WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 5.990
Volume 4, Issue 5, 1168-1180. Research Article ISSN 2277– 7105

SYNTHESIS OF 2-HYDROXY-1-NAPHTHALDEHYDE-P-HYDROXYBENZOICHYDRAZONE (HNHBH) AND ITS APPLICATIONS IN DIRECT AND DERIVATIVE SPECTRO PHOTOMETRIC DETERMINATION OF PALLADIUM (II)

P. Govinda Chowdary[1] and V. Saleem Basha[2*]

[1]Department of Chemistry, Vignan Institute of Technology and Sciences, Deshmuki, Nalgonda, Telangana.

[2]Department of chemistry, Govt, College (UG &PG), Anantapur, A.P, INDIA. 515001.

Article Received on
23 Feb 2015,

Revised on 14 March 2015,
Accepted on 06 April 2015

***Correspondence for Author**
V. Saleem Basha
Department of chemistry, Govt, College (UG &PG), Anantapur, A.P, INDIA. 515001.

ABSTRACT

A new chromophore, 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone (HNHBH) has been synthesized, characterized and its analytical applications for the determination of palladium (II) are investigated. Palladium (II) reacts with the organic reagent in aqueous dimethyl formamide (DMF) in wide pH range forming greenish yellow coloured 1:1 (M: L) soluble complex with λ_{max} at 430 nm. The colour formation was instantaneous and was stable more than 48 hours in a neutral micellar medium (Triton X-100). Beer's law obeys in the range 0.212-7.660 µg mL^{-1} of Pd(II). The molar absorptivity, Sandell's sensitivity, detection limit, determination limit and relative standard deviation are calculated as 2.48 x 10^4 L $mol^{-1}cm^{-1}$, 0.0057 µg cm^{-2}, 0.042 µg mL^{-1}, 0.127 µg $mL^{-}1$ and 1.31 % respectively. The second and third order derivative spectrophotometric methods are also developed for the determination of palladium (II) which showed greater sensitivity and selectivity. Proposed direct and derivative methods are applied for the determination of palladium in activated charcoal, soil samples, industrial effluents, alloys and in soil, river waters.

KEYWORDS: Palladium, Spectrophotomtry, HNHBH, activated charcoal, alloys, soil samples and industrial effluents.

INTRODUCTION

Palladium and its alloys have wide range of applications both in chemical industry and in instrument making.[1] Palladium acts as good catalyst and is used to speed up hydrogenation and dehydrogenation reactions, as well as in petroleum cracking. Due to most use of Pd, Pt and Rh for use of catalytic converters in motor vehicles, the emission of these metals in to the environment has increased[2] It is alloyed with gold to produce white gold used in jewellery. Palladium is also used in dentistry, watch making, in aircraft spark plugs and in the production of surgical instruments and as electrical contacts. Palladium salts are employed in making special photographic printing paper. Palladium chloride was at one time prescribed in tuberculosis treatment at the rate of 0.065 grams per day (approximately one milligram per kilogram of body weight). Palladium is thought to be one of the allergent in view of health hazards[3] so it is an important research activity for an analytical and bio-analytical chemist to determine palladium in trace levels or ultra trace levels. Review of literature reveals that various analytical methods used for the determination of palladium including AAS method[4], neutron activation analysis[5] and spectrophotometric methods.[6-15] Most of the other spectrophotometric methods reported for palladium determination involve use of spurious organic solvents as extracting media[16-17]. Among the reported methods in aqueous medium, most of them are either less sensitive[18-20] or less selective.[21-22] In the present paper rapid, non-extractive, sensitive and selective direct, second and third derivative spectrophotometric methods are reported in micellar medium for the determination nanogram quantities of palladium(II) using a simple chromogenic reagent, 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone. The metal ion reacts with the reagent in wide pH range (1.0-7.0) forming greenish yellow coloured solution in Triton X-100. The colour formation was instantaneous and stable for more than 48 hours.

MATERIALS AND METHODS

All chemicals and solvents used were of analytical reagent grade.

Palladium (II) solution

A 0.01 M solution of palladium (II) was prepared by dissolving 0.1774 g of palladium chloride (Sigma-Aldrich) in minimum volume of 2 N hydrochloric acid and diluting to 100 ml with distilled water in a 100 ml volumetric flask. This stock solution was standardized gravimetrically using dimethyl glyoxime. Solutions of lower concentrations were prepared freshly by diluting the stock solution to carry out the analysis.

Buffer solutions

Buffer solutions of various pH values were prepared by mixing 1 M hydrochloric acid and 1 M of sodium acetate (pH 1.0-3.0), 0.2 M acetic acid and 0.2 M sodium acetate (pH 3.5-7.0), 0.2 M acetic acid and 0.1 M sodium acetate (pH 7.0) and 2M ammonium chloride and 2 M ammonium hydroxide (pH8.0-10.0) solutions in appropriate ratios. The pH of the solutions was checked with pH meter.

Triton X-100 solution

A 1% solution of Triton X-100 (Sigma chemicals) was prepared by dissolving 1 ml of concentrated Triton X-100 in boiled distilled water cooled and diluted to 100 ml with distilled water.

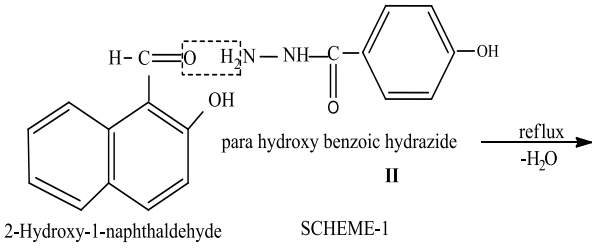
Instrumentation

The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV -160A) fitted with 1 cm Quartz cells and ELICO digital pH meter model LI – 120 respectively. The pH meter has temperature compensate arrangement and has reproducibility of measurement within ± 0.01 pH.

Reagents

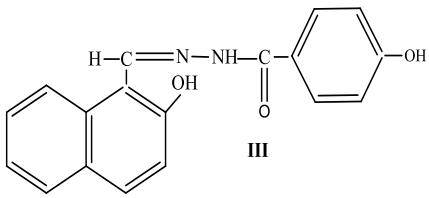
2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone (HNHBH)

Equimolar solutions of 2-hydroxy-1-naphthaldehyde (I) in methanol and parahydroxybenzoichydrazide (II) in hot aqueous ethanol were refluxed for two hours on water bath and cooled. The greenish yellow coloured product formed (III) was filtered and recrystallized from aqueous ethanol in the presence of activated charcoal (m.p.272-274^{0}c).



2-Hydroxy-1-naphthaldehyde
I

SCHEME-1



III

2-Hydroxy-1-naphthaldehyde-p-hydroxy benzoic hydrazone

Characterization

The compound was characterized by IR, NMR, Mass and UV spectral analysis The IR peaks at 3185 cm^{-1} (–OH), 3292 cm^{-1} (–NH), 1735 cm^{-1} (>C=O), 1635cm^{-1} (>C=N-) and 1383 cm^{-1} (>C=N-) and NMR peaks at δ 12.10 ppm, (–OH), δ 10.50 ppm (–NH) and δ 9.49 ppm (–CH) confirm the structure of hydrazone formed as shown in (III).

1×10^{-2} M solution of the reagent was prepared by dissolving 0.3100 g in 100 ml of dimethyl formamide (DMF). Working solutions were prepared by diluting the stock solution with DMF.

Preparations of sample solutions

Charcoal sample[25]

0.1 g of Pd-charcoal was weighed and mixed with 50 ml of 1 M nitric acid in a beaker. The mixture was heated on a hot plate until it is dried. The residue was mixed with 50 ml of distilled water, then filtered and washed with distilled water. The filtrate was finally diluted to 250 ml with distilled water. 2.0 ml of the solution was used to determine palladium present in it using the proposed method. The results are compared with those obtained by a standard procedure using nitroso-R salt.

Alloy samples[24]

A known amount of each sample was weighed and fused with five times to its weight of a fusion material, sodium carbonate, at 1050 – 1150^{o}C. Different cations present in the ore were first converted into fluorides, which were then converted into sulphates with less volatile sulphuric acid. Subsequent ignition at 1000 – 1100^{o}C for five minutes, converted the sulphates back into the corresponding oxides. The oxides formed were boiled with concentrated nitric acid until near dryness, cooled and diluted to 250ml with distilled water.

Soil sample[24]

The soil sample (5.0g) was weighed into a 250 ml teflon high pressure microwave acid digestion bomb and 50 ml of aqua-regia were added. The bomb was sealed tightly and then positioned in the carousel of a microwave oven. The system was operated at full power for 30 min. The digested material was evaporated to incipient dryness. Then, 50 ml of 5% hydrochloric acid were added and heated close to boiling to leach the residue. After cooling, the residue was filtered and the un dissolved residue was washed two times with 5% hydrochloric acid. The filtrates were quantitatively collected in a 200 ml volumetric flask and

diluted to the mark with distilled water and known amount palladium was added. The palladium content in known aliquots of the resultant solution was determined by the proposed method**.** An ICP-MS method was used as a reference method.

Industrial effluent[23]

The industrial effluent was decomposed in a 50 ml round bottom flask by heating with 10 ml of a mixture containing concentrated nitric and sulphuric acid (10+1) on a hot plate and then finally heated to near dryness. The drop wise addition of concentrated nitric acid was needed to obtain a colourless residue. The residue, neutralized with dilute sodium hydroxide solution, was then dissolved in distilled water and diluted to an appropriate volume. The palladium content was analyzed and compared with those obtained by ICP-MS method.

Applications in second order derivative spectrophotometry

The second order derivative spectrophotometric method was applied for the determination of palladium in soil sample and river water.

Direct spectrophotometry

In each of a set of 10 ml volumetric flasks, 4 ml of buffer solution (pH 4.0) (Fig.1), and 0.3 ml of HNHBH ($1x10^{-2}$M) were taken and various volumes of $1x10^{-4}$M palladium (II) solution were added. The resultant solutions were made up to the mark with distilled water. The absorbance was measured at 430 nm against the reagent blank (Fig. 2). The calibration plot was prepared by plotting the absorbance against the amount of palladium (II) (Fig.3).

Second and third order derivative spectrophotometry

Second and third order derivative spectra were recorded for the above solutions with a scan speed of fast (nearly 2400 nm min^{-1}), split width of 1 nm with nine degrees of freedom in the wavelength range 350-600 nm. The derivative amplitudes were measured at 415 nm, 465 nm for the second derivative and 427 nm and 475 nm for the third derivative curves and plotted against amount of palladium (II) to obtain the calibration plots.

RESULTS AND DISCUSSION

Direct method

The absorption spectra of [Pd(II)-HNHBH] solution and HNHBH solution at pH 4.0 were recorded in the wave length region 380-520 nm against the reagent blank and buffer blank respectively and presented in fig 1. The metal complex showed absorption maximum at 430

nm where the reagent has very low absorbance. Therefore, Pd (II) was determined by measuring the absorbance of experimental solutions at 430 nm.

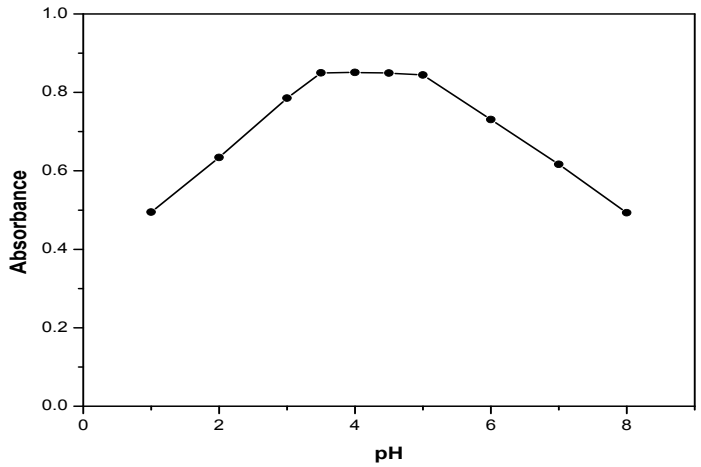


Fig. 1 Effect of pH on the absorbance of Pd (II) – HNHBH system

[Pd (II) = 5×10^{-5} M; [HNHBH] = 7.5×10^{-4} M

Wavelength = 430 nm; [Triton X-100] = 0.02%

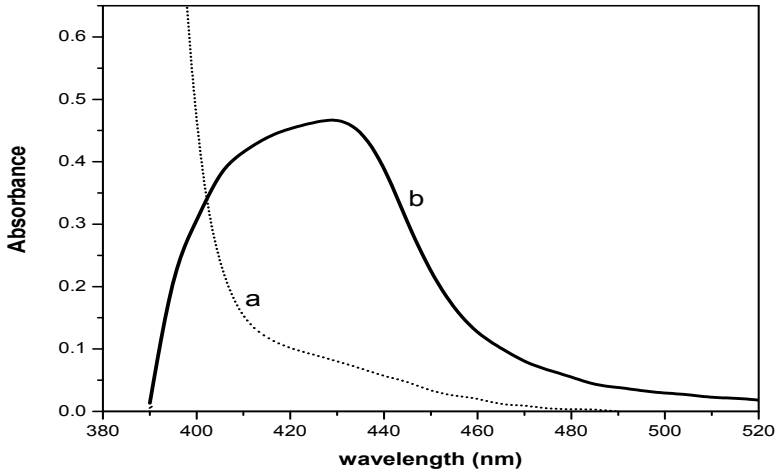


Fig. 2 Absorption spectra of (a) HNHBH Vs buffer blank

(b) Pd(II) – HNHBH Vs reagent blank

[Pd(II)] = 3×10^{-5}M ; [HNHBH] = 3×10^{-4}M

pH = 4.0 ; [TRITON-X-100] = 0.05%

Experimental data revealed that the maximum sensitivity can be obtained in the pH range 3.5-5.0. Therefore, pH 4.0 was taken as the optimum pH for the determination of Pd(II). The colour intensity of the metal complex was found to increase significantly in the presence of

0.05% triton X-100. Hence, further analysis was carried out in the presence of 0.05% of triton X-100 surfactant. The absorbance verses the amount of palladium (II) plot followed regression equation A_{430}=0.1979C + 0.004. Beer's law was obeyed in the range 0.212-7.660 μg mL^{-1} of Pd (II). The Sandell's sensitivity, detection limit, determination limit and other statistical parameters are evaluated and presented in **table 1**.

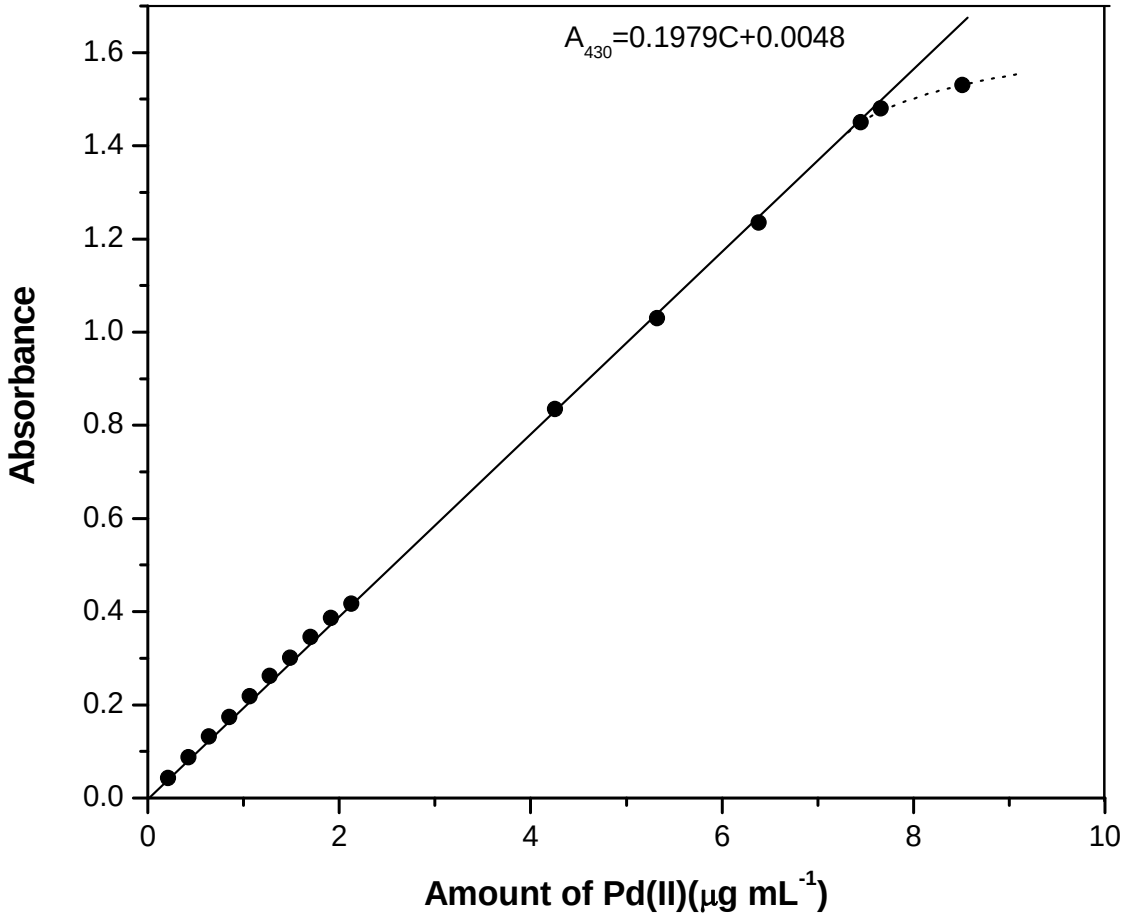


Fig. 3 Applicability of Beer's law

[HNAHBH] = 7.5 x 10^{-4}M; Wavelength = 430 nm

pH = 4.0 ; [Triton X-100] = 0.02%

Table. 1 Analytical characteristics of [Pd (II)- HNHBH]

Parameter	Direct method	Second derivative		Third derivative	
	430 nm	415 nm	465 nm	427 nm	475 nm
Beer' law range (μg mL^{-1})	0.212 - 7.660	0.044 - 2.021	0.106 - 2.021	0.020 - 2.021	0.031 - 2.021
Angular coefficient (m)	0.1979	0.0951	0.2152	0.4187	0.2808
Y-intercept (b)	+0.004	+0.0017	+0.0019	+0.0046	+0.0021

Correlation coefficient (r)	0.9995	0.9997	0.9999	0.9996	0.9999
RSD (%)	1.31	0.13	0.51	0.43	0.24
Detection limit ($\mu g\ mL^{-1}$)	0.042	0.015	0.011	0.008	0.005
Determination limit ($\mu g\ mL^{-1}$)	0.127	0.045	0.033	0.024	0.015

Effect of foreign ions

The tolerance levels of various anions and cations associated with palladium (III) were determined in the present investigations and given in **table 2**. Large number of diverse ions was found to possess reasonably high tolerance levels. Good number of metal ions which showed serious interference was masked using suitable masking agents (**table 3**). The stoichiometry of the soluble complex was calculated using Job's, molar and slope ratio methods and obtained as 1:1 (Metal:Ligand). The formation constant of the complex species was determined by Job's method as 2.48×10^6.

Table2. Tolerance limits of foreign ions

Foreign ion	Tolerance limit (folds)	Foreign ion	Tolerance limit(folds)
Citrate	4081	Mg(II)	1850
Sulphate	1920	Na(I)	1724
Phosphate	1900	Ca(II)	1685
Oxalate	1760	K(I)	1600
Bromide	1598	Ba(II)	1585
Tartrate	1480	Sr(II)	1479
EDTA	1432	Pb(II)	42
Iodide	1335	Cd(II)	38
Nitrate	1240	Te(IV), Ce(IV)	29
Carbonate	1200	Se(IV)	21
Chloride	709	Tl(III)	10
Thiocyanate	341	Zr (IV),Ag(I)	7
Fluoride	380	Mn(II)	3
Thiosulphate	67	Ir(III), Au(III), Th(IV), U(VI)	2
Thiourea	15	Sn(II)	1
		Mo	1
		Zn(II),Co(II), Ni(II), Cu(II)	<1

Amount of Pd (II) taken =1.0$\mu g\ mL^{-1}$ pH = 4.0

The method was successfully applied for the determination of palladium in activated charcoal, alloys, and soil samples and in industrial effluents. Suitable aliquots of the sample solutions were treated with required amount of reagent and surfactant and the absorbance of the resultant solutions were measured at 430 nm. The amounts of palladium present were evaluated from predetermined calibration plot.

Table.3. Elimination of interference by adding masking agents

Masking agent (µg)	Foreign ion	Tolerance limit (folds)
EDTA : 400	Ni(II)	35
	Co(II)	30
	Cu(II)	30
	Mn(II)	20
	Zn(II)	20
Citrate : 400	Mo(VI)	145
Tartrate: 1000	Th(IV)	350
	U(VI)	12

Derivative methods

The second and third order derivative spectra of [Pd(II) - HNHBH] complex solution were recorded in the wave length region 350-600 nm and shown in figures **4** and **5** respectively. The second order curve showed maximum amplitude at 415 nm and 465 nm with zero cross at 447 nm. The third order curve showed peaks and valleys at 427 nm and 475 nm with zero cross 465.5 nm. Beer's law was obeyed in the range 0.044-2.021 µg mL^{-1} at 415 nm and 0.106-2.021 µg mL^{-1} at 495 nm by the second order derivative curves. The third order curves showed Beer's law ranges 0.020-2.021 µg mL^{-1} and 0.031-2.021 µg mL^{-1} of Pd(II) at 427 nm and 477 nm respectively. The effect of diverse ions on the derivative amplitudes showed that some metal ions which interfered seriously in zero order method were tolerable at higher levels in the derivative methods **(table 4).** This is clear evidence that the derivative methods are more selective than the direct method. The second order derivative spectrophotometric method was used to determine the amount of palladium in soil and river waters.

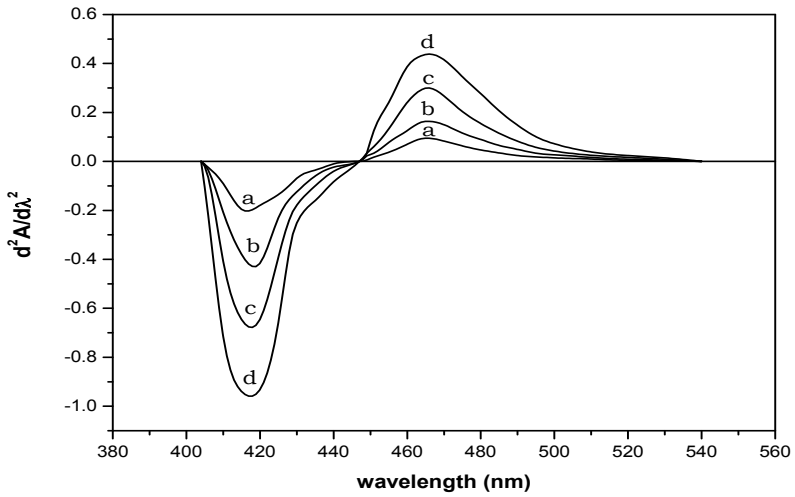


Fig.4 Second derivative spectra of Pd(II) –HNHBH

Amount of Pd(II) (µg ml^{-1}) : a. 0.425; b. 0.744; c. 1.383; d. 2.021

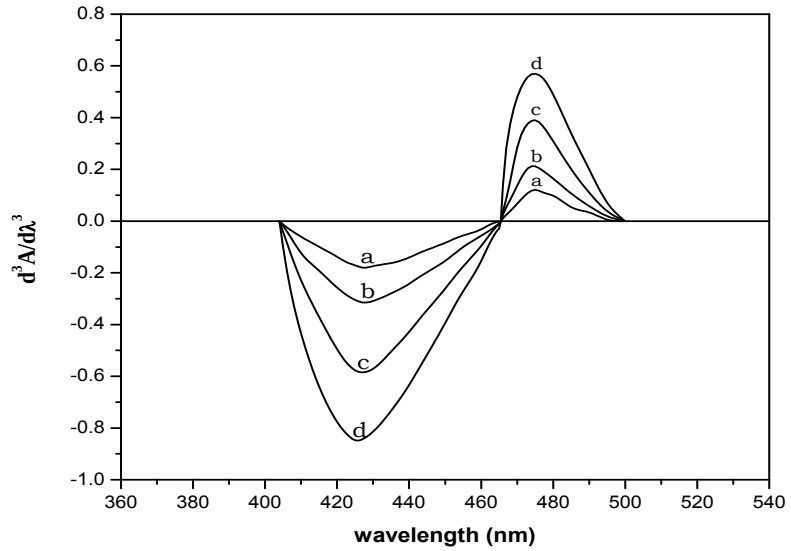


Fig.5 Third derivative spectra of Pd(II) –HNHBH

Amount of Pd (II) (µg ml^{-1}); a. 0.425; b. 0.744; c. 1.383; d. 2.021.

Table.4. Tolerance limits of foreign ions

Foreign ion	Tolerance limit(in folds)				
	Zero order	Second derivative		Third derivative	
		415 nm	465 nm	427 nm	475 nm
Ga(III)	<1	>100	interferes	>100	interferes
In(III)	<1	equal	>100	equal	interferes
La(III)	<1	interferes	interferes	>100	>100
Y(III)	<1	interferes	interferes	interferes	interferes
V(V)	<1	>100	10	>100	equal
Al (III)	<1	interferes	interferes	interferes	interferes

Table. 5 Determination of palladium in activated charcoal and alloy samples

Sample	Palladium content(%)			
	Present method*	RSD (%)	Reference method[ref]	RSD (%)
Pd- Charcoal[a]	5.154 ± 0.02	1.4	4.862 ± 0.03	1.64
			Certified value (%)	
Palladium alloy-2[b]	72.2 ± 0.008	0.84	72	-
Palladium –cobalt alloy[c]	49.5 ± 0.012	1.12	50	-

*Average of five determinations ± SD

a - 5%Pd-95%C

b- 26%Ag-2%Ni

c- 50%Pd-50%Co

Table.6 Determination of palladium in soil samples and industrial effluents

Sample	Amount of palladium (µg mL^{-1})			ICP-MS method
	Added	Found *	Actually present in the sample	
Soil	2.650	2.770 ± 0.002	0.220	0.210
Industrial effluent	1.500	1.535 ± 0.001	0.035	0.032

*mean value of five determinations ± SD

Table.7 Determination of palladium in soil and River water

Sample	Amount of Pd(II) found * (µg ml^{-1})		RSD (%)
	Proposed method	AAS method	
Soil[a]	0.174 ± 0.006	0.170 ± 0.003	1.18
River water[b]	0.083 ± 0.004	0.091 ± 0.001	2.27

*Average of five determination ± SD

a = Soil sample was procured from Geological Survey of India, Bangalore

b = water collected from Krishna river, Near Kurnool, India.

Applications

The method was successfully applied for the determination of palladium in activated charcoal, alloys, and soil samples and in industrial effluents and water samples. Suitable aliquots of the sample solutions were treated with required amount of reagent and surfactant and the absorbance of the resultant solutions were measured at 430 nm. The amounts of palladium present were evaluated from predetermined calibration plot. The results found to be in good agreement with those obtained by the standard known methods (**tables 5,6 and 7).**

Table.8. Comparison of analytical results of the present methods with already reported methods.

Reagent	Beer's law range (µg mL^{-1})	ε x 10^4 (L $mol^{-1}cm^{-}$)	Interference	Ref.
2-Mercapto-4-methyl-5-phenylazo-pyrimidine	0.7-8.4	2.05	Fe(III),Mn(II),Bi(III),Hg(II) Zn(II),Mo(VI), F^-,CN^-, PO_4^{3-}	[26]
2-Mercaptonicotinic acid	Upto 19.1	1.0	-	[27]
2-Acetylthiophene guanylhydrazone	Upto 12	0.7491	-	[28]
1-(2-Pyridylazo)-2-naphthol	0.5-10.0	1.2	Ni(II),Fe(III),I^-,SCN^-	[29]
Cyclohexylxanthate and Triton X-100	2.65-5.0	0.912	Al(III),Zn(II),Cu(II),U(VI), Ni(II),Co(II),Fe(II),EDTA	[30]
Polyethyleneglycol-ammonium sulfate-nitroso-R-salt	0-0.2	1.58	-	[31]
2-(2,3,5-Triazolylazo)-5-[(N,N-dicarboxymethyl)amino]benzoic acid	0-12	1.72	-	[32]
3-Phenoxybenzaldoxime	0.4-4.0	0.2434	-	[33]
2-Arylthiophenylnitroacetophenone	2.5-20.0	0.1612	-	[34]
Pyridoxal-4-phenyl-3-thiosemicarbazone	0.4-6.4	2.2	Co(II),Cd(II),Ni(II),Fe(II), Fe(III),Zn(II),$S_2O_3^{2-}$	[35]
1,3-Bis(hydroxymethyl) benzimidazole-2-thione	Upto 6.0	1.543	-	[36]
α-Benzilmonoxime-Triton X-100	0.2-24.0	0.80	-	[37]
2-Hydroxy-1-naphthaldehide-p-hydroxybenzoichydrazone	0.212 - 7.660	1.84	Mn(II), U(VI), Mo(VI),Th(IV), Cu(II), Zn(II), Co(II), Ni(II) interference eliminated by masking agents.	Present method (zero order)
2-Hydroxy-1-naphthaldehide-p-hydroxybenzoichydrazone	0.021 - 2.021	-	Ga(III), In(III), La(III), V(V), Tolerable upto 5 fold excess	Present method (third derivative)

CONCLUSION

Comparison of the analytical results of already reported methods and present method shown in **table 8** (Referances 26-37clearly indicates that the present proposed method is more sensitive and reasonably selective than number of other methods. All these findings cause great concern regarding public health demanding an accurate determination of these metal ions at trace levels the present study may provide awareness among the public.

ACKNOWLEDGEMENTS

The authors are thankful to the authorities of Sri Krishnadevaraya University, Anantapur for providing necessity facilities. The authors also thankful Dr. B.V. Subba Reddy IICT, Hyderabad for providing IR NMR and Mass spectral data.

REFERENCE

1. R. Sahu, S.M. Sondhi and B. Gupta, Talanta, 1995; 42(3): 401-405.
2. K. Pyrzynska, Talanta, 1998; 47(4): 841.
3. S. Caroli, A. Alimonti, F. Petrucci, B. Bocca, M. Krachler, F. Forastere, M T Sacerdote and S. mallone Spectro chim acta Part B., 2001; 56(7): 1241.
4. G. Absalan, A. Safavi & A. Massoumi, Microchemical J, 1988; 37: 212.
5. S. Lahiri, S. Dey, T K Baidya, M Nandy, D Basu & N R Das, AppI Radiat Isotopes, 1997; 48: 549.
6. H. Eskandari & G.I.Karkaragh, Bull Koreati C/tern Soc, 2003; 24: 1731.
7. D.M.Rao, K.H. Reddy & D.V.Reddy, Talanta, 1991; 38: 1047.
8. O.W. Rollins & M.M. Oldham, Anal Chem, 1971; 43: 262.
9. P. Parameshwara, J. Karthikeyan , A. Nityananda Shetty & Prakash Shetty, Ann Chini, 2007; 97: 1097.
10. I.L.Garcia, J.M. Aviles & M.H. Cordoba, Talanta, 1986; 33: 411.
11. K. Kuroda , N. Yoshikuni & Y. Kamimura, Anal Chi,iz Ada, 1972; 60: 71.
12. S.Jaya , T. Rao & T.V. Ramakrishna, J Less Common Met. 1983; 91: 261.
13. Z. Marczenko, Separation and Spectrophotometric Determination of Elements (John Wiley and Sons), 1973; 566.
14. B.K. Reddy, K.J.Reddy, J.R.Kumar, A.K. Kumar & A.V.Reddy Anal Sd, 2004; 20: 925.
15. A.K. Chhakkar & L.R.Kakkar, Fresenius J Anal Chem, 2004; 350: 127.
16. A.D. Langade and V.M. Shinde, Analyst, 1982; 107: 708-711.
17. J. Pramanik and H.R. Das, J.Indian Chem.Soc, 1982; 59: 397-400.
18. M. Blanco and S. Maspoch, Microchim Acta, 1983; 81: 11-20.
19. A.T. Gowda and H.S. Gowda, Anal.Chem, 1983; 55: 1816-1817.
20. S.P. Bag and B. Bhattacharya, J.Indian Chem.Soc, 1983; 60: 204-205.
21. A.K. Singh, B. Roy and R.P. Singh, Analyst, 1983; 108: 1203-1204.
22. K.H. Reddy and D.V. Reddy,Indian J.Chem, 1983; 22A: 723-724.
23. M.I. Toral, P. Richter and L. Silva, Talanta, 1993; 40: 1405.
24. W. Yang, Q. Hu, Z. Huang, J. Yin, G. Xie and J. Chen, J.Serb.Chem.Soc, 2006; 71(7): 821-828.
25. H. Eskandari and A.G. Saghseloo, Anal.Sci, 2003; 19: 1513-1518.