

**A Rabid and Sensitive Spectrophotometric  
Determination of copper (II) and platinum (II) using new reagent  
of  
5-[(4-hydroxy phenyl) azo]-4,6-di hydroxy-2-mercapto pyrimidine**

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**Abstract**

A new reagent of 5-[(4-hydroxy phenyl) azo]-4,6-di hydroxy-2-mercapto pyrimidine (HPAdMPm-HL) has been synthesized and used as a sensitive and selective analytical reagent for spectrophotometric determination of micrograms of copper (II) & platinum (II) .

HPAdMPm reacts with copper (II) & platinum (II) in PH (5) to form an intense color soluble product , that is stable and has a maximum absorption at (621,612) nm with molar absorptivity ( $0.109 \times 10^4$  ,  $0.576 \times 10^4$ )  $L \cdot mol^{-1} \cdot cm^{-1}$  respectively.

Beer's law is obeyed in the concentration range (0.05 - 10)  $mg \cdot ml^{-1}$  for copper and (0.05 - 15)  $mg \cdot ml^{-1}$  for platinum . A repetition of the method is checked by finding the relative standard deviation % (R.S.D) for copper & platinum (n=7) which is (3.28 , 0.6) % respectively . The composition of Cu (II) – HpAdMPm & Pt (II) – HpAdMPm complex is established as 1:1 by molar ratio and continuous variation .

The interferences of ions (  $Fe^{3+}$  ,  $Ag^+$  ,  $Ni^{2+}$  ,  $Zn^{2+}$  ,  $Cr^{3+}$  ,  $Co^{2+}$  ,  $NO_2^-$  ,  $SO_4^{=}$  ,  $Cl^-$  ,  $CO_3^{=}$  ,  $F^-$  ,  $NO_3^-$  ) were studied and masked by using appropriate masking agents .

**الخلاصة :-**

تضمن البحث تحضير الكاشف 5- [ (4- هيدروكسي فنيل ) أزو ] - 4 , 6 – ثنائي هيدروكسي -2- مركبتو بريميدين واستخدم في تقدير كميات مايكروغرامية من ايون النحاس (II) والبلاتين (II) بطريقة طيفية سهلة وحساسة وسريعة . الكاشف تفاعل مع كل من ايون النحاس (II) والبلاتين (II) في PH (5) وتنتج معقدات ذائبة ملونة وثابتة ولها اعلى امتصاص عند الطول الموجي (612,621) نانومتر ومعامل امتصاص مولاري ( $10^4 \times 0.576$  ,  $10^4 \times 0.109$ ) لتر.مول<sup>-1</sup>.سم<sup>-1</sup> على التوالي .

تم بناء منحني المعايرة الذي اظهر مدى من الخطية عند مدى التركيز (0.05 – 10) مايكروغرام \ مل للنحاس و (0.05 – 15) مايكروغرام \ مل بالنسبة للبلاتين .

حددت دقة وضبط الطريقة من خلال ايجاد R.S.D % (n = 7) وكانت لمعقدي النحاس (II) والبلاتين (II) (0.6 , 3.28) % على التوالي .

تم تحديد نسبة الفلز الى الكاشف بطريقتين مور والتغيرات المستمرة حيث وجد انها تساوي 1:1 بالنسبة لمعقدي النحاس والبلاتين .

درس تأثير الايونات المتداخلة التالية :

(  $Fe^{3+}$  ,  $Ag^+$  ,  $Ni^{2+}$  ,  $Zn^{2+}$  ,  $Cr^{3+}$  ,  $Co^{2+}$  ,  $NO_2^-$  ,  $SO_4^{=}$  ,  $Cl^-$  ,  $CO_3^{=}$  ,  $F^-$  ,  $NO_3^-$  ) وحجبت باستخدام عوامل الحجب المناسبة .

## **Introduction**

In a search of new sensitive and selective reagents, studies of some azo compounds containing various heterocyclic have been made<sup>(1-6)</sup>. This class of azo compounds possess active ( $\pi$ -acidic) azo imine ( $-\text{N}=\text{N}-\text{C}=\text{N}-$ ), function and efficient agents to stabilize low valent metal oxidation states<sup>(7,8)</sup>. due to the presence of azo centered  $\pi^*$ -molecular orbital, for this reason a number of these azo compounds were synthesized and their abilities as chelating ligands<sup>(9-11)</sup>. Heterocyclic azo dyes often react with the metal ions as a tridentate ligands forming coordinative bond with the heterocyclic moiety,  $-\text{OH}$  or  $-\text{COOH}$  group and azo group<sup>(12)</sup>.

Platinum has exceptional catalytic properties and is used in the chemical and petroleum industries in hydrogenation, isomerization, cyclization, dehydration and oxidation reaction<sup>(13)</sup>.

Neutron activation analysis is a sensitive method for the detection of platinum in plants, rocks and soils<sup>(14)</sup>.

Copper is one of the several metal ions that play an important role in the biological system. It is used in the electrical industry as fine wires and high conductivity tubes. In addition, it is a hazardous pollutant in the environment resulting from the industrial effluents, in the form of particulate or soluble copper waste from the electroplating, chemical and textile industries<sup>(15,16)</sup>.

Spectrometry and spectrophotometry have been widely used for the determination of trace metal ions because of the relatively simple and inexpensive equipment required.

The application of UV-Vis absorption to the determination of metals is still popular in many laboratories. The technique provides easy determination of many metals from low to high concentration at an affordable cost.

In this paper, a UV-Vis spectrophotometric method is proposed for the determination of Cu(II) and Pt(II) in aqueous solution.

The method is based on the reaction of Cu(II) and Pt(II) with HPAdMPm (Figure 1). The proposed method is simple, sensitive, and the complex formed is stable.

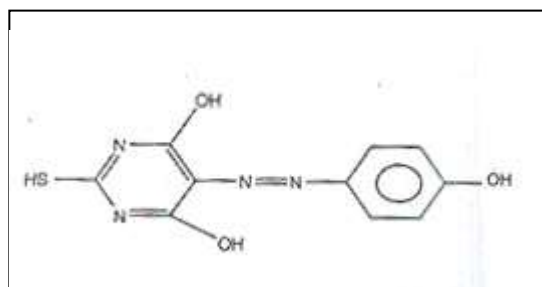


Figure (1) : Structural formula of HPAdMPm

## **Experimental**

### **\* Apparatus**

Absorption spectra were made with Shimadzu (1650 – UV – Visible) spectrophotometer scientific equipment. UV – Visible (spectra – SC, U.S.A) spectrophotometer was used in other measurements of absorbance of solution, both apparatus with 1.0 cm quartz cells. Measurements of pH were made using an in-lab (Philips, pw 9421 – England) pH-meter. Digital balance, Sartorius (Bp 3015 – Germany), and water bath (90, Hamburg – England).

**\* Reagents**

All chemicals used were of analytical – grade reagents except of the reagent 5 – [(4 – hydroxy phenyl azo) – 4,6 – di hydroxy – 2 – mercapto pyrimidine was prepared and purified according to the method mentioned in the literature <sup>(17)</sup> .

- The standard stock solution of copper (II) ( $100 \text{ Mg.ml}^{-1}$ ) was prepared by dissolving ( ) gm of ( ) in water in a 100 ml volumetric flask .

- The standard stock solution of Platinum (II) ( $1000 \text{ Mg.ml}^{-1}$ ) was prepared by dissolving (0.2128) gm of  $\text{K}_2\text{PtCl}_4$  in water in 100 ml volumetric flask . Working solution were prepared by diluting the stock solution to an appropriate volume .

- Solution of the studied interfering ions of suitable concentrations were prepared using grade reagents .

-  $1 \times 10^{-3} \text{ M}$  (HpAdMPm) prepared by dissolving (0.006) gm in (250) ml of absolute ethanol . A solution of ( $1 \times 10^{-4}$ ) M was prepared by diluting 10 ml of stock solution in 100 ml of absolute ethanol which was used in all measurements .

**\* General procedure**

In each of asset of 5 ml standard flasks , transfer 1 ml of sample containing  $\leq 3 \text{ Mg.ml}^{-1}$  of Cu (II) & Pt (II) and (2 ml) of 0.1 mM of (HpAdMPm) ethanol solution . The complexes formed were solubilized in water in and diluted up to five ml distilled water and allow the reaction mixture to stand for 10 minute measure the absorption at 621 nm for Cu (II) & at 612 nm for Pt (II) at 25 °C in a 1cm cell against a reagent blank prepared in a similar way but without the presence of the ion under test .

**Results and Discussion**

**\* properties of (HpAdMPm) and its metal chelate**

The reagent is a bi dentate with coordination of azo group , hydroxy group ; the structural formula of reagent is given in figure (1) .

Owing to the large conjugated system , the compound showed excellent chelating ability to form inner metal chelates .

HPAdMPm & their metals chelates can be easily solubilized in aqueous solutions .

**\*Absorption spectra**

The absorption spectrum of the Cu (II) – HPAdMPm & Pt (II) – HPAdMPm complexes is recorded against the reagent blank . Similarly , the absorption spectrum of the reagent is recorded against the solvent as blank . The absorption spectra of reagent & both complexes are shown in figure (2) (A,B,C) .

The spectra obtained reveal that Cu (II) , Pt (II) complexes and the reagent have maximum absorbencies at (621 , 612 & 450) nm , respectively . The reagent has a minimum absorbance at the maximum absorbance of the complexes & hence dose not interfere with the determination of copper & Platinum . Thus , further absorbance measurements of the complexes are made at (621 , 612) nm . The effect of various parameters on absorbance intensity of the formed products were studied and the reactions conditions were optimized .

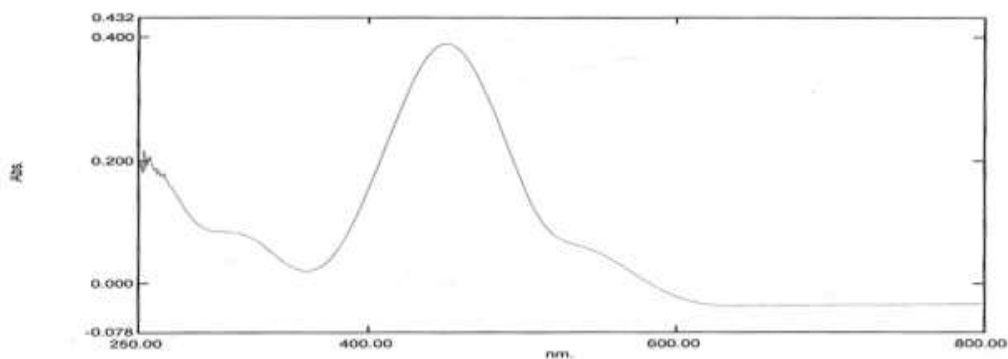


Figure (2 - A) : Absorption spectra of reagent

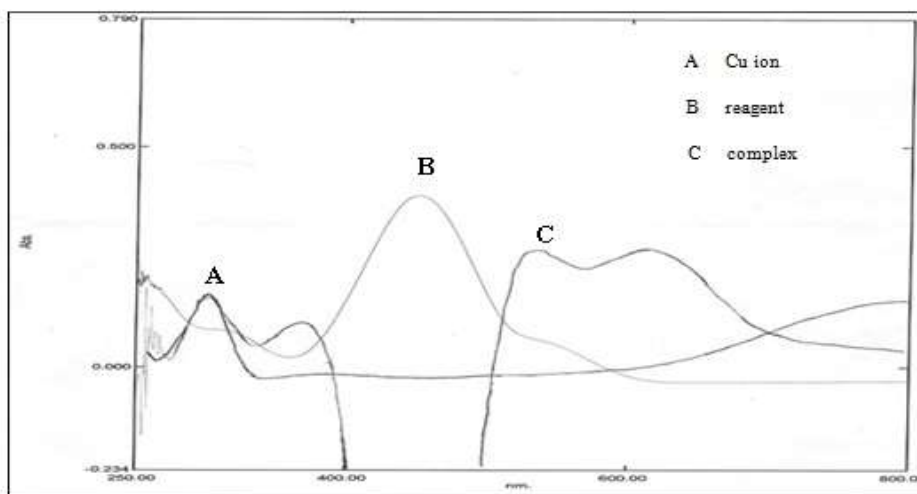


Figure (2 - B) : Absorption spectra of Cu (II) – HPAdMPm

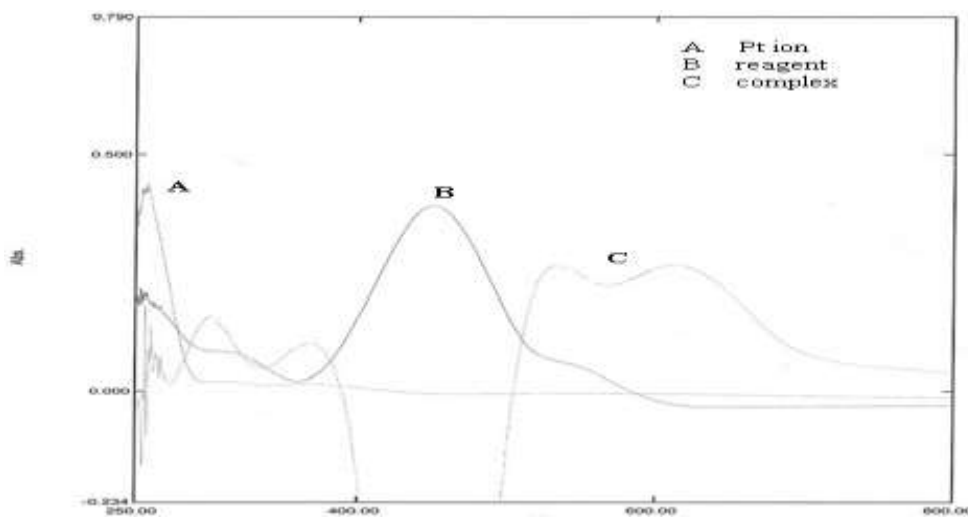


Figure (2 - C) : Absorption spectra of Pt (II) – HPAdMPm

**\* Effect of PH**

The influence of PH on Cu (II) – HPAAdMPm & Pt (II) – HPAAdMPm complexes was studied over (1-10) adjusted by using dilute solutions (0.1) M NaOH & HCl , and the effect on absorbance was studied fig 3 (A&B) demonstrated that the absorbance of the complexes in the range (4-6) , therefore the optimum PH was at(5)for both complexes were the absorbance was maximum & stable.

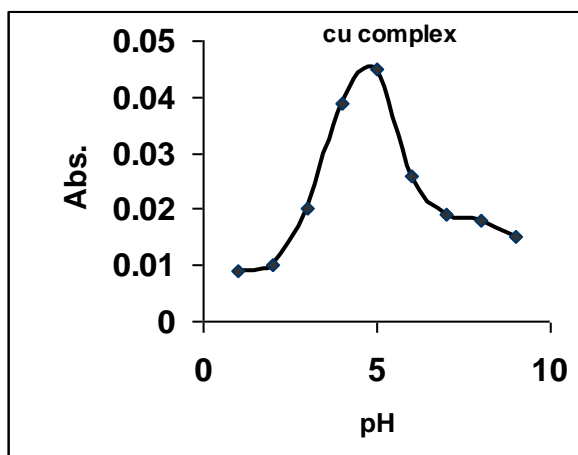


Fig 3 (A)

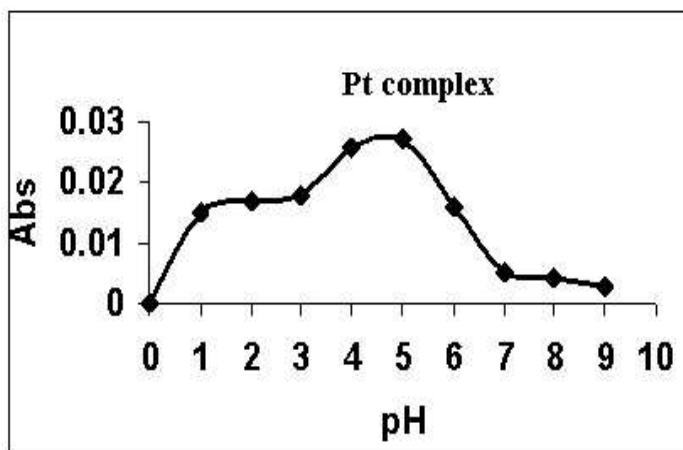


Fig 3 (B)

Fig 3 (A&B):Effect of PH on the absorbance of (A)Cu (II)–HPAdMPm & (B) Pt (II) - HPAAdMPm at room temperature .

**\* Effect of time**

The color of the complexes system and absorbance reach a maximum value after (5) minute , therefore five minute development time was selected as optimum in the general procedure . The color obtained were stable for about 24 hours for both complexes fig 4 (A,B)

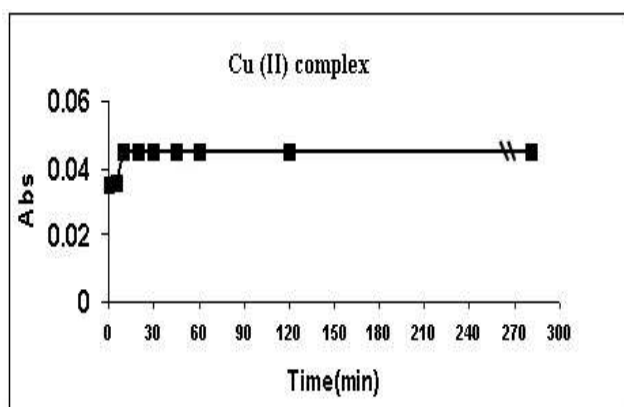


Fig 4 (A)

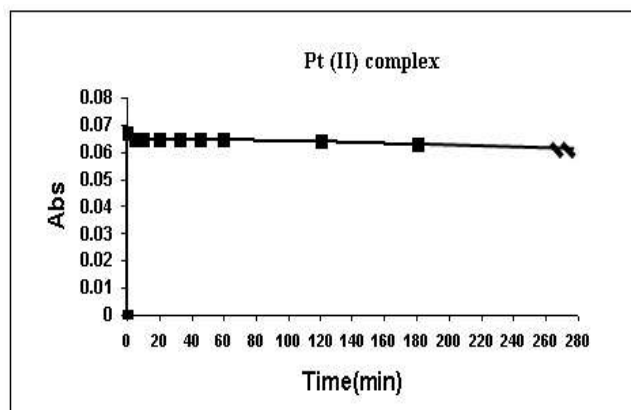


Fig 4 (B)

Fig 4 (A , B) : Effect of time on the absorbance of (A) Cu complex , (B) Pt complex at room temp.

**\* Effect of temperature**

The effect of temperature on the absorbance of the complexes was studied , the same absorbance were obtained when the color was developed at room temperature (25 – 30) °C complexes , but when the temperature higher than 40 °C the absorbance decreased and stability were observed , therefore it is recommended that the color reactions should be carried out at room temperature for complexes fig 5 (A & B) .

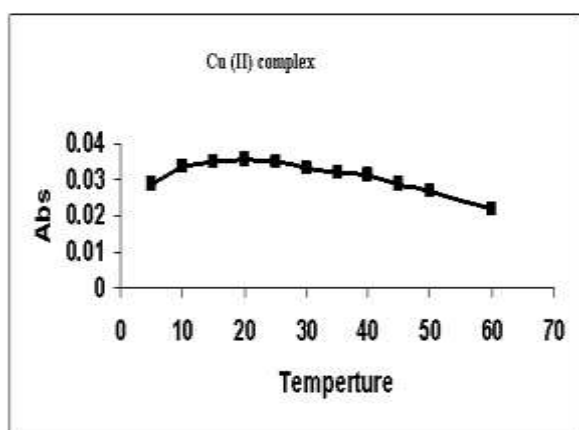


Fig 5 (A)

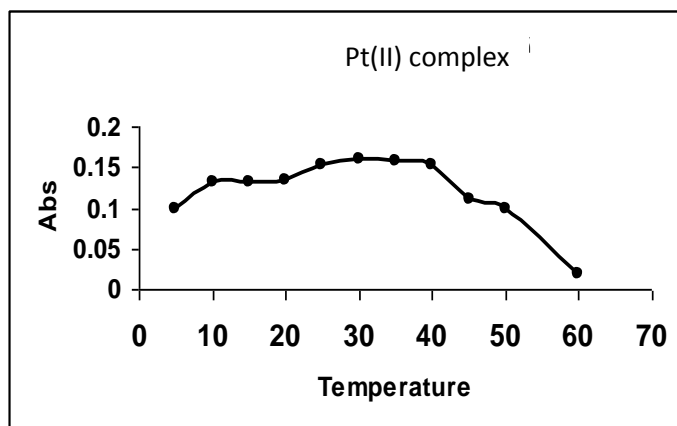


Fig 5 (B)

Fig 5 (A & B) : Effect of temperature on the absorbance of (A) Cu complex , (B) Pt complex

**\* Calibration graph**

The present studies indicate that Beer's law is obeyed for copper (II) over the concentration range (0.25 – 10) Mg. cm<sup>-1</sup> & for platinum (0.25 – 15) . The molar absorptivity of the (Cu & Pt) complex is calculated as [(0.109 , 0.576) \* 10<sup>4</sup>] L.mol<sup>-1</sup>.cm<sup>-1</sup> . Since the colored complexes are stable for 24 hours fig 6 (A&B) . The correlation coefficient detection limit , precision & Accuracy of the analytical procedure are given in table (1)

Table (1) : Analytical characteristics of [(Cu & Pt) – HPAdMPm] complexes

Characteristic	Cu (II)	Pt (II)
Absorption maximum ( nm )	621	612
Beer's law rang ( Mg . cm <sup>-3</sup> )	( 0.25 – 10 )	( 0.25 – 15 )
PH rang	( 4 – 6 )	( 3 – 6 )
Molar absorptivity ( L . mol <sup>-1</sup> . cm <sup>-1</sup> )	0.109 × 10 <sup>4</sup>	0.576 × 10 <sup>4</sup>
Correlation coefficient	0.996	0.9971
Detection limit ( Mg . cm <sup>-3</sup> )	0.1971	0.981
R . S . D %	3.28 %	0.6 %
% E rel	- 1.15 %	- 2 %

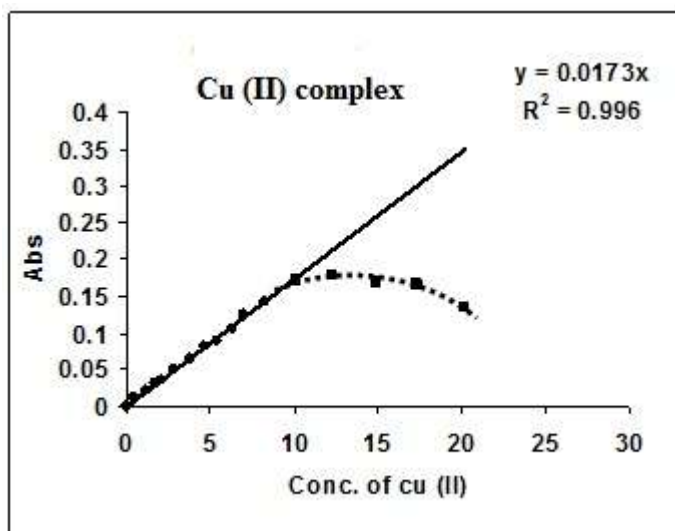


Fig 6 (A)

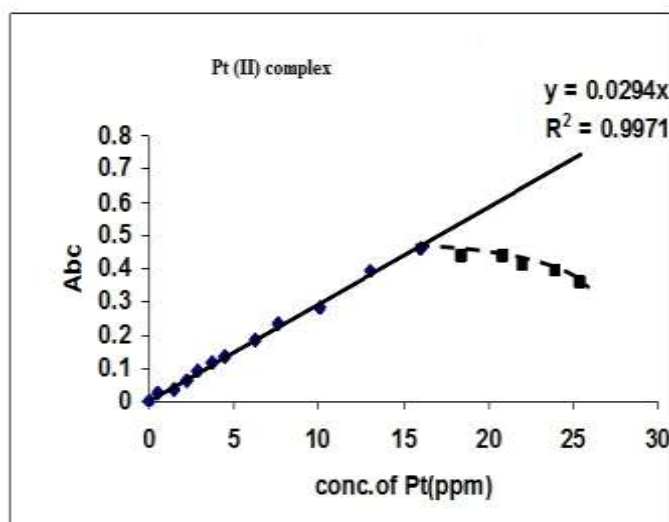


Fig 6 (B)

Fig 6 (A&B) :- Calibration curve of [ Cu(II) & Pt (II) ] – HPA<sub>d</sub>M<sub>P</sub>m complex

**\* Stoichiometry and stability constant**

The stoichiometry of the complexes were investigated by Job's <sup>(18)</sup> continuous variation method and mole ratio method <sup>(19)</sup> and were found to be 1:1 (metal : ligand) for cu & Pt complexes fig 7 (A & B).

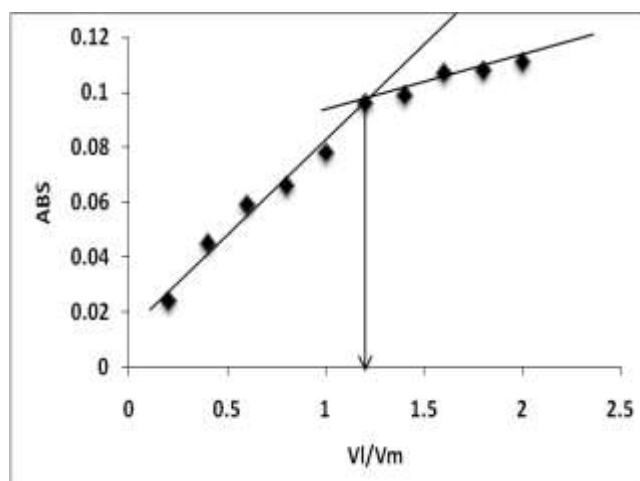


Fig 7 (A)

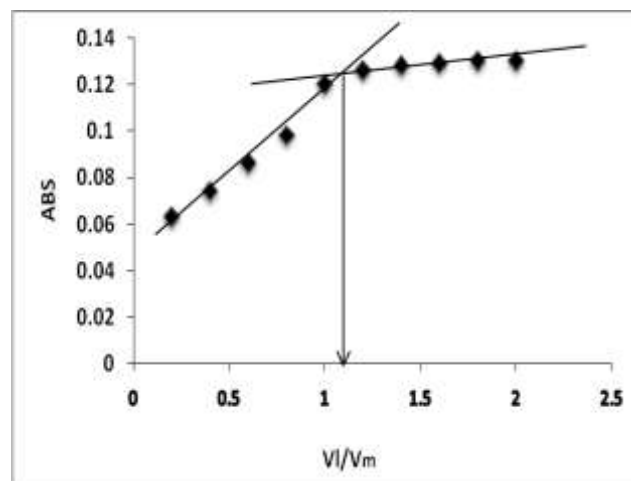


Fig 7 (B)

Fig 7 (A & B) mole ratio method for Cu complex & Pt complex

A careful comparison of the IR spectrum of Cu (II) & Pt (II) – HPA<sub>d</sub>M<sub>P</sub>m complexes with that of HPA<sub>d</sub>M<sub>P</sub>m showed that HPA<sub>d</sub>M<sub>P</sub>m acts as a bi dentate ligand . The chelate formation through N atoms are confirmed by the shift in  $\nu_{C=N}$  to frequencies (15 – 20)  $\text{cm}^{-1}$  as compared to ligand ( $\nu_{C=N} = 1656$ )  $\text{cm}^{-1}$  . ( $\nu_{N=N} = 1508$ )  $\text{cm}^{-1}$  <sup>(20)</sup> band in free ligand is shifted to lower with low intensity upon complication suggesting chelation via the ( M – N ) <sup>(21)</sup> . The ( $\nu_{OH}$ ) band shifts to lower frequency upon complication , This suggests the O – coordinatination of the phenolic group <sup>(22)</sup> The bonding of oxygen to the metal ion is provided by occurrence of bonds at ( 525 , 515 )  $\text{cm}^{-1}$  as the

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result of ( $\nu_{M-O}$ )<sup>(23)</sup>. The FT.IR bands of ( HPAAdMPm ) & its complexes ( Cu – HpAdMPm & Pt – HPAAdPm ) with their probable assignment are given in table 2

Table (2) : Selected IR data of ( HpAdMPm ) and its complexes with Cu (II) , Pt (II)

compound	$\nu$ (OH)	$\nu$ (C=N)	$\nu$ (N=N)	$\nu$ (M-N)	$\nu$ (M-O)
Cu-HpAdMPm	3468 m	1642 s	1490 m	455 w	520 w
Pt-HpAdMPm	3460 m	1635 s	1495 m	460 w	530 w
HpAdMPm	3475 m	1656 s	1508 m	-	-

s = sharp , m = medium , w = weak

On the basis of IR , and astoichiometric data .

The most probable structure of the complexes can be suggested as follows Fig 8 ( A & B )

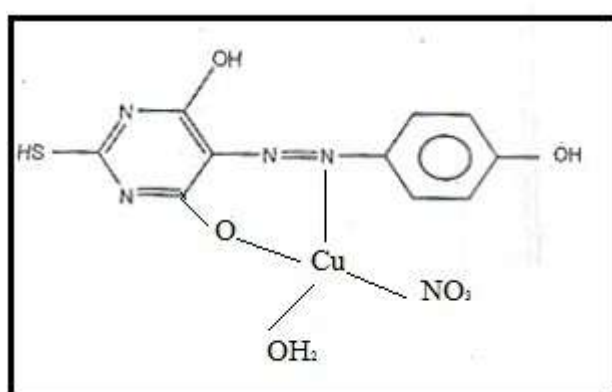


Fig 8 (A)

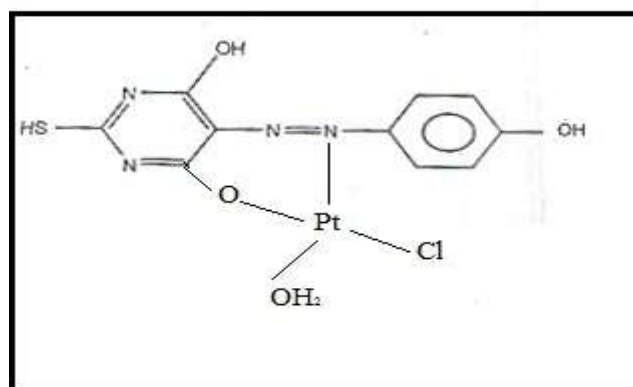


Fig 8 (B)

**Fig 8 ( A & B ) :- proposed structure of ( Cu complex , Pt complex )**

The stability constant of complexes ( Cu , Pt ) were determined to be (  $2.58 \times 10^4$  ,  $1.34 \times 10^5$  )

### **Interference of foreign ions :**

Various salts and metal were added to the solution containing (2) Mg . ml<sup>-1</sup> of ( Cu & Pt ) and the general procedure was applied<sup>(23)</sup>.

The results obtained are given in table 3 . Among the anions examined (  $CO_3^{=}$  ,  $NO_2^-$  ,  $SO_4^{=}$  ,  $NO_3^-$  ,  $F^-$  ,  $Cl^-$  ) all of it not interfered with Pt , but the (  $F^-$  ,  $Cl^-$  ) interfered with Cu .

Among the metal ions studied , many did not interfere at milligram level . The interference from ( Cd & Pb ) on Cu complex can be masked by addition of ( 2ml of tartaric acid & 3 ml of ascorbic acid ) respectively , while sodium cyanide have no effect on the absorbance of Pt complex in presence of Cu complex only . Thus , the proposed method can be applied for determination of ( Cu & Pt ) in standard alloys and water samples .



Table (3) :- Effect masking agents

Masking agent [0.01] M , ( ) ml	Interference ion / 2 Mg . ml <sup>-1</sup>	
	Cu	Pt
Tartaric acid (2)	Cd <sup>2+</sup>	-
Ascorbic acid (3)	Pb <sup>2+</sup>	-
Sodium cyanide (2)	-	Cu
Ascorbic acid (3.5)	Cl <sup>-</sup>	-
Citric acid (2.5)	F <sup>-</sup>	-
Tartaric acid (3)	Pt <sup>2+</sup>	-

## Conclusion

The proposed method using HPAdMPm offers the advantages of high sensitivity , selectivity and simplicity for the determination of Cu (II) & Pt (II) without the need for organic solvent extraction pre-concentration or pre-separation , its can be used as an alternative method for the determination of those ions in an environmental and industrial sample .

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