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Determination of Co^{2+} and Cd^{2+} by using 2-[(2-Benzimidazolyl) azo]-4-methoxyphenol

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Abstract

Co^{2+} and Cd^{2+} are determined by using (BIAMP) reagent, the maximum absorption of the two formation complex are (522) and (627).
Optimum conditions are recorded pH (9) , (7), temperature (20), (30), Bear's low (0.03-1.7), (0.02-1.5) ppm, detection limits were (0.0015), (0.0005) for Co^{2+} and Cd^{2+} complexes.
RSD, R^2, r and molar absorptivity were recorded, also interferences of ions are studying.

الخلاصة

يتضمن البحث تقدير الكوبلت (II) والكادميوم (II) باستعمال الكاشف الجديد (BIAMP) ، وجد ان اعلى امتصاص للمعقدين كان عند الطول الموجي (522 nm) و (627 nm) لكل من الكوبلت والكادميوم.
حددت الظروف المثلى لتكوين المعقدين من داله حامضية (٩) و (٧) ودرجة حرارة (٢٠) و (٣٠) مئوية، تم بناء منحني المعايره عند مدى من التراكيز تراوحت بين (0.03-1.7 ppm) و (0.02-1.5 ppm) لكل من الكوبلت والكادميوم.
وجد ان حد الكشف لهذه الطريقة هو (0.0015 ppm) و (0.0005 ppm) ، درس تاثير الايونات المتداخلة وحجبت باستخدام عوامل الحجب المناسبة.

Introduction

Trace and ultra trace determination of cadmium in several samples are becoming of increasing interest owing to the high toxicity of this metal, several highly sensitive and selective analytical techniques have been applied for the determination of such low levels of cadmium including ETAAs, ICP-AES and ICP-MS[1-4].

Several systems for the generation of volatile cadmium species have been developed[5-9].

Cobalt is present in trace amounts in virtually all living tissues, Cobalt have been determined in low concentration in beer in the range of 0.2 ppm with a claimed accuracy of ± 0.02 ppm[10]. 2-nitroso-1-napthol used as a reagent to determined of cobalt[11]. Direct and derivative spectrophotometric determination of cobalt with 5-bromosalicylaldehydethiosemicarbazone[12].

A graphite furnace atomic absorption spectrometry method have been used for determination of lead and cadmium in biological material[13].

In the present investigation we report asimple and sensitive spectrophotometric method for determination of cadmium and cobalt by using a newly synthesized reagent.

Experimental

Apparatus

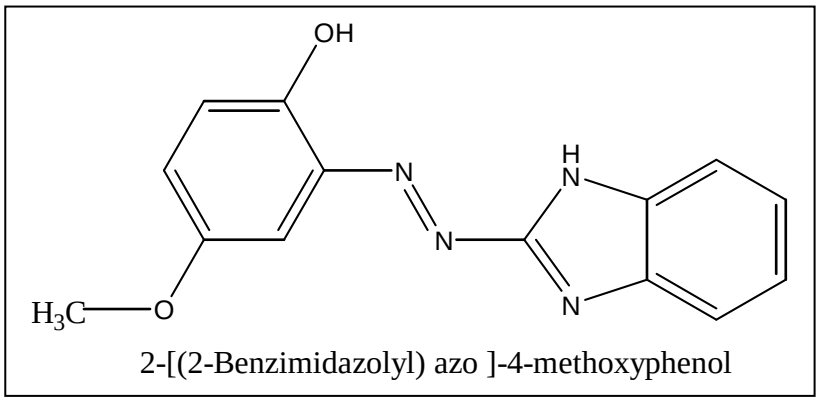
A UV-Probe model (UV-1650) spectrophotometer (Schimadzu-Japan) and spectronic-21 model U.V-Visible single beam with 1 cm cells Bausch and Lomb (USA) was used for all absorbance measurements, pH measurements were made with Knick-Digital pH meter (England), Digital Balance, Sartorius, (BP 3015- Germany) 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

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

A 2-amino-benzoimidazole (2.66 g, 20 mmol) was dissolved 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, 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 reagent as shown below.



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

Standard Solutions

A solution of Co^{2+} (20 ppm) was prepared by dissolving (0.0049 g) of $Co(NO_3)_2.6H_2O$ in 50 ml distilled water

A solution of Cd^{2+} (20 ppm) was prepared by dissolving (0.0027 g) of $Cd(NO_3)_2.4H_2O$ in 50 ml distilled water.

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

A solution of ($1x10^{-2}$ M) was prepared by dissolving (0.0670g) 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 0.4 ppm of Co^{2+} or 0.3 ppm of Cd^{2+} ions and (1 ml) of $1x10^{-4}$ M ethanolic reagent (BIAMP) solution dilute to volume with deionized water, mix well and after 10 minutes measure the absorbance at 522 nm for Co^{2+} and 627 nm for Cd^{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 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 effect of pH on the absorbance value of the complex was investigated by changing the pH value of the solution in the range of (2-12) and the results are shown in, figures (1&2).

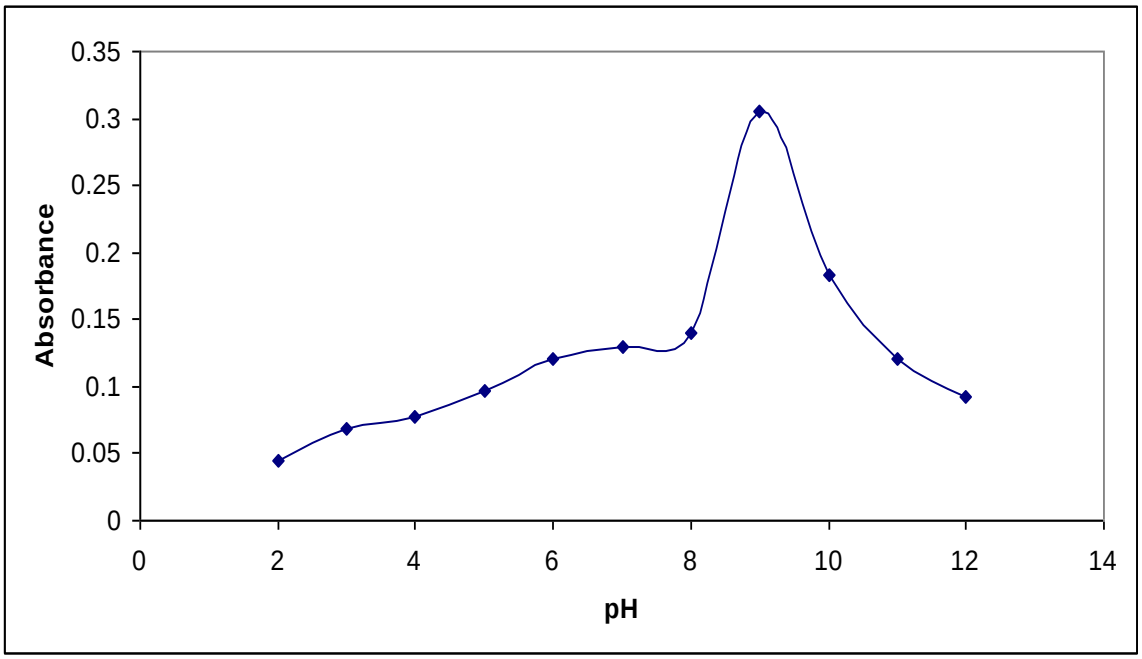


Fig.(1) Effect of pH on the absorbance of Co-BIAMP complex .

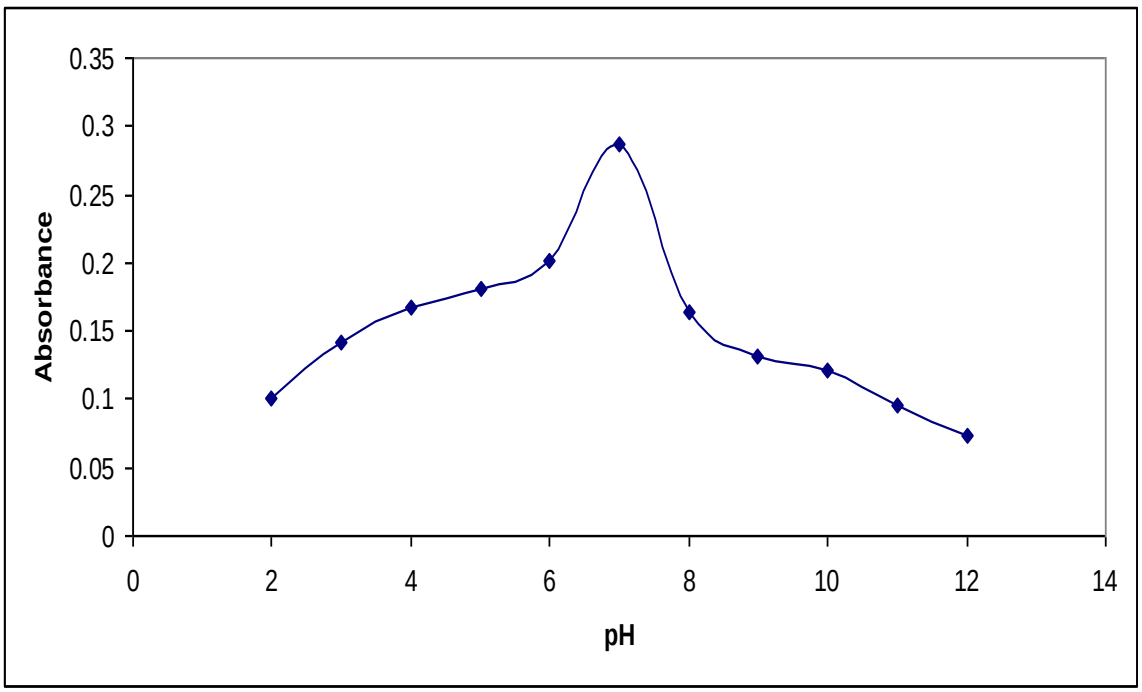


Fig.(2) Effect of pH on the absorbance of Cd-BIAMP complex.

From figures (1&2) the best pH value of Co-BIAMP complex (9), while for Cd-BIAMP complex (7).

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-BIAMP and Cd-BIAMP was studied figures (3&4) show this effect.

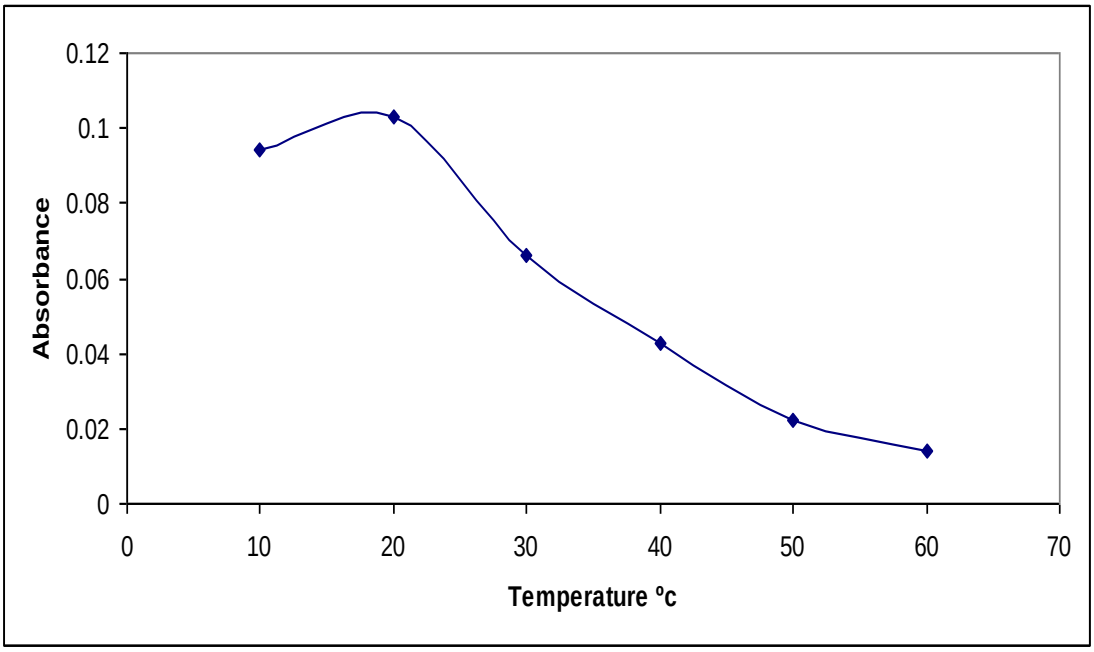


Fig.(3) Effect of temperature on the absorbance of Co-BIAMP complex.

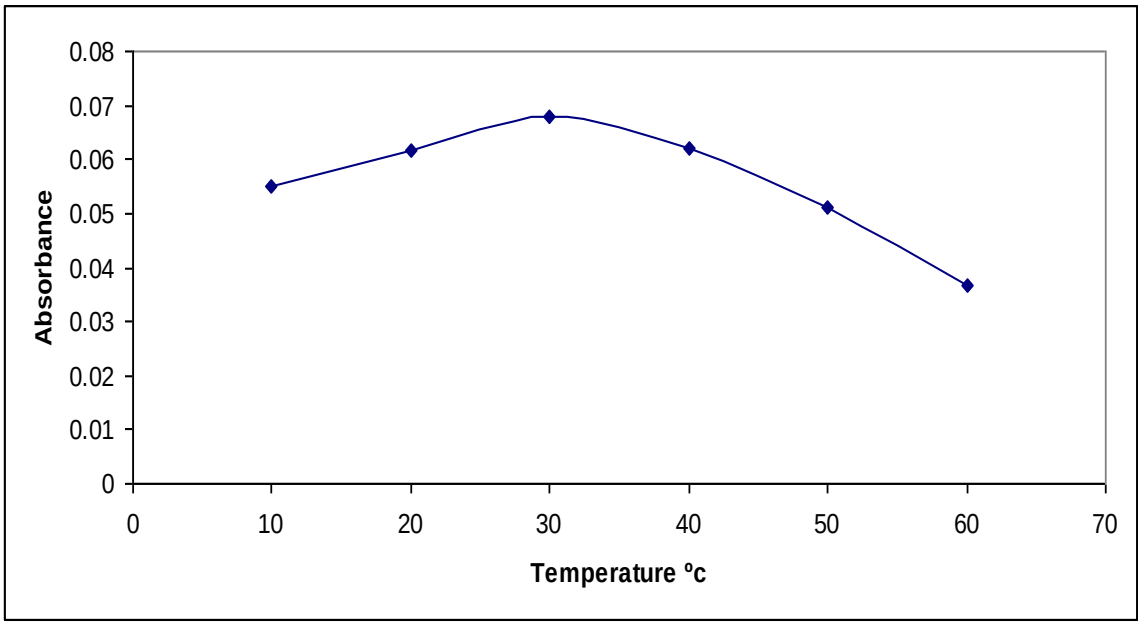


Fig.(4) Effect of temperature on the absorbance of Cd-BIAMP complex.

The effect of temperature on the absorbance of two complexes was studied in the range (10-60) ºc, the maximum absorption was obtained at 20 ºc and for Co-BIAMP and 30 ºc Cd-BIAMP, 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[14] method of continuous variation and molar ratio[15] methods, the composition of two complexes were shown in figures (5-8).

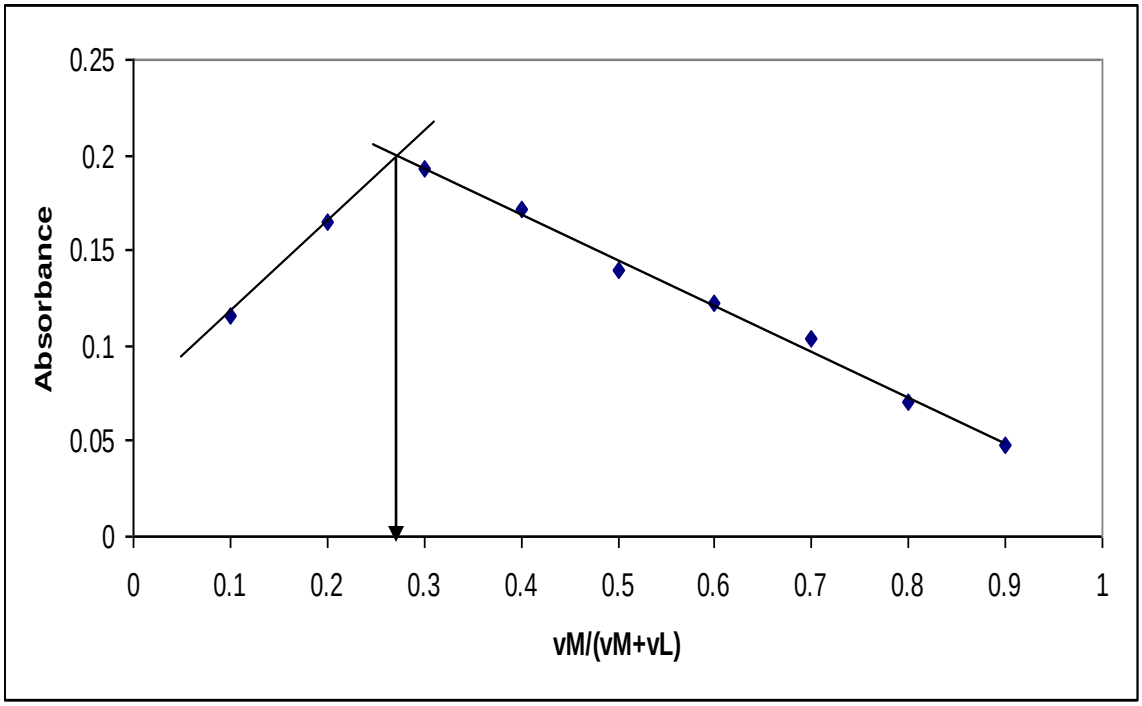


Fig.(5) continuous variation method for Co-BIAMP complex at optimum conditions.

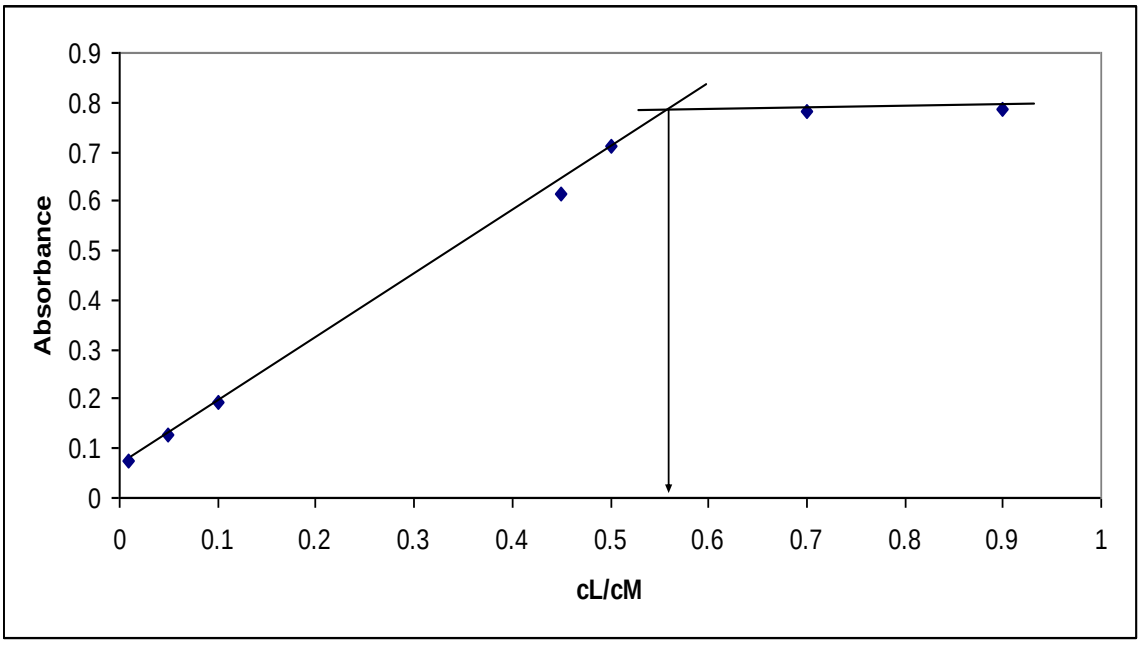


Fig.(6) molar ratio method for Co-BIAMP complex at optimum condition.

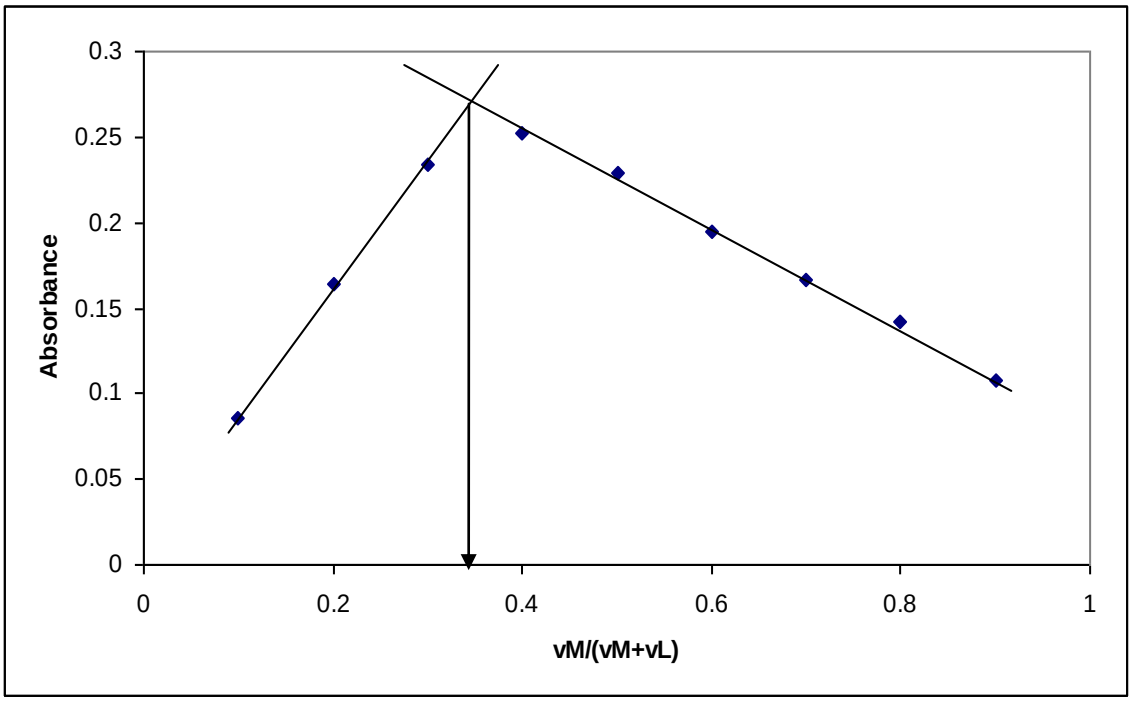


Fig.(7) continuous variation method for Cd-BIAMP complex at optimum conditions.

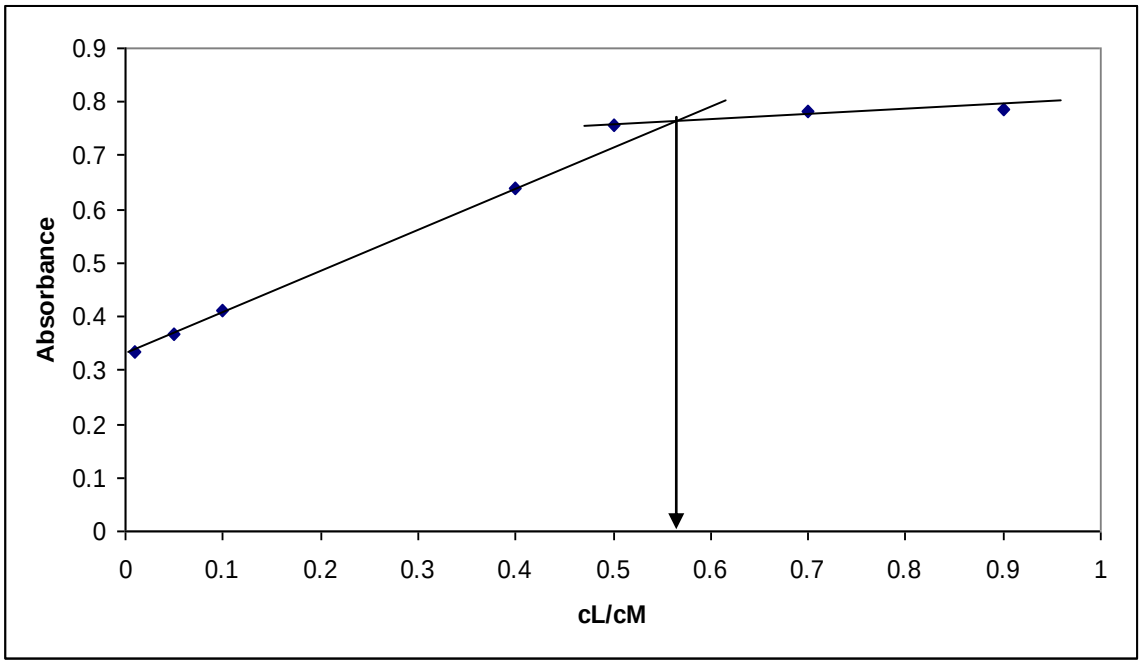


Fig.(8) molar ratio method for Cd-BIAMP complex at optimum conditions.

From the results of continuous variation and molar ratio methods show in figures (7-10), the ratio between Co^{2+} to BIAMP is (1:2), and between Cd^{2+} to BIAMP is (1:2) and the stability constant[16] ($K_{sta.}$) was ($1.19x10^{5}$ $L^{2}.mol^{-2}$) for Co-BIAMP comlex and ($3.48x10^{6}$ $L^{2}.mol^{-2}$) for Cd-BIAMP complex, figures (9,10) shows the proposed composition of the two complexes

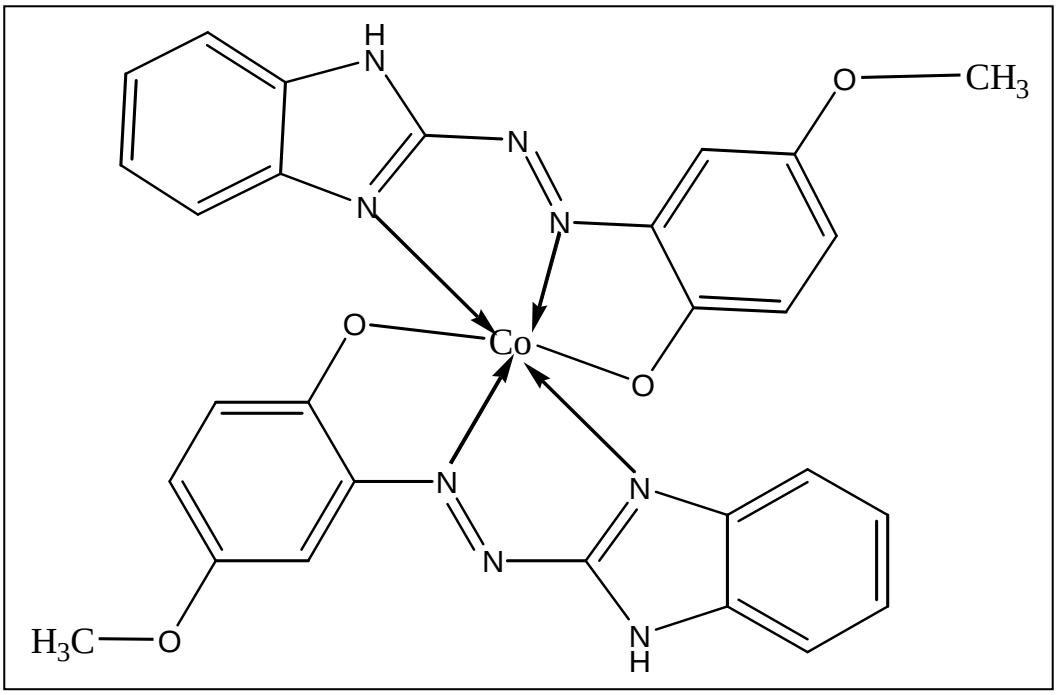


Fig. (9) the composition of Co-BIAMP complex

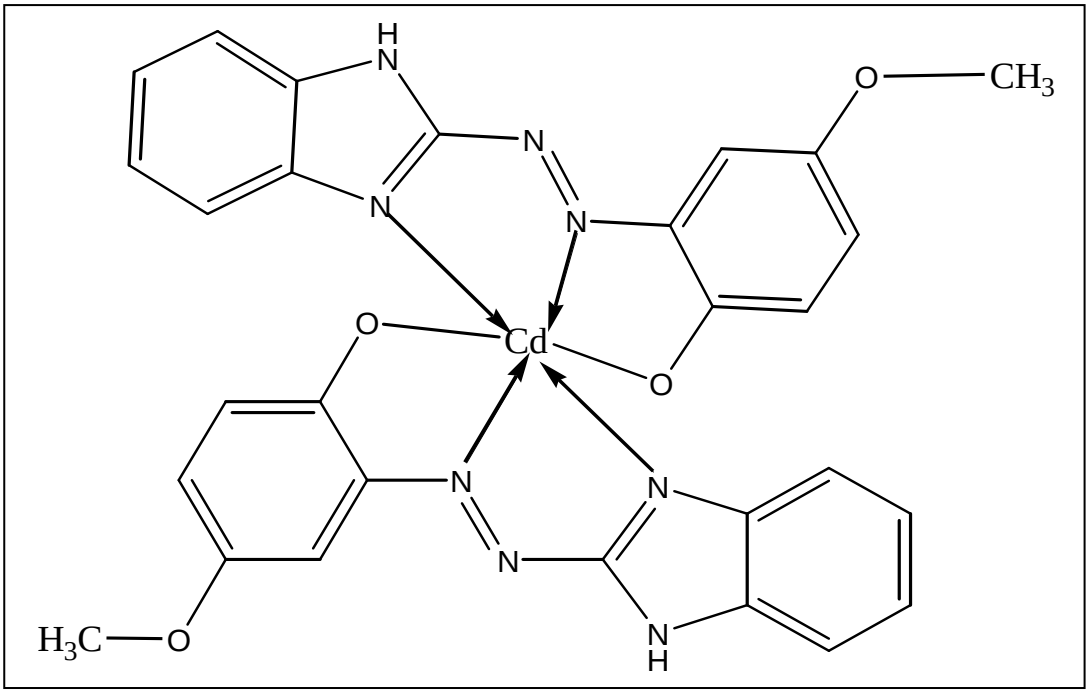


Fig. (10) the composition of Cd-BIAMP complex

Beer's low

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

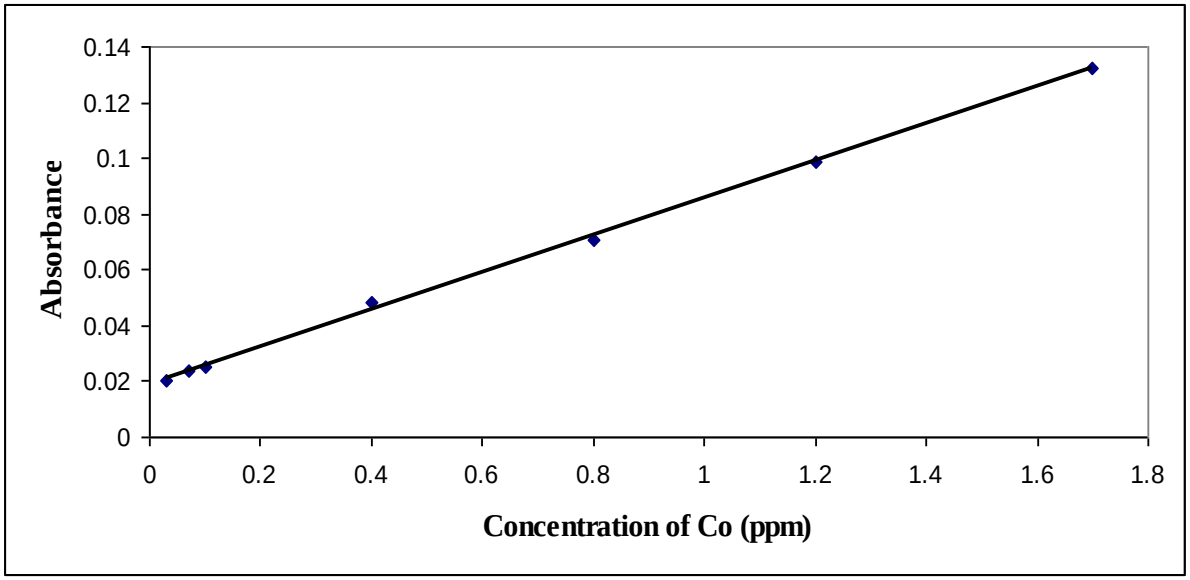


Figure (11) calibration curve of Co^{2+} ion.

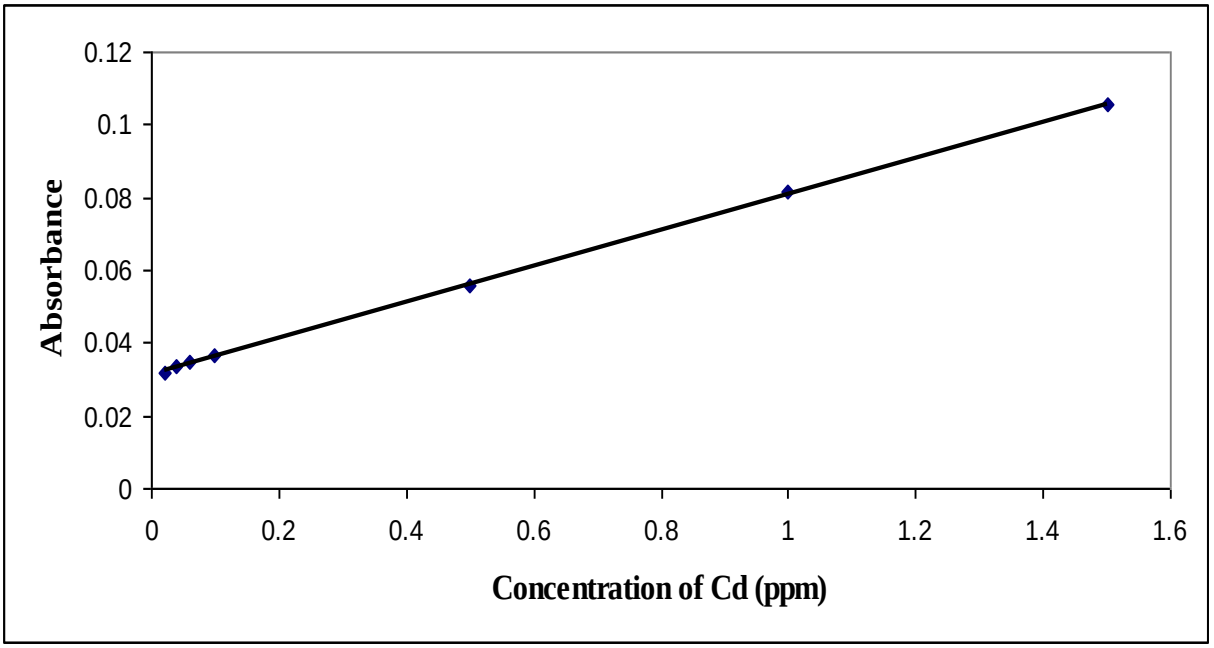


Figure (12) calibration curve of Cd^{2+} ion.

The results indicated that Beer's law was obeyed over the concentration range (0.03-1.7) ppm for Co^{2+} and (0.02-1.5) ppm for Cd^{2+}, linearity (R^2) for Co^{2+}, Cd^{2+} ions were (0.9992) and (0.9997) respectively, the detection limit was (0.0015) ppm for Co^{2+} and (0.0005) ppm for Cd^{2+}.

The molar absorption coefficient and Sandell's sensitivity were calculated to be ($6.65001x10^{4}$), ($8.72x10^{-5}$) for Co^{2+} and ($4.9400x10^{4}$), ($2.27x10^{-4}$) for Cd^{2+}.

The relative standard deviation R.S.D % was (1.65) and (0.87) for Co^{2+} and Cd^{2+} respectively, (Re %) and (E_{rel}%) were (96.75), (-3,25) for Co^{2+} and (97.03), (-2, 97) for Cd^{2+}.

The precision and accuracy of the method were found to be excellent.

Effect of interference ions[17,18]

The selectivity of Co-BIAMP and Cd-BIAMP complexes were tested by measuring the absorbance of complex of 1 ppm of Co^{2+} and 1 ppm Cd^{2+} at optimum conditions in presence of different foreign ions of 5 ppm concentration which are able to form complexes with (BIAMP).
Table (1) shown that ions (Cd^{+2}, Ni^{+2} and Zn^{+2}) were the absorbance value varying by more than 5% from the expected value for Co^{2+} complex and (Co^{+2} and Zn^{+2}) ions for Cd^{2+}.

Table (1) effect of interference ions

Interference ions 5 ppm	Interference %	
	Co-BIAMP	Cd-BIAMP
Cd^{2+}	+7.33	----------
Co^{2+}	-------	+8.43
Mn^{2+}	+3.97	+2.47
Fe^{2+}	+2.24	+3.11
Ni^{2+}	+5.13	+3.33
Cu^{2+}	+4.55	+4.89
Zn^{2+}	+6.48	+5.01
Pb^{2+}	+1.98	+2.26
Sn^{2+}	+3.85	+1.14
Al^{3+}	+3.37	+2.58

Effect of masking agents[19]

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
Co-BIAMP	0.165	0.167	0.207	0.206	0.205	0.163	0.244
Cd-BIAMP	0.017	0.016	0.054	0.029	0.045	0.042	0.018

Table (2) shown the best masking agents for Co-BIAMP complex were (Tartaric acid and KCN) but for Cd-BIAMP were (Tartaric acid and NaF), other masking agents are less effect comparatively.

Absorption spectra

The absorption spectra of the two complexes and the reagent5 are shown in figure (13) under optimum conditions

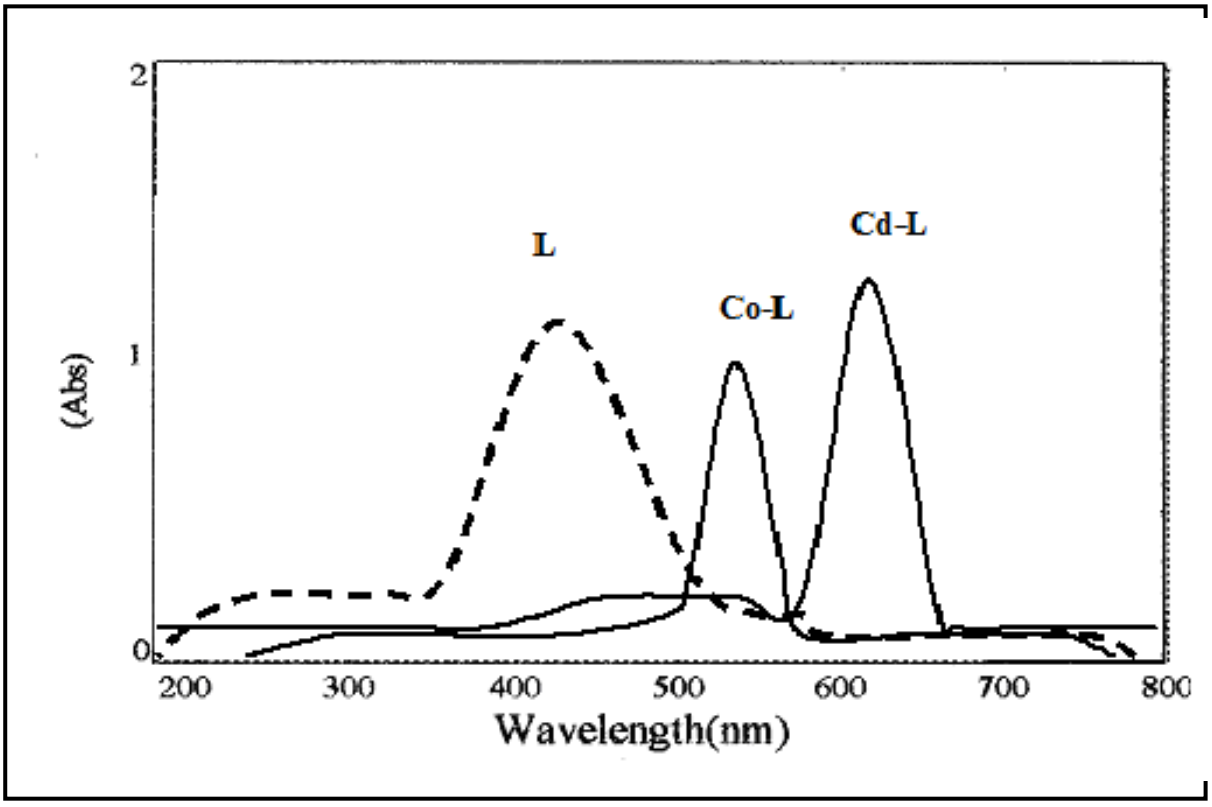


fig.(13) absorption spectra of the two complexes and the reagent.

Absorption spectra show that the λ_{max} of absorption of the reagent (BIAMP) at 449 nm, Co (BIAMP) complex at 522 nm and Cd (BIAMP) complex at 627 nm, this a new λ_{max} mean red shift in λ_{max} of complexes.

FTIR spectrum of (BIAMP)

FTIR spectrum of the reagent (BIAMP) show in figure (14)

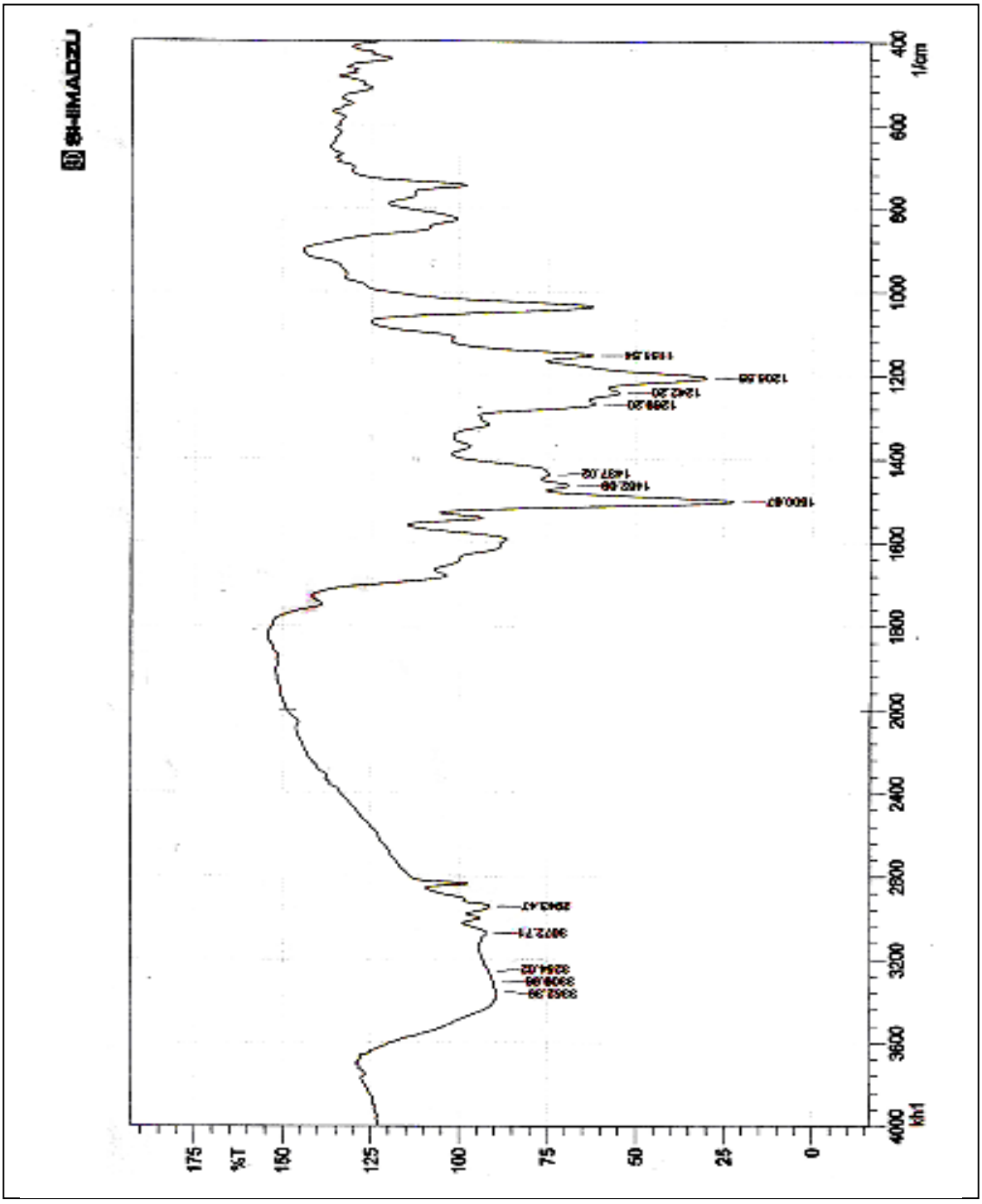


Fig.(14) FTIR spectrum of (BIAMP)

The infrared spectrum show in figure (14) give an evidence for the formation of the reagent 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 (Co-BIAMP) complex

FTIR spectrum of (Co-BIAMP) complex show in figure (15)

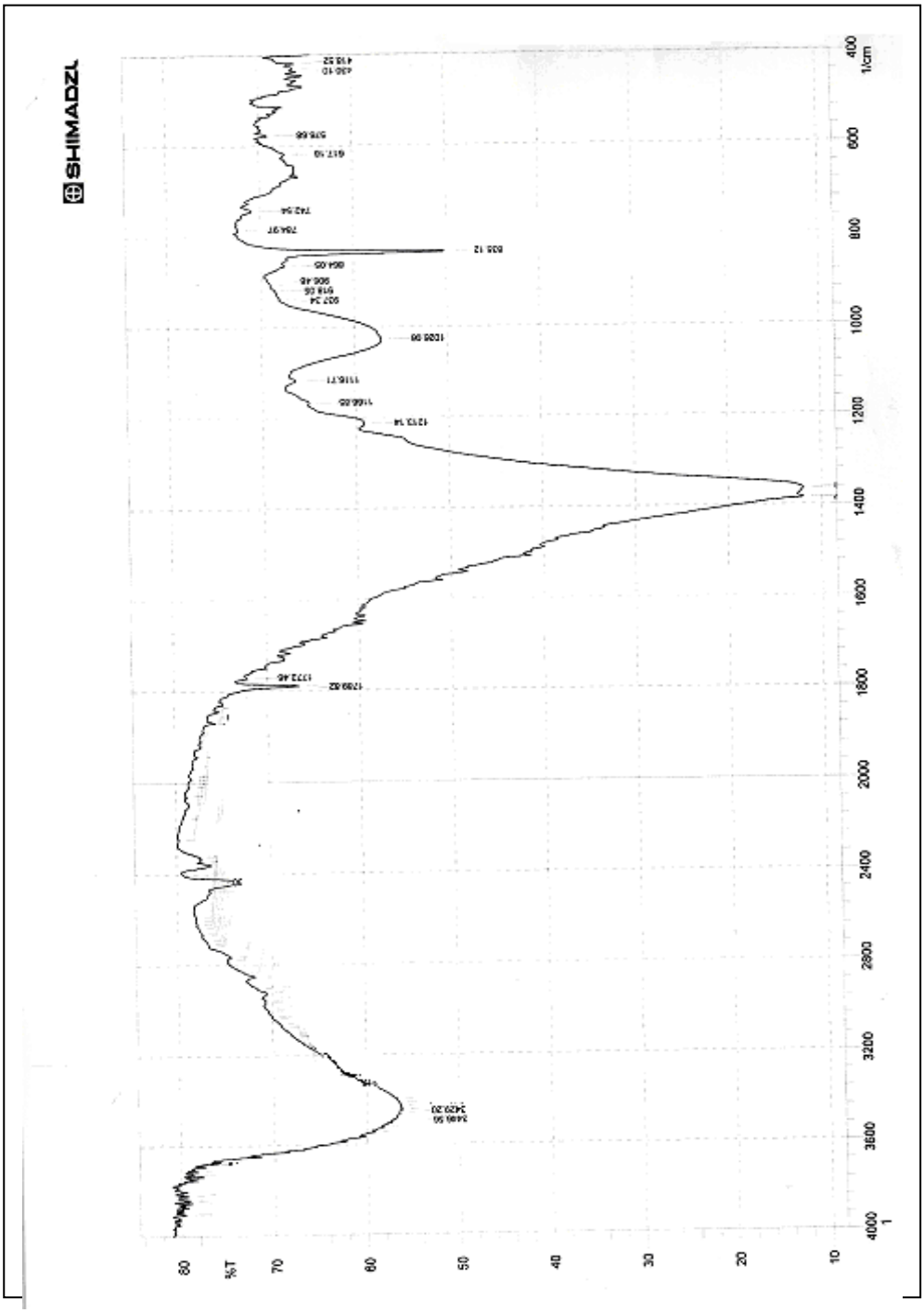


Fig.(15) FTIR spectrum of (Co-BIAMP) complex

FTIR spectrum of (Cd-BIAMP) complex

FTIR spectrum of (Cd-BIAMP) complex show in figure (16)

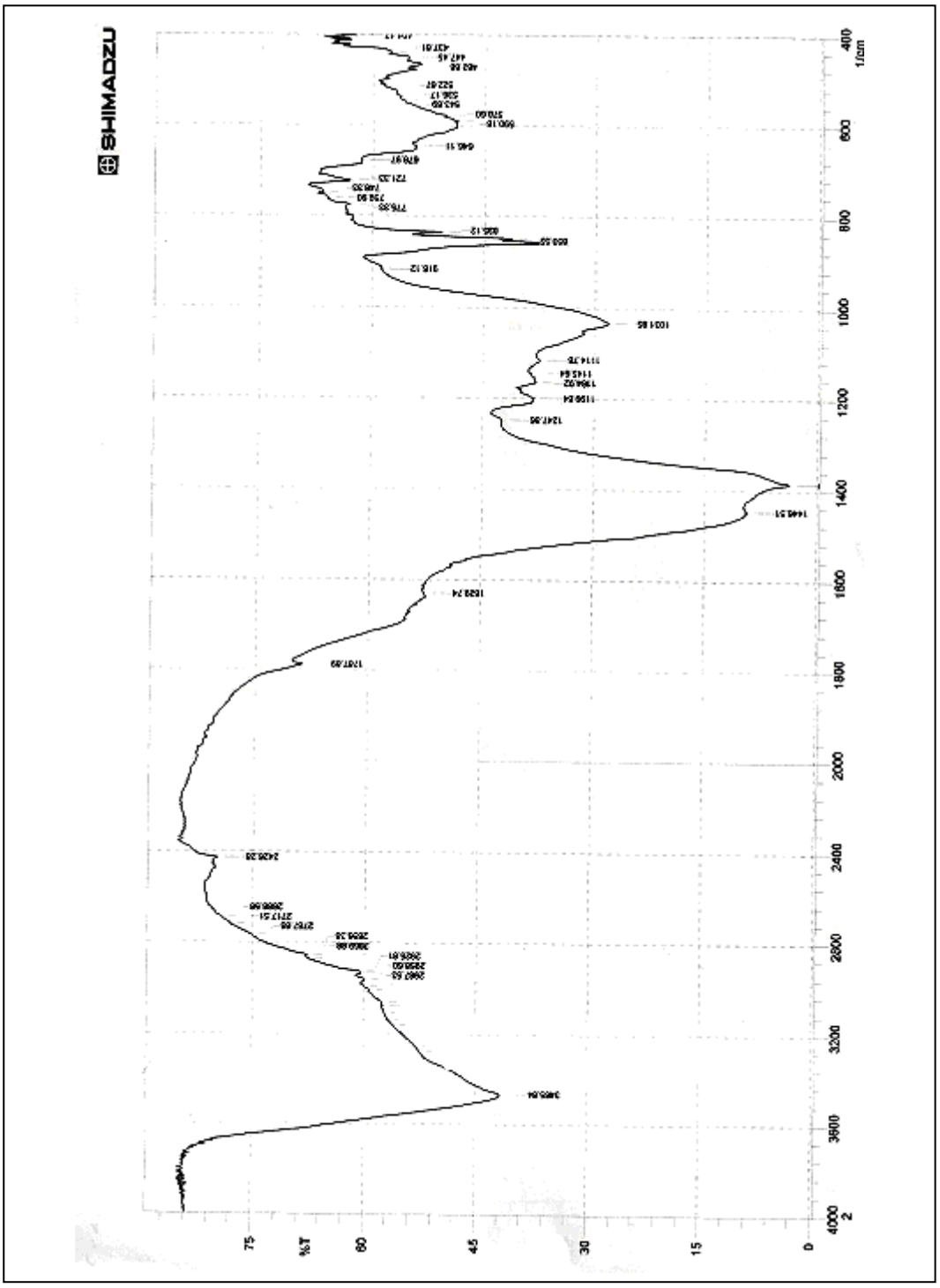


Fig.(16) FTIR spectrum of (Co-BIAMP) complex

The comparison between spectra of the reagent with those of the coordination complexes have revealed certain characteristic differences, these difference was shown in figures (15 and 16).
From figure (15 and 16) all metal complexes show that (BIAMP) behaves as monobasic tridentate reagent, coordinating via (C=N, N=N and phenolic OH) groups with displacement of hydrogen atoms from the latter.

The absence of broad band at 3413-3446 cm^{-1} in (Co-BIAMP) complex spectrum and at 3465 cm^{-1} in (Cd-BIAMP) complex spectrum indicate the deprotonation of phenolic oxygen and cleavage of the hydrogen bond with the involvement of the oxygen in bonding[20,21].

The spectra of the BIAMP reagent 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 (1394 cm^{-1}) and (1446 cm^{-1}) in (Co-BIAMP) and (Cd-BIAMP) complex spectrums, these shift suggest the linkage of metal ion with nitrogen of imidazol ring[22,23]. A (N=N) band at (1500 cm^{-1}) in BIAMP reagent figure (14) was shifted to (1375 cm^{-1}) and (1380 cm^{-1}) in figures (15 and 16) this shift could contributed to the metal-azo linkage[24].

A new bands appeared in (418-460 cm^{-1}) and (437-462 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 (Co-BIAMP) and (Cd-BIAMP) [25,26].

Applications

This method was applied to determine Pb^{2+} and Al^{3+} standard solutions, the results show in table (4)

Table (4) the results of standard method

Ion	True Value	Experimental Value
Co^{2+}	1 ppm	0.979 ppm
Cd^{2+}	1 ppm	1.020 ppm

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