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Micro-Determination of Palladium Using 2,6-*Bis*(1-hydroxy-2-naphthylazo)pyridine as an Analytical Ragent

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A simple, selective and sensitive spectrophotometric method was developed for the micro-determination of palladium(II) using 2,6-*bis* (1-hydroxy-2-naphthylazo)pyridine (PBN). Alcoholic solution of 2,6-*bis*(1-hydroxy-2-naphthylazo)pyridine formed two complexes with palladium(II) at different pH, a green coloured complex having λ_{max} 650 nm in the pH range 3.5-5.0 and a reddish-brown complex absorbing maximum at 570 nm in the pH range 7.5-9.0 on warming for *ca.* 5 min on a water bath. At pH 3.5-5.0, the green coloured Pd(II)-PBN complex had molar absorptivity and Sandell's sensitivity 1.06×10^4 L mol^{-1} cm^{-1} and 0.010 µg cm^{-2}, respectively. The validity of the Beer's law was followed upto 14 ppm with an optimum concentration range for accurate determination of 0.8-12.5 ppm. The molar composition of the complex was 1:1 (M:L) as determined by Job's method of continuous variations. In the pH range 7.5-9.0, the reddish-brown Pd(II)-PBN complex had molar absorptivity of 1.0×10^4 L mol^{-1} cm^{-1} showing the Sandell's sensitivity of 0.010 µg cm^{-2}. Beer's law was followed upto 11.8 ppm with the optimum concentration range of 0.8-10.5 ppm. The reddish-brown complex had the molar composition of 1:2 (M:L). A number of foreign ions tested for their interferences and use of masking agents whenever necessary were investigated during the micro-determination of palladium(II). Analytical method established at low pH showed good sensitivity and its application was extended to determine Pd(II) in some synthetic solutions equivalent to that of some alloys, hydrogenation catalyst *etc*.

Key Words: 2,6-*Bis*(1-hydroxy-2-naphthylazo)pyridine, Palladium(II), Spectrophotometry.

INTRODUCTION

The high melting points of palladium and its alloys provide high resistance to corrosion. Therefore, it is widely used in electrical devices. Palladium and its alloys are also applied as dental restorative materials; palladium-gold alloys are used in jewellary as a substitute for many gold alloys. Thus it is important to explore the possibilities of developing a simple, sensitive and selective method for the determination of palladium traces in various synthetic mixtures, alloys, as a component in the three-way catalysts in automobile exhaust gas catalytic beads and hydrogenation catalyst processes[1-4]. For the quantitative determination of palladium in trace amount, there are several frequently adopted methods such as atomic absorption spectrophotometry, X-ray fluorescence spectroscopy, spectrofluorometry, spectrophotometry, *etc*. Among these, spectrophotometric methods are preferred as they are more economical, easy to handle, with a comparable sensitivity and accuracy and good precision. It is one of the most commonly used techniques for routine analysis of metals[5-10].

This paper reports, 2,6-*bis*(1-hydroxy-2-naphthylazo)-pyridine (PBN) as an analytical reagent for the micro-determination of palladium(II) spectrophotometrically, whereas a limited number of heterocyclic azo dyes find their use for the determination of noble metals. Comparatively this reagent has been found a potential reagent for palladium(II).

EXPERIMENTAL

A Bausch and Lomb Spectronic 2000 spectrophotometer with 10 mm matched glass cells was used for recording spectra and a Beckman pH meter was used for pH measurements.

Reagents 2,6-*bis*(1-hydroxy-2-naphthylazo)pyridine (PBN) solution: PBN as synthesized earlier[11], was used as a 1×10^{-3} M solution prepared by dissolving 0.419 g in 1 L of pure ethanol. Solutions more than a week old were discarded.

Standard palladium(II) solution: A stock solution of palladium(II) was prepared by dissolving appropriate amounts of palladium chloride (Johnson and Mathey, UK) in 2 N hydrochloric acid. The solution was standardized gravimetrically with dimethylglyoxime.

Acetate buffer, pH 4.0: An acetate buffer solution was prepared by mixing 800 mL of 0.2 N acetatic acid and 200 mL of 0.2 N sodium acetate solution in a 1 L measuring flask. M/5 Sodium acetate solution was prepared and used for pH adjustments.

All other reagents were of analytical grade and doubly distilled water was used throughout.

Detection method for the determination of palladium(II)

At low pH: To a suitable volume of sample containing 20-312 µg of palladium(II), add 2 mL of 1×10^{-3} M PBN solution followed by 2 mL of 1 M acetate-HCl buffer. Dilute to 25 mL with water and ethanol keeping 50 % (v/v) ethanol concentration. Heat the solution on the boiling water bath for 10 min, cool and add ethanol to compensate the loss of volume on heating. Measure the absorbance at 650 nm against a corresponding reagent blank prepared under identical conditions.

At high pH: To a suitable aliquot containing 20-252 µg of palladium(II), add 2 mL of 1×10^{-3} M PBN solution followed by 2 mL of 0.2 M sodium acetate. Dilute to 25 mL with water and ethanol keeping 50 % (v/v) ethanol concentration. Heat the solution on the boiling water bath for 10 min, cool and add ethanol to compensate the loss of volume on heating. Measure the absorbance at 570 nm against a corresponding reagent blank prepared under identical conditions.

RESULTS AND DISCUSSION

Palladium is the easiest to determine analytically amongst the platinum metals and a number of organic reagents are known comparatively against other platinum metals. Heterocyclic azo dyes comprise an important class of sensitive reagents for palladium; some important of them are given in Table-1. 2,6-*Bis*(1-hydroxy-2-naphthylazo)pyridine formed two complexes with Pd(II) in an ethanol-water mixture maintaining at least 40 % ethanol (v/v) *i.e.*, a green coloured complex in the pH range 3.5-5.0 and a reddish-brown coloured complex at higher pH (7.5-9.0). The colour intensity developed maximum if each of the complex was heated on a boiling water bath for *ca.* 5 min.

It was observed that equimolar solution of PBN and palladium(II) gave maximum colouration for green coloured complex and maintaining a pH with an acetate buffer of any pH value between 3.5-5.0 the composition of the complex as determined by Job's method of continuous variation was 1:1 (M:L). The reddish-brown coloured complex developed in the alkaline medium with 0.2 N sodium acetate had maximum colour if 2-molar excess of PBN was used and this complex had molar composition of 1:2 (M:L). Fig. 1 shows the spectra of the complexes recorded against the corresponding reagent blank at different pH levels. The optimum conditions and other optical constants determined for both the complexes are shown in Table-2.

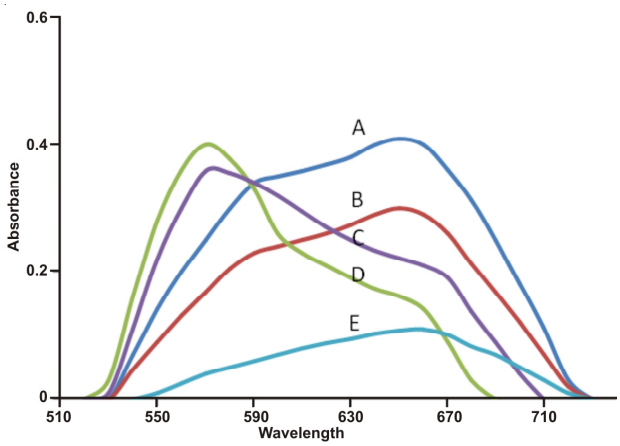

Fig. 1. Absorption spectra of Pd(II)-PBN complexes at different pH with Pd(II): 4×10^{-5} M and PBN: 8×10^{-5} M; curve A at pH, 3.5-5.0; B pH, 5.5; C pH 9.5; D pH 7.5-9; E pH 2

TABLE-2
PHYSICO-CHEMICAL CHARACTERISTICS OF THE PALLADIUM(II)-PBN COMPLEXES

Characteristics	Green complex	Reddish brown complex
λ_{max} (nm)	650	570
pH range	3.5 - 5.0	7.5-9.0
Reagent required for full complexation (mol)	1	2
Beer's law range (ppm)	0.0-14.0	0.0-11.8
Optimum concentration range (ppm)	0.8-12.5	0.8-10.5
Sandell's sensitivity (µg cm^{-2})	0.010	0.011
Molar absorptivity (ε) (L mol^{-1} cm^{-1})	1.06×10^4	1.0×10^4
Composition (M:L) by Job's method	1:1	1:2

TABLE-1
COMPARISON OF SENSITIVITIES OF VARIOUS SPECTROPHOTOMETRIC REAGENTS FOR PALLADIUM(II)

Reagent	λ_{max} (nm)	Molar absorptivity (L mol^{-1} cm^{-1})	References
1-(2-Pyridylazo)-2-naphthol /90 ºC	–	1.2×10^4	12
5-Chlorosalicylalaldehyde guanylhydrazone	–	7.27×10^4	13
5-(Benzothioazolylazo)-2,5-naphthalenediol	638	6.150×10^4	14
1-(2-Benzothiazolylazo)-2-hydroxy-3-naphthoic acid	677	7.27×10^4	14
5- (2-Benzothioazolylazo)-8-hydroxyquinoline	656	5.80×10^4	14
2-(5-Nitro-2-pyridylazo)-5-(N-propyl-N-3-sulphnopropylamino)phenol	612	6.2×10^4	15
3-Hydroxy-2-methyl-1-phenyl-4-pyridine	345	1.89×10^4	16
Benzoyloxybenzaldehyde-thiosemicarbazone	365	0.4×10^4	17
4-(N,N-Diethylamino)-benzaldehyde thiosemicarbazone	408	3.33×10^4	18
Benzildithiosemicarbazone	395	3.018×10^4	19
1-(2-Naphthalene)-3-(2-thiazo)-triazene	–	4.07×10^4	20
2-Hydroxy-5-methyl-acetophenoneisonicotinoylhydrazone	385	5.32×10^3	21
4-Hydroxy-3,5-dimethoxy benzaldehyde-4-hydroxy benzoyl hydrazone	373	7.5×10^4	22
Cinnamaldehyde-4-hydroxy benzoylhydrazone	375	6.0×10^4	22
4-(2,6-Diamino-4-pyrimidylazo)phenol	625	1.8×10^4	23
1-Methyl-3-(2-pyridyl)thiourea	490	0.96×10^4	24
2, 6-*Bis*(1-hydroxy-2-naphthylazo)pyridine	650	1.06×10^4	This work
	570	1.0×10^4	

Effect of diverse ions: In the determination of palladium (II) at the 4.25 µg/mL level; chloride, bromide, acetate, phosphate, citrate, alkaline earths, lanthanides, Al(III), Ga(III), In(III), Pt(IV), Ir(III), Rh(III), Ru(II)/(III), Os(VIII), Au(III), Th(IV) and UO_2(II) ions did not interfere while using the present methods. However, EDTA, fluoride, oxalate, iodide, thiosulfate, thiocynate, nitrite, thiourea, thiosemicarbazide, borate, sulphide, tartrate and cyanide interfered seriously in green coloured complex. In reddish brown coloured complex EDTA, thiosulphate, thiourea and thiosemicarbazide interfered seriously.

Under the appropriate conditions investigated for palladium(II), about 20-fold cyanide and 15-fold sulphide were found not to interfere for reddish brown complex, which were used to mask a number of transition metals. Other noble metals like gold(III), platinum(II), osmium(VIII), iridium(IV), rhodium(III) and ruthenium(III) did not show any colour reaction with PBN, even on warming for *ca.* 20 min. However, prolonged heating showed some colour reaction with platinum(IV) only. Palladium (II) can therefore be determined selectively in presence of the base metals as well as noble metals.

Table-3 represents the tolerance limits in ppm of various other ions in solution that caused a deviation smaller than ± 2 % in absorbance for the determination of palladium(II).

TABLE-3
TOLERANCE LIMITS OF DIVERSE IONS IN THE DETERMINATION OF 4.25 µg/mL OF PALLADIUM(II)

Foreign ions	Green complex tolerance limits (ppm)	Reddish brown complex tolerance limits (ppm)
NO_3^-	–	300
NO_2^-	100	–
Tartrate	25	–
Cr(III)	20[a]	10[a]
Mn(II)	25	15
Fe(II)	6[b]	6[c]
Co(II)	6	6
Ni(II)	10	3
Zn(II)	15[a]	7[a]
Cd(II)	10	5
Cu(II)	2	3[d]
Hg(II)	7[b]	10[c]
Ag(I)	20[a]	15[a]
Tl(I)	60[a]	20[a]
Pb(II)	40[a]	10[a]

[a]Masked by 1 % PO_4^{3-}. [b]Masked by 1 % citrate. [c]Masked by 1 % cyanide. [d]Masked by 1 % sulphide.

Application for determining Pd(II) in various synthetic samples: The most important feature of the present reagent is that almost no colour reaction is produced by any base metal. Only copper(II) ions showed 5 % interference in the colour intensity if equal amount of the copper(II) ions are present. If the micro-determination of palladium is made at 3.5-4 other base metals showed their colour reactions above pH 7. Hence the analytical method developed at pH 4 is highly selective. To check the selectivity of the method palladium(II) ions were determined in synthetic solution equivalent to the composition of some palladium alloys. Analytical data of the analytical method has been presented in Table-4.

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TABLE-4
MICROANALYSIS OF PALLADIUM(II) IN SOME SYNTHETIC SAMPLES

Sample analyzed	Sample composition(ppm)	Pd(II) found in six samples(ppm)	Meanvalue(ppm)	Standard deviation
18-Cr white gold	Au(75), Pd(20), Ag(5)	20.5, 20.3, 20.6, 19.9, 19.8, 20.5	20.22	0.3563
	Au(75), Pd(15), Ag(10)	15.2, 15.2, 15.0, 15.1, 14.5, 15.1	15.0	0.2915
	Au(75), Pd(10), Ag(15)	9.8, 9.7, 10.1, 10.5, 9.8, 9.8	9.98	0.3271
18-Cr gold	Au(75), Pd(10), Ag(10.5), Cu(3.5), Zn(0.1), Ni(0.9)	10.5, 10.2, 10.7, 10.1, 9.8, 10.0	10.3	0.2915
	Au(75), Pd(6.4), Ag (9.9), Cu(5.1), Zn(3.5), Ni(1.1)	6.6, 6.7, 6.7, 6.8, 6.5, 6.4	6.66	0.1140
	Au(75), Pd(15), Cu(3.0), Ni(7.0)	14.8, 14.9, 15.6, 15.1, 15.0, 15.5	15.08	0.3114
14-Cr gold	Au(58), Pd(20), Ag (6), Cu(3.5), Zn(1.5), Ni(1.0)	20.8, 20.5, 20.3, 20.5, 20.2, 19.9	20.46	0.2302
	Au(58.5), Pd(5), Ag (32.5), Cu(3.5), Zn(1.5)	4.8, 4.9, 5.3, 5.2, 5.2, 5.0	5.08	0.2167
Lindlar catalyst (Pd-$CaCO_3$)	Pd(5), Rest $CaCO_3$	5.1, 5.0, 5.3, 4.8, 5.2, 4.7	5.08	0.1923
Pd-Charcoal catalyst	Pd(5), Rest charcoal	5.3, 5.4, 5.0, 5.1, 5.0, 5.1	5.16	0.1816