

Non-Extractive Spectrophotometric Determination of Palladium in Biological Samples Using Pyridoxal Thiosemicarbazone (PTSC)

Dr. M. Renuka¹, M. Obula Reddy²

¹Chemistry Lecturer, Loyola Degree College, Pulivendula, Kadapa(Dist), Andhra Pradesh, India.

²Physics Lecturer, Loyola Degree College, Pulivendula, Kadapa(Dist), Andhra Pradesh, India.

Abstract— A very simple, highly selective and non-extractive spectrophotometric method for the trace amounts of palladium(II) has been developed. Pyridoxal thiosemicarbazone (PTSC) has been proposed as a new analytical reagent for the direct non-extractive spectrophotometric determination of palladium (II). The reagent reacts with palladium in acidic medium (pH 2.0, CH₃COONa and Con. HCl) to form a pale yellow coloured 1: 2 (M : L) complex. The reaction is instantaneous and the maximum absorption was obtained at 420 nm and remains stable for 2 hrs. The molar absorptivity and sandell's sensitivity were found to be $1.63 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.635 \mu\text{g cm}^{-2}$ respectively. Linear calibration graphs were obtained for 0.9- 10.0 $\mu\text{g/ml}$ of palladium(II). The method is highly selective for palladium and successfully used for determination of palladium in various hydrogenation catalysts.

Keywords— Spectrophotometric determination, Pyridoxal thiosemicarbazone, Molar absorptivity, Sandelle's sensitivity and hydrogenation catalysts.

I. INTRODUCTION

Palladium is a rare and lustrous silvery white metal that resembles platinum. It is the least dense and has the lowest melting point of the platinum group metals. It is soft and ductile when annealed and greatly increases its strength and hardness when it is cold-worked. Palladium dissolves slowly in sulfuric, nitric and hydrochloric acid [1]. It plays a key role in catalytic converters. Palladium and its alloys have wide range of applications both in chemical industry and in instrument making [2]. Palladium is utilized in many electronic devices including computers, cell phones, multi-layer ceramic capacitors and low voltage electrical contacts as well as in dentistry and medicine [3]. Palladium is also used in jewellery, watch making and in blood sugar strips. Palladium is found in Lindlar catalyst, also called as Lindlar's palladium. Palladium is one of the three most

popular metals used to make white gold alloys [4]. A survey of literature has revealed that several analytical techniques have been reported for the determination of palladium which include atomic absorption spectrometry [5], neutron activation analysis [6], and pre-concentration and separation of palladium, such as flow injection method, hollow fiber micro extraction, solid-phase micro extraction and spectrophotometry [7-33].

In the present investigation we report a simple, selective and non-extractive derivative spectrophotometric determination of palladium (II) using a newly synthesized reagent pyridoxal thiosemicarbazone. The ligand is synthesized by reacting thiosemicarbazide with Pyridoxal, Pyridoxal is one of the three natural forms of vitamin B₆, along with pyridoxamine and pyridoxine. All of these forms are converted in the human body into a single biologically active form, pyridoxal 5-phosphate. All three forms of vitamin B₆ are heterocyclic organic compounds. Green plants are a natural source of pyridoxal, and its deficiency in the human body can lead to serious complications such as epilepsy and seizures.

In continuation of our ongoing work, we report here the spectrophotometric determination of palladium in biological samples. A close literature survey reveals that PTSC is so far not been employed for the spectrophotometric determination of palladium (II). This method is far more selective, simple and rapid than the existing spectrophotometric methods.

II. MATERIALS AND METHODS

Materials

Pyridoxalhydrochloride and thiosemicarbazide were procured from Merck, India and purified by rectified spirit. Ethanol of AR grade, Merck and used as received. Solvent like N,N-dimethyl formamide was used after distillation.

Synthesis of reagent Pyridoxal thiosemicarbazone (PTSC)

Pyridoxalhydrochloride (2g, 0.01M, dissolved in 20ml of ethanol) and thiosemicarbazide (0.9 g, 0.01mol dissolved in 10ml of H₂O) were mixed in a clean round bottom flask. Suitable quantity of (~ 10ml) of ethanol was added to the reaction mixture and refluxed with stirring for 3 hrs. The intense yellow coloured product was separated out on cooling. It was collected by filtration, washed several times with cold water. This compound was recrystallized from methanol and dried in vacuo. The yield was found to be 78 %, and melting point is 209 – 211°C. The reaction route for the synthesis is shown in Fig. 1.

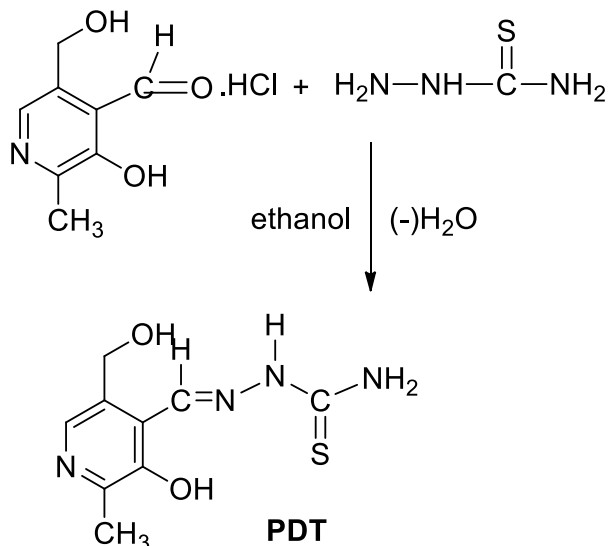


Fig.1: Synthesis of reagent Pyridoxal thiosemicarbazone (PTSC)

Preparation of reagent solution

The reagent solution (0.01M) was prepared by dissolving 0.060 gm of the compound in dimethylformamide (DMF) in 25ml volumetric flask. The reagent solution was stable for atleast 10 hrs.

Preparation of palladium (II) ion solution

A 1×10^{-2} M stock solution of divalent palladium was prepared by dissolving requisite quantity (0.22g) of PdCl₂ in doubly distilled water containing few drops of conc. HCl and made up to 100 ml volumetric flask. The stock solution was standardized gravimetrically [34]. Dilute solutions were prepared from this stock solution. Solutions of large number of inorganic ions, complexing agents were prepared from their analR grade (or) equivalent grade water soluble salts.

Procedure

An aliquot of the solution containing palladium in optimum concentration range , 10ml of buffer solution (pH 2.0) and

1ml of 0.01M reagent solution were combined in 25ml volumetric standard flask and resulting solution was diluted to the mark with distilled water. The absorbance of the solution was measured at 420 nm against reagent (PTSC) blank. The measured absorbance was used to compute the amount of palladium from predetermined calibration plot.

Determination of Palladium (II) in hydrogenation catalysts

About 0.3g of the catalyst sample was treated with 10ml of aquaregia. The solution was then evaporated to 5ml, cooled and diluted with 20ml distilled water and filtered. The residue was washed into the filtrate first with 20ml of 2N nitric acid and then with small volume of distilled water. Finally the solution was made up to the mark with distilled water in 100ml volumetric flask. The palladium content in known aliquots of the resultant solution is determined by the proposed method and the results are given in Table 4.

Apparatus

A Perkin – Elmer (Lambda 25), UV – Visible spectrophotometer equipped with 1.0 cm(path length) quartz cell and Elico model LI- 610 pH meter were used in the present study.

III. RESULTS AND DISCUSSION

Characterization of reagent

The newly synthesized reagent pyridoxal thiosemicarbazone has been characterized using IR, NMR and Mass spectral data.

IR spectra

The infrared spectrum of PTSC is shown in Fig 2. From the spectra it has been revealed that the reagent show sharp strong peak at 3422 cm^{-1} may be assigned for the stretching vibrations of –OH and 3381 cm^{-1} may be assigned for the assymmetric stretching of –NH₂ groups . The sharp peaks appeared at 3262 cm^{-1} may be assigned for stretching vibrations of secondary –NH group. The band at 3172 cm^{-1} may be assigned for stretching vibration of secondary thioamide –NH group, band at 1620 cm^{-1} may be assigned for plane bending vibration of –NH group, band at 1524 cm^{-1} may be assigned for stretching vibraton of ring C=C group, band at 1413 cm^{-1} may be assigned for stretching vibration of –C=S group band at 1290 cm^{-1} may be assigned for stretching vibration of –C-NH group, band at 1262 cm^{-1} may be assigned for plane bending vibration of -OH group and band at 823 cm^{-1} may be assigned for stretching vibrations of 4-substituted pyridine.

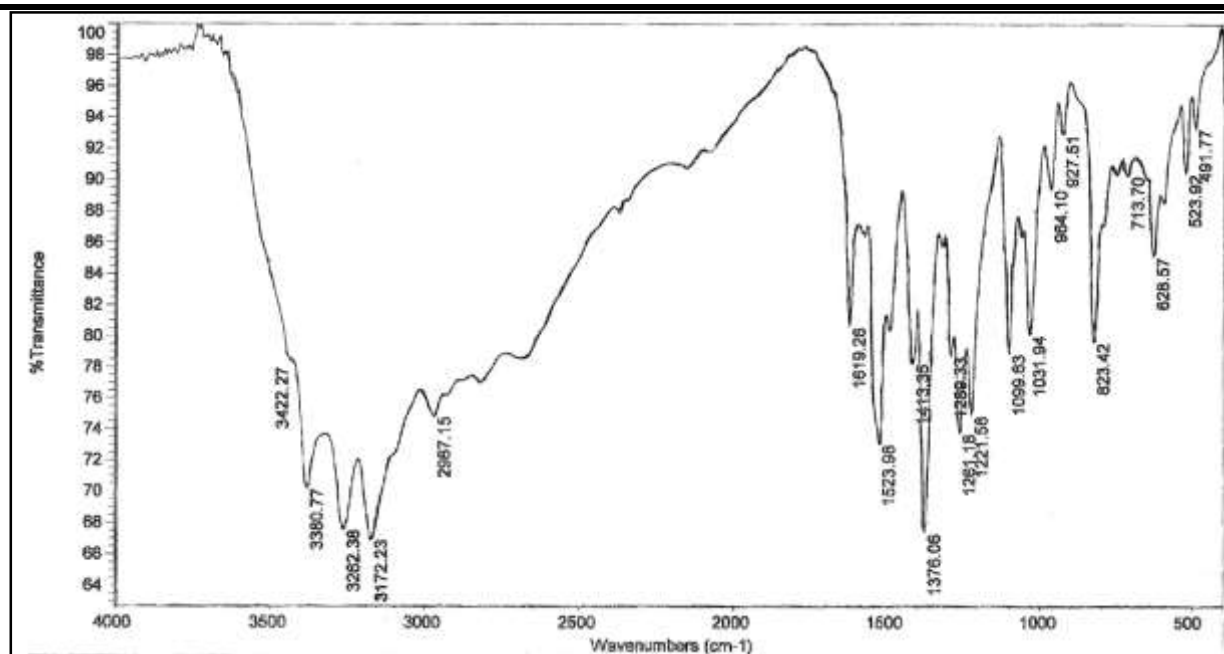


Fig.2: Infrared Spectrum of PTSC in KBr disc

^1H – NMR spectra

The ^1H – NMR spectra of reagent was scanned in $\text{DMSO}-d_6$ solvent and are shown in the Fig 3. From the spectral data, the singlet obtained at 2.40(δ) ppm may be due to the methyl proton, the multiple signals at 4.58(δ) ppm may be due to amine protons, the singlet signal at 5.26(δ) ppm may be due to $-\text{OH}$ protons, the singlet signal at 7.99(δ) ppm may be due to $-\text{CH}$ protons, the singlet signal at 8.57(δ) ppm may be due to $-\text{CH}_2\text{OH}$ protons and the singlet signal at 11.59(δ) ppm may be due to phenyl ring protons and NMR spectrum of PTSC is shown in Fig 3.

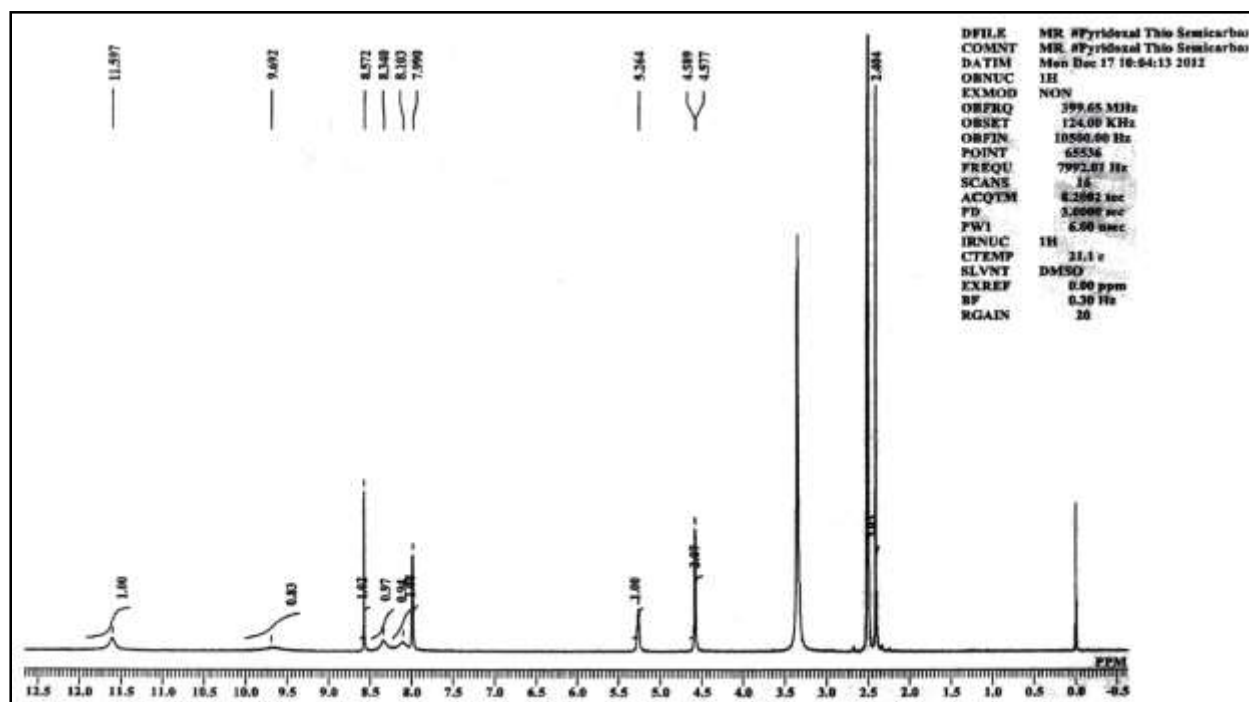


Fig.3: ^1H -NMR Spectrum of PTSC in $\text{DMSO}-d_6$ medium

Mass spectra

Mass spectrum of PTSC is shown in Fig.4. It shows the molecular ion peak at m/z 240. The peak observed at m/z values of 239 is due to the loss of $-H$ radical, peak observed

at m/z values of 224 is due to the loss of $-NH_2$ radical and peak observed at m/z values of 207 due to the loss of $-SH$ radical. Thus mass spectrum is consistent with the structure of PTSC.

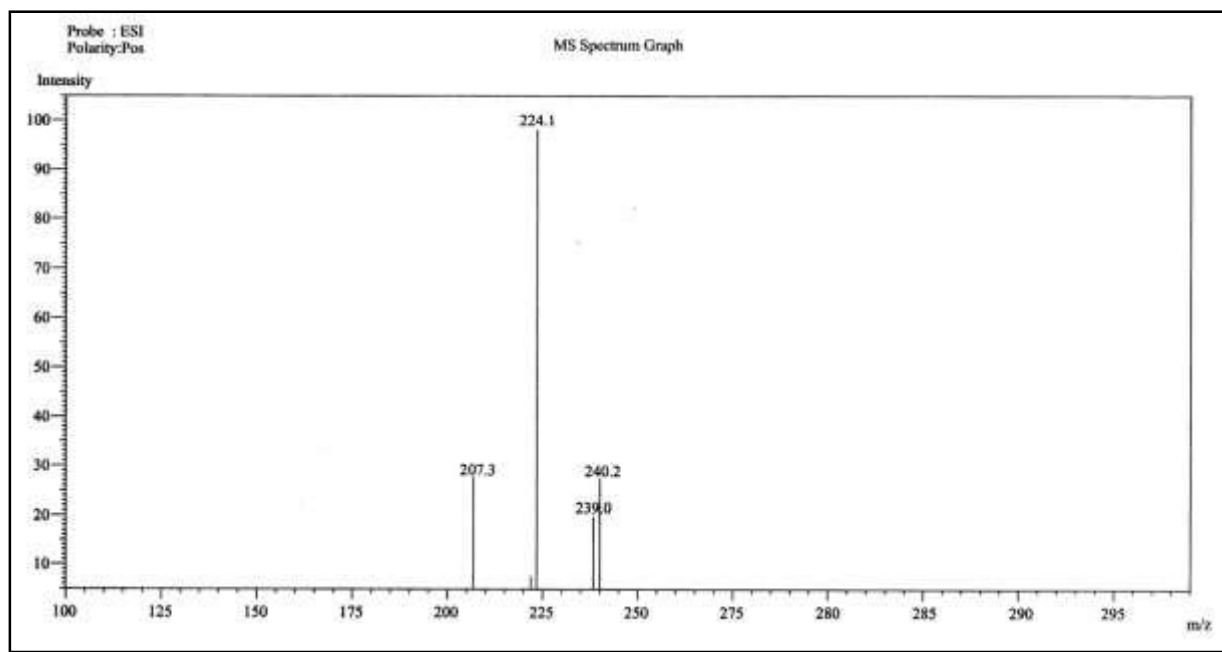


Fig.4: Mass spectrum of PDT

UV-Visible spectra

Absorption spectrum of 2×10^{-5} solution of PTSC at different pH values were recorded and pK_a values were determined spectrophotometrically using Phillip and Merrit method [35]. The bathochromic shift from 295 – 365 nm indicates that in solution on increasing pH the $>C=S$ group

of the reagent (PTSC) is enolised and dissociated. The values of PTSC are 3.0(pK_1) and 9.0 (pK_2) respectively. The pK_1 and pK_2 values are presumably due to keto – enol tautomerism and deprotonation of $-SH$ group respectively and UV-visible spectra is shown in Fig 5.

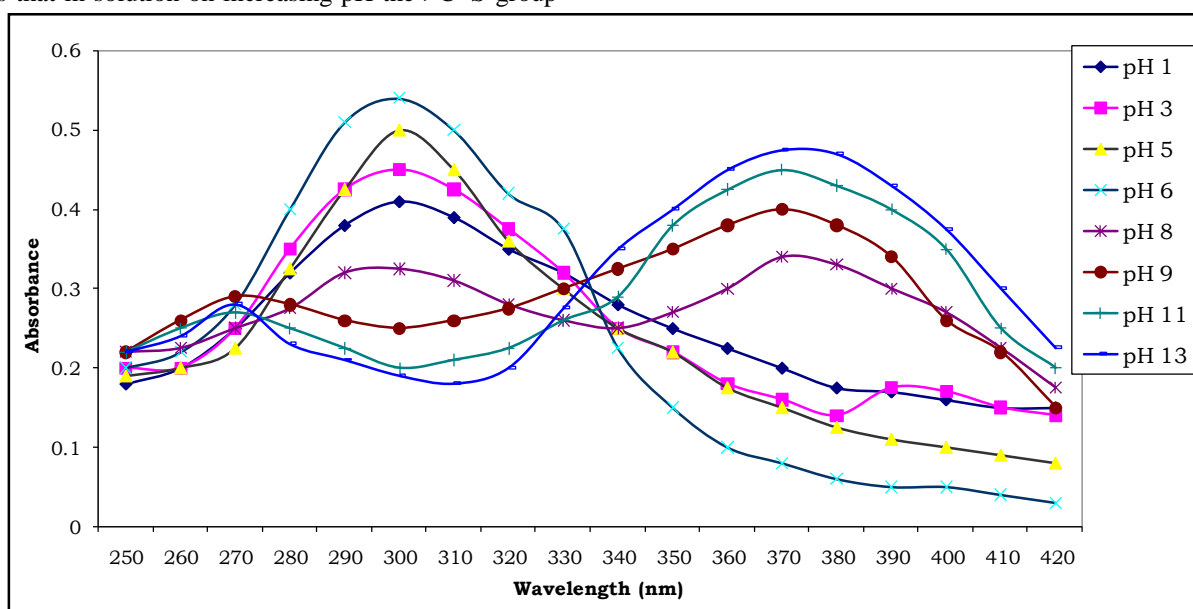


Fig.5: Absorption spectra of $2 \times 10^{-5}M$ of PTSC at different pH values

Effect of pH

The effect of pH on the colour intensity of the Pd(II) – PDT complex was studied results are shown in Fig 6. The graph

indicates that the complex shows maximum and constant absorbance in the pH range 1.0 – 3.0. Hence, buffer solution of pH 2.0 is chosen for subsequent studies.

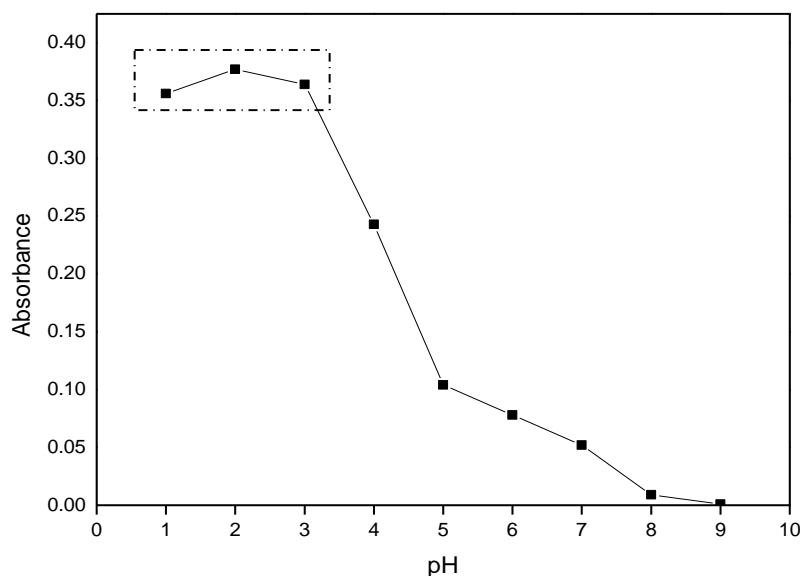


Fig.6: Effect of pH on the absorbance of Pd(II) – PDT complex Adherence of Beers law, Molar absorptivity, and Sandells sensitivity

Beer's law was obeyed over a concentration range of 0.9-10.0 $\mu\text{g/ml}$ of palladium(II) and shown in Fig 7. Molar

absorptivity and Sandells sensitivity were found to be $1.63 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.635 \mu\text{g cm}^{-2}$ respectively.

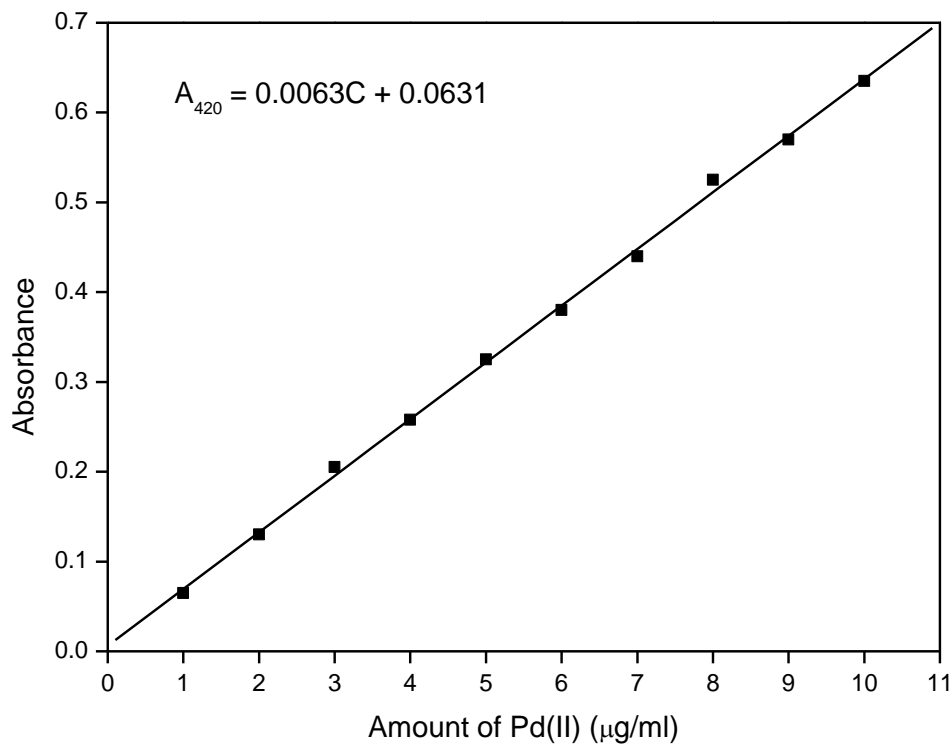


Fig.7: Calibration plot for Pd(II) determination

Effect of reagent concentration

The amount of reagent necessary for full colour development are presented in Table 1. The data indicate that a 10 fold molar excess of reagent is sufficient for full colour development.

Table.1: Effect of PDT concentration of the absorbance of Pd(II) complexes

Pd : PTSC	Absorbance
1:0.5	0.402
1: 10	0.420
1: 20	0.418
1: 30	0.410
1:40	0.415
1: 50	0.435

Effect of time

The absorbance of Pd(II) – PTSC complex was measured at different time intervals to ascertain the time stability of the complex. The absorbance of the Pd(II) complex was measured at 420 nm. The colour development is instantaneous and remains constant for 2 hrs and thereafter showed gradual decrease in intensity with increasing time.

Precision

The precision of the method was checked by ten replicate analysis containing 5ml of Palladium(II)solution. The standard deviation and relative standard deviation were found to be ± 0.0056 and $\pm 2.47\%$ respectively.

Effect of foreign ions

The validity of the method was assessed by investigating the effect of various cations and anions on the determination of palladium(II) by the developed method, by taking 1ml amount of palladium(II) solution was taken in a set of 25ml volumetric flasks containing 10 ml of buffer solution, appropriate amount of foreign ion and the reagent solution was added at the end. The contents were made up to the mark with distilled water. The absorbance of the solution in each flask was measured at 420 nm from which the tolerance limit of the foreign ion was determined. The amount of foreign ion which brings about a change in absorbance by $\pm 2\%$ was taken as its tolerance limit and results of these experiments are shown in Table 2. Larger amounts of Mo(IV) and Fe(III) do not interfere in the presence of masking agents. Interference of molybdenum(IV) and iron(III) are masked with ascorbic acid.

Table.2: Tolerance limit of foreign ions in the determination of 2.12 $\mu\text{g/ml}$ of palladium

Ion added	Tolerance limit $\mu\text{g/ml}$	Ion added	Tolerance limit $\mu\text{g/ml}$
EDTA	1490	Cd(II)	450
Chloride	1472	Zn(I)	260
Hypo	632	Mn(II)	220
Tartrate	592	Pb(II)	83
Sulphate	384	Se(V)	32
Oxalate	352	Cr(VI)	21
Ascorbic acid	320	Ni(II)	7.6
Bicorbamate	242	Hg(II)	1.6
Carbonate	240	Os(VIII)	1.2
Acetate	236	V(III)	0.41
Thiocyanate	232	Mo(IV)	0.39 ^a
Ascorbate	230	Fe(III)	0.38 ^a
Fluoride	70	Pt(IV)	0.08
Iodide	51	Co(II)	0.02

^a Masked with 200 $\mu\text{g/ml}$ of ascorbic acid.

Determination of the composition of the complex

The composition of the complex (M: L= 1 : 2) was determined by Job's continuous variation method and Molar ratio method and were shown in Fig.8. and Fig.9 respectively. CH₃COONa (1M) - Conc. HCl (0.1M) buffer (pH 2.0) is used in these studies. The dissociation constant

(α) and concentration (c) of the reagent at intersecting point were used in the calculation of stability constant of the complex. Stability constant of the complex 1: 2 (M : L) complex is given by $1-\alpha / 4\alpha^3c^2$. The structure of Pd(II) – PDT is given in Fig 10.

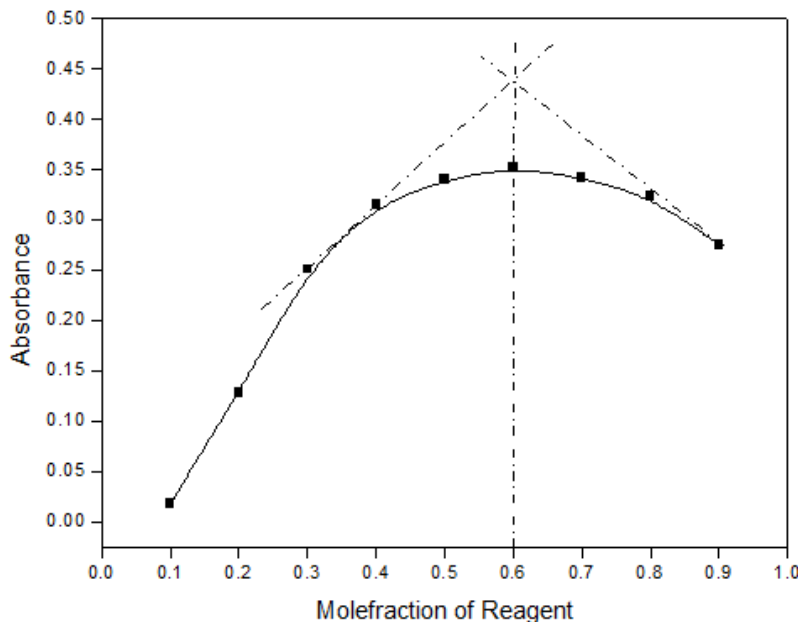


Fig.8: Job's curve

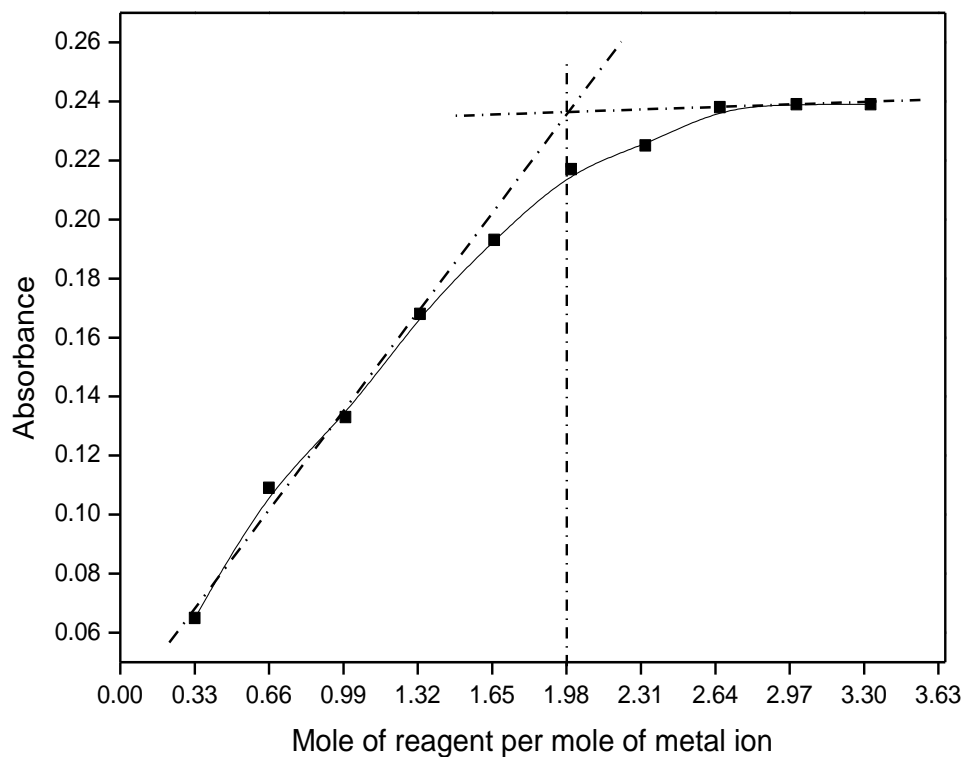


Fig. 9: Molar ratio plot

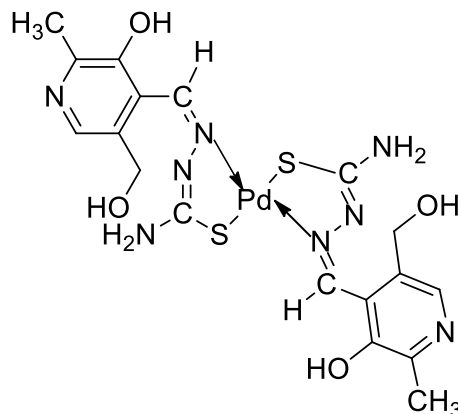


Fig.10: The predicted structure of Pd(II) – PTSC Complex

Various physico – chemical and analytical characteristics of palladium complex are summarized in Table 3.

Table.3: Physico – chemical and analytical characteristics of Pd(II) – PTSC Complex

S. No.	Characteristics	Results
1	λ_{\max} (nm)	420
2	pH range (optimum)	1.0 – 3.0
3	Mole of reagent required per mole of metal ion for full colour development	10
4	Time stability of the complex (in hrs)	2
5	Beer's law validity range ($\mu\text{g/ml}$)	1.0 – 9.90
6	Molar absorptivity ($\text{lit mol}^{-1}\text{cm}^{-1}$)	1.63×10^4
7	Specific absorptivity ($\text{ml g}^{-1}\text{cm}^{-1}$)	0.15
8	Sandell's sensitivity $\text{my of Cu(II) cm}^{-2}$	0.651
9	Composition of the complex as obtained in Job's and molar ratio methods(M:L)	1 : 2
10	Stability constant of the complex	1.90×10^{10}
11	Mean absorbance	0.226 ± 0.0005
12	Standard deviation in the determination of 2.12 $\mu\text{g/ml}$ of Cu(II) for ten determinations	0.0056
13	Relative Standard deviation (RSD) %	2.47
14	Y–intercept	0.0631
15	Angular coefficient	0.063
16	Detection limit ($\mu\text{g/ml}$)	0.0743
17	Determination limit ($\mu\text{g/ml}$)	0.2230

Determination of Palladium (II) in hydrogenation catalysts:

The results of determination of Pd(II) in hydrogenation catalyst are presented in Table.4.

Table.4: Determination of amount of Pd(II) in Hydrogenation catalysts

Catalyst	Amount of Pd(II)*%		Relative error (%)	Standard deviation(%)
	Present	Found		
Pd-CaCO ₃	5.00	5.02	-0.78	±0.038
Pd-BaCO ₃	5.00	4.98	-0.62	±0.029
Pd-BaSO ₄	5.00	5.04	0.80	±0.039
Pd activated charcoal	10.00	9.93	-0.38	±0.030

*Average of five determinations

The Comparison of Spectrophotometric Methods For The determination of Palladium (II) with various ligands are presented in the Table. 5.

S.No	Name of the reagent	$\lambda_{max}(nm)$	pH range	Determination ($\mu g/ml$)	$\epsilon \times 10^4$ ($L mol^{-1} cm^{-1}$)	Reference
1.	Sodium isoamylxanthate	360	4.5-7.0	3.0-3.8	0.95	36
2.	1-amino-4-hydroxy Anthraquinone(AMHAQ)	620	0.3-6.5	3.0-14.5	1.1	37
3.	2-hydroxy-5-methyl acetophenoneisonicotinoyl hydrazone (HMAINH)	385	2.0	2.0-9.0	0.532	38
4.	Propericiazine(PPC)	474	1.10-4.10	0.2-24.2	0.41	39
5.	Gemifloxacin	430	acidic	1.0-10.0	1.36	40
6.	1-(2-quinolylazo)-2,4,5-Trihydroxy benzene(QATB)	620	3.0-5.5	1.9-7.95	1.25	41
7.	Pyridoxal thiosemi carbazone(PTSC)	420	2.0	0.9-10.0	1.63	PM

PM-Present method

IV. CONCLUSION

The synthesized reagent Pyridoxal thiosemicarbazone (PTSC) is characterized by analytical and spectral studies. The reagent forms a yellow coloured complex with Pd(II). The Pd(II)-PTSC complex structure is predicted and various physico-chemical and analytical characteristics are determined. This reagent PTSC is successfully used for the determination of Palladium(II) in various biological samples.

ACKNOWLEDGEMENT

The authors thank M. Subbalakshmi of IICT, Hyderabad for her help in recording IR and NMR spectras of reagent samples.

REFERENCES

- [1] Sahu R, Sondhi SM and Gupta B, *Talanta*, 42(3) (1995) 401.
- [2] Zhang L., Ma, D., Li, J., and Wang, Y., *Anal. Sci.*, 2006. 222 (7), 989-992.
- [3] Yang, b., Zhu, L., Huang, Z., Yang, G., and Yin, J., *Guijinshu*, 2005, 26(1), 39-42. M. Swetha et al *Adv. Appl. Sci. Res.*, 2013, 4(2):298-304 *Pelagia Research Library*.
- [4] Absalan G, Safari A and Massoumi A, *Microchemical J*, 37 (1988) 212.
- [5] Lahiri S ,Dey S, Badiya T K, Nandy M, Balu D and Das NR, *Appl Radial Isotopes*, 48(1997) 549.
- [6] Eskandari H & Karkaragh G I, *Bull Korean Chem Soc*, 24(2003) 1731.
- [7] Sayed Juned A and Bhole Arjun B *Annals of Biological Research*, 2011,2(1): 9-16

- [8] Parameshwara P, Karthikayan J, Nityananda Shetty A & Prakash Shetty, *Ann Chim*, 97 (2007) 1097.
- [9] Hall I H, Lackey C B, Kistler T D, Durham R W Joud E M, *pharmazie*, 55 (2000) 937.
- [10] Reddy B k, Reddy K J, Kumar J R, Kumar A k & Reddy Av *Anal Sci*, 20 (2004) 925.
- [11] Chhakar AK & Kakkar L R, *Fresenius' J Anal Chem*, 350 (2004) 127.
- [12] Prakash Shetty, Nityananda Shetty A, Gadag R, *Indian J Chem Technol*, 10 (2003) 287.
- [13] Kaluram N. Vidhata, Santosh S. Katkar, Balasaheb R. Arbad and Machhindra K. Lande *Advances in Applied Research*, 2012, 3(2): 713-719
- [14] Lakshmi narayana S, Janardhan Reddy K, Narayana Reddy SA, Kumar JR & Reddy AV, *J Chin Chem Soc*, 54(2007)1233.
- [15] Janardhana Reddy K, Kumar Jr, Ramachandiraiah C, Reddy SA & Reddy Av, *Environ Monit Assess*, 136 (2008) 337.
- [16] Biju Mathew, Mini .V and Ancy Vinnifred., *Der Chemica Sinica*, 2010, 1 (3): 7-14.
- [17] Karthikeyan J, Parameshwara P, Nityananda S A, *Environ monit Assess*, 173 (2011) 569.
- [18] Gangadarappa, M., and Reddy, P.R., *J. Indian Chem. Soc*, 2006, 83, 1130-1134.
- [19] M.Rameswara Rao and K. B.Chandrasekhar, *Der pharma chemical*, 2011, 3(2): 358- 369.
- [20] Long, W.R., Cao, Q.E., Li, C.N., Wang, J.L., Guanpu Shiyanshi, 2004, 21 (5), 1037- 1040.
- [21] Ahmed, I.S., *Instrumentation Sci. & Tech.*, 2005, 33(1), 33-45.
- [22] S. Satyasree, V. Krishna Reddy and P. Raveendra Reddy., *Der Chemica Sinica*, 2012, 3(6):1415-1420.
- [23] Reddy, K.V., and Paul, A., *India J.Chem*, 1984, 23A, 703-704.
- [23] Gaurav B P, Subhash G B, Mrunmayee DJ & Anand SA, *Adv Appl Sci Research* 1 (2010) 58.
- [24] Jeffery G H, Bassett J, Mendham J & Denney R C, *Vogel's Text Book of Quantitative Chemical Analysis*, 5th ed (Addition Wesley Longman Ltd), 1997, 469.
- [25] G.G.Mohammed, *J.Pharma Biomed Anal* 24(4), 2001, 561-587.
- [26] V.S.Anasuya Devi, V.Krishna Reddy and K. Mohan Reddy *Archives of Applied Science Research*, 2011, 3(4):265-279.
- [27] D. Nagarjuna Reddy, K. Vasudeva Reddy, T. Sreenivasulu Reddy and K. Hussain Reddy., *Advances in Applied Science Research*, 2011, 2 (4):328-337
- [28] D.Gopalakrishna, N.Devanna and K.B Chandrasekhar, *International Journal of Applied Biology and Pharmaceutical Technology*, Aug-oct-2012, Volume: I: Issue-2:643-659
- [29] Hanna, W.G., *Talanta*, 1999, 50(4), 809-818.
- [30] Prakash, S., Shettyand, A.N., and Gadag, R.V., *Indian J. Chem .Tech.* 2003, 10(3), 287- 290
- [31] Gholovand, M.B., and Nozari, N., *Talanta*, 2000, 52(6), 1055-1060.
- [32] M.Rameswara Rao and K. B.Chandrasekhar, *Der Pharma Chemica*, 2011, 3(2): 358-369.
- [33] Vogel Al. A text book of quantitative inorganic analysis, 3 rd edn., ELBS and Longman, 1975; 325.
- [34] Phillip J.P. and Merrit T.L. *American chem.. Soc.* 1978, 70, 410.
- [35] Malik A.K., Kaul A.N., Lark B.S., Faubel W, RAo. ALJ., *Turk.jou. chem.*, 2001, 25, 99-105.
- [36] Kamal.A. Idris., Magada.S. Salesh., Mohammad.M., Saleima, FATma S. Hassan, Sherif.K. Idris., *Monatshefte fur Chemie/ Chemical monthly* 1990: 121 (8-9), 625-634.
- [37] Gaurav.B Petha, Subhash. G. Bhadange, Mrunmayee. D. Joshi and Anand. S. Aswar., *Adv App Sci Res* 2010; 1(2), 58-64.
- [38] Thimme Gowda . A, Sanke. Gowda. H and Made Gowda N.M ., *Anal Chem* 1983: 55(11), 816-817.
- [39] Madhuri. D, Chandrasekhar K.B, Devanna.N, Somasekhar G, *Rasayan J Chem* 2010., 3(1): 159-165.
- [40] Prathap Singh Kadyan, Devender Singh, *Der Pharma Chemica* 2011, 316, 70-74.