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Sensitive Derivative Spectrophotometric Determination of Palladium(II) Using 3,5-Dimethoxy-4-hydroxybenzaldehydeisonicotinoylhydrazone in presence of Micellar medium

M. Rameswara Rao[†]* and K. B. Chandrasekhar[¶]

[†] Department of Quality Control, Chemical Technical Operations Unit-1, Dr. Reddy's Laboratories Pvt. Ltd, Bollaram, Jinnaram, Medak (Dist), India
[¶] Department of Chemistry, College of Engineering, Jawaharlal Nehru Technological University Anantapur, Anantapur, Andhra Pradesh, India

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ABSTRACT

A simple and sensitive spectrophotometric method has been developed for the determination of palladium(II) using newly synthesized reagent 3,5-Dimethoxy-4-hydroxy benzaldehydeisonicotinoylhydrazone (DMHBIH) reagent in a micellar medium of Triton X-100 (neutral surfactant). Palladium(II) forms a bright yellow coloured water soluble complex with the reagent in acidic buffer medium pH 5.5. Beer's law obeyed in the range 0.1064 to 2.1284 μg/mL of Pd(II) at λmax 382 nm. The molar absorptivity and Sandell's sensitivity of coloured species are 2.44 x 10^4 L.mol^{-1}.cm^{-1} and 0.0044 μg/cm^2 respectively. Palladium(II) forms (M: L) 1:1 complex and stability constant of the complex is 2.2 x 10^7. The developed derivative spectrophotometric method was employed for the determination of palladium(II). This method has been satisfactorily applied for the determination of Pd(II) in alloy samples, hydrogenation catalyst samples and real water samples.

Keywords: Palladium(II), Derivative spectrophotometery, alloy samples, hydrogenation catalyst samples, water samples.

INTRODUCTION

Palladium is a rare and lustrous silvery white metal. It is an important industrial catalyst. It has strong resistance to corrosion in air and to the action of acids (except nitric acid) at ordinary temperatures. Palladium has lowest melting point and least dense of these platinum group metals. The metal exists in the oxidation states, +2 and +4. Palladium(II) compounds are more stable. It also exists in mineral like stibiopalladinite, brageite and several nickel sulphite ores. For increasing density, it is alloyed with silver, gold and copper. Palladium has great affinity for nitrogen containing ligands. It is used in the watch bearings, springs and balance wheels, air craft spark plugs, blood sugar test strips and also for mirrors in scientific instruments. Palladium is also used in dentistry, medicine and ground water treatment. It is used as a catalyst in the manufacture of sulphuric acid and hydrogenation process. Palladium is widely employed in jewellary and may be alloyed with platinum or substituted for it. Palladium found in many electronics including computers, mobile phones, multilayer ceramic capacitors, component plating, low voltage electrical contacts and LED/LCD televisions. Palladium salts are employed in making special photographic printing paper. Besides all these applications palladium has some adverse health effects, palladium is cytotoxic and kills or damages cells. It also causes considerable damage and inhibits enzyme activity and function. Palladium causes significant numbers allergic reactions as well as contact dermatitis, stomatitis, lichinoid reactions and periodontal gum disease [1-3].

Hydrazones are important organic analytical reagents for the determination of metal ions in microgram quantities. They react with many metal ions forming coloured complexes and act as chelating agents. In general, the technique of solvent extraction is widely used in the spectrophotometric determination of metal ions [4-5]. However, organic solvents such as benzene and chloroform are often carcinogenic, toxic and cause environmental pollution. It is significant to develop a method which does not involve solvent extraction. The potential application of hydrazone derivatives for the spectrophotometric determination of metal ions has been reviewed by Singh.et.al [6]. In the light of good analytical characteristics of hydrazones, herein we report direct and first order derivative spectrophotometric determination of Pd(II) using 3,5-Dimethoxy-4-hydroxybenzaldehydeisonicotinoyl hydrazone (DMHBIH) in presences of micellar medium without involving any extraction.

Derivative spectrophotometry is a very useful technique, in the sense that, it decrease the interference i.e. increase the tolerance limit value of the foreign ions. The great interest towards derivative spectrophotometry is due to the increased resolution of spectral bands, allowing the detection and location of the wavelengths of poorly resolved components of complex spectra and reducing the effect of spectral background interferences. Because of these characteristics, the process of isolation and pre-concentration of active components, usually required in qualitative and quantitative spectrophotometric procedures applied in the analysis of complex systems, is completely avoided. Derivative spectrophotometric methods for the determination of metal ions [7-9] are not exploited much. A micellar solution of a surfactant has the ability to enhance the stability of metal complex and has been utilized as a medium for the spectrophotometric determination of the metal chelate [10-12].

MATERIALS AND METHODS

Apparatus

A Shimadzu 160A, microcomputer based UV-VIS spectrophotometer equipped with 1.0 cm quartz cells was used for all spectral measurements. The instrumental parameters were optimized and the best results were obtained with a scan speed 145 nm/min., slit width of 1.0 nm and $\Delta\lambda$ = 2 nm for the first order derivative mode in the wavelength range 350-650 nm. ELICO LI-120 digital pH meter was used for the pH adjustments. The reproducibility of the measurements is within 0.01 pH. Sartorius BS/BT 2245 model (Germany make) electronic analytical balance having maximum capacity of 220 g and sensitivity of ± 0.1 mg was used for weighing purpose.

Reagents

All chemicals used were of A.R grade unless stated. All solutions were prepared with doubly distilled water.

Palladium(II) stock solution: The standard Pd(II) solution (0.01 M) was prepared by dissolving accurately weighed 0.1773 g of $PdCl_2$ (AR Johnson Matthey & Co. Ltd, London) in a few mL of dilute hydrochloric acid and made up to the mark with doubly distilled water in a 100-mL of volumetric flask and standardized [13]. The working solutions were prepared by diluting the stock solution to an appropriate volume.

Triton X-100 solution: Aqueous solution of 5% Triton X-100 prepared by diluting 5 mL of Triton X-100 (GR Merk) to 100mL with doubly distilled water.

Buffer Solutions: Buffer solutions were prepared by 1.0 M Hydrochloric acid- 1.0 M Sodium acetate (pH 0.5-3.5); 0.2 M Acetic acid – 0.2 M Sodium acetate (pH 4.5- 7.0); 0.25 M Sodium tetra borate decahydrate - 0.1 M Hydrochloric acid (pH 8.0 – 9.1); 0.25 M Sodium tetra borate decahydrate - 0.1 M sodium hydroxide (pH 9.2-10.8). Solutions of various diverse ions of suitable concentrations were prepared using AR grade chemicals.

Synthesis of 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH)

The reagent 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH) was synthesized by refluxing equimolar amounts of 3,5-dimethoxy-4-hydroxy benzaldehyde and isonicotinoylhydrazide. In a 250 mL round bottom flask hot ethanolic solutions of 3,5-dimethoxy-4-hydroxybenzaldehyde (1.8218 g, 0.01 mole) and isonicotinoyl hydrazide (1.3714 g, 0.01 mole) are mixed and refluxed using water condenser for 5 hours. On cooling the reaction mixture, a light greenish coloured crystalline product was separated out, collected by filtration and washed several times with (20%) ethanol in water and dried in vacuo. The resulting hydrazone was recrystalised by using ethanol (Yield, 76%; mp 221^{0}C).

The infrared spectrum of the reagent shows bands at ν 3429.03 (NH), 2924.16 (OH), 1658.62 (>C=O), 1578.92 (C=N), 1514.12 (C=N pyridine ring), 1372.71 (N-H primary amide). The ^{1}H NMR (200 MHz) spectrum of the reagent was recorded in DMSO solvent. It shows signals corresponding to δ 11.9 (s, 1H, NH), 8.97 (s, 1H, OH phenolic), 8.78 (d, 2H, ArH pyridine ring), 8.34 (s, 1H, N=C-H), 7.8 (d, 2H, ArH pyridine ring), 7.01 (s, 2H, ArH aldehydic), 3.8 (s, 6H, $-OCH_3$ (2 methoxy)), 3.3 (s, 2H, water in solvent), 2.5 (s, 6H, DMSO solvent). The mass spectrum shows that molecular ion peak at m/z 302.2 (M+1). The structure of DMHBIH was confirmed based upon above IR, NMR and mass spectral data, given in Figure 1. The product is sparingly soluble in methanol but easily soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Hence, reagent stock solution (0.01 M) was prepared by dissolving 301.30 mg of DMHBIH in 100 mL of DMF. The reagent solution is stable for 48 hours.

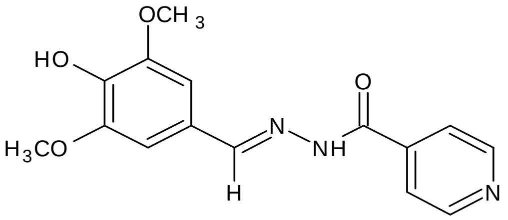

Figure 1. Structure of 3,5-dimethoxy-4-hydroxybenzaldehydeisonicotinoylhydrazone(DMHBIH).

Analytical properties of DMHBIH

The reactions of some important metal ions were tested at different pH values. The samples were prepared in 25-mL volumetric flasks by adding 10 mL of buffer solution (pH 1.0 – 11.0), 0.5 mL of 1×10^{-3} M metal ion, 1.0 mL of Triton X-100 (5%) and 0.5 mL of 1×10^{-2} M DMHBIH reagent solution. The mixture was diluted up to the mark with doubly distilled water. The absorbance measured in 350-700 nm range against reagent blank. The results are summarized in Table 1.

Table 1. Characteristics of DMHBIH complexes in solution

Metal ion	λmax (nm)	pH	Surfactant used	Colour of the complex	Molar absorptivity (L.mol^{-1}.cm^{-1})
Pd(II)	382	5. 5	Triton X-100	Bright yellow	2.44×10^4
Cu(II)	400	8.0	Triton X-100	Bright yellow	1.08×10^4
Au(III)	384	4.0	SDBS	Yellow	2.9×10^4
Ru(III)	390	4.25	Triton X-100	Brownish yellow	1.7×10^4

Recommended procedure

Determination of Pd(II) (Zero order spectrophotometry)

An aliquot of the solution containing 0.1064 – 2.1284 µg/mL of Pd(II), 10 mL of buffer solution pH 5.5, 1.0 mL of Triton X-100 (5%) and 1.0 mL of 5×10^{-3} M DMHBIH reagent solution were taken in a 25-mL volumetric flask and the solution was diluted up to the mark with doubly distilled water. The absorbance was measured at 382 nm in a 1.0 cm cell against reagent blank prepared in the same way, without metal ion. The measured absorbance is used to compute the amount of Pd(II) from the pre-determined calibration curve.

First order derivative spectrophotometry

For the above solutions, first-order derivative spectra of Pd(II)-DMHBIH were recorded with scan speed fast having a degree of freedom 9, in the wavelength range from 350-650 nm. The derivative peak height was measured by peak-zero method at 414 nm. The peak height was plotted against the amount of Pd(II) to obtain the calibration curve.

Analysis of alloy samples

0.5 g sample of alloy was digested in 15 mL of aqua-regia by warming and the solution was evaporated to dryness. The residue was dissolved in 10 mL of diluted HCl and resulting solution concentrated to 5.0 mL, diluted to 50 mL with doubly distilled water, filtered and made up to the mark in a 100-mL volumetric flask.

Analysis of hydrogenation catalyst samples

About 0.3 g of catalyst sample was transferred into 250-mL beaker, treated with 5.0 mL of 2.0 M HNO_3 and covered. When the solution of gas had diminished 10 mL of aqua-regia was added and the solution was evaporated to near dryness on a sand-bath. The residue was dissolved in 5.0 mL of 2.0 M HNO_3 and diluted to mark with doubly distilled water in a 250 mL volumetric flask. Suitable aliquots were taken and analyzed for palladium(II) using recommended procedure discussed above.

Real water samples [14]

Each filtered (with whatman No. 40) river water sample (250 mL) was mixed with 10 mL of concentrated nitric acid in 500 mL distillation flask. The sample was digested in the presence of excess potassium permanganate solution according to the method recommended by Fifield et.al [15]; the solution was cooled and neutralized with a dilute NH_4OH solution. The digest was transferred into a 25-mL standard flask and diluted up to the mark with double distilled water.

RESULTS AND DISCUSSION

The reagent 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH) was easily synthesized as any other Schiff base reagent. The new chromogenic reagent DMHBIH was not used for the spectrophotometric determination of the Pd(II). Aldehyde-isonicotinoylhydrazone reagents are not exploited much for spectrophotometeric determination of metal ions. Moreover, the derivative methods using this class of reagents are scare.

The de-protonation constants of DMHBIH have been determined by recording UV-Visible spectra of µM (1.2×10^{-6} M) at various pH values [16] and by taking the arithmetic mean of the values obtained from the measurements at five different wavelengths. The values of de-protonation of ligand are 5.1 (pK_1) and 8.2 (pK_2). The possible species which may be formed at different pH values are shown in Figure 2. In acidic medium, the ligand presumably exists in enolic form and co-ordinates the metal ion as mono-anion to give neutral complexes. The colour reactions of some important metal ions with DMHBIH are summarized in Table 1. The colour reactions are mainly due to complex formation of DMHBIH with divalent, trivalent metal ions such as Pd(II), Cu(II) Au(III) and Ru(III) in acidic medium to give intense coloured complexes.

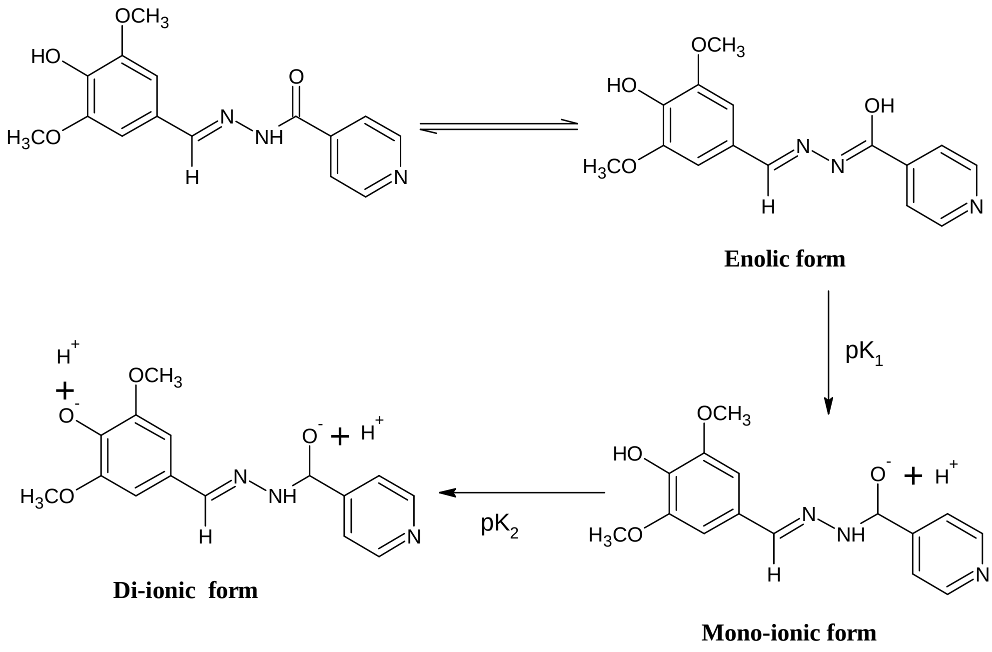

Figure 2. Different species of DMHBIH at different pH values.

Absorption spectra

The absorption spectra of DMHBIH and its Pd(II) complex under the optimum conditions are shown in Figure 3. The Pd(II)-DMHBIH complex shows the maximum absorbance at 382 nm, where the reagent blank does not absorb appreciably.

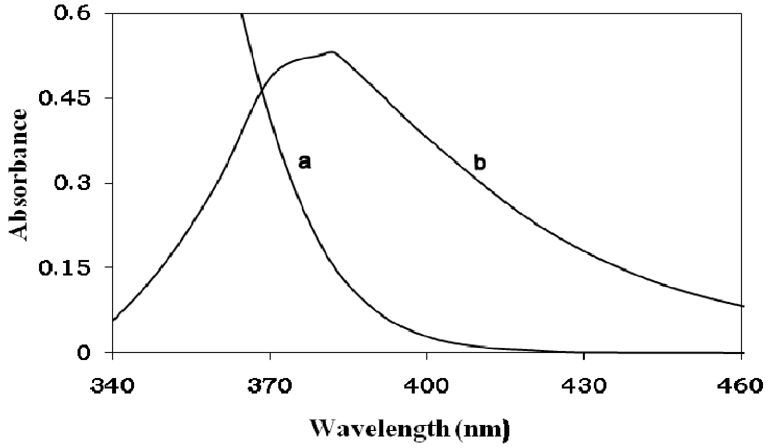

Figure 3. Zero order absorption spectra of

a) Reagent (DMHBIH) vs. buffer blank.
b) Pd(II)-DMHBIH complex vs. reagent blank.
Pd(II) = 0.1064 µg/mL, [DMHBIH] = 2 x 10^{-4} M, pH = 5.5,
Triton X-100 (5%) = 1.0 mL.

Effect of pH

It was observed that the colour reaction between Pd(II) and the reagent DMHBIH was instantaneous even at room temperature in pH range 2.0 to 7.0. The study of the effect of pH on the colour intensity of the complex showed that the maximum constant absorbance was obtained in the pH range 4.5 to 7.0. Therefore, pH 5.5 was kept constant throughout the experiment.

Effect of Time

A slow decrease in absorbance was observed for the coloured species after 15 min. The stability of the complex was increased by adding surfactant. The absorbance of Pd(II)-DMHBIH remain constant for more than 6 hours in presence of neutral surfactant Triton X-100.

Effect of Surfactants

The effect of various surfactants such as Triton X-100, Sodium Dodecyl Benzene Sulphonate (SDBS) and Cetyl Trimethyl Ammonium Bromide (CTAB) on the absorption profiles of the Pd(II)–DMHBIH system has been investigated and presented in Table 2. In presence of Triton X-100 the complex is more stable and exhibited maximum absorbance. Hence, Triton X-100 is selected for further studies.

Table 2. Effect of various surfactants on the Pd(II)-DMHBIH complex

Surfactant (5%)	Nature of Surfactant	Absorbance at 382 nm
None	-	0.475
Triton X-100	Neutral	0.531
CTAB	Cationic	0.257
SDBS	Anionic	0.422

Conditions: 1.0 mL of surfactant (5%), 10 mL of buffer pH 5.5,
1.0 mL of DMHBIH (5 x 10^{-3} M) reagent, 0.1064 µg/mL Pd(II).
Blank prepared in same conditions without metal ion.

Effect of Triton X-100

A study on the effect of volume of Triton X-100 on absorbance of the complex indicates that, absorbance of the metal complex remains constant over a range of 1.0 to 4.0 mL of Triton X-100 (5%). Therefore, 1.0 mL of Triton X-100 (5%) was sufficient in all analytical studies. Triton X-100 serves to stabilize and sensitize the metal complex.

Effect of DMHBIH concentration

When varying the volume of reagent DMHBIH (5 x 10^{-3} M) from 0.5 mL to 4.0 mL, the constant absorbance was obtained from 0.5 mL to 2.0 mL. A slow decrease in the absorbance of complex was observed from 2.5 mL to 4.0 mL (i.e. above 25-fold molar of reagent). Therefore, a 5-fold molar excess of reagent is adequate for complete and constant colour development.

Order of addition of reactants

The order of addition of metal ion, DMHBIH Reagent, buffer solution and surfactant has no adverse effect on the absorbance of the Pd(II)-DMHBIH coloured complex.

Calibration Graphs and Analytical Characteristics

From the calibration plots it was observed that, the system obeyed Beer's law in the range 0.1064 – 2.1284 μg/mL of Pd(II) with excellent linearity in terms of correlation coefficient value (r = 0.99). However, the practical range of determination of Pd(II) obtained from Ringbom's curve is 0.4256 - 2.1284 μg/mL at 382 nm. The molar absorptivity and Sandell's sensitivity of the Pd(II)-DMHBIH complex are 2.44 x 10^4 L.mol^{-1}.cm^{-1} and 0.0044 μg.cm^{-2} respectively. The specific absorptivity of the complex is 0.229 mL.g^{-1}.cm^{-1}. The precision of the method in terms of relative standard deviation (n =10) for the determination of 1.0642 μg/mL of Pd(II) is 0.02%. Important analytical parameters of Pd(II)-DMHBIH are summarized in Table 3.

Table 3. Important Analytical parameters of Pd(II)-DMHBIH complex

Parameter	Results	
	Zero order	first order derivative
λmax (nm)	382	414
Detection limit (μg/mL)	0.1100	-
Limit of Quantization (μg/mL)	0.3299	-
Regression equation Y= a + bx		
Slope (b)	0.2247	0.0768
Intercept (a)	0.0258	0.0101
Correlation coefficient (r)	0.9985	0.9979

Composition and stability of the complex

The composition of the complex is determined by Job's continuous variation method and molar ratio method is found to be 1:1 [Pd(II): DMHBIH]. The stability constant of the complex is determined as 2.2 x 10^7 by Job's method.

Derivative spectrophotometry is a useful technique because it decreases the interference i.e. increase the tolerance limit value of foreign ions and may be advantageously used for the determination of metal ion having overlapping spectra. The conceptual simplicity, relatively quick and easy realization, increased selectivity in the analysis of minor components is the main reasons why the interest in derivative spectra is constantly growing for practical applications. The recommended derivative procedure has been employed for the determination of palladium(II) using DMHBIH.

The first derivative spectrum (Figure 4) shows maximum amplitude at 414 nm with a zero cross at 387 nm. The derivative amplitudes were measured by following peak-zero method. The typical first order derivative spectra of the Pd(II)–DMHBIH complex recorded at different amounts of palladium(II) under the optimum experimental conditions and shown in Figure 5. This shows that, the derivative amplitudes measured at 414 nm for first order were found to be proportional to the amount of palladium(II).

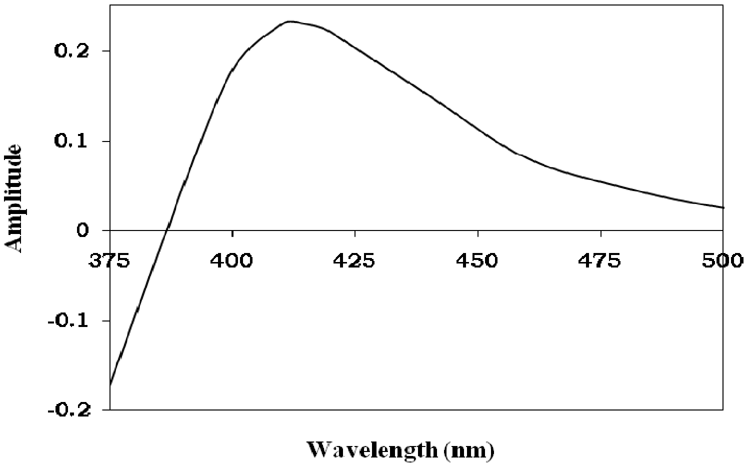

Figure 4. First order derivative spectrum of Pd(II)-DMHBIH vs. reagent.

Pd(II) = 0.1064 µg/mL, [DMHBIH] = 2 x 10^{-4} M, pH = 5.5, Triton X-100 (5%) = 1.0 mL.

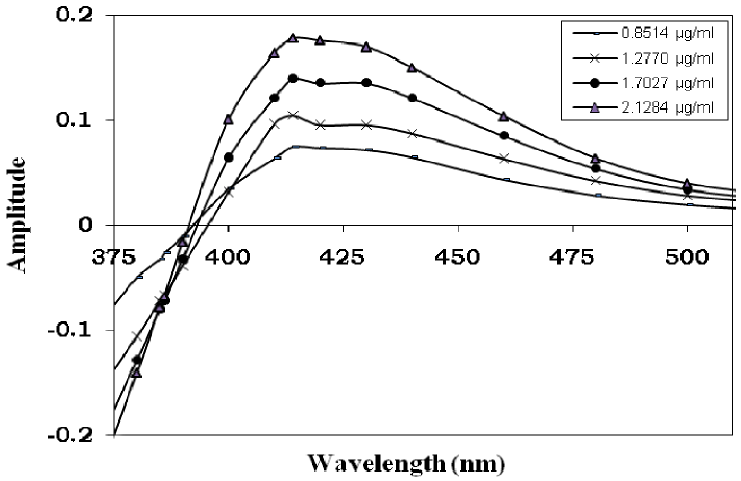

Figure 5. Typical first order derivative spectra of Pd(II)-DMHBIH vs. reagent.

Pd(II) (µg/mL) = 0.8514; 1.2770; 1.7027; 2.1284. [DMHBIH] = 2 x 10^{-4} M, pH = 5.5, Triton X-100 (5%) = 1.0 mL.

Effect of diverse ions

The effect of various diverse ions in the determination of Pd(II) was studied to find out the tolerance limit of foreign ion in the present method.

Table 4. Tolerance limit of foreign ions in the determination of 1.0642 µg/mL of palladium(II).

Ion added	Tolerance limit (µg/mL)	
	Zero order	First order derivative
Sulphate	3843	3843
Oxalate	2289	2289
Iodide	2284	2792
Nitrate	2108	2480
Bromide	1438	2078
Acetate	1417	1653
Urea	845	1207
Fluoride	646	760
Citrate	227	379
Phosphate	190	380
Tartarate	59	178
Borate	49	246
Ascorbic acid	6.0	57
Thiocynade	2.3	7.0
Thiourea	0.2	1.0
U(VI)	476	761
Sb(III)	390	487
Cd(II)	382	450
Ba(II)	302	385
Sr(II)	298	351
Zr(IV)	237	292
La(III)	195	222
Mn(II)	100	121
Mg(II)	100	120
Se(IV)	100	126
Co(II)	94	118
Al(III)	68	84
Pb(II)	66	83
Bi(III)	60	85
Hg(II)	40	80
OS(III)	45	75
Ni(II)	33	47
Mo(VI)	27	38
Zn(II)	26	52
As(III)	25	30
W(VI)	5.0	15
Sn(II)	5.0	48
Ce(IV)	5.0	6.0
V(V)	5.0	10
Ag(I)	4.0	22
Fe(III)	2.2 [a], 3.4 [b]	5.0 [a,b]
Rh(II)	3.0	4.0
Pt(II)	2.3	7.0
Cu(II)	0.3, 0.5 [c]	1.3, 3.0 [c]
Cr(VI)	0.4	1.0
Au(III)	0.3	0.2
Ru(III)	0.2	2.0

'a' Masked with 152 µg/mL of phosphate,
'b' Masked with 228 µg/mL of fluoride
'c' Masked with 0.2 µg/mL of thiourea

The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error ± 2% in the absorbance or amplitude. The results are given in Table 4.

The data obtained in derivative method is also incorporated. The data suggest that several commonly associated anions and cations do not interfere when they present in large excess. Sulphate, oxalate, iodide and nitrate do not interfered when they are present more than 2000 µg/mL. Bromide and acetate do not interfered up to 1400 µg/mL. The larger amounts (> 300 µg/mL) of cations such as uranium(VI), antimony(III), cadmium(II), and barium(II) do not interfered. Metals like strontium(IV), zirconium(IV), lanthanum(III), manganese(II), magnesium(II) and selenium(IV) do not interfered when they present up to 100 µg/mL. Whereas, the metals copper(II), chromium(VI), gold(III) and ruthenium(III) are seriously interfered. The tolerance limit of many anions and cations are more in derivative method when compared to zero order. This shows that derivative method is more selective than zero order spectrophotometric method. The metal like iron(III) is masked with phosphate, fluoride and Copper(II) is seriously interfered even after adding masking agent such as thiourea.

Applications

The spectrophotometric determination of Pd(II) in the alloy samples, hydrogenation catalyst samples and real water samples were carried out by employing the recommended procedure. A known aliquot of the sample solution was taken in a 25-mL volumetric flask containing 10 mL of buffer solution pH 5.5, 1.0 mL of Triton X-100 (5%) and 1.0 mL of $5x10^{-3}$ M DMHBIH reagent solutions. The contents in the flask were made up to the mark with doubly distilled water. The amount of palladium(II) present in these samples was computed from a pre-determined calibration plot and results are summarized in Table 5, 6 and Table 7 respectively.

Table 5. Determination of palladium(II) in alloy samples

Sample composition	Proposed method			
	Amount found* (%)		RSD (%)	
	Zero order	First order derivative	Zero order	First order derivative
Pd, 72; Ag, 26; Ni, 2 %;	72.4	72.3	- 0.55	- 0.42
Pd, 96, Ru, 2; Rh, 2%;	94.7	95.2	+ 1.35	+ 0.83
Stibiopalladinite mineral (Pd, 75%; Sb, 25%)	74.1	74.4	+ 1.20	+ 0.79

* *Average value of five determinations*

Table 6. Determination of palladium(II) in hydrogenation catalyst

Sample	Amount of Pd(II) present (%)	Present method			
		Amount found* (%)		RSD (%)	
		Zero order	First order derivative	Zero order	First order derivative
Pd-$CaCO_3$	5	4.93	5.09	+1.4	-1.8
Pd-$BaCO_3$	5	5.14	4.96	- 2.8	+ 0.8
Pd-$BaSO_4$	5	4.88	4.94	+ 2.4	+ 1.2
Pd-charcoal	10	9.89	9.91	+ 1.1	+ 0.9

* *Average value of five determinations*

Table 7. Determination of palladium(II) in real water samples

sample	Pd(II) added (µg/mL)	Palladium(II) found (µg/mL)			Recovery (%)	
		AAS method	Present method			
			Zero order	First order derivative	Zero order	First order derivative
River water sample	5.0	4.96	4.58	4.59	91.8	91.80
Well water sample	100	9.88	9.78	9.87	97.8	98.7
Pond water sample	12	11.94	11.79	11.87	98.3	98.9

** Average value of best three among five determinations*

CONCLUSION

The present method using 3,5-dimethoxy-4-hydroxybenzaldehydeisonicotinoyl hydrazone (DMHBIH) as Spectrophotometric reagent for the determination of palladium(II) in aqueous medium is sensitive and simple. This method was favorably compared with previously reported spectrophotometric methods [17-23] presented in Table-8.

Table 8. Comparison of spectrophotometric methods for the determination of palladium(II)

Reagent	λmax (nm)	pH	Beer's law range (µg/mL)	Molar absorptivity (L.mol^{-1}.cm^{-1})	Extraction/ heating	Ref.
2,2'-dipyridyl-2-pyridylhydrazone (DPPH)	560	4.0	-	3.0 x104	Extn CHCl$_3$	17
Isonitroso-4-methyl-2-pentane	330	4.0	0.10-10.0	5.4 x 10^{4}	Extraction	18
Pyridoxal-4-phenyl-3-thiosemicarbazone	460	3.0	0.40-6.40	2.2 x 10^{4}	Extn. Benzene	19
di4-(2-pyridylazo)-resorcinol (PAR)	520	9.0-11.0	0.11-2.03	8.0 x 10^{5}	At 90^{0}C Extn. Molten Napthalene	20
Furfuraldehyde thiosemicarbazone (FFTSC)	360.5	1.0-5.0	0.17-1.70	3.99 X 10^{4}	Aqueous	21
2-(2-Quinolylazo)-5-ethyl amino benzoic acid	625	1.0-2.0	0.01-0.60	1.51 x 10^{5}	Aqueous	22
O-Hydroxyacetophenone thiosemicarbazone	370	6.0	0.42-10.6	9 x 10^{3}	Aqueous	23
3,5-dimethoxy-4-hydroxy benzaldehydeisonicotinoyl hydrazone	382	5.5	0.1064 – 2.1284	2.44 x 10^{4}	Aqueous	Present method

Most of the spectrophotometric methods involve either extraction [17-19] or heating of the reaction mixture [20]. However, heating at a specific temperature for a long time or extraction of components is laborious and time consuming. The present method is not laborious and there is no need of heating the components or pre-extraction. Although the 4-Hydroxy-3,5-dimethoxybenzaldehyde-4-Hydroxybenzoylhydrazone and Cinnamldehyde-4-hydroxy benzoylhydrazone [9] methods are sensitive, they suffer from the serious interference of molybdenum(IV), magnesium(II) and uranium(VI). Large amounts of sulphate, acetate, oxalate and uranium, moderate amount of the molybdenum(VI), magnesium(II) do not interfere in the present method. This method is also free from the interference of tin(IV), arsenium(III) and other rare earth metals. Further the Triton X-100 enhances the stability of the metal complex.

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