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### SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

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#### ABSTRACT

Phenanthraquinonemonothiosemicarbazone (PTS) with palladium (II) forms two coloured complexes, one is green at lower pH and the other one is brown at higher pH. Both the complexes are soluble in dimethyl formamide (DMF). The maximum absorbance of the green complex in acidic medium having HCl (0.28-1.14 M) is 590 nm whereas of brown complex at pH 8.0 - 9.5 is 540 nm in 70 % DMF concentration. Validity of Beer's law for the green and brown complexes are 23.41 and 7.23 ppm respectively. Sandell's sensitivity of green and brown complexes are  $2.53 \times 10^{-2}$  and  $8.35 \times 10^{-3}$   $\mu\text{g Pd/cm}^2$  respectively. PTS has been found to be a sensitive and highly selective reagent for the determination of palladium

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#### I. INTRODUCTION

Palladium(II) forms two coloured complexes with phenanthraquinonemonothio-semicarbazone(PTS). One is green and it is formed at lower pH's and the other is brown, formed at higher pH's. It has been observed that colour development (at higher pH's) is slow at room temperature and is accelerated on warming. Maximum complexation takes place on heating for about 8-10 minutes on a boiling water bath. At lower pH's, complexation takes place instantaneously. Both are soluble in DMF and the absorbance remains constant when DMF concentration (v/v) is 70% or more. The brown complex is stable for at least six hours and the green complex for fifteen hours. These observations have been utilized in developing a new spectrophotometric method for the determination of the metal.

#### II. EXPERIMENTAL

##### Preparation of PTS:

PTS was prepared by oxidation of phenanthrene (Fluka, AG) to phenanthraquinone by the method of Schultz and was purified. Then equimolar amounts of phenanthraquinone and thiosemicarbazide (E. Merck GR) were dissolved separately in minimum amounts of methanol and then mixed. After mixing, the solution was refluxed for three hours on a boiling water bath. The hot solution was filtered under suction and cooled. Red crystals of PTS were obtained which were recrystallised from methanol (m.p, 191-192). The purity of the ligand has been checked by elemental analysis and thin layer chromatography. The wavelength of maximum absorption of PTS is at pH 0.7, 6.5 and 11.9 is at 250, 254 and 207 nm respectively. PTS solution was prepared by dissolving it in dimethyl formamide (DMF) because of its greater solubility in this solvent. The solution is stable for two days.

##### Palladium (II) solution

Stock solution of palladium (II) was prepared by dissolving requisite amount of palladium chloride (Johnson and Matthey, London) in 2N hydrochloric acid. The solution was standardised gravimetrically with dimethylglyoxime.

##### Absorption spectra

Absorption spectra of the two complexes were recorded against corresponding reagent blanks, prepared under identical conditions. The brown complex shows maximum absorbance at 540 nm and the green complex at 590 nm. Hence, subsequent studies have been carried out at these wavelengths for the two complexes respectively.

**Effect of pH****(i) Brown complex**

A series of solutions containing 1.0 ml of  $5 \times 10^{-4}$  M palladium (II) and excess of the PTS solution at different pH's were prepared keeping all other variables constant. The pH's were adjusted with dilute solutions of sodium hydroxide and hydrochloric acid. The solutions were heated on a boiling water bath for nearly 10 minutes, cooled to room temperature and the volume was made up to 10 ml in each case, keeping 70% DMF concentration. The absorbance of these solutions recorded at 540 nm against the corresponding reagent blank and are plotted against pH's of the solutions. It was found that absorbance is maximum in the pH range 8.0 – 9.6. In view of this, subsequent studies have been carried out at pH 8.5.

**(ii) Green complex**

The green complex is formed in acidic medium. The effect of hydrochloric acid on the formation of the complex was, therefore, studied. Absorbance of the solutions having different amounts of acid and 70% DMF concentration, were measured at 590 nm against the corresponding reagent blanks. It has been found that absorbance remains constant when the final concentration of hydrochloric acid is in range of 0.28-1.14 M. In subsequent studies, 1 ml of 5M hydrochloric acid was added.

**Effect of reagent concentration**

To a series of solutions containing a fixed amount of palladium (II), increasing moles of reagent were added and pH was adjusted to 8.5 with dilute sodium hydroxide for brown complex and 1 ml of 5M hydrochloric acid was added for green complex. The brown complex was warmed for 10 minutes, cooled and diluted to 10 ml, maintaining 70% DMF. On the other hand, the green complex was also diluted to 10 ml, keeping 70% DMF medium. Absorbances were recorded at the corresponding  $\lambda_{\max}$  against reagent blank in each case. It has been observed that only 3- times molar excess of the ligand is required for maximum complexation in the case of the green complex and 7-times in the case of the brown complex. In subsequent studies, 10times molar excess of the ligand was used in both the cases.

**Physical constants of the complexes**

The physical constants of the two complexes were determined. The values are given below (first corresponds for the green complex and second for the brown complex).

$\lambda_{\max}$ (nm)	590 ; 540
Validity of Beer's law (ppm)	23.41 ; 7.23
Optimum determination range (ppm)	3.47-18.20 ; 1.32-6.76
Molar extinction coefficients ( $\epsilon$ ) (1 mole <sup>-1</sup> cm <sup>-1</sup> )	4200 ; 12740
Sandell's sensitivity ( $\mu\text{g Pd/cm}^2$ )	$2.53 \times 10^{-2}$ ; $8.35 \times 10^{-3}$

**Procedure for determination of palladium**

To a suitable aliquot containing 13.2-67.6  $\mu\text{g}$  (for brown complex) or 34.7-182.0  $\mu\text{g}$  (for green complex) of palladium (II) is added ten times of reagent solution. For the brown complex the pH is adjusted between 8.0 to 9.5 with dilute sodium hydroxide and/or hydrochloric acid. The mixture is warmed on a boiling water bath for nearly 10 minutes, cooled and diluted to 10 ml, maintaining 70% DMF (v/v) medium. For the green complex, add 1 ml of 5M hydrochloric acid and dilute to 10 ml, maintaining 70% DMF (v/v) medium. The absorbance is measured at 540 nm for the brown complex and at 590nm for the green complex respectively, against the corresponding reagent blank, prepared under identical conditions. Knowing the absorbance, the amount of palladium is deduced from the calibration curve.

**Molar composition of the complex**

The stoichiometries of the complex have been determined by the method of continuous variations and the mole ratio method. Both the methods show that in case of the brown complex, the composition is 1:2. Similar plot for the green complex indicates the metal to ligand ratio to be 1:1.

**Absorbance deviations**

The absorbances of eight solutions were noted under experimental conditions, containing 10.64 ppm (for green complex) and 5.32 ppm (for brown complex). The results are given below (first corresponds for the green complex and second for the brown complex).

Mean absorbance	0.420 ; 0.637
Average relative deviation (%)	0.29 ; 0.67
Maximum relative deviation (%)	0.69 ; 0.92
Standard deviation	0.003 ; 0.005

**Effect of diverse ions**

The effect of diverse ions was studied by taking suitable amounts of palladium (10.64  $\mu\text{g/ml}$  for green complex or 5.32  $\mu\text{g/ml}$  for brown complex) and varying amounts of diverse ions. The absorbances were measured at 540 nm (for brown complex) and at 590 nm (for green complex), against corresponding reagent blank. Attempts to mask copper(II) failed in both the systems. The concentrations of different ions tolerated (in ppm) are given in parenthesis (first corresponds for the green complex and second for the brown complex).

Chloride (1500 , 500 ) ; Bromide (2000 , 500) ; Iodide (100 , Interferes) ; Fluoride (150 , 200) Nitrate (2000 , 600) ; Nitrite (1200 , 100) ; Tartrate (800 , 200) ; Oxalate (500 , Interferes) ; Phosphate (800 , 250) ; Citrate (700 , 70) ; EDTA (600 , 150) ; Borate (1000 , 400) ; Calcium (II), Barium (II) ( 150 each ; 80 each) Magnesium (II) (300 , 100) ; Iron (II) (100 , 20<sup>a</sup>) , Iead (II) , (100 , Interferes ) ; Aluminium (III) (100 , 40) Cobalt (II), nickel (II) (100 each ; Interferes ) Zine (II) (150 , 5<sup>b</sup>) ; Cadmium (II) (200 , 10<sup>b</sup>) ; Mercury (II) (100 , 10<sup>b</sup>) ; Arsenic (III) (50 , 5) Silver (I) (150 , 10<sup>c</sup>) ; Gold (III) (150 , 20<sup>d</sup>) ; Ruthenium (III) (50 , 3 ) ; Rhodium (III), Osmium (VIII) ,and Platinum (IV) (50 each ; Interferes) ,Iridium (III) (100 , Interferes ) ; Uranyl (II) (300 , 50 ) ; Titanium (IV) (200 , 30 ) ; Thorium (IV) (200 , 50) ; Vanadium (V) (150 , 10)

\* (a, b, c and d shows the masking with  $\text{PO}_4^{3-}$ , EDTA,  $\text{Cl}^-$  &  $\text{Br}^-$  respectively)

**III. DISCUSSION**

Palladium gives colour reactions with many chromogenic reagents with varying selectivity and no reagent has outstanding preference. Dithizone is important among many organic spectrophotometric reagents for palladium. It is a sensitive reagent in acidic medium, but other noble metals such as Au, Pt(II), Hg and Cu also react with dithizone. Certain nitroso compounds are sensitive spectrophotometric reagents for palladium. p - Nitrosodimethylaniline and p-nitrosodiphenylamine are of particular value. The disadvantage of the methods is that both of them cannot be used in presence of large amounts of neutral salts such as sodium chloride, since the absorbance decreases.

Oxime reagents give highly selective extraction methods for determination of palladium. Dimethylglyoxime is very selective, but insensitive. Phenyl  $\alpha$  – pyridylketoxime is a sensitive and relatively selective reagent, but absorbance maximum lies in U.V. region (340nm).

Many azo compounds have been suggested as sensitive reagents for palladium. Among them, palladiazole is a sensitive reagent. The method is selective but bismuth(III), cerium (III), lead(II) and rare earths interfere in the determination.

A very sensitive method using o-hydroxyquinolphthalein has been developed. The method is based upon the ternary complex formed by palladium with hexadecyltrimethyl ammonium bromide and methyl cellulose. Fe(II), Cu (II), Al (III) and Cr (III) interfere, but Cu(II) and Al(III) can be masked by citric acid.

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Phenanthraquinonemethiosemicarbazone (PTS) form a green complex with palladium (II) at 0.28-1.14N hydrochloric acid concentration. The reagent does not form complex with other metals except copper at this acid concentration and thus the advantage of the method is that palladium (II) can be determined in presence of a large number of other metals. At higher pH's (8.0-9.5), a brown complex is formed. Since EDTA does not interfere, therefore, it has been used for masking some of the common metals. In brief, PTS is highly selective at lower pH and sensitive at higher pH.