EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM METAL AT TRACE LEVEL USING (p-METHOXYPHENYL) ETHANE-1, 2-DION-1-OXIME AS AN ANALYTICAL REAGENT

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ABSTRACT

A simple and selective method for spectrophotometric determination of palladium (II) has been developed using a new analytical reagent (p-methoxyphenyl)ethane-1, 2-dion-1-oxime (HMPEDO). The method is based on formation of yellow colored 1 : 2 complex of palladium (II) with HMPEDO extracted into chloroform in the pH range 1.1-3.2. The absorbances were measured at 420 nm as λ_{max}. This method obeys Beer's law in the optimum concentration range 1-20 μgcm^{-3} and indicates an excellent linearity between the two variables with good molar absorptivity of 3.087×10^4 $dm^3mol^{-1}cm^{-1}$ and Sandell's sensitivity of 3.45×10^{-3} μgcm^{-2}. The instability constant of the complex calculated from mole ratio method is 2.68×10^{-4} and that of Asmus' method is 2.76×10^{-4} at room temperture. The repetability of this method was checked by finding the relative standard deviation for n = 10, that was derived as 1.665%. The developed method was successfully applied for determination of palladium in synthetic mixtures and real samples.

Key words: Carbonyl oxime, Palladium metal, Extractive spectrophotometry, Solvent extraction, p-Methoxyphenyl)ethane-1, 2-dion-1-oxime.

INTRODUTION

Palladium belongs to platinum group metals, which played plentiful applications like a good catalyst in the hydrogenation reactions. A major use of palladium is in jewelry, dentistry[1] and its alloys are used in low voltage electrical contacts. The use of dental metal palladium and its alloys causes the risk of illness like metal toxicity in many people. The palladium can be easily methylated, which is more toxic than methylated mercury.

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Palladium is cytotoxic and thus, damages cells[2-4]. It inhibits enzyme activities. It also causes number of allergic reactions[5]. Due to these toxic effects and high mobility, palladium dental alloys are banned in many countries. Besides all the adverse effects of palladium; it is largely used in many industries at various concentration levels. Consequently, it is necessary to develop a rapid, versatile and sensitive method for determination of palladium.

Various complexing agents have been reported[6-14] (Table 1) for extractive spectrophotometric determination of palladium (II). However, they suffer from their own limitations such as low sensitivity and selectivity, slow extraction, long time for color development, small Beer's range and interference by many diverse ions. In present investigation, extraction of palladium (II) with (p-methoxyphenyl)ethane-1,2-dion-1-oxime (HMPEDO) has been studied under wide range of experimental conditions.

EXPERIMENTAL

Apparatus

Absorbance measurements were taken on the Elico SL-150 digital UV-Visible spectrophotometer using 1 cm^2 quartz cells and pH measurements were carried out on Equiptronics EQ-614.

Reagents and samples

A. R. grade chemicals and reagents were used. All the solutions were prepared in deionised double distilled water.

Palladium (II) solution

A stock solution of palladium (II) was prepared by dissolving calculated amount of palladium chloride in deionised double distilled water containing few drops of HCl. The stock solution was standardized gravimetrically by DMG method[15]. For experimental purposes, solutions of different concentrations were prepared diluting the stock solution suitably.

Preparation of the reagent (HMPEDO) solution

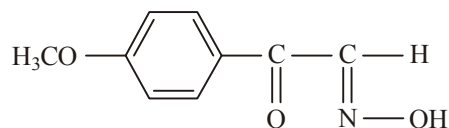The reagent was prepared by using the known method[16]. The structure of reagent is as shown below -

Table 1: Comparison of the method with other spectrophotometric methods for the determination of palladium (II)

Reagent	pH	λ_{max} (nm)	$\varepsilon(dm^3\ mol^{-1}\ cm^{-1}) \times 10^4$	M : L	Beers law validity range (µg)	Remarks	Ref.
1-Phenyl-1-hydrazony 1-2-oximino-1, 2-ethanedione	2.0	480	0.681	1 : 2	0.5-12	Cu (II), Hg (II) Ag (I), Ru (III) Interfere	6
1-Phenyl- 1, 2-butanedione dioxime	7.5	380	0.374	1 : 2	0.5-9	Cu (II), Mn (II), Fe (II), Ni (II) Interfere	7
3-Phenoxybenzaldoxime	4.0	435	0.243	NR	0.4-4	Less sensitive	8
2-Arylthio-phenyl-nitroacetophenone	5.0	430	0.161	NR	0.25-2	Less sensitive	9
5-Methyl- 2, 3-hexanedione dioxime	0.5-1.5	379	0.389	1 : 2	0.5-9	Less sensitive	10
2-Oxo-4'-hydroxyphenyl acetaldehyde oxime	1.5-4.2	420	2.27	1 : 2	0.5-5.1	Less sensitive	11
5, 6-Dimethyl-1, 3-indanedione-2-oxime	5.5	370	2.980	1 : 2	0.15-3.9	Less sensitive	12
Isonirtrosomalondianilide	2 - 4.25	385	2.128	1 : 2	0.2-3.5	Cu (II), Pb (II), Ru (III), Pt (IV), Rh (III), Au (III), Ag (I) Interfere	13
p-Nitroisonitroso-acetophenone	5.4-5.6	425	1.355	1 : 2	0.1-10	EDTA, Thiourea, Sulphite, Iodine Interfere	14
(p-Methoxyphenyl) ethane 1, 2-dion-1-oxime.	1.1-3.2	420	3.087	1 : 2	1-20	Highly sensitive and selective	PM

NR = Not reported; PM = Present method; M : L = Metal : Ligand

Recommended procedure

To an aliquot of solutions containing 1-20 µg palladium (II) in a separating funnel, 0.3 cm^3 of 0.1% ethanolic solution of HMPEDO was added. The pH was adjusted to 1.59 by a phosphate buffer. The volume was made to 10 cm^3 with deionsed double distilled water and equilibrated with 10 cm^3 of chloroform for 60 seconds. Two phases were allowed to separate and absorbance of the organic extract was measured at 420 nm against reagent blank. Palladium (II) reacts with HMPEDO to form yellow colored complex. The colored organic extract can be directly employed for further spectrophotometric determination of palladium (II).

RESULTS AND DISCUSSION

Absorption spectra

The yellow colored organic complex of palladium (II) formed with HMPEDO was extracted into chloroform has maximum absorbance at 420 nm, whereas the reagent has relatively very low absorbance value at this wavelength (Fig. 1). Hence, all the further spectral studies of the complex were carried out at 420 nm as λ_{max}.
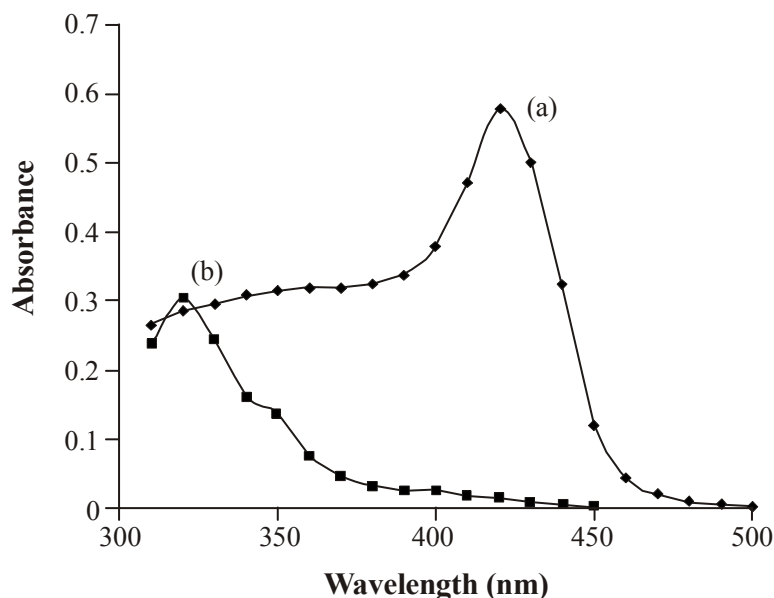

Fig. 1: Absorption spectra of (a) Pd (II)-HMPEDO complex and (b) HMPEDO

Effect of pH

The extraction behavior of the complex was investigated over the pH range 1.1-3.2, and it was found that the optimum extraction was in the pH range 1.58-1.63. All the extractions were therefore carried out at pH 1.59, (Fig. 2).
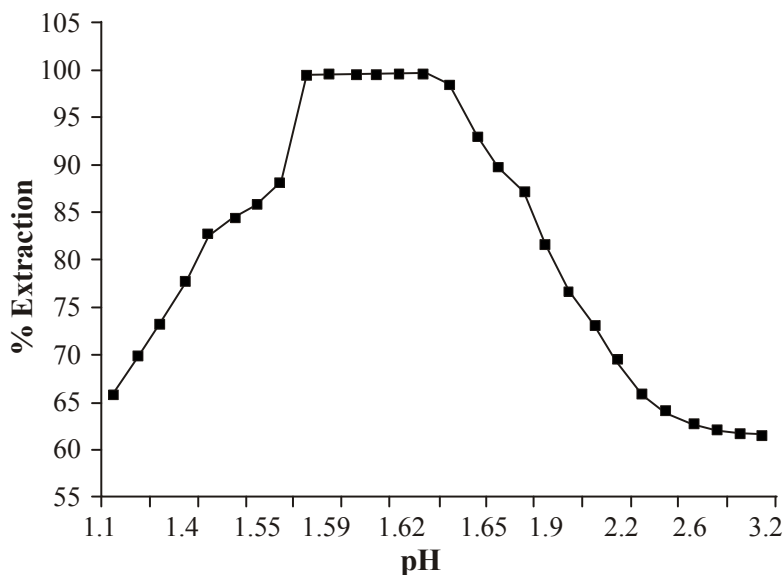

Fig. 2: Effect of pH on Pd-HMPEDO complex

Extraction using various solvents

Solvent study was carried out at λ_{max} of 420 nm, using several organic solvents such as chloroform, chlorobenzene, carbon tetrachloride, xylene, toluene, benzene, iso-amyl alcohol, n-butanol, iso-butyl methyl ketone and ethyl acetate. The optimum extraction of palladium (II) was found to be quantitative in chloroform, which was therefore chosen as solvent for further studies.

Effect of reagent (HMPEDO) concentration

The effect of variation in the concentration of HMPEDO from 2.790×10^{-4} mol dm^{-3} to 2.232×10^{-3} mol dm^{-3} was studied keeping other parameters constant. It is found that 1.674×10^{-3} mol dm^{-3} solution of HMPEDO in ethanol is sufficient for complete extraction and color development with palladium (II). However, excess of reagent concentration did not have any effect on the extraction of palladium (II) from aqueous phase to organic phase.

Effect of equilibration time and stability of complex

The effect of equilibration time of palladium (II) was studied by varying the time from 10 seconds to 90 seconds. It was found that the equilibration period of 60 seconds was sufficient for the extraction of palladium (II) complex and hence, it was employed for the further studies. The absorbance of the colored complex remained constant for 8 hrs. at room temperature and then decreases gradually due to decomposition of the complex; this concludes that the complex formed is fairly stable for 8 hrs.

Validity of Beer's law, molar absorptivity and Sandell's sensitivity

The Pd (II)-HMPEDO complex system followed Beer's law in the range 1-20 μg cm^{-3}. The molar absorptivity of the extracted species was found to be 3.087×10^4 dm^{3}mol^{-1}cm^{-1} and the Sandell's sensitivity of the complex was found to be 3.45×10^{-3}μgcm^{-2}.

Ringbom's plot for the Pd (II)-HMPEDO complex

The Ringbom's plot to know the optimum range of the concentration for the system was drawn between the log of concentration of palladium (II) against percentage transmittance. The plot has sigmoid shape with linear segment at intermediate values ranging from 2 - 20 μgcm^{-3}, which indicates that palladium (II) can be determined in the range of 2 – 20 μgcm^{-3}.

Diverse ion effect

Interference studies were carried out for extraction and spectrophotometric determination of 20 μg palladium (II) with various diverse ions (prepared by dissolving their commonly available chemically pure salts in deionised double distilled water or in dilute acids to give ≤ 10 mg cm^{-3} concentration of the cations and ≤ 20 mg cm^{-3} concentration of the anions) in 10 cm^3 of aqueous phase. The tolerance limit of these diverse ions is tabulated in (Table 2). Interfering ions detected were masked using suitable masking agents.

Nature of the extracted complex

The extraction into nonpolar organic solvent suggests that palladium (II) was probably extracted as a neutral species into the organic phase. Studies by Job's continuous variation method indicate that the colored complex was formed by the reaction of equimolar solutions (1.879×10^{-4} mol dm^{-3}. Palladium (II) and HMPEDO were in the ratio of 1 : 2 (M : L) i.e. Pd : [HMPEDO]. The composition of Pd (II)-HMPEDO complex was also determined by slope analysis method. The distribution coefficient (D) of palladium (II) was

calculated at different molar concentrations of HMPEDO. The logarithmic plot of D versus [HMPEDO] (Fig. 3) gives a straight line with a slope of 2.0 indicating that the composition of extracted species is 1 : 2. This was verified by mole ratio method.
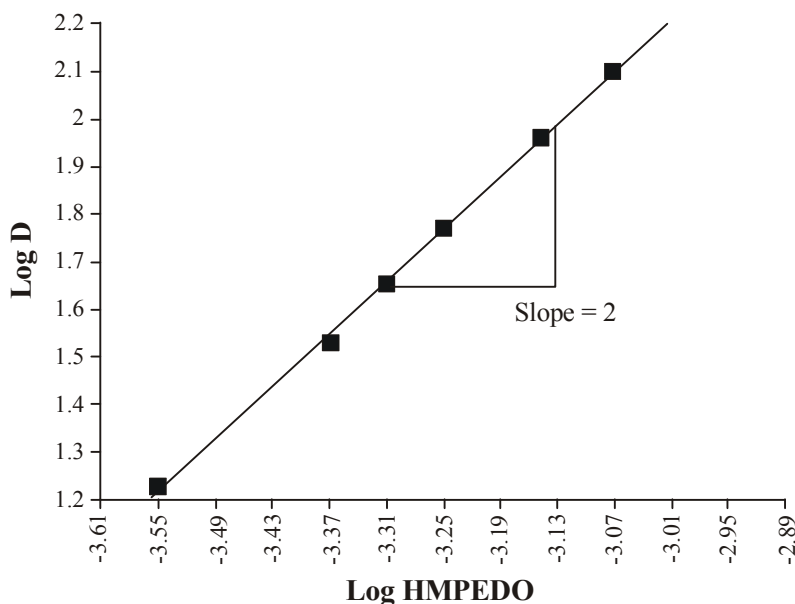

Fig. 3: Determination of Pd (II)-HMPEDO complex by slope ratio method

Instabilty constant of the Pd (II)-HMPEDO complex

The instability constant of the Pd (II)-HMPEDO complex was calculated using mole ratio method as well as Asmus' method. The absorbance values of organic extracts were obtained at 420 nm by equilibrating the solution with chloroform, containing fixed volume of palladium (II) i.e. (1 cm^3 of 1.879×10^{-4} mol dm^{-3}) and a buffer (pH 1.59) with different known volumes of 1.879×10^{-4} mol dm^{-3} HMPEDO. The instability constant of the Pd (II)-HMPEDO complex was calculated to be 2.68×10^{-4} at room temperature by mole ratio method. In Asmus' method, instability constant of the Pd (II)-HMPEDO complex was calculated to be 2.76×10^{-4} at room temperature. This value is in perfect agreement with the value obtained by mle ratio method.

Precision and accuracy

The precision and accuracy of the proposed method were determined by analyzing solutions containing known amount of palladium (II). The standard deviation and relative standard deviation (RSD) for the average of ten determinations with 20 µg palladium (II)

solution per cm^3 at λ_{max} 420 nm was found to be 0.333 and 1.665%, respectively. The variation from mean at 95% confidence limit was 20 ± 0.238.

Applications

The applicability of the developed method was tested by successful analyses of variety of synthetic as well as real samples containing palladium. In order to examine the efficiency of this method, the method was applied to the determination of palladium in some synthetic mixtures, real samples like different hydrogenation catalysts[17] and dental alloy.

Table 2: Tolerance limit for diverse ions in the determination of palladium (II)

Diverse ions	Tolerance limit (mg)
Br$^-$, I$^-$, ClO$_3^-$, S$_2$O$_8^{2-}$, Thiourea, EDTA	15
Cl$^-$, SCN$^-$, S$_2$O$_5^{2-}$, S$_2$O$_7^{2-}$, Citrate, Urea, W (VI), Mn (II), Mg (II), Se (II), Cu (II)	10
H$_2$PO$_4^-$, Sb (II) ,Pt (IV),Re (VII)	6
F$^-$, BrO$_3^-$, IO$_3^-$, NO$_3^-$, HSO$_4^-$, Oxalate, Tartarate, Li (I), Ca (II), Cd (II), Zn (II), Hg (II), Pb (II), In (III),Bi (III), Ti (IV), V (V)	5
HPO$_4^{2-}$, Ag (I), Ba (II), Ni (II)	4
CO$_3^{2-}$, Fe (II), Sr (II), Al (III), Mo (VI)	2.5
S$_2$O$_3^{2-}$, NO$_2^-$, SO$_4^{2-}$, Acetate, Ru (III), Fe (III)	1
SO$_3^{2-}$ masked with potassium permanganate and sulphuric acid, Cr (III) and Co (II) masked with EDTA	Interfere

Determination of palladium in synthetic mixtures

The present method was applied to the determination of palladium in various synthetic mixtures containing zinc, copper, nickel, mercury, lead, cadmium and molybdenum (Table 3).

Table 3: Determination of Pd (II) in synthetic mixture

Synthetic mixture (µg)	Palladium found[a] (µg)	SD	RSD %
	HMPEDO method		
Pd (20) + Zn (100) + Cu (100)	19.76	0.064	0.32
Pd (20) + Ni (50) + Hg (50)	19.76	0.064	0.32
Pd (20) + Pb (50) + Cd (100)	19.90	0.061	0.31
Pd (20) + Mo (100)	19.79	0.105	0.53

a = Average of three determination

Determination of palladium in real samples

Pd (5%) on charcoal: Palladium charcoal sample was accurately weighed in a silica crucible. After ashing the carbon for 7 hrs, the sample was treated with 4 cm^3 of formic acid (1 : 3) and dried by heating on a hot plate. The residue was dissolved in 4 cm^3 of aqua-regia and diluted with deionised double distilled water to 250 cm^3. An aliquot of this solution was taken for the determination of palladium by the developed method as well as the alternate method[18].

Pd (5%) on BaSO₄ and Lindlar catalyst: Each sample was accurately weighed in a separate silica crucible. After ashing both the samples for 7 hrs, each sample was treated with 3 cm^3 of aqua-regia and 2 cm^3 of perchloric acid and dried by heating on a hot plate. Each residue was dissolved in 4 cm^3 of aqua-regia and diluted with deionised double distilled water to 250 cm^3. An aliquot of this solution was taken for the determination of palladium by the developed method as well as the alternate method.

Pd-Ag alloy: Accurately weighed Pd dental alloy sample was first treated with 4 cm^3 of aqua-regia and 3 cm^3 of perchloric acid and heated on a hot plate. After cooling the solution, it was treated with 3 cm^3 of aqua-regia and evaporated to dryness. The residue was dissolved in 5 cm^3 of 5 M HCl and diluted with deionised double distilled water to 250 cm^3. An aliquot of this solution was taken for the determination of palladium by the developed method as well as the alternate method.

Table 4: Determination of for Pd (II) in hydrogenation catalysts and dental alloy

Hydrogenation catalyst	Palladium found[a] (%)		Certified value (%)	SD	RSD %
	Alternate method	HMPEDO method			
Pd- Activated charcoal	4.98	4.96	5.00	0.015	0.30
Pd-BaSO$_4$	4.97	4.96	5.00	0.014	0.28
Lindlar catalyst	4.98	4.97	5.00	0.015	0.30

Alloy	Palladium found [a](%)		Certified value (%)	SD	RSD %
	Alternate method	HMPEDO method			
Pd-Ag Alloy	24.97	24.95	25.00	0.035	0.14

a = Average of three determinations.

CONCLUSION

The developed method offers advantages like high selectivity, reliability and reproducibility towards palladium; in addition to its simplicity, instant color development and less interference by various diverse ions. This method has been successfully applied for the determination of palladium metal at microgram level from synthetic mixtures as well as some real samples. The results obtained by developed method are in good agreement with the certified values and the values from the alternate method. In conclusion, the simplicity of this method and the use of inexpensive facility makes this technique potentially capable for its use in industrial fields.

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