

Comparative study of Palladium (II) using 4-Hydroxy 3, 5 dimethoxy benzaldehyde 4-hydroxy benzoyl hydrazone and Cinnamaldehyde 4-hydroxy benzoylhydrazone in presence of micellar medium by Spectrophotometry

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Abstract:

Two simple, sensitive, rapid and selective spectrophotometric methods have been developed for the determination of Palladium (II) using newly synthesized reagents 4-Hydroxy3,5dimethoxy benzaldehyde-4-hydroxybenzoylhydrazone (HDMBHBH) and Cinnamaldehyde 4-hydroxy benzoylhydrazone (CMHBH) in presence of neutral surfactant TritonX-100-5% (micellar medium). Palladium (II) forms a brown coloured water-soluble complex with HDMBHBH and CMHBH-in the pH range 1.0-6.0. The Pd (II)-HDMBHBH complex shows maximum absorbance at λ_{max} 373 nm in the pH range 3.0-4.0 and Pd (II)-CMHBH shows at λ_{max} 375 nm in the pH range 4.0-5.0. At these wavelengths (λ_{max}), the complex shows maximum absorbance while the reagent blanks shows negligible absorbance. Hence, analytical studies were carried out at λ_{max} 373 nm at pH 3.0 for HDMBHBH and 375 nm at pH 4.0 for CMHBH against reagent blanks. Beer's law is obeyed in the range 0.106-1.064 $\mu\text{g ml}^{-1}$ and the optimum concentration range from ringbom plot is 0.212-0.957 $\mu\text{g/ml}$ of Palladium (II) for both reagents. The molar absorptivity and Sandell's sensitivity for the coloured solution were found to be $7.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0015\text{-}\mu\text{g. cm}^{-2}$ for HDMBHBH, $6.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0017\text{-}\mu\text{g. cm}^{-2}$ for CMHBH respectively. The interference effects of various diverse ions have been studied. Palladium (II) forms 1:1 complex with HDMBHBH and CMHBH stoichiometry with stability constant 7.29×10^6 for HDMBHBH and 3.55×10^6 for CMHBH. The standard deviation in the determination of $0.638\text{-}\mu\text{g ml}^{-1}$ of Palladium (II) is 0.003 for HDMBHBH and 0.008 for CMHBH. The Relative standard deviation is 0.71% for HDMBHBH and 2.5% for CMHBH. First and second order derivative spectroscopic methods were developed at λ_{max} 422 nm and 444 nm for HDMBHBH and at 402 nm and 438 nm for CMHBH respectively, for the determination of Palladium (II), which is more sensitive than the zero order method. The developed method has been employed for the determination of Palladium (II) in hydrogenation catalyst samples, synthetic alloy samples and in water samples. The results are in good agreement with the certified values.

Keywords: Comparative study of Palladium (II), Spectrophotometry, Hydrogenation catalyst samples, Synthetic alloy samples, water samples, micellar medium, HDMBHBH, CMHBH.

Introduction

The potential analytical applications of hydrazones and its derivatives have been reviewed by Singh et al [1]. Hydrazones are important class of known analytical reagents. Due to analytical potentialities of hydrazones herein we report the synthesis, characterization and analytical properties of reagents 4-Hydroxy3, 5dimethoxybenzaldehyde-4-hydroxybenzoylhydrazone (HDMBHBH) and Cinnamaldehyde 4-hydroxy benzoylhydrazone (CMHBH). As the light of the above herein we report the direct and derivative

spectrophotometric methods for determination of Palladium (II) using HDMBHBH and CMHBH in hydrogenation catalyst samples, synthetic alloy samples and in water samples. Derivative spectrophotometry is a very useful approach for determining the concentration of single component in mixtures with overlapping spectra as it may eliminate interferences.

Palladium was discovered by William Hyde Wollaston in 1803.^{[2][3]} 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.^[4] This metal also does not react with oxygen at normal temperatures (and thus does not tarnish in air). Palladium heated to 800°C will produce a layer of palladium (II) oxide (PdO). It lightly tarnishes in moist atmosphere containing sulfur.

The largest use of palladium today is in catalytic converters.^[5] Palladium is also used in jewelry, in dentistry,^[5] watch making, in blood sugar test strips, Palladium is found in the Lindlar catalyst, also called Lindlar's Palladium. Palladium is one of the three most popular metals used to make white gold alloys.^[6] In aircraft spark plugs and in the production of surgical instruments and electrical contacts.^[7] When it is finely divided, such as in palladium on carbon. Palladium is also a versatile metal for homogeneous catalysis and speeds up hydrogenation and dehydrogenation reactions, as well as in petroleum cracking.. It is used in combination with a broad variety of ligands for highly selective chemical transformations. Palladium is an effective catalyst for making carbon-fluoride bonds.^[8]

Palladium itself has been used as a precious metal in jewelry, as an alternative to platinum or gold. With the platinotype printing process photographers make fine-art black-and-white prints using palladium salts. Often used with platinum, palladium provides an alternative to silver.^[9]

Palladium and its alloys have a wide range of applications, both in chemical industry and in instrument masking. It is also has widespread use in dental and medical devices and the manufacture of jewelry^{[10][11]}.

For the determination of Palladium (II) at microgram quantities, a number of hydrazone derivatives and several analytical techniques such as AAS, ICP-AES, ICP, X-Ray fluorescence spectroscopy and UV-visible spectrophotometry were employed. Among them, spectrophotometric methods are preferred because they are cheaper and easy to handle.

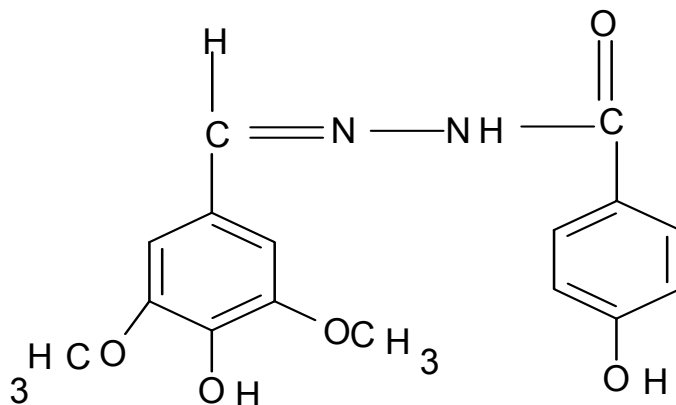
Hydrazones and its derivatives reacts with many metal ions forming colour complexes and act as chelating agents. In general the technique of solvent extraction is widely used in the spectrophotometric determination of metal ions. However, organic solvents such as benzene and chloroform are often carcinogenic, toxic and cause environmental pollution. It is significant to develop a method which does not involve solvent extraction. A micellar solution has the ability to enhance the stability of metal complex and has been utilized as a medium for the spectrophotometric determination of the metal chelate¹²⁻¹⁵.

Materials and methods: The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV-160A) fitted with 1.0 cm Quartz cells and Elico digital pH meter (Model LI 120) respectively. Suitable settings for derivative were as follows. The spectral band length was 5 nm, the wavelength accuracy was 0.5 nm with automatic wavelength correction and the recorder was a computer controlled thermal graph printer with a cathode ray tube and one degree of freedom in the wavelength range 300 – 800 nm.

The reagents (HDMBHBH and CMHBH) were prepared by the Sah and Daniels^[16] procedure

Preparation of HDMBHBH: 1.82 g of 4-hydroxy 3, 5 dimethoxy benzaldehyde (I) and 1.52 g of 4-Hydroxy benzhydrazide (II) were dissolved in sufficient volume of Carbinol and the mixture is refluxed for 4 hours. The contents were allowed to cool and the product was separated by filtration. A crude sample (yield 80%) is obtained (C₁₆H₁₆N₂O₅). The resultant product is recrystallised twice from hot methanol. Pure light greenish coloured crystals

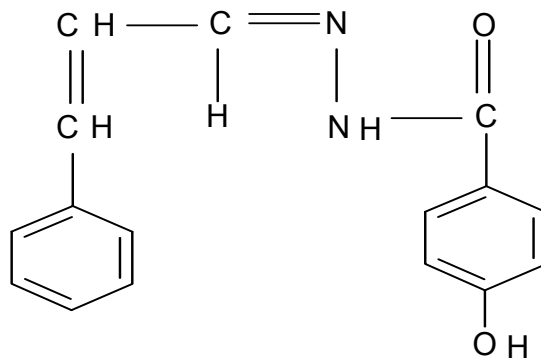
of 4-Hydroxy 3, 5 domethoxy benzaldehyde 4-hydroxy benzoylhydrazone (HDMBHBH) (III) (m.p. 292-294°C.) was obtained.



Structure of HDMBHBH

Preparation of CMHBH:

1.32 ml of Cinnamaldehyde (I) and 1.52 g of 4-Hydroxy benzhydrazone (II) were dissolved in sufficient volume of methanol and the mixture is refluxed for 4 hours. The contents are allowed to cool and the product was separated by filtration. A crude sample (yield 80%) is obtained ($C_{16}H_{13}O_2N_2$). The resultant product is recrystallised twice from hot methanol. Pure light yellowish crystals of Cinnamaldehyde-4-hydroxy benzoylhydrazone (CMHBH) (III) (m.p. 242-244°C.) was obtained.



Structure of CMHBH

Table: 1.Spectral data of Reagents (HDMBHBH and CMHBH)

Assignments	IR Spectral bands(cm^{-1}) of		Assignments	The 1H NMR (300 MHz) spectrum of in DMSO solvent	
	HDMBHBH	CMHBH		HDMBHBH	CMHBH
v NH stretching	3529	3452	NH	11.54 (S, 1H)	δ 11.57(S,1H)
v OH stretching	3075	3218-3092	OH (phenolic)	10.13 (S, 1H)	10.74 (S, 1H)
v > C=O stretching	1642	1620	N=C-H	8.1 (S, 1H)	8.19-8.22 (S, 1H)
v C=N stretching	1609	1577	ArH (pyridine ring)	7.77 – 7.80 (D, 2H)	7.77 – 7.80 (D,2H)
			ArH (aldehydic)	6.84 –6.96 (M,4H)	7.60 – 7.62 (D,2H)
			-OCH ₃ (2 Methoxy)	6.63 (S, 6H)	

The mass spectrum of HDMBHBH and CMHBH shows that molecular ion peak at m/z 317.1 ($M+1$) and 267 ($M+1$) respectively.

The structures of HDMBHBH and CMHBH were confirmed based upon above IR, NMR and mass spectral data

A 0.01 solution of Palladium (II) was prepared by dissolving requisite amount of $PdCl_2$ [17-21] in distilled water [22] and then standardized. The stock solution of Palladium (II) was diluted as required.

A 0.01M solutions of HDMBHBH and CMHBH in Dimethyl formamide (DMF) were employed in the present studies. The reagent (HDMBHBH and CMHBH) solutions (0.01M) were prepared by dissolving suitable quantity (0.316 g for HDMBHBH and 0.264 for CMHBH) of the compound in 100 ml of dimethyl formamide. The reagent solution is stable for 12 hours in presence of micellar medium. The working solutions were prepared daily by diluting the stock solution to an appropriate volume. All other chemicals used were of analytical grade.

Results and Discussion

The reagents 4-Hydroxy 3, 5-dimethoxy benzaldehyde 4-hydroxy benzoylhydrazone (HDMBHBH) and Cinnamaldehyde 4-hydroxy benzoylhydrazone (CMHBH) were easily synthesized as any other Schiff base reagent. In acidic medium, the ligands presumably co-ordinates the metal ions as di-anion to give neutral complexes. The absorption spectra of reagents (HDMBHBH, CMHBH) and Palladium (II) complex under the optimum conditions are shown in Figure1&2.

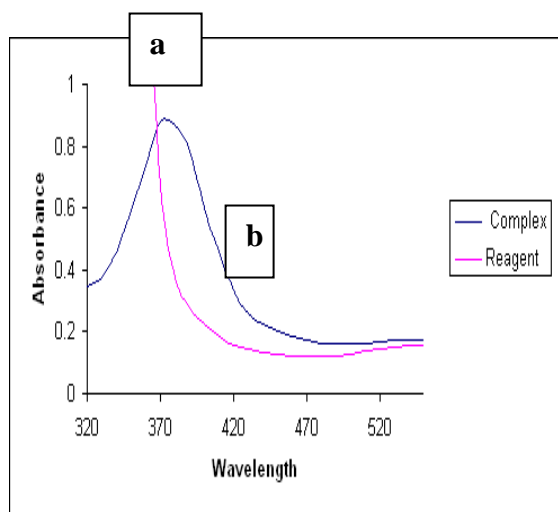


Fig-1 Absorption spectra of

(a) HDMBHBH Vs Buffer blank
(b) Pd (II)-HDMBHBH Vs Reagent blank
HDMBHBH -2×10^{-3} M (0.5 ml)
Pd (II) -2×10^{-4} M (0.5 ml)
pH 4.0 (3.0 mL)
Triton-X-100 (5%) -1.0 ml

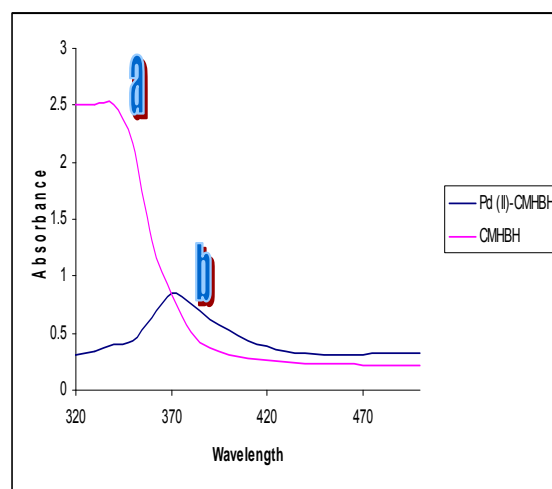


Fig-2 Absorption spectra of

(a) CMHBH Vs Buffer blank
(b) Pd (II)-CMHBH Vs Reagent blank
CMHBH -2×10^{-3} M
Pd (II) -2×10^{-4} M (0.5 ml)
pH 4.0 (3.0 mL)
Triton-X-100 (5%) -1.0 ml

Effect of reagent (HDMBHBH and CMHBH) concentration

A 10-fold molar excess of reagent (HDMBHBH and CMHBH) was necessary for complex and constant colour development. Excess of the reagent has no effect on the absorbance of the complex. The absorbance of the complex solution was found independent of the order of the addition of the reagents.

Effect of time Time stability of the coloured solution

The absorbance of the solution was measured at different time intervals to ascertain the time stability of the colour of the complex. The colour reaction between Palladium (II) with HDMBHBH and CMHBH was found to be instantaneous at room temperature. A slow decrease in absorbance was observed for the coloured species after 10 min. The stability of the complex was increased by adding neutral surfactant Triton X-100 (5%) and the colour remained stable for more than 12 hours.

The effect of surfactants

The effect of various surfactants such as Triton X-100, Sodium dodecyl benzene sulphonate (SDBS) and Cetyltrimethyl ammonium bromide (CTAB) on the absorption profiles of the system has been investigated and presented in Table 2. In presence of Triton X-100 (5%) both complex were more stable and exhibited maximum absorbance, hence Triton X-100 (5%) has been selected for further studies.

Table: 2. Influence of different surfactants

Surfactant	Absorbance of Pd(II)-HDMBHBH complex at λ_{max} 373 nm	Absorbance of Pd(II)-CMHBH complex at λ_{max} 375 nm
None	0.452	0.402
Triton X-100	0.876	0.808
CTAB (5%) (Cationic)	0.724	0.683
SDBS (5%) (Anionic)	0.654	0.523

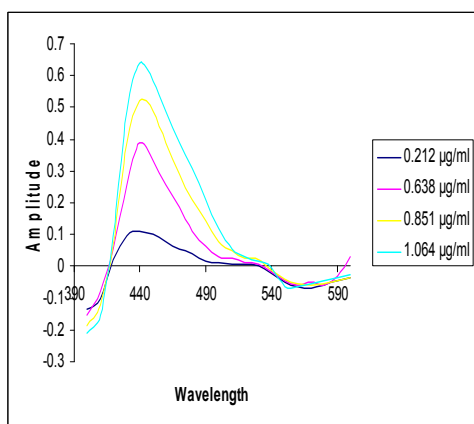
Optical characteristics, precision and accuracy data.

Beer's law limits, molar absorptivity and Sandell's sensitivity values, regression equation and correlation coefficients for Palladium (II)-HDMBHBH and Palladium (II)-CMHBH complex were compared and presented in Table 3. From this it was noticed that in derivative spectra the peak position shift towards higher wavelengths and Beer's law range was also improved compared to zero order method.

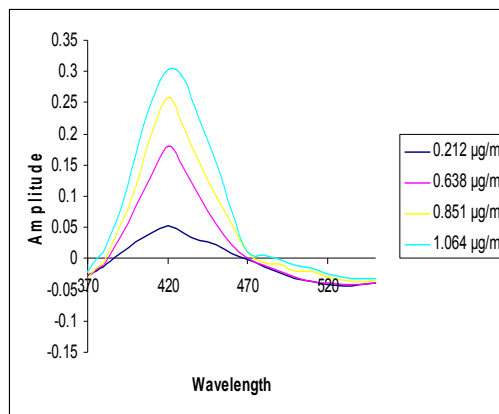
Table: 3. Optical characteristics, precision and accuracy data.

Characteristics	Results	
	HDMBHBH	CMHBH
λ_{max}	373 nm	375 nm
pH range	1.0-6.0	1.0-6.0
Optimum pH range	3.0-4.0	4.0-5.0
Mole of reagent required per mole of metal ion for full colour development	10 (folds)	10 (folds)
Molar absorptivity ($L \cdot mol^{-1} \cdot cm^{-1}$)	7.5×10^4	6.0×10^4
Sandal's sensitivity ($\mu g/cm^2$)	0.0015	0.0017
Beer's law validity range ($\mu g/ml$)	0.106-1.0640.	0.106-1.064
Optimum concentration range ($\mu g/ml$)	0.212-0.957	0.212-0.957
Composition of complex (M: L) obtained in Job's and molar ratio method	1:1	1:1
Stability constant of the complex	7.29×10^6	3.55×10^6
Standard deviation in the determination of 0.638 $\mu g/ml$ of Palladium (II) for ten determinations.	0.003	0.008
Relative standard deviation (%)	0.71	2.5
Regression coefficient	0.9997	0.9999
Detection limit ($\mu g/ml$)	0.009	0.024
Determination limit ($\mu g/ml$)	0.027	0.072

The calibration graph follows the straight-line equation $Y = a + bX$; where c is the concentration of the solution, Y is measured absorbance or peak height and a and b are constants. By substituting the Pd (II)- HDMBHBH complex experimental data in the above equation, the calibration equations were calculated as λ_{\max} 373 nm = $0.67056X - 0.00124$ for zero order data and λ_{\max} 422 nm = $0.28662X + 7.12539 \times 10^{-4}$ for first derivative data, λ_{\max} 444 nm = $0.60427X + 9.20195 \times 10^{-4}$ for second derivative data which gives the straight lines.

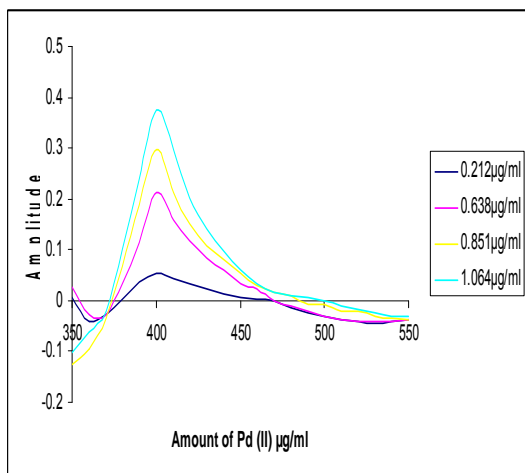


Pd (II)-HDMBHBH - Beer's law
Second order derivative spectra
HDMBHBH- 2×10^{-3} M (0.5 ml)
Pd (II) - 2×10^{-5} M (0.5 ml)
pH --3.0 (3.0 ml)
Triton-X-100 (5%)-1.0 ml
 λ_{\max} -----444 nm

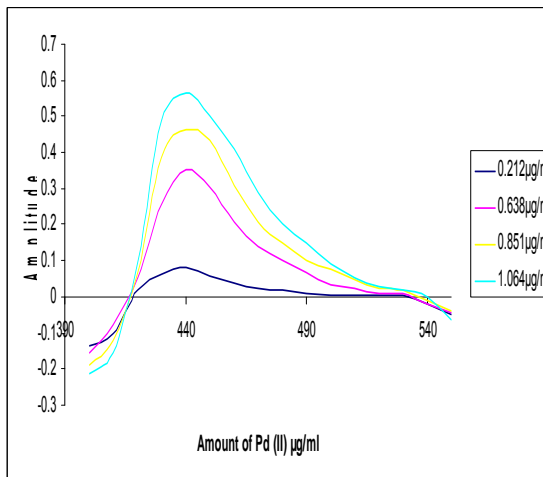


Pd (II)-HDMBHBH - Beer's law
first order derivative spectra
HDMBHBH- 2×10^{-3} M (0.5 ml)
Pd (II) - 2×10^{-5} M (0.5 ml)
pH --3.0 (3.0 ml)
Triton-X-100 (5%)-1.0 ml
 λ_{\max} -----422 nm

By substituting the Pd (II)-CMHBH complex experimental data in the above equation, the calibration equations were calculated as λ_{\max} 375 nm = $0.55906X - 0.04704$ for zero order data and λ_{\max} 402 nm = $0.37978X - 0.0278$ for first derivative data, λ_{\max} 438 nm = $0.64254X - 0.05306$ for second derivative data which gives the straight lines.



Pd (II)-CMHBH beer's law
First order derivative spectra
CMHBH - 2×10^{-3} M (0.5 ml)
Pd (II) - 2×10^{-5} M (0.5 ml)
pH -4.0 (3.0 mL)
Triton-X-100 (5%)-1.0 ml
 λ_{\max} -----402 nm



Pd (II)-CMHBH beer's law
second order derivative spectra
CMHBH- 2×10^{-3} M
Pd (II) - 2×10^{-5} M (0.5 ml)
pH 4.0 (3.0 mL)
Triton-X-100 (5%)-1.0 ml
 λ_{\max} -----438 nm

Zero order method: The developed spectrophotometric method proposed in the present studies was applied for the determination of Palladium (II) in Synthetic alloy samples, Hydrogenation catalyst samples and in water samples. The results are in good agreement with the certified values.

Application to Synthetic alloy samples: 0.5 g sample of alloy was digested in 15 ml of aquaregia by warming and the solution was evaporated to dryness. The residue was dissolved in 10 ml of diluted HCl and the resulting solution concentrated to 5 ml, diluted to 50 ml with distilled water, filtered and made up to the mark in a 100 ml volumetric flask.

A suitable aliquot of the sample solution was taken in a 10 ml standard flask containing 3.0 ml buffer solution, and 0.5 ml of (2×10^{-3} M) reagent (HDMHBH and CMHBH) solution. The contents were diluted to 10 ml with distilled water and its absorbance was measured at λ_{max} against the reagent blank. The absorbance values were referred to the pre-determined calibration plot to compute the amount of Palladium present. The results are presented in table 4&5

Table: 4.Determination of Palladium (II) in synthetic mixtures

Sample composition	Proposed method						Amount found* %					
	HDMHBH						CMHBH					
	Zero order	RSD (%)	D1	RSD (%)	D2	RSD (%)	Zero order	RSD (%)	D1	RSD (%)	D2	RSD (%)
Pd, 72; Ag, 26; Ni, 2 %;	71.6	0.55	71.4	0.833	71.2	1.11	71.3	0.97	71.5	0.69	71.8	0.27
Pd, 95; Ru, 4; Rh, 1 %	94.3	0.73	94.6	0.42	95.2	-0.21	94.1	0.94	94.5	0.52	94.7	0.31
Stibio palladinite mineral (Pd, 75; Sb, 25%)	74.1	1.2	74.6	0.533	75.1	-0.13	74.4	0.80	74.7	0.40	75.9	0.13
Pd, 60; Au 40 %;	58.7	2.16	59.3	1.16	59.6	0.66	59.1	1.5	59.4	1.0	59.7	0.5

Table: 5. Determination of Palladium (II) in synthetic mixtures

Synthetic mixture composition $\mu\text{g/ml}$	Pd (II) added $\mu\text{g/ml}$	AAS Method	Pd (II) Found					
			HDMHBH			CMHBH		
			Present method	S.D.	R.S.D %	Present method	S.D.	R.S.D %
3.0 Fe (III)+ 2.0 Ag (I) +2.0 Zn (II)	9.0	8.96	8.90	0.0872	0.98	8.92	0.0891	0.99
	10.0	9.92	9.80	0.1098	1.12	9.84	0.0982	0.98
	9.0	8.95	8.92	0.1168	1.31	8.97	0.0895	0.99
2.0 Mo (VI) +2.0 Ni (II) +2.0 Mn (II)	10.0	9.96	9.93	0.0963	0.97	9.95	0.0993	0.99
3.0 Fe (II)+3.0 Cu (II) +1.0 CU (II)	9.0	8.95	8.93	0.1036	1.16	8.92	0.0892	0.99
	10.0	9.97	9.96	0.1215	1.22	9.96	0.1215	1.22

Application to Hydrogenation catalyst samples:

About 0.3 g of catalyst sample was transferred into 250 ml beaker, treated with 5 ml of 2 M HNO₃ 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 ml of 2M HNO₃ and diluted to 250 ml in a volumetric flask. Suitable aliquots were taken and analyzed for palladium using the procedure discussed above.

Table: 6. Determination of Palladium (II) in Hydrogenation catalyst samples

Sample	Amount of Pd (II) present	Proposed method						Amount found* %					
		HDMBHBH						CMHBH					
		Zero order	RSD (%)	D1	RSD (%)	D2	RSD (%)	Zero order	RSD (%)	D1	RSD (%)	D2	RSD (%)
Pd-CaCO ₃	5	4.93	1.4	4.94	1.2	4.96	0.8	4.95	1.0	4.97	0.60	4.99	0.20
Pd-BaCO ₃	5	4.90	2.0	4.93	1.4	4.94	1.2	4.93	1.4	4.95	1.0	4.97	0.6
Pd-BaSO ₄	5	5.01	-0.2	5.03	-0.6	5.05	-1.2	4.94	1.2	4.95	1.0	4.98	0.4
Pd-Charcoal	10	9.90	1.0	9.94	0.6	9.96	0.4	9.92	0.8	9.95	0.5	9.97	0.3

Analysis of Palladium (II) in Water samples:

Various water samples were prepared with different compositions of Palladium (II) and analyzed by employing the proposed developed procedure. The results are in perfect agreement with those obtained by direct atomic absorption spectrophotometry. The results are given in the table 7.

Table: 7. Determination of Palladium (II) in water samples.

Palladium (II) added µg/ml	Palladium (II) found AAS	Proposed method						Amount found* %					
		HDMBHBH						CMHBH					
		Zero order	R %	D1	R %	D2	R %	Zero order	R %	D1	R %	D2	R %
Sample 1 8.0	7.89	7.54	94.25	7.56	94.5	7.58	94.75	7.55	94.37	7.57	94.62	7.59	94.87
Sample 2 10.0	9.89	9.56	95.60	9.58	95.8	9.62	96.2	9.53	95.3	9.55	95.5	9.67	96.7
Sample 3 12.0	11.92	11.70	97.50	11.74	97.83	11.76	98.0	11.77	98.08	11.84	98.66	11.9	99.16

R-Recovery %

Precision and accuracy

The precision and accuracy of the proposed methods were studied by analyzing (10 replicates) 0.638 µg/ml of Palladium (II) and the RSD values were found to be less than 2.5 %.

Effect of diverse ions

In order to assess the analytical potential of the proposed methods, the effects of some diverse ions which often accompany Palladium (II) were examined by carrying out the determination of 0.532µg/ml Palladium (II) in the presence of foreign ions. An ion was considered to interfere in the determination if the absorbance observed differed by more than ± 2% from that for Palladium (II) alone. The results presented in Table 8 indicate that many metal ions and anions do not interfere in the determination of Palladium (II). However, Cu (II), Fe (III), Mo (VI) interferes seriously as they readily form coloured species with HDMBHBH and CMHBH. The tolerance limit of Cu (II), Fe (III), and Mo (VI) were enhanced by using masking agents of fluoride, phosphate and tartarate.

Table:8 Tolerance limits of diverse ions in the determination of 0.532µg/ml Palladium (II)

Ion Added	HDMBHBH Tolerance Limit (µg/ml)			CMHBH Tolerance Limit (µg/ml)		
	Zero order	D1	D2	Zero order	D1	D2
ZIodide	1903	2157	2157	1269	1269	1269
Sulphate	576	576	576	960	960	960
Urea	600	720	720	240	300	300
Thiocyanide	2.3	7	7	581	697	697
Bromide	800	960	960	639	799	799
Thiourea	0.2	1.0	1.0	761.2	761.2	761.2
Nitrate	1550	1612	1612	868	992	992
Tetra borate	98	246	491	1524	1524	1524
Acetate	118	177	177	118	177	177
Phosphate	189.94	284.91	378.44	474.85	474.85	474.85
Chlorides	213	248	248	355	426	426
Tartarate	500	750	750	250	250	250
Citrate	189.22	378.44	378.44	567	756	756
Fluoride	475	532	532	190	190	190
Oxalate	264	264	264	264	264	264
Thiosulphate	224	359	359	920	920	920
U ⁺⁶	142.84	190.47	190.47	119.04	142.85	166.66
Sn ⁺²	3.56	4.74	4.74	118.71	118.71	118.71
La ⁺³	138.9	166.8	166.8	250.02	277.8	277.8
Pb ⁺²	41.44	62.16	62.16	62.18	103.5	165.76
Na ⁺	23	42	42	575	575	575
Hg ⁺²	20.09	60.07	60.07	62.17	100.29	160.47
Ba ⁺²	205.99	274.66	274.66	137.33	164.79	205.99
W ⁺⁶	9.19	11.03	11.03	12.86	18.38	18.38
Zr ⁺⁴	200.69	218.93	218.93	164.20	182.44	200.69
Zn ⁺²	19.61	26.15	26.15	19.61	19.61	19.61
Bi ⁺³	41.79	62.98	62.98	104.98	104.98	104.98
Ni ⁺²	29.34	35.21	35.21	17.6	29.34	29.34
Ce ⁺⁴	2.80	4.20	4.20	14.01	19.61	21.01
Fe ⁺³ **	1.11	1.67	1.7	2.79	2.79	2.79
Cu ⁺² *	1.27	2.5	2.5	3.17	3.17	3.17
Ru ⁺³	1.01	2.02	2.02	5.45	6.54	6.54
Ag ⁺	2.15	3.23	3.23	10.78	19.41	21.57
Pt ⁺⁴	2.85	3.80	3.80	4.74	5.70	5.70
Sb ⁺²	390	487	487	487	487	487
Sr ⁺²	26.28	26.28	26.28	157.71	175.24	192.96
Se ⁺⁴	23.66	23.66	23.66	63.18	78.96	78.96
V ⁺⁵	5.09	10	10	10.18	25.47	25.47
Os ⁺⁸	19.02	38.04	38.04	38.04	57.06	76.09
Cd ⁺²	202.3	224.82	224.82	112.41	134.89	168.61
Sr ⁺²	219.05	236.57	236.57	157.71	175.24	192.76
Mn ⁺²	82.39	98.87	98.87	65.91	82.93	93.38
Mg ⁺²	53.46	60.75	60.75	60.75	65.61	65.61
Se ⁺⁴	78.96	94.75	94.75	63.18	78.96	78.96
Co ⁺²	70.071	88.39	88.39	29.46	47.14	58.93
Al ⁺³	40.47	45.86	45.86	26.98	32.37	40.47
Mo ⁺⁶ #	0.954	0.954	0.954	1.91	1.91	1.91
Cr ⁺⁶	1.55	2.07	2.07	2.59	2.59	2.59
Au ⁺³	1.96	3.93	3.93	9.84	15.75	15.75

Table: 9. masking agents for interfering ions of HDMHBH and CMHBH

HDMHBH	CMHBH
*Masked by 189 µg /ml of Phosphate	*Masked by 474.85 µg /ml of Phosphate
** Masked by 199.51 µg /ml of Fluoride	**Masked by 190 µg /ml of Fluoride
# masked by 187.5 µg /ml of Tartarate	# masked by 250 µg /ml of Tartarate

Conclusion

The proposed methods are simple, accurate and have advantages over the reported methods which suffer from interference by large number of ions or require either heating or extraction or are less sensitive.

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Table: 10. Comparison of spectrophotometric methods for the determination of Palladium (II)

Reagent	λ_{max} (nm)	pH	Molar absorptivity (L mol ⁻¹ cm ⁻¹)	Extraction/ Heating	Beer's law Range µg/ml	Ref
Salcylaldehyde thiosemicarbazone	674	1.5-4.0	5.2×10^4	Aqueous	1-7.2	23
1-Amino-4hydroxy anthroquinone	620	3.8	5.3×10^4	Aqueous	0.35 µg /25 ml	24
Indane-1,2,3-trione mono thiosemicarbazone	460	3.0	1.5×10^4	Aqueous	0.42-3.63	25
O-hydroxyacetophenone thiosemicarbazone	370	6.0	9×10^3	Aqueous	0.42-10.6	26
Nicotinaldehyde-4-phenyl-3-thiosemicarbazone	365	3.0	2.81×10^4	Aqueous	0.5-8.0	27
2-Aminoacetophenone isonicotinoyl hydrazone	500	4.0	3.0×10^4	Aqueous	0.30-3.00	28
2,2'-dipyridyl- 4-2pyridylhydrazone (DPPH)	560	4.0	3.0×10^4	Extn CHCl ₃	0.30-3.00	29
Pyridoxal-4-phynyl-3-thiosemicarbazone	460	3.0	2.20×10^4	Extn Benzene	0.4-6.4	30
4-Hydroxy-3,5 dimethoxy benzaldehyde 4hydroxybenzoylhydrazone (HDMHBH)	373	3.0	7.5×10^4	Carbinol	0.106-1.064	31
Cinnamaldehyde 4 hydroxy benzoylhydrazone (CMHBH)	375	4.0	6.0×10^4	Ethanol	0.106-1.064	Present method

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