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RESEARCH ARTICLE

Extractive Spectrophotometric Determination of Palladium (II) Using Novel Salen Ligand

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Abstract

2-[(E)-N-(2—{[2-[(E)-[(2-hydroxyphenyl) methylildene] amino] phenyl} (methyl) amino} phenyl) carboximidoyl] phenol (HHMCP) was synthesized and employed to develop an extractive spectrophotometric method for the determination of Pd (II). The reagent forms a complex with Pd (II) and can be quantitatively extracted in Chloroform at pH = 9.0. The extracted species showed an absorption maximum at 560nm with molar absorptivity of 0.47×10^2 L mol^{-1} cm^{-1}. A systematic study of the extraction was carried out by varying the parameters like pH, reagent concentration and equilibration time. The method has been successfully applied for the determination of Palladium in synthetic mixtures and real samples such as catalyst.

INTRODUCTION

Palladium, platinum, rhodium, ruthenium, iridium and osmium form a group of elements referred to as the platinum group metals (PGMs). These have similar chemical properties, but palladium has the lowest melting point and is the least dense of them. Palladium finds very important and extensive use in alloys, catalyst and in low voltage electrical contacts. Hence its recovery, purification and determination are vital processes. Many spectrophotometric methods of determining palladium have been reported (1-9).

Palladium is a rare and lustrous silvery-white metal discovered in 1803 by William Hyde Wollaston. Palladium compounds are more stable. Unlike other platinum metals palladium is soluble in concentrated HNO_3. Palladium gives stable amine, nitrite, cyanide, chloride, bromide and iodide complexes. Platinum group metals especially palladium is very important to industry.

Extraction of palladium from acidic solution is generally carried out from acidic medium. (10-13) Limited data have been reported on the extraction of palladium from nitric acid (14, 15) and sulphuric acid (16, 17) solution. The higher prices of platinum group metals have stimulated investigation of their separation, concentration and purification by solvent extraction techniques. (18, 19)

The determination of palladium is always an expensive procedure usually involving procedures such as flame atomic absorption spectrometry, emission spectrometry or neutron activation analysis (NAA). (20) Techniques like neutron activation analysis are expensive and available in few laboratories only.

The liquid-liquid extraction methods have been reported for palladium-dimethylglyoximate is specially extracted from dilute acid from chloroform. (21) Dithiocomplexes of palladium (II) are also extractable into chloroform. (22) Extraction of palladium-halide complexes affords convenient separations. (23) The extraction of palladium (II) from iodide solutions with methyl isobutyl ketone, alcohols and from thiocyanate solution with alcohols has been used for the separation from other metals. Pyridine and its derivatives may also be used for the extraction of palladium (II) from solutions. Extraction of palladium (II) with amines from citrate or tartarate and

thiocyanate solutions, with quaternary ammonium salts from chloride and bromide and thiocyanate solution have been reported.(24)

In continuation of the studies on the analytical application of HX for the determination of metals, it is used as extracting and spectrophotometric reagent to determine palladium (II). The extraction of Pd-HX complex from sulphuric acid and perchloric acid was applicable to the spectrophotometric determination of palladium (II). Palladium from synthetic mixtures containing gold is successfully determined by using 3-hydroxy-2-methyl-1-phenyl-4-pyridone ligands. (25) Palladium (II) is also determined by using sodium isoamylxanthate in presence of surfactants spectrophotometrically. (26)

A higher sensitive and selective spectrophotometric method for the determination of palladium by using thiosalicylic acid as a ligand in neutral medium has been reported (27), where the coloured metal complex is extractable into chloroform in presence of hexylamine.

The present method for extractive spectrophotometric determination of trace amount palladium (II) offers advantage of simplicity, sensitivity, rapidity and stability. It is also applicable for determination of palladium from real samples such as catalyst etc.

MATERIALS AND METHODS

All absorbance measurements were made on Systronics Digital Double Beam spectrophotometer model-2101 with 1 cm quartz cell. Standard volumetric flasks, 125ml separatory funnels, beakers were used for volumetric measurements. All dilutions were made using double distilled water. Solvents like chloroform, ethanol were used after double distillation. All interfering ion solutions were prepared in double distilled water

A stock solution of Pd (II) was prepared by dissolving 1 g Palladium chloride in 250 ml double distilled water and standardized. A working solution of 100µg/ml was prepared by dilution of the stock solution with double distilled water in a standard volumetric flask. 2-[(E)-N-(2—{[2-[(E)-[(2-hydroxyphenyl) methylildene] amino] phenyl} (methyl) amino} phenyl) carboximidoyl] phenol (HHMCP) was synthesized. (28) A solution of HHMCP (10^{-2} M) was always prepared by dissolving 0.478 g of HHMCP in 100 ml chloroform and used. .

EXTRACTION PROCEDURE

To an aliquot of solution containing 100 µg of Pd (II) in a separatory funnel, 10 ml of buffer solution of pH 9.0 and 10 ml 10^{-2} M HHMCP in chloroform were added. After shaking for 1.5 minutes, separatory funnel was kept for equilibrium and allowed to separate into two layers. The absorbance of the extracted yellow complex was recorded at 560 nm against chloroform black. A calibration graph was prepared and unknown amount of Pd (II) was determined from the calibration curve. Raffinates were analyzed for determination of Pd(II).

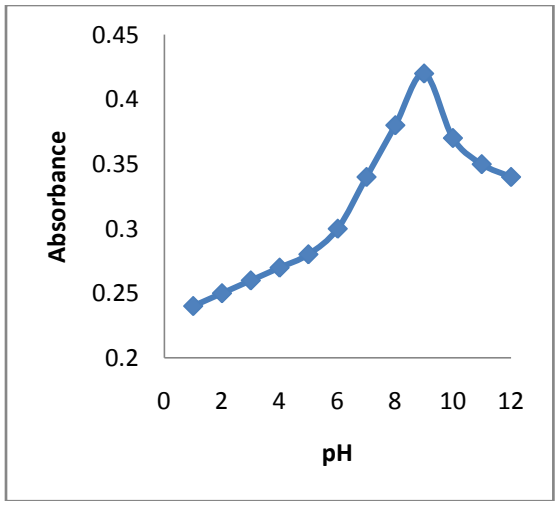
RESULTS AND DISCUSSION

1. **Absorption Spectrum**:

After extraction, Pd (II): HHMCP complex present in organic phase was scanned from 200 nm to 1000 nm against reagent blank. Maximum Absorbance value was observed at 560 nm. Therefore 560 nm was selected for the absorbance measurement throughout the experiments.

2. **Effect of pH:**

The absorbance of the organic phase was measured as a function of pH of the aqueous phase. The complexation of Pd (II) was carried out at pH range from 1-12. The data obtained shows maximum absorbance at pH 9.0. (Figure 1)



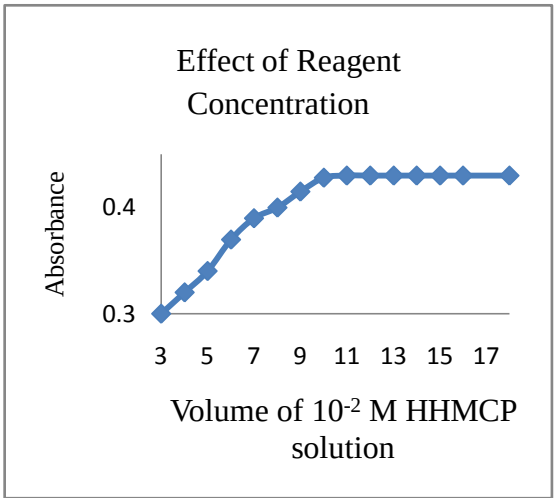
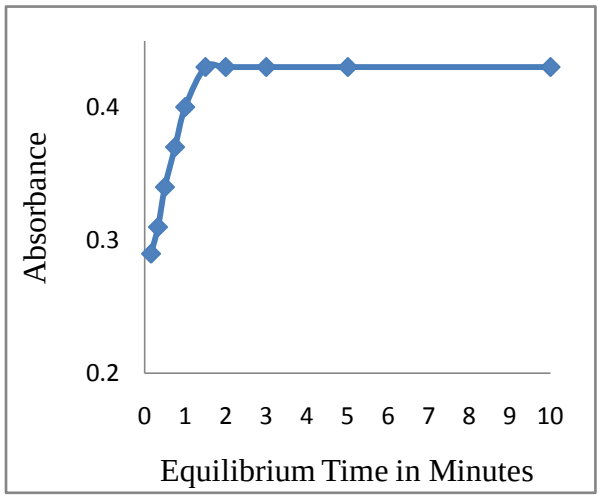


Fig. 1 Effect of pH **Fig.2 Effect of** HHMCP **reagent Concentration**

3. Effect of HHMCP reagent concentration

The minimum amount of reagent required for complete complexation of 100µg of Pd (II) was studied by varying the concentration of HHMCP. The results obtained from the plot of absorbance versus concentration of HHMCP indicate that 10 ml of 10^{-2} M reagent solution was sufficient for the quantitative extraction and spectrophotometric determination of 100µg Pd (II) (Figure 2). Addition of more reagent did not interfere with complexation and extraction of the complex. Further study of complexation was carried out by using 12 ml of 10^{-2} M HHMCP solution in chloroform to ensure the complete complexation.



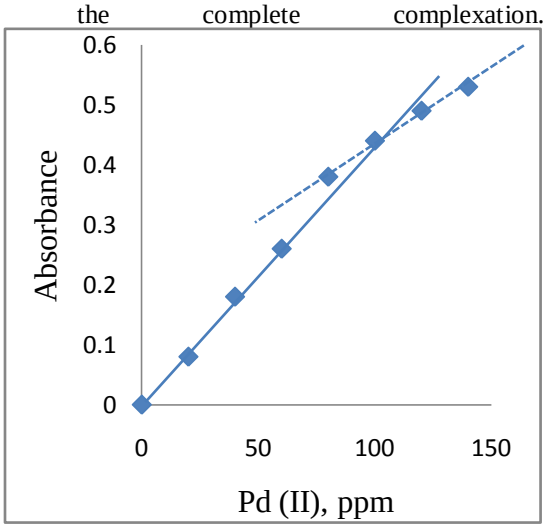


Fig.3 Effect of Effect of equilibrium time **Figure 4: Calibration Curve**

4. Effect of equilibrium time

The minimum equilibrium time for complete complexation of 100µg Pd (II) was studied by varying the equilibrium period from 5 seconds to 10 minutes. The results obtained from the plot of absorbance versus equilibrium time indicated that minimum 1.5 minute equilibrium time was required for the quantitative extraction and spectrophotometric determination of 100µg of Pd (II) (Figure 3). It was also observed that equilibrium time above 1.5 minute did not affect the complexation and extraction of the complex.

5. Calibration curve:

A calibration graph of Pd (II) was prepared by complexing varying amount of Pd (II) in the range 0µg to 160µg with 12 ml 10^{-2} M HHMCP in chloroform. Plot of absorbance versus concentration of Pd (II) gave a straight line indicating that that Beer's range up to 100µg of Pd (II) at 560 nm. (Figure 4)

6. Mole ratio method:

Mole Ratio Method is used to determine the composition of the complex. Complexation was carried out by treating equimolar solutions of Pd (II) and HHMCP. Plot of absorbance versus mole ratio gave two lines intercepting each other at mole fraction 1. This indicates metal to ligand ratio 1:1. (Figure 5)

7. Job's continuous variation method:

Job's Continuous Variation Method is also used to determine the composition of the complex. Complexation was carried out by treating equimolar solutions of Pd (II) and HHMCP For complexation of Pd (II) varying moles of Pd (II) were treated with varying moles of HHMCP in chloroform to obtain mole fraction 0.1 to 1.0. Plot of absorbance versus mole fraction also suggest metal to ligand ratio 1:1. (Figure 6)

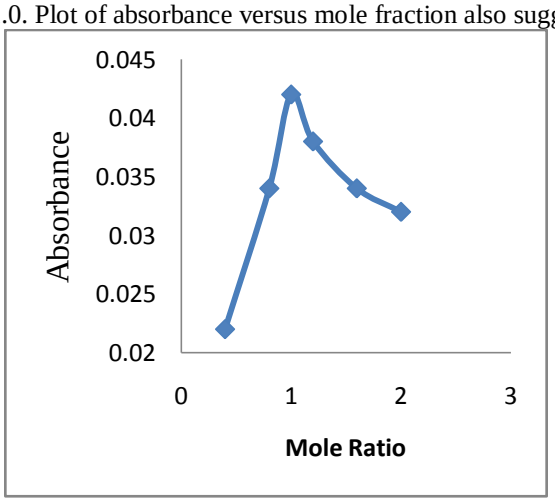


Figure 5: Mole Ratio Method

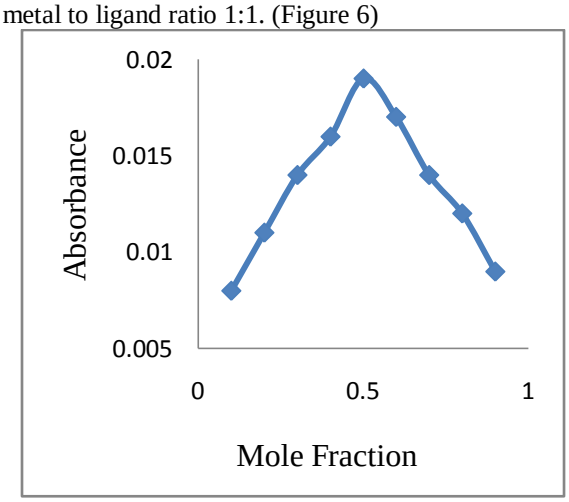


Figure 6: Job's Continuous Variation Method

8. Effect of foreign ions:

Under the optimum conditions the effect of various cations and anions on the extraction and spectrophotometric determination of 100µg Pd (II) was studied by adding known amount of foreign ion in interest to Pd (II) aqueous solution before adjusting the required pH. Complexation was carried out as per the method mentioned above.(Table 1)

In case of intensive interference of some foreign ions the test was repeated with successively smaller amount of the same foreign ion. The tolerance for the added foreign ion was decided as the largest amount that give error less than 2 % in the extractive determination of Pd (II) at 560 nm

Foreign Ion added	Amount Tolerated in µg *
Ni (II)	10
Sn (II)	10
Ru (III)	20
Mn (II)	10
Fe (II)	15
Co (II)	15
Cu (II)	15
Zn (II)	10
Cd (II)	15
Cr (VI)	20
Fe (III)	20
Hg(II)	20
Pb(II)	15
Al(III)	20
Mg(II)	20
Ba(II)	20

Table 1: Effect of Foreign Ions on Extraction of Pd (II)
*** Average of five determinations**

9. Applications:

To study the analytical applicability of the proposed method, it was applied for separation and spectrophotometric determination of Pd (II) from real samples such as Pd (II) from different catalyst formulations etc. (Table 2). The results were compared with those obtained using the traditional methods. As seen, the results of two different methods are in satisfactory agreement.

Samples	Pd (II) content		
	Amount of Pd(II) in µg	From Conventional Methods *	From Complexation with HHMCP *
Palladium Catalyst (5% Pd on $BaSO_4$)	100	99	98
Palladium Catalyst (10% Pd on $BaSO_4$)	100	98	98
5% Pd(II) on Asbestos	100	98	99
10% Pd(II) on Asbestos	100	98	98

Table 2: Determination of Pd (II) from real Samples

∗ Average of five determinations

Conclusions

An extractive spectrophotometric method was developed for estimation of Palladium (II) and successfully used for quantitative extraction of Palladium (II) at pH 9.0. Since the equilibration time is very less, the method is very quick. The method is applicable for determination of Palladium (II) from different synthetic mixtures and catalysts.

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