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2, 4-Dihydroxy benzaldehyde isonicotinoyl hydrazone as a Spectrophotometric reagent for the determination of palladium (ii)

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ABSTRACT

A new reagent, 2,4-dihydroxy benzaldehyde isonicotinoyl hydrazone has been used for the determination of palladium (II). The reagent reacts with palladium (II) in aqueous dimethyl formamide in wide P^H range forming yellow coloured 2:3 (M:L) soluble complex with λ_{max} at 435nm. Beer's law is obeyed in the range $0.213-2.129 \mu\text{g mL}^{-1}$ and $0.213 - 2.139 \mu\text{g mL}^{-1}$ of Pd (II) in direct and derivative methods, respectively. The molar absorptivity, Sandell's sensitivity, detection limit, determination limit and relative standard deviation are found to be $2.08 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, $0.0051 \mu\text{g cm}^{-2}$, $0.015 \mu\text{g mL}^{-1}$, $0.046 \mu\text{g mL}^{-1}$ and 0.43%, respectively. The second and third derivative spectrophotometric methods develop for the determination of palladium (II) shows greater sensitivity and selectivity. The proposed direct and derivative methods are applied for the determination of palladium in standard alloy samples.

Keywords: Palladium (II), 2,4-dihydroxy benzaldehyde isonicotinoyl hydrazone, derivative spectrophotometry.

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INTRODUCTION

Palladium has found great application as a catalyst with the increasing use of palladium in jewellery and cosmetic industry in the form of alloys, a need has arisen for the development of rapid and effective methods for the determination of palladium (II) in real samples. It has strong resistance to corrosion in air to the action of acids (except nitric acid) at ordinary temperatures. Solution of palladium chloride and potassium sulphite is used for detecting carbon monoxide in the air at industrial areas. Due to the introduction of palladium, platinum and rhodium for use in catalytic converters in motor vehicles, the emission of these metals into the environment has increased. In addition, an increased uptake of palladium by plants has led to polluted soil [1]. Palladium is thought to be one of the strongest allergens from a health hazard view point [2].

For these reasons, rapid and accurate palladium determination methods for process, quality and pollution control are valuable. For the determination of palladium at micro levels, there are several frequently adopted methods using analytical techniques such as atomic absorption spectrophotometry, spectrofluorimetry and other techniques. Among these, spectrophotometric methods are preferred because they are cheaper and easier to handle but with comparable sensitivity.

Several organic reagents have been used for the spectrophotometric determination of Pd (II). We report herein a simple, rapid, non-extractive, sensitive and selective direct and derivative spectrophotometric method in micellar medium for the determination of micro and nanogram quantities of palladium (II) [3] using 2,4-dihydroxy benzaldehyde isonicotinoyl hydrazone (DHBINH) as a chromogenic agent.

MATERIALS AND METHODS

The absorbance and P^H measurements were made on a Shimadzu UV-Vis Spectrophotometry (160A) and ELICO digital P^H meter (LI-120), respectively. 2,4-Dihydroxy benzaldehyde isonicotinoyl hydrozone (DHBINH) was synthesized by adopting the reported procedure⁴. 0.01M solution of the reagent in dimethyl formamide (DMF) was used in further studies. Palladium(II) (Sigma-Aldrich) (0.01M) solution was prepared in distilled water and standardized. Buffer solutions of P^H 1.0-8.0 were prepared by suitable mixture of 0.2M CH_3COOH -0.2M CH_3COONa and 2M NH_4Cl – 2M NH_4OH , respectively.

Direct spectrophotometry : In each of the 10 ml volumetric flasks, 4 ml of buffer solution (P^H 5.0), and 0.3 ml of DHBINH ($2 \times 10^{-4}M$) were taken and various volumes of $2 \times 10^{-5}M$ palladium (II) solutions were added. The resultant solutions were made up to the mark with distilled water. The absorbance was measured at 435nm against the reagent blank. The calibration plot was prepared by plotting the absorbance against the amount of palladium (II).

Derivative spectrophotometry: The second and third order derivative spectra were recorded for the above solutions with a scan speed of fast (nearly 2400nm min⁻¹), split width of 1nm with nine degrees of freedom in the wave length range 350 – 600nm and presented in figures 1 and 2. The second order derivative spectra gave a trough at 440nm and a crust at 510nm with Zero cross at 463nm (fig:1). In the third derivative spectra, a large crust at 415nm, a small crust at 525nm and a relatively large trough at 485nm with zero crosses at 432nm and 500nm (fig:2) respectively. Hence, Pd(II) was determined by measuring the derivative amplitude at 440nm and 510nm for second order derivative and 415nm, 485nm and 525nm for third order derivative spectra.

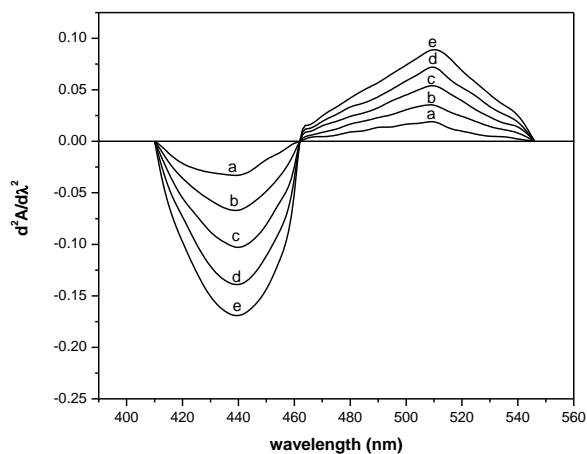


Fig.1: Second order derivative spectra of Pd (II) - DHBINH
Amount of Pd (II) ($\mu\text{g mL}^{-1}$) : a. 0.425; b.0.852; c. 1.277; d. 1.703; e. 2.129 [DMF] =15%

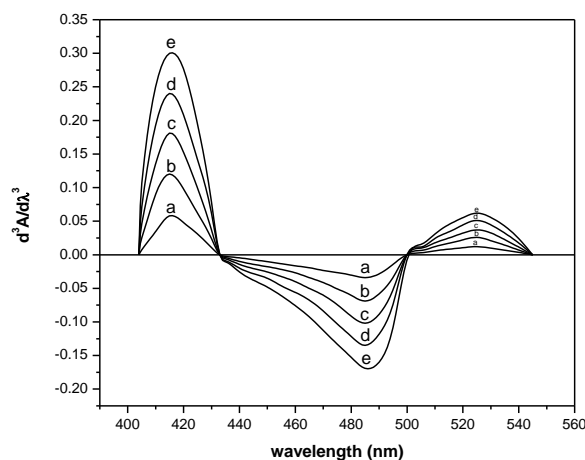


Fig.2: Third order derivative spectra of Pd (II) - DHBINH
Amount of Pd (II) ($\mu\text{g mL}^{-1}$) : a. 0.425; b.0.852; c. 1.277; d. 1.703; e. 2.129

RESULTS AND DISCUSSION

Direct method: Palladium(II) react with DHBAINH in the P^H range 1.0-8.0 forming yellow coloured solution. The absorption spectrum of the coloured solution showed maximum absorbance at 435nm.

The calibration plot followed the regression equation $A_{435} = 0.1974 C - 0.00014$. Beer's law was obeyed in the range $0.213-2.124 \mu\text{g mL}^{-1}$ of Pd(II) at P^H 5.0. The various analytical and statistical parameters are evaluated and shown in table: 1. The studies on effect of diverse ions showed that large number of anions and cations do not interfere (table: 2) . The possible interferences of some metal ions are reduced by masking them with appropriate masking agents.

Table 1: Comparison of results

Parameter	Direct method	Second derivative		Third derivative		
	435 nm	440 nm	510 nm	415 nm	485 nm	525 nm
Beer's law range ($\mu\text{g mL}^{-1}$)	0.213-2.129	0.213-2.139	0.426-2.129	0.027-2.129	0.106-2.129	0.213-2.129
Molar absorptivity, ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)	2.08×10^4	-	-	-	-	-
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.0051	-	-	-	-	-
Angular coefficient (m)	0.1974	0.0808	0.0426	0.1418	0.079	0.0296
Y- intercept (b)	-0.0001	-0.0011	-0.0005	-0.009	0.00007	0.0003
Correlation coefficient (r)	0.9999	0.9997	0.9992	0.9994	0.9998	0.9991
Relative standard deviation (%)	0.43	1.39	1.85	0.70	1.17	1.12
Detection limit ($\mu\text{g mL}^{-1}$)	0.015	0.048	0.070	0.019	0.034	0.061
Determination limit ($\mu\text{g mL}^{-1}$)	0.046	0.145	0.211	0.057	0.103	0.182
Composition (Metal: ligand)	2 : 3	-	-	-	-	-
Stability constant	1.48×10^{20}	-	-	-	-	-

Derivative method: Derivatization of the absorption spectrum of the yellow coloured [Pd(II)-DHBAINH] complex solution showed that Pd(II) was determined by measuring the derivative amplitude at 510nm for the second order and 415nm, 485nm and 525nm for third order spectra. The calibration plots in the figures 3 and 4 reveal that the third order derivative spectra at wavelength 415nm is more sensitive with wider Beer's law range than the zero order and

second order derivative method. The effect of diverse ions in the derivative amplitudes (table 3) showed that the metal ions interfere seriously in zero order method are greatly enhanced in the derivative methods indicating the grater selectivity of derivative methods than the direct method.

Table 2: Tolerance limits of foreign ions

Foreign ion	Tolerance limit ($\mu\text{g mL}^{-1}$)	Foreign ion	Tolerance limit ($\mu\text{g mL}^{-1}$)
Tartrate	2960	Mg(II)	1600
Sulphate	1920	Ba(II)	1250
Bromide	1500	Ca(II)	1120
Citrate	1460	Sr(II)	950
Nitrate	1200	Na(I)	810
Carbonate	1200	K(I)	740
Iodide	1200	W(VI)	360
Chloride	710	Cd(II)	60
EDTA	700	Hg(II)	40
Thiosulphate	690	Ir(III)	30
Phosphate	560	Tl(III)	30
Oxalate	470	Mo(VI)	20
Fluoride	380	Ce(IV)	20
Thiocyanate	290	U(VI)	15
Thiourea	140	Zr(IV)	10
Ascorbic acid	60	Bi(III)	10
		Co(II)	6, 120 ^a
		Ni(II)	6, 80 ^a
		Zn(II)	6, 75 ^a
		Cr(VI)	6, 85 ^a
		Au(III)	6, 110 ^b
		Sn(II)	6, 55 ^c
		Ag(I)	4, 45 ^b
		Th(IV)	2, 65 ^a
		Ru(III)	2
		V(V)	0.3, 90 ^a
		Cu(II)	0.3, 60 ^a
		Ga(III)	0.2, 55 ^a
		Fe(III)	0.2, 60 ^a
		Al(III)	0.6, 70 ^c
		In(III)	0.5, 65 ^c

a = in presence of 500 ppm of EDTA b = in presence of 600 ppm of thiosulphate

c = in presence of 1000 ppm of tartrate

Amount of Pd(II) = 2.129 $\mu\text{g mL}^{-1}$ pH = 5.0

Table 3: Tolerance limit foreign ions (in folds)

Foreign ions	Tolerance limit (in folds)		
	Zero order	Second derivative	Third derivative
Co(II)	6	75	40
Ni(II)	6	110	70
Zn(II)	6	55	80
Cr(VI)	6	75	40
Au(III)	6	30	50
Sn(II)	6	25	75
Ag(I)	4	120	60
Th(IV)	2	85	55
Ru(III)	2	45	15
V(V)	<1	85	60
Cu(II)	<1	70	40
Fe(II)	<1	55	25
Al(III)	<1	130	50
In(III)	<1	45	35

Applications : Using the second order derivative method Pd(II) was determined in platinum – Iridium alloy and oakay allow. The Pd (II) content was determined and the results are presented in table: 4 and 5.

Table 4: Determination of Pd(II) in Pd-Charcoal

Sample Composition (%)	Found *
Pd – Charcoal : Pd – 10% ; C – 90%	9.85 ± 0.067

*Average of four determinations ± SD

Table 5: Determination of Pd(II) in alloys samples

Sample	Certified Composition(%)	Pd(II) (µg)		Relative error (%)
		Taken	Found *	
Ookayalloy	Pd-20.5; Ni-60.0;V-19.5	18	17.8	-1.1
Pt-Ir alloy	Pd-3.5;Pt-550; Ru-7.0;Cu-30; Fe-3.5;Ir-28.0	22	22.2	+0.91

*Average of five determinations.

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