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Determination of Palladium (II) Using Cinnamaldehyde Isonicotinoyl Hydrazone by Derivative Spectrophotometric Technique

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ABSTRACT

A simple and derivative spectrophotometric method has been developed for the determination of palladium (II) using cinnamaldehyde isonicotinoyl hydrazone (CINH) reagent in aqueous medium. Palladium (II) forms a yellow colored water soluble complex with the CINH reagent in acidic buffer range of pH 3.0-6.0. Beer's law obeyed in the range 0.106 to 2.128 µg mL^{-1} of Pd (II) λ_{max} at 412 nm. The molar absorptivity and Sandell's sensitivity of colored species are 1.03 x 10^{4} L.mol^{-1}cm^{-1} and 0.0054µg cm^{-2} respectively. Palladium (II) forms (M: L) 1:1 complex and stability constant of the complex is 9.3 x 10^{4}. The developed derivative spectrophotometric methods were employed for the determination of palladium (II) in alloy samples and hydrogenation catalyst samples.

Keywords: Derivative spectrophotometry, Cinnamaldehyde isonicotinoyl hydrazone (CINH), Palladium (II), Alloy samples.

INTRODUCTION

The potential application of hydrazone derivatives for the spectrophotometric determination of metal ions has been reviewed by Singh.et.al [1]. Hydrazones are important organic analytical reagents for the determination of metal ions in microgram quantities. They react with many metal ions forming colored complexes and act as chelating agents. In general, the technique of solvent extraction is widely used in the spectrophotometric determination of metal ions [2-3]. 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. In the light of good analytical characteristics of hydrazones, herein we report direct (zero order) and derivative spectrophotometric determination of Palladium (II) using cinnamaldehyde isonicotinoyl hydrazone (CINH) 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 [4-9] are not exploited much.

MATERIALS AND METHODS

Apparatus: All absorption measurements were made in a Shimadzu 160A microcomputer based UV-Visible spectrophotometer equipped with 1.0 cm quartz cells. The instrumental parameters were optimized and the best results obtained in the wavelength range 300- 650 nm with a scan speed fast, spectral band width 2 nm, wavelength readability 0.1 nm increments and wavelength accuracy ± 0.5 nm with automatic wavelength correction.

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.

Palladium (II) stock solution: The standard Pd(II) solution (0.01 M) was prepared by dissolving accurately weighed 0.1773 g of palladium chloride (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 [10]. The working solutions were prepared by diluting the stock solution to an appropriate volume.

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 analytical reagent grade chemicals. All solutions were prepared with doubly distilled water.

Cinnamaldehyde isonicotinoyl hydrazone Solution: The reagent cinnamaldehyde isonicotinoyl hydrazone (CINH) was synthesized by refluxing equimolar amounts of Cinnamaldehyde and 4-isonicotinoyl hydrazide [11]. The structure of CINH was confirmed by infrared spectroscopy, proton nuclear magnetic resonance spectroscopy and mass spectrometry and given in figure 1.

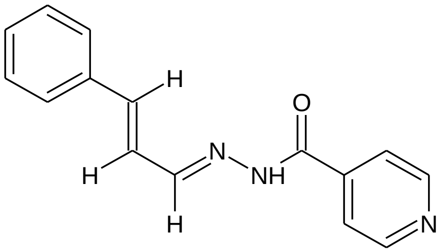

Figure 1 - Structure of cinnamaldehyde isonicotinoyl hydrazone (CINH)

The reagent solution (0.01 M) was prepared by dissolving 0.2512 g of CINH in 100 mL of dimethylformamide (DMF). The reagent solution is stable for 48 h.

Procedure for the determination of palladium(II) (Zero order): An aliquot of the solution containing 0.106 to 2.128 µg/mL of Pd(II), 10 mL of buffer pH 4.5, and 1.0 mL of CINH reagent 1x 10^{-2} M were taken in a 25mL volumetric flask and the solution was diluted up to the mark with doubly distilled water.

The absorbance of the solution was recorded λ_{max} at 412 nm in a 1.0 cm cell against reagent blank prepared under identical conditions. The measured absorbance was used to compute the amount of palladium (II) from the calibration plot.

Procedure for the determination of palladium (II) by first order derivative spectrophotometry: For the above solution of Pd(II)-CINH first order derivative spectrum was recorded with a scan speed having degrees of freedom 9 in a wavelength range 350 to 650 nm. The first order derivative peak-height (h) was measured by peak-zero method at 438 nm. The peak-height was plotted against the amount of Pd (II) to obtain the calibration curve.

Procedure for the determination of palladium (II) by second order derivative spectrophotometry: For the above solution, second order derivative spectrum of Pd(II) - CINH system was recorded with reference to reagent blank with 9 degrees of freedom, in a wavelength range 350 nm to 650 nm. In the second order derivative spectrum peak-height at 451 nm was measured from the zero line of spectrum. Calibration plots were constructed by plotting the derivative amplitude against the amounts of palladium (II).

Analysis of synthetic alloy samples: Synthetic alloy samples whose composition corresponds to industrial, dental alloys and stibiopalladinite mineral are prepared and analyzed for the determination of palladium (II) by adopting the recommended procedure. 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 100mL volumetric flask.

Analysis of hydrogenation catalyst samples: About 0.3 g of catalyst sample was transferred into 250 mL beaker, treated with 5 mL of 2 M nitric acid and covered. When the solution of gas diminished 10 mL of aqua-regio was added and the solution was evaporated to near dryness on a sand bath. The residue was dissolved in 5 mL of 2M nitric acid and diluted to 250 mL in a volumetric flask. Suitable aliquots were taken and analyzed for palladium using procedure discussed above.

RESULTS AND DISCUSSION

The reagent cinnamaldehyde isonicotinoyl hydrazone (CINH) was easily synthesized as any other Schiff base reagent. The color reactions are mainly due to complex formation of CINH with divalent and tetravalent metal ions in aqueous medium. In acidic medium, ligand presumably exists in enolic form and co-ordinates the metal ion as mono-anion to give neutral complexes. Palladium (II) reacts with CINH over a wide range of pH (1.0- 10.0) to form a water soluble yellow colored complex.

Absorption spectra: The absorption spectra of CINH and [Pd (II)-CINH] complex recorded in optimum conditions against buffer solution and reagent blank respectively shown in figure 2. The complex shows absorption maxima at 412 nm, where the reagent does not show appreciable absorbance. Therefore, analytical wavelength 412 nm was used for all measurements.

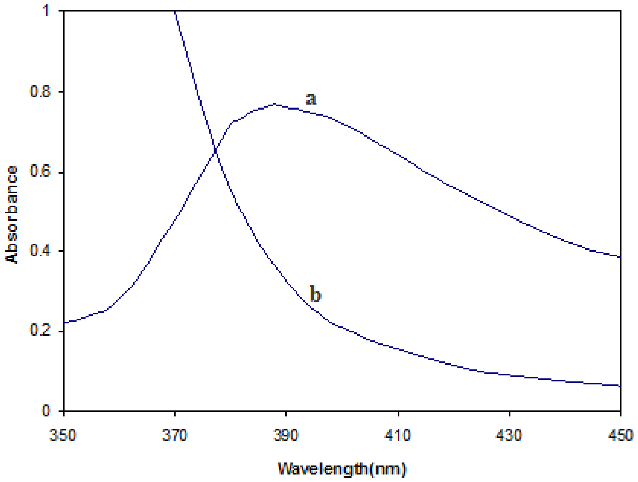

Figure 2 : Zero order absorption spectra of, Reagent (CINH) vs. buffer blank.
a) Pd(II)-CINH complex vs. reagent blank. Pd(II)=2.128 µg mL^{-1}, [CINH] = 4 x 10^{-4} M, pH (4.5) = 10 mL

Effect of pH: It was observed that the color reaction between Pd(II) and the reagent CINH was instantaneous in pH range 1.0 to 10.0 The study of the effect of pH on the color intensity of the complex showed that the maximum constant absorbance was obtained in the pH range 3.0 to 6.0. Therefore, pH 4.5 was kept constant throughout the experiment.

Color stability of the complex: The absorbance of palladium (II)-CINH complex was measured at different time intervals to ascertain the stability of the complex. The full color development of the complex remains constant upto five hours. The precision of the method in terms of relative standard deviation (n =10) for the determination of 2.128 µg mL^{-1} of Pd(II) is 3.20%.

Effect of CINH concentration: The amount of reagent necessary for full color development of Pd(II)-CINH was established and tabulated in table 1. The studies revealed that a 10-fold molar excess of CINH reagent is sufficient for complete and constant color development. Excess of reagent has no effect on the absorption of the complex.

Table 1: Effect of CINH concentration on the absorbance of the Pd (II)-CINH complex

Pd(II) : CINH	Absorbance
1:10	0.426
1:20	0.429
1:30	0.423
1:40	0.439
1:50	0.446

Pd(II) = 2.128 µg/mL, pH (4.5) = 10 mL, wavelength 412 nm.

Order of addition of reactants: The order of addition of metal ion, buffer solution and CINH reagent has no adverse effect on the absorbance of the colored complex.

Applicability of Beer's law: From the calibration plots (Figure 3) it was observed that, the system obeyed Beer's law in the range 0.106 to 2.128 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 0.426 to 2.128 µg mL^{-1} at 412 nm. The molar absorptivity and Sandell's sensitivity of the Pd(II)-CINH complex are 1.03 x 10^4 $L.mol^{-1}.cm^{-1}$ and 0.0054 $µg.cm^{-2}$ respectively. The straight line obeyed the equation $A_{412} = 0.0890 X + 0.0152$.

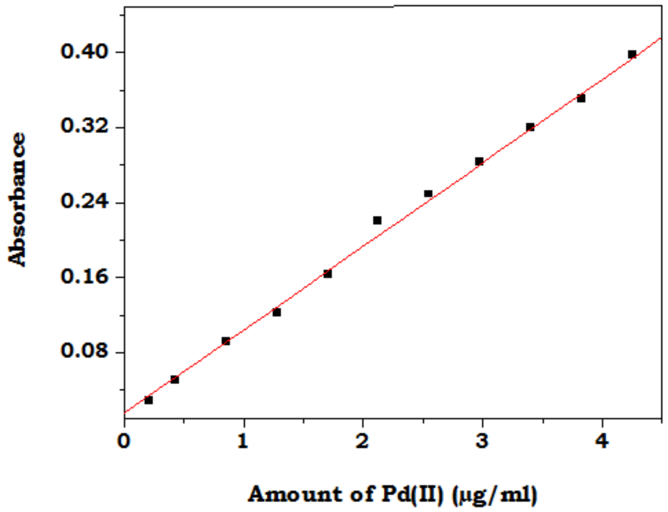

Figure 3: Absorbance vs. amount of Pd(II) (µg mL^{-1}).
[CINH] = 4 x 10^{-4} M, pH (4.5) =10 mL, Wavelength = 412 nm.

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): CINH]. The stability constant of the complex is determined as 9.3 x 10^{4} by Job's method. The Jobs curve for the Pd (II)-CINH complex was shown in figure 4.

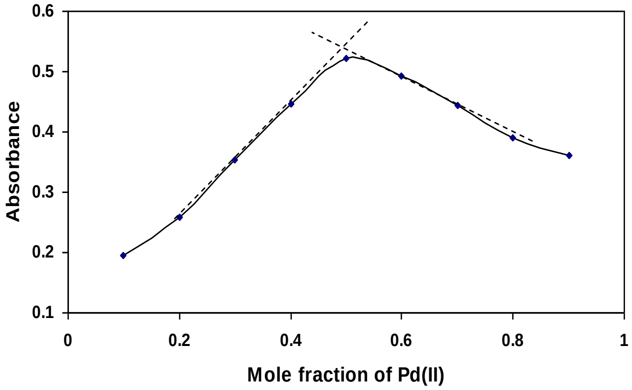

Figure 4: Job's curve of Pd(II)-CINH complex
pH (4.5) =10 mL, Wavelength = 412 nm

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).

The typical first order and second order derivative spectra are shown in figure 5 and figure 6 respectively. This shows that, the derivative amplitude measured at 438 nm for first order and 451 nm for second order was found to be proportional to the amount of palladium (II).

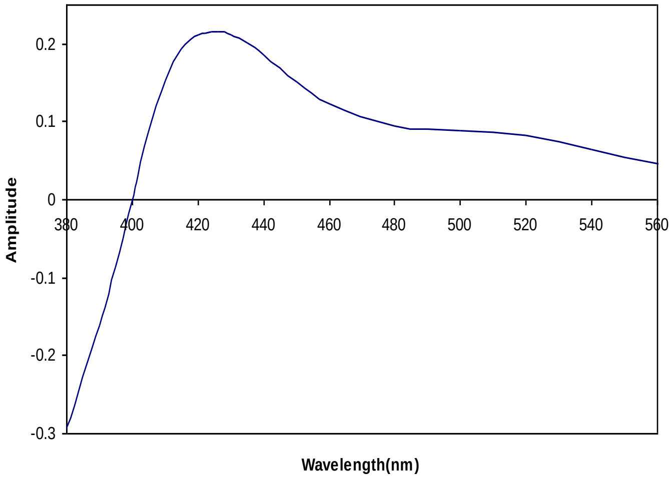

Figure 5: Typical first order derivative spectra of Pd (II)-CINH vs. reagent. Pd(II) = 2.128 µg mL^{-1}, [CINH] = 4 x 10^{-4} M, pH (4.5) = 10 mL.

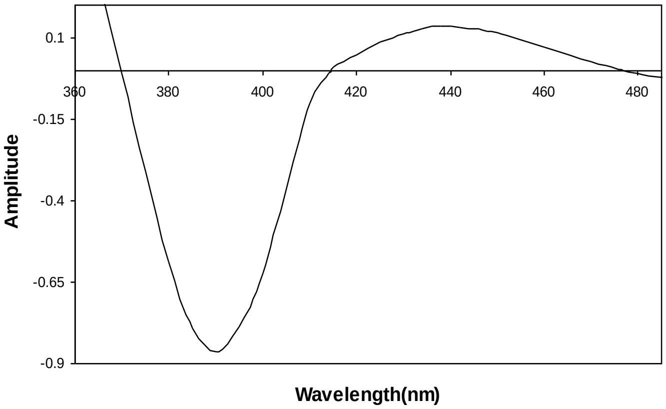

Figure 6: Typical Second order derivative spectra of Pd(II)-CINH vs. reagent Pd(II) = 2.128 µg mL^{-1}, [CINH] = 4 x 10^{-4} M, pH (4.5) = 10 mL

Effect of diverse ions: The effect of various diverse ions in the determination of Pd(II) was studied to determine the tolerance limit of foreign ion in the present method. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error ± 2% in the absorbance. The results are given in table 2.

Table 2: Tolerance limit of foreign ion in the determination of 2.128 µg mL^{-1} of palladium (II)

Ion added	**Tolerance limit (µg mL^{-1})**	**Ion added**	**Tolerance limit (µg mL^{-1})**
Tartarate	2925	La(III)	30
Tetraborate	2456	Ce(IV)	25
Sulphate	1920	Ru(III)	51
Bromide	1915	Ag(I)	22
Phosphate	1889	Cd(II)	15
Nitrate	1225	Au(III)	12
Urea	1206	Hg(II)	14
Acetate	609	Mo(VI)	0.2
Fluoride	310	Zn(II)	8.0
Citrate	72	W(VI)	6.0
Thiourea	66	Ti(IV)	4.0

Ascorbic acid	32	U(VI)	4.0
Oxalate	32	Zr(IV)	3.0
Pd(II)	418	Li(I)	3.0
Sb(III)	218	Rh(II)	2.5
Bi(III)	154	Fe(III)	2.2 [a, b]
Ba(II)	165	Cr(VI)	2.0
Se(IV)	150	Co(II)	25.0
Mn(II)	120	Ni(II)	30.0
As(III)	77	Th(IV)	1.0
Sn(II)	54	Cu(II)	0.2 [c], 0.1 [d]
Sr(II)	32	V(V)	0.2

‘a’ Masked with 228 µg/ml of fluoride
‘b’ Masked with 760 µg/ml of phosphate
‘c’ Masked with 61 µg/ml of thiourea
‘d’ masked with 35 µg/ml of ascorbic acid

The data suggest that several commonly associated anions and cations do not interfere in the determination of Pd(II) using CINH reagent, when they present in large excess. However, metals like Mo (VI), Cu (II),Th (IV) and V(V) were 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 Cu (II) metal was interfered even masking with thiourea or ascorbic acid. The interference of associated metal ion such as Fe (III) was decreased by masking with fluoride and phosphate.

APPLICATIONS

The spectrophotometric determination of Pd (II) in the alloy samples and hydrogenation catalyst 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 4.5 and 1.0 mL of CINH reagent $1x10^{-2}$ M 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 3 and table 4 respectively.

Table 3: Determination of Pd (II) in alloy samples

Sample composition	**Amount found* (%)**			**RSD (%)**		
	Zero order	**First order**	**Second order**	**Zero order**	**First order**	**Second order**
Stibio palladinite mineral (Pd, 75;Sb, 25%;)	74.1	74.4	74.2	+ 1.2	+ 0.79	+1.06
Pd, 96, Ru, 2; Rh, 2%;	94.4	95.2	95.4	+ 0.63	+ 0.83	+ 0.63
Pd, 72; Ag, 26; Ni, 2 %;	72.4	72.3	71.8	- 0.55	- 0.42	+ 0.27

* Average value of five determinations.

Table 4: Determination of Pd (II) in hydrogenation catalyst samples

Sample	**Amount of Pd(II) Present (%)**	**Amount found* (%)**			**RSD (%)**		
		Zero order	**First order**	**Second order**	**Zero order**	**First order**	**Second order**
Pd-charcoal	10	9.89	9.91	10.08	+ 1.1	+ 0.9	- 0.8
Pd-$CaCO_3$	5	4.91	5.09	4.94	+1.8	-1.8	+1.2
Pd-$BaCO_3$	5	4.89	4.96	4.96	+ 2.2	+ 0.8	+ 0.8
Pd-$BaSO_4$	5	5.12	4.94	4.93	- 2.4	+ 1.2	+ 1.4

* Average value of five determinations.

CONCLUSIONS

The present method, using CINH as spectrophotometric reagent for the determination of Pd(II) is simple, rapid, reasonably sensitive. Physico-Chemical and analytical characteristics of Pd(II)-CINH complex were tabulated in table 5.This method was favorably compared with previously reported spectrophotometric methods [12-21]. Most of the spectrophotometric methods involve either extraction [12-14] or heating of the reaction mixture [15]. 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. Large amounts of tartarate, tetraborate, sulphate, bromide, phosphate, nitrate, lead(II), antimony(III), barium(II), bismuth(III), selenium(IV) and manganese(II), moderate amount of the tin(II), ruthenium(III), nickel(II), cobalt(II), silver(I), cadmium(II), gold(III) and mercury(II) do not interfere in the present method. This method is also free from the interference of lanthanum (III), cerium (IV), arsenic (III) and other rare earth metals.

Table 5: Physico-Chemical and analytical characteristics of Pd(II)-CINH complex

Characteristics	Results
λ_{max} (nm)	412
pH range (optimum)	3.0-6.0
Mole of reagent required per mole of metal ion for full colour development	10- folds
Molar absorptivity (L.mol^{-1}.cm^{-1})	1.03 x 10^4
Sandell's sensitivity (µg.cm^{-2})	0.0054
Beer's law validity range (µg/mL)	0.106 to 2.128
Optimum concentration range (µg/mL)	0.426 to 2.128
Relative standard deviation (%)	3.20
Composition of complex (M:L) obtained in Job's and mole ratio method	1: 1
Stability constant of the complex	9.3x 10^4

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