مجلة القادسية للعلوم الصرفة المجلد 13 العدد 1 لسنة 2008
المؤتمر العلمي الاول لكلية العلوم المنعقد في 26-27 اذار لسنة 2008

# PREPARATION AND SPECTROPHOTOMTRIC DETERMINATION OF PALLADIUM(II) COMPLEX WITH NEW REAGENT
# 5-[PHENYL AZO]-4,6-DI HYDROXY-2- MERCAPTO PYRIMIDINE

***Abid Allah.M.Ali &* Hussain. J. Mohammed &**Khalid .J. AL-adely**
** College of Education for Girls / Dept.Chemistry/ Kufa University*
*** College of Science/ Dept.Chemistry/ Al-Qadisia University*

***الخلاصة*** :

تضمن البحث تقدير البلاديوم الثنائي بأستعمال الكاشف الجديد 5-[ فنيل أزو ] -6,4- ثنائي هيدروكسي -2-مركب بريميدين بتراكيز واطئة . كان المعقد المتكون بين البلاديوم (II) والكاشف PDMP ذائب في المحاليل المائية وفي وسط حامضي ضعيف. أظهر المعقد أعلى قيمة أمتصاص عند الطول الموجي 572 نانوميتر وبمعامل أمتصاص مولاري $0.76*10^4$ لتر .مول$^{-1}$. سم$^{-1}$. وكذلك كانت العلاقة خطية للتراكيز المحصورة بين ( 5-0.1( جزء في المليون تحت الطول الموجي الاعظم المذكور. وكانت قيم الدقة والتكرارية للتراكيز المعلومة المحضرة مختبرياهي أفضل من 0.55% و 0.60% على التتالي.كما تم دراسة تأثير التداخلات الممكن حصولها من الايونات السالبة والموجبة وبيان أنتقائية الطريقة. أما ثابت الاستقرار للمعقد تحت الظروف المثلى ودرجة حرارة الغرفة كان $1.2*10^8$ لتر. مول$^{-1}$ .

***Abstract***

5-[phenyl azo ]-4,6-dihydrexoy-2-mercapto pyrimidin.(PDMP)has been used for the determination of palladium (Π) at trace levels .The inner complex of pd (II) with PDMP at acidic pH , is soluble in aqueous solutions .The complex has a maximum absorption at 572 nm and $\varepsilon_{max}$ of 0.76 x $10^4$ L. mol$^{-1}$.cm$^{-1}$ . A linear correlation (0.1-5 µg/ml) was found between absorbance at $\lambda_{max}$ and concentration .The accuracy and reproducibility of the determination method for various known amounts of palladium(Π) were tested .The results obtained are both precise (RSD was better than 0.60%) and accurate (relative error was better than 0.55%).The effect of diverse ions on the determination of palladium(Π) to investigate the selectivity of the method were also studied .The stability constant of the product under optimized conditions and at room temperature was 1.25x$10^8$ L. mol$^{-1}$.

***Keywords*:** Palladium , Spectrophotometry , PDMP.

## *Introducation*

The azo dye compounds, such as 5-[(2-hydroxy phenyl)azo] 4,6-dihydroxy -2-mercapto pyrimidine[(1)] or imidazole azo and thiazolyl azo [(2)], have been synthesized and proposed for the determination of several metales ions .These heterocyclic azo compounds reacted with iron(Π), copper(Π), nickel(Π), cobalt (Π), thallium(I) and palladium, they are suitable for the analysis of trace heavy metals .

Various spectrophotometric methods for the assay of palladium (II) have been reported .Solvent extraction of sorption –spectrophotometry[(3)], high –performance liquid chromatographic-spectrophotometry [(4)],spectrophotometric procedures using low-melting-point[(5)], simple spectrophotometric methods in aquatic media[(6)], derivative spectrophotometry[(7)], flow injection and stopped flow–based techniques[(8)], and spectrophotometry in the solutions containing co solvent or micelles [(9)]. Among the proposed methods, simplicity[(10,11)] speed [(5,11)], sensitivity [(4,11)], and selectivity [(12,13)] limitations have been observed .This work reports on a simple,sensitive and selective method for the determination of palladium(Π). The method is based on the formation of the complex of pd(Π) ion with azo dye 5-[phenyl azo]-4,6-dihydroxy-2-mercapto pyrimidine in weak acid media.

## *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)°C, and left to stand 30 min .This solution was pourd in beaker containing (4,6-dihydroxy-2-mercapto pyrimdine dissolved in 150 ml of ethanol and 50 ml of (2N) NaOH at (0-5) °C. The mixture was allowed to stand over night.The precipitate was filtered off, washed with distilled water, and recrystallized from ethanol, Scheme .1.

### B. Preparation of Pd(II)as Pd $(phCN)_2CI_2$ Salt .

dissolve 0.5gm of $PdCl_2$ in 30 ml of benzonitrile .The mixture was refluxed for 1hr. A yellow precipitate of $Pd(phCN)_2$ $Cl_2$ is formed after addition of 50 ml of diethyl ether .The precipitate was filtered and washed with ether.[(15)]

### *C -Preparation of complex [Pd(PDMP)Cl $H_2O$]*

The complex was prepared by mixing stoichiomretic amounts of Pd $(phCN)_2Cl_2$ and ligand (PDMP)in a 1:1 ratio in aqueous ethanolic solution. The mixture was stirred at room temperature for 5 min. The pH of solution was adjusted to 6.0 then left for 24 hr. The solution was filtrate and washed with distilled water and dried at 70 °C.

### *Apparatus*

Spectral and absorbance measurements were made with Shimadzu UV-Visible 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 .

### *Reagents*

All chemicals used are of analytical reagent grade.

### *Standard Pd(II)solution (1000 µg/ml):-*

Dissolve 0.3591 gm of Pd $(phCN)_2$ $Cl_2$ in 100 ml distilled water, working standard palladium(Π) solutions were prepared by simple dilution of the appropriate volume of standard palladium(Π) solution (1000 µg/ml) with distilled water .

### *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$^{-3}$ with ethanol.

### **Procedure for determination of palladium** (Π)

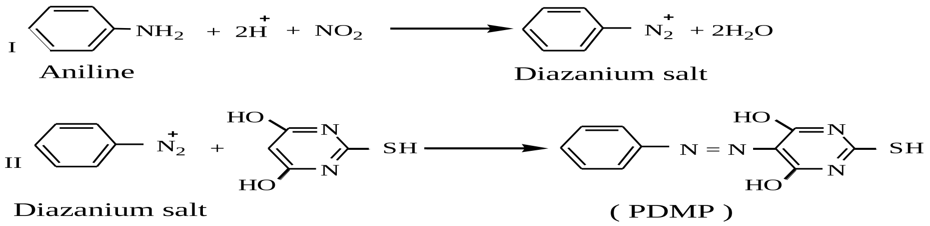
Into a series of 10 ml calibrated flask , transfer increasing volumes of palladium(Π) solution (10 µg/ml) to cover the range of the calibration graph and 4ml of lx10$^{-4}$ M (PDMP) solution and the pH was adjusted by (0.05 N) of HCl and NaOH, dilute the solution to the mark with distilled water and allow the reaction mixture to stand for 5 min. Measure the absorbance at 572 nm against reagent blank, prepared in the same way but containing no palladium ion using 1cm cells.

## Results and discussions

The results of this investigation indicated that the reaction between palladium and (PDMP) at pH 6.0 yield highly soluble product which can be utilized as a suitable assay procedure for palladium, This product has a maximum absorption at 572 nm, at which the blank at this wave length 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-mercepto pyrimidin 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 palladium (II) ion with the azo reagent, minimum blank value and relatively rapid reaction rate), the effect of pH (2-12) was studied . Only pH 6.0 was found to be optimum .Neutral and alkaline results in low sensitivity and was not stable.

### Effect of (PDMP) concentration

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

### 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 palladium (Π) is obtained which shows that Beer's law is obeyed over the concentration range of (1-50 µg per 10 ml 0.1-5 ppm) with correlation coefficient of 0.9994 and an intercept of 0.0040. The molar absorptivity of the product with reference to palladium was $0.76x10^4$ L. $mole^{-1}.cm^{-1}$.

### Accuracey and precision

To determine the accuracy and precision of the method, palladium was determined at three different concentrations. The results are shown in table 1, indicate that satisfactory precision and accuracy could be attained with proposed method.

**Table 1 . Acuracy and precision of the method**

| Palladium µg/ml | Error % | R.S.D % * |
|---|---|---|
| 0.5 | +0.55 | 0.60 |
| 1 | -0.30 | 0.25 |
| 2 | -0.015 | 0.15 |

*Result of five determinations

## Interferences

The effect of diverse ions on determination of palladium (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 2 .

**Table 2 . Effect of foreign ions**

| Foreign ions | Amount added µg | Interference % E |
|---|---|---|
| $Pt^{+2}$ | 500 | +0.7 |
| $Zn^{+2}$ | = | 1.3 |
| $Cu^{+2}$ | = | -2.1 |
| $Rh^{+3}$ | = | -0.01 |
| $Ag^{+}$ | = | 0.0 |
| $Cr^{+3}$ | = | +4.3 |
| $Ni^{+2}$ | = | -3.0 |
| $SO_4^{-2}$ | = | -0.02 |
| $Cl^{-1}$ | = | +0.01 |
| $Br^{-}$ | = | -0.08 |

| | | |
|---|---|---|
| $NO_2^-$ | = | +2.5 |
| $NO_3^-$ | = | -1.6 |

**Structure of the complex**

The I.R. bands of the (PDMP) and its palladium (Π) complex with their probable assignment are give in table 3. 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 1545 $cm^{-1}$ 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 25$cm^{-1}$ to lower frequency. The coordination of both N and O atoms to the pallaium 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 (16,17) **.**

The stoichiometry of the reaction between palladium(Π) and (PDMP) was investigated using the molar ratio method(18). The results obtained Fig.4 , show a 1:1 complex formed between palladium(Π) and (PDMP) at 572 nm . The apparent stability constant was calculated by comparing the absorbance of a solution containing stoichiometric amount of palladium 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 $1.25x10^8$ L. $mole^{-1}$. On the basis of the I.R, and a stoichiometric data the structure of complex can be suggested as follows :

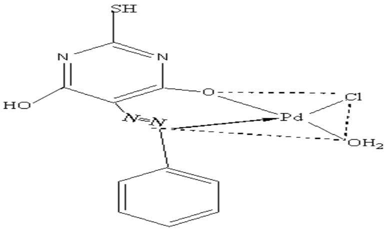


**Table (3):Selected I.R.bands of PDMP and it pd (II)complex**

| compound | Thioamide I | Thioamide II | Thioamide III | υ C=N | υ N=N | υ O-H | υ C-H Aromatic | υ M-N | υM-o |
|---|---|---|---|---|---|---|---|---|---|
| **PDMP** | **1545<br>(M)<br>1530<br>(W)** | **1270<br>(M)** | **965<br>(S)** | **1645<br>(S)<br>1610<br>(M)** | **1465(S)<br>1360<br>(W)** | **3390<br>(M)** | **3108<br>(W)** | **-------** | **-------** |
| **Pd[PDMP] $Cl_2$** | **-** | **1340<br>(s)** | **975(m)** | **1620<br>(w)<br>1580** | **1445<br>(m)** | **3410<br>(w)** | **3110<br>(w)** | **540<br>(w)** | **505<br>(w)** |

S=strong , m= medium , w=weak

***Acknowledgements***

The authors would like to express his thanks to their ex-research Rafaah Abd –Al-Amer and Ranaa Shaker for their help in the experimental work .

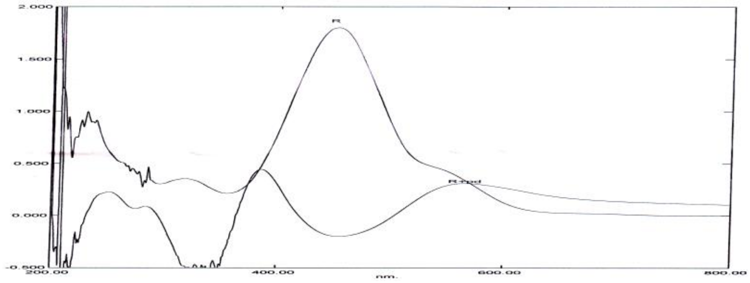
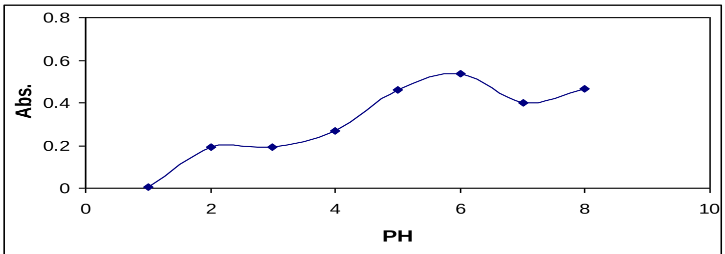
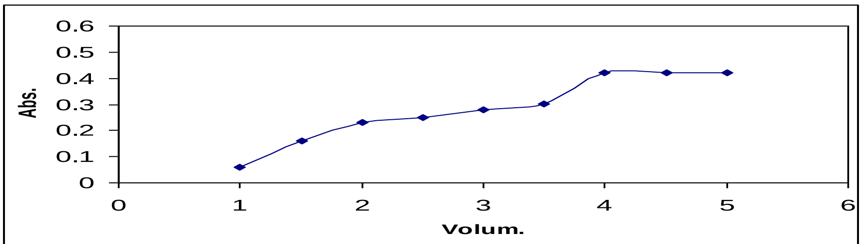


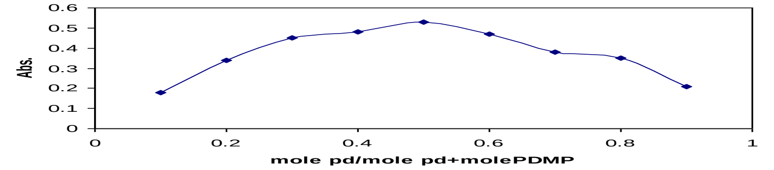
**Fig1.-Absorption spectra of(R+pd) 5ppm treated as described under procedure and measured against a reagent blank and R the reagent blank against ethanol**



Fig(2):-Effect of PH on the coloured reaction product



Fig(3):-Effect of the concentration of PDMP on yhe coloured reaction product



Fig(4):-Study of the mole ratio of the reaction between pd and PDMP

## References

1. M. Al- Haar M .Sc .Thesis , Univ. of kufa , Iraq,2006.
2. N. Al-Dahan ,H.J.Mohammed and A.M.Ali,J.Al-Qadisiah for Pure Sci, accept 2007.
3. A. A.Jewad, K.H.Kadhim, and A.N.Al-Sharefy, Nat.J. of Chem, 19,2005,493
4. K. Watanabe, M. Hojjatie, T.Nakamura , and I. Aoki, Anal. Chim Acta.218,1989,111.
5. S. Igarashi ,N. Ide, and Y.Takagai.Anal.Chim.Acta,424,2000,263.
6. R.K.Sharma,K.Shravah,and S.K. Sindh wani ,Analyst,112,1987,175.
7. D.Ma,F.Cui,D.Xia,and Y.wany,Anal.Lett,35,2002,413.
8. A.Y.EL-Sayed and F.A.Abu –shanab,mikrochim,Acta,129,1998,225.
9. D.G.Themelis,G.A.Zachariadis,andJ.A.Stratis,Analyst,120,1995,1593.
10. N.Pourreza andS.Rastegarzadeh,Anal.Chim.Acta,437 ,2001,273.
11. C. Shima ,I.Nukatuka,and Chzeki,Anal.Sci.14,1998,337.
12. T.Nagahiro, M. Satak ,J.Lin and B.K.Puri,Analyst,109,1984,163.
13. C.I.Park K.W.Cha .Talanta,46,1998,1515.
14. M.S.Carvalho,I.C.S.Fraga,K.C.M.Neto,andE.Q.Sliva Talanta,43, 1996,1675.
15. M.Hussain jasem.Iraqi.J.sci,37,No2,1996,513.
16. E.G.Rodnw.Inorg.Synth.8,1960,204.
17. K.Nukamoto,Infrared Spectra of Inorganic and Coordination Compounds,J.Wiely,1963 .
18. L.G.Hargis Analytical Chemistry,prentice –Hall Inc.,New Jersey.1988.