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Direct, derivative spectrophotometric determination of micro amounts of Palladium (II) by 5-bromo salicylaldehyde isonocotinoyl hydrazone (5-BrSAINH)

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ABSTRACT

A simple and highly selective spectrophotometric method have been developed for the determination of trace amounts of Pd (II) using newly synthesized reagent 5-bromo salicylaldehyde isonocotinoyl hydrazone (5-BrSAINH) in aqueous DMF medium. Palladium (II) forms a brown colored soluble complex with 5-BrSAINH in the pH range 1.0-5.0. The Pd (II) – 5-BrSAINH complex shows maximum absorbance at 445nm in the pH range 2.5-3.0 where the reagent blank shows negligible absorbance. Hence analytical studies were carried out at 445nm and at pH 3.0.Beer's law was obeyed in the range 1.06-10.64μgmL^{-1} *of Pd (II).The molar absorptivity and sandell's sensitivity for the colored solution were found to be* 1.30×10^{4} $L.mol^{-1}cm^{-1}$ *and* $0.81X10^{-2}$ μgcm^{-2}*, respectively.The brown colored complex has 1:1 Stoichiometry .The interference effect of various diverse ions have been studied .The stability constant of the complex was determined as* $7.24X\ 10^{6}$ *by Job's method. First and second order derivative spectrophotometric methods were developed which were found to be more sensitive than zero order method. The developed method have been employed for the determination of palladium (II) in hydrogenation catalyst samples, alloy steel samples and in water samples. The results were in good agreement with certified values.*

Key words: Spectrophotometer, 5-BrSAINH, determination of palladium (II), hydrogenation catalyst samples, synthetic alloy samples, water samples.

INTRODUCTION

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 [1]. It plays a key role in catalytic converters. Palladium and its alloys have wide range of applications both in chemical industry and in instrument making [2]. Palladium is utilized in many electronic devices including computers, cell phones, multi-layer ceramic capacitors and low voltage electrical contacts as well as in dentistry and medicine [3]. Palladium is also used in jewellery, watch making and in blood sugar strips. Palladium is found in Lindlar catalyst, also called as Lindlar's palladium. Palladium is one of the three most popular metals used to make white gold alloys [4].

A survey of literature has revealed that several analytical techniques have been reported for the determination of palladium which include atomic absorption spectrometry [5], neutron activation analysis [6], and pre-concentration and separation of palladium, such as flow injection method, hollow fiber micro extraction, solid-phase micro extraction and spectrophotometry [7-33].

Hydrazones and their derivatives react with many metal ions forming colored complexes. 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 carcinogenic, and cause environmental pollution. It is significant to develop a method which does not involve solvent extraction.

MATERIALS AND METHODS

Apparatus

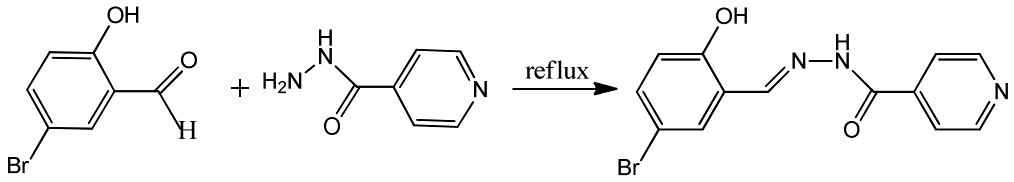
The absorbance and pH measurements were made on a Perkin Elmer (LAMDA 25) UV-Visible spectrophotometer (Model UV-160A) controlled by a computer fitted with 1cm path length quartz cells and an ELICO digital P^H meter of (Model LI 613), respectively.

Reagents

All chemicals used were of analytical grade. A stock solution of Pd (II) was prepared by dissolving 1 gram of palladium chloride in hydrochloric acid solution (2M,5ml) and made up to the mark in a 250ml volumetric flask. The resulting solution was standardized and working solutions were prepared by suitable dilution. Solutions of the studied interfering ions of suitable concentrations were prepared using A.R.grade salts.

PREPARATION OF 5-BrSAINH

Equimolar solutions of 5-bromo salicylaldehyde (I) and isonicotinic acid hydrazide (II) were dissolved in sufficient volume of methanol and the mixture was refluxed for 1 hour. The contents were allowed to cool and the product was separated by filtration. A crude sample (yield 80%) was obtained. The resultant product was recrystallized thrice from hot methanol. Pure light yellowish green colored crystals of 5-bromo salicylaldehyde isonicotinoyl hydrazone (III) ($238\text{-}240^0$c) were obtained (m.p $238\text{-}240^0$c)



5-bromo salicylaldehyde
I

Isonicotinicacidhydrazide
II

5-bromosalicylaldehydeisonicotinoylhydrazone
III

Procedure

General method

Aliquots of solutions containing 2.0-20.0µg of palladium (II) were transferred into a series of 10ml volumetric flasks. To these 5-BrSAINH (0.1%, 0.5ml) was added and the contents were diluted to the mark with distilled water and mixed well. The absorbance was measured at 445nm against the reagent blank. The calibration graph was constructed by plotting the absorbance against the concentration of Pd (II) ions.

Derivative method

For the solutions as prepared above the first and second derivative spectra were recorded with reference to the reagent blank in the wavelength range 350-600nm. The derivative amplitudes were measured at 455nm for first order and 470nm for second order curves. Calibration graphs were constructed by plotting the derivative amplitudes against the concentration of Pd (II) ions.

RESULTS AND DISCUSSION

Absorption spectra

The reaction of 5-BrSAINH with Pd (II) at room temperature gives a brown colored soluble complex. The Pd (II) - 5-BrSAINH complex shows maximum absorbance at 445nm where the reagent blank does not absorb appreciably.

Effect of pH on the absorbance of the experimental solution:

The plot between absorbance and of pH reveals that the metal complex shows maximum and constant absorbance in the pH range 2.5-3.0. Therefore, pH 3.0 was selected for further studies.

Effect of reagent concentration on absorbance of the complex solution:

The minimum amount of reagent to acquire maximum color intensity with a given amount of Pd (II) was evaluated from the absorbance measurements of experimental solution with different amounts of reagents. The results prove that a 15-fold molar excess of the reagent was required for the development of maximum color intensity with a given amount of palladium (II).

Composition and stability of the complex:

The composition of the complex was determined using Job's continuous variation method. The results indicate a 1:1 stoichiometry between the metal ion and the reagent. The stability constant of the complex was determined as 7.24X 10^6 by Job's method.

Validity of Beer's law:

The calibration plot between absorbance and concentration of Pd (II) showed that Beer's law was obeyed by the system in the concentration range 1.06-10.64µgmL^{-1} of Pd (II). The straight line obeys the equation A_{445}=0.0713C+0.00954. The molar absorptivity and sandell's sensitivity of the method were found as 1.30 x 10^4 L.mol^{-1}cm^{-1} and 0.81X 10^{-2} µgcm^2, respectively.

Effect of Foreign Ions:

The effect of various anions and cations normally associated with Pd (II) on the absorbance of the experimental solution was studied. The tolerance limits of the tested foreign ions which bring about a change in the absorbance by +2% were calculated and presented in table 1. Almost all the tested anions possess high tolerance levels (>100 fold). The metal ions Co (II), V (V) and Fe (II), were tolerable up to 15-40 fold excess and Fe (III) and Hg (II) interfere seriously.

Table.1 Tolerance limits of foreign ions

Amount of Pd (II) taken = 2.66µg mL^{-1}, pH = 3.0

Foreign ion	Tolerance Limit (µg mL^{-1})	Foreign ion	Tolerance Limit (µg mL^{-1})
Iodide	1,850	Te (IV)	950
oxalate	1710	Cd(II)	820
chloride	1320	W(VI)	760
Formate	1140	K(I)	690
Thiosulphate	1000	Li(I)	650
urea	950	Ce(IV)	520
DTA	700	Na(I)	500
sulphate	550	Mg(II)	450
Bromide	500	Mo(VI)	400
Tatarate	320	Ti(IV)	395
Flouride	250	Al(III)	260
Thiocyanate	170	Pt(IV)	130
Citrate	160	Co(II)	80
		V(V)	60
Thiourea	60	Fe(II)	50
Nitrate	120	Ru (III)	10^a,190
		Fe(III)	6^a,108
		Hg(II)	2^b,120

a) in the presence of 1300 µg mL^{-1} of Cl$^-$ b) in the presence of 1800 µg mL^{-1} of I$^-$

Derivative Method

In order to improve the sensitivity and selectivity of the direct spectrophotometric method developed; the absorbance data was derivatised once and twice and plotted against the wavelength(350-600) which gave the corresponding first and second order derivative curves (fig 1and 2).. The first derivative curve shows a peak at 455nm. At this wavelength, the derivative amplitudes were proportional to the amount of Pd (II) in the range 0.426-11.7 µg mL^{-1}

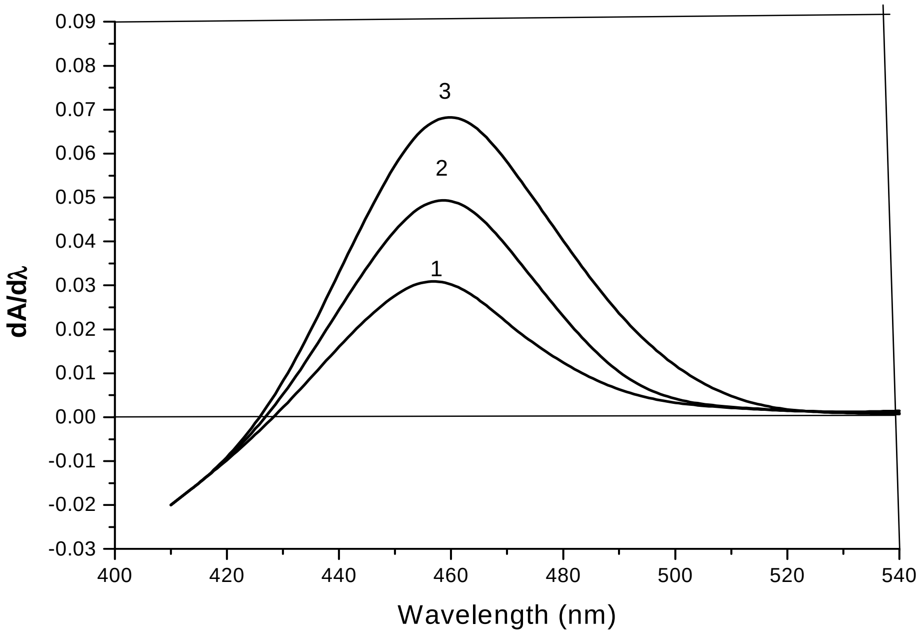


Fig.1: First Order derivative spectra of Pd (II)–5Br–SAINH Vs Reagent blank Pd (II) (μg mL^{-1}) = (1) 1.06; (2) 4.26 (3) 7.45

The second derivative spectra show a peak at 470nm. At this wavelength, the derivative amplitudes were proportional to the amount of Pd (II) in the range 0.426-10.64 µg mL^{-1}.

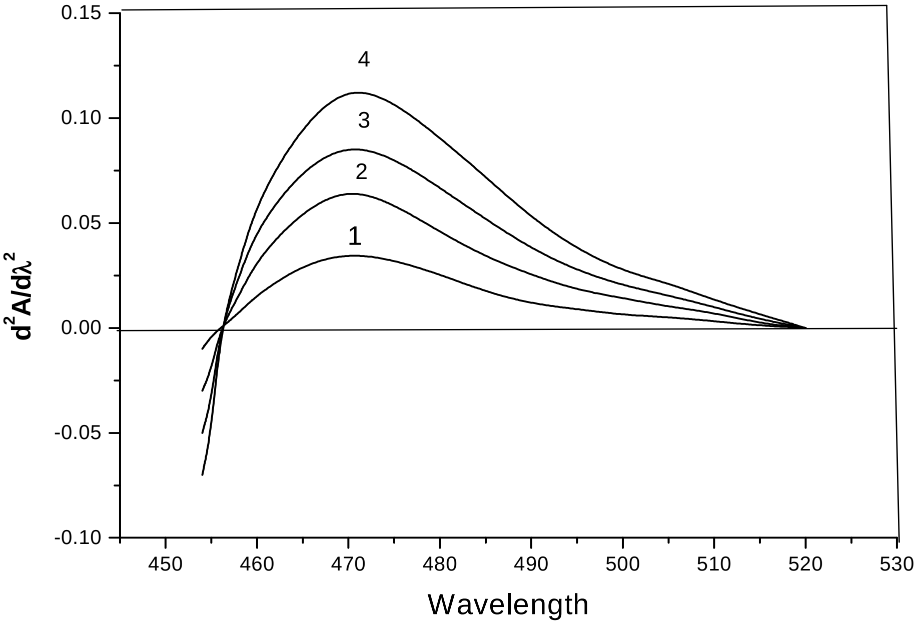


Fig.2: Second Order derivative spectra of Pd (II)–5Br–SAINH Vs Reagent blank Pd (II) (μg mL^{-1}) = (1) 1.06; (2) 4.26 (3) 7.45

The analytical results of both direct and derivative methods were summarized and presented in Table 2. The tolerance limits of some cations in derivative methods were compared with those in direct method and presented in Table 3

Table 2: Analytical Characteristics of Pd (II) -5-BrSAINH

Parameter	Zero order	First Derivative	Second Derivative
Analytical Wavelength (nm)	445 nm	455	470
Molar absorptivity (L mol^{-1} cm^{-1})	1.3007 X 10^4	-	-
Beer's law range	1.06-10.64	0.426-11.7	0.426-10.64
Sandell's sensitivity	0.0081	-	-
Angular coefficient (m)	0.0713	0.0232	0.0490
Y-intercept(b)	0.00954	-0.0014	0.0380
Correlation coefficient (r)	0.9998	0.9986	0.9997
Relative Standard deviation	1.12%	0.46%	0.93%
Stability constant	7.24 X 10^6	-	-
Detection limit (µgmL^{-1})	0.00159	0.0008	0.0005
Determination limit (µgmL^{-1})	0.00482	0.0032	0.0011

Table.3: Tolerance limits of foreign ions

Foreign ion	Tolerance limit in folds		
	Zero order (445nm)	First derivative (455nm)	Second derivative (470nm)
Co(II)	80	95	110
V(V)	60	75	100
Mn (II)	55	70	90
Fe (II)	50	70	85
Ru (III)	10	45	65
Fe (III)	6	35	50
Hg (II)	2	15	30

It can be observed from table 3 that the tolerance limits of metal ions which interfere in zero order method were greatly enhanced in the derivative methods indicating the greater selectivity of derivative methods than the direct method

Applications

Zero order method:

The developed spectrophotometric method was employed for the determination of palladium (II) in alloy steel samples, hydrogenation catalyst samples and in water samples.

Determination of Palladium (II) in hydrogenation catalysts

About 0.3g of the catalyst sample was treated with 10ml of aquaregia. The solution was then evaporated to 5ml, cooled and diluted with 20ml distilled water and filtered. The residue was washed into the filtrate first with 20ml of 2N nitric acid and then with small volume of distilled water. Finally the solution was made up to the mark with distilled water in 100ml volumetric flask. The palladium content in known aliquots of the resultant solution is determined by the proposed method and the results are given in

Table 4: Analysis of Palladium (II) in Hydrogenation Catalysts

Catalyst	Amount of palladium(II)* %		Relative error (%)	Standard deviation (%)
	Present	Found		
Pd-$CaCO_3$	5.00	5.02	-0.78	±0.038
Pd-$BaCO_3$	5.00	4.98	-0.62	±0.029
Pd-$BaSO_4$	5.00	5.04	0.80	±0.039
Pd activated charcoal	10.00	9.93	-0.38	±0.030

**Average of five determinations*

Alloy steel sample solutions

A 0.1-0.5g of steel sample was dissolved in minimum volume of aquaregia by slow heating on sand bath and then heated to fumes of oxides of nitrogen. After cooling, 5-10ml of 1:1 H_2SO_4 was added and evaporated to dryness. Sulphuric acid treatment was repeated three times to remove all the nitric acid. The residue dissolves in 20ml of distilled water, filtered and the filtrate was made up to 100ml in a volumetric flask with distilled water. The sample solution was appropriately diluted to obtain the concentration in the required range. This solution was used to determine palladium in it, using the proposed method and the results were given in Table 5

Table: 5 Determination of Pd (II) of Alloy Steel samples

Certified composition of the alloy sample	**Amount of Pd (II) (µgml^{-1})**		**Relative error (%)**	**Standard deviation (µgml^{-1})**
	Certified	**Found**		
Co-Pd alloy 95 %Co,5%Pd	5.00	5.07	1.6	±0.038
Ni-Pt-V-Pd (okay alloy) 60% Ni, 20% Pt, 9.5% V,10.5% Pd	10.50	10.58	1.3	± 0.035

**Average of five determinations*

Analysis of Water samples:

Three different samples of natural water were spiked with known amounts of Pd (II) and the resultant samples were analyzed for their Pd (II) content by the proposed method. The samples were simultaneously analyzed by flame atomic absorption spectrophotometry and the results obtained are compared in table 6

Table: 6 Determination of palladium (II) in water samples

Palladium (II) found	**Proposed method**	
Palladium(II) added µgmL^{-1}	AAS method	Palladium found
Sample 1 8.0	7.89	7.68
Sample 2 10.0	9.89	9.43
Sample 3 12.0	11.92	11.89

Derivative method:

The second order derivative method was applied for the analysis of some synthetic hard and resistant alloys of palladium with good accuracy and precision results are presented in Table 7

Table: 7 Analysis of Synthetic mixtures

Alloy composition	**Characteristic**	**Amount of Pd (II) found (%)**	**Relative error**
Pd 60% Au 40%	Jewellery alloy	58.9	+0.65
Pd (II) 6.00 Ag (I) 6.00	High resistance to corrosion	6.02	-1.31

CONCLUSION

Rapid color development, simplicity and selectivity are the advantages of the proposed method. The intensity of the colored species will not be affected by slight variation of the experimental parameters such as concentration of the reagent. The proposed method does not involve extraction, heating or any other stringent reaction conditions and offers the advantage of high color stability (24h). The commonly associated metal ions, especially Ti (IV), Al (III), Pt (IV) and Co (II) could be tolerated in considerable excess, which is an advantage over other reported reagents. The proposed method can be used as an alternative method for the determination of trace amounts of palladium in alloy steel samples, hydrogenation catalysts and water samples.

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