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Spectrophotometric Determination of Trace Amounts of Copper (II) Using 5 - (phenyl azo) – 4,6 – dihydroxy -2- mercapto pyrimidine .

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Abstract :

A new , simple , sensitive and rapid spectrophatometric method is proposed for the determination of trace amounts of copper (II) . The method is based on the formation of a 1 : 2 complex with 5- (phenyl azo) – 4,6 – dihydroxy -2- mercapto pyrimidine (PDMP) as a new reagent is developed . The complex has a maximum absorption at 490 nm and ε_{max} of 0.85×10^4 L . mol^{-1} cm^{-1} . A linear correlation (0.2-3 μg /ml) was found between absorbance at λ_{max} and concentration . The accuracy and reproducibility of the determination method for various known amounts of copper (II) were tested . The results obtained are both precise (RSD was better than 0.50%) and accurate (relative error was better than 0.21%) the effect of diverse ions on the determination of copper (II) to investigate the selectivity of the method were also studied . The stability constant of the product under optimized conditions and at room temperature was 1.43×10^{10} l.$mole^{-1}$ The method was applied to the determination of Cu (II) ion in some standard practical samples .

Key Words : 5- (phenyl azo) – 4 , 6 –dihydroxy -2- mercapt pyrimidine , Copper (II) determination , Spectrophotometry

الخلاصة :

تم تطوير طريقة طيفية جديدة وسريعة وحساسة في تقدير الكميات الضئيلة للنحاس الثنائي . اعتمدت الطريقة على أساس تكوين معقد 2:1 فلز كاشف مع الكاشف الجديد 5- (فينل ازو)- 4 , 6- تنائي هدروكسي 2- مركبتو بيرميدين PMDP , يمتلك المعقد أعلى قمة امتصاص عند الطول ألموجي 490 نانوميتر ومعامل امتصاص مولا ري 10^4 *0.85 لتر . مول$^{-1}$. سم$^{-1}$. كانت العلاقة الخطية بين الامتصاص عند الطول ألموجي الأعظم والتركيزات تتراوح بين (0.2 - 3.0) جزء في المليون إما دقة وضبط الطريقة أعطت نتائج تراوحت بين أفضل من 0.50% بالنسبة إلى RSD و 0.21% بالنسبة إلى الخطأ النسبي . ولبيان انتقائية الطريقة تم دراسة تأثير عدد من الايونات السالبة والموجبة على الطريقة . كان ثابت الاستقرار للمعقد تحت الظروف الفضلى ودرجة حرارة الغرفة $1.43*10^{10}$ لتر. مول . تم تطبيق الطريقة في تقدير النحاس (II) في عدد النماذج القياسية العملية .

Introduction :

It is known that aromatic azo compounds are widely used because of their very good chelatogenic characteristics[1]. Metal complexes of azo compounds containing heteroaryl ring systems find various applications . These type of molecules have several advantages , for example the azo group is photocromic , redox responsive , stabilize low valent metal oxidation states due to the presence of a low – lying azo centered π^* molecular orbital serves as a molecular switch , is used as a metal ion indicator , dyes and Pigments in industry [2-4]. Also , heteroaryl ring azo compounds are of considerable interest because of their chemistry and potentially beneficial biological activities , such as antibacterial , antiviral and anti-malarial activities[5-7] . Many of these compounds such as azo pyrimidine[8,9] , thiazolyl azo[10] and azo imidazole [11 , 13] , have been synthesized and proposed for the determination of several metal ions . These heterocyclic azo compounds reacted with iron (II) copper (II) , nickel (II) , nickel (II) , cobalt (II) , cadmium (II) , zinc (II) and palladium (II) , and have been suitable for analysis of truce heavy metals . various methods for the assay of copper (II) have [14 , 15] been reported . Differential pulse stripping voltammetry extraction and reverse phase high performance liquid , chromatography [16 , 17] flow injection and flow injection – catalytic

spectrophotom etric method [18 – 20] and simple spectrophotometric method [21 , 25] . According to the best of our knowledge , this reagent has not been reported in the literature as being used for any cation determination . In this study , We wish to report this reagent as a selective reagent in spectrophotometric determination of micro amounts of copper (II) .

Apparatus

Spectral and absorbance measurements were made with Shimadzu UV-Vis 1700 double beam spectrometer using 1 cm glass cells. Vibrational spectra were recorded on Testscan Shimadzu FT.IR 8000 series. pH measurements was cared out using Hanna pH meter model HI 9321 . The conductance measurements were carried out using Al- pha- 800 digital conductivity meter.

Reagents

All chemicals used are of analytical reagent grade without any purification.

5- (phenyl azo)]- 4,6-dihyroxy -2-mercapto pyrimidine (lxl0^{-3})M.

Dissolve 0.062 gm of (PDMP) in 200 ml of ethanol. Working (PDMP) was prepared by simple dilution of the appropritate volume of the reagent (PDMP) solution 1x10^{-3} M with ethanol.

StandardCu(II) (100 µg/ml).

Dissolve 0.0392 gm of $CuSO_4.5H_2O$ in 100 ml distilled water, working standard copper(II) solutions were prepared by simple dilution of the appropriate volume of standard copper solution (100 µg/ml) with distilled water.

Experimental:

A-Preparation of the reagent (PDMP)

The reagent was prepared by coupling reaction of diazonium salt solution of aniline with appropriate 4,6-dihydroxy-2-mercapto pyrimidine as coupling component in alkaline solution .A diazonium solution was prepared by dissolving 2.0 gm of aniline in 2ml of concentrated HCl and 10 ml distilled water, To this mixture 20 ml of 15% sodium nitrite is added drop wise at (0-5)$^{\circ}$C, and left to stand 30 min .This solution was poured in beaker containing (4,6-dihydroxy-2-mercapto pyrimdine dissolved in 150 ml of ethanol and 50 ml of (2N) NaOH at (0-5) $^{\circ}$C. The mixture was allowed to stand overnight . The precipitate was filtered off, washed with distilled water, and recrystallized from ethanol, Scheme .1.

Preparation of complex [Cu(PDMP)$_2$ H$_2$O]

The complex was prepared by mixing stoichiometric amounts of $CuSO_4$ and ligand (PDMP)in a 1:2 ratio in aqueous ethanolic solution. The mixture was stirred at room temperature for 5 min. The pH of solution was adjusted to 7.0 then left for 24 hr. The solution was filtrate, washed with distilled water and dried at 70 $^{\circ}$C.

Procedure for determination of Copper (Π)

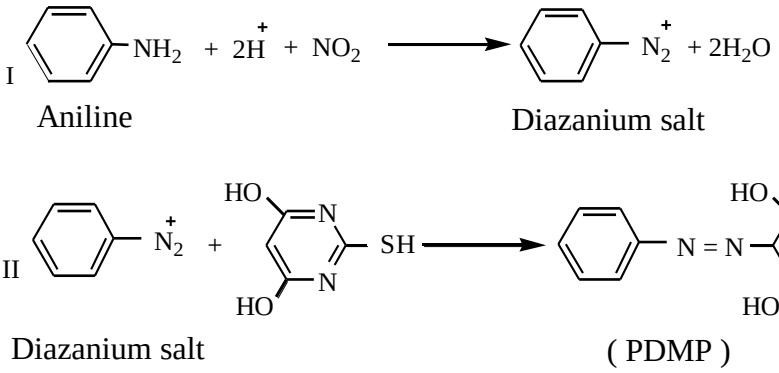
Into a series of 10 ml calibrated flask , transfer increasing volumes of copper(Π) solution (10 µg/ml) to cover the range of the calibration graph and 2.5ml of lx10^{-4} M (PDMP) solution and the pH was adjusted by (0.05 N) of HCl and NaOH, dilute the solution to the mark with distilled water and allow the reaction mixture to stand for 5 min. Measure the absorbance at 490 nm against reagent blank, prepared in the same way but containing no copper ion using 1cm cells.

Results and discussions

The results of this investigation indicated that the reaction between copper (II) and (PDMP) at pH 7.0 yield highly soluble product which can be utilized as a suitable assay procedure for copper, This product has a maximum absorption at 490 nm, at which the blank at this wavelength shows zero absorbance Fig .1. was adopted in all subsequent experiments.

The mechanism of reagent reaction

The reaction sequence in procedure of reagent involves two steps. In the firstly aniline reacts with nitrite ion in acidic media to form diazonium ion and the second including the coupling reaction of diazonium ion with 4,6-dihydroxy-2-mercapto pyrimidine to form yellow azo dye .



Scheme.1: Mechanism of the preparation of reagent (PDMP)

The effect of various parameter on the absorption intensity of the formed products were studied and the reaction condition were optimized.

Effect of pH

To establish the optimum condition (stability of the product from the reaction of copper (II) ion with the azo reagent, minimum blank value and relatively rapid reaction rate), the effect of pH (2-12) was studied . Only pH 7.0 was found to be optimum .Neutral and alkaline results in low sensitivity and was not stable. pH change on the electronic absorption spectra of the complex was studied by adding a small amount of 0.1M HCl and NaOH. The UV-Visible spectra of Cu (II) complex gives the band centered at 498 nm in ethanol which may be assigned to $^{2}E_g1 \rightarrow {}^{2}T_2g$ [26] . The bands appearing in the range of 270- 321 nm are attributed to $\pi \rightarrow \pi^*$ transition. The other band observed in the region of 490 nm is attributed to $n \rightarrow \pi^*$ electronic transition[27,28]Fig.2. .

Effect of (PDMP) concentration

various concentrations of 5- (phenyl azo)- 4,6- dihydroxy-2-mercapto pyrimidine was added to fixed concentration of copper (Π), 2.5 ml of $1x10^{-4}$ M (PDMP) solution was sufficient and gave minimum blank value, under 2.5 ml, the absorbance of blank value was increased causing a decrease in the absorbance of the sample. Therefore 2.5ml of $1x10^{-4}$ M of PMDP was used in all subsequent experiments Fig.3 .

Order of addition of reagents

To obtain the optimum results, the order of addition of materials should be followed as give by the procedure , otherwise , a loss in stability are observed.

Calibration graph

Employing the conditions described under procedure a linear calibration graph of copper (Π) is obtained which shows that Beer's law is obeyed over the concentration range of (2-30 μg per 10 ml 0.2-3 ppm) with correlation coefficient of 0.9995 and an intercept of 0.0042. The molar absorptivity of the product with reference to copper was $0.85x10^{4}$ L. $mole^{-1}.cm^{-1}$.

Table1. Analytical data of copper (II) complex of (PDMP)

compound	% Yield	colour	Mp. ºC	Conductance $\Omega^{-1}cm^2mole^{-1}$
$C_{10}H_8N_4O_2$	92	Dark red	210-212*	-
$C_{20}H_{14}N_8O_4Cu$	75	Dark brown	305-307*	18

***decomposition point.**

Molar Conductance data

The solubility of complex in ethanol acetone permitted determination of the molar conductivity of the 10^{-3}M Solution at 27^0C and , by comparison , the electrolytic nature for complex . The low value of the molar conductance data listed in Table . 1 indicate that the complex non electrolyte .

Accuracey and precision

To determine the accuracy and precision of the method, copper was determined at three different concentrations. The results are shown in table 2, indicate that satisfactory precision and accuracy could be attained with proposed method.

Table 2 . Acuracy and precision of the method

Cu(II) µg/ml	Error %	R.S.D % *
0.5	+0.21	0.50
1	-0.11	0.13
2	-0.02	0.22

*Result of five determinations

Interferences

The effect of diverse ions on determination of copper (II) was studied .To test of diverse ions were determined by the general procedure, in the presence of their respective foreign ions.The metal ion can be determined in the presence of a 10 or more fold excess of cation and anion. Table 3 .

Table 3 . Effect of foreign ions

Foreign ions	Amount added µg	Interference % E
Pt^{+2}	500	+0.6
Ni+2	=	0.09
Pd+2	=	-1.5
Rh^{+3}	=	-0.02
Ag^{+}	=	0.01
Cr^{+3}	=	+2.2
Zn+2	=	-1.01
SO_4^{-2}	=	-0.05
Cl^{-1}	=	0.0
Br^{-}	=	0.0
NO_3^{-}	=	1.8
NO_2^{-}	=	-1.02

Structure of the complex

The I.R. bands of the (PDMP) and its copper(Π) complex with their probable assignment are give in table 4. The two bands due to υ(S-H) and thioamide moiety present in the ligand appeared in the spectrum of the complex. Thioamide band I which is due to δ(N-H) major υ(C=N) minor appeared at 1596 cm^{-1} as medium and sharp band disappeared in the case of the complex , this indicates the involvement of N-atom in coordination to the metal, this is further indicated by the

shift of (N=N) group by 45cm^{-1} to lower frequency. The coordination of both N and O atoms to the copper atom is further indicated by the observation a new bands at 540 and 505 cm^{-1}. These bands had not been appeared in the reagent spectra [30,31] .The stoichiometry of the reaction between copper(II) and (PDMP) was investigated using the Jobs method[29]. The results obtained Fig.4 , show a 1:2 complex formed between copper(II) and (PDMP) at 490 nm . The apparent stability constant was calculated by comparing the absorbance of a solution containing stoichiometric amount of copper and PDMP with of a solution containing a five – fold excess of (PDMP) reagent. The average conditional stability constant of complex in water ,under the described experimental conditions is 1.43x10^{10} L. mole^{-1}. On the basis of the I.R, and a stoichiometric data the structure of complex can be suggested as follows :

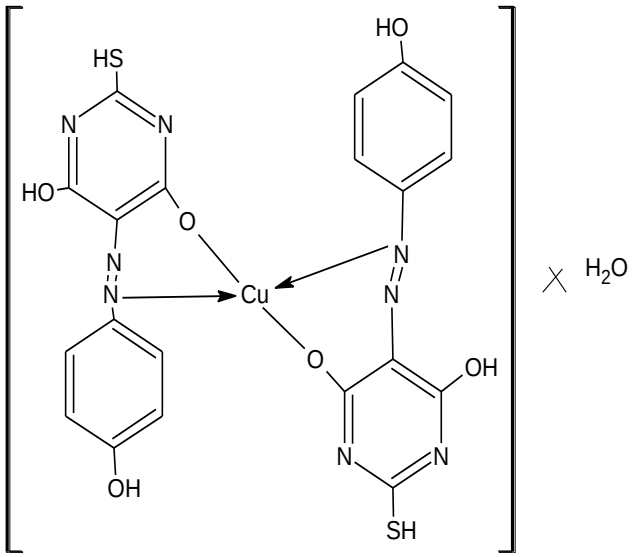


Table. 4. Selected IR data (4000- 400cm-1) of PDMP and its complex .

Compound	(C=N)	(N=N)	Pyrimidine Ring	ν (c-o)	ν (S-H)	ν (M-O)	ν (M-N)
PDMP	1625 s	1550 m	1478 s	1185s	2340w	-	-
(Cu(PDMP)$_2$)	1569 s	1520 m	1480 s	1215 s	2335w	520w	422 w

S ; sharp , m; mediume, w; weak

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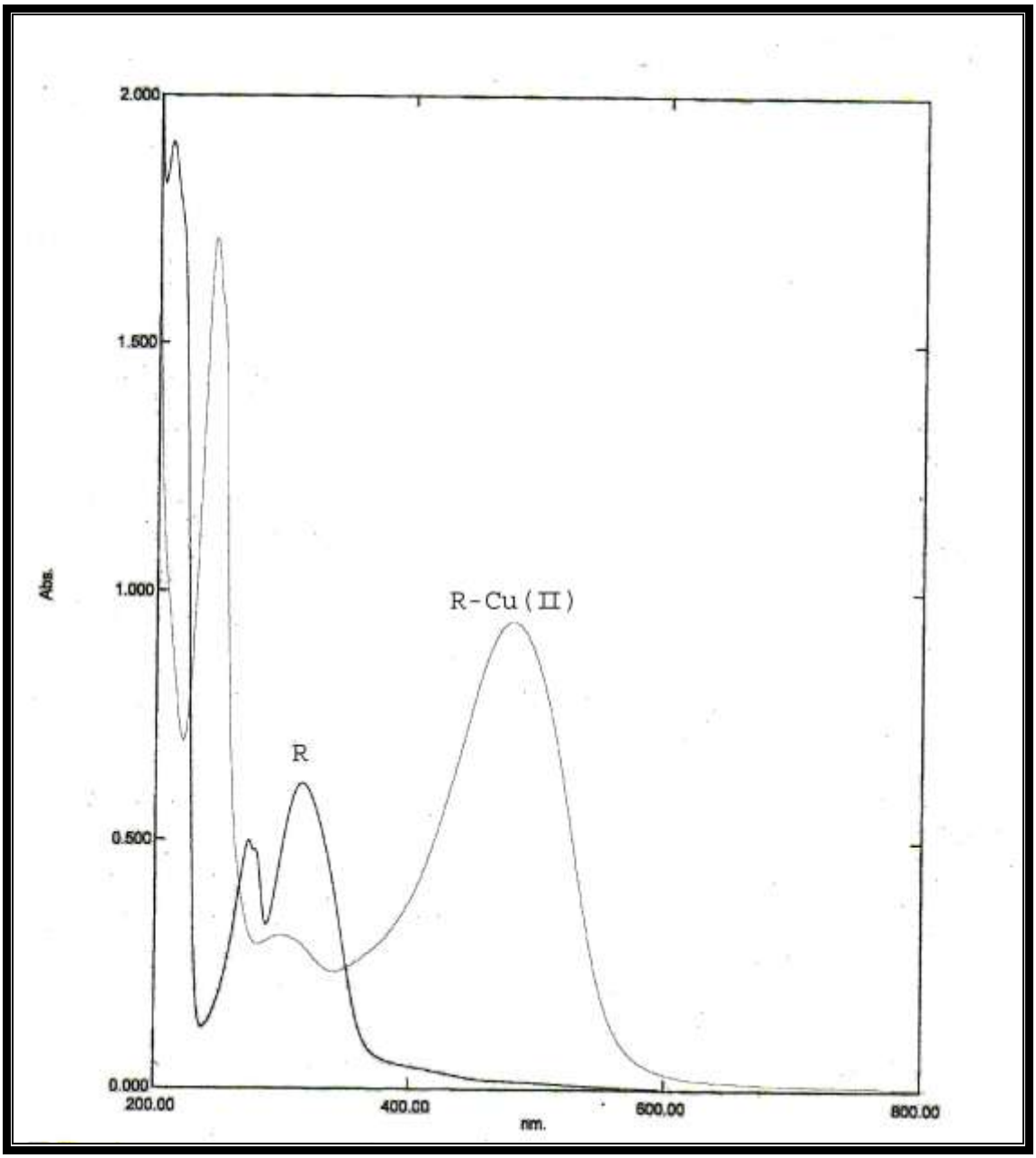

Fig 1:- Absorption spectra of (Cu –PDMP) 2PPm treated as described under procedure and measured against a reagent blank and PDMP the reagent blank against ethanol .

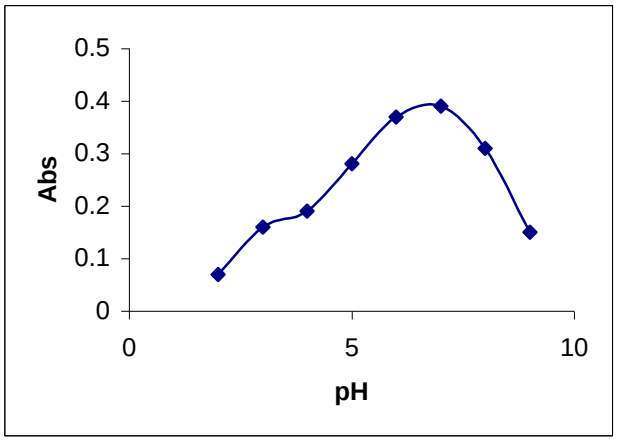

Fig 2:- Effect of pH the coloured reaction product

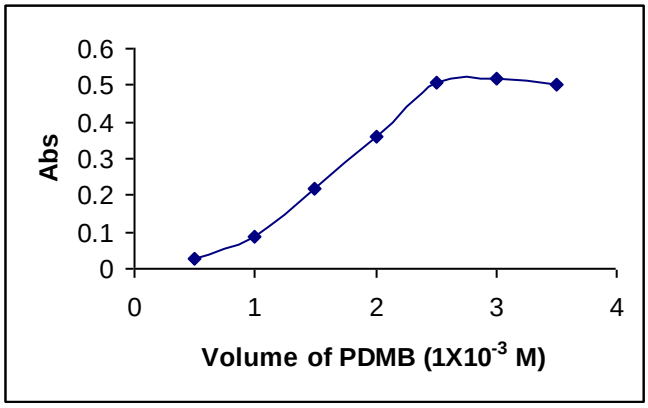

Fig 3:- Effect of the concentration of PDMP on the coloured reaction product .

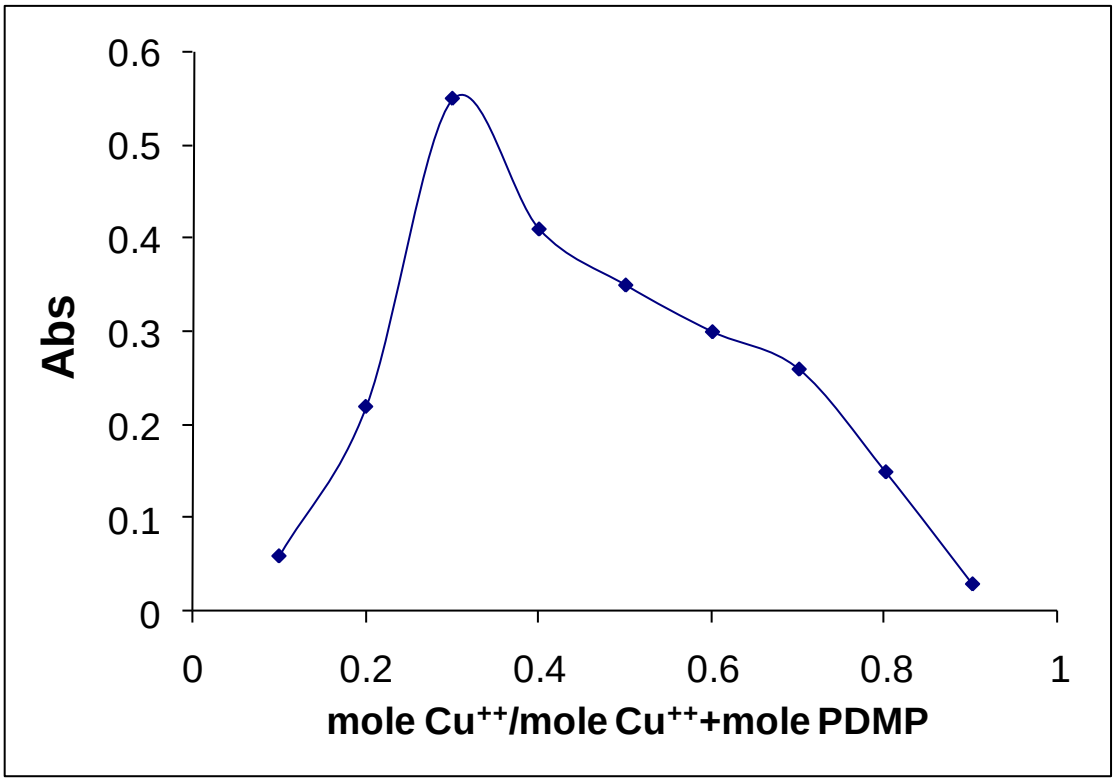

Fig 4:- Job curve for the complex of Cu(II) with PDMP at PH =7