



5- [(4-Hydroxy phenyl)azo]- 4,6-dihydroxy-2-mercapto pyrimidine as Selective Reagent for Spectrophotometric Determination of Palladium (II)

Zahraa Lateef Razzaq

College of dentistry / Department of Basic science/ University of Kufa

Summary

A Selective and sensitive method has been advanced for the estimation of Pd (II) This work is based on the coordination of Pd(II) with 5- [(4-Hydroxy phenyl)azo]- 4,6-dihydroxy-2-mercapto pyrimidine (HADP) to form color product ,that has a maximum absorption at(605) nanometer and ϵ of(1.11×10^4) L. mol⁻¹.cm⁻¹. The relative error ,relative standard deviations and stability constant for Pd(II) were (-0.8 ,+1.2%) ,(0.51,0.72%) and 4.12×10^8 L².mole⁻² .The new reagent and it complex have been prepared in ethanolic solution. Conductivity values for complex is consistent with those predicted an electrolyte.

Keywords : HADP, Spectrophotometry ,Chelation , Palladium (II)

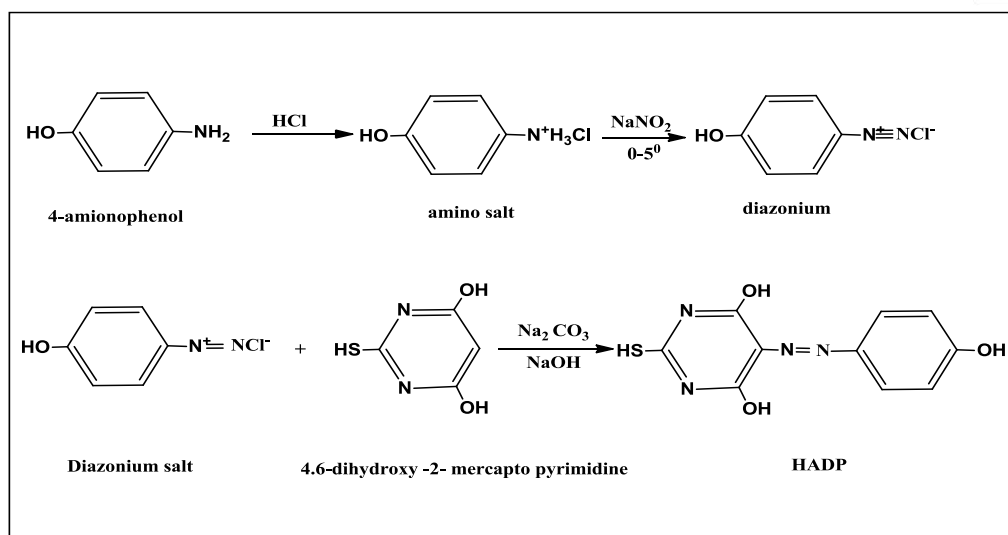
Introduction

Palladium group metals (PGM) are used in different chemical process. They exhibit good chemisorption ,high activity towards reactant and at high temperature resistance to oxidation processes¹.Interested of Palladium-complexes that are active structures in the biological and deferent fields of sciences²⁻⁴. Azo compounds are sensitive chromogenic reagents as well as complexing agent . They have been utilized for extraction –photometric and spectrophotometric determination of many metal ions due to excellent selective and sensitive above a wide extent of pH and because they are relatively convenient to prepare and purity⁵⁻⁸.Some determination methods are derivative spectrophotometry⁹⁻¹² ,atomic absorption¹³,electrochemical¹⁴⁻¹⁶ , chromatography^{17,18} and flow injection analysis^{19,20}. This research reports a simple , Selective and , highly sensitive spectrophotometric technique for the estimation of Pd(II).The method is depend on the selective chelating formation of Pd(II) with 5- [(4-Hydroxy phenyl)azo]- 4,6-dihydroxy-2-mercapto pyrimidine (HADP).

Experimental

The chemical used were of analytical grade except Pd (phCN)₂Cl₂ was prepared by reported method²¹.

A- 5- [(4-Hydroxy phenyl)azo]- 4,6-dihydroxy-2-mercapto pyrimidine HADP reagent was prepared according to the following²² Scheme .1.



Scheme.1.Preparation of HADP reagent

B- preparation of complex [Pd (C₁₀H₇N₄O₃S)Cl₂]

The compound was synthesized by stichiometric from ligand in 25 ml of ethanol. ,then poured drop wise with stirring to equalize 1:1 Pd chloride salt in 25 ml hot distilled water. The solid precipitate was filtered off, recrystallized with ethanol and dried.

Apparatus

Spectrophotometric measurements were made with [UV-visible – 1700] double beam spectrophotometer using 1 cm quartz cells. Conductivity measurements were made at room temperature utilizing an [Alpha digital conductivity model -800]. The pH values were performed with WTW PH-meter 720.

Reagents

Palladium (II) stock solution (1000µg.ml⁻¹)

Dissolve 0.3591 g of Pd (phCN)₂Cl₂ in 100ml of deionized water, working standard Pd(II) solutions were prepared by simple dilution of the suitable volume of standard Pd(II) solution 100 µg.ml⁻¹ with deionized water .

5- [(4-Hydroxy phenyl)azo]- 4,6-dihydroxy-2-mercapto pyrimidine (1x10⁻³M)

0.066 g of reagent HADP prepared dissolved in 250 ml of ethanol , working HADP solutions was prepared by simple dilution of suitable volume of reagent solution (1x10⁻³M) with ethanol .

Foreign ion solution (100µg.ml⁻¹)

These solution were prepared by dissolving an amount of the compound in deionized water

Procedure of determination of Pd(II) as complex with HADP

Into a chain of 10 ml volumetric flask, transfer rising volume of Pd(II) working solutions 100µg.ml⁻¹ to the extent of the Calibration group , add 1.5 ml of 1x10⁻³M of HADP. The PH was adjusted by 0.05 M HCl and NaOH .The complex formed in water and diluted up



to 10 ml with deionized water at room temperature. Measure the absorbance at 605nm for complex versus a reagent blank prepared in the similar way but containing no Pd(II) .

Results and discussion

Spectra

The result of this work indicated that the reaction of Pd(II) with HADP yields soluble coloured complex which can be used for determination of Pd(II) .This coloured product has a maximum absorption at 605 nm Fig. 1. The bonds showing in the range of (290-445) nm are assigned to $[\pi \rightarrow \pi^*]$ transition other bands spotted in the zone of 605 nm is attributed to $[n \rightarrow \pi^*]$ electronic transition^{23,24} .

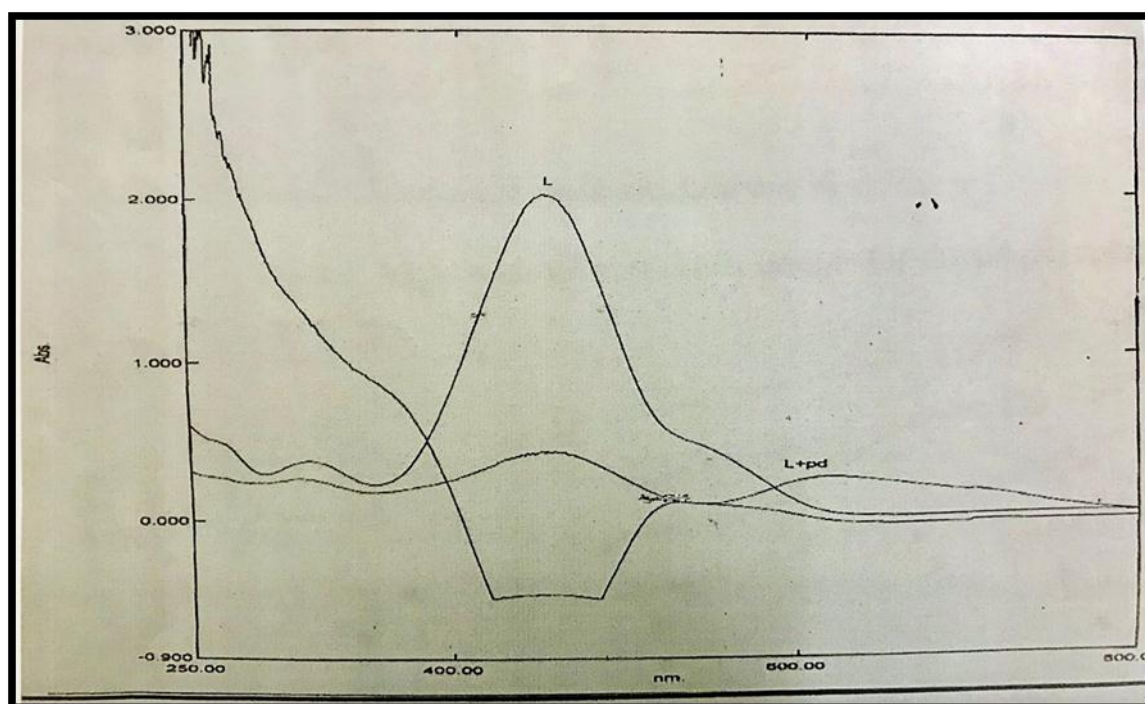


Fig .1. Absorption spectra of the reagent HADP (L) versus ethanol as blank and the complex of Pd (II) with HADP (L+Pd) versus HADP as blank.

The influence of different parameters on the absorption of color complex was investigated and the reaction condition were optimized.

Effect of reagent of concentration

Different Concentration of HADP solution were added to constant quantities of Pd(II) . 1.5 ml of 1×10^{-3} M reagent was found sufficient to improve the color to be optimum for the concentration range($0.5-10 \mu\text{g} \cdot \text{ml}^{-1}$) of Pd (II) Fig .2.

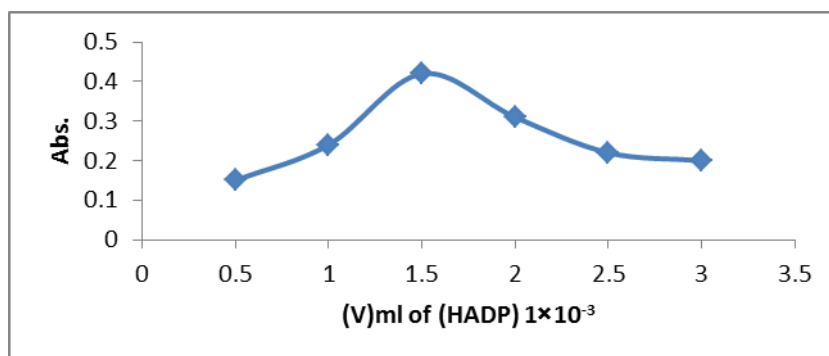


Fig.2. Effect of the concentration of HADP

Effect of pH

The effect on absorbance was studied via added adjusted of 0.05 M hydrochloric acid and sodium hydroxide. The absorbance of the complex was maximum and constant in the pH extent shown in Table 1, Fig 3.

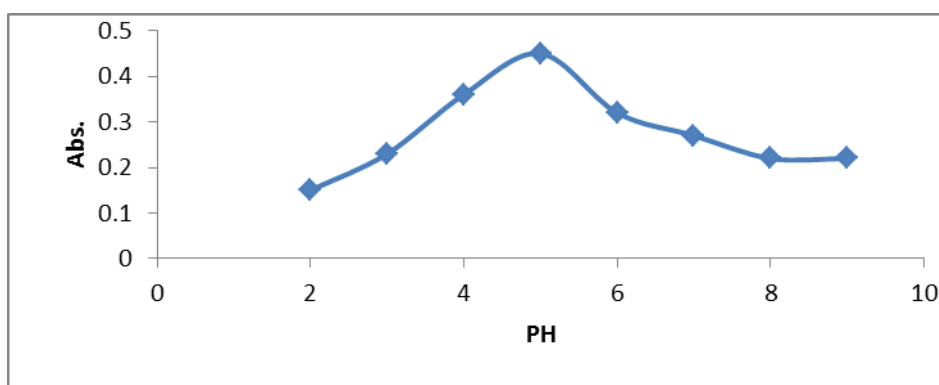


Fig.3. Effect of pH on the color intensity of [HADP-Pd(II)]

Table .1. Analytical factors of Pd(II) –HADP complex

Characteristic	Pd(II)
Absorption maxima (nm)	605
PH range	4-6
Beer'slaw range ($\mu\text{g/ml}$)	0.2-5.0
Molar absorptivity ($\text{L.mol}^{-1}.\text{cm}^{-1}$)	1.11×10^4
Sandell's sensitivity ($\mu\text{g.cm}^2$)	0.00224
Stability constant ($\text{L}^2.\text{mole}^{-2}$)	4.12×10^8

Effect of reaction time and temperature

Colour intensity of Pd(II) complex with HADP reached a maximum after reacted immediately and became stable after one min in the general procedure and the colour was constant for at least 72 hrs. In practice, the same absorbance was obtained when the colour was developed at room temperature ($25-30^\circ\text{C}$), but when the volumetric flask were placed in

URL: <http://www.uokufa.edu.iq/journals/index.php/ajb/index>

<http://iasj.net/iasj?func=issues&jid=129&uiLanguage=en>

Email: biomgzn.sci@uokufa.edu.iq



an ice –bath (0 °C) or in water bath at (45 °C) a loss in colour and constancy were observed ,therefore it is recommend that the colour reaction should be made at room temperature for complex of Pd(II) with HADP.

Calibration Graph

Under the recommended conditions of procedure, a linear calibration graph of Pd(II) was obtained , that Beer's law is followed over the concentration extent of (0.2-5.0) $\mu\text{g/ml}$ with a correlation coefficient 0.9655 and an intercept of 0.0611 Fig.4 The molar absorptivity and Sandell's sensitivity are given in Table 1.

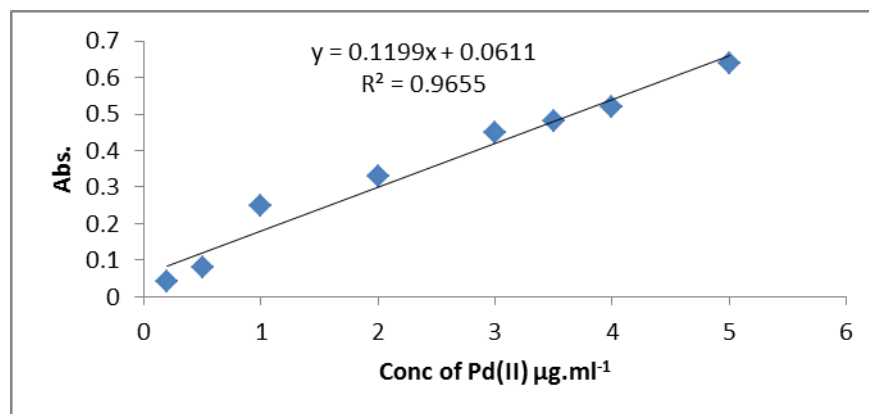


Fig.4 . Calibration graph of Pd(II) as complex with HADP

Conductivity measurement

The solubility of complex in acetone and ethanol allowed of the molar conductivity of(10^{-3}) M solution at 25 °C and ,by comparison the electrolytic nature for complex . The low Values of molar conductance data list in Table. 2 indicate that the complex is non electrolyte.

Table .2. Conductivity Value of complex

Complex	Molar conductivity $\text{S.mole}^{-1}.\text{cm}^2$	
	Acetone	Ethanol
Pd ($\text{C}_{10}\text{H}_7\text{N}_4\text{O}_3\text{S}$)Cl	18	30

Accuracy and precision

The accuracy and precision of the method, Pd(II) was determined at three concentrations. The results are shown in Table.3 indicate precision and accuracy suggested method.

**Table .3. Accuracy and precision of the proposed method For five determinations**

Amount taken ($\mu\text{g/ml}$)pd(II)	E%*	R.S.D.%*
1	0.6-	0.51
2	0.8-	0.72
3	1.2+	0.60

Interferences

The influence of foreign ions on the estimation of this ion was examined .To exam of foreign ions were estimated by the general procedure, in the presence of their respective interference ions . Each of these metal ions can be estimated without any interference in the presence of a more than a 20 fold excess of cations and anions Table .4.

Table .4. Effect of foreign ions

interference ions	Amount added $\mu\text{g.ml}^{-1}$	E %
Ni^{++}	10	1.2+
Cu^{++}	10	+3.4
Pb^{++}	10	3.5+
Cd^{++}	10	0.0
Zn^{++}	10	1.5+
Ag^+	10	1.2-
Ba^{++}	10	1.3-
Cl^-	10	0.4-
Br^-	10	1.3-
CO_3^-	10	2.3-

Composition of Complex

The composition of the complex was studied via mole ratio method²⁵ Fig.5. A fracture at 1:1 suggested the formation of $[\text{Pd}(\text{C}_{10}\text{H}_7\text{N}_4\text{O}_3\text{S})\text{Cl}_2]$ Fig .6.

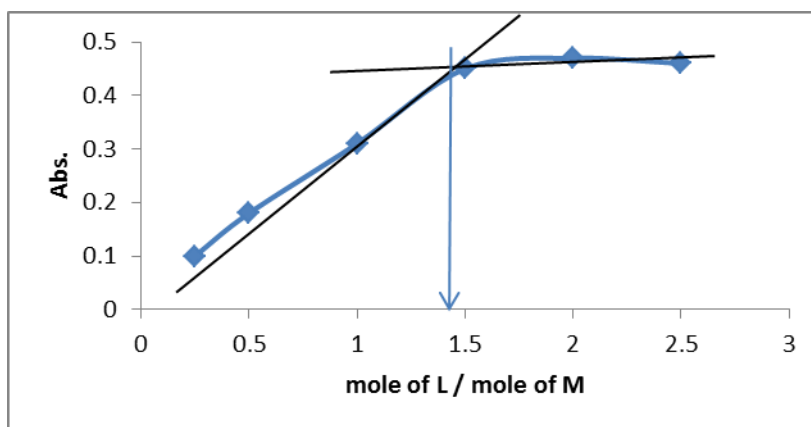


Fig. 5. Mole ratio method of the complex [Pd(II) – HADP]

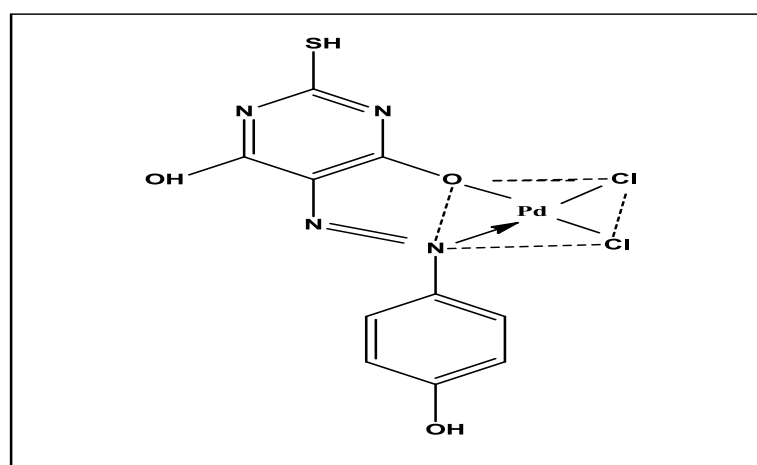


Fig.6.The Suggested the formation of [Pd (C₁₀H₇N₄O₃S)Cl₂]

References

- 1-F.R.Hartley "Chemistry of the Platinum Group Metals" Elsevier Amsterdam ,1991.
- 2-H.Watarai ; Tr.Anal. chem , 12 , 1993 ,313 .
- 3-A.G.Volkov and D.W. Deamer , "liquid –liquid " interfaces ,Theory Methods , CRC Press ,Boca Raton ,1996.
- 4-K.Inagaki and Y.Kideni ; Anal. Chim. Acta , 80 , 1983 ,171.
- 5-H.R.Hovind.Analyst,100 ,1975 ,769.
- 6-T.I.Shurupova and V.M.Ivano ;Zh. Analit.khim ,31,1976,31.
- 7- O.Navratil ; and R.W.Frei , Anal.Chim .Acta ;52,1970,221.
- 8-L.Sommer and V.M.Ivanov ; Talanta,14,1967,171.
- 9-H.B.Singh ; N.K.Agnihotri and V.K.Singh ;Talanta ,48,1999,623.
- 10-P.Parameshwara; J.Karthikeyan,A.Nityan and a Shetty and S.Prakash ;Chemica Acta.Turcica ,34(2,3),2006 ,21-26.
- 11-M.Biju and I.Dayana ;Asian.J.Chem, 22(10),2010,7551-7556.



- 12-P.B.Gaurav; B.G.Subhash;J.D.Mrunmayee and A.S.Adnan;
Adv.Appl.Sci.Res,1(2),**2010**,58-64.
- 13-X.Jia ; T.Wang and J.Wu ;Talanta , 54(4),**2001**,741-751.
- 14-V.Murugan ;T.Balamurugan ;M.Shen;A.M.Fahad; A.Ajmal and E.Mohammed ;J.Colloid
.Inter.Sci,485,**2017**,123-128.
- 15-B.K.Majid ; B.Mohammad; S.Ali ;A.Bahareh; F.Alireza and
B.Alcbar;Electro.Acta,149,**2014**,108-116.
- 16-Z.Jing;J.Yangxuan ;D.Haifeng;W.Wenchang. and C:Zhidong;J.Anal.Lett,49,**2016**,2741-
2754.
- 17-M.Bruzzoniti ;C.Mucchino ;Tarasco;C.Sarzanini ;j.Chromatogr.A,1007(1-2),**2003**,93-100.
- 18-E.Diaz ;S.Ordonez ;A.Vega and J.CoCa ;Chromatographia ;61(5-6),**2005**,285-290.
- 19-K.Mohsen ;R.Behazd and A.Khadijeh ;Anal.Bioanal.Chem.Res ;4(1),**2017**,11-20.
- 20-S.Serife and K.Senol ;Talanta ,109,**2013**,26-30.
- 21-E.G.Rochow; Inorg.Synth ;8,**1960**,204.
- 22-S.AL-Bdere, M.Sc, Thesis University of kufa **2008**.
- 23-S.Naskar, S.Biswas ,D.Mishra, T.Solerand and S.Chattopadhyay ;Inorg.
Chim.Acta,357,**2004**,4257.
- 24-R.Gup and B.Kikan ; Spectrochim.Acta, 62,**2005**,1188-1195.
- 25-A.Pielesz ;J.Mol.Struc ,511,**1999**,337-344.