



ORIGINAL RESEARCH PAPER

Pathology

Non-Extractive Spectrophotometric Determination of Palladium in water Samples Using Pyridoxal Thiosemicarbazone (PTSC).

KEYWORDS:

Spectrophotometric determination, Pyridoxal thiosemicarbazone, Molar absorptivity, Sandelle's sensitivity and water samples.

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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 (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, CH₃COONa 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 x 10⁴ L mol⁻¹ cm⁻¹ and 0.635 µg cm⁻² respectively. Linear calibration graphs were obtained for 0.9- 10.0 µg/ml of palladium(II). The method is highly selective for palladium and successfully used for determination of palladium in various hydrogenation catalysts.

Introduction:

Palladium is a rare and lustrous silvery white metal that resembles platinum. It is the least dense and has the lowest melting point of the platinum group metals. It is soft and ductile when annealed and greatly increases its strength and hardness when it is cold-worked. Palladium 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]. Palladium 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 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 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:

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 (DMF) was used after distillation.

Synthesis of reagent Pyridoxal thiosemicarbazone (PTSC)

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 %, and melting point is 209 – 211°C. The reaction route for the synthesis is shown in Fig. 1.

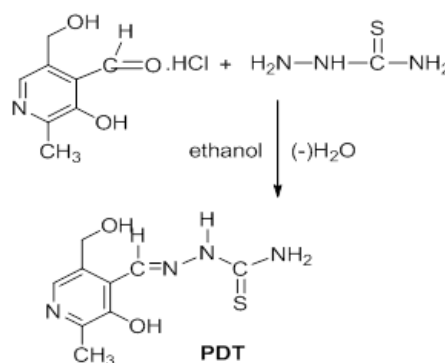


Fig.1. Synthesis of reagent Pyridoxal thiosemicarbazone (PTSC)

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 10 hrs.

Preparation of palladium (II) ion solution

A 1x10⁻² 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 [21]. Dilute solutions were prepared from this stock solution. Solutions of large number of inorganic ions, complexing agents were prepared from their analR 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 (PTSC) blank. The measured absorbance was used to compute the amount of palladium from

predetermined calibration plot.

Analysis of Water samples:

Three different samples of natural water were spiked with known amounts of Pd (II) and the resultant samples were analyzed for their Pd (II) content by the proposed method. The samples were simultaneously analyzed by flame atomic absorption spectrophotometry and the results obtained are compared in table.2.

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 PTSC 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 –NH₂ 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.

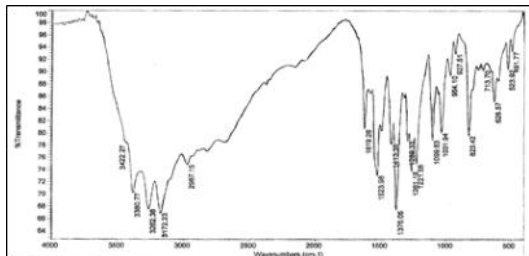


Fig.2. Infrared Spectrum of PTSC in KBr disc

¹H – NMR spectra

The ¹H – NMR spectra of reagent was scanned in DMSO –d₆ solvent and are shown in the Fig 3. From the spectral data , the singlet obtained at 2.40(□) ppm may be due to the methyl proton, the multiple signals at 4.58(□) ppm may be due to amine protons, the singlet signal at 5.26(□) ppm may be due to –OH protons, the singlet signal at 7.99(□) ppm may be due to –CH protons, the singlet signal at 8.57(□) ppm may be due to –CH₂OH protons and the singlet signal at 11.59(□) ppm may be due to phenyl ring protons and NMR spectrum of PTSC is shown in Fig 3.

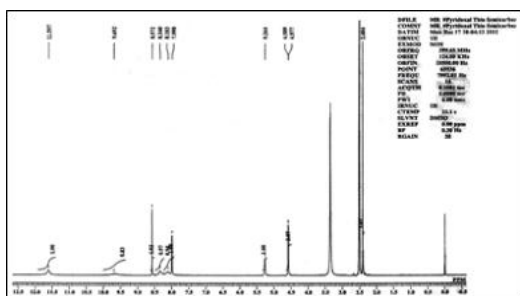


Fig.3. ¹H-NMR Spectrum of PTSC in DMSO – d₆ medium

Mass spectra

Mass spectrum of PTSC is shown in Fig.4. It 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 –NH₂ 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 PTSC.

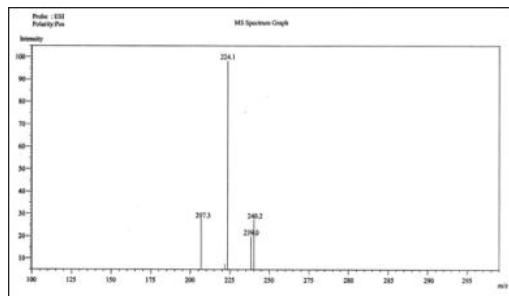


Fig.4. Mass spectrum of PTSC

Effect of pH

The effect of pH on the colour intensity of the Pd(II) – 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.

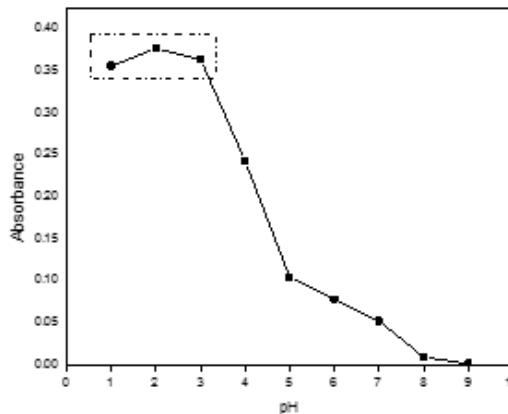


Fig.5. Effect of pH on the absorbance of Pd(II) – PDT complex Adherence of Beers law, Molar absorptivity, and Sandells sensitivity Beer's law was obeyed over a concentration range of 0.9-10.0 µg/ml of palladium(II) . Molar absorptivity and Sandells sensitivity were found to be 1.63 x 10⁴ L mol⁻¹ cm⁻¹ and 0.635 µg cm⁻² respectively.

Effect of reagent concentration

10 fold molar excess of reagent is sufficient for full colour development.

Effect of time

The absorbance of Pd(II) – PTSC 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 ± 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. 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 $\mu\text{g/ml}$ of palladium

Ion added	Tolerance limit $\mu\text{g/ml}$	Ion added	Tolerance limit $\mu\text{g/ml}$
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)	0.39a
Ascorbate	230	Fe(III)	0.38a
Fluoride	70	Pt(IV)	0.08
Iodide	51	Co(II)	0.02

aMasked with 200 $\mu\text{g/ml}$ of ascorbic acid.

Determination of the composition of the complex

The composition of the complex (M: L= 1 : 2) was determined by Job's continous variation method and Molar ratio method. respectively. CH_3COONa (1M) - Conc. HCl (0.1M) buffer (pH 2.0) is used in these studies. The dissociation constant (K) 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 $1/K^2/4c^2$. The structure of Pd(II) – PTSC is given in Fig 6.

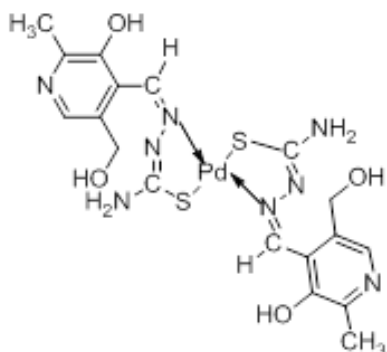


Fig. 6. The predicted structure of Pd(II) – PTSC Complex

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

Table.2. Determination of amount of Pd(II) in water samples

Palladium found		Proposed method	
Palladium(II) added ($\mu\text{g/mL}$ -1)	AAS method	Palladium found	
Sample 1	8.0	7.88	7.75
Sample 2	10.0	9.75	9.50
Sample 3	12.0	11.80	11.65
Sample 4	14.0	13.85	13.78

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	λ_{max} (nm)	pH range	Determination ($\mu\text{g/ml}$)	$\epsilon \times 10^4$ ($\text{L mol}^{-1} \text{cm}^{-1}$)	Reference
1.	Sodium isoamylxanthate	360	4.5-7.0	3.0-3.8	0.95	22
2.	1-amino-4-hydroxy Anthraquin	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.	Pyridoxal thiosemicarbazone (PTSC)	420	2.0	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. This reagent PTSC is successfully used for the determination of Palladium(II) in different water samples.

Acknowledgement:

The authors thank M. Subbalakshmi of IICT, Hyderabad for her help in recording IR and NMR spectras of reagent samples.

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