



# Non-Extractive Spectrophotometric Determination of Palladium (II) in Soil samples using Pyridoxal Thiosemicarbazone(PTSC)

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## Abstract:

Pyridoxal thiosemicarbazone (PTSC) 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<sub>3</sub>COONa 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 various soil samples.

**Keywords:** Spectrophotometric determination, Pd(II), Pyridoxal thiosemicarbazone soil samples.

## Introduction:

Palladium is a soft and ductile when annealed and greatly increases its strength and hardness when it is cold-worked. It dissolves slowly in sulfuric, nitric and hydrochloric acid [1]. It plays a key role in catalytic converters. Palladium and its alloys have wide range of applications both in chemical industry and in instrument making [2]. Palladium is utilized in many electronic devices including computers, cell phones, multi-layer ceramic capacitors and low voltage electrical contacts as well as in dentistry and medicine [3]. It is also used in jewellery, watch making and in blood sugar strips. Palladium is found in Lindlar catalyst, also called as Lindlar's palladium. Palladium is one of the three most popular metals used to make white gold alloys [4]. A survey of literature has revealed that several analytical techniques have been reported for the determination of palladium which include atomic absorption spectrometry [5], neutron activation analysis [6], and pre-concentration and separation of palladium, such as flow injection method, hollow fiber micro extraction, solid-phase micro extraction and spectrophotometry [7-20].

In the present investigation we report a simple, selective and non-extractive spectrophotometric determination of palladium (II) using pyridoxal thiosemicarbazone as a new Chromogenic reagent. The ligand is synthesized by reacting thiosemicarbazide with Pyridoxalhydrochloride. Pyridoxal is one of the three natural forms of vitamin B<sub>6</sub>, 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 B<sub>6</sub> 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 biological 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:

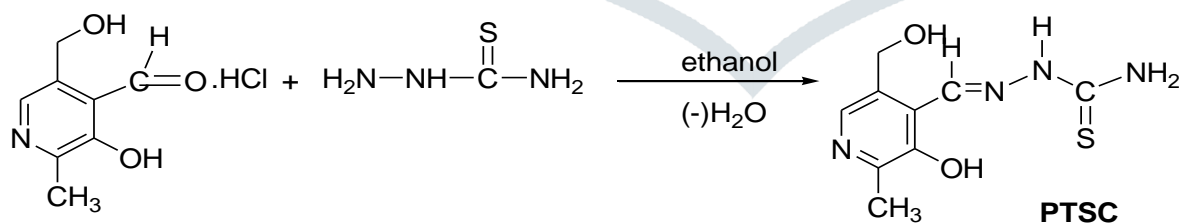
A Perkin – Elmer (Lambda 25), UV – Visible spectrophotometer equipped with 1.0 cm (path length) quartz cell and Elico model LI- 610 pH meter were used in the present study.

### Preparation of Reagent and solutions

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

### Synthesis of Pyridoxal thiosemicarbazone (PTSC)

Equimolar concentration of Pyridoxalhydrochloride (2g, dissolved in 20ml of ethanol) and thiosemicarbazide (0.9g dissolved in 10ml of H<sub>2</sub>O) solutions were mixed in a round bottom flask containing 10ml ethanol, the reaction mixture was refluxed for 3 hrs. The intense yellow coloured product Pyridoxal thiosemicarbazone (PTSC) (Scheme.1) 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 80 %, and melting point is 209 – 211°C.



### Scheme.1. Synthesis of Pyridoxal thiosemicarbazone (PTSC)

#### Preparation of PTSC solution

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

## Characterisation of reagent

The compound was characterized using IR, NMR and Mass spectral data. Infrared spectrum of PTSC shows sharp strong peak at  $3422\text{ cm}^{-1}$  may be assigned for the stretching vibrations of  $-\text{OH}$  and  $3381\text{ cm}^{-1}$  is for asymmetric stretching of  $-\text{NH}_2$  groups. The sharp peaks appeared at  $3262\text{ cm}^{-1}$  which is may be for stretching vibrations of secondary  $-\text{NH}$  group,  $3172\text{ cm}^{-1}$  is for stretching vibration of secondary thioamide  $-\text{NH}$  group, band at  $1620\text{ cm}^{-1}$  is for plane bending vibration of  $-\text{NH}$  group,  $1524\text{ cm}^{-1}$  is for stretching vibration of ring  $\text{C}=\text{C}$  group, band at  $1413\text{ cm}^{-1}$  may be assigned for stretching vibration of  $-\text{C}=\text{S}$  group and  $1290\text{ cm}^{-1}$  is for stretching vibration of  $-\text{C}-\text{NH}$  group,  $1262\text{ cm}^{-1}$  is for plane bending vibration of  $-\text{OH}$  group and band at  $823\text{ cm}^{-1}$  may be assigned for stretching vibrations of 4-substituted pyridine.

The  $^1\text{H}$  – NMR spectrum of PTSC ( $\text{CdCl}_2 + \text{DMSO}-d_6$ ) showed signals at singlet obtained at 2.40 (s), 4.58 (m), 5.26 (s), 7.99 (s), 8.57 (s), 11.59 (s) are due to methyl proton, amine proton,  $-\text{OH}$  proton, CH proton,  $-\text{CH}_2\text{OH}$  protons, phenyl ring protons respectively.

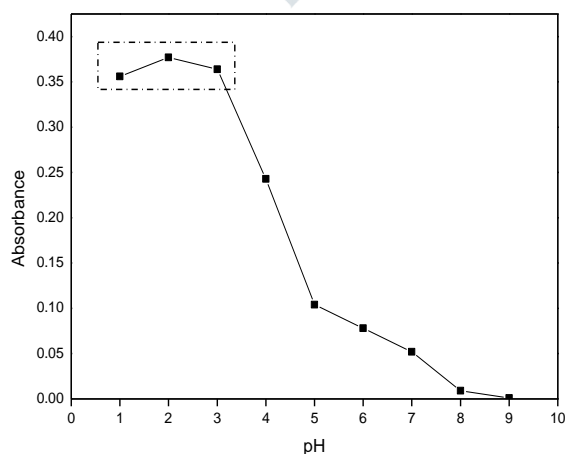
Mass spectrum of PTSC shows the molecular ion peak at  $m/z$  240. The peak observed at  $m/z$  values of 239 is due to the loss of  $-\text{H}$  radical, peak observed at  $m/z$  values of 224 is due to the loss of  $-\text{NH}_2$  radical and peak observed at  $m/z$  values of 207 due to the loss of  $-\text{SH}$  radical. Thus mass spectrum is consistent with the structure of PTSC.

## Preparation of palladium (II) solution

A  $1 \times 10^{-2}$  M stock solution of  $\text{Pd}^{2+}$  was prepared by dissolving 0.22g of  $\text{PdCl}_2$  in doubly distilled water containing few drops of conc. HCl and made up to the mark in a 100 ml volumetric flask. The stock solution was standardized gravimetrically [21]. Dilute solutions were prepared from this stock solution. Solutions of large number of inorganic ions, complexing agents were prepared from their analaR grade water soluble salts.

## Buffer Solution

The effect of pH on the colour intensity of the  $\text{Pd(II)} - \text{PTSC}$  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.



**Fig.5. Effect of pH on the absorbance of Pd(II) – PTSC complex**

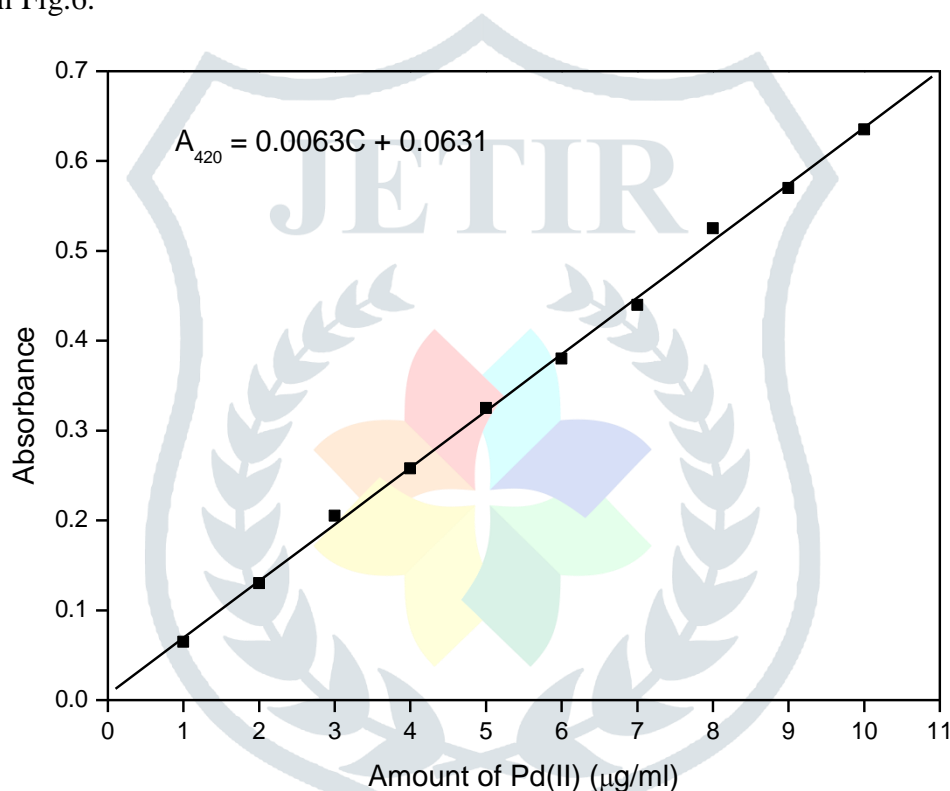
## Procedure

An aliquot of the  $\text{Pd}^{2+}$  solution in optimum concentration range, 10ml of buffer solution (pH 2.0) and 1ml of 0.01M reagent solution were taken in a 25ml volumetric standard flask and resulting solution was diluted to the mark with distilled water. The absorbance was measured at 420 nm against reagent (PTSC) blank. The measured absorbance was used to compute the amount of palladium from predetermined calibration plot.

## RESULTS AND DISCUSSION

Beer's law was obeyed over a concentration range of 0.9-10.0  $\mu\text{g/ml}$  of palladium(II) .

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 shown in Fig.6.



**Fig.6. Calibration plot for Pd(II) determination**

pH = 2.0 ; [PDT] =  $4 \times 10^{-4}\text{M}$ ; Wavelength( $\lambda$ ) = 420 nm; DMF = 10% (V/V)

## Precision

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

## Interference 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, 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.1. 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.

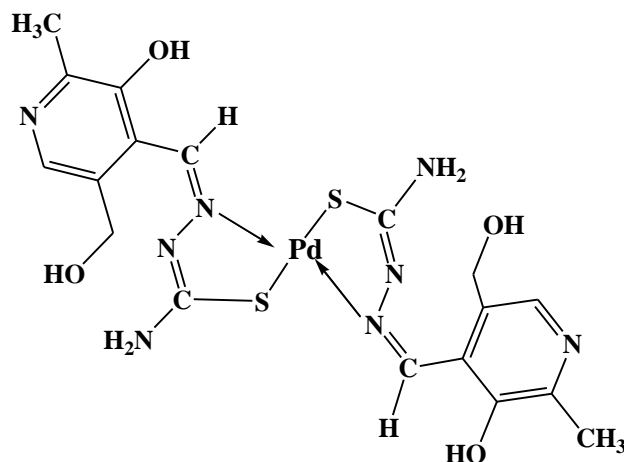
**Table .1. Tolerance limit of foreign ions in the determination of 2.12 µg/ml of palladium**

Ion added	Tolerance limit µg/ml	Ion added	Tolerance limit µg/ml
EDTA	1490	Cd(II)	450
Chloride	1472	Zn(I)	260
Hypo	632	Mn(II)	220
Tartrate	592	Pb(II)	83
Sulphate	384	Se(V)	32
Oxalate	352	Cr(VI)	21
Ascorbic acid	320	Ni(II)	7.6
Bicorbamate	242	Hg(II)	1.6
Carbonate	240	Os(VIII)	1.2
Acetate	236	V(III)	0.41
Thiocyanate	232	Mo(IV)	0.39 <sup>a</sup>
Ascorbate	230	Fe(III)	0.38 <sup>a</sup>
Fluoride	70	Pt(IV)	0.08
Iodide	51	Co(II)	0.02

<sup>a</sup> Masked with 200µg/ml of ascorbic acid.

### Determination of the composition of the complex

The composition of the complex (M : L) was determined by Job's Continuous Variation method and Molar Ratio Methods. The dissociation constant ( $\alpha$ ) 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  $1-\alpha / 4\alpha^3 c^2$ . The structure of Pd(II) – PTSC is given in **Fig 7**.



**Fig. 7. Structure of (M:L - 1: 2) Pd(II) – PTSC Complex**

### Determination of Pd(II) in soil samples:

A (5.0 g) soil sample was taken into a 250 mL Teflon high pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China) and added 50 mL of aqua regia. It was sealed tightly and then positioned in the carousel of a microwave oven (Model WL 5001, 1000 W). The system was operated at full 826 Yang et al. power for 30 min. The digested material was evaporated to dryness. Then, 50 mL of 5.0% hydrochloric acid was added and it is heated close to boiling to leach the residue. After cooling, the residue was filtered and the undissolved residue was washed two times with 5.0% hydrochloric acid. The filtrates were quantitatively collected in a 200 mL volumetric flask and the palladium content was analyzed according to the general procedure.

The results of determination of Pd(II) in various soil samples are presented in Table.2.

**Table.2. Determination of amount of Pd(II) in various soil samples**

Sample	Present method	AAS method	RSD (%)	Recovery(%)
<sup>a</sup> Soil (Road side)	91.5(ng/g)	91.0 (ng/g)	1.7	99.21
<sup>a</sup> Soil(general)	34.4(ng/g)	34.2(ng/g)	3.1	99.15
<sup>a</sup> Soil(marine)	110.0(ng/g)	112.2(ng/g)	1.2	98.5
<sup>a</sup> Soil(Industrial)	350(ng/g)	355(ng/g)	0.2	99.23

a = average of five determinations

The Comparison of Spectrophotometric Methods for The determination of Palladium (II) with various ligands are presented in the Table.3.

**Table.3. The Comparison of Spectrophotometric methods for The determination of Pd(II) with various ligands.**

S. No	Name of the reagent	$\lambda_{\max}$ (nm)	pH range	Determination ( $\mu\text{g/ml}$ )	$\epsilon \times 10^4$ ( $\text{L mol}^{-1} \text{cm}^{-1}$ )	Refer ence
1.	Sodium isoamylxanthate	360	4.5-7.0	3.0-3.8	0.95	22
2.	1-amino-4-hydroxy Anthraquinone(AMHAQ)	620	0.3-6.5	3.0-14.5	1.1	23
3.	2-hydroxy-5-methyl acetophenoneisonicotinoylhydrazone (HMAINH)	385	2.0	2.0-9.0	0.532	24
4.	Propericiazine(PPC)	474	1.10-4.10	0.2-24.2	0.41	25
5.	Gemifloxacin	430	acidic	1.0-10.0	1.36	26
6.	1-(2-quinolylazo)-2,4,5-Trihydroxy benzene(QATB)	620	3.0-5.5	1.9-7.95	1.25	27
7	2-hydroxy-1-naphthaldehyde-phydroxybenzoichydrazone (HNHBH)	430	3.0 -6.0	0.212-7.0	2.48	28
8.	Pyridoxal thiosemi carbazone(PTSC)	420	1.0 -3.0	0.9-10.0	1.63	PM

PM-Present method

### Conclusion:

The synthesized reagent Pyridoxal thiosemicarbazone(PTSC) is characterized by analytical and spectral studies. The reagent forms a yellow coloured complex with Pd(II). The Pd(II)-PTSC complex structure is predicted and various physico-chemical and analytical characteristics are determined. PTSC is successfully used for the determination of Palladium(II) in various soil samples.

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