Determination of Pb^{2+} and Al^{3+} by using a new ligand2-[(2-Benzimidazolyl) azo]-4-methoxyphenol

داخل ناصر طه
جامعة بابل / كلية العلوم / قسم الكيمياء
عبد الله محمد علي ايمن عبد الرسول جواد
جامعة الكوفة / كلية التربية للبنات جامعة الكوفة / كلية الصيدلة
شيرين رضا رسول يحيى فاهم حسين عبد الكاظم زينب هاشم
جامعة بابل / كلية العلوم / قسم الكيمياء

Abstract

This paper involve the determine of Pb^{2+} and Al^{3+} by using a new reagent 2-[(2-Benzimidazolyl) azo]-4-methoxyphenol (BIAMP), the wavelengths of maximum absorption of two complexes are (530 nm) and (633 nm) for Pb-BIAMP and Al-BIAMP.

Optimum condition were constructed like pH (9), (9) and temperature (30 ºc), (50 ºc) for Pb^{2+} and Al^{3+} , Beer's law was obeyed in the range (0.03-2), (0.01-1) ppm, detection limit was (0.0003), (0.00034) ppm, linearity (R^2) was (0.9995), (0.9991) correlation factor (r) was (0.9997), (0.9995), molar absorbitivty (ε) was 2.17 x 10^4 $L.mol^{-1}.cm^{-1}$, 1.02 x 10^5 $L.mol^{-1}.cm^{-1}$ for Pb and Al.

The stoichometry of metal to reagent were (1:2) of two complexes, Precision and accuracy of the analytical procedure was R.S.D % (0.33, 1.13) % and $E_{rel.}$%, R_e % were (-1.85, -2.33) %, (98.15, 97.67) % for Pb and Al. The interferences of ions were study and masked by using suitable masking agents.

الخلاصة

يتضمن البحث تقدير الرصاص (II) والالمنيوم (III) باستعمال الكاشف الجديدBIAMP)) ، وجد ان اعلى امتصاص للمعقدين كان عند الطول الموجي (530 nm) و (633 nm) لكل من الرصاص والالمنيوم، حددت الظروف المثلى لتكوين المعقدين من داله حامضية (9) و (9) ودرجة حرارة (30) و (50) مئوية، تم بناء منحني المعايره عند مدى من التراكيز تراوحت بين (0.03-2 ppm) و (0.01-1ppm) لكل من الرصاص والالمنيوم.وجد ان حد الكشف لهذه الطريقة هو (0.0003 ppm) و (0.00034 ppm) وبخطية (R^2) مساويه الى (0.9995) و (0.9991(وقيمة معامل الارتباط (0.9997) و (0.9995)، اما قيمة معامل الامتصاص المولاري هي $2.17x10^4$ $L.mol^{-1}.cm^{-1}$ و $1.02x10^5$ $L.mol^{-1}.cm^{-1}$ لكل من الرصاص والالمنيوم على التوالي.تم تحديد نسبة الفلز الى الكاشف حيث وجد انها تساوي (2:1) لكلا المعقدين كما تم تحديد دقة وضبط الطريقة التحليلية حيث وجد ان قيمة 0.33 %) R.S.D%) و (1.13 %(اما E_{rel} بلغت (-1.85 %) و (-2.33 %) 98.15 %) R_e) و (97.67 %) لكل من الرصاص والالمنيوم على التوالي ، كما درس تاثير الايونات المتداخلة وحجبت باستخدام عوامل الحجب المناسبة.

Introduction

Lead is recognized as a highly toxic accumulative element, even at low levels[1].In humans, lead is chronically accumulated in bone and some soft tissues, thus triggering injuries to the health, such as hematological damage, anemia, kidney malfunctioning and brain damage most contamination to humans by lead originates from drinks and food[2-4].

Several method have been used for determination of lead , atomic absorption[5-7], various kinds of flow-injection on-line column preconcentration systems, such as coprecipitation[8], ion exchange[2], solvent extraction[9] have been combined with atomic spectrometry for trace lead determination in water[10-11].

Aluminum is an abundant element, it is distributed among the body tissues, organs and bones, but it is exact biological functions are not known fully, aluminum have been detected in the brains of dead patients[12,13].

Stripping voltammetry has been widely used to measure the low concentration of aluminum[14].

Solochome violt SR[15], calmagit[16], cupferro[17] and alizarin[18] are most frequently used for aluminum complex.

In this study, the employment of sensitive and reproducible method was developed for the determination of lead and aluminum by using 2-[(2-Benzimidazolyl) azo]-4-methoxyphenol as a new 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.

Reagents

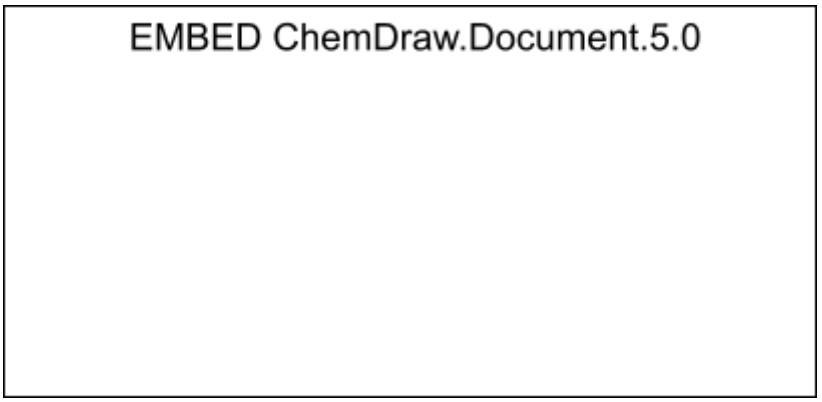
Synthesis of 2-[(2-Benzimidazolyl) azo]-4-methoxyphenol (BIAMP)

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.



Standard Solutions

Solution of Pb^{2+} (20 ppm) was prepared by dissolving (0.0016 g) of $Pb(NO_3)_2$ in 50 ml distilled water.

Solution of Al^{3+} (20 ppm) was prepared by dissolving (0.0050 g) of $AlCl_3$ 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 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 0.3 ppm of Pb^{2+} and 0.5 ppm of Al^{3+} 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 530 nm for Pb^{2+} and 633 nm for Al^{3+} 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 from (2-12) and the results are shown in, figures (1&2).

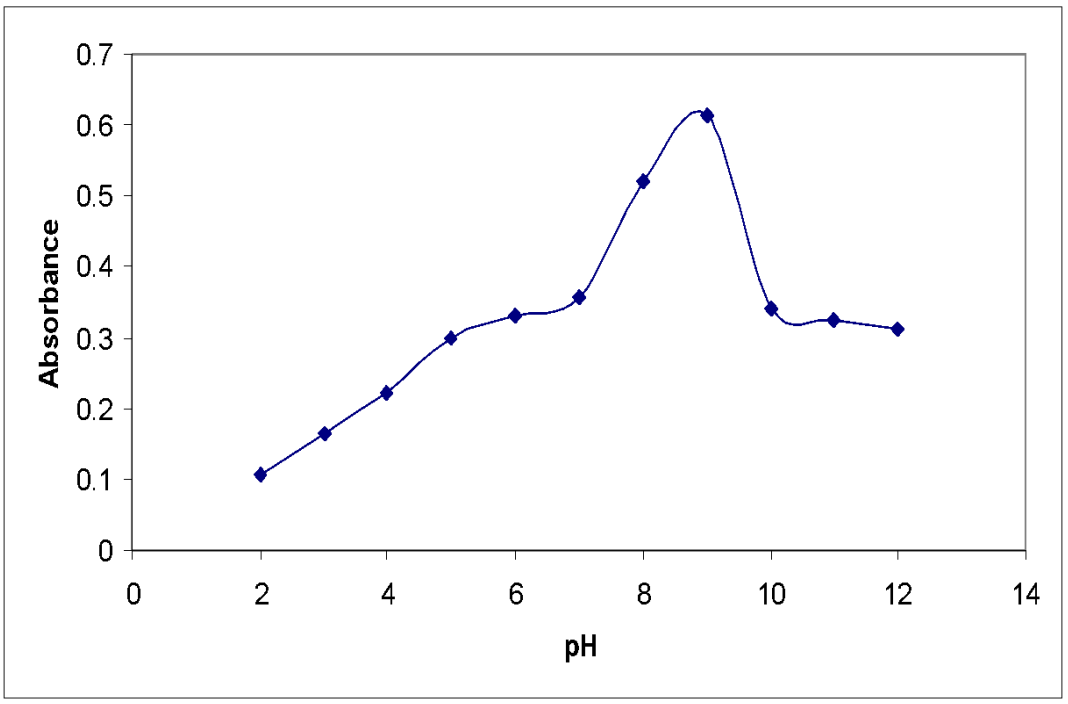


Fig.(1) Effect of pH on the absorbance of Pb-BIAMP complex .

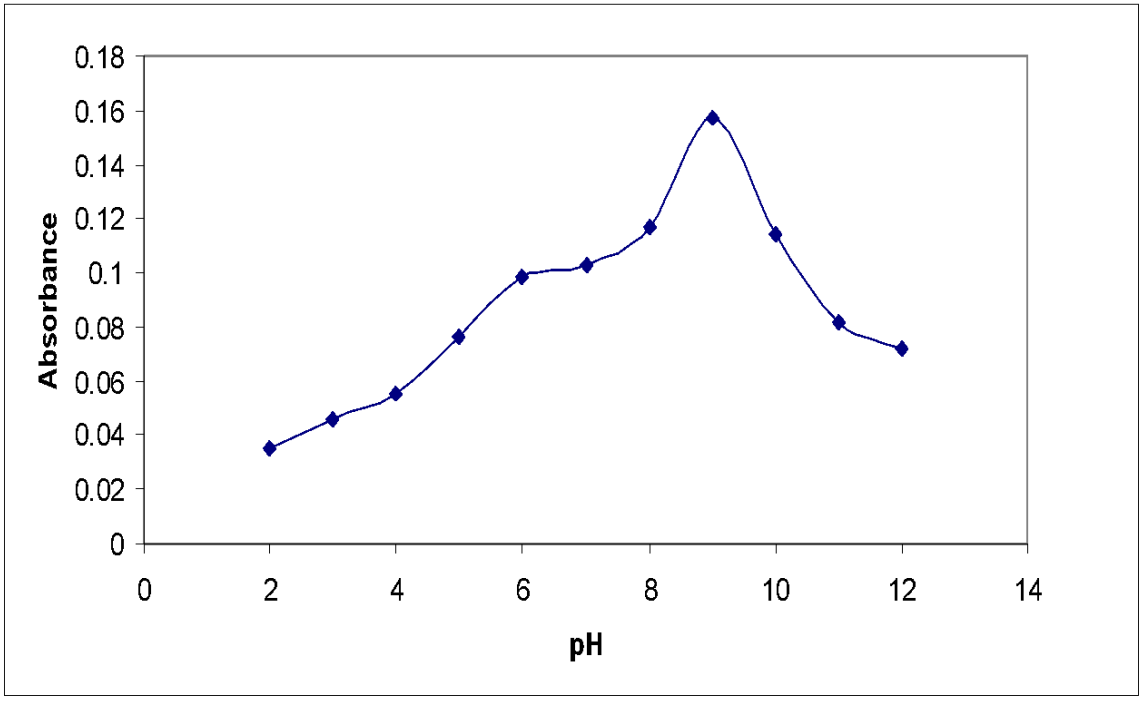


Fig.(2) Effect of pH on the absorbance of Al-BIAMP complex.

From figures (1&2) the best pH value of Pb-BIAMP complex is in the range (8-9.5) and pH (9) was adopted as optimum while for Al-BIAMP complex is in the range (8.5-9.5) and the pH (9) was adopted as optimum pH.

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

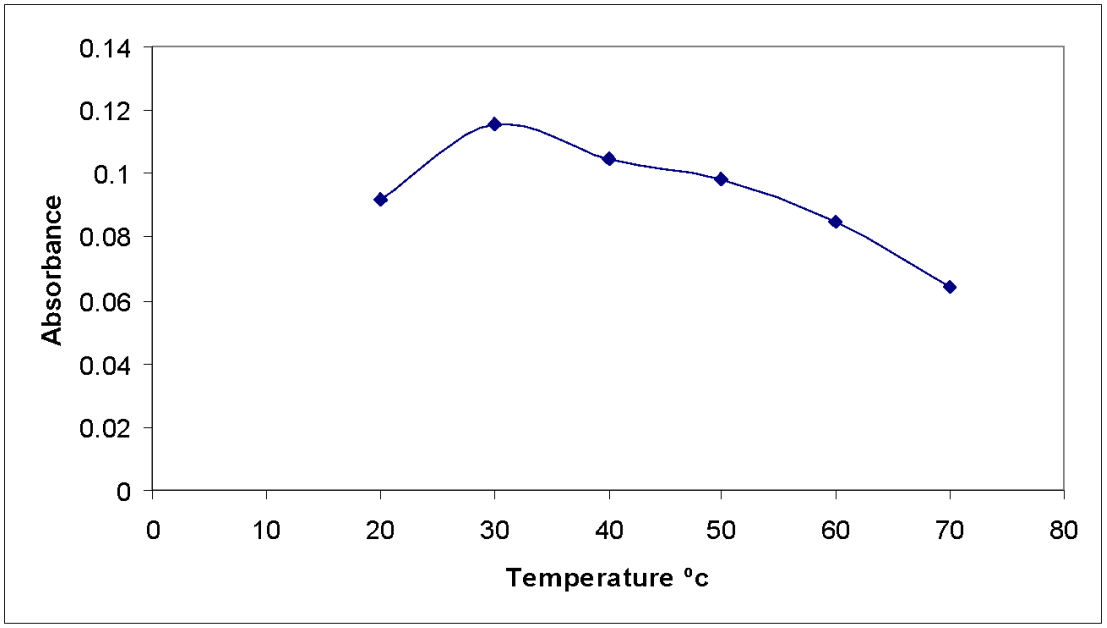


Fig.(3) Effect of temperature on the absorbance of Pb-BIAMP complex.

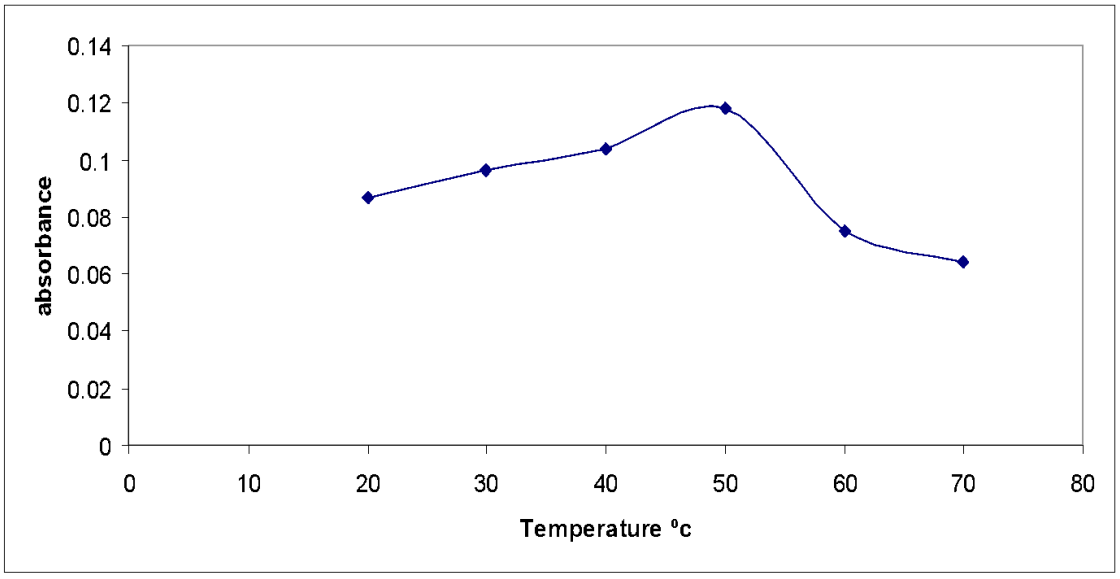


Fig.(4) Effect of temperature on the absorbance of Al-BIAMP complex.

The effect of temperature on the absorbance of two complexes was studied in the range (20-70) °c, the maximum absorption was obtained at 30 °c and for Pb-BIAMP

and 50 ºc for Al-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[13] method of continuous variation and molar ratio[14] methods, the composition of two complexes were shown in figures (5-8).

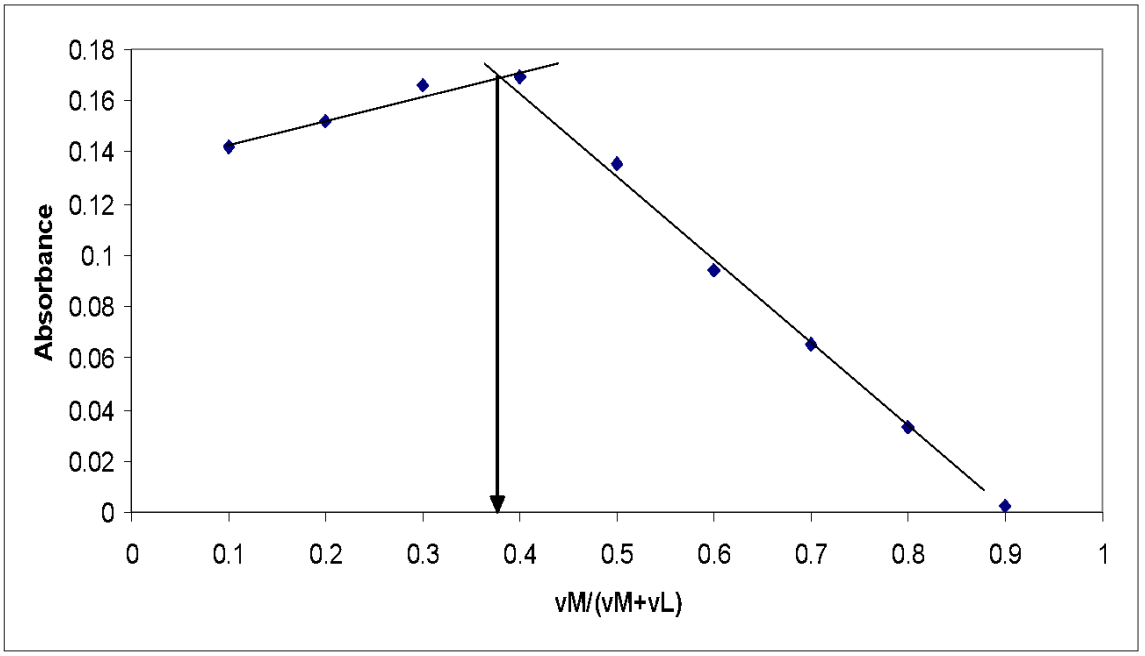


Fig.(5) continuous variation method for Pb-BIAMP complex at optimum conditions.

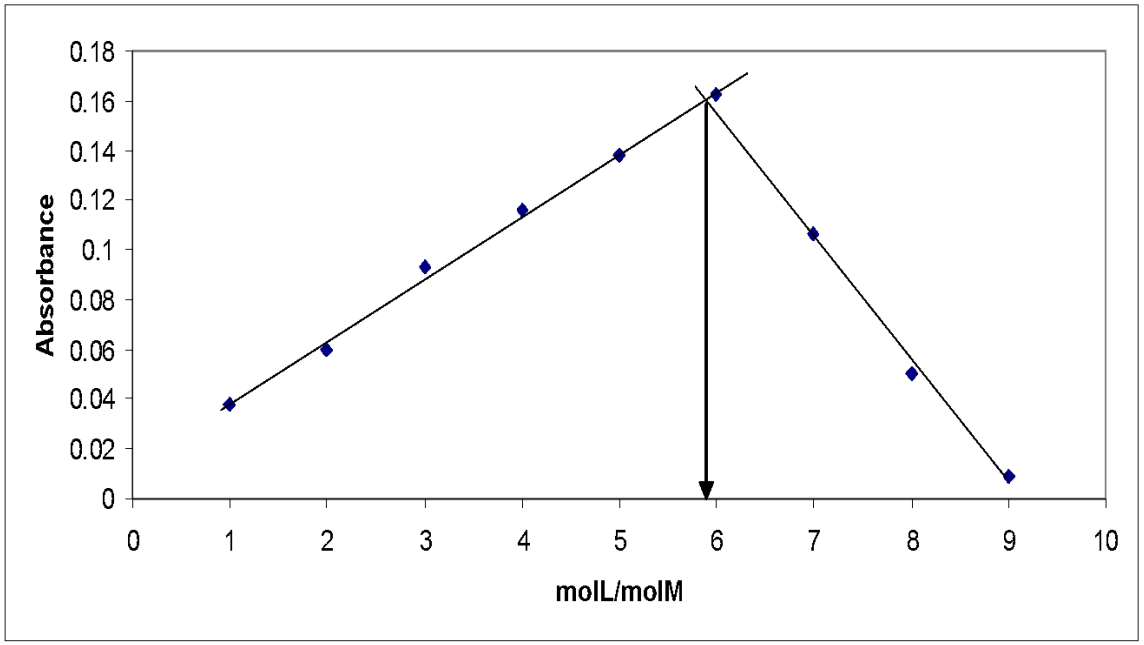


Fig.(6) molar ratio method for Pb-BIAMP complex at optimum condition.

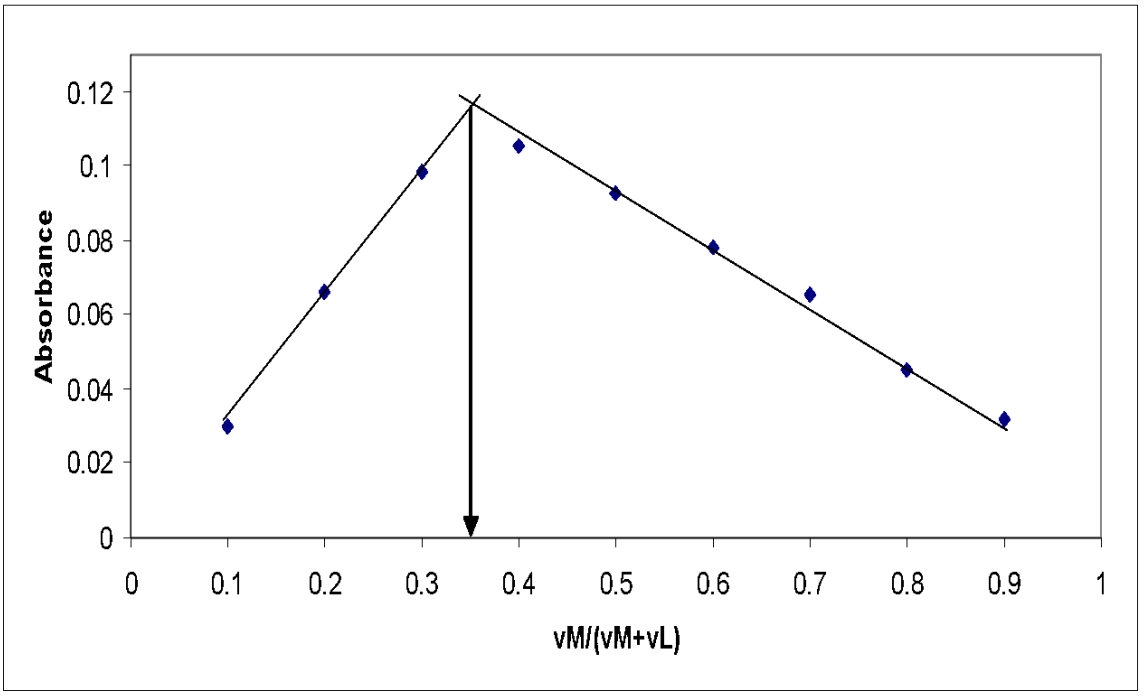


Fig.(7) continuous variation method for Al-BIAMP complex at optimum conditions.

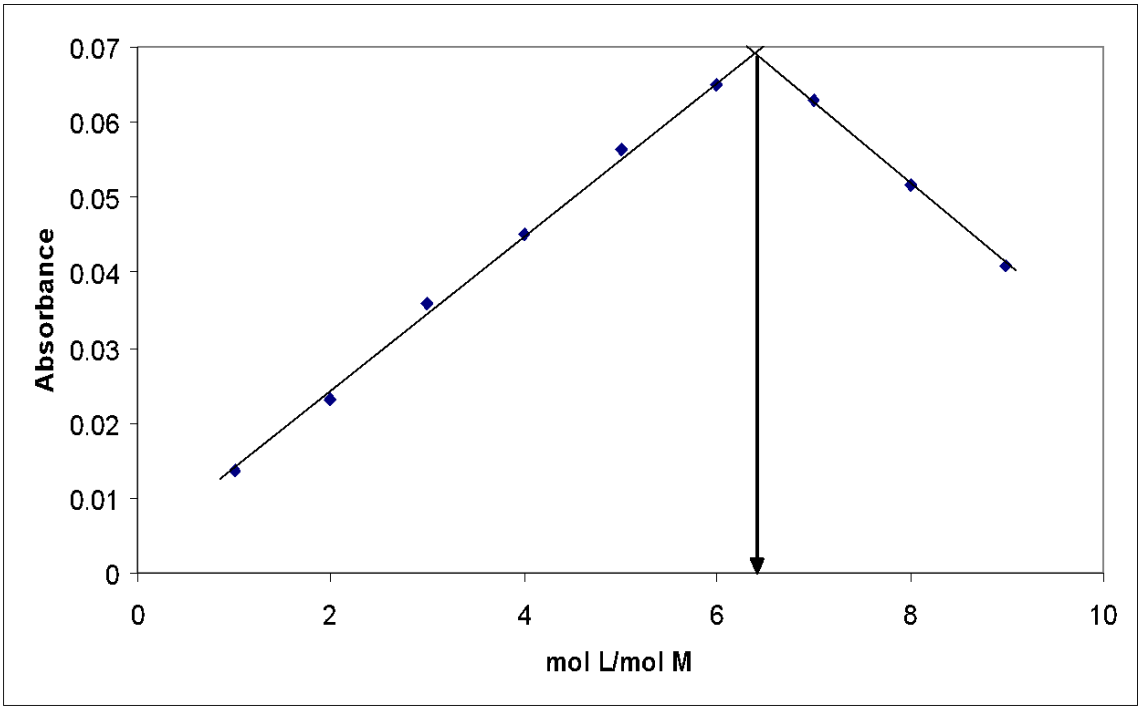


Fig.(8) molar ratio method for Al-BIAMP complex at optimum conditions.

From the results of continuous variation and molar ratio methods show in figures (5-8), the ratio between Pb^{2+} to BIAMP is (1:2), and between Al^{3+} to BIAMP is (1:2) and the stability constant[15] ($K_{sta.}$) ($4.32x10^5$ $L^2.mol^{-2}$) for Pb-BIAMP complex and ($1.02x10^6$ $L^2.mol^{-2}$) for Al-BIAMP complex, figures (9, 10) shows the proposed composition of the two complexes

EMBED ChemDraw.Document.5.0

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

EMBED ChemDraw.Document.5.0

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

Beer's low

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

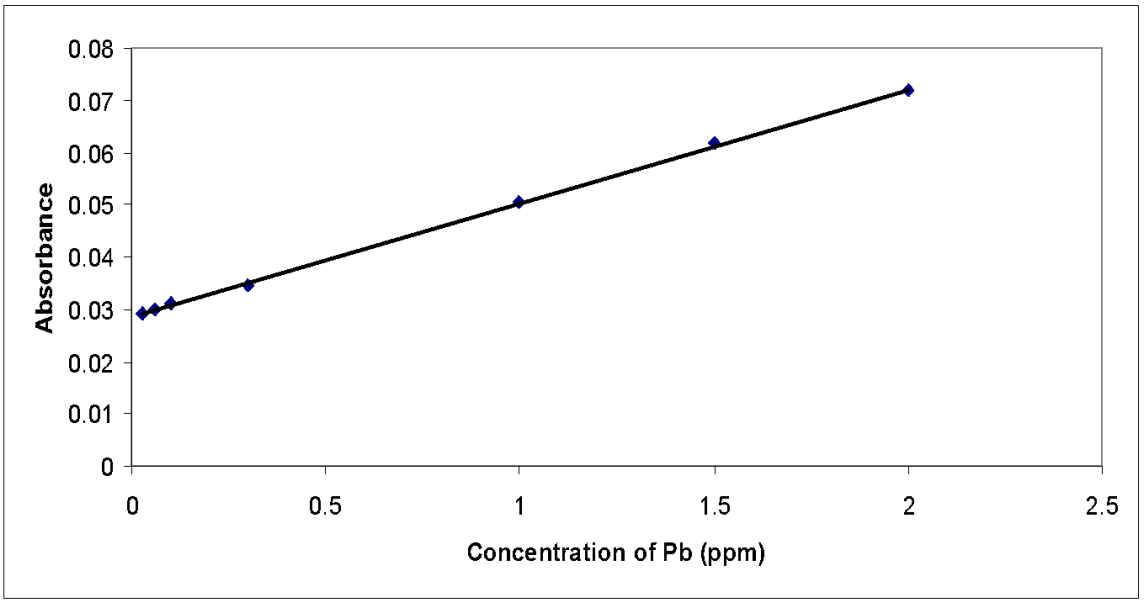


Figure (11) calibration curve of Pb^{2+} ion.

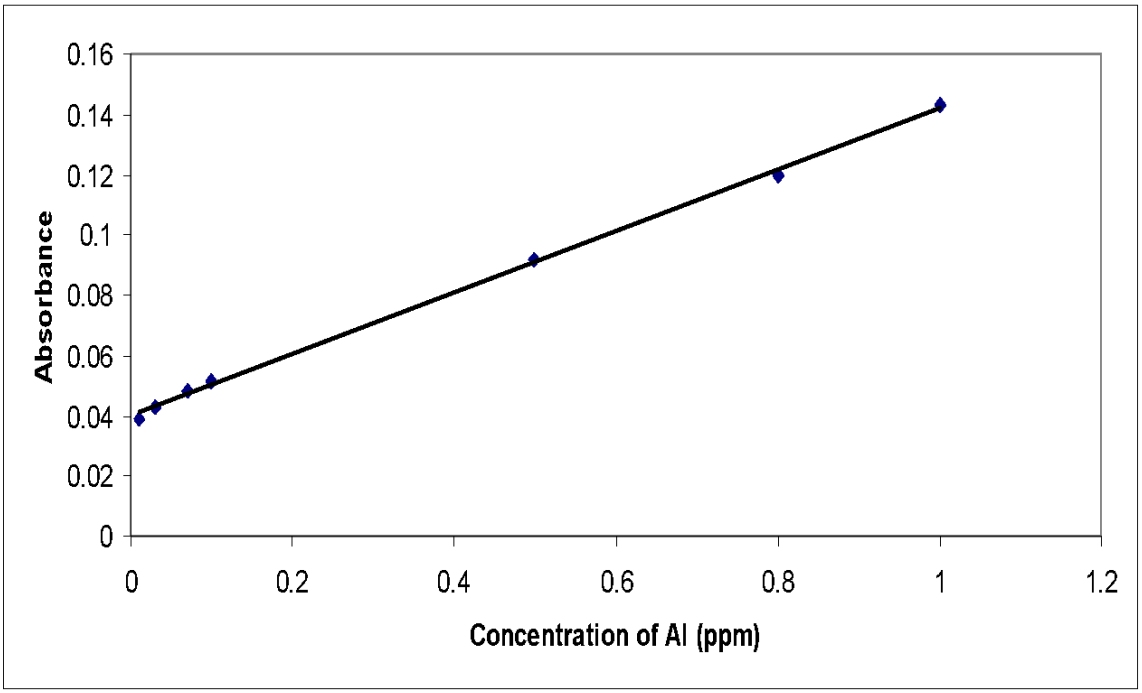


Figure (12) calibration curve of Al^{3+} ion.

The results indicated that Beer's law was obeyed in the range (0.03-2), (0.01-1) ppm, detection limit was (0.0003), (0.00034) ppm, linearity (R^2) was (0.9995), (0.9991) correlation factor (r) was (0.9997), (0.9995), molar absorbitivty (ε) was 2.17 x 10^4 $L.mol^{-1}.cm^{-1}$, 1.02 x 10^5 $L.mol^{-1}.cm^{-1}$ for Pb and Al.Sandell's sensitivity were calculated to be ($9.54x10^{-5}$) for Pb^{2+} and ($2.55x10^{-5}$) for Al^{3+}.Precision and accuracy of the analytical procedure was R.S.D % (0.33, 1.13) % and $E_{rel.}$%, R_e % were (-1.85, -2.33) %, (98.15, 97.67) % for Pb and Al.The precision and accuracy of the method were found to be excellent.

Effect of interference ions[16,17]

The selectivity of Pb-BIAMP and Al-BIAMP complexes were tested by measuring the absorbance of complex of 1 ppm of Pb^{2+} and 1 ppm Al^{3+} 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	Interference %	
	Pb-BIAMP	Al-BIAMP
Mn^{2+}	+1.53	+0.84
Fe^{2+}	+3.88	+6.63
Co^{2+}	+3.18	+1.49
Ni^{2+}	+4.66	+2.67
Cu^{2+}	+7.73	+3.65
Zn^{2+}	+3.54	+2.09
Cd^{2+}	+6.37	+5.01
Sn^{2+}	+3.93	+4.25

Pb^{2+}	-------	+4.24
Al^{3+}	+1.29	-------

Table (1) shown that ions ($Cu^{+2}$and Cd^{+2}) were the absorbance value varying by more than 5% from the expected value for Pb^{2+} complex and (Fe^{+2} and Cd^{+2}) ions for Al^{3+}.

Effect of masking agents[18]

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
Pb-BIAMP	0.176	0.078	0.179	0.126	0.129	0.108	0.099
Al-BIAMP	0.018	0.063	0.017	0.032	0.020	0.058	0.041

Table (2) shown the best masking agents for Pb-BIAMP complex was (Oxalic acid) but for Al-BIAMP were (Oxalic acid and Ascorbic acid), other masking agents are less effect comparatively.

Absorption spectra

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

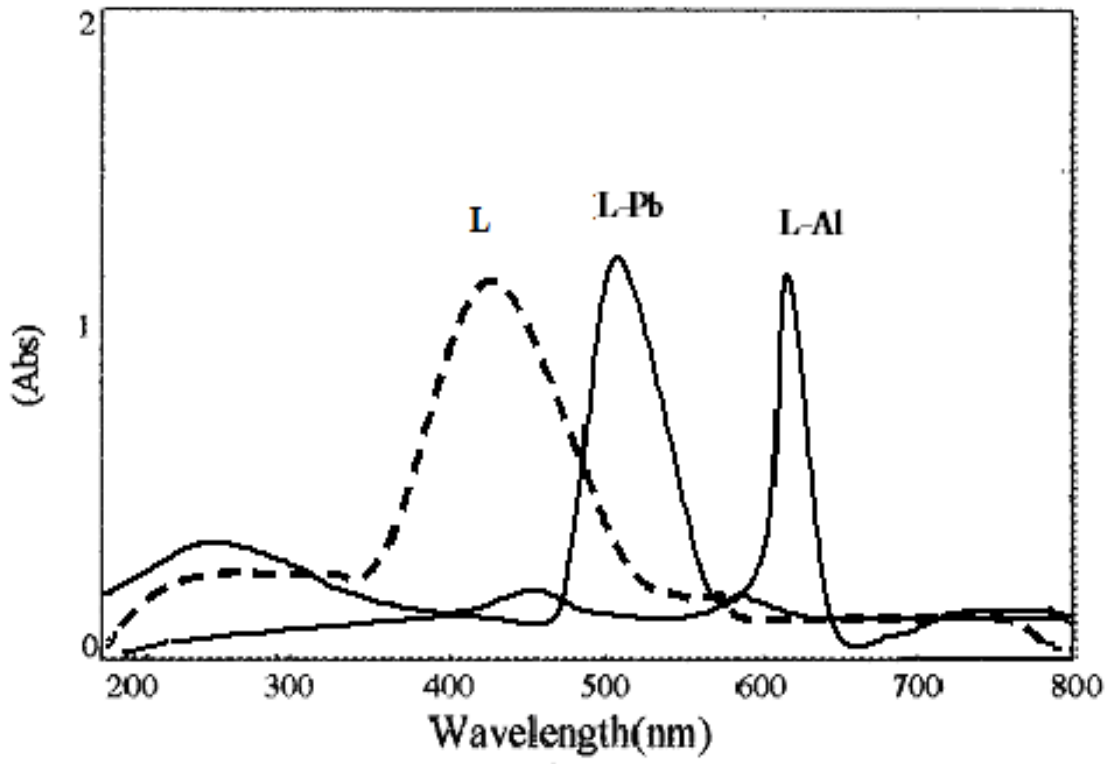


fig.(13) absorption spectra of the two complexes and the reagent.

Absorption spectra show that the λ_{max} of absorption of the reagent (BIAMP)

at 449 nm, Pb (BIAMP) complex at 530 nm and Al (BIAMP) complex at 633 nm, this a new λ_{max} mean red shift in λ_{max} of complexes.

FTIR spectrum of (BIAMP) reagent

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

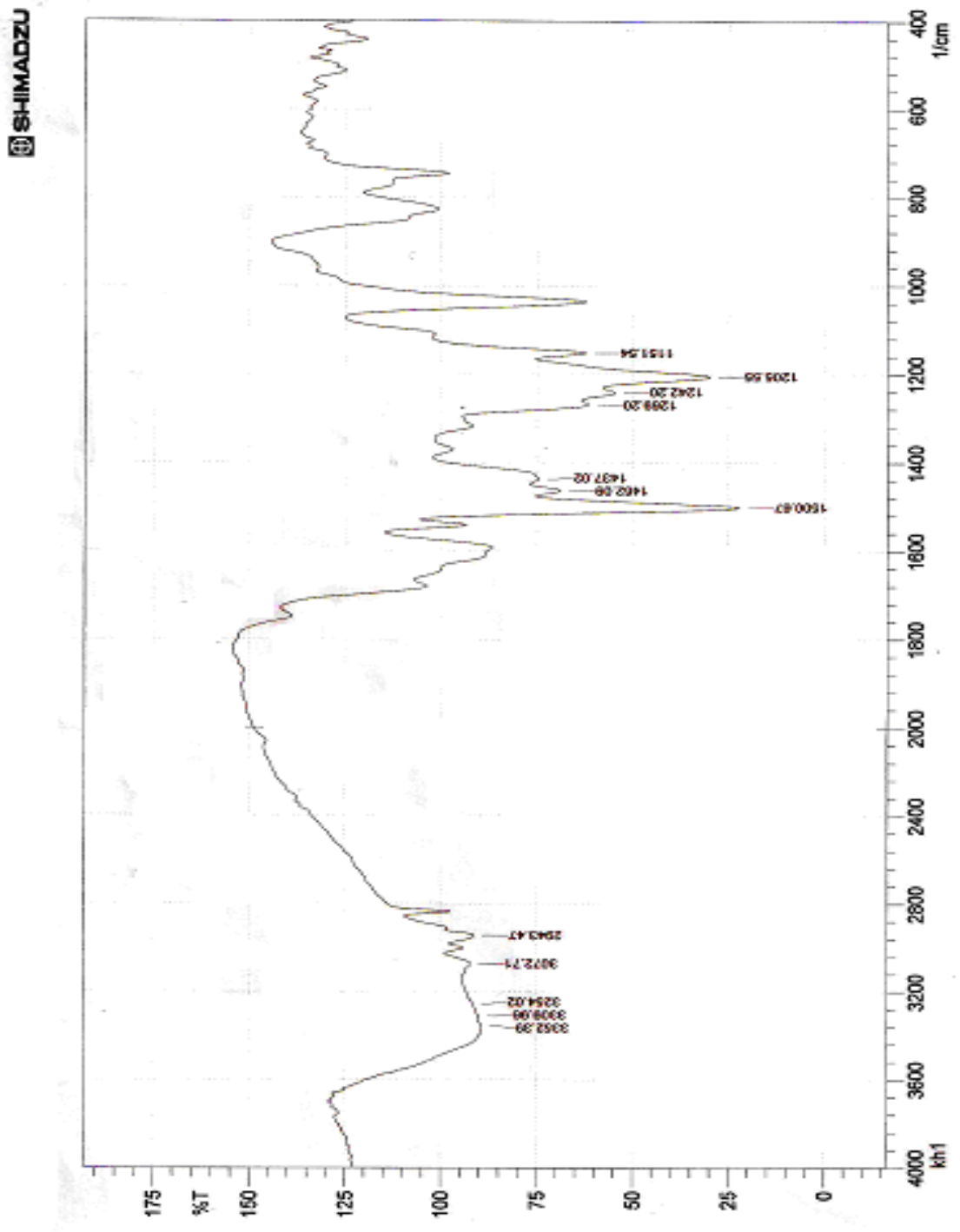


Fig.(14) FTIR spectrum of (BIAMP)

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 (BIAMP -Al) complex

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

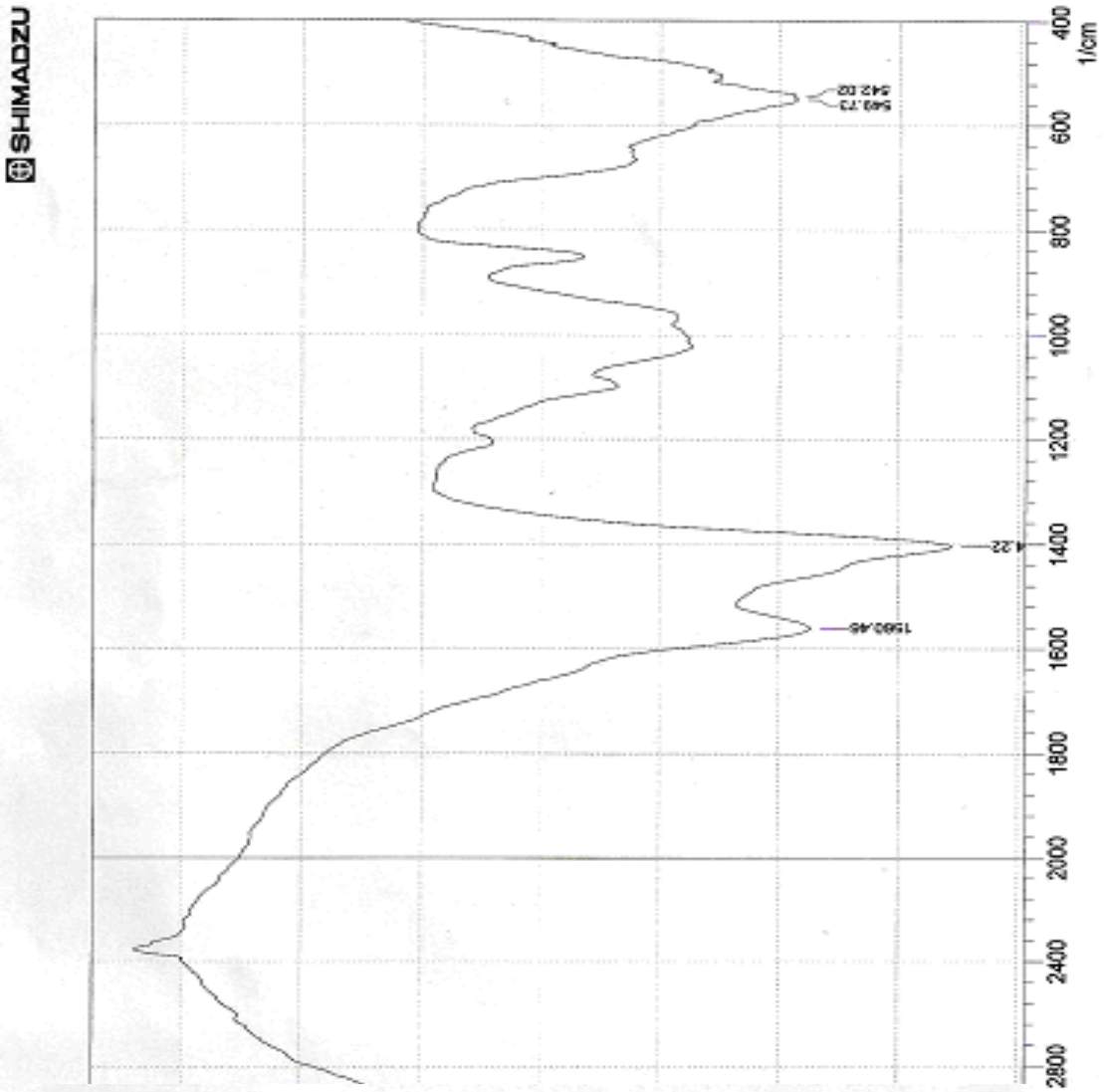
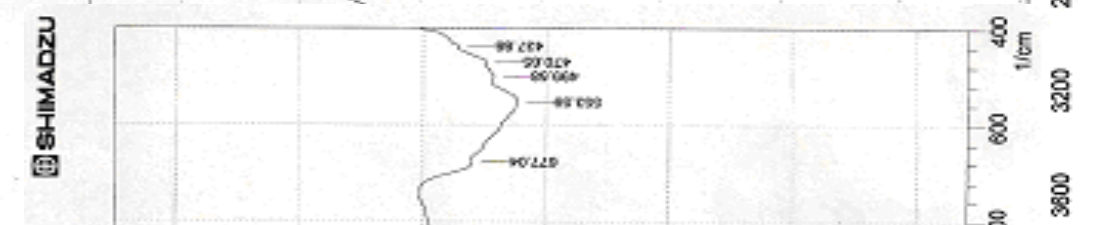


fig.(15) FTIR spectrum of (BIAMP -Al) complex

FTIR spectrum of (BIAMP -Pb) complex



FTIR spectrum of (BIAMP -Pb)

complex show in figure (16)

Fig.(16) FTIR spectrum of (BIAMP -Pb) 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 (15 and 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 3311-3422 cm^{-1} in (Al-BIAMP) complex spectrum and at 3300-3419 cm^{-1} in (Pb-BIAMP) complex spectrum indicate the deprotonation of phenolic oxygen and cleavage of the hydrogen bond with the involvement of the oxygen in bonding[19,20].

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 (1560 cm^{-1}) and (1520 cm^{-1}) in (Al-BIAMP) and (Pb-BIAMP) complex spectrums, these shift suggest the linkage of metal ion with nitrogen of imidazol ring[21,22]. A (N=N) band at (1500 cm^{-1}) in BIAMP ligand figure (14) was shifted to (1404 cm^{-1}) and (1408 cm^{-1}) in figures (15 and 16) this shift could contributed to the metal-azo linkage[23].

A new bands appeared in (420-458 cm^{-1}) and (437-470 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) and (M-Cl) stretching for (Al-BIAMP) and (M-O) and (M-N) stretching for (Pb-BIAMP) [24,25].

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
Pb^{2+}	0.7 ppm	0.698 ppm
Al^{3+}	0.5	0.501 ppm

References

1- W.Chuachuad & J. Tyson, J. Ana. At. Spectrum., (2005), 20, 282.
2- L. Wan, Z-R. Xu & J-H. Wong, Analyst, (2006), 131, 141.
3- M.S. Bispo, M.G.A. Korn, E.S.B. Borte & L.S.G. Teixeira, Spectrochim. Acta, Part B, (2002), 57, 2175.
4- Y.P. Depena, B. Paredes, W. Rondona, M. Bargurea, J. Burgurea, C. Rondona, P. Carreo & T. Capote, Talanta, (2004), 64, 1351.
5- J.H. Wang, Y.L. Lu, Z. Du & Z.L. Fang, J. Anal. At. Spectrom., (2004), 19, 1559.
6- J.X. Li, F. Lu, Z. Du & K.I. Tsunoda, Anal. Chem. Acta, (2000), 419, 65.
7- J.F. Tyson, R.I. Ellis, G. Carnrick & F. Fernandez, Talanta, (2000), 52, 403.
8- G.A. Zachariadis, A.N. Anthemidis, P.G. Bettas & J.A. Stratis, Talanta, (2003), 57, 919.
9- R.G. Wuilloud, A.H. Gonzalez, E.J. Marchevsky, R.A. Olsina & L.D. Martine, J.AOAC Int., (2001), 84, 1555.
10- G.H. Tae & Z.L. Fang, Fresenius J. Anal. Chem., (1998), 360, 156.
11- J. Nakajima, Y. Hirano & K. Oguma, Anal. Sci., (2003), 19, 585.
12- I.S. Parkinson, M.K. Ward & D.N.S. Kerr, J. Clin. Pathol., (1981), 34, 12, 1285.
13- Jop, Ann. Chem, (Paris), (1928), ***9***, 113.
14- J.A. Yoe & A.L. Jones, Chem. Anal. Ed., (1944), ***11***, 16.
15- W.C. Vosburgh & G.R. Cooper, J. Am. Chem. Soc., (1941), ***63***, 437.
16- H. Shuker, ***M.Sc. Thesis***, Mousl University, (1992).
17- C.B. Ojeda, A.G. Detorres, F.S. Rojas & J.M. Canopavon, Analyst, (1987), ***112***, 1499.
18- W. Abd Al-Azezz, ***Ph.D Thesis***, Mosul University, (1990).
19- A.M. Ali, N.J.C., (2007), 28, 676.
20- F.A. Snavely & C.H. Yodeer, J. Org. Chem., (1968), 33, 513.
21- K.G. Al-Adely, N.J.C., (2007), 28, 585.
22- O.Yamach & H.Tanaka, Talanta, (1970), 20, 203.
23- M.W.Bes, S.F.Kettle & D.B.Powell, Spectrochem. Acta., (1974),30(A), 139.
24- S.N.Duby & K.Beena, Indian J.Chem. Acta., (1985), 24(A), 950.
25- X.Kumar & S.P.Tolani, Croat. Chem. Acta, (1989), 62(1), 73.