Determination of Traces of Pd(II) in Spiked Samples by Using 3,4-Dihydroxybenzaldehydeisonicotinol-hydrazone as a Chelating Agent with UV Visible Spectrophotometer

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Abstract: A simple, rapid, sensitive and inexpensive method has been developed for the determination of trace amounts of palladium(II) using 3,4-dihydroxybenzaldehydeisonicotinoylhydrazone (3,4-DHBINH). The metal ion gives a yellow colored complex with 3,4-DHBINH in acetate buffer of pH 3.0 with 1:1 (metal: ligand) composition. The complex shows maximum absorption at 380 nm. Beer's law is obeyed in the range 0.5-20.0 ppm of Pd(II). The molar absorptivity, Sandell's sensitivity and detection limit were found to be $0.53 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, $0.02 \mu\text{g cm}^{-2}$ and $0.0948 \mu\text{g mL}^{-1}$, respectively. The correlation coefficient and regression coefficient of the Pd(II)-3,4-DHBINH complex were 1.08 and 0.04 respectively. Major cations and anions did not show any interference. Antimicrobial activity of the Pd(II)-3,4-DHBINH has been studied. The developed method has been successfully applied to the analysis of Pd(II) in spiked samples. Comparing the results with those obtained using an atomic absorption spectrophotometer tested the validity of the method

Keywords: Trace, Palladium, Spectrophotometer, Chelating agent

Introduction

Palladium and its alloys have a wide range of applications both in the chemical industry and in instrument making¹. Environmental contamination by the platinum group element (PGEs),

mainly related to automotive catalytic converters, is exponentially increasing and reliable and accurate quantification is a mandatory task. The wide use of palladium not only in automotive catalytic converters but also as a drug and in food production has led to a more uncontrolled release of those metals in the environment². Palladium is one of the precious metals. Owing to its corrosion resistant nature and alloying ability, palladium is an important element in metallurgy. Its alloys are used in dental and medicinal devices and in jewelry manufacture. Palladium-cobalt alloys show catalytic activity in the hydrogenation of nitrile function³. Moreover, palladium is used in automobile catalysts together with Pt and Rh⁴.

For the determination of palladium at micro amount levels, there are several frequently adopted methods using analytical techniques, such as AAS, ICP-AES, ICP-MS, X-ray fluorescence spectroscopy, spectrophotometry, spectrofluorometry and such other techniques. Among these, spectrophotometric methods are preferred because they are cheaper and easy to handle. Many physiologically active hydrazones find application in the treatment of diseases like tuberculosis, leprosy and mental disorders. Hydrazones also act as herbicides, insecticides, nematocides, rodenticides and plant growth regulators.

Isonicotinoylhydrazide (INH) is an important antitubercular agent and has potential sites for formation of complexes with metal ions. The potential use of hydrazone derivatives in analytical chemistry, for the spectrophotometric determination of ions has been reviewed by Singh *et al.*⁵. It appeared through the scan of the available literature that little attention has been paid to the use of isonicotinoylhydrazones of substituted carbonyl compounds for spectrophotometric determination of palladium. Since, focus of interests in the study of the analytical usefulness of 3, 4-dihydroxybenzaldehydeisonicotinoylhydrazone, for the spectrophotometric determination of such important metal palladium(II), a new method for the spectrophotometric determination of Pd(II) using 3,4-dihydroxybenzaldehydeisonicotinoylhydrazone (3,4-DHBINH) is proposed in this work. This method is rapid, sensitive, inexpensive and superior to most of the reported methods⁶⁻¹⁵ in simplicity.

Experimental

Apparatus

A recording spectrophotometer (model Shimadzu 2450) was employed in photometric studies. A Perkin – Elmer 2380 atomic - absorption spectrophotometer was employed for the comparison of the results of the samples. A digital pH meter (model Elico LI – 129) was used for measuring the pH of the solutions.

Preparation of a stock solution of palladium(II)

1.664 g of palladium(II) chloride was dissolved in a minimum amount of 2M hydrochloric acid solution in a one liter volumetric flask, and was finally made up to the mark with 2M hydrochloric acid solution. This stock solution was standardized gravimetrically using dithizone¹⁶.

Preparation of 3, 4- dihydroxybenzaldehydeisonicotinoylhydrazone

Equimolar quantities of 3,4-dihydroxybenzaldehyde (3,4-DHB) dissolved in alcohol and aqueous isonicotinoylhydrazide (INH) were taken in a 500 mL round bottom flask and refluxed for 2-3 h. The contents were cooled and then filtered. The product (Scheme 1) obtained was washed with aqueous methanol and finally recrystallized from rectified spirit. The purity of the reagent was checked by TLC and melting point analysis (m.p. 218 – 219 °C).

It is evident from I.R. spectrum of the ligand that, C=N group is present in the compound because the peak appears at 1600 cm⁻¹. C=O(Stretching) amide peak appears at 1656.9 cm⁻¹. -OH group peak appears at 3484.6 cm⁻¹, -NH peak appears at 3245 cm⁻¹. From the above data it is

confirmed the formation of 3,4-dihydroxybenzaldehydeisonicotinoylhydrazone. A 0.1 M stock solution was prepared by dissolving 2.57 g of 3,4-DHBINH in 40% aqueous dimethyl formamide.

Scheme 1. Formation of 3, 4-DHBINH

Buffer solutions

Solutions of 1.0 M sodium acetate and 1.0 M acetic acid were prepared in double distilled water. Suitable portions of these solutions were mixed to get the desired pH of the solution.

Procedure for determination of Pd(II)

1.0 mL of Pd(II) solution was placed in a test tube; the pH was adjusted to 3.0 by the addition of $\text{CH}_3\text{COOH}+\text{CH}_3\text{COONa}$ buffer. 1.0 mL of 3,4- DHBINH solution was added. The contents in the test tube were diluted to 10.0 mL. The absorbance was measured at 380 nm against a reagent blank.

Results and Discussion

Absorption spectra

The absorption spectra in the 300-600 nm range for 3,4- DHBINH and Pd(II)- 3,4-DHBINH complex are shown in Figure 1. The formation of the 380 nm band in figure 1 must be connected with chelate formation between Pd(II) and 3,4-DHBINH .

Figure 1. Absorption spectra of (a) 3,4-DHBINH; (b) Pd(II)-3,4-DHBINH complex; Pd(II): 1 mL of 1.0×10^{-4} M; 3,4-DHBINH: 1.0 mL of 1.0×10^{-3} M ; pH: 3.

Effect of pH

The effect of pH on the absorption of the complex was studied at 380 nm with solutions containing 1.0×10^{-4} M Pd(II) solution and 1.0×10^{-3} M 3,4-DHBINH. The spectrum of the Pd(II)-3,4-DHBINH solution was strongly dependent on the pH of the solution. Our experiments showed that the complex has maximum absorbance at pH 3.0. The optimum working pH was found to be pH 3.0. The plot between pH and absorbance of complex is shown in Figure 2.

Figure 2. Effect of pH on Pd(II) - 3,4-DHBINH complex; Pd(II): 1 mL of 1.0×10^{-4} M; 3,4-DHBINH: 1.0 mL of 1.0×10^{-3} M; $\lambda_{\max}$: 380 nm.

Effect of reagent concentration

The influence of excess of reagent concentration on the absorbance of the complex was studied. The absorbance of 1.0×10^{-4} M Pd(II) solution after the addition of varying concentrations of 3, 4-DHBINH ranging from 1.0×10^{-4} M to 20×10^{-4} M at pH 3.0 was measured at 380 nm; the reaction of Pd(II) with 3,4-DHBINH solution increased in sensitivity with increasing solution concentration. It is almost consistent after ten fold excess of the reagent concentration with respect to metal concentration. Hence ten fold molar excess of reagent was considered for further studies.

Applicability of Beer's law

Known aliquots of 10.0 mL solutions, each containing constant volumes of 4.0 mL of buffer (pH = 3.0), 1.0 mL of 10.0×10^{-4} mol L⁻¹ reagent and 1.0 mL of Pd(II) containing 0.5–28.0 $\mu\text{g mL}^{-1}$ were prepared. The absorbance of these solutions was measured at 380 nm. A graph plotted between the amount of Pd(II) and its absorbance is shown in Figure 3. It can be observed from the graph that a linear plot passing through the origin obeys Beer's law in the range 0.5–20.0 $\mu\text{g mL}^{-1}$ of Pd(II).

Figure 3. Applicability of Beer's law to Pd(II)- 3,4-DHBINH complex; 3,4 -DHBINH: 1.0 mL of 1.0×10^{-3} M; pH: 3.0; $\lambda_{\max}$: 380 nm.

Molar absorptivity, Sandell's sensitivity and correlation co-efficient

The molar absorptivity of the complex was calculated to be $0.533 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity of the complex obtained from Beer's law data was $0.02 \mu\text{g cm}^{-2}$ at 380 nm. The correlation coefficient of the Pd(II)-3,4-DHBINH complex was 1.00, which indicated an excellent linearity between the two variables.

Ringbom plot for the Pd-3,4-DHBINH complex

A Ringbom plot is an established standard adopted to know the optimum range of concentration for a system that obeys Beer's law. A Ringbom plot was drawn between $\log C$ of Pd(II) and $(1-T)$, where T is transmittance. The plot has a sigmoid shape with a linear segment at intermediate absorbance values (0.371-0.650) and concentration values (8.0 - $14.0 \mu\text{g mL}^{-1}$). The slope of the Ringbom plot from Figure 4, is 0.534. Hence the ratio between the relative error in concentration and photometric error is 4.3127 for a one percent photometric error, $\Delta P = 0.01$. Hence the relative error in the concentration is 0.0431.

Figure 4. Ringbom's plot of Pd(II) – 3,4-DHBINH complex ; Pd(II) : 2000 - $24000 \mu\text{g L}^{-1}$; 3,4 –DHBINH: $1.0 \text{ mL of } 1.0 \times 10^{-3} \text{ M}$; pH: 3.0; λ_{max} : 380 nm.

Precision and accuracy of the method and detection limit of the method

To assess the precision of the method, determinations were carried out with different concentrations of Pd(II) under optimum conditions. The standard deviation was found to be not more than 0.0015 and the relative standard deviation was less than 0.427%. It is evident from these results that the method is precise, besides being accurate. The detection limit was determined as the amount of Pd(II) corresponding to thrice the standard deviation blank value. A value of $0.095 \mu\text{g mL}^{-1}$ was obtained.

Composition of the Pd(II)- 3,4-DHBINH complex

Job's method of continuous variation, the molar-ratio method and Asmus's method were employed to elucidate the composition of the complex. Equimolar solutions of Pd(II) and 3,4 -DHBINH ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) were used to determine the metal to ligand ratio by Job's method of continuous variation. The absorbance values were recorded at 380 nm against the reagent blank. A plot was drawn between the absorbance and V_M/V_M+V_L , where V_M and V_L are the volumes of the reagent and metal, respectively. The obtained curve shown in Figure 5 is indicative of 1:1 stoichiometry in the complex. This was further confirmed by molar-ratio

method (Figure 6). Finally the composition of the complex was verified by Asmus's method. Based on these experiments the probable structure of the complex is deduced as follows.

Figure 5. Job's method of continuous variation of Pd(II) - 3,4-DHBINH complex; Pd(II) and 3,4-DHBINH: 1.0 mL of 1.0×10^{-4} M; pH:3.0; $\lambda_{\max}$: 380 nm.

Figure 6. Mole- ratio method of Pd(II) - 3,4-DHBINH complex; Pd(II) and 3,4- DHBINH: 1.0 mL of 1.0×10^{-4} M; pH:3.0; $\lambda_{\max}$: 380 nm.

Effect of foreign ions

The effect of foreign ions on complexation was studied by taking 1.0 mL of Pd(II) solution, 1.0 mL of required concentration of the foreign ion solution, 4.0 mL of buffer (pH = 3.0) and 2.0 mL of 3,4- DHBINH solution in a 10.0 mL standard flask. The total volume of the

solution was brought to 10.0 mL with double distilled water. The experiment was repeated by changing the concentration of the diverse ion. The absorbances were measured at 380 nm. A change of ± 0.02 was taken as the tolerance limit for interference. The interference of various ions in the determination of Pd(II) is reported in Table 1.

Applications

The developed extractive spectrophotometric method for palladium(II) was successfully applied for its determination in water samples and synthetic mixtures.

Analysis of palladium(II) in water samples

Various water samples were prepared¹⁷ 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 spectrometry. The results are given in Table 2.

Table 1. Tolerance limit of diverse ions in the determination of Pd(II)

Diverse ion	Tolerance limit $\mu\text{g.mL}^{-1}$	Diverse ion	Tolerance limit $\mu\text{g.mL}^{-1}$
Ascorbic acid, Thiocyanate	15000	Mg(II),Ca(II)	6000
Sulphate	10000	Ba(II), Mn(II) Fe(III)	4500
Thiourea	8500	Al(III), NI(II),Ag(I)	3500
Iodide	5500	Zn(II)	2500
Tartrate	3000	Cu(II)	500
Oxalate	2750		
Phosphate	2500		

Table 2. Determination of palladium(II) in water samples

S.No.	Palladium(II) added $\mu\text{g mL}^{-1}$	Palladium(II) found		S.D.	R.S.D.
		AAS	Present method		
Sample 1	0	0	0	--	--
Sample 2	5	4.95	4.89	0.0357	0.737
Sample 3	10	9.98	9.92	0.0234	0.236
Sample 4	15	14.96	14.85	0.0245	0.165
Sample 5	20	19.97	19.70	0.023	0.117

Analysis of palladium(II) in synthetic mixtures

Various synthetic mixtures were prepared¹⁷ and analyzed by employing the proposed developed procedure. The results are in perfect agreement with those obtained by direct atomic absorption spectrometer. The results are given in Table 3.

Table 3. Determination of Palladium in synthetic mixtures

Synthetic mixture composition $\mu\text{g. mL}^{-1}$	Pd(II) added $\mu\text{g mL}^{-1}$	Palladium(II) ^a found		S.D.	R.S.D %
		AAS	Present method		
4.0 Fe(III)+ 4.0 Mn(II) + 1.0 Cu(II)*	10.00	9.98	9.85	0.0291	0.296
2.0 Al(III) + 3.0 Ni(II) + 3.0 Ag(I)	12.00	11.95	11.86	0.0283	0.239
3.0 Co(II)+3.0 Mn(II)+ 2.0 Zn(II)	14.00	13.97	13.89	0.0223	0.160

^a. Average five determinations

* The interference of Cu(II), is eliminated by using EDTA as a masking agent

Conclusion

3,4-Dihydroxybenzaldehydeisonicotinolhydrazone a new reagent is proved to be the best reagent for the determination of palladium(II) when compared to some other spectrophotometric methods reported earlier⁷⁻¹⁶ (Table 4). This method was successfully applied for the determination of palladium(II) in water samples and synthetic mixtures.

Table 4. Comparison of the present method with the other spectrophotometric methods for the determination of palladium(II)

S.No.	Reagent	pH	$\lambda_{\max}$ nm	$\epsilon_{\max}, \times 10^4 /$ $\text{Lmol}^{-1} \text{cm}^{-1}$	M:L	Beer's law range $/\mu\text{g} \cdot \text{mL}^{-1}$	Ref
1	5-Methyl-2,3-hexanedione dioxime	0.5-1.5	379	0.389	1:2	50-9000	7
2	Glyoxalb(4-phen-yl-3-thiosemicarba- zone)	9.6	635	0.320	1:1	N.R	8
3	Phenanthraquinine monothiosemicarbazone	N.R	540	0.420	N.R	1.3-6.7	9
4	3-Phenoxybenzal-doxime	4.0	435	0.2434	N.R	0.4-4.0	10
5	Furfurylacroline thiosemicarbozone	2.0-10.0	390	0.41	N.R	N.R	11
6	Benzoyloxybenzaldehyde-thiosemicarbazone	5.0	365	0.4	1:1	5.0-60 $\mu\text{g/mL}$	12
7	2-Arylthio-phenyl-nitroaceto-phenone	5-0	430	0.1612	NR	2.5-2-0	13
8	2-Mercapto – 5 anilino 1,3,4 – thiadiazole.	Basic medium	312 260	0.3209 0.2329	1:2	0.33-10.66	14
9	Chromocitromin B-H	2-3	470	0.1	1:1	NR	15
10	7-Iodo – 8 – hydroxy quinoline – 5 – Sulphonic acid	NR	430	0.0958	NR	2.5-wide range	16
11	3,4-Dihydroxybenzaldehydeisonicotinoyl-hydrazone	3.0	380	0.533	1:1	0.5-20.0	Present method

N.R.: Not Reported

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