DIRECT AND DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM (II) IN PRESENCE OF MICELLAR MEDIUM IN HYDROGINATION CATALYST SAMPLES, SYNTHETIC ALLOY SAMPLES AND IN WATER SAMPLES USING 4-HDROXY 3, 5 DIMETHOXY BENZALDEHYDE-4-HYDROXY BENZOYLHYDRAZONE (HDMBHBH)

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ABSTRACT : A rapid, simple, sensitive and selective spectrophotometric method has been developed for the determination of Palladium (II) using newly synthesized reagent 4-Hdroxy3,5dimethoxybenzaldehyde-4-hydroxybenzoylhydrazone (HDMBHBH) in neutral surfactant of TritonX-100-5% (micellar medium). Palladium (II) forms a brown coluored water-soluble complex with 4-Hdroxy 3, 5dimethoxybenzaldehyde-4-hydroxybenzoylhydrazone in the pH range 1.0-6.0. The complex shows maximum absorbance at λmax 373 nm and in the pH range 3.0-4.0. However, at this wavelength, the reagent shows considerable absorbance. At λmax 373 nm, the complex shows maximum absorbance while the reagent blank shows negligible absorbance. Hence, analytical studies are carried out at λmax 373 nm and at pH 3.0 (Phosphate buffer) against reagent blank. Beer's law is obeyed in the range 0.106-1.064 µg ml^{-1} and the optimum concentration range from ringbom plot is 0.212-0.957 µg/ml of Palladium (II). The molar absorptivity and Sandell's sensitivity for the coloured solution are found to be 7.5 x 10^4L mol^{-1} cm^{-1} and 0.0015-µg. cm^{-2} respectively. The interference effect of various diverse ions has been studied. The complex shows 1:1 [Pd (II): HDMBHBH] stoichiometry with stability constant 7.29 x 10^6. The standard deviation of the method in the determination of 0.638 - µg ml^{-1} of Palladium (II) is 0.003 and the Relative standard deviation is 0.71%. First and second order derivative spectroscopic method is developed at λmax 422 nm and λmax 444 nm 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 and in synthetic alloy samples. The results are in good agreement with the certified values.

Keywords: Determination of Palladium (II), Spectrophotometry, hydrogenation catalyst samples, synthetic alloy samples, biological materials, HDMBHBH.

INTRODUCTION

The potential analytical applications of hydrazone derivatives have been reviewed by Singh et al [1] Hydrazones are important class of known analytical reagents. In the light of analytical potentialities of hydrazones herein we report the synthesis, characterization and analytical properties of reagent 4-Hdroxy3, 5dimethoxybenzaldehyde-4-hydroxybenzoylhydrazone (HDMBHBH). In the light of the above herein we report the direct and derivative spectrophotometric determination of Palladium (II) using HDMBHBH in hydrogenation catalyst samples and in synthetic alloy 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. In this paper a first and second order derivative spectrophotometric method is described for the determination of Palladium (II) in hydrogenation catalyst samples and in synthetic alloy samples.

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 forms a versatile catalyst and speeds up hydrogenation and dehydrogenation reactions, as well as in petroleum cracking.

Pd is also a versatile metal for homogeneous catalysis. 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 white gold.With the platinotype printing process photographers make fine-art black-and-white prints using platinum or 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]. Due its wide applications, the need arose of applications; the need arose for the development of simple and rapid methods for the quantitative determination of Palladium (II). For the determination of Palladium (II) at micro level, several analytical techniques such as AAS, ICP-AES, ICP, X-Ray fluorescence spectroscopy and spectrophotometer are employed. Among the, spectrophotometric methods are preferred because they are cheaper and easy to handle.

EXPERIMENTAL PART

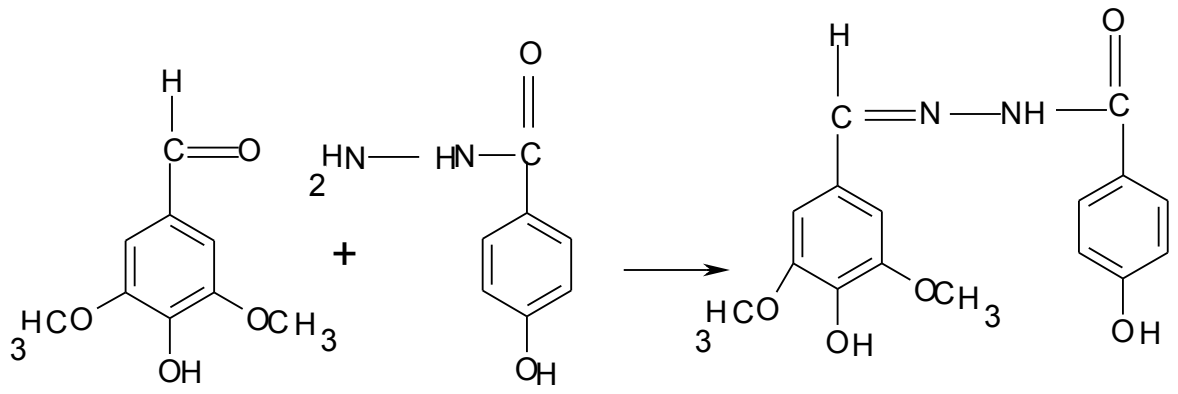
The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV-160A) fitted with 1.0 cm Quartz cells and Elico digital pH meter (Model LI 120) respectively. Suitable settings for derivative were as follows. The spectral band length was 5 nm, the wavelength accuracy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

REAGENTS

Preparation of 4-Hydroxy 3, 5-dimethoxy benzaldehyde-4hydroxy benzoylhydrazone (HDMBHBH)

The reagent (HDMBHBH) is prepared by the Sah and Daniels [12] procedure. 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 are allowed to cool and the product was separated by filtration. A crude sample (yield 80%) is obtained ($C_{16}H_{16}N_2O_5$). 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.) were obtained. The infrared spectrum of the reagent shows bands at ν 3529 (NH), 3075 (OH), 1642(C=O), 1609 (C=N). The 1H NMR (300 MHz) spectrum of the reagent was recorded in DMSO solvent. It shows signals corresponding to δ 11.54 (s, 1H, NH), 10.13 (s, 1H, OH phenolic), 8.92 (s, 1H, OH phenolic) 8.1 (s, 1H, N=CH), 7.77 – 7.80 (d, 2H, ArH), 6.84 – 6.96 (m, 4H, ArH), 6.63 (s, 6H, O – CH3). The mass spectrum shows that molecular ion peak at m/z 317.1 (M+ 1). The structure of HDMBHBH was confirmed based upon above IR, NMR and mass spectral data.

Figure.1: structure of 4-hydroxy 3, 5-dimethoxy benzaldehyde 4-hydroxy benzoylhydrazone



I (**4-hydroxy 3, 5 dimethoxy Benzaldehyde**) + II **(4-Hydroxy benzoylhydrazine)** (4-HBH) → III **(HDMBHBH)**

A 0.01M solution of HDMBHBH in Dimethyl formamide (DMF) was employed in the present studies. The reagent (HDMBHBH) solution (0.01M) was prepared by dissolving suitable quantity (0.316 g) of the compound in 100 ml of dimethyl formamide. The reagent solution is stable for 12 hours.

A 0.01 solution of Palladium (II) was prepared by dissolving requisite amount of $PdCl_2$ [13-18] in distilled water [19] and then standardized. The stock solution of Palladium (II) was diluted as required.

The working solutions were prepared daily by diluting the stock solution to an appropriate volume. All other chemicals used were of analytical grade.

Buffer solutions :(Phosphate)

0.2M KCl and 0.2M HCl (pH-1.0), 0.2M KCl and 0.02M HCl (pH-2.0), 0.1M Potassium Dihydrogen phosphate and 0.1M HCl (pH-3.0 and 4.0), 0.1M Potassium Dihydrogen phosphate and 0.1M Sodium hydroxide (pH-5.0 and 6.0). The pH of these solutions was checked with a digital pH meter**.**

Procedure : Direct spectrophotometry

In each set of different 10 ml volumetric flasks, 3.0 ml of buffer solution (pH 3.0), 0.5 ml of 4-hydroxy 3, 5-dimethoxy benzaldehyde 4-hydroxy benzoylhydrazone (**$2x10^{-3}$** M) and various volumes of ($2x10^{-5}$ M) Palladium (II) solution were taken and made up to the mark with distilled water. The absorbance was measured at λmax 373 nm against the reagent blank. The calibration plot was prepared.

First order derivative spectrophotometry:

For the above solutions, first order derivative spectra were recorded with a scan speed of fast (nearly 2400 nm min^{-1}); slit width of 1 nm with nine degrees of freedom, in the wavelength range 360 – 600 nm. The First order derivative peak height was measured by the peak-zero method at λmax 422 nm. The peak height was plotted against the amount of Palladium (II) to obtain the calibration plot.

Second order derivative spectrophotometry:

For the above solutions, second order derivative spectra were recorded with a scan speed of fast (nearly 2400 nm min^{-1}), slit width of 1 nm with nine degrees of freedom, in the wavelength range 360-600nm. The second order derivative peak height was measured by the peak-zero method at λmax 444nm. The peak height was plotted against the amount of Palladium (II) to obtain the calibration plot. The calibration graph follows the straight-line equation Y= a c + b; where c is the concentration of the solution, Y is measured absorbance or peak height and a and b are constants. By substituting the corresponding experimental data substituted in the above equation, the calibration equations were calculated as A λmax 373 nm = 0.67056x-0.00124 for zero order data and A λmax 422 nm = $0.28662x + 7.12539X10^{-4}$ for first derivative data, A λmax 444 nm = $0.60427x + 9.20195X10^{-4}$ for second derivative data which gives the straight lines.

Preparation of buffer solutions

Synthetic 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 the resulting solution concentrated to 5 ml, diluted to 50 ml with distilled water, filtered and made upto the mark in a 100 ml volumetric flask.

Hydrogenation catalyst samples:

About 0.3 g of catalyst sample was transferred into 250 ml beaker, treated with 5 ml of 2 M HNO_3 and covered. When the solution of gas had diminished 10 ml of acqua-regia was added and the solution was evaporated to near dryness on a sand bath. The residue was dissolved in 5 ml of 2M HNO_3 and diluted to 250 ml in a volumetric flask. Suitable aliquots were taken and analyzed for palladium using the procedure discussed above.

RESULTS AND DISCUSSION

Absorption spectra of HDMBHBH and the Palladium (II) complex:

The absorption spectra of the solution containing Palladium (II) complex against the reagent blank and that of the reagent solution against the corresponding buffer blank were recorded in the wavelength region 350-500 nm at pH 3.0. Typical spectra are presented in Fig-1. The spectra show that Palladium (II) complex has an absorption maximum at λmax 373 nm. However, at this wavelength, the reagent shows considerable absorbance. At λmax 373 nm, the complex shows maximum absorbance while the reagent blank shows negligible absorbance. Hence the analytical studies were carried out at λmax 373 nm

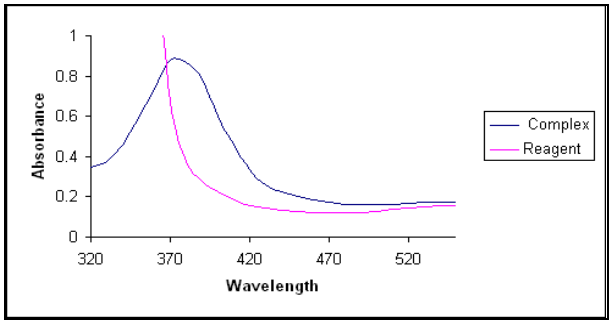


Figure - 1. Absorption spectra of

(a) HDMBHBH Vs Buffer blank, (b) Pd (II)-HDMBHBH Vs Reagent blank Pd (II) - $2x10^{-4}$ M (0.5 ml), HDMBHBH- $2x10^{-3}$ M (0.5 ml), Buffer pH-3.0 (3.0 ml), Triton-X-100 (5%)-1.0 ml

Effect of pH on the absorbance of the complex

The study of the effect of pH on the colour intensity of the reaction mixture showed that the maximum colour was obtained in the pH range 3.0-4.0. Analytical studies were therefore, carried out at pH 3.0 Figure-2

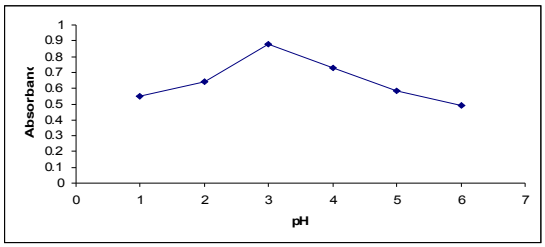


Figure-2- Effect of pH on Absorbance of Pd (II)-HDMBHBH, Pd (II)-$2x10^{-4}$ M (0.5 ml), HDMBHBH -$2x10^{-3}$ M (0.5 ml), Buffrer pH 3.0 - (3.0 ml), Triton-X-100 (5%)-1.0 ml, λmax ------ 373 nm

Effect of reagent (HDMBHBH) concentration

A 10-fold molar excess of HDMBHBH 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 reactants.

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) and HDMBHBH was found to be instantaneous at room temperature and the colour remained stable for more than 12 hours.

Applicability of Beer's law

For the possible determination of Palladium (II) at micro levels, the absorbance of the solutions containing different amounts of metal ion was measured. Calibration plot drawn between absorbance and amount of Palladium (II) Fig 3 showed that Beer's law was obeyed in the concentration range 0.106-1.064 µg ml^{-1} of Palladium (II). The straight line obeyed the equation A λmax 373 nm =0.67056x-0.00124. The molar absorptivity and Sandall's sensitivity were 7.29 x $10^6 Lmol^{-1}cm^{-1}$ and 0.003ug/cm^2 respectively. The correlation coefficient of the calibration curve for experimental data was 0.999. The standard deviation of the method for ten determinations of 0.638-µg ml^{-1} of Palladium (II) was 0.003.

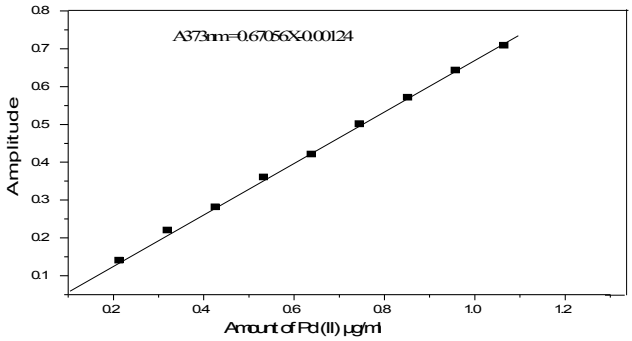


Figure-3: Pd (II)-HDMBHBH-Zero order Beers law
HDMBHBH-2X10^{-3} M (0.5 ml) (Constant), Pd (II)-2X10^{-5} M,
Buffer pH -3.0 (3.0 ml), Triton-X-100 (5%)-1.0 ml (Constant), λmax --373 nm

Determination of Palladium (II) first order derivative method

The first order derivative method has been employed for the determination of Palladium (II) employing HDMBHBH in trace quantities. The second derivative spectra Figure-4 (a) showed maximum amplitude at λmax 422 nm. The derivative amplitudes at λmax 422 nm were proportional to the concentration of Palladium (II). The straight line obeyed the equation A λmax 422 nm = 0.28662x + 7.12539X10^{-4}

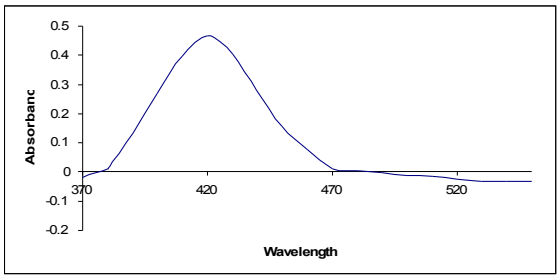


Figure-4 (a) Pd (II)-HDMBHBH- Fist order derivative spectra HDMBHBH -2X10^{-3} M (0.5 ml) (Constant), Pd (II)-2X10^{-5} M Buffer pH -3.0 (3.0 ml), Triton-X-100 (5%)-1.0 ml (Constant) λmax ---------- 422 nm

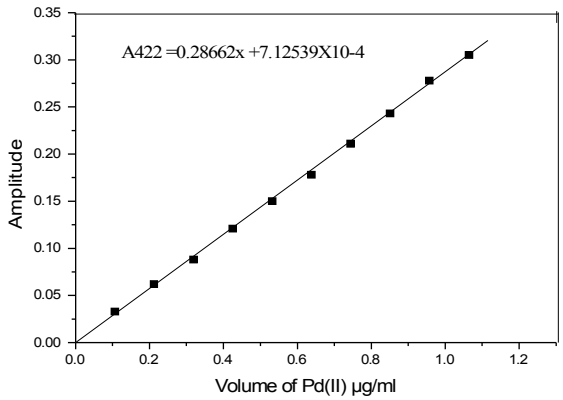


Figure-4 (b): Pd (II)-HDMBHBH- First order Beers law HDMBHBH -2X10^{-3} M (0.5 ml) (Constant), Pd (II)-2X10^{-5} M Buffer pH -3.0 (3.0 ml), Triton-X-100 (5%)-1.0 ml (Constant), λmax ----------422 nm

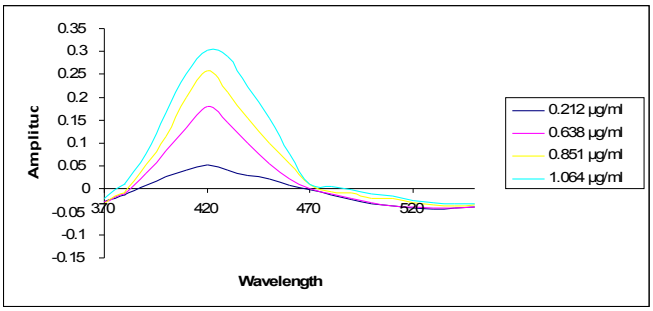


Figure.4 (c) Pd (II)-HDMBHBH- Beers law first order derivative spectra, HDMBHBH -1X10^{-3} M (0.5ml) (Constant), Pd (II)-1X10^{-5} M , Buffer pH --3.0 (3.0 ml), Triton-X-100 (5%)-1.0 ml (Constant), λmax------422 nm

Determination of Palladium (II) by second order derivative method

The second order derivative method has been employed for the determination of Palladium (II) employing HDMBHBH in trace quantities. The second derivative spectra Fig-5 (a) showed maximum amplitude at λmax 444 nm. The derivative amplitudes at λmax 444 nm were proportional to the concentration of Cadmium (II). The straight line obeyed the equation A λmax 444 nm = 0.60427x + 9.20195X10^{-4}

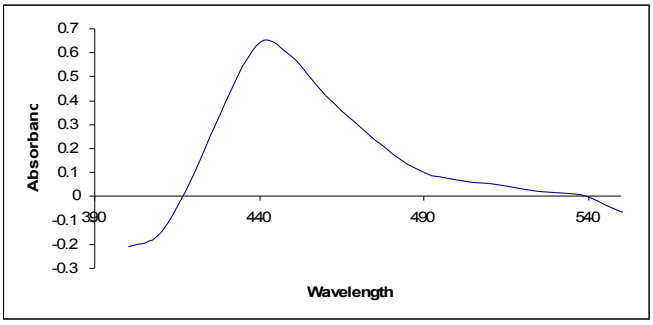


Figure-5 (a) Pd (II)-HDMBHBH- Second order derivative spectra HDMBHBH-2X10^{-3} M (0.5 ml), Pd (II) -2X10^{-4} M (0.5 ml) Buffer pH --3.0 (3.0 ml), Triton-X-100 (5%)-1.0 ml (Constant) λmax------444 nm

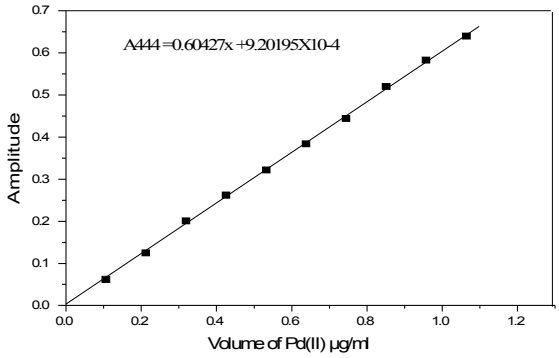


Figure-5 (b): Pd (II)-HDMBHBH - Second order Beers law HDMBHBH-2X10^{-3} M (0.5 ml), Pd (II) -2X10^{-5} M (0.5 ml) Buffer pH --3.0 (3.0 ml), Triton-X-100 (5%)-1.0 ml (Constant) λmax------444 nm

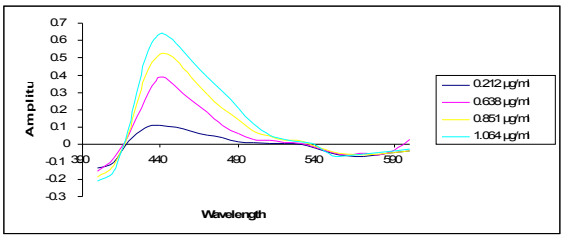


Figure.5 (c) Pd (II)-HDMBHBH - Beers's law second order derivative spectra HDMBHBH-2X10^{-3} M (0.5 ml), Pd (II) -2X10^{-5} M (0.5 ml) Buffer pH --3.0 (3.0 ml), Triton-X-100 (5%)-1.0 ml (Constant) λmax----------444 nm

Composition and stability of the complex

The stoichiometry of the complex was determined by Job's continuous variation method and molar ratio method and found to be 1:1 (M: L), the stability constant was determined by Job's method as 7.29 x 10^{6}.

Precision, Accuracy and Detection limit of the method.

The method has a good reproducibility for a set of ten measurements. The standard deviation (0.003) and relative standard deviation (0.71%) values clearly indicate that the precision and accuracy of the method are good.

Ringbom Plot for the Pd (II)-HDMBHH Complex.

A Ringbom plot is an established standard method adopted to know the optimum range of concentration for a system that obeys Beer's law. The Ringbom plot is sigmoid shape with a linear segment at intermediate absorbance values of 0.212-0.957**.**

Effect of diverse ions:

The tolerance limits (µg ml^{-1}) of various diverse ions in the present method are given in Table1 Tolerance limit was set as the amount of foreign ion that caused an error in the absorbance by ± 2%. The effect of several diverse ions on the determination of Palladium (II) was examined under the optimum conditions.The extent of interference by various anions and cations was determined by measuring the absorbance of solutions containing a constant amount of Palladium (II) and varying amounts of diverse ions.

The effect of various diverse ions in the determination of 0.532µg/ml Palladium (II) was studied to find out the tolerance limit of foreign ions 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 1. 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, thiosulphate, Nitrate, Urea, bromide, Uranium (I), Strantiam (III), Cadmium (VI) and zirconium (IV). The tolerance limit values for many anions and cations are more in derivative method. The interference of associated metal ions such as iron (III), copper (II) and Molybdenum (VI) is decreased by adding masking agents Fluoride and Phosphate, Tartarate respectively.

APPLICATIONS

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 alloys:

A suitable aliquot of the sample solution was taken in a 10 ml standard flask containing 3.0 ml of buffer of pH 3.0, and 0.5 ml of ($2x10^{-3}$ M) HDMBHBH solution. The contents were diluted to 10 ml with distilled water and its absorbance was measured at λmax 373 nm 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 2

Certified samples of bearing metal alloy samples were not available. Therefore, synthetic mixtures whose composition corresponds to bearing metal alloy were prepared. The present developed was applied to the determination of Palladium (II) in synthetic mixtures.Synthetic alloy samples (Table-3) whose composition corresponds to industrial, jewellery, dental and stibiopalldinite mineral are prepared and analyzed for the determination of palladium (II) by adopting the above recommended procedure and from a pre –determined calibration plot.The interference of Cu (II), Fe (III) (II), and Mo (VI) is eliminated by masking Phosphate, Fluoride and Tartarate respectively. The catalyst sample solution was prepared by employing the procedure given above .The suitable aliquots of the samples were analyzed by the above recommended procedure and the amount of palladium (II) was computed from a pre –determined calibration plot.

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 4.

Table: 1Tolerance limit of foreign ions in the determination of 0.532 µg/ml of Pd (II)

Ion Added	Tolerance (µg/ml) (Zero order) 373 nm	Limit	Tolerance (D1) 422 nm	Limit(µg/ml)	Tolerance (µg/ml) (D2) 444 nm	Limit
Iodide	1903		2157		2157	
Sulphate	576		576		576	
Ascorbic acid	35		56		56	
Urea	600		720		720	
Thiocyanide	2.3		7		7	
Bromide	800		960		960	
Thiourea	0.2		1.0		1.0	
Nitrate	1550		1612		1612	
Tetra borate	98		246		491	
Acetate	118		177		177	
Phosphate	189.94		284.91		378.44	
Chlorides	213		248		248	
Tartarate	500		750		750	
Citrate	189.22		378.44		378.44	
Flourude	475		532		532	
Oxalate	264		264		264	
Thiosulphate	224		359		359	
U^{+6}	142.84		190.47		190.47	
Sn^{+2}	3.56		4.74		4.74	
La^{+3}	138.9		166.8		166.8	
Pb^{+2}	41.44		62.16		62.16	
Na^{+}	23		42		42	
Hg^{+2}	20.09		60.07		60.07	
Ba^{+2}	205.99		274.66		274.66	
W^{+6}	9.19		11.03		11.03	
Zr^{+4}	200.69		218.93		218.93	
Zn^{+2}	19.61		26.15		26.15	
Bi^{+3}	41.79		62.98		62.98	
Ti^{+4}	38.30		38.30		38.30	
Ni^{+2}	29.34		35.21		35.21	
Ce^{+4}	2.80		4.20		4.20	
Fe^{+3} **	1.11		1.67		1.7	
Cu^{+2} *	1.27		2.5		2.5	
Ru^{+3}	1.01		2.02		2.02	
Ag^{+}	2.15		3.23		3.23	
Pt^{+4}	2.85		3.80		3.80	
Sb^{+2}	390		487		487	
Sr^{2+}	26.28		26.28		26.28	
Se^{+4}	23.66		23.66		23.66	
V^{+5}	5.09		10		10	
Os^{+3}	19.02		38.04		38.04	
Cd^{+2}	202.3		224.82		224.82	
Sr^{+2}	219.05		236.57		236.57	
Mn^{+2}	82.39		98.87		98.87	
Mg^{+2}	53.46		60.75		60.75	
Se^{+4}	78.96		94.75		94.75	
Co^{+2}	70.071		88.39		88.39	
Al^{+3}	40.47		45.86		45.86	
Mo^{+6} #	0.954		0.954		0.954	
Cr^{+6}	1.55		2.07		2.07	
Au^{+3}	1.96		3.93		3.93	
As^{+3}	14.98		22.47		22.47	

*Masked by 189 µg /ml of Phosphate, ** Masked by 199.5l µg /ml of Fluoride, # Masked by 187.5 µg /ml of Tartarate

Table.2: Determination of Palladium (II) in synthetic alloy samples

S.No	Sample composition	Proposed method					
		Amount found %					
		Zero Order	RSD (%)	D1	RSD (%)	D1	RSD (%)
1	Pd, 72; Ag, 26; Ni, 2 %;	71.6	0.55	71.4	0.833	71.2	1.11
2	Pd, 95; Ru, 4; Rh, 1 %	94.3	0.73	94.6	0.42	95.2	-0.21
3	Stibio palladinite mineral (Pd, 75; Sb, 25%)	74.1	1.2	74.6	0.533	75.1	-0.13
4	Pd, 60; Au 40 %;	58.7	2.16	59.3	1.16	59.6	0.66

*Mean of five determinations

Table.3 Determination of Palladium (II) in synthetic mixtures

Synthetic mixture composition µg/ml	Pd (II) added µg/ml	Pd (II) found			
		AAS	Present method	S.D.	R.S.D %
3.0 Fe (III)+ 2..0 Ag (I) +2.0 Zn (II)	9.0 10.0 9.0	8.96 9.92 8.95	8.90 9.80 8.92	0.0872 0.1098 0.1168	0.98 1.12 1.31
2.0 Mo (VI) +2.0 Ni (II) +2.0 Mn (II)	10.0	9.96	9.93	0.0963	0.97
3.0 Fe (II)+3.0 Cu (II) +1.0 CU (II)	9.0 10.0	8.95 9.97	8.93 9.96	0.1036 0.1215	1.16 1.22

Average of five determinations

Table 4 Determination of Palladium (II) in water samples.

S.No	Palladium(II) added µg/ml	Palladium (II) found AAS	Proposed method					
			Amount found %					
			Zero Order	Recovery (%)	D1	Recovery (%)	D2	Recovery (%)
Sample 1	8.0	7.89	7.54	94.25	7.56	94.5	7.58	94.75
Sample 2	10.0	9.89	9.56	95.60	9.58	95.8	9.62	96.2
Sample 3	12.0	11.92	11.70	97.50	11.74	97.83	11.76	98.0

Physico-chemical and analytical characteristics of Pd (II)-HDMBHBH complex (Table-5)

The results obtained in zero order and derivative spectrophotometric methods for Palladium (II)-HDMBHBH complex were compared and presented in Table 6. 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: 5. Physico-chemical and analytical characteristics of Pd (II) - HDMBHBH complex

Characteristics	Results
λ_{max}	373 nm
pH range	1.0-6.0
Optimum pH range	3.0-4.0
Mole of reagent required per mole of metal ion for full colour development	10 (folds)
Molar absorptivity ($L.mol^{-1}cm^{-1}$)	7.5×10^4
Sandal's sensitivity ($\mu g/cm^2$)	0.0015
Beer's law validity range (µg/ml)	106-1.0640.
Optimum concentration range (µg/ml)	0.212-0.957
Composition of complex (M: L) obtained in Job's and molar ratio method	1:1
Stability constant of the complex	7.29×10^6
Standard deviation in the determination of 0.638 µg/ml of Pd (II) for ten determinations.	0.003
Relative standard deviation (%)	0.71
Regression coefficient	0.99971
Detection limit (µg/ml)	0.009
Determination limit (µg/ml)	0.027

Table.6: Comparison of spectrophotometric methods for the determination of Palladium (II)

Reagent	λmax (nm)	pH	Molar absorptivity (L mol^{-1} cm^{-1})	Extraction/ Heating	Beer's law Range µg/ml	Ref
Salciladehyde thiosemicarbazone	674	1.5-4.0	5.2×10^4	Aqueous	1-7.2	18
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	27
Nicotinaldehyde-4-phenyl-3-thiosemicarbazone	365	3.0	2.81×10^4	Aqueous	0.5-8.0	33
2-Aminoacetophenone isonicotinoyl hydrazone	500	4.0	3.0×10^4	Aqueous	0.30-3.00	39
2,2'-dipyridyl- 4-2pyridylhydrazone (DPPH)	560	4.0	3.0×10^4	Extn $CHCl_3$	0.30-3.00	40
Pyridoxal-4-phynyl-3-thiosemicarbazone	460	30.	2.20×10^4	Extn Benzene	0.4-6.4	41
Furfuraldehyde thiosemicarbazone (FFTSC)	360	1.0-5.0	3.9911×10^4	At 90^0C Extn.Molten Napthalene	0.170- 1.703	48
1-Amino-4hydroxy anthroquinone	620	3.8	5.3×10^4	Aqueous	0.35 µg /25 ml	23
4-Hydroxy-3,5 dimethoxy benzaldehyde isonicotinoylhydrazone (HDMBINH)	382	5.5	2.44×10^4	Ethanol	0.1064-2.1284	-
4-Hydroxy-3,5 dimethoxy benzaldehyde 4hydroxybenzoylhydrazone (HDMBHBH)	373	3.0	7.5×10^4	Carbinol	0.106-1.064	Present method

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