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1-(2-Quinolylazo)-2,4,5-trihydroxybenzene as Spectrophotometric Reagent for Micro-determination of Palladium (II)

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ABSTRACT

Alcoholic solution of 1-(2-quinolylazo)-2,4,5-trihydroxybenzene (QATB) forms two colored complexes with palladium (II) in different pH ranges, (red wine - λ_{max} 620 nm, pH 3.0-5.5 and green- λ_{max} 675 nm, in alkaline medium). The red wine complex had molar absorptivity and the Sandell's sensitivity 1.25 $X10^4$ $L.mol^{-1}cm^{-1}$ and 0.0085 $\mu g.cm^{-2}$ respectively. Beer's law was followed upto 8.5 ppm with an optimum concentration range of 1.9- 7.95 ppm. The green coloured Pd(II)-QATB complex had molar absorptivity of 1.2 $X10^4$ $L.mol^{-1}cm^{-1}$ showing Sandell's sensitivity of 0.0087 $\mu g.cm^{-2}$. Beer's law was followed upto 9.4 ppm with the optimum concentration range of 1.6-8.5 ppm. Effect of foreign ions tested for their interferences and use of masking agents have been tabulated in the micro-determination of palladium(II). Analytical method established at low pH showed good selectivity and its application was extended to determine Pd(II) in some synthetic solutions equivalent to that of some alloys, hydrogenation catalysts etc.

Keywords: 1-(2-quinolylazo)-2,4,5-trihydroxybenzene, palladium(II), spectrophotometry.

INTRODUCTION

Palladium is a rare and lustrous silvery white metal that resembles with platinum. It is also used in jewellery as an alternative to platinum or gold, in dentistry [1], watch making, in blood sugar test strips. Palladium is one of the three most popular metals used to make white gold alloys, in aircraft spark plugs and in the production of surgical instruments and electrical contact [2]. The largest use of palladium today is in catalytic converters [3]. It is used in the Lindlars' catalyst, also called Lindlars' palladium. Palladium is a versatile metal for homogenous catalysis and speeds up hydrogenation and dehydrogenation reactions. It is used in combination with a broad variety of ligands for highly selective chemical transformation. Palladium is an effective catalyst for making carbon-fluoride bonds.

This paper reports, 1-(2-quinolylazo)-2,4,5-trihydroxybenzene (QATB) as an analytical reagent for the micro-determination of palladium(II), whereas, a very limited number of heterocyclic azo dyes find their uses for the determination of noble metals. Comparatively this reagent has been found a potential reagent for palladium (II).

MATERIALS AND METHODS

Reagents and Chemicals

1-(2-Quinolylazo)-2,4,5-trihydroxybenzene (QATB) Solution

QATB as synthesized earlier [4], was used as a 1 X 10^{-3} M solution prepared by dissolving 0.281 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, U.K) in 2N hydrochloric acid. The solution was standardized gravimetrically with dimethylglyoxime [5].

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

Determination of Palladium(II)

At low pH

To a suitable volume of sample containing 19.0-79.5 µg of palladium(II), add 2 mL of 1X10^{-3} M QATB solution followed by 1 mL of 1 M acetate-HCl buffer. Dilute to 10 mL with water and ethanol keeping 50%(v/v) ethanol concentration. Heat the solution on the boiling water bath for 10 minutes, cool and add ethanol to compensate the loss of volume on heating. Measure the absorbance at 620 nm against a corresponding reagent blank prepared under identical conditions.

At high pH

To a suitable aliquot containing 16.0 – 85.0 µg of palladium(II), add 2 mL of 1X10^{-3} M QATB solution followed by 1 mL of 0.2 N sodium hydroxide. Dilute to 10 mL with water and ethanol keeping 50%(v/v) ethanol concentration. Heat the solution on the boiling water bath for 10 minutes, cool and add ethanol to compensate the loss of volume on heating. Measure the absorbance at 675 nm against a corresponding reagent blank prepared under identical conditions.

Apparatus

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

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 are an important class of sensitive reagents for palladium; some important of them are given in Table 2. QATB formed two complexes with Pd(II) in an ethanol-water mixture maintaining at least 30% ethanol (v/v) i.e. a dark wine colored complex in the pH range 3.0-5.5 and a green colored complex at higher pH. The color intensity developed maximum if each of the complex was heated on a boiling water bath for about 10 minutes.

The dark wine red colored complex had maximum color development when 3-molar excess of QATB was used and maintaining a pH with an acetate-HCl buffer of any pH value between 3.0-

5.5. The composition of the complex as determined by Job's method of continuous variation was 1:1 (M : L). The green colored complex developed in the alkaline medium with 0.2 N sodium hydroxide had maximum color if 4-molar excess of QATB 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 1.

Effect of diverse ions

In the determination of palladium (II) at the 4.24 µg/mL level; fluoride, nitrate, nitrite, sulfate, sulfite, citrate, tartrate, alkali metals, 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 uranyl(II) ions did not interfere while using the present methods. On the other hand, iodide, thiosulfate and manganese interfered seriously.

Under the appropriate conditions found for palladium (II), about 20-fold cyanide and 15-fold EDTA were found not to interfere, 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 color reaction with QATB, even on warming for 10 minutes. However, prolonged heating showed some color 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 ions in solution that caused a deviation smaller than ± 2% in absorbance for the determination of palladium (II).

Application for determining Pd(II) in various synthetic samples

The reagent QATB was applied for determining Pd(II) in synthetic alloys samples, applied for dental purposes, used in jewellery and in hydrogenation catalyst samples. Alloys samples were synthetically prepared by mixing the appropriate amount of metal ions equivalent to that of the known composition of the alloys and analyzed for the palladium concentration present in them applying the present method with additional amount of 1 mL of 1% KCN solution and then using the acetate-HCl buffer pH 4.0.

For hydrogenation catalyst samples

An appropriate weighed amount of the catalyst sample was treated with 2M HNO_3 and heated to degas, then treated with aqua regia. The sample was heated almost to dryness and then the residue was dissolved in 2M HNO_3 and diluted to 100 ml in a volumetric flask. Suitable aliquots were taken and analyzed for palladium by adding 1 mL of KCN solution and using acetate-HCl buffer of pH 4.0.

Table 1: Physico-chemical characteristics of the palladium (II)-QATB complexes

Characteristics	Wine red complex	Green complex
λ max.(nm)	620	675
pH range	3.0 - 5.5	Alkaline medium (1 – 4 X10^{-2} N NaOH)
Reagent required for full complexation (mol)	3	4
Beer's law range (ppm)	0.0 - 8.5	0.0 – 9.4
Optimum concentration range (ppm)	1.9 - 7.95	1.6 – 8.5
Sandell's sensitivity (µg cm^{-2})	0.0085	0.0087
Molar absorptivity (є) (l. mol^{-1} .cm^{-1})	1.25 X 10^4	1.20 X 10^4
Composition (M:L) by Job's method	1:1	1:2

The results obtained are summarized in table 4.

Table 2: 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 /90^0C	678	$1.2 X 10^4$	6
5-(Benzothioazolylazo)-2,5-naphthalenediol	638	$6.150 X 10^4$	7
1-(2-Benzothiazolylazo)-2-hydroxy-3-naphthoic acid	677	$7.27 X 10^4$	7
5- (2-Benzothioazolylazo)-8-hydroxyquinoline	656	$5.80 X 10^4$	7
2-(5-Nitro-2-pyridylazo)-5-(N-Propyl-N-3-sulphopropylamino)phenol	612	$6.2 X 10^4$	8
3-Hydroxy-2-methyl-1-phenyl-4-pyridine	345	$1.89 X 10^4$	9
Benzoyloxybenzaldehyde-thiosemicarbazone	365	$0.4 X 10^4$	10
4-(N,N-Diethylamino)-benzaldehyde thiosemicarbazone	408	$3.33 X 10^4$	11
Benzildithiosemicarbazone	395	$3.018 X 10^4$	12
1-(2-Naphthalene)-3-(2-thiazo)-triazene	----	$4.07 X 10^4$	13
2-Hydroxy-5-methyl-acetophenoneisonicotinoylhydrazone	385	$5.32 X 10^3$	14
4-Hydroxy-3,5-dimethoxy benzaldehyde-4-hydroxy benzoyl hydrazone	373	$7.5 X 10^4$	15
Cinnamaldehyde-4-hydroxy benzoylhydrazone	375	$6.0 X 10^4$	15
4-(2,6-Diamino-4-pyrimidylazo)phenol	625	$1.8 X 10^4$	16
1-(2- Quinolylazo)-2,4,5-trihydroxybenzene	620 675	$1.25 X 10^4$ $1.2 X 10^4$	This work

Table 3: Tolerance limits of diverse ions on the determination of 4.24 µg/mL of palladium(II)

Foreign ions	Dark wine complex Tolerance limits (ppm)	Masking agents	Green complex Tolerance limits (ppm)	Masking agents
Cl^-	500	------	500	------
Br^-	500	------	500	------
SCN^-	50	------	80	------
CN^-	100	------	100	------
$C_2O_4^{2-}$	50	------	50	------
EDTA	60	------	50	------
BO_3^{3-}	50	------	5	------
PO_4^{3-}	100	------	80	------
UO_2(II)	5	------	10	------
Cd(II)	20	------	25	------
Hg(II)	20	------	25	------
Fe(II)	20	Masked by 1% CN^-	20	Masked by 1% CN^-
Zn(II)	40	” ” ” ” ” ”	20	” ” ” ” ” ”
Cu(II)	40	” ” ” ” ” ”	20	” ” ” ” ” ”
Co(II)	20	” ” ” ” ” ”	20	” ” ” ” ” ”
V (V)	5	” ” ” ” ” ”	20	” ” ” ” ” ”
Ag(I)	40	” ” ” ” ” ”	10	” ” ” ” ” ”
Pb(II)	10	” ” ” ” ” ”	10	” ” ” ” ” ”

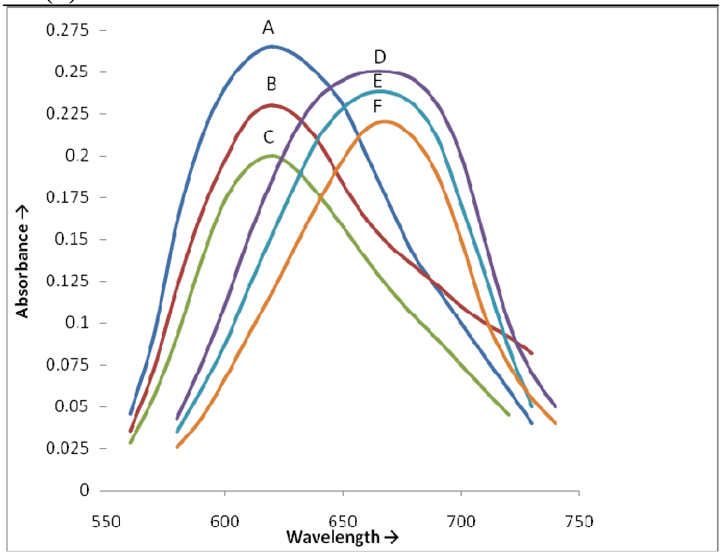

Fig. 1. Absorption spectra of Pd(II)-QATB complexes at different pH with Pd(II): $2X10^{-5}$ M and QATB: $1X10^{-4}$ M; curve A at pH, 3.0-5.5; B pH, 6.5; C, pH 2.2; D with 1- $4X10^{-2}$ N NaOH; E, $5X10^{-3}$ N NaOH; F, $1X10^{-3}$N NaOH.

Table 4: Microanalysis of palladium(II) in different synthetic samples

Sample analyzed	Sample composition (ppm)	Pd(II) found in six samples (ppm)	Mean value (ppm)	Standard Deviation
18-Cr white gold	Au(75), Pd (20), Ag (5)	19.8, 20.1, 20.1, 20,2, 21.0, 19.7	20.15	0.497
	Au(75), Pd(15), Ag (10)	15.3, 15.2, 15.4, 14.9, 14.8, 15.5	15.2	0.279
	Au(75), Pd (10), Ag (15)	10.1, 10.5, 10.2, 10.1, 9.8, 10.1	10.13	0.225
18-Cr gold	Au(75), Pd(10), Ag (10.5), Cu(3.5), Zn(0.1), Ni(0.9)	10.0, 9.9, 9.8, 10.1, 10.0, 9.8	9.9	0.126
	Au(75), Pd(6.4), Ag (9.9), Cu(5.1), Zn(3.5), Ni(1.1)	6.3, 6.4, 6.2, 6.5, 6.3, 6.3	6.33	0.13
	Au(75), Pd(15), Cu(3.0), Ni(7.0)	14.7, 15.1, 15.2, 14.8, 15.3, 15.2	15.05	0.243
14-Cr gold	Au(58), Pd(20), Ag (6), Cu(3.5), Zn(1.5), Ni(1.0)	20.2, 20.3, 19.8, 19.7, 19.8, 19.9	19.95	0.242
	Au(58.5), Pd(5), Ag (32.5), Cu(3.5), Zn(1.5)	5.0, 5.1, 5.1, 4.9, 5.0, 5.2	5.05	0.234
Dental Alloy	Pd(78), Co(9.5), In(4.0), Sn(8.0), Al(0.2), Re(0.3)	77.5, 77.6, 78.3, 78.5, 77.9, 78.3	78.0	0.5
	Pd(76), Co(9.0), In(6.0), Sn(8.5), Al(0.1), Re(0.4)	77.0, 76.6, 76.3, 75.7, 75.5, 75.6	76.1	0.61
Lindlar Catalyst (Pd-$CaCO_3$)	Pd(5), Rest $CaCO_3$	5.3, 5.2, 5.0, 5.3, 5.4, 4.9	5.2	0.195
Pd-Charcoal catalyst	Pd(5), Rest charcoal	5.0, 4.8, 4.7, 5.3, 5.0, 5.2	5.0	0.22

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