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## Facile and direct spectrophotometric determination of palladium (II) with L-Cystine

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**Abstract**

A simple, rapid and highly sensitive spectrophotometric determination of palladium (II) by using L-Cystine as complexing agent is described. The reagent forms a 1:2 yellow coloured complex with Pd (II) at pH 4, showed maximum absorbance at 369nm. The Beer's law obeyed over the concentration range 2.12 to 16.9  $\mu\text{gL}^{-1}$  of palladium (II). The molar absorptivity and sandell's sensitivity of the coloured complex are found to be  $2.69 \times 10^4 \text{L mol}^{-1} \text{cm}^{-1}$  and  $7.89 \times 10^{-4} \mu\text{g/cm}^2$  respectively. The effect of various diverse ions on the estimation of Pd (II) has been studied. The application of the proposed methods was extended to determine Pd (II) in synthetic alloy samples and in hydrogenation catalyst samples.

**Keywords:** Alloy sample, Hydrogenation catalyst, L-cystine, Palladium determination, Spectrophotometry.

**1. Introduction**

Palladium is a lustrous silver-white metal. It forms many compounds and several complex salts. Palladium is the least dense and has a low melting point of the platinum group metals. It is an important industrial catalyst. The largest use of palladium today is in catalytic convertor [1]. It has strong resistance to corrosion in air and to the action of acids (except nitric acid) at ordinary temperatures. The metal exists in the oxidation states, +2 and +4. Palladium (II) compounds are more stable. It also exists in mineral like stibiopalladinite, brageite and several nickel sulphite ores. For increasing density, it is alloyed with silver, gold and copper. It is used in the watch bearings, springs and balance wheels, air craft spark plugs, blood sugar test strips and also for mirrors in scientific instruments. Palladium is also used in dentistry [2], medicine and ground water treatment. It is used as a catalyst in the manufacture of sulphuric acid and hydrogenation process. Palladium is widely employed in jewellery [3] and may be alloyed with platinum or substituted for it. Palladium found in many electronics, including computers, mobile phones, multilayer ceramic capacitors, component plating, low voltage electrical contacts and LED/LCD televisions [4]. Palladium salts are employed in making special photographic printing paper [5]. Besides all these applications palladium has some adverse health effects, palladium is cytotoxic and kills or damages cells. It also causes considerable damage and inhibits enzyme activity and function. Palladium causes a significant number of allergic reactions as well as contact dermatitis [6-8], stomatitis, lichenoid reactions and periodontal gum diseases.

Many sensitive methods, such as spectrofluorometry, X-ray fluorescence spectrometry, neutron activation analysis, atomic absorption spectrophotometry have been used for determination of palladium. However spectrophotometric methods have gained popularity for palladium determination as advantageous in respect of simplicity and low operating costs. Palladium has great affinity for nitrogen containing ligands. Many organic compounds being recommended as the complexing agents for spectrophotometric determination of palladium, which includes hydrazones and its derivatives reacts with many metal ions forming colour complexes and act as chelating agents. In general the technique of solvent extraction is widely used in the spectrophotometric determination of metal ions. However, organic solvents such as benzene and chloroform are often carcinogenic, toxic and cause environmental pollution. It is significant to develop a method which does not involve solvent extraction. A micellar solution has the ability to enhance the stability of metal complex and has been utilized as a medium for the spectrophotometric determination of the metal chelates which includes Benzidithiosemicarbazone [9], Pyridoxal-4-phenyl-3-thiosemicarbazone [10].

4-(N, N-diethylamino) benzaldehyde thiosemicarbazones <sup>[11]</sup>, 1-(2-pyridylazo)-2-naphthol <sup>[12]</sup>, 2, 4 dihydroxy acetophenone thiosemicarbazone <sup>[13]</sup>, bromosalicylaldehyde isonicotinylhydrazine <sup>[14]</sup>, 4, 5(bromo-2-pyridyl)-azo-1, 3-diaminobenzene <sup>[15]</sup>, 1-(2-Quinolyazo)-2,4,5-trihydroxybenzene <sup>[16]</sup> and 4-hydroxy benzoylhydrazone <sup>[17]</sup>. However the majority of them involve multistep synthesis, and hence not economically viable methods for the determination of palladium. So this study aimed to introduce the readily available L-Cystine as a reagent for spectrophotometric determination of Pd (II).

## 2. Method and Materials

### 2.1. Instruments and Chemicals

Jasco model V-630, UV-Visible spectrophotometer with 1cm quartz cell and Equip-tronics, digital pH meter model EQ-610. All chemicals used were analytical grade and their solutions being prepared by using distilled water. Palladium (II) chloride solution was prepared by dissolving 0.1773g of PdCl<sub>2</sub> in a minimum volume of dilute KCl solution followed by dilution to known volume and standardised gravimetrically as palladium dimethylglyoxime <sup>[18]</sup>. A 0.02M solution of L-Cystine was prepared by dissolving in dilute hydrochloric acid and then diluted using deionised water.

Buffer solution (phosphate): 0.2M KCl and 0.2M HCl(pH-1.0), 0.2M KCl and 0.02M HCl (pH-2), 0.1 M Potassium dihydrogen phosphate and 0.1M HCl (pH-3.0 and 4.0), 0.1M Potassium dihydrogen phosphate and 0.1M sodium hydroxide (pH-5.0 and 6.0).

### 2.2. Procedure

In each set of different 25 mL volumetric flask 5 mL of buffer solution (pH 4.0), 6mL of 0.02 M solution of L-cystine and various volumes of 0.02 M Pd (II) were taken and made up to the mark with same buffer solution. The absorbance was taken  $\lambda_{max}$  369 nm against the reagent blank. The calibration plot was prepared.

### 2.3 Application of method

#### 2.3.1 Alloy samples

0.5 g sample of the synthetic alloy composition was digested in 15 mL of aqua regia by warming and the solution was evaporated to dryness. The residue was dissolved in 10 mL of diluted HCl and the resulting solution concentrated to about 3 mL, followed by dilution to 50 mL with distilled water, filtered to 100 mL volumetric flask and made up to the mark, applied the proposed method to estimate the amount of palladium(II). Results given in the Table-1.

**Table 1:** Microanalysis of palladium in synthetic mixture of alloy composition

Alloy sample		Present method( $\lambda_{max}=369nm$ ) <sup>[19]</sup>			Reference method ( $\lambda_{max}=405nm$ ) <sup>[19]</sup>		
Metal content	Composition	Pd found	RSD(%)n=5	RE (%)	Pd found	RSD(%)n=5	RE (%)
* Pd-Pt-Cu-Zn	15+15+35+35	15.09	0.48	+0.6	14.07	0.68	-6.2
*Pd-Co-In-Sn-Al	78+9.5+4+8+0.5	77.06	0.79	-1.2	76.94	0.42	-1.35
**Pd-Cu	95+5	94.18	0.81	-0.86	93.83	0.78	-1.23
**Pd-Ru-Rh	95+4+1	94.34	0.34	-0.69	94.3	0.63	-0.73
**18cr white gold Au-Pd-Ag	75+20+5	75.24	0.56	+0.32	73.77	0.44	-1.64

\*Dental alloy \*\* Jewellery alloy

### 2.3.2 Catalyst samples

Exactly weighed 0.5 g of catalyst sample was transferred in to 100 mL beaker, treated with 5mL of dilute nitric acid and covered, when gas from the solution is diminished about 5 mL of aqua regia was added and the solution was evaporated to

dryness on a sand bath, The residue was dissolved in 5mL of 2M nitric acid and diluted to 100mL volumetric flask. Suitable aliquots were taken and analyzed as per the proposed procedure. Results given in the Table-2

**Table 2:** Determination of palladium in catalysts

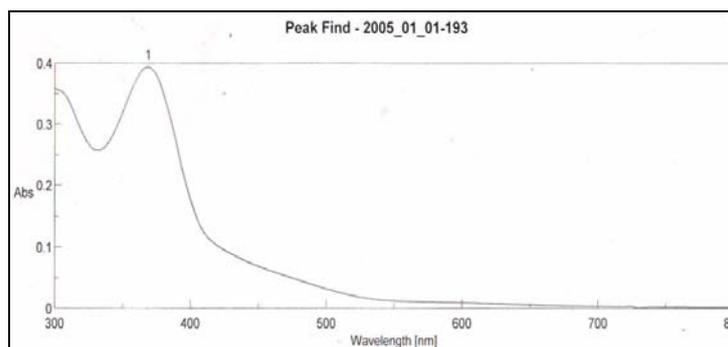
Catalyst		Present method( $\lambda_{max}=369nm$ ) <sup>[19]</sup>			Reference method ( $\lambda_{max}=405nm$ ) <sup>[19]</sup>		
Name of catalyst	Pd claimed	Pd found	RSD(%)n=5	RE (%)	Pd found	RSD(%)n=5	RE (%)
Lindlar catalyst Pd-CaCO <sub>3</sub>	5.0	4.79	0.47	-4.2	5.12	0.52	+2.4
Pd-activated charcoal	10	9.58	0.66	-4.2	10.21	0.44	+2.1

## 3. Result and discussion

### 3.1. Absorption spectra of L-Cystine and Palladium (II) Complex

The absorption spectra of the solution containing palladium(II) – L-Cystine complex against reagent blank and that of reagent

solution against the corresponding buffer blank were recorded in the wavelength region 300- 800nm at pH = 4. Typical spectra are presented in fig-1



**Fig 1:** Absorption spectra of palladium (II) –L-cystine complex

### 3.2. Effect of pH on the absorbance of the complex

The study of the effect of pH on the colour intensity of the reaction mixture showed that the maximum colour was produced at pH 4. Analytical studies were therefore carried out at pH 4.0 fig-2

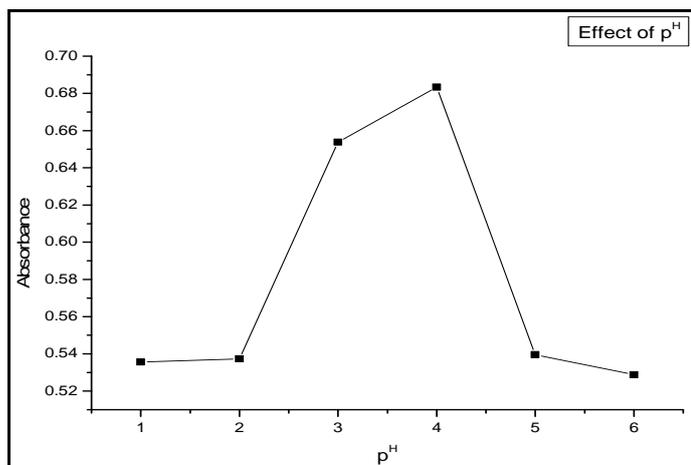


Fig 2: Effect of pH on absorbance (optimum pH at 3 to 4)

### 3.3. Effect of reagent (L-Cystine) concentration

The effect of reagent concentration was studied by taking 4mL of 0.002M PdCl<sub>2</sub> solution by varying volume of 0.002M L-cystine solution, It was observed that absorbance remains constant from 3mL to 9 mL. Hence half of the volume of equivalent molar concentration metal ion solution as complexing reagent was recommended for determination of palladium (II) for the further studies.

### 3.4. Beer's Law sensitivity and calibration plot

For the determination of palladium (II) at the micro level, the absorbance of the solution containing different amount of metal ion under the optimum condition was measured at 369nm and a calibration plot was constructed (figure-3) where optimum concentration range for effective spectrophotometric determination being determined.

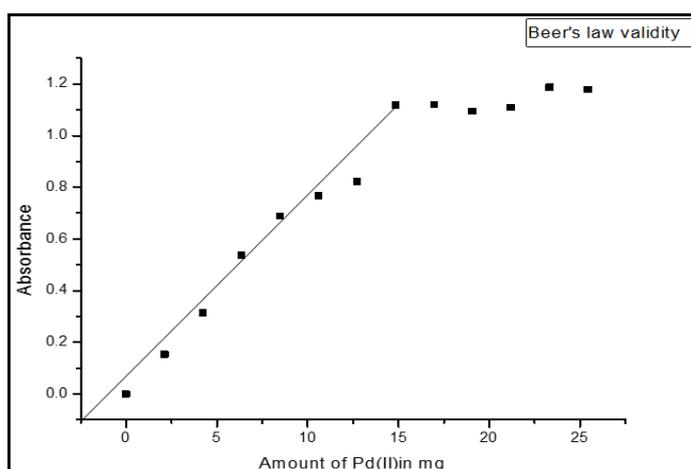


Fig 3: Beer's law verification, calibration curve

### 3.5. The stoichiometry and nature of the complex

The composition of the complex formed was determined by Job's continuous variation method (figure-4). It was found to be molar composition metal to ligand (M: L) is 2:1

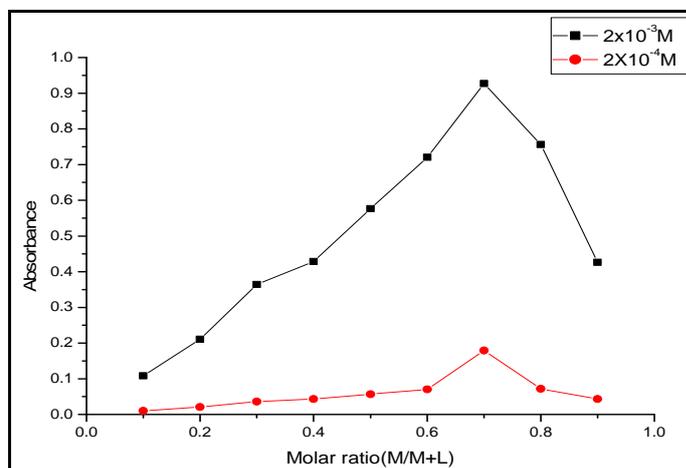


Fig 4: Job's method: metal to ligand molar ratio 2:1 (M<sub>2</sub>L)

### 3.6. Effect of diverse ions

The effect of various foreign ions was investigated in the determination of 7.6µg/mL palladium (II) to find out the tolerance limit of diverse ions in the present method. The tolerance limit of foreign ions was taken as the amount of foreign ion required to cause an error of ±2% in the absorbance. Ag(I) (05), Ca(II) (10), Al(III) (75), Ce(III) (25), Tl(III) (24), Fe(III) (25), Bi(III) (10), Na(I) (50), K(I) (50), Mg(II) (100), Pb(II) (70), Zn(II) (60), Cu(II) (40), Ni(II) (48), Mn(II) (4), Cd(II) (20), Ti(III) (24), Sn(IV) (45), acetate(100), chloride(100), sulphate(100), oxalate(100), tartarate(100), phosphate(100). The data suggest that several associated anions and cations do not interfere when they are present in large excess.

### 3.7. Precision and accuracy

For the study of reproducibility and accuracy of the method, absorbance measurement with eight different identical solutions containing 8.5µg of palladium was determined. The average of these eight readings and standard deviation were calculated. The standard deviation was found to be 0.0316. The entire analytical data have been listed in the Table-3. The results obtained by this method applied for alloy composition and hydrogenation catalysts are being compared with determination of palladium content in the above mentioned samples analysed by a reported spectrophotometric method using Salicylaldehyde thiosemicarbazone<sup>[19]</sup> the experimental results of proposed method are in close agreement with that of reference method<sup>[19]</sup>.

Table 3: Physico-chemical and analytical characteristics of Pd (II) – L-Cystine complex

Characteristics	Results
λ <sub>max</sub> .	369nm
Optimum pH range.	3 to 4
Mole of the Reagent required per mole of metal ion for full colour	0.5 fold
Beer's law validity range	2.12 µg to 16.9µg
Optimum concentration range	2.5 to 11.5
Composition of the complex (M:L)	2:1
Standard deviation in the determination of 8.5µg/mL Pd(II) for eight determinations	0.0316
Relative standard deviation	0.81%
Molar absorptivity	2.69x10 <sup>4</sup> L mol <sup>-1</sup> cm <sup>-1</sup>
Sandell's sensitivity	7.89x10 <sup>-4</sup> µg/cm <sup>2</sup>
Detection limit	0.0375µg L <sup>-1</sup>
Quantization limit	0.1137µg L <sup>-1</sup>

#### 4. Conclusion

A simple, rapid and reliable spectrophotometric method has been developed and successfully applied for determination of Pd (II) in alloy composition, hydrogenation catalyst and artificial Palladium solution. The proposed method does not require extraction, heating and interference free. This reagent is nontoxic and readily available.

#### 5. Acknowledgements

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