ISSN 0974 - 9373

Vol. 15 No.1 (2011) **Journal of International Academy of Physical Sciences** pp. 95-104

Direct and Derivative Spectrophotometric Determination of Pd (II) Using 3,5-Dimethoxy-4-hydroxybenzaldehyde benzoylhydrazone(DMBBH) in Presence of Micellar Medium

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(Received December 24, 2010)

Abstract: A simple and sensitive spectrophotometric method has been developed for the determination of Palladium(II) using 3,5-Dimethoxy-4-hydroxy benzaldehyde benzoyl hydrazone (DMBBH) in a neutral surfactant of Triton X-100(5%) (micellar medium). Palladium (II) forms an yellow coloured water soluble complex with the reagent in acidic medium pH 4.25. The molar absorptivity and Sandell's sensitivity of coloured species are 1.86 x 10^4 L.mol^{-1} cm^{-1} and 0.0054 μg/cm^2 respectively. Beer's law is obeyed in the range 0.266-3.1926 μg/ml of Pd(II) at λ_{max} at 376 nm. The developed derivative spectrophotometric method was employed for the determination of palladium (II). This method has been satisfactorily applied for the determination of palladium (II) in Alloys and hydrogenation catalyst .

Keywords: Palladium (II), 3,5-dimethoxy-4-hydroxybenzaldehyde benzoylhydrazone (DMBBH), Micellar Medium, derivative spectrophotometry.

1. Introduction

The potential analytical applications of hydrazone derivatives have been reviewed by Singh et al[1]. Hydrazones are important classes of known analytical reagents[2-8.] These reagents are formed by the condensation of hydrazine and carbonyl compound. Hydrazones are also found to have biological activities. These compound contain azomethine nitrogen atom and this is responsible for their reactivity with number of transition metal ion which form coloured complex.In continuation of our ongoing work on the analytical application of hydrazone ,we reported herein spectrophotometric determination of Palladium (II) using 3,5-dimethoxy-4-hydroxy benzaldehyde benzoylhydrazone (DMBBH).

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. It always occurs with platinum group metals and is found in native metallic form. All the platinum group metals share similar chemical properties, but palladium is unique in the sense that it 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. It has great affinity to absorb hydrogen. For increasing density, it is alloyed with Ag, Au and Cu. 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. 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 SED/OLED/LCD televisions. Palladium salts are employed in making special photographic printing paper. Solutions of palladium chloride or the palladium, potassium sulphite are used for detecting carbon monoxide in the air of industrial areas. Palladium(II) forms an yellow coloured water soluble complex with DMBBH in acidic pH solution. The Stability of the complex was increased by adding neutral surfactant triton X-100.The absorbance of [Pd(II)-DMBBH] remains constant for more than 2 hours.

2. Experimental

A shimadzu 160A, microcomputer based UV-VIS spectrophotometer equipped with 1.0cm quartz cells was used for all spectral measurements. The instrumental parameters are optimized and the best results were obtained with scan speed fast, slit width of 1nm and $\Delta\lambda$=2nm for first order derivative mode in the wavelength range 350-650nm. ELICO L1-120 digital pH meter was used for the pH adjustments.

All chemicals used were of A.R grade unless stated. All solutions were prepared with doubly distilled water. The standard Palladium (II) solution (0.01M) was prepared by dissolving accurately weighed 0.1773 g of $PdCl_2$ was dissolved by adding few drops of Hydrochloric acid and dissolved by using doubly distilled water and made up to the mark in a 100-ml of volumetric flask. The stock solution was standardized by standard procedure. The working solutions were prepared by diluting the stock

solution to an appropriate volume. Aqueous solution of 5% TritonX-100 was prepared by diluting 5ml of TritonX-100 (A.R Merck) to 100ml with doubly distilled water. Buffer solutions (phosphate buffers) were prepared by using 0.1M HCl, 0.1M NaOH, 0.1M disodium hydrogen phosphate and 0.1M potassium dihydrogen phosphate. Solutions of various ions of suitable concentrations were prepared using AR grade chemicals.

The reagent 3, 5-dimethoxy-4-hydroxybenzaldehy debenzoylhydrazone (DMBBH) was synthesized by refluxing equimolar amounts of 3, 5-dimethoxy-4-hydroxybenzaldehyde and benzhydrazide. In a 250 ml round bottomed flask hot ethanolic solution of 3,5-dimethoxy-4-hydroxybenzaldehyde (1.8217g, 0.01 mole) and hot ethanolic solution of benzhydrazide(1.3615g, 0.01mole) were mixed and refluxed using water condenser for 3 hours. On cooling the reaction mixture, an yellow coloured product separated out, which was collected by filtration and washed with double distilled water. The resulting hydrazone was recrystallized using 50% ethanol (yield, 76%, mp 225^0C) and the structure of DMBBH shown in figure -1.

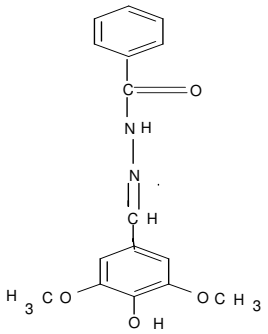

Fig.1. Structure of 3,5-Dimethoxy-4-hydroxybenzaldehyde benzoylhydrazone(DMBBH)

The resulting hydrazone was recrystalized using 50% ethanol (yield, 76%, mp 225^0C). The reagent solution (0.01 M) was prepared by dissolving 0.30032 g of DMBBH in 100 ml of Dimethylformamide (DMF). The reagent solution is stable for 48 hours. The reaction of some important metal ions was tested at different pH values. The samples were prepared in 10ml volumetric flasks by adding buffer solution 3.0 ml (pH 3-5), metal ion 0.5 ml of $1x10^{-3}$M, Tritonx-100 (5%) 0.5ml and DMBBH 0.5 ml of $1x10^{-2}$M solution. The mixture was diluted up to the mark with distilled water. The absorbance was measured in 300-700nm range against reagent blank.

For the spectrophotometric determination of Palladium (II), an aliquot of the solution containing 0.2660-3.1926 μg/ml of Palladium (II), 3.0ml of buffer solution (pH 5.0), 0.5ml of 5% TritonX-100 and 0.5ml of $5x10^{-3}$M

DMBBH reagent solution were taken in 10 ml volumetric flask and the solution was diluted up to the mark with doubly distilled water. The absorbance was read at 376 nm in a 1.0cm cell against reagent blank prepared in the same way is shown in figure -2. The measured absorbance was used to compute the amount of Palladium (II) from the predetermined calibration curve.

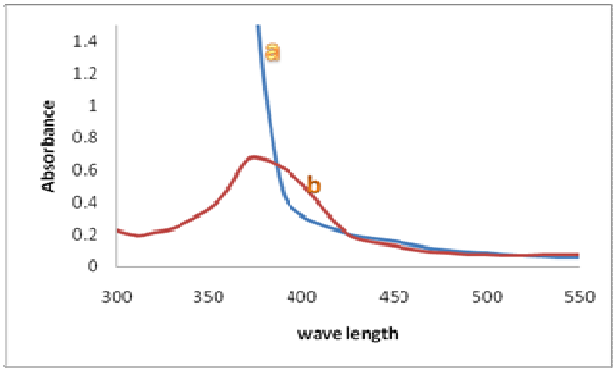

Fig.2. Zero order Absorption spectra (a) Reagent (DMBBH) Vs DMF blank. (b) Pd(II)-DMBBH complex of µg/ml Pd(II)

The first-order derivative spectrum was recorded with scan speed fast having a degree of freedom 9, in the wave length range from 350-650nm. The first-order derivative peak height was measured at 435nm is shown in figure-4. The peak height was plotted against the amount of Palladium (II) to obtain the calibration curve. The second order derivative spectrum of [Pd (II)-DMBBH] system was recorded peak height at 446nm.The third order derivative spectrum was recorded peak height at 464 nm and The fourth order derivative spectrum was recorded peak height at 508 nm. Calibration plot was constructed by plotting the derivative amplitude against the amount of Pd (II).

3. Results and discussion

The reagent 3, 5-dimethoxy-4-hydroxybenzaldehyde benzoylhydrazone (DMBBH) was easily synthesized as any other Schiff base reagent. The new chromogenic reagent DMBBH was used for the spectrophotometric determination of Pd(II). The colour reactions of some important metal ions with DMBBH are summarized in Table-1.

The absorption spectrum of DMBBH and its Pd (II) complex under the optimum conditions are shown in Figure-2. The [Pd (II)-DMBBH] complex shows the maximum absorbance at 376 nm, where the reagent blank does not absorb appreciably.

Table-1: The colour reactions of some important metal ions with DMBBH

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Metalion	P^H	λ_{max} (nm)	Molar absorptivity (ε) ($L.mol^{-1}cm^{-1}$)
Au(III)	4.25	380	2.32×10^4
Cu(II)	9	435	$3.16x\ 10^4$
Pd(II)	5	376	$1.86 \times 10^{4*}$

Palladium (II) reacts with DMBBH in acidic buffer to give yellow coloured water soluble complex. The colour reaction between Pd (II) and DMBBH was instantaneous even at room temperature in pH range 3.0-5.0, the maximum colour intensity was observed at pH 4.25 in presence of neutral surfactant Tritonx-100(5%).

A slow decrease in absorbance was observed for the coloured species after 15 min. The stability of the complex was increased by adding neutral surfactant Tritonx-100. The absorbance of [Pd (II) – DMBBH] remains constant for more than 2 hours.

The effect of surfactants such as Tritonx-100, Sodium dodecyl benzene sulphonate (SDBS) and cetyl trimethyl ammonium bromide (CTAB) on the absorption profiles of the system has been investigated and presented in Table-2. In presence of Tritonx-100(5%) the complex is more stable and exhibited maximum absorbance. Hence Tritonx-100(5%) has been selected for further studies.

Table-2. Influence of different surfactants on the [Pd (II)-DMBBH] complex

Surfactant	Type	Absorbance at 380 nm
None		0.421
Tritonx-100(5%)	Neutral	0.651
CTAB(5%)	Cationic	0.517
SDBS(5%)	Anionic	0.588

When varying amounts of 5% Tritonx-100 solution from 0.5ml to 4.0 ml, the constant absorbance was obtained from 0.5ml. The absorbance remains constant up to 4.0ml of 5% Tritonx-100. Hence 0.5ml of 5% Tritonx-100 was sufficient in all analytical studies. Tritonx-100 serves to stabilize and sensitize the metal complex. Similarly when varying the volume of reagent DMBBH ($1x10^{-3}$M) from 0.5ml to 4.0ml, the constant absorbance was obtained from 0.5 ml. therefore a 10 fold molar excess of reagent is adequate for full colour development.

The order of addition of buffer solution, metal ion, Tritonx-100 and reagent has no adverse effect on the absorbance of [Pd (II)-DMBBH] complex. Beer's law obeyed in the range 0.2660-3.193 μg/ml. The Molar

absorptivity and Sandell's sensitivity is $1.86x10^4$ L.mol $^{-1}cm^{-1}$ and 0.0054 $\mu g/cm^2$. [Pd (II)-DMBBH] complex was obtained from the Beer's law. The linear regression analysis of absorbance at 376 λ_{max} of the complex against metal ion (μg/ml) shows a linear fit shown in figure-3. The various important Physico-Chemical and analytical characteristics of [P(II)-DMBBH] complex are summarized in Table-3.The first order beers law graph was shown in Figure-5. This shows that the derivative amplitudes measured at 435 nm for first order were found to be proportional to the amount of Pd (II).The stoichiometry of the complex was found to be 1:1 (metal : ligand) investigated by Job's continuous variation method and molar ratio method, with a stability constant $1.0363x10^6$.

Table-3: Physico-Chemical and Analytical Characteristics of [Pd (II)-DMBBH]

Characteristics	**Results**
Colour	Yellow
λ_{max}(nm)	376
p^H range (optimum)	3.0-5.0
Mole of reagent required per mole of metal ion for full colour development	10 folds
Molar absorptivity(L.mol $^{-1}cm^{-1}$) (ε)	$1.86x10^4$
Sandell's sensitivity($\mu g/cm^2$)	0.0054
Beer's law validity range(μg/ml)	0.266-3.193
Optimum concentration range(μg/ml)	0.532 -2.927
Composition of complex(M:L) obtained in Job's and mole ratio methods	1:1
Stability constant of the complex	$1.0363x10^6$
Standard deviation	0.0002
Relative standard deviation(%)	0.02

The effect of various diverse ions in the determination of 1.3302μg/ml Pd(II) and tolerance limit of foreign ions was studied in the present method. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of ±2% in the absorbance or amplitude. The results are given in Table-4. The data obtained in the derivative method is also incorporated. The data suggest that several associated anions and cations do not interfere when they are present in large excess, such as iodide, nitrate, thiosulphate, thiocyanide, bromide, sodium (I), calcium (II), bismuth (III), tungsten (VI). The tolerance limit values for many anions and cations are more in derivative method. The interference of associated metal ion such as Copper (II) is decreased by adding masking agent thiourea.

Table 4. Tolerance limit of foreign ions in the determination of 1.330 µg/ml Palladium(II)

Ion added	Tolerance limit µg/mL	Ion added	Tolerance limit µg/mL
Tartarate	2202	Ba^{2+}	206
Citrate	1125	Hg^{2+}	201
Chloride	1068	Co^{2+}	118
Sulphate	960	Cd^{2+}	112
Tetraborate	670	Sr^{2+}	88
Phosphate	665	Ni^{2+}	88
Nitrate	620	Sn^{2+}	59
Acetate	565	Cr^{3+}	52
Fluoride	379	Mn^{2+}	27
Ascorbic acid	26	Ru^{3+}	2
W^{6+}	368	Ca^{2+}	1
Sb^{3+}	244	Cu^{2+}	0.63 1.27*

*masked by thiourea 245 µg/ml.

4. Applications

The proposed method was applied for the determination of Palladium (II) in synthetic alloys and hydrogenation catalyst.

Estimation of Palladium (II) in synthetic alloy samples:

Synthetic alloy samples whose composition corresponds to industrial, Jewellery, dental[9-10] alloys[11] and stibiopalladinite mineral are prepared and analyzed for the estimation of palladium by adopting the recommended procedure. The results are presented in Table-5

Table 5. Determination of Pd(II) in synthetic alloys

Sample	Sample Composition .	Proposed method	
		Amount found(%)	RSD(%)
1	Stibiopalladinite mineral (Pd,75;Sb,25%))	73.90	+1.46
2	Pd,60;Au 40%	59.30	+1.16
3	Pd,72; Ru ,4; Rh,1 %	71.50	+0.69
4	Pd, 72; Ag ,26;Ni 2%	71.20	+1.11

***average of best three determinations among five determinations**

Estimation of Palladium (II) in hydrogenation catalyst samples

The catalyst sample solution was prepared by employing the procedure and suitable aliquots of the above samples were analyzed the amount of palladium (II) present in these samples were computed from a predetermined calibration plot and results are presented in Table 6.

Table 6. Determination of Pd(II) in hydrogenation catalyst samples.

Samples	Amount of Pd(II) present(%)	Present method	
		Amount found*(%)	RSD (%)
Pd-charcoal	10	9.89	+1.1
Pd-$CaCO_3$	5	4.91	+1.8
Pd-$BaCO_3$	5	4.89	+2.2
Pd-$BaSO_4$	5	4.83	+3.4

*average of best three determinations among five determinations

5. Conclusion

The present method using 3, 5-dimethoxy-4-hydroxybenzaldehyde benzoylhydrazone (DMBBH) as spectrophotometric reagent for the determination of Pd (II) in aqueous medium in presence of TritonX-100 surfactant is sensitive and simple. Many of the methods involve either heating at a specific temperature or extraction of the reaction mixture. However heating at a specific temperature for a long time is laborious and time consuming. The determination of Pd (II) using DMBBH is not laborious and there is no need of heating or extraction of the components. Further the reagent is easy to synthesize using available chemicals. More over the present method is simple, rapid, selective and more precise for the determination of Pd (II).

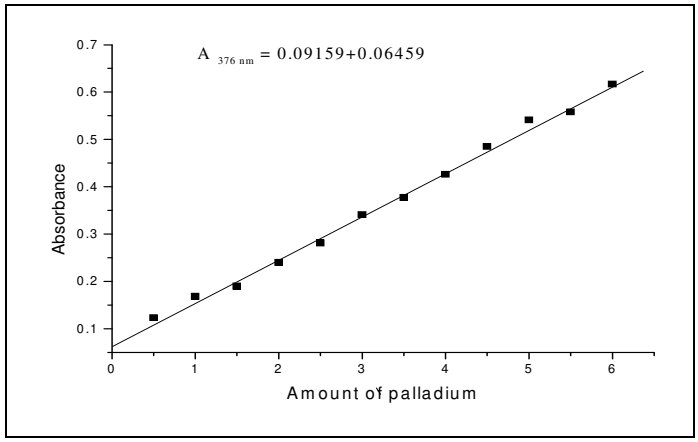

Fig.3. Zero order Beer's law plot of [Pd(II)-DMBBH] complex

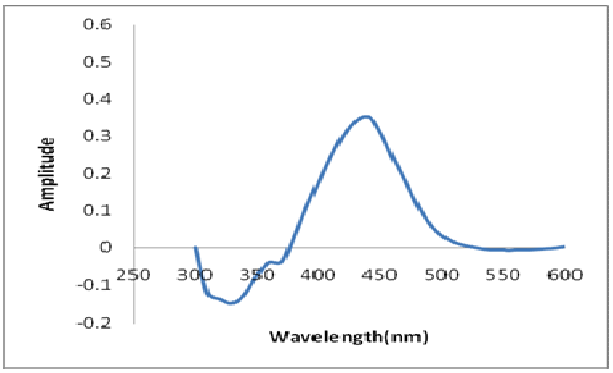

Fig.4. First order derivative spectrum of [Pd(II)-DMBBH] complex

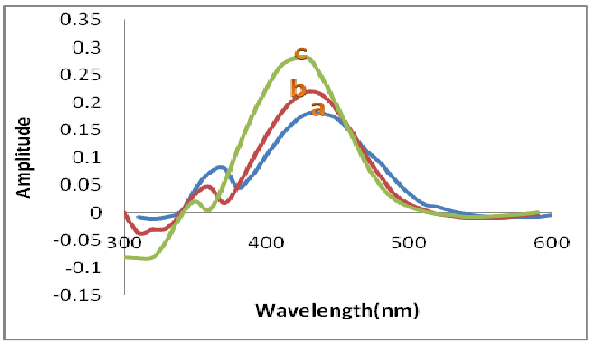

Fig.5. First order derivative Beers law of [Pd(II)-DMBBH] complex

(a) 1.59µg/ml of Pd(II)
(b) 2.12 µg/ml of Pd(II)
(c) 2.66 µg/ml of Pd(II)

6. Acknowledgements

Authors thank Jawaharlal Nehru Technological University, Anantapur for providing research facilities.

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