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Non-Extractive Spectrophotometric Determination of Palladium in Alloys Samples Using Pyridoxal Thiosemicarbazone.

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ABSTRACT

A very simple, highly selective and non-extractive spectrophotometric method for the trace amounts of palladium(II) has been developed. Pyridoxal thiosemicarbazone (PDT) has been proposed as a new analytical reagent for the direct non-extractive spectrophotometric determination of palladium (II). The reagent reacts with palladium in acidic medium (pH 2.0, CH_3COONa and Con. HCl) to form a pale yellow coloured 1: 2 (M : L) complex. The reaction is instantaneous and the maximum absorption was obtained at 420 nm and remains stable for 2 hrs. The molar absorptivity and Sandell's sensitivity were found to be $1.63 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.635 \mu\text{g cm}^{-2}$ respectively. Linear calibration graphs were obtained for 0.9- 10.0 $\mu\text{g/ml}$ of palladium(II). The method is highly selective for palladium and successfully used for determination of palladium in several standard reference materials (steels and alloys).

Keywords: Spectrophotometric determination, Pyridoxal thiosemicarbazone, Alloy and steel samples, Molar absorptivity and Sandell's sensitivity.

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INTRODUCTION

Palladium and its alloys are widely used in the chemical industry and in instrument making [1]. Palladium is extensively used in jewellery. 'White gold' is obtained when palladium is added to gold, with or without other elements. The yellow colour of gold fades and the alloy becomes quite white. Palladium is also used in watch making. Palladium is widely used in hydrogenation catalysts, micro contactors in electronics, hard alloy in dentistry, fertilizers industry and in last few years as a component in auto-catalysts that reduce vehicle exhaust emissions of hydrocarbons, carbon monoxide and oxides of nitrogen. 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 [2]. Palladium is thought to be one of the strongest allergens from a health hazard viewpoint [3]. Hence, accurate determination of trace amounts palladium using simple and sensitive method is of great importance. Spectrophotometric methods occupy special position due to their simplicity, less expensive instrumentation and high sensitivity. Among various organic chromogenic reagents containing sulphur and nitrogen as donor atoms, thiosemicarbazones occupy a unique place. The metal chelates of these sulphur and nitrogen containing organic reagents find a wide range of applications in medicine and agriculture [4]. Most of these methods are less sensitivity [5-13], also chloroform used for extraction in some of these methods is considered to be hazardous. The most widely used method for the determination of palladium is extractive dithizone method [14], but it suffers serious interferences and also there is only a slight difference between colours of the complex and the free reagent. In the present investigation we report a simple, selective and non-extractive derivative spectrophotometric determination of palladium (II) using a newly synthesized reagent pyridoxal thiosemicarbazone. The ligand is synthesized by reacting thiosemicarbazide with Pyridoxal, Pyridoxal is one of the three natural forms of vitamin B₆, along with pyridoxamine and pyridoxine. All of these forms are converted in the human body into a single biologically active form, pyridoxal 5-phosphate. All three forms of vitamin B₆ are heterocyclic organic compounds. Green plants are a natural source of pyridoxal, and its deficiency in the human body can lead to serious complications such as epilepsy and seizures.

In continuation of our ongoing work, we report here the spectrophotometric determination of palladium in various alloy samples. A close literature survey reveals that PTSC is so far not been employed for the spectrophotometric determination of palladium (II). This method is far more selective, simple and rapid than the existing spectrophotometric methods.

MATERIALS AND METHODS

Materials

Pyridoxalhydrochloride and thiosemicarbazide were procured from Merck, India and purified by rectified spirit. Ethanol of AR grade, Merck and used as received. Solvent like N,N-dimethyl formamide was used after distillation.



Synthesis of reagent Pyridoxal thiosemicarbazone (PDT)

Pyridoxalhydrochloride (2g, 0.01M, dissolved in 20ml of ethanol) and thiosemicarbazide (0.9 g, 0.01mol dissolved in 10ml of H₂O) were mixed in a clean round bottom flask. Suitable quantity of (~ 10ml) of ethanol was added to the reaction mixture and refluxed with stirring for 3 hrs. The intense yellow coloured product was separated out on cooling. It was collected by filtration, washed several times with cold water. This compound was recrystallized from methanol and dried in vacuo. The yield was found to be 78 % melting point is 209 – 211°C. The reaction route for the synthesis is shown in Fig. 1.

Preparation of reagent solution

The reagent solution (0.01M) was prepared by dissolving 0.060 gm of the compound in dimethylformamide (DMF) in 25ml volumetric flask. The reagent solution was stable for atleast 10hrs.

Preparation of palladium (II) ion solution

A 1×10^{-2} M stock solution of divalent palladium was prepared by dissolving requisite quantity (0.22g) of PdCl₂ in doubly distilled water containing few drops of conc. HCl and made up to 100 ml volumetric flask. The stock solution was standardized gravimetrically [15]. Dilute solutions were prepared from this stock solution. Solutions of large number of inorganic ions, complexing agents were prepared from their analaR grade (or) equivalent grade water soluble salts.

Procedure

An aliquot of the solution containing palladium in optimum concentration range, 10ml of buffer solution (pH 2.0) and 1ml of 0.01M reagent solution were combined in 25ml volumetric standard flask and resulting solution was diluted to the mark with distilled water. The absorbance of the solution was measured at 420 nm against reagent (PDT) blank. The measured absorbance was used to compute the amount of palladium from predetermined calibration plot.

Preparation of Alloy sample

100mg of alloy sample was dissolved in aquaregia and evaporated on hot water bath to dryness. The residue was dissolved in minimum amount of dilute hydrochloric acid and transferred into 50ml standard flask quantitatively. The contents were diluted to the mark with distilled water.

Apparatus

A Perkin – Elmer (Lambda 25), UV – Visible spectrophotometer equipped with 1.0 cm (path length) quartz cell and Elico model LI-610 pH meter were used in the present study.

RESULTS AND DISCUSSION

Characterisation of reagent

The newly synthesized reagent pyridoxal thiosemicarbazone has been characterized using IR, NMR and Mass spectral data.

IR spectra

The infrared spectrum of PDT is shown in Fig 2. From the spectra it has been revealed that the reagent show sharp strong peak at 3422 cm^{-1} may be assigned for the stretching vibrations of -OH and 3381 cm^{-1} may be assigned for the asymmetric stretching of -NH_2 groups. The sharp peaks appeared at 3262 cm^{-1} may be assigned for stretching vibrations of secondary -NH group. The band at 3172 cm^{-1} may be assigned for stretching vibration of secondary thioamide -NH group, band at 1620 cm^{-1} may be assigned for plane bending vibration of -NH group, band at 1524 cm^{-1} may be assigned for stretching vibration of ring C=C group, band at 1413 cm^{-1} may be assigned for stretching vibration of -C=S group, band at 1290 cm^{-1} may be assigned for stretching vibration of -C-NH group, band at 1262 cm^{-1} may be assigned for plane bending vibration of -OH group and band at 823 cm^{-1} may be assigned for stretching vibrations of 4-substituted pyridine.

^1H – NMR spectra

The ^1H – NMR spectra of reagent was scanned in $\text{DMSO}-d_6$ solvent and are shown in the Fig 3. From the spectral data, the singlet obtained at $2.40(\delta)$ ppm may be due to the methyl proton, the multiple signals at $4.58(\delta)$ ppm may be due to amine protons, the singlet signal at $5.26(\delta)$ ppm may be due to -OH protons, the singlet signal at $7.99(\delta)$ ppm may be due to -CH protons, the singlet signal at $8.57(\delta)$ ppm may be due to $\text{-CH}_2\text{OH}$ protons and the singlet signal at $11.59(\delta)$ ppm may be due to phenyl ring protons.

Mass spectra

Mass spectrum of PDT shows the molecular ion peak at m/z 240. The peak observed at m/z values of 239 is due to the loss of -H radical, peak observed at m/z values of 224 is due to the loss of -NH_2 radical and peak observed at m/z values of 207 due to the loss of -SH radical. Thus mass spectrum is consistent with the structure of PDT.

UV-Visible spectra

Absorption spectrum of 2×10^{-5} solution of PDT at different pH values were recorded and pKa values were determined spectrophotometrically using Phillip and Merrit method [16]. The bathochromic shift from 295 – 365 nm indicates that in solution on increasing pH the $>C=S$ group of the reagent (PDT) is enolised and dissociated. The values of PTSC are $3.0(pK_1)$ and $9.0(pK_2)$ respectively. The pK_1 and pK_2 values are presumably due to keto – enol tautomerism and deprotonation of -SH group respectively and UV-visible spectra is shown in Fig 4.

Effect of pH

The effect of pH on the colour intensity of the Pd(II) – PDT complex was studied results are shown in Fig 5. The graph indicates that the complex shows maximum and constant absorbance in the pH range 1.0 – 3.0. Hence, buffer solution of pH 2.0 is chosen for subsequent studies.

Adherence of Beers law, Molar absorptivity, and Sandells sensitivity

Beer's law was obeyed over a concentration range of 0.9-10.0 $\mu\text{g/ml}$ of palladium(II) and shown in Fig 6. Molar absorptivity and Sandells sensitivity were found to be $1.63 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.635 \mu\text{g cm}^{-2}$ respectively.

Effect of reagent concentration

The amount of reagent necessary for full colour development was are presented in Table 1. The data indicate that a 10 fold molar excess of reagent is sufficient for full colour development.

Effect of time

The absorbance of Pd(II) – PDT complex was measured at different time intervals to ascertain the time stability of the complex .The absorbance of the Pd(II) complex was measured at 420 nm. The colour development is instantaneous and remains constant for 2 hrs and thereafter showed gradual decrease in intensity with increasing time.

Precision

The precision of the method was checked by ten replicate analysis containing 5ml of Palladium(II) solution. The standard deviation and relative standard deviation were found to be ± 0.0056 and $\pm 2.47\%$ respectively.

Effect of foreign ions

The validity of the method was assessed by investigating the effect of various cations and anions on the determination of palladium(II) by the developed method, by taking 1ml amount of palladium(II) solution was taken in a set of 25ml volumetric flasks containing 10 ml of buffer solution, appropriate amount of foreign ion and the reagent solution was added at the end. The contents were made up to the mark with distilled water. The absorbance of the solution in each flask was measured at 420 nm from which the tolerance limit of the foreign ion was determined. The amount of foreign ion which brings about a change in absorbance by $\pm 2\%$ was taken as its tolerance limit and results of these experiments are shown in Table 2. Larger amounts of Mo(IV) and Fe(III) do not interfere in the presence of masking agents. Interference of molybdenum(IV) and iron(III) are masked with ascorbic acid.

Table 1: Effect of Reagent(PTSC) Concentration On The Absorbance of Pd(II) Complexes

Pd(II) : PTSC	Absorbance (nm)
1 : 0.5	0.402
1 : 10	0.420
1 : 20	0.418
1 : 30	0.410
1 : 40	0.415
1 : 50	0.435

Table 2 : Tolerance Limit of Foreign Ions in the Determination of 2.12 $\mu\text{g/ml}$ of palladium

Ion added	Tolerance limit	Ion added	Tolerance limit
EDTA	1490	Cd ⁺²	450
Chloride	1472	Zn ⁺¹	260
Hypo	632	Mn ⁺²	220
Tartarate	592	Pb ⁺²	83
Sulphate	384	Se ⁺⁵	32
Oxalate	352	Cr ⁺⁶	21
Ascorbic acid	320	Ni ⁺²	7.6
Bicarbamate	242	Hg ⁺²	1.6
Carbonate	240	Os ⁺⁸	1.2
Acetate	236	V ⁺³	0.41
Thiocyanate	232	Mo ⁺⁴	0.39 ^a
Ascorbate	200	Fe ⁺³	0.38 ^a
Flouride	70	Pt ⁺⁴	0.08
Iodide	51	Co ⁺²	0.02

^amasked with 200 mg/ml of ascorbic acid.

Determination of composition of the complex

The composition of the complex (M : L = 1 : 2) was determined by Job's continuous variation method and molar ratio method and were shown in Fig 7 and Fig 8 respectively. CH₃COONa(1M) – Conc. HCl (0.1M) buffer (pH 2.0) is used in these studies. The dissociation constant (α) and concentration (c) of the reagent at intersecting point were used in the calculation of stability constant of the complex. Stability constant of the complex 1: 2 (M : L) complex is given by $1-\alpha/4\alpha^3c^2$. The structure of Pd(II) – PDT is given in Fig 9.

Table 3: Physico – Chemical and Analytical Characteristics of Pd(II)- PTSC Complex

Characteristics	Pd(II) – PTSC
λ_{max} (nm)	420
pH – range (optimum)	1.0 – 3.0
Mean absorbance	0.226±0.0005
Mole of reagent required per mole of metal ion for full color development	10 fold
Time stability of the complex (h)	2
Beers law validity range ($\mu\text{g/ml}$)	1.0 – 9.90
Molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$)	1.63×10^4
Specific absorptivity ($\text{ml g}^{-1} \text{cm}^{-1}$)	0.15
Sandell's sensitivity ($\mu\text{g/cm}^2$)	0.651
Composition of the complex as obtained from Jobs and Molar ratio method (M : L)	1 : 2
Stability constant of the complex	6.34×10^4
Standard deviation in the determination of 2.12 $\mu\text{g/ml}$ of Pd(II)	0.0056
Relative standard deviation	2.47
Detection limit ($\mu\text{g ml}^{-1}$)	0.0743
Determination limit ($\mu\text{g ml}^{-1}$)	0.22

Table 4: Determination of Palladium in Certified Reference Materials

Name of the certified reference material	Amount of palladium(%)		%Error
	Certified Value	Found ^a	
Stark palladium silver alloy ^b	72.0	72.35	0.48
Palladium gold ^c	60.0	60.19	0.32

^aAverage of five determinations,

^bStark palladium silver alloy - Pd 72%, Ag 26%, Ni 2%

^cPalladium gold - Pd 60%, Au 40%.

Various physico – chemical and analytical characteristics of palladium complex are summarized in Table 3.

Table 5: The Comparison of Spectrophotometric Methods For The Determination of Palladium (II)

Name of the reagent	λ_{\max} (nm)	pH	Determination range ($\mu\text{g/ml}$)	$\epsilon \times 10^4$ ($\text{L mol}^{-1} \text{cm}^{-1}$)	Reference
Sodium isoamylxanthate	360	4.5-7.0	3.0-38	0.95	17
1-amino-4-hydroxy anthraquinone(AMHA)	620	0.3-6.5	3.0-14.5	1.1	18
2-hydroxy-5-methyl Acetophenone isonicotinoyl Hydrazone(HMAINH)	385	2.0	2.0-9.0	0.532	19
Propericiazine(PPC)	474	1.10-4.10	0.2-24.2	0.41	20
Gemifloxacin	430	acidic	1.0-10.0	1.36	21
1-(2-quinolyazo)-2,4,5-Trihydroxy benzene (QATB)	620 675	3.0-5.5 alkaline	1.9-7.95 1.6-8.5	1.25 1.20	22
Pyridoxal thiosemicarbazone (PTSC) PM-Present method	420	2.0	0.9-10.0	1.63	PM

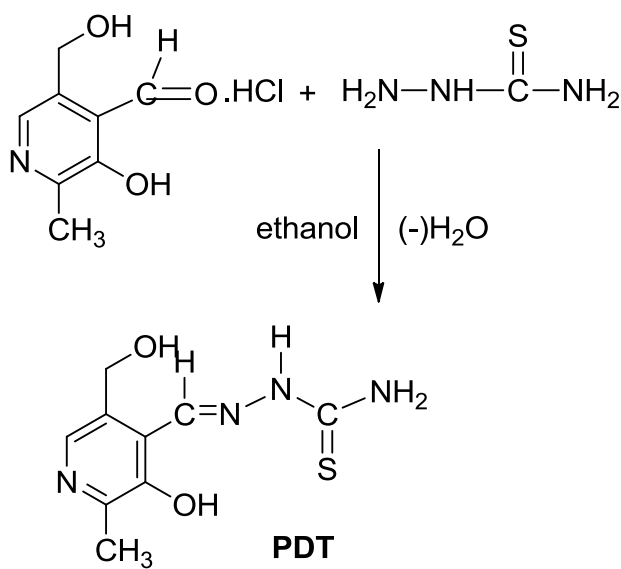


Figure 1 : Synthesis of pyridoxal thiosemicarbazone(PDT)

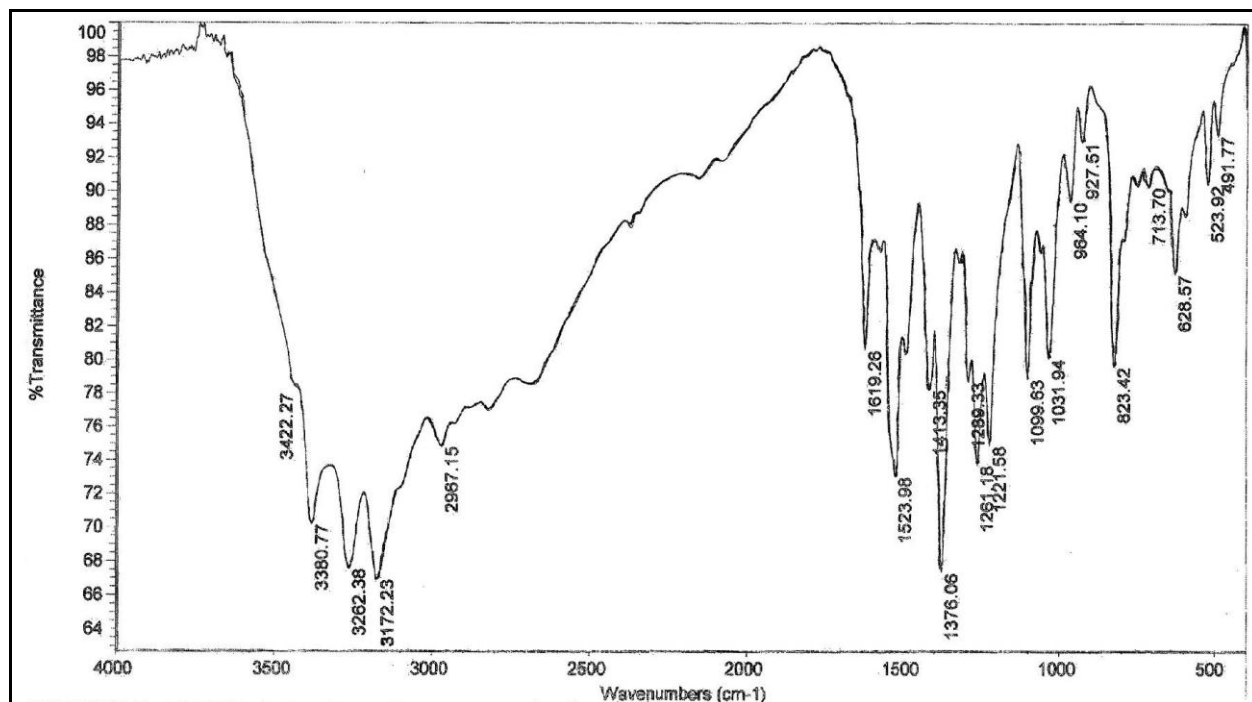


Figure 2 : Infrared Spectrum of PDT in KBr disc

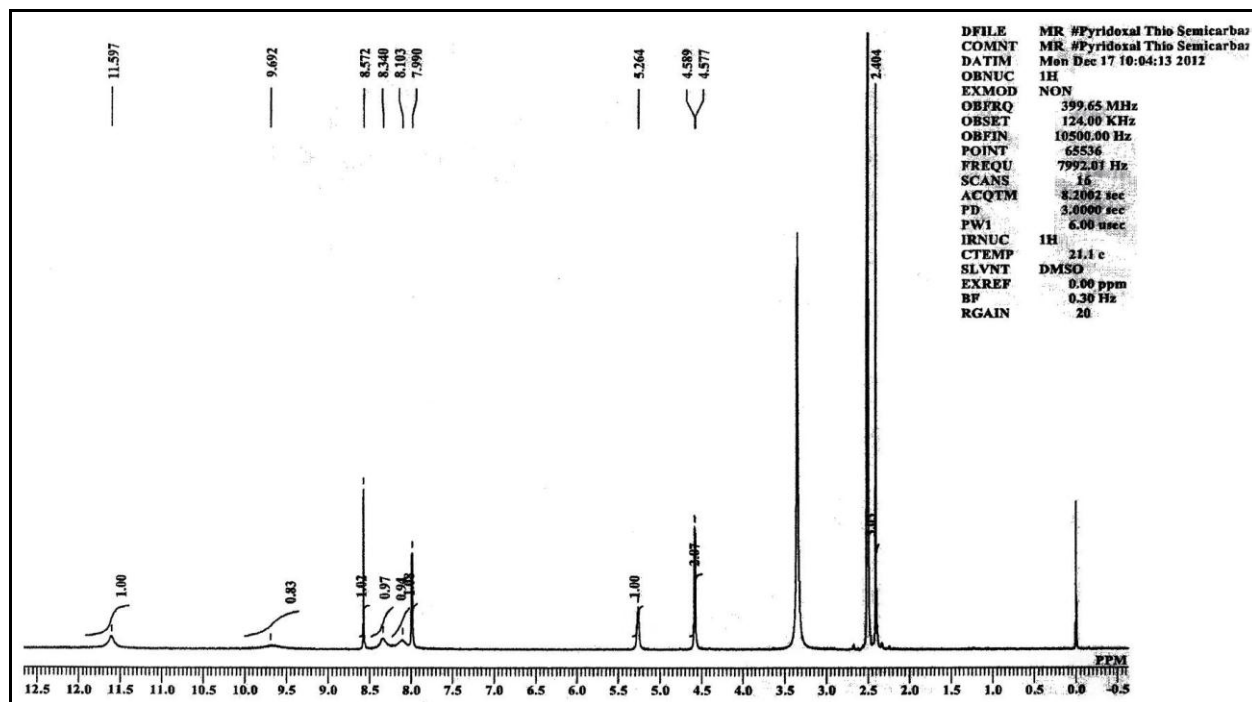


Figure 3: ¹H-NMR Spectrum of PDT in DMSO – d₆ medium

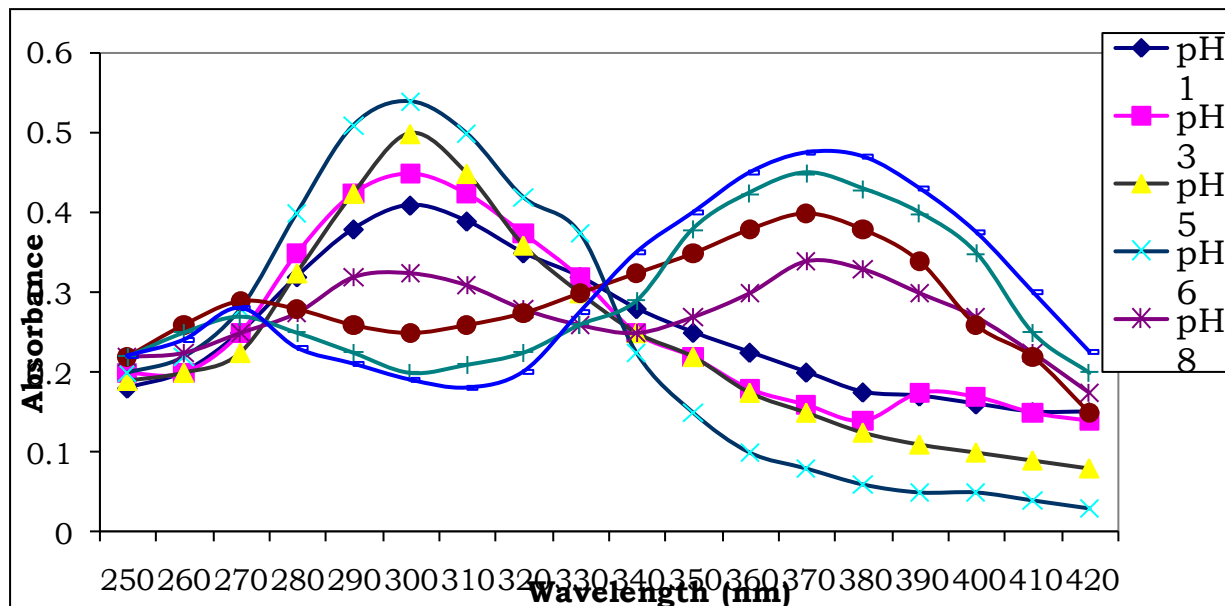


Figure 4 : Absorption spectra of 2×10^{-5} M of PDT at different pH values

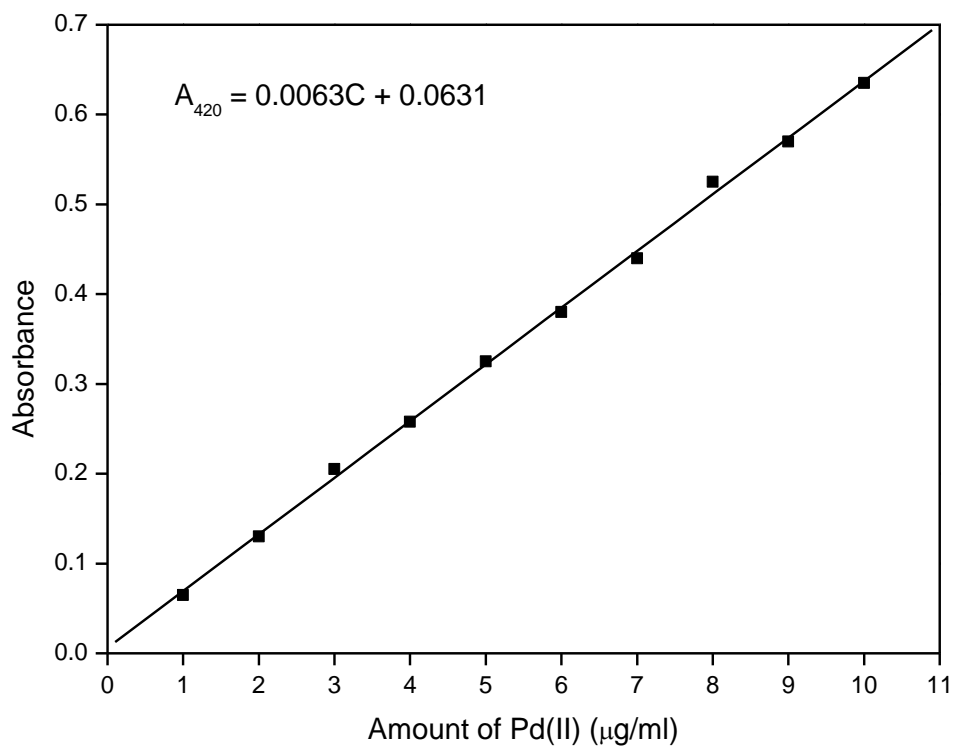


Figure 5 : Calibration plot for Palladium (II) determination

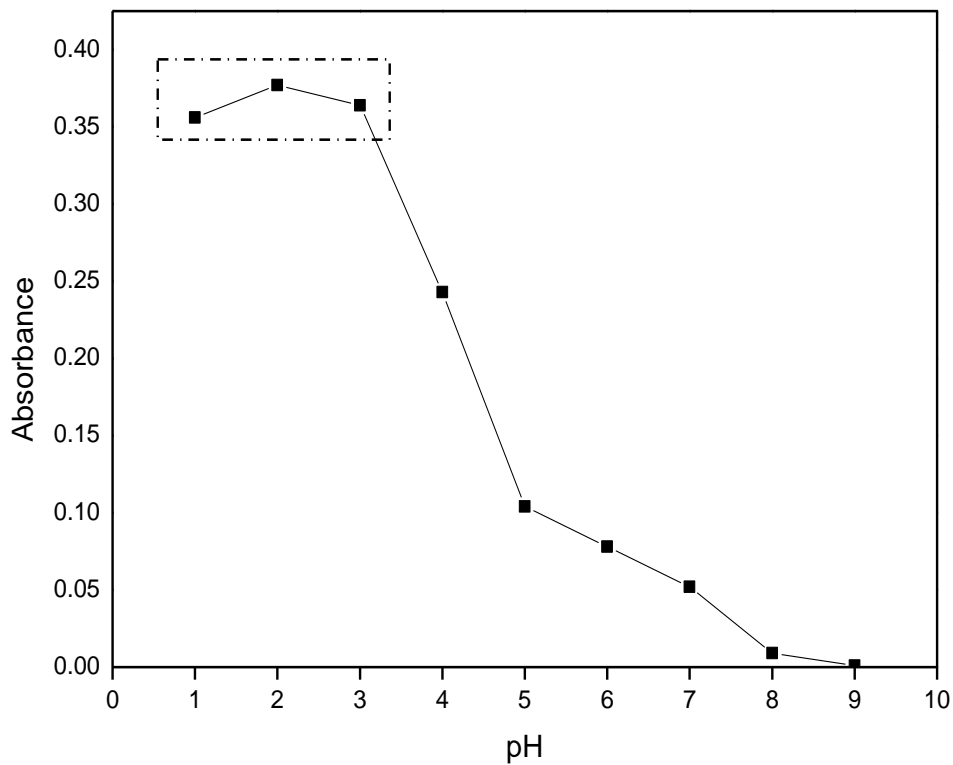


Figure 6 Effect of pH on the absorbance of Pd(II) – PDT complex

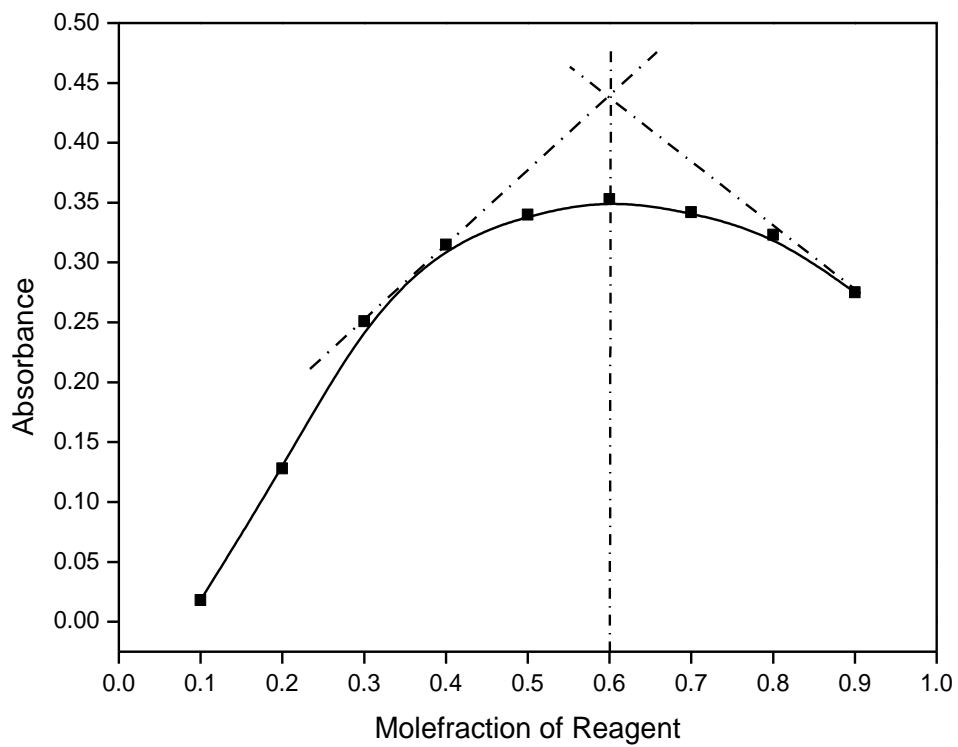


Figure 7 : Jobs curve

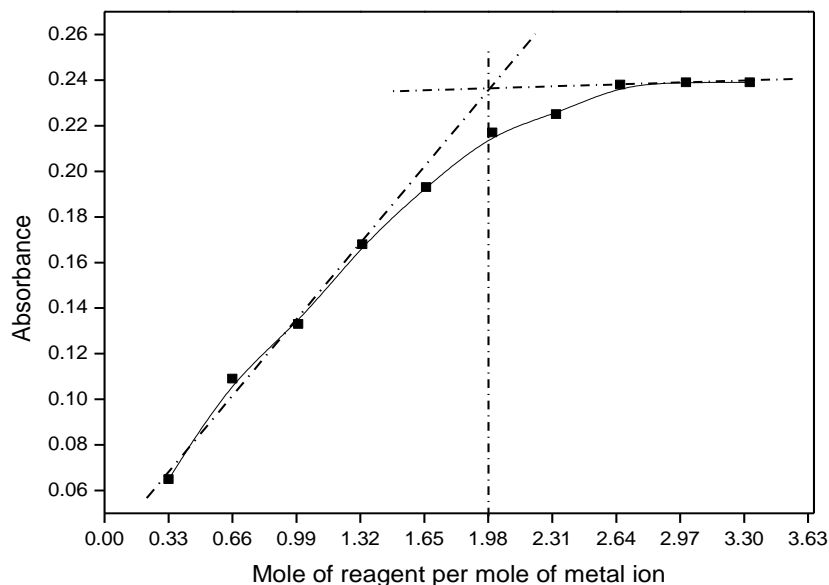


Figure 8: Molar ratio plot

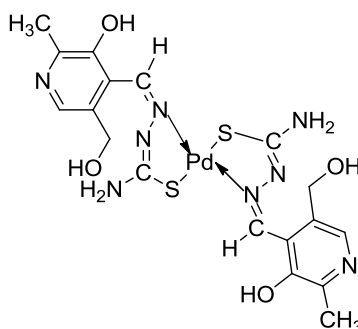


Figure 9 : The Proposed structure of Pd-PDT complex

Applications

The amount of palladium present in synthetic samples whose composition corresponding to Stark palladium silver alloy, Palladium gold was determined by the developed method, by taking a known aliquot of the sample solution in a 25 ml standard flask containing 10 ml of buffer solution, 2.5 ml of DMF and reagent [1.0ml of 1×10^{-2} M PDT] solution and made up to the mark with distilled water. The absorbance of the complex was measured at 420 nm against the reagent blank prepared under the similar experimental conditions. The absorbance values were referred to the predetermined calibration plot to compute the amount of the metal ion in alloy samples and the data are given in Table 4.

CONCLUSION

This paper describes the non - extractive spectrophotometric determination of palladium (II) using pyridoxal thiosemicarbazone (PDT) in aqueous medium. The present

method is simple, rapid and more sensitive than other reported methods for determination palladium. It is successfully applied for the determination of palladium in various alloy samples. The comparison of the proposed method with other spectrophotometric methods are presented in Table 5.

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