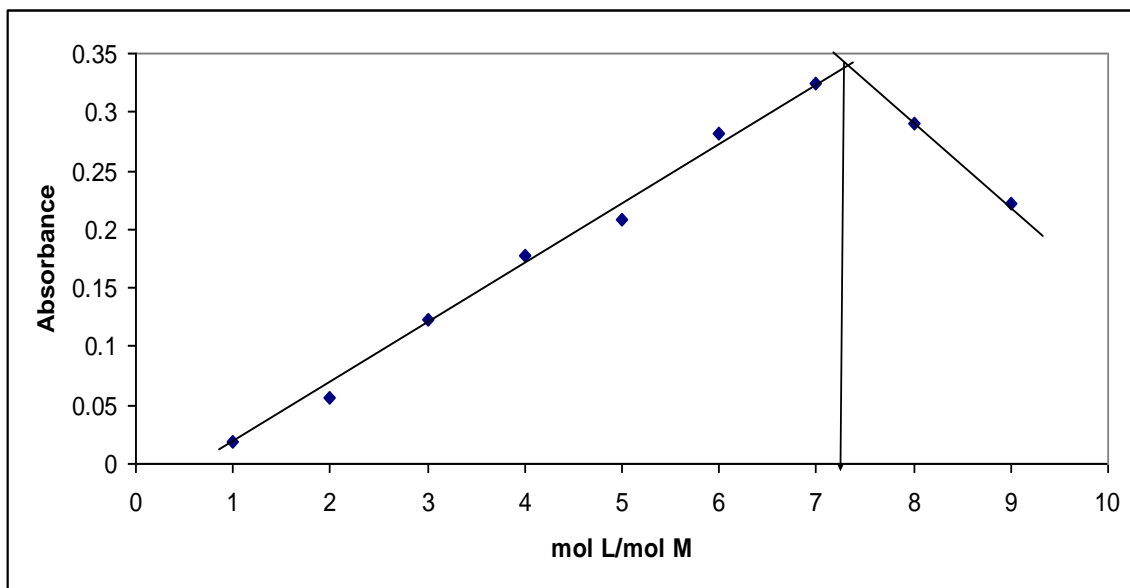Fig.(5) continuous variation method for Co-MBTAMP complex at optimum conditions.

Fig.(6) molar ratio method for Co-MBTAMP complex at optimum   conditions.
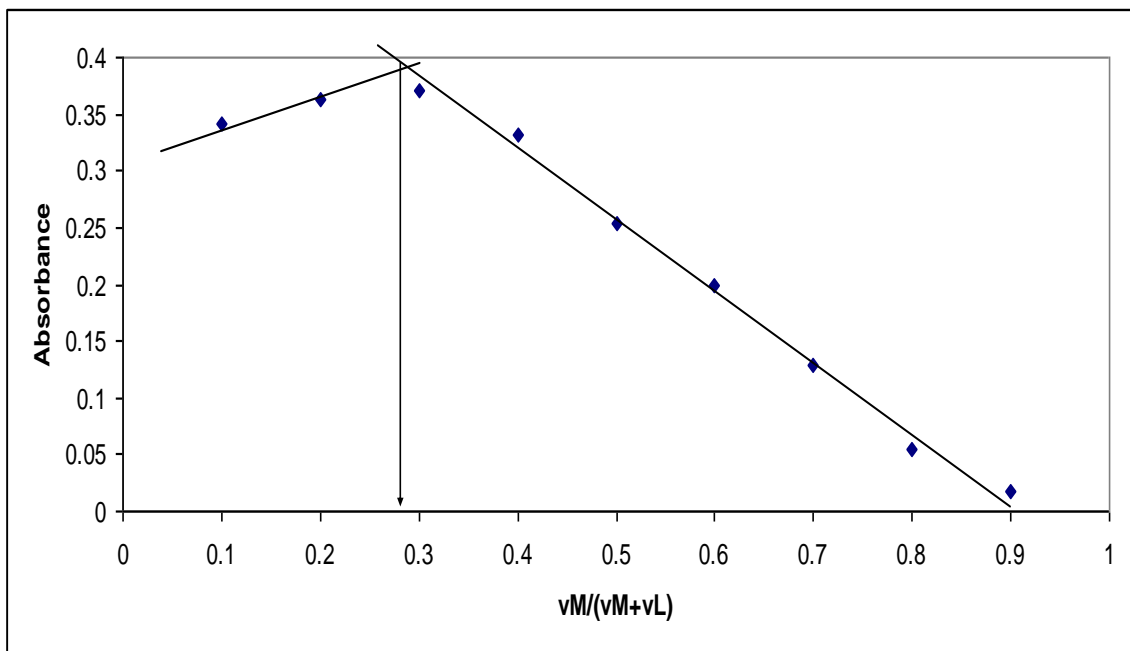
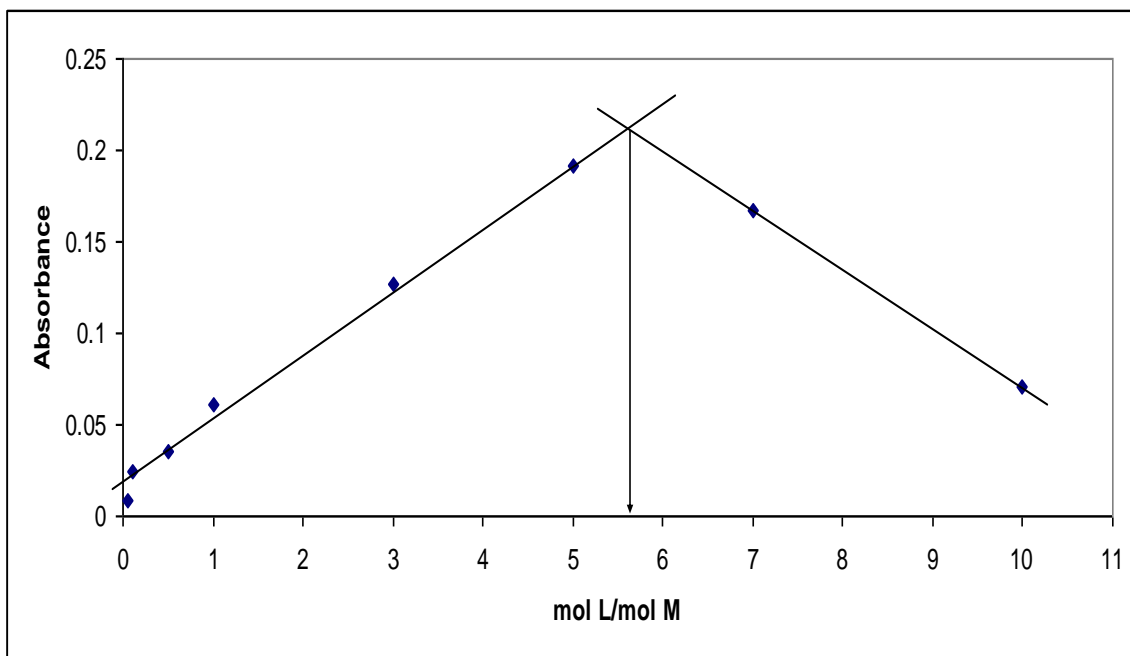Fig.(7) continuous variation method for Ni-MBTAMP complex at optimum conditions.

Fig.(8) molar ratio method for Ni-MBTAMP complex at optimum conditions.

From the results of continuous variation and molar ratio methods show in figures (5-8), the ratio between Co^{2+} to MBTAMP is (1:2), and between Ni^{+2} to MBTAMP is (1:2) and the stability constant[31] ($K_{sta.}$) was (8.80×10^5 $L^2.mol^{-2}$) for Co-MBTAMP complex and (6.14×10^6 $L^2.mol^{-2}$) for Ni-MBTAMP complex, figures (9,10) shows the proposed composition of the two complexes
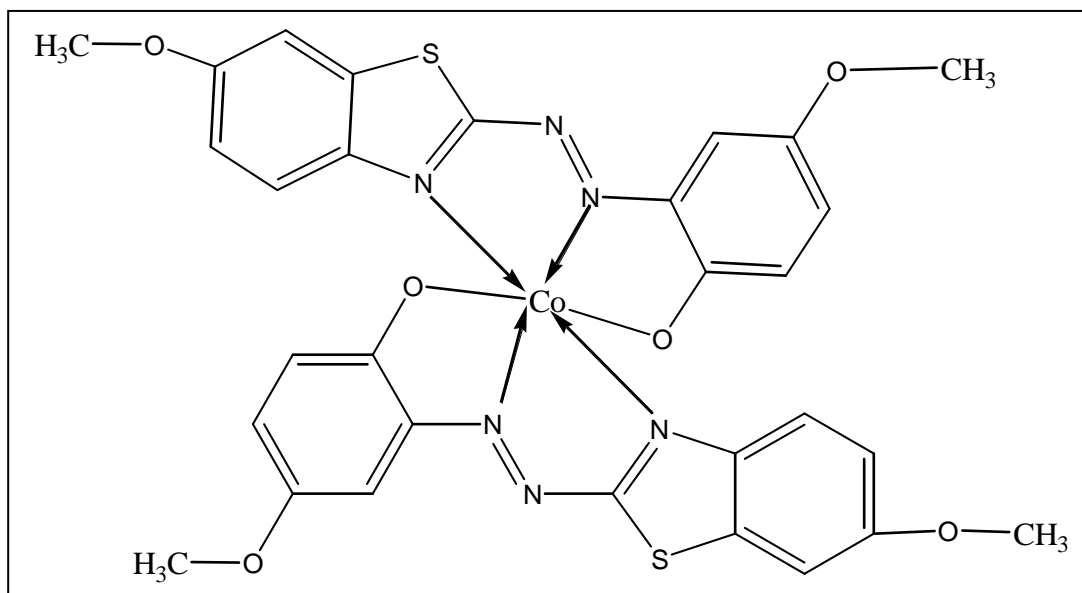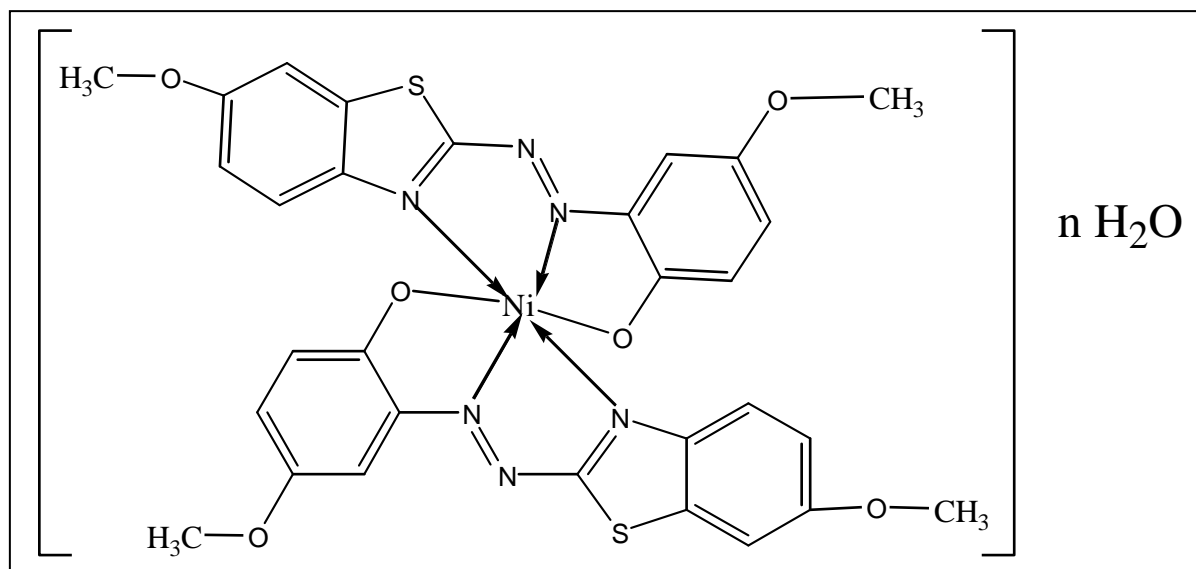
Fig. (9) the composition of Co-MBTAMP complex

$n\ H_2O$

Fig. (10) the composition of Ni-MBTAMP complex

Beer's low

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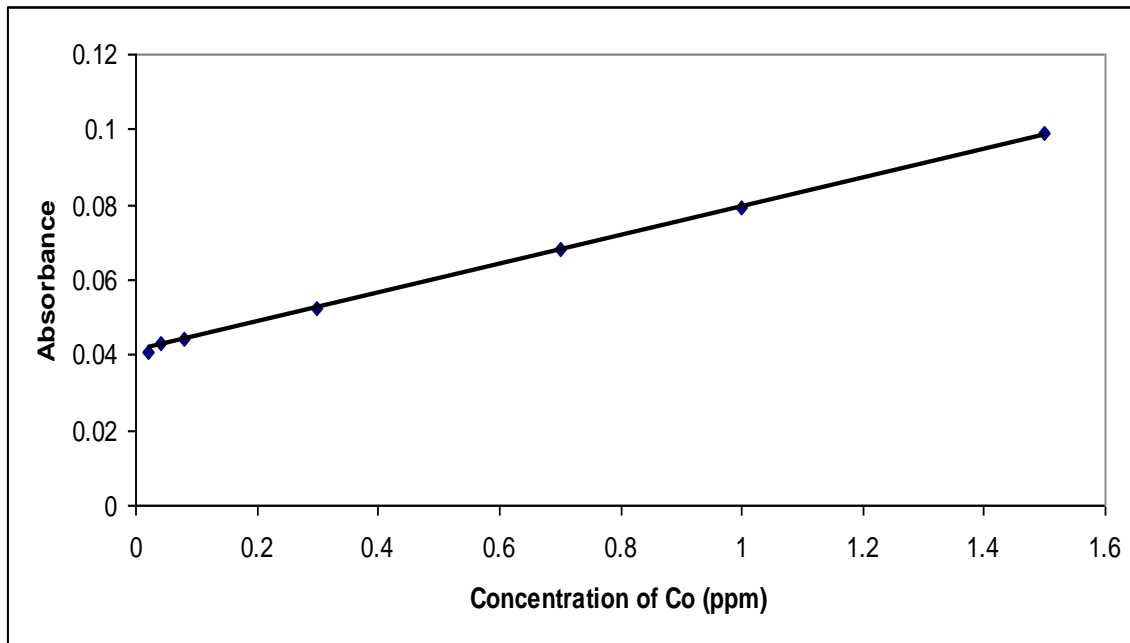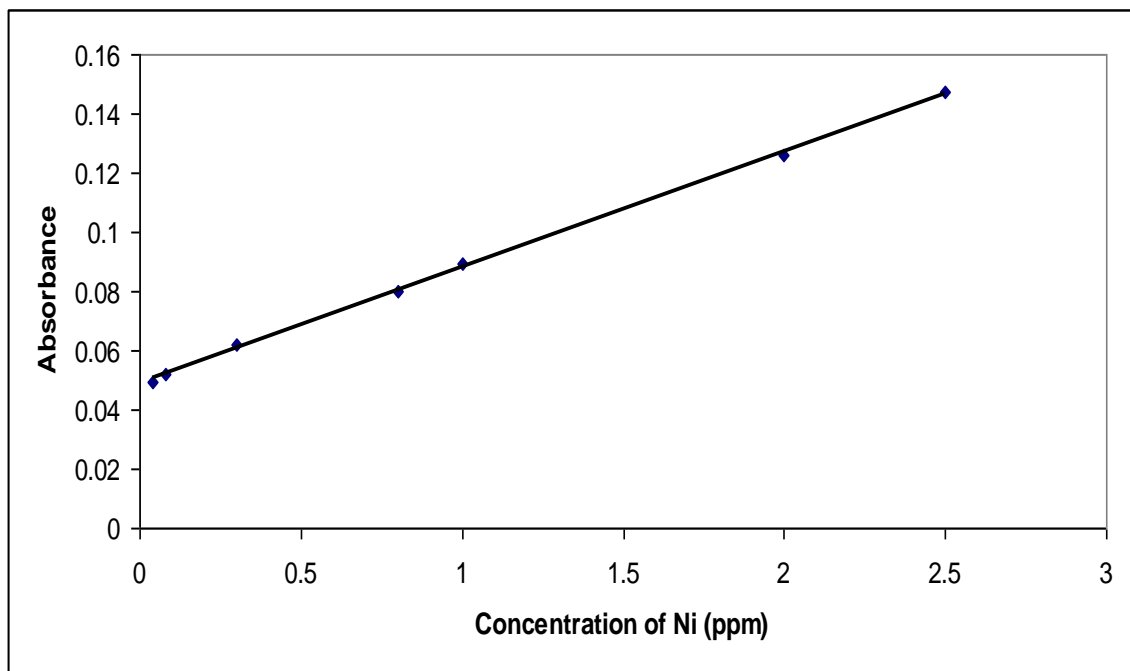

Figure (11) calibration curve of Co^{2+} ion.

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

Beer's law was obeyed in the range (0.02-1.5), (0.04-2.5) ppm, detection limit was (0.0002), (0.0010) ppm, linearity (R^2) was (0.9994), (0.9992) correlation factor (r) was (0.9997), (0.9995), molar absorbitivty (ε) was $3.84x\ 10^4$ L.mol^{-1}.cm^{-1}, $3.9\ x\ 10^4$ L.mol^{-1}.cm^{-1} for Co and Ni.

Precision and accuracy of the analytical procedure was R.S.D % (0.43, 0.84) % and $E_{rel.}$% and R_e % were   (-3.11, -2.32) %, (96.89, 97.68) % for Co and Ni, Sandell's sensitivity were calculated to be $(1.15x10^{-4})$ for Co^{2+} and $(1.49x10^{-4})$ for Ni^{+2}.

Effect of interference ions[32,33]

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

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

Table (1) represent the effect of interference ions

Interference ions 5 ppm	Interference %	
	Co-MBTAMP	Ni-MBTAMP
Ni^{2+}	+2.02	-------
Co^{2+}	-------	+1.09
Pb^{2+}	+3.75	+6.11
Cu^{2+}	+5.72	+1.88
Zn^{2+}	+3.94	+3.32
Cd^{2+}	+1.10	+2.17
Mn^{2+}	-1.81	-2.29
Fe^{2+}	-8.11	-6.32
Fe^{3+}	-4.46	-3.14

Table (1) shown the absorbance value of Cu^{2+} ion varying by more than 5% from the expected value for Co^{2+} complex and Pb^{2+} ion for Ni^{+2}.

Effect of masking agents[34]

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

Table (2) represents the effect of masking agents

	Complex without any addition	Tartaric acid	Oxalic acid	Citric acid	Ascorbic acid	KCN	NaF
Co-MBTAMP	0.052	0.032	0.081	0.011	0.041	0.050	0.031
Ni-MBTAMP	0.049	0.068	0.063	0.044	0.022	0.087	0.050

Table (2) shown the best masking agent for Co-MBTAMP complex was (Citric acid) but for Ni-MBTAMP was (KCN), other masking agents are less effect comparatively.

Absorption spectra

The absorption spectra of the ligand and two complexes are shown in figures (13,14 and 15) under optimum conditions
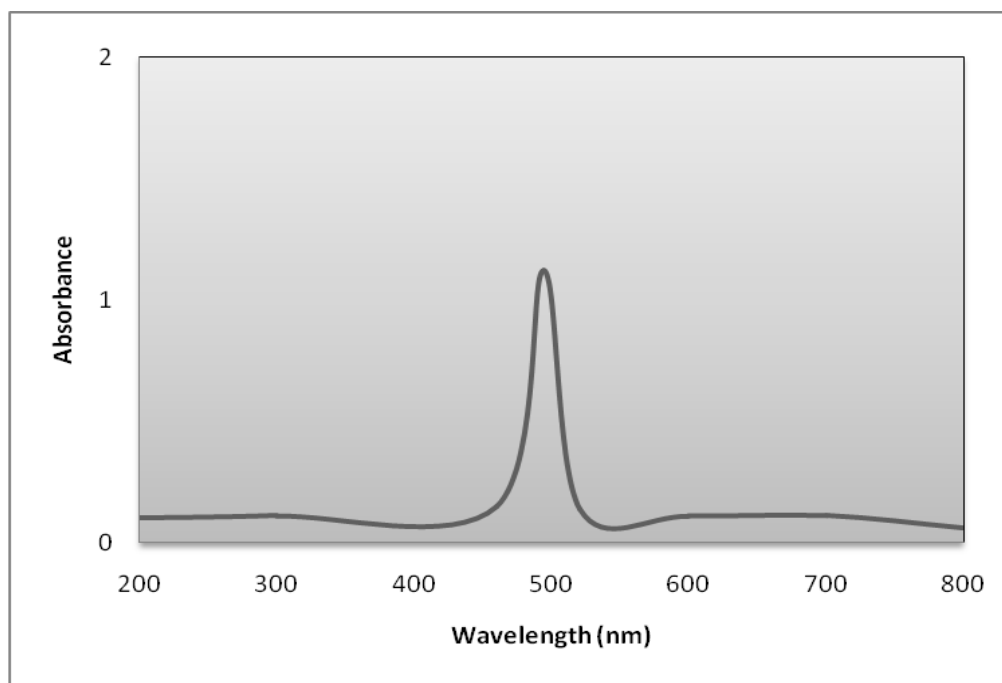

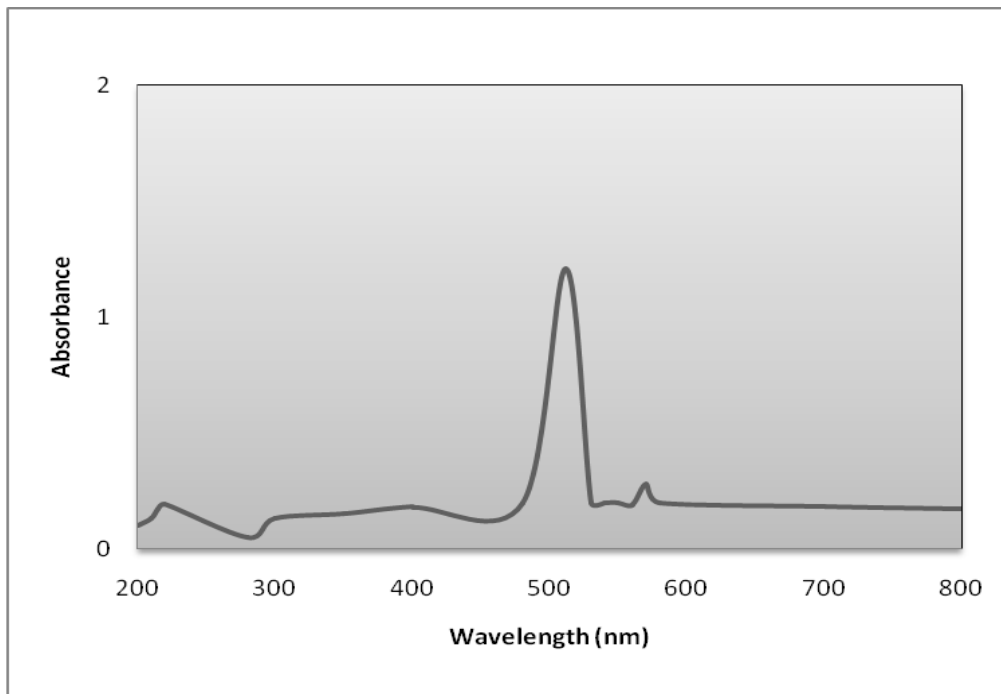fig.(13) absorption spectra of the ligand.

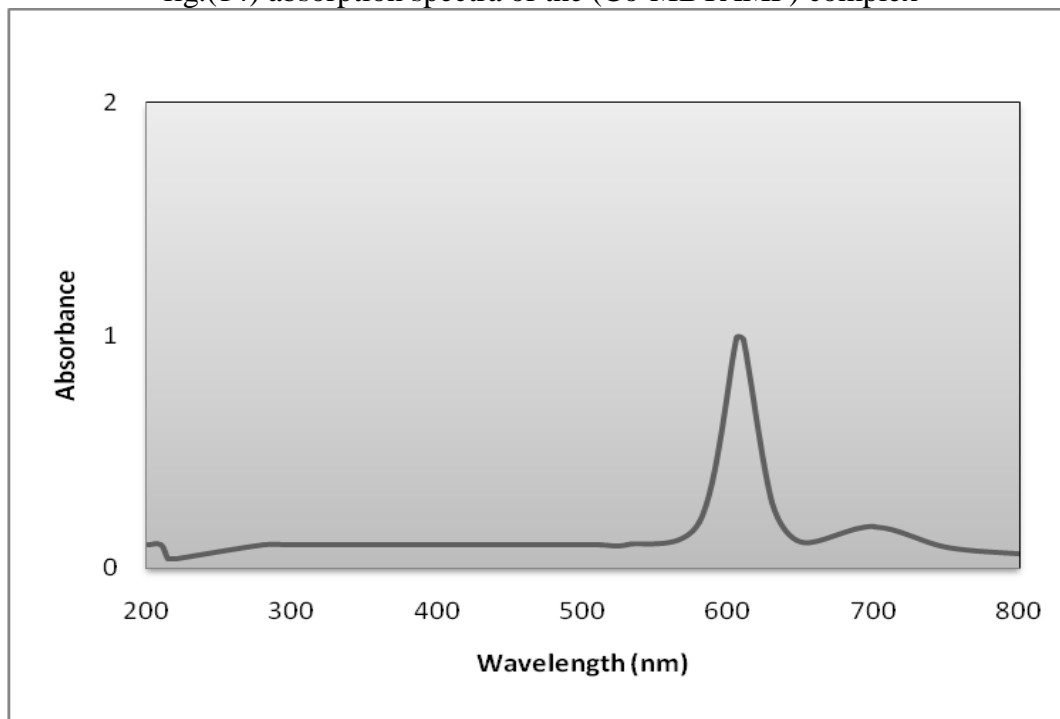fig.(14) absorption spectra of the (Co-MBTAMP) complex

fig.(15) absorption spectra of the (Ni- MBTAMP) complex

Absorption spectra show that the λ_{max} of absorption to the ligand (MBTAMP) at 494 nm, (Co-MBTAMP) complex at 512 nm and (Ni-MBTAMP) complex at 605 nm, this a new λ_{max} of two complexes mean red shift in λ_{max} and formation theses complexes.

FTIR Spectroscopic Study

FTIR specta of the ligand (MBTAMP), (Co- MBTAMP) and (Ni- MBTAMP) complexes are shown in figure (16-18)
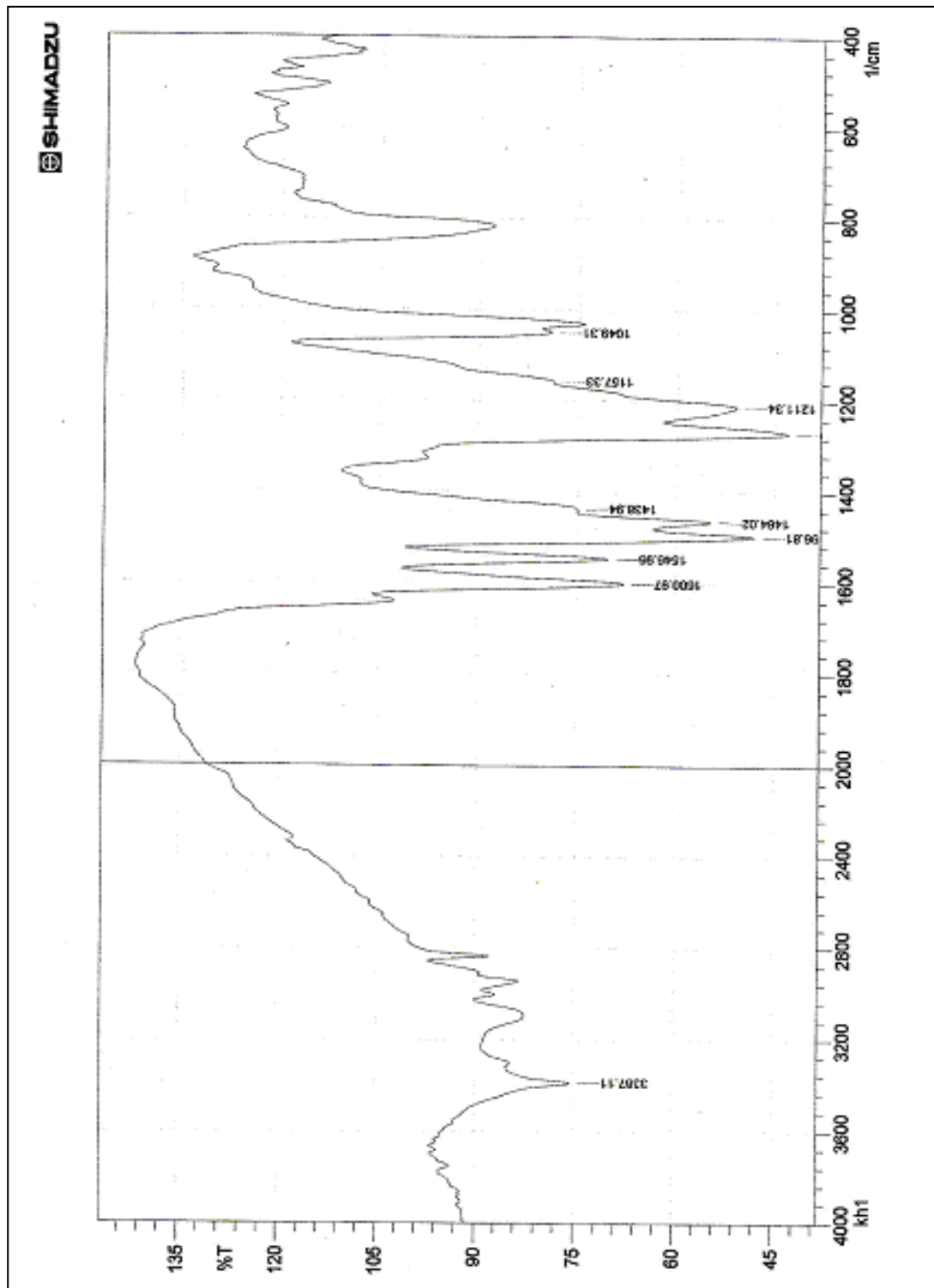

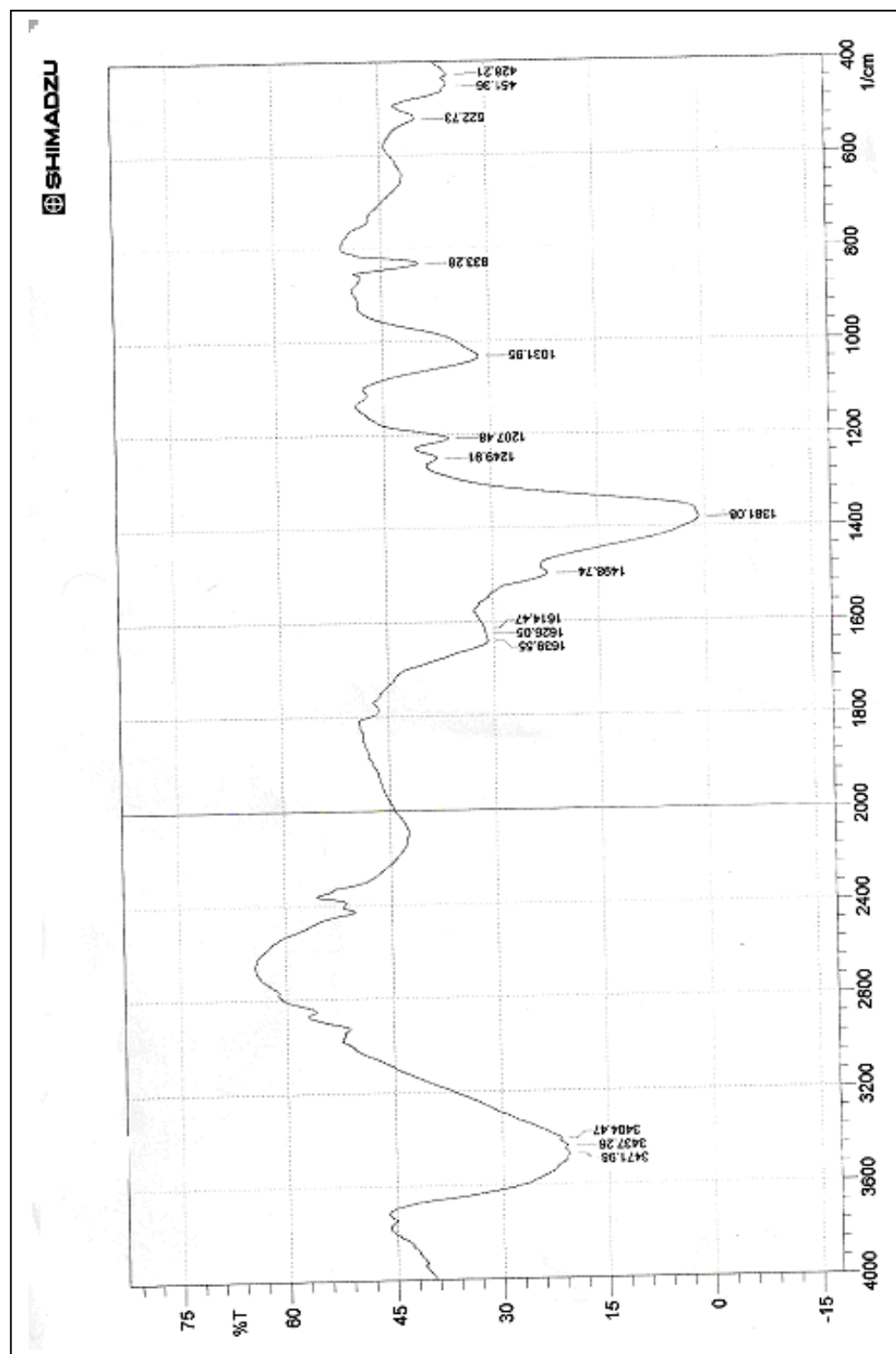Fig.(16) FTIR spectrum of (MBTAMP)

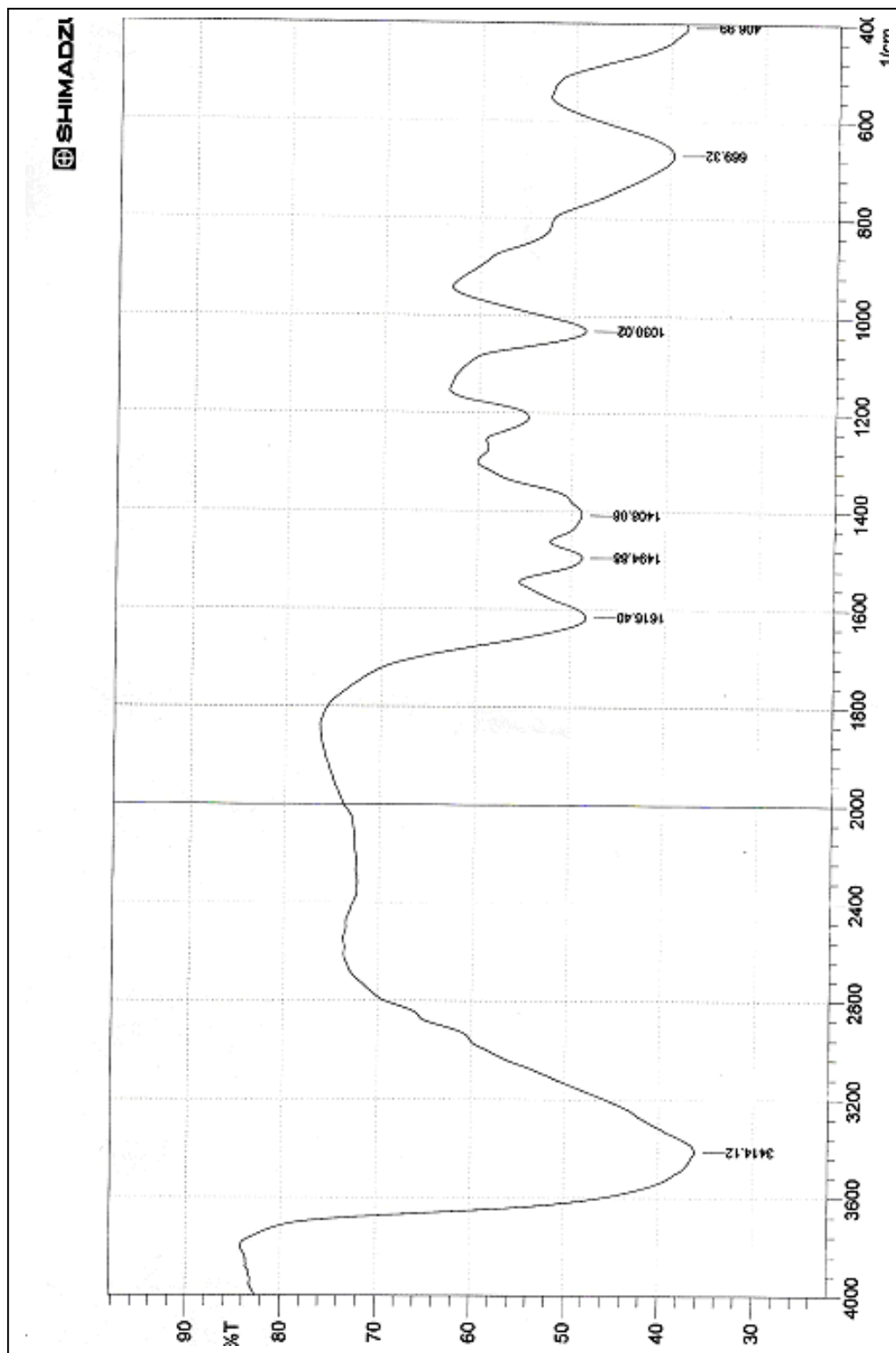Fig.(17) FTIR spectrum of (Co-MBTAMP)

Fig.(18) FTIR spectrum of (Ni-MBTAMP)

The infrared spectrum show in figure (16) give an evidence for the formation of the reagent MBTAMP, table (3) show the main absorbance peaks

Table (3) represent FTIR absorbance peaks

Value cm^{-1}	Conclusion
3387	Hydrogen bond between H atom in –OH group and N in N=N
3260	N-H stretching in thiazol ring
3100	C-H aromatic stretching
2900	C-H aliphatic stretching
1600	C=N stretching of amidazol ring that is fusion with benzene ring
1545	N=N stretching
1211	C-S stretching

The comparison between spectrum of the ligand with those of the coordination complexes have revealed certain characteristic differences, these difference was shown in figures (17 and 18).

From figure (175 and 18) all metal complexes show that (MBTAMP) behaves as monobasic tridentate ligand, coordinating via (C=N, N=N and phenolic OH) groups with displacement of hydrogen atoms from the latter.

The presence of broad band at 3404-3471 cm^{-1} in (Co-MBTAMP) complex spectrum and disappear the broad band at 3387 cm^{-1} in (Ni-MBTAMP) complex spectrum indicate the deprotonation of phenolic oxygen and cleavage of the hydrogen bond with the involvement of the oxygen in bonding[35,36].

The broad band at 3414 cm^{-1} in (Ni-MBTAMP) complex spectrum back to hydrogen bonds of water molecules in the complex.

The spectrum of the MBTAMP ligand figure (14) shown a single strong absorption bands at (1600 cm^{-1}) due to (C=N) stretching of thiazol ring, this band was reduced and shift to (1498 cm^{-1}) and (1494 cm^{-1}) in (Co-MBTAMP) and (Ni-MBTAMP) complex spectrums, these shift suggest the linkage of metal ion with nitrogen of imidazol ring[37,38]. A (N=N) band at (1545 cm^{-1}) in MBTAMP ligand figure (14) was shifted to (1381 cm^{-1}) and (1408 cm^{-1}) in figures (17 and 18) this shift could contributed to the metal-azo linkage[39].

A new bands appeared in (428-451 cm^{-1}) and (406-413 cm^{-1}) in the spectrum of the complexes that does not appeared in MBTAMP spectrum, this may be back to the (M-O), (M-N) stretching for (Co-MBTAMP) and (Ni-MBTAMP) [40,41].

The fixed position of C-S band in thiazol ring means that the sulfur atom of thiazole ring does not participate in coordination[42].

Applications

This method was applied to determine Co^{2+} and Ni^{2+} standard solutions, the results show in table (4)

Table (4) the results of standard method

Ion	True Value	Experimental Value
Co^{2+}	0.6 ppm	0.569 ppm
Ni^{2+}	0.7 ppm	0.681 ppm

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