Preparation of Antipyriylazo Salicylic acid and use it for theSpectrophotometric determinationof Pd (II)In Urea

Nabaa karim saeed&Hussain.J.Mohammed*
*Chemistry Department / Faculty of Science / KufaUniversityP.O.Box(21),Iraq
* E-mail :ibrahiem _ af @ yahoo . com

***Abstract*-- A new , simple , sensitive and rapid spectrophotometric method is proposed for the determination of trace amount of palladium (II) . The method is based on the formation of a 2:1 complex with 3-(4′- antipyriylazo) Salicylic acid (APASA) as a new reagent is developed . The complex has a maximum absorption at 540 nm and ε_{max} of 1.2×10^5 L. mol^{-1}. cm^{-1} . A linear correlation (0.1 – 4µg. ml^{-1}) was found between absorbance at λ_{max} and concentration . The accuracy and reproducibility of the determination method for various known amounts of palladium (II) were tested . The results obtained are both precise (RSD was better than0.77 %) and accurate (relative error was better than 0.7 %) . The effect of diverse ions on the determination of palladium (II) to investigate the selectivity of the method were also studied . The stability constant of the product was 3×10^9 L. mol^{-1} . The proposed method was successfully applied to the analysis of synthetic mixtures and raw milk without any preliminary concentration or separation.**

***Index Term*-- Palladium (II) determination , spectrophotometry , antipyriylazo Salicylic acid , Biological sample .**

INTRODUCTION

Pyrazolonesazo versatile heterocycles, which have very important application in both chemistry and biology due to the great flexibility and diverse structural aspects, a wide range of pyrazolon have been synthesized and their complexation behavior studied [1-5] . Moreover, pyrazoles attached to a sulphanilamido moiety through an azo linkage have been reported to exhibit biological activity [6] .It is known that pyrazoloneazo compounds are widely used because of their very good chelatogenic characteristics. The activity of pyrazoloneazo is thought to be due to their power of chelation with traces of metal ions present in biological systems [7-11] . By various methods has been developed determination of different ions such as Palladium (II) . Many of these method require complicated and expensive instruments, therefore, development of Palladium (II) in different samples seem desirable[12-15].The aim of the present work is to develop an easy, rapid method for the determination of palladium(II). The method is based on the reaction of antipyriylazo salicylic acid (APASA), with forms coloured complex which forms coloured complex with Pd(II) ion.

MATERIALS AND METHODS

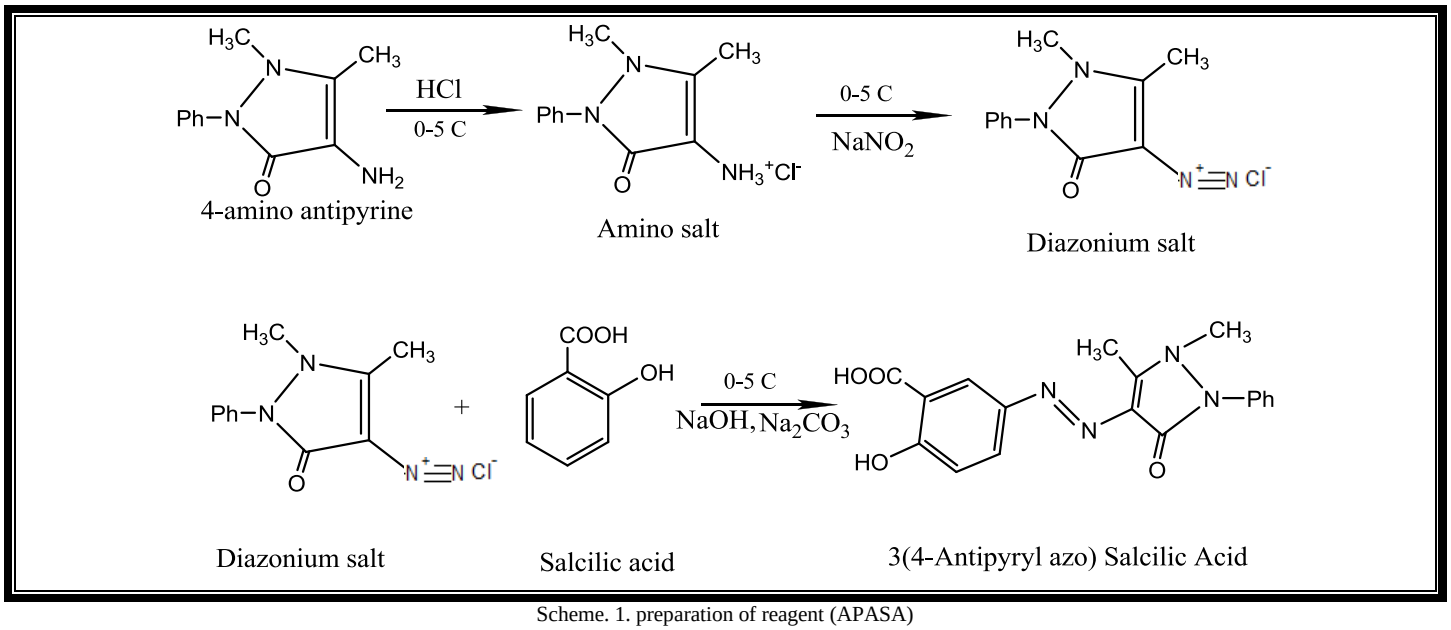
Equipments

Spectrophotometric measurement were made with ***Shimadzu UV – visible – 1650PC double beam spectrophotometer*** using 1.00 cm glass cells . Conductivity was measured in DMSO (10^{-3}) solution with an Alpha digital ***conductivity model -800***. The pH measurements were performed with a***WTW pH- meter720***. Vibrational spectra were recorded on ***Test scan Shimadzu FT.IR 8000 series*** . Atomic absorption measurements were carried out with an***Spectrophotometry - 6300 Japan.***

A)Preparation of reagent (APASA)

The reagent was prepared by coupling salicylic acidwithdiazotate 4- amino antipyrine in alkaline alcoholic Adiazonium solution was prepared by taking 1g 4- amino antipyrine in 25 ml of ethanol and concentrated hydrochloric acid with 7 ml of distilled water.

And adding sodium nitrite solution dropwiseat(0-5C).Salicylic acid 1g was dissolved in25 ml of ethanol and 25 ml of 4Nfrom NaOH were added at (0-5C) .The mixture was left to stand over night. The precipitate was filtered off and recrystallized from ethanol. Scheme. 1.



Scheme. 1. preparation of reagent (APASA)

B) Preparation of palladium complex:-

The complex was prepared by stoichiometric amount from ligand in 100 mL of ethanol thenadded drop wise with stirring to a stoichiometric amount 2:1 for pallaium salt in 50 ml distilled water. The solid product thus formed off, washed with ethanol and dried

palladium (II)stock solution (1000 μgml^{-1})

Dissolve0.0666 g of PdCl2 (99% Riedel-DehaengSeelz-Hannover) in4 ml from ConcentrationHCl and dilution the volume to 200 ml with distilled water working Standard Pd (II) solutions were prepared by dilution of the appropriate volume of Standard Pd (II) solution (1000µg.ml-1)with distilledwater

(4 –pyrazolon azo) Salicylic acid(1×10^{-3}M).

A 0.0698g of reagent (APASA) was dissolved in 200 ml of ethanol working (APASA) solution (3×10^{-3}M) was prepared by simple dilution of appropriate volume of the reagent solution (1×10^{-4}M) with ethanol

Recommended procedure for determination of Pd (II) Complex:-

In to a series of 10 ml calibrated flask, transfer increasing volumes of Pd(II) working solution 10 ppm to cover the range of calibration curve, add 3 ml 0f 1Mm of (APASA) solution and pH was adjusted to 8. The complex formed was solubilized in water and diluted up to 10 ml in a standard flask . The absorbance of the resulting solution was measured at the respective absorption maxima against a reagent blank prepared under similar condition .

RESULTS AND DISCUSSION

Properties of APASA and it metal chelate APASA is a Didentate with coordination of azo group nitrogen and carbonyl groups. Owing to the large conjugated, thecompound showed excellent chelationcompound showed excellent chelationability to form metal chelates. APASAand its metal chelates can be easilysolubilized in an aqueous solution.

Absorption spectra

The results of this investigation indicated that the reaction of Pd(II) and with 4(4 –pyrazolon azo) salicylicacid yields highly soluble coloured complex which can be utilized as a suitable assay procedure for determination of Pd(II) . This colour complex has maximun a absorption at 540 nm for Pd(II) ,the blank at this wavelength show zero absorbonce (Fig 1). The bands appearing in the range of 200-570 nm are attributed to $\pi\rightarrow\pi^*$ transition. The other bands observed inthe region of540 nm for Pd(II)is attributed to n $\rightarrow\pi^*$ electronic transition [10,11].

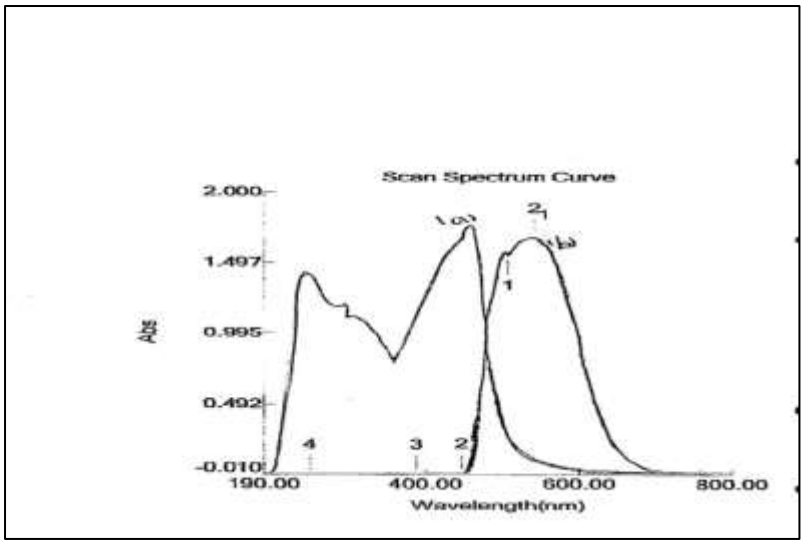


Fig. 1. Absorption spectra of [Pd (II) + APASA] treated as described under procedure and against a reagent blank and reagent blank against ethanol

The effect of various parameters on the absorbance intensity of the formed products were studied and the reaction conditions were optimized .

Effect of pH

The pH of metal complex solution was adjusted using dilute solutions of 0.05 N HCl and 0.05 N NaOH. The effect on absorbance was studied. The absorbance of the complex was maximum and constant in the pH range (6-10) for pd (II) Fig 2 .

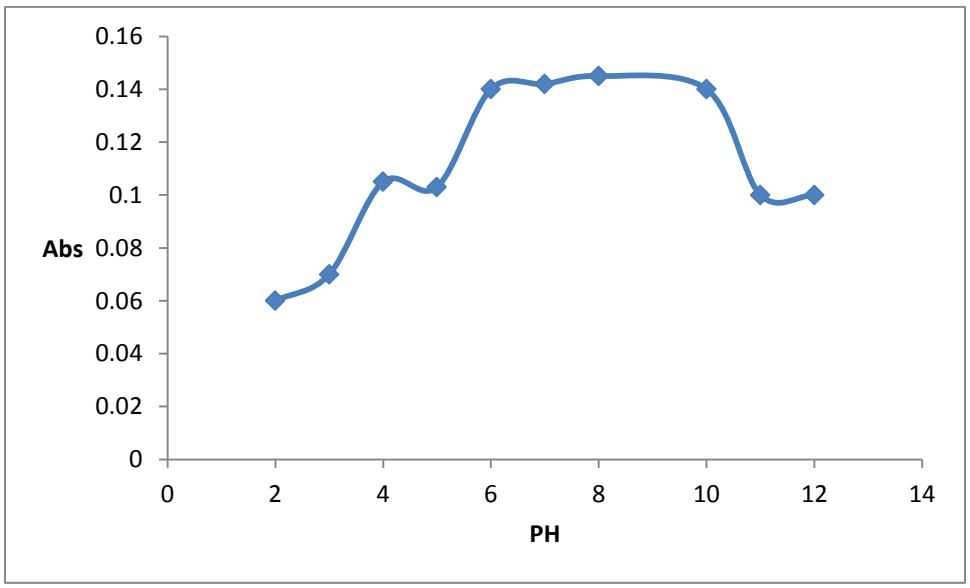


Fig. 2. Effect of PH

Effect of reagent concentration

various concentrations of APASA solution were added to a fixed amount of Pd(II) 3 ml of 3×10^{-3}M where found enough to develop the colour to it full intensity and give a minimum blank value and was considered to be optimum for the concentration range 0.1-4 µg/ml of Pd(II) Fig 3.

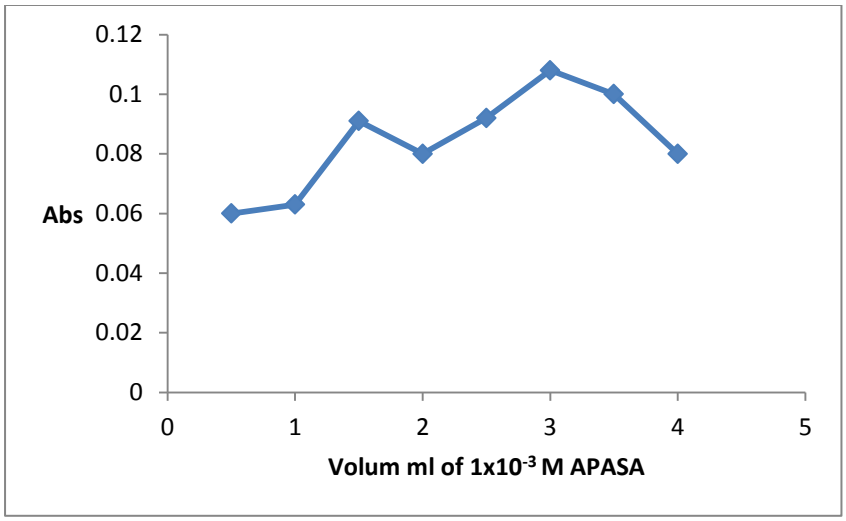


Fig. 3. Effect of (APASA) concentration

Effect of time on the stability of complex

The colour intensity reached a maximum after the Pd(II) has been reacted immediately with APASA, therefore one minute development time was selected as optimum in the general procedure. The colour obtained was stable for a least24 hours

Fig 4.

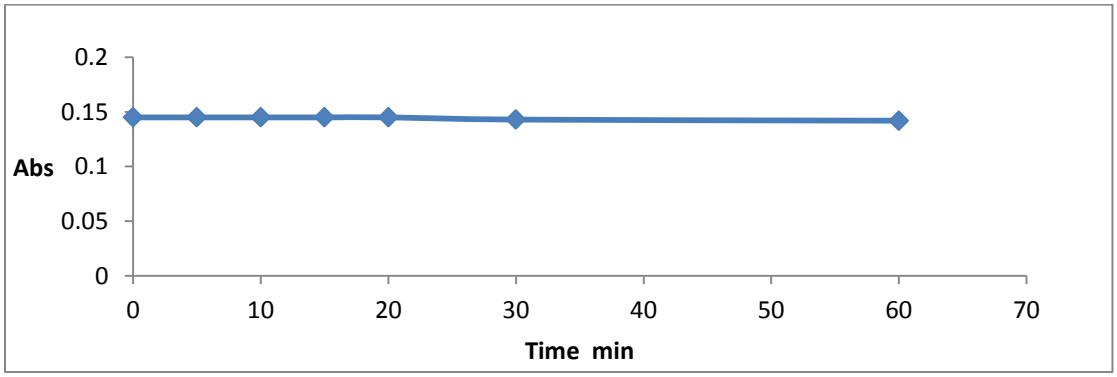


Fig. 4. Effect of time on complex of $Pd[APASA]_2$

Effect of temperature

The effect of temperature on the colour intensity of the product was studied .In practice, the same absorbance was obtained when the colour was developed at roomtemperature (25-30°C), but when the volumetric flask was placed in an ice bath at (0°C) or in a water-bath at(40°C) a loss in colour intensity and stability was observed ,therefore it is recommended that the colour reaction should be carried out at room temperature forcomplex Fig 5 .

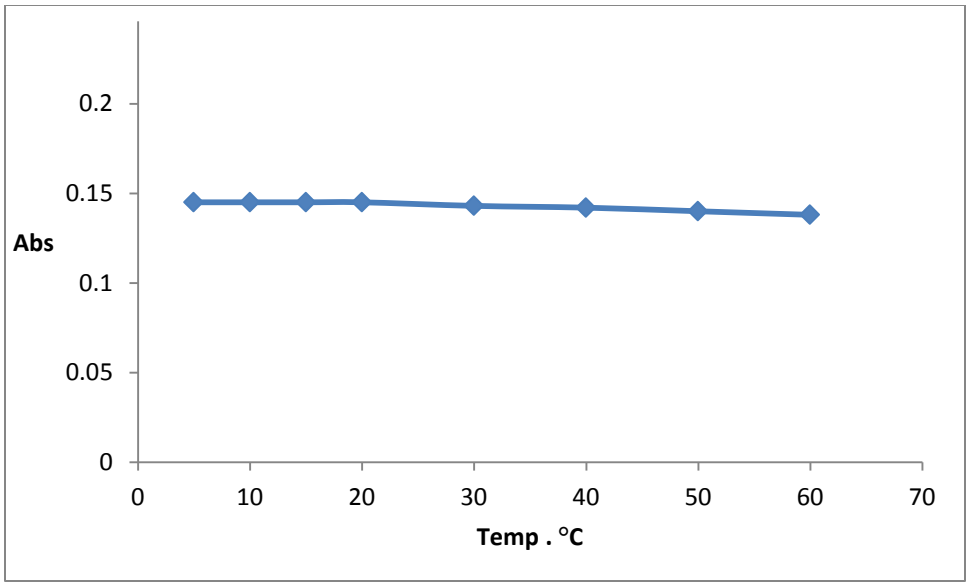


Fig.5. Effect of temperatures on complexPd[APASA]$_2$

Calibration Graph

At optimum condtions ,a linearcalibration graphs for Pd (II) was obtained ,that Beers low isobeyed over the concentration range of(0.1-4.0 ppm) with a correlation coefficient (0.9942). The results of analytical performance are summarized in Table .I

Table I
Analytical characteristics of Pd-APASA complex

Absorption maximum (nm)	540
Beer's law range (ppm)	(0.1-4)
pH range	(8-10)
Sandell's sensitivity µg . cm-2	0.0087
Molar absorptivity (L. mol-1. cm-1)	0.121X 10^5
Stability constant (L. mol-1)	3×10^9
Melting point for reagent °C	199-200
Melting point for pd (II) – complex °C	400

Conductivity measurements:

The solubility of the complex in dimethysulfoxide and ethanol permitted of the molar conductivity of(10^{-3}M) solution at 25C□□and , bycomparison, the electrolytic nature forcomplex .The low values of themolar conductance data listed in Table II indicate that the complexes are non electrolytes.

Table II
Conductivity values of complex

Complex	Molar conductivity, S. mole^{-1} .cm^2
Pd-$(APASA)_2.XH_2O$	34.77

Interferences

The effect of diverse ions in the determination of this metal ion was studied. To test of diverse ions was determined by the general procedure, in the presence of their respective foreign ions. This metal ion can be determined with different Interference ions.The metal ion can be determined in the presence of a 8 or more fold excess of cation and anion Table.3. In the experiment , a certain amount of standard Co (II) solution , coexisting ion solution and masking agent (or absence of masking agent) were added . It is found some of studied ions interfere seriously . However , their interferences are masked efficiently by addition 1.0 ml of 0.1 M of (Na2HPO4 , $NO_2$and NO_3).

Table III
effect of foreign ions.

Foreign ions	Concentration ppm	Pd % Erel
Fe^{+3}	100	15.74
Ni^{+2}	100	29.6
Zn^{+2}	100	7.40
Co^{+2}	100	38.8
Cu^{+2}	100	52.7
V^{+5}	100	4.62
Hg^{+2}	100	10.18
Cl^{-1}	100	9.25
Br^{-1}	100	11.1
SO_4^{-2}	100	6.48
CO_3^{-2}	100	-18.5
I^{-1}	100	18.5
$S_2O_8^{-2}$	100	1.85

Infrared spectra of the regent and it Pd(II) complex:-

The FT- IR bands of the (APASA) and its palladium (II) complex with their probable assignment is given in Table 4. The IR Spectrum of the ligand shows band at3483 cm-1and 3421 cm^{-1},which can be attributed to the carboxylic and OH group . However ,the *v* (N=N) stretching band in the free ligand is observed at 1482 cm-1 .This band has been shifted to lower with high intensity 1456 cm-1frequency value upon complexation suggesting chelation via the (M-N) [16-18] .The IR Spectrum of the ligand revaled a sharp band at 1676 cm-1 dueto *v* (C=O)of pyrozol azo .The band of (C=O) has been shifted to lower frequency with lower intensity at 1647 cm^{-1} in the complexes indication to that it has been affected upon chelation to the metal ion[19] .The bonding of oxygen to the metal ion is provided by the occurrence of bands at 526 cm^{-1}as .the result of *v* (M-O) [20]

Table IV
Selected FT.IR data of (APASA) and it's complex with pd (II)

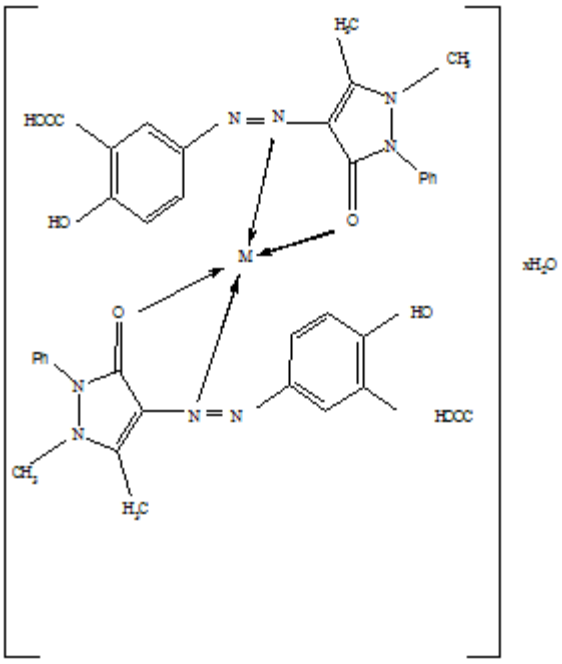
Compound	**υ (OH)**	**υ (C-H) arom.**	**υ (N=N)**	**υ (C=O)**	**υ (M-O)**	**υ (M-N)**
APASA	3483m	3062w	1482m	1676s	--------	--------
$[Pd(APASA)_2]XH_2O$	3435b	3035w	1456m	1647m	526w	470w

s=strong , m= medium , w=weak, b=broad

The composition ofPd (II) complex:-

The composition of complex was studied in the excess of reagent solution by the mole – ratio and job, s method a break at a 1:2 (M:L) moleration suggested the formation of complex where M=Pd(II),L=APASA under the given condition[21,22](.Fig.6&7).

On the basis of the FT IR, stoichiometric and molar conductivity data the structure of complex can be suggested as the following:-.



Structure of complex Pd(APASA)$_2$

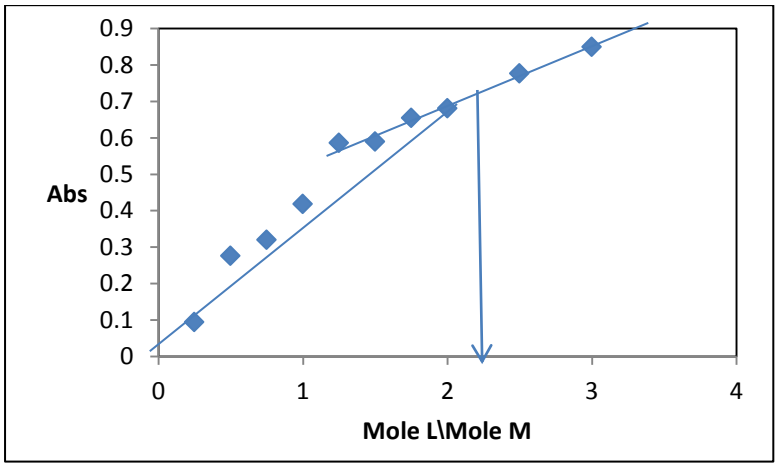


Fig. 6. Mole-ratio method for Pd[1-APASA]$_2$ complex

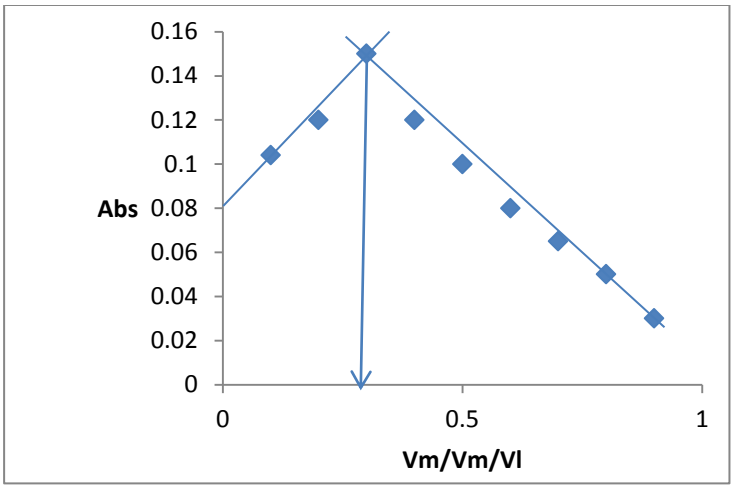


Fig. 7. Job s method for Pd[1-APASA]$_2$ complex

Applications

1-Determination of Pdt (II) in practical samples .

To determine the accuracy and precision of the method , Palladium (II) was determined at two different concentrations with different interferences ions and masked these ions by using masking reagent . The results are shown in Table.5 , indicate that satisfactory precision and accuracy could be attained with proposed method.

Table V
Determination of Pd (II) in synthetic samples

Amount taken of Pd (II) p.p.m	Recovery%	*R.S.D%
1.5	99.30	0.77
2	99.11	1.01

*For five determinations

2-Determination of Pd(II)in urin by recommended method and flame atomic absorption.

For human urine sample,taking an appropriate volume(human urine 50ml) of sample in a 500ml flask.the sample was concentrated to about 5ml by heating in ahotplate ,and transferred into the 50ml beaker. To which. 2ml of concentrated HNO_3 and3ml of 30% v/v H_2O_2 was added. The digest was evaporated to near dryness. The residue was dissolved with 5mlof5% HCl and transferred into a25mlof calibrated flask quantitatively. Then diluted the solution to volume with (5%) HCland then ready for UV-Visible spectrophotometric analysis and atomic absorption [23] Table VI.

Table VI
Pd(II) levels (µg.g-1) in biological sample

Biological sample (InUrea)	Amount found by proposed Spectrophotometric method, µg.g-1	Amount found by atomic absorption method, µg.g-1
Pd(II)	0.145	0.143

REFERENCES

[1] E. . Paul, L . Jean, and R. Paquin, *Can. J. Chem.*, vol. 31, 1025–1039, 1953.

[2] S. Sugiura, O. Ohtani, K. Izumi, T. Kitamildo, H. Asa, K. Kato, M. Hori, and H. Fujimura, *J. Med. Chem.*, . 20, . 80, 1977.

[3] A. Farghaly and A. Behit, *Arch. Pharm (Weinheim)*, vol. 333, 7–53, 2000.

[4] S. Manfrendini, R. Bazzanini, P. Baraldi, M. Bonora, M. Marangoni, D. Simoni, A. Pani, F. Scintu, E. Pinna, L. Pisana, and P. Lacolla, *Anticancer. Drugs*, vol. 11, no. 3, 194–204, 1996.

[5] A. Farghaly, F. Soliman, M. Elsemary, and A. Rostom, *pharmazie*, vol. 56, No. 1, 18–32, 2001.

[6] S. Nigram, G. Saharia, and H. Sharma, *Indian Chem.*, vol. 60, 583, 1983.

[7] K. Yogesh, N. Rathis, S. Mayur, B. Shipra, and C. Sumitra, *J. Serb. Chem. Soc.*, vol. 12, No. 69, 991–998, 2004.

[8] H. J.Mohammed and A. Mohee, and A. Header, *E. J. Chem.*8(S1),.426-433, 2011.

[9] H.J . Mohammed and M .H.Shaimaa, Inte.J.Eng &Tech-IJENS,14,No 2,102-111,2014.

[10] H.J . Mohammed and M .Walla, Inte.J.Civil &Envi-IJENS,13,No 6,102-111,2013.

[11] H.J . Mohammed and A.A.Masar, Chem .Sci.Trans,3(3),102-111,2014

[12] Y. Altun, F. Köseoğlu, H. Demirelli, I. Yilmaz, A. Çukurovali, and N. Kavak, *J. Braz. Chem. Soc.*, vol. 20,. 299–308, 2009.

[13] B. Dimitrova, K. Benichedda, E. Iranova and F. Adams, *J. Anal. At. Spectrum*, 19(10),1396, 2004.

[14] F. Vanhaeske, M.Resamo, E. Garcia. Ruiz, L.Balcaen. K. R. Koch and K. Meintoch, *J. Anal At spectrum*, 19, (2004).

[15] S.A. Abbasi, *Anal. Lett*, 20, (1987), 1013-1027.

[16] T.Z. Liu, and T.F. Lin . *Stern,FreeRadical Bio Med*, 23,155-161,1997.

[17] K.Fatma, and K. Eser. ,*Spectro Chim. Acta*.54:242 -249, 2007.

[18] G.Pandey .and K.K.Narng .2004. . *Metog. Chem*.34:291 298.

[19] G.G.Mohamed and A.M Zayed. , *Spectro Chim. Acta*.58:3 167 -175Z.M Zaki,*Spectro Chim. Acta.* 56:1917 -1926, 2000.

[20] A.E. Haervy and D.L. Manning, :*J.Am.Chem.Soc*.,72,4488 ,1950.

[21] W.C.Vosburgh and G.R.Cooper,: *J.Am.Chem.Soc*.,63,437 ,1941.

[22] X.Dong.Y.Han,Q .Hu, J.Chen.J and G. Yang.,*J.Braz.Soc*.,Vol17,No1,189-193,2006.