Determination of Sn^{2+} by using a new ligand 2-[(2-Benzimidazolyl) azo]-4-methoxyphenol

داخل ناصر طه
جامعة بابل / كلية العلوم
عبد الله محمد علي — جامعة الكوفة / كلية التربية للبنات
عزت حسين زمام — جامعة الكوفة / كلية العلوم
شيرين رضا رسول — جامعة بابل / كلية العلوم
علاء رشيد — جامعة بابل / كلية العلوم
بان احمد — جامعة بابل / كلية العلوم
زينه عباس — جامعة بابل/ كلية التمريض

Abstract

BIAMP was used to determine Sn^{2+}, optimum conditions were maximum absorption of complex at (523 nm), pH (9), temperature (40 ºc) .
Beer's law was obeyed in the range (0.02-1.8) ppm, detection limit was (0.0009) ppm, linearity (R^2) was (0.9995), correlation factor (r) was (0.9997), molar absorbitivty (ε) was 4.09 x 10^4 $L.mol^{-1}.cm^{-1}$.

The ratio between metal to ligand was (1:2) of complex, Statistical units were recorded, R.S.D % (1.63) % and $E_{rel.}$% and R_e % were (-1.66) %, (98.34) % . The interferences of ions were study.

الخلاصة

استخدم الكاشف (BIAMP) لتقدير Sn^{2+} ، وجد ان اعلى امتصاص للمعقد كان عند الطول الموجي (523 nm)، الظروف المثلى لتكوين المعقد من داله حامضية (٩) ودرجة حرارة (٤٠) مئوية، تم بناء منحني المعايره عند مدى من التراكيز تراوحت بين (0.02-1.8 ppm) .
كان حد الكشف لهذه الطريقة هو (0.0009 ppm) وبخطية (R^2) مساويا الى (٠.٩٩٩٥) وقيمة معامل الارتباط (٠.٩٩٩٧)، اما قيمة معامل الامتصاص المولاري هي 4.09 x 10^4 $L.mol^{-1}.cm^{-1}$.
سجلت نسبة الفلز الى الكاشف حيث وجد انها تساوي (٢:١) واجريت تحاليل احصلئية فكانت قيمة R.S.D% (% ١.٦٣) اما $E_{rel.}$ بلغت (% 1.66-) اما R_e (%٩٨.٣٤)، وتمت دراسة تاثير الايونات المتداخلة.

Introduction

Tin is an element of group 14 of the periodic table, metallic tin is normally covered with a thin protective film of tin oxide(1). Tin is a soft, silvery metal that is a naturally occurring element, tin occurs naturally in food and it is also present in food stored in tin cans, tin is present in air, water and soil, it is found in humans at low levels, tin combined with a substance like chlorine or sulfur is called an inorganic tin compound, tin combined with substances containing carbon is called an organic compound or organic tin(2).

Inorganic tin compounds are in toothpaste, soaps and dyes, the inorganic tins are not very toxic due to poor absorption by all routes of exposure, organ tins are used to make pesticides, plastics and food packaging(3).

Many ways established for tin determination inorganic tin determination by used atomic absorption spectroscopy(4). Tin was determined in biological samples(5), water(6), vegetable(7). In added X-Ray fluorescence to determine the tin concentration in river water, which found detection limit of 0.25-0.4 mg/l for ionic metals(8). Organotin compound can be determine using dithizone in compounds(9). Fluorometric technique has been developed for the determination of tin in potato samples(10,11).

The aim of present study is to develop a simpler direct spectrophotometric method for the trace determination of tin in aqueous solution using a new organic 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.

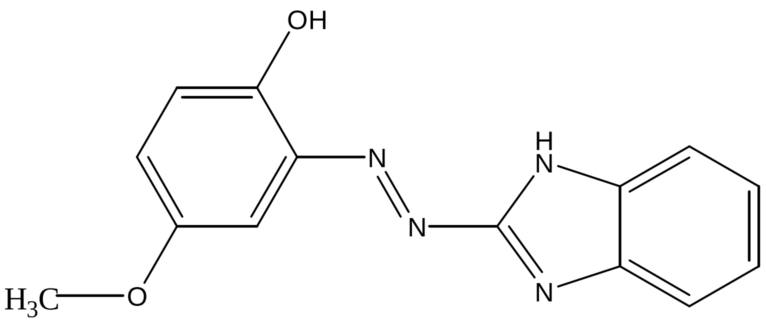
Reagents

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

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.



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

Standard Solutions

A solution of Sn^{2+} (20 ppm) was prepared by dissolving (0.0019 g) of $SnCl_2.2H_2O$ 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 0.5 ppm of Sn^{2+} ion 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 523 nm 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

Effect of pH on the absorbance show below in figure (1).

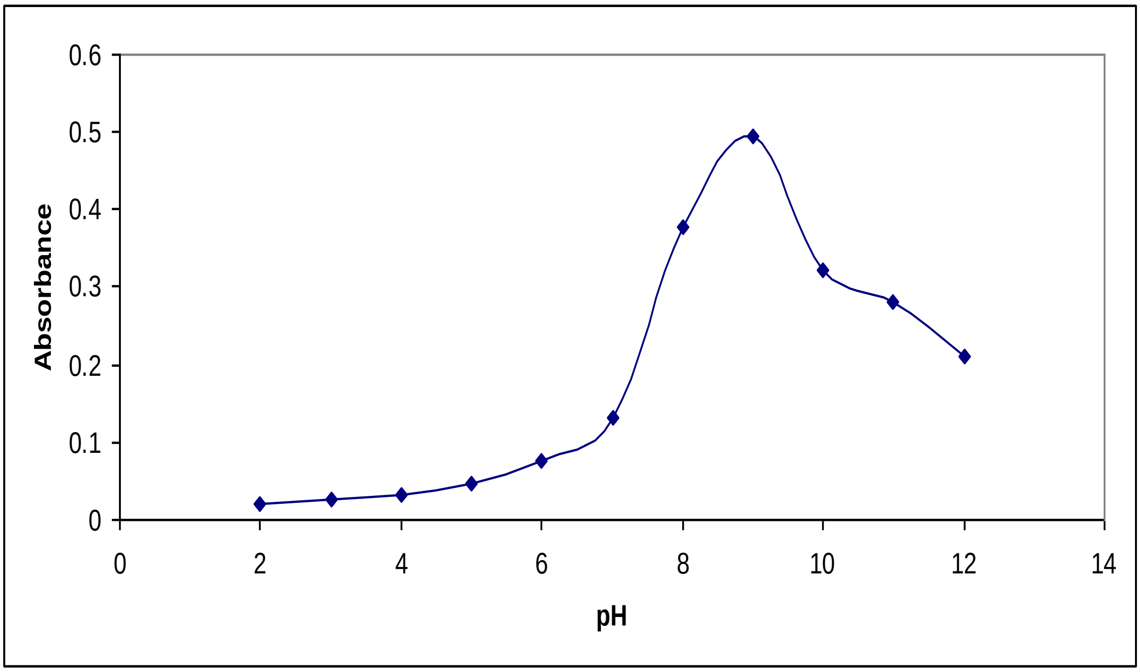


Fig.(١) Effect of pH on the absorbance of Sn-BIAMP complex.

From figure (1) the best pH value of Sn-BIAMP complex is in the range (8.5-9.5) and the pH (9) was adopted.

Stability of complexes with the time

A stability of the complex with the time was studied, the color of the 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 complex Sn-BIAMP was studied, figures (2) show this effect.

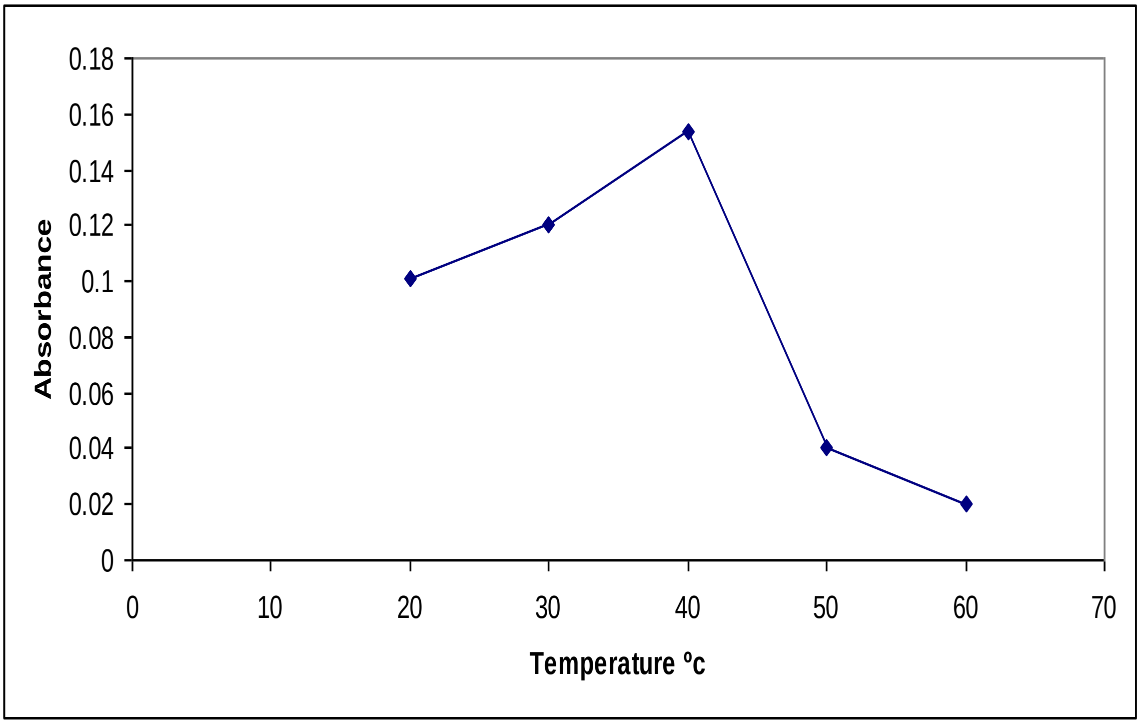


Fig.(2) Effect of temperature on the absorbance of Sn-BIAMP complex.

The maximum absorption was obtained at 40 °c, above this temperature the complex may be dissociation.

Composition of the complex

The composition of the complex was determined by Job's[12] method of continuous variation and molar ratio[13] methods, the composition of complex was shown in figures (3,4).

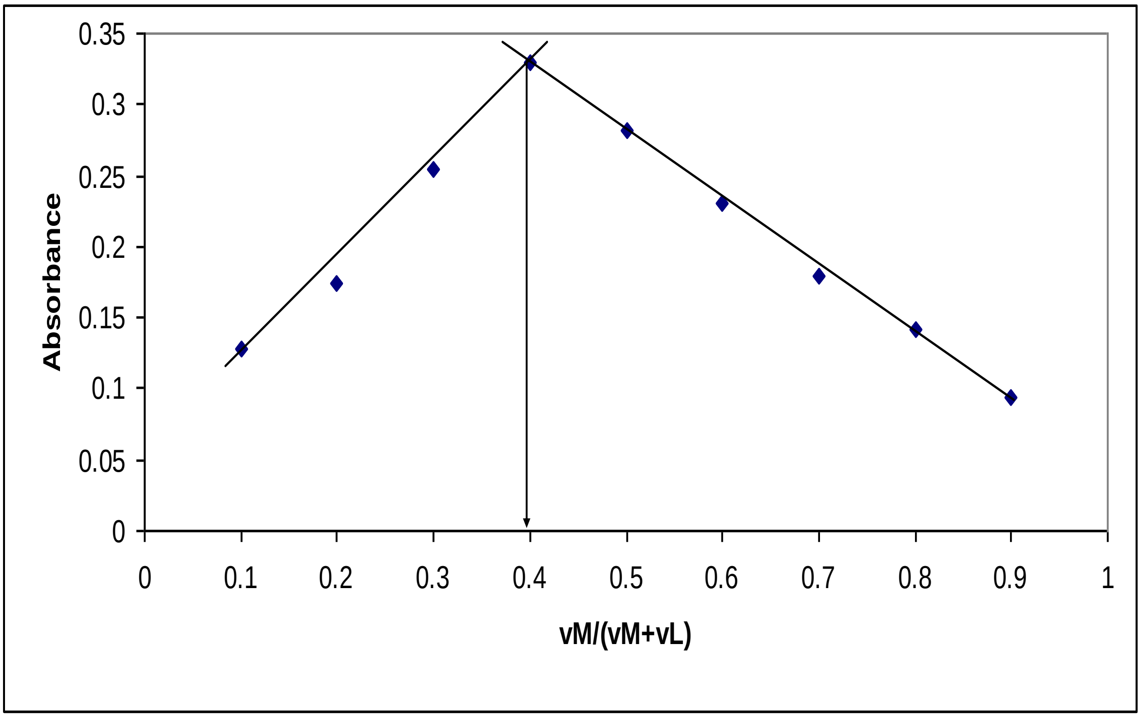


Fig.(3) continuous variation method for Sn-BIAMP complex at optimum conditions

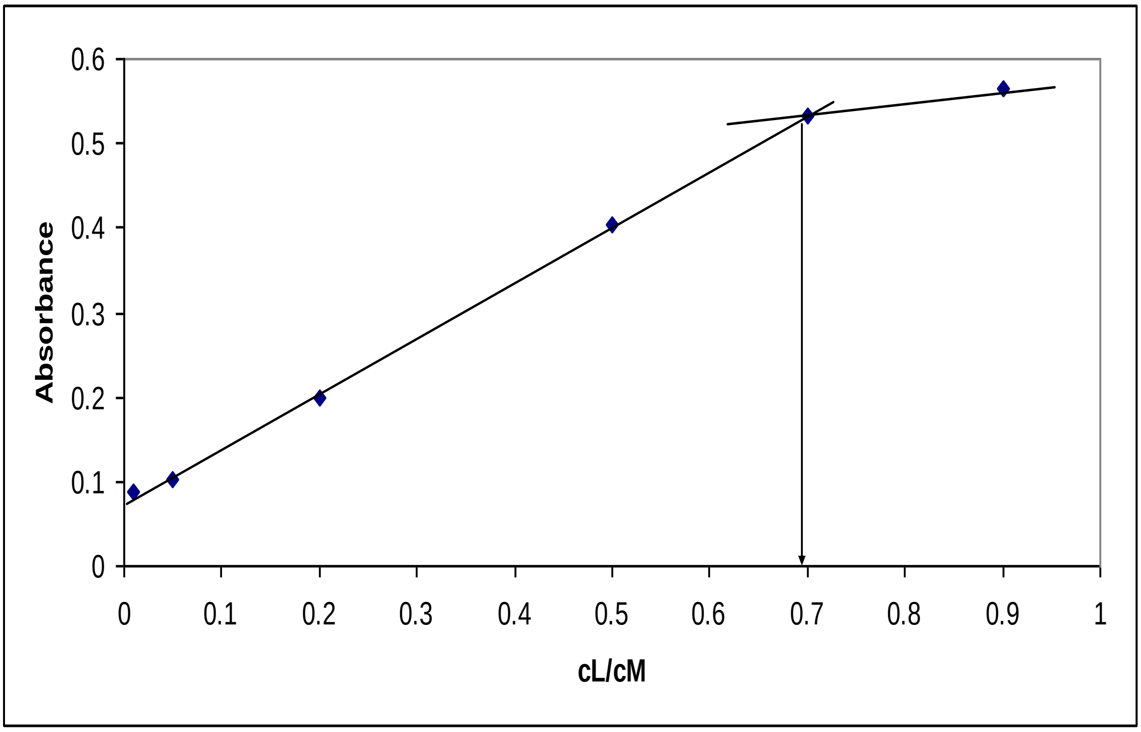


Fig.(4) molar ratio method for Sn-BIAMP complex at optimum conditions.

From the results of continuous variation and molar ratio methods show in figures (3 and 4), the ratio between Sn to BIAMP is (1:2), and the stability constant(14) ($K_{sta.}$) was ($1.59x10^6$ $L^2.mol^{-2}$), figure (5) shown the proposed composition of the complex.

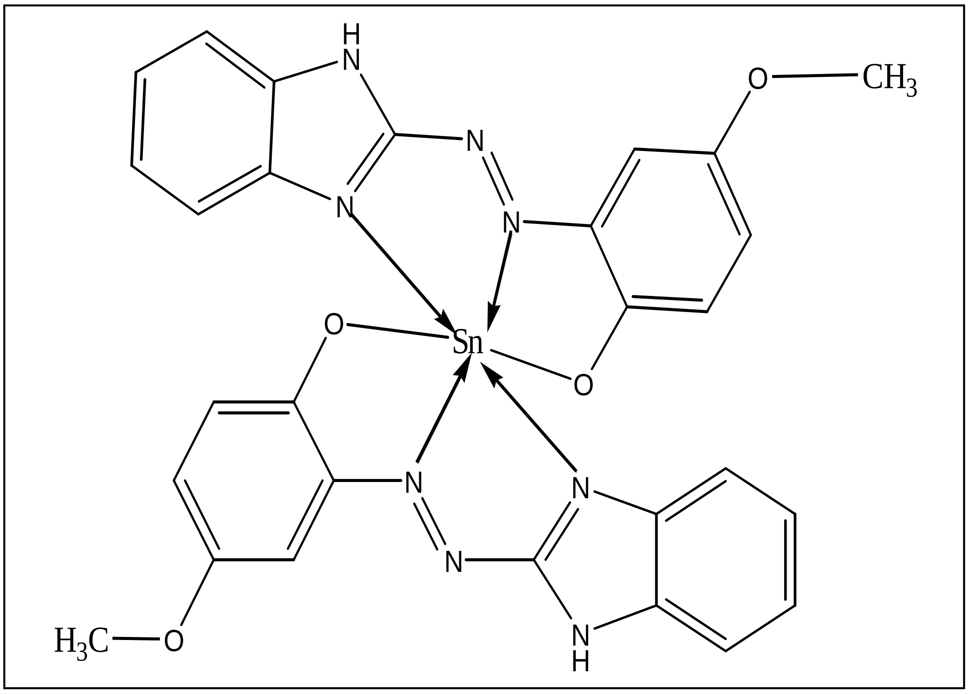


Fig. (5) the composition of Sn-BIAMP complex

Beer's low

Calibration curve for the complex was obtained by following the proposed procedure under the optimum conditions in figures (6).

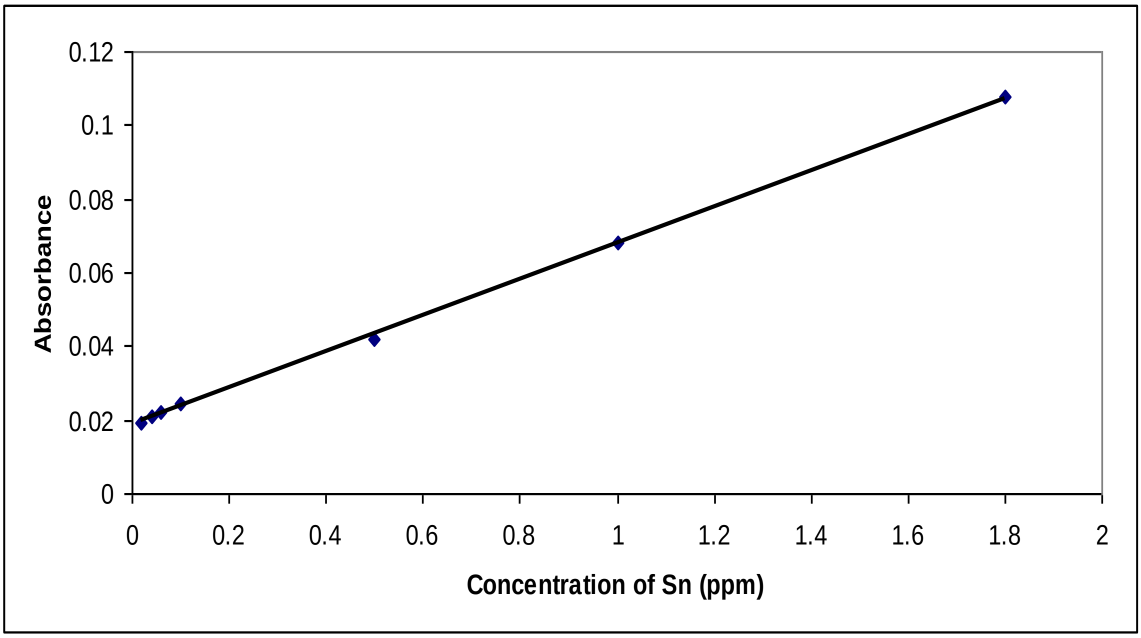


Figure (6) calibration curve of Sn^{2+} ion.

Beer's law was obeyed in the range (0.02-1.8) ppm, detection limit was (0.0009) ppm, linearity (R^2) was (0.9995), correlation factor (r) was (0.9997), molar absorbitivty (ε) was 4.09 x 10^4 $L.mol^{-1}.cm^{-1}$, Sandell's sensitivity was $2.4x10^{-4}$.

Precision and accuracy of the analytical procedure was R.S.D % (1.63) % and $E_{rel.}$% and R_e % were -1.66) %, (98.34) % .

Effect of interference ions

The selectivity of Sn-BIAMP complexes were tested by measuring the absorbance of complex of 1 ppm at optimum conditions in presence of different foreign ions of 5 ppm concentration which are able to form complexes with (BIAMP)[15, 16].

The extent of reaction of these ions is shown in table (1), table (1) shown that ions (Zn^{+2}, Pb^{+2} and Al^{+3}) were the absorbance value varying by more than 5% from the expected value for Sn^{+2} complex.

Table (1) effect of interference ions

Interference ions 5 ppm	Interference % Sn-BIAMP
Ni^{2+}	+1.22
Zn^{2+}	+8.43
Mn^{2+}	+4.61
Fe^{2+}	+3.21
Co^{2+}	+1.34
Cu^{2+}	+1.11
Cd^{2+}	+3.23
Pb^{2+}	+9.27
Al^{3+}	+6.25

Effect of masking agents[17]

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

Table (2) shown the best masking agent was KCN, NaF for Sn-BIAMP, complex other masking agents are less effect comparatively.

Table (2) the effect of masking agents

	Complex without any addition	Tartaric acid	Oxalic acid	Citric acid	Ascorbic acid	KCN	NaF
Sn-BIAMP	0.052	0.073	0.012	0.042	0.021	0.052	0.051

Absorption spectra

The absorption spectra of the complex and the ligand are shown in figure (7) under optimum conditions

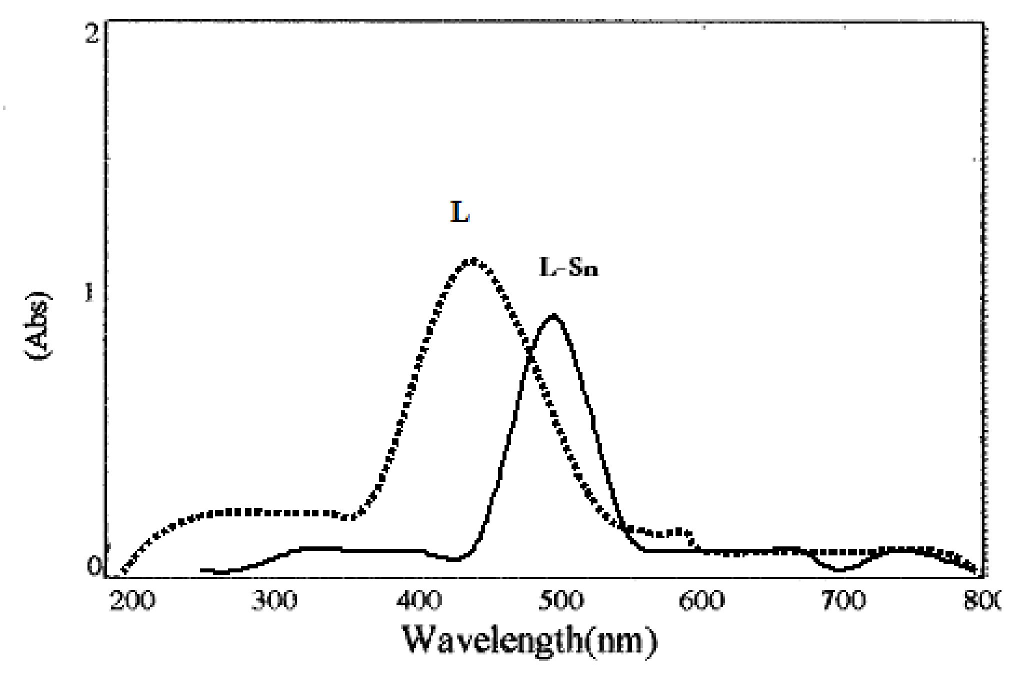


fig.(7) absorption spectra of the two complexes and the reagent.

Absorption spectra show that the λ_{max} absorption of the reagent (BIAMP) at 449 nm, Sn-BIAMP complex at 523 nm, this a new λ_{max} mean red shift in λ_{max} of complexes.

FTIR spectrum of (CNPAI) reagent

FTIR spectrum of the ligand (BIAMP) show in figure (8)

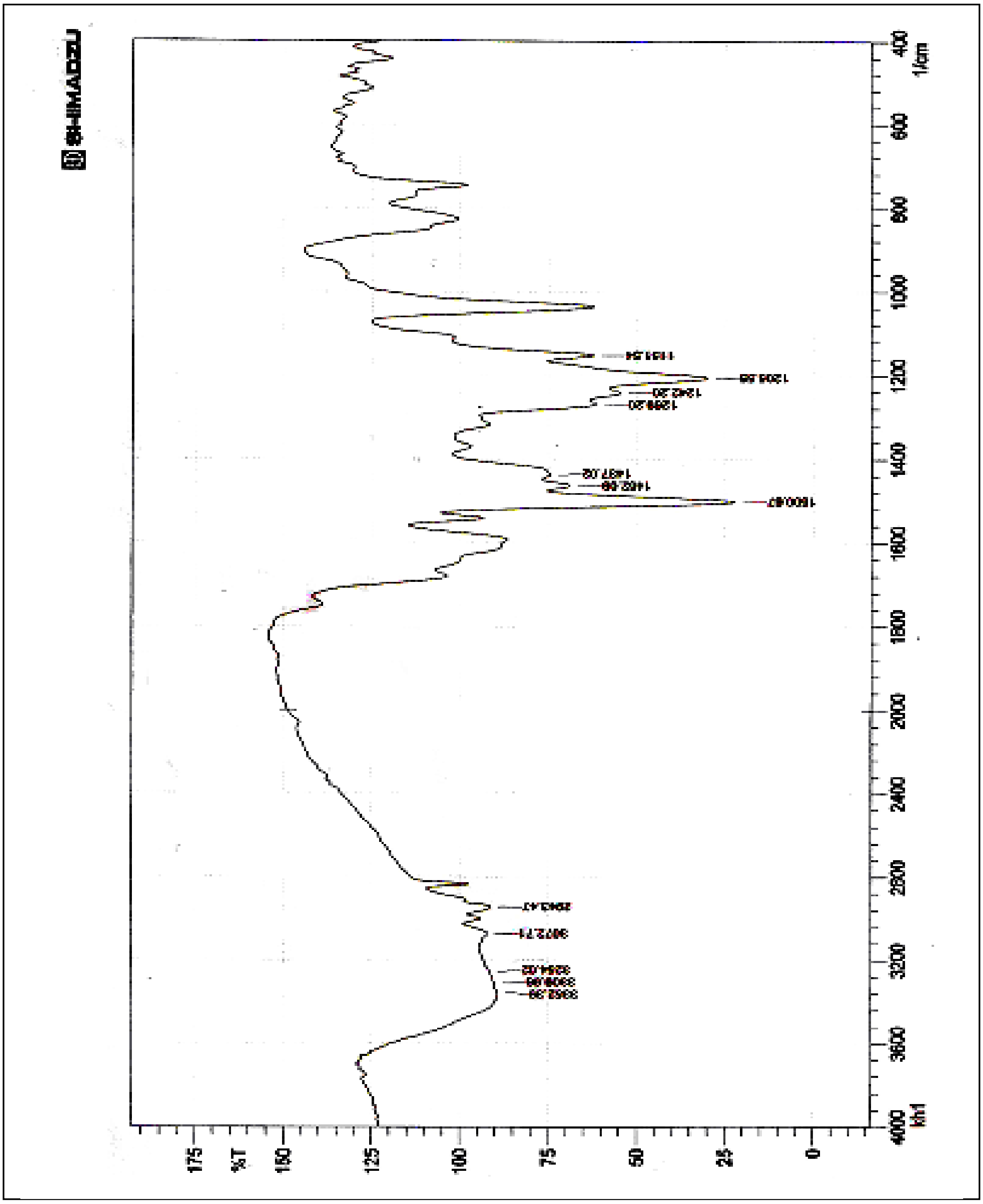


Fig.(8) FTIR spectrum of (BIAMP)

The infrared spectrum show in figure (8) 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 -Sn) complex

FTIR spectrum of (BIAMP -Sn) complex show in figure (9)

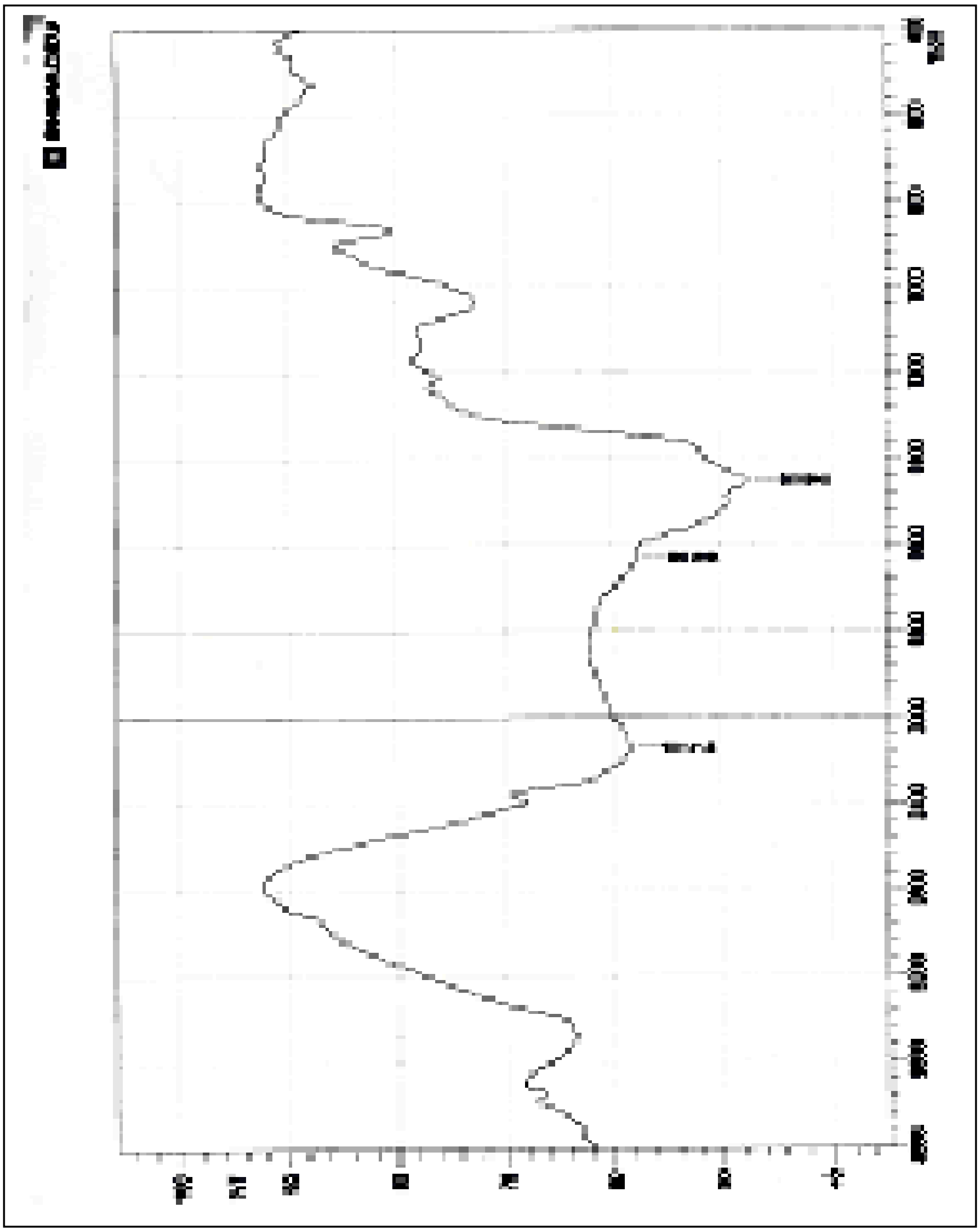


Fig.(9) FTIR spectrum of (Sn-BIAMP) complex

The comparison between spectra of the ligand with this of the coordination complex has revealed certain characteristic differences, these difference was shown in figure (9).
From figure (9) metal complex 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 3225-3280 cm^{-1} in (Sn-BIAMP) complex spectrum indicate the deprotonation of phenolic oxygen and cleavage of the hydrogen bond with the involvement of the oxygen in bonding[18,19].
The spectra of the BIAMP ligand figure (8) 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 (1631 cm^{-1}), these shift suggest the linkage of metal ion with nitrogen of imidazol ring[20,21]. A (N=N) band at (1500 cm^{-1}) in BIAMP shifted to (1450 cm^{-1}) this shift could contributed to the metal-azo linkage[22].
A new bands appeared in (440-460cm^{-1}) in the spectrum of the complex that does not appeared in BIAMP spectrum, this may be back to the (M-O) and (M-N) stretching for (Sn-BIAMP) [23,24].

Applications

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

Table (4) the results of standard method

Ion	True Value	Experimental Value
Sn^{2+}	0.8 ppm	0.779 ppm

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