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Liquid-Liquid Extraction of Palladium (Ii) with Cyanex 301

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ABSTRACT

This paper describes experimental work of solvent extraction of Pd (II) from acidic aqueous media with Cyanex 301 as extractant in chloroform. Various parameters such as acid concentration, reagent concentration, shaking time, effect of diluents and effect of foreign ions were studied. Quantitative extraction of Pd (II) in 0.5M HCl was possible with 0.05 M Cyanex 301 after 60 seconds of shaking .The pale yellow coloured Pd-Cyanex 301 complex exhibits maximum absorption 310 nm where extraction of reagent was found to be negligible. The complex is stable more than 48 hrs. The probable composition of the species has been deduced from the extraction data. Beer-Lambert law is obeyed in the concentration range 6µg -80µg with Sandell's sensitivity of 1.09 x 10-3 µg/mL/cm2 and molar absorptivity of 91,166 mole-1.cm-1.dm3. A study of effect of diverse ions on the extraction showed that several metals ions like Ti+4, Mg+2, Ce+4, Al+3, Mn+2 do not interfere during the extraction and estimation of Palladium. The data have been successfully employed for the separation of binary mixtures containing the non interfering metal ions. The optimized conditions of separation have been successfully utilized to recover metal from real samples.

KEYWORDS Extraction, Palladium, Cyanex 301, Chloroform.

1. Introduction

Palladium is a chemical element with symbol Pd and atomic number 46. It is a rare and lustrous silvery-white metal discovered in 1803 by William Hyde Wollaston . Common oxidation states of palladium are 0, +1, +2 and +4. There are relatively few known compounds with palladium unambiguously in the +3 oxidation state, though such compounds have been proposed as intermediates in many palladium-catalyzed cross-coupling reactions. [1] In 2002, palladium (VI) was first reported.[2,3] Palladium dissolves slowly in concentrated nitric acid, in hot, concentrated sulfuric acid, and, when finely divided, in hydrochloric acid.[4]

Naturally occurring palladium is composed of seven isotopes, which includes six stable isotopes. The most stable radioisotopes are 107Pd with a half-life of 6.5 million years (found in nature), 103Pd with a half-life of 17 days, and-^{100}Pd with a half-life of 3.63 days. Eighteen other radioisotopes have been characterized with atomic weights ranging from 90.94948(64) u (^{91}Pd) to 122.93426(64) u (^{123}Pd).[5] Most of these have half-lives that are less than thirty minutes, except ^{101}Pd (half-life: 8.47 hours), ^{109}Pd (half-life: 13.7 hours), and ^{112}Pd (half-life: 21 hours).[6]

Palladium(II) chloride is the principal starting material for many other palladium catalysts. It is used to prepare heterogeneous palladium catalysts: palladium on barium sulfate, palladium on carbon, and palladium chloride on carbon.[7] It reacts with triphenylphosphine in coordinating solvents to give bis(triphenylphosphine)palladium(II) dichloride, a useful catalyst.[8]

The largest use of palladium today is in catalytic converters.[9] Palladium is also used in jewelry, dentistry,[9,10] watch making, blood sugar test strips, aircraft spark plugs and in the production of surgical instruments and electrical contacts.[11]Palladium is also used to make professional transverse flutes.[12] As a commodity, palladium bullion has ISO currency codes of XPD and 964. Palladium is one of only four metals to have such codes, the others being gold, silver and platinum.[13]Because of its ability to absorb hydrogen, palladium is a key component of the controversial cold fusion experiments that began in 1989.

The second-biggest application of palladium in electronics is in the manufacture of multilayer ceramic capacitors[14] in which palladium (and palladium-silver alloys) are used as electrodes.[9] Palladium (sometimes alloyed with nickel) is used in connector platings in consumer electronics.[15, 16]

Palladium is used in small amount (about 0.5%) some alloys of dental amalgam in order to decrease corrosion and increase the metallic lustre of the final restoration.[17]

Finely divided palladium metal can be pyrophoric. As a platinum-group metal, the bulk material is quite inert. Although contact dermatitis has been reported, the amount of data on the effects of exposure to palladium is limited. It has been shown that people with an allergic reaction to palladium also react to nickel, making it advisable to avoid the use of dental alloys containing palladium on those so allergic. [18, 19, 20, 21, 22]

Reference reveals that several reagents have been used for the spectrophotometric determination of Palladium .[23-53] Palladium is also extractable from the acidic medium with various reagents. [54-63.]

From literature survey, it is obvious that existing methods for the determination of Palladium have their own limitations[64-69]. The proposed method is simple, rapid for the separation and spectrophotometric determination of Palladium using Cyanex 301. Cyanex-301 [bis (2, 4, 4 trimethylpentyl) dithiophosphonic acid] marketed by Cytec Inc. Canada has been used as an extractant for some metal ions [70-87].

2. Materials and Methods:

2.1 Stock Solution

All the chemicals (E. Merck) and diluents used in the present experimental studies were of Analytical Reagent grade. The extractant Cyanex 301 was supplied by Cytec Inc. Canada was used without further purification.

Stock solutions of various cations, anions were prepared from their respective salts. (Table .3) by taking proper precautions.

Pd (II) stock solution was prepared by dissolving 0.166gm of $PdCl_2$ in a 100 mL std. measuring flask with distilled water containing about 5 mL conc. HCl.

2.2 Standardization of Palladium by gravimetric method:
Palladium was standardized gravimetrically by dimethylglyoxime (DMG) method[88]. The solution containing Pd (II) in 0.25 M HCl was taken in a flask and to it 5.0 mL of dimethylglyoxime (DMG) solution was added and ammonium hydroxide solution was added till the solution became alkaline when scarlet red precipitate was obtained. It was stirred and digested on water bath for 1 hr, cooled and filtered through a previously weighed sintered glass crucible. The precipitate was washed with 1% reagent and then with hot distilled water. The precipitate was dried at 110^{O}C and palladium was weighed as Pd – $(DMG)_2$ to constant weight.

All absorbance measurements were carried out on **'Spectronic Genesis 8'**UV- Visible spectrophotometer using 10mm path length quartz cuvettes.

2.3 General Extraction Procedure:
To an aliquot of the aqueous solution containing Palladium (II) was added to concentrated hydrochloric acid to make it 0.5 M in a total volume of 15mL. The solution was transferred into a 125mL separating funnel and shaken for 60 sec. with 15 mL of 0.05M Cyanex 301 solution in chloroform. After allowing the two phases to separate, the organic phase was collected in a 25mL standard measuring flask and diluted up to the mark with chloroform. A small quantity of anhydrous Sodium Sulphate was added to all the 25mL flasks to absorb the moisture. The absorbance of the extract was measured between 200 to 400 nm against blank. A Pd (II) - Cyanex 301 complex in organic phase exhibits maximum absorption at 310 nm where absorption of reagent was found to be negligible. Hence the wavelength 310 nm was chosen for further studies.

3. Results and Discussion:
3.1. Absorption Spectrum:
The absorption of Palladium- Cyanex complex was studied over a wavelength range of 200-400 nm. The pale yellow coloured complex exhibited absorption maxima at 310nm (Fig 1). At this wavelength the absorption of the reagent was negligible. Therefore, the wavelength of 310nm was chosen for all further measurements (fig.1)

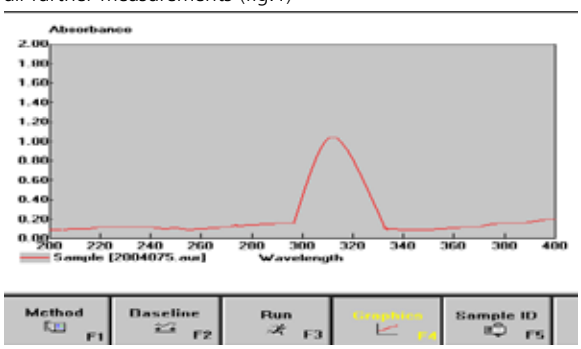


Fig.1. Absorption Spectra
3.2. Effect of reagent concentration:
The optimum concentration of Cyanex 301 for quantitative extraction of Pd (II) was ascertained by extraction with varying concentrations of Cyanex 301 from 0.01-0.10 mol dm^{-3} in chloroform. The extraction was quantitative with 0.05 mol dm^{-3} Cyanex 301 (Fig 2). Hence 15mL of 0.05 mol dm^{-3} Cyanex 301 in Chloroform was used throughout the study.

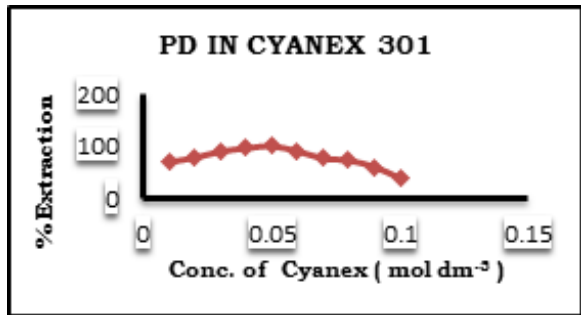


Fig.2. Cyanex Concentration

3.3. Effect of Hydrochloric acid concentration:
The effect of the molarity of hydrochloric acid concentration on the absorbance of the extract was studied using the recommended procedure. By varying concentration of HCl between 0.1 to 0.9 mol dm^{-3}. The absorbance of extract was found to be maximum at 0.6 mol dm^{-3}. Thus 0.6 mol dm^{-3} HCl concentration was used for subsequent studies.(Fig. 3)

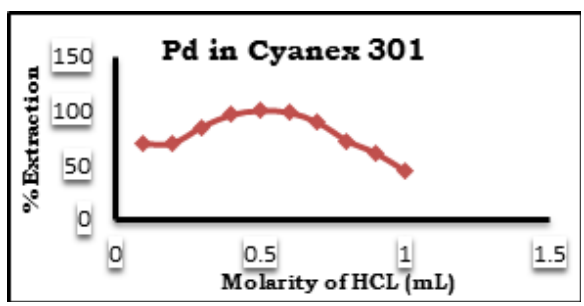


Fig.3. HCl Concentration

3.4. Effect of various Diluents:
To find out the effect of diluents on extraction, the reagent 0.05 mol dm^{-3} of Cyanex 301 was prepared in different diluents and was used for extraction from aqueous phase containing 100 µg of Palladium in 0.6 mol dm^{-3} HCl. For the diluents study the absorbance and % extraction of Palladium decreased in the order: Chloroform (99.99%), Toluene (95.34%), Carbon Tetrachloride (96.12%), Benzene (74.29%), Xylene (89.75%), Cyclohexane (63.85%). (Fig.4) Chloroform gave quantitative extraction and hence for all further studies chloroform was chosen as diluents.

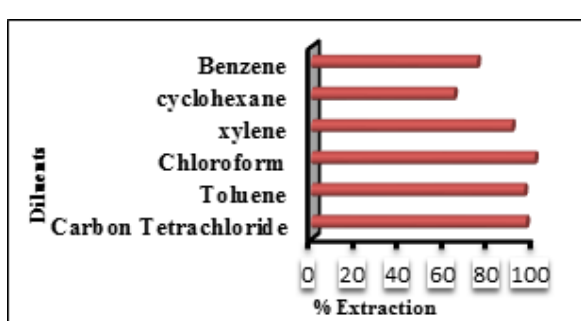


Fig.4. Effect of Diluents

3.5. Effect of Shaking period:
The absorbance of the extract obtained by shaking the aqueous phase containing 100µg Palladium (II) + 15mL with 0.5 M Hydrochloric acid, with an organic phase containing 0.05 M Cyanex 301 in Chloroform was measured, for varying time periods from 15 sec to 120 sec. It was observed that the extraction was quantitative after 60 sec. of equilibration. Hence, optimum period chosen for shaking was 60 sec. (Fig. 5)

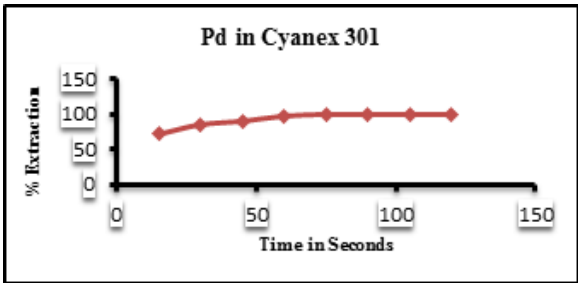


Fig. 5 Equilibration Period

4. Optimum Conditions for Extraction of Platinum (Table.1)

Parameter	Optimum Condition
Palladium(II)	100 µg/mL
Hydrochloric acid concentration	0.5 mol dm^{-3}
Cyanex 301 concentration	0.05 mol dm^{-3}
Shaking Time	60 seconds
Diluent	Chloroform

4.1 Validity of Beer-Lambert law:

A calibration graph for determination of Palladium was prepared under optimum experimental condition (0.5 mol dm^{-3} HCl, and 0.05 mol dm^{-3} Cyanex in Chloroform). Beer's law was found to be obeyed in the range of 6 µg to 80 µg of Palladium at 310 nm. (Fig.6)

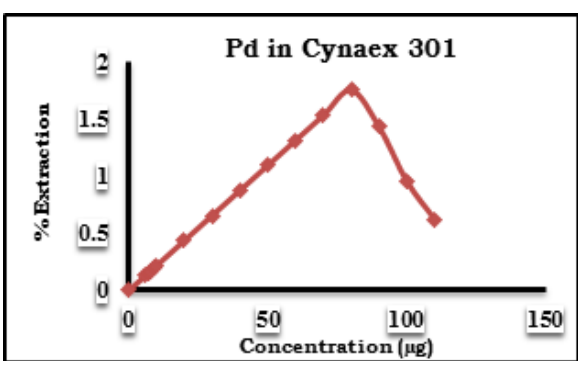


Fig 6. Beer's law plot

4.2. Spectrophotometric Data for the Determination of Palladium after Extraction with Cyanex 301 (Table.2)

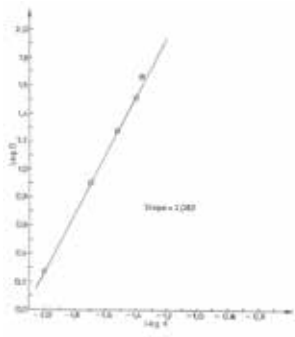
The molar absorptivitiy of complex calculated was found to be 91,166 x 10^4 $mole^{-1}.cm^{-1}.dm^3$. At 310 nm, Sandell's sensitivity calculated on the basis of total Palladium present is 1.09 x10^{-3} µg cm^{-2} .The spectral characteristic are given in (Table. 2)

Molar absorptivity	91,166 x $10^4 mole^{-1}.cm^{-1}.dm^3$
Sandell's sensitivity	1.09 x10^{-3} µg cm^{-2}
Mean absorbance of 6 determinations	1.094
Beer's law range	6 to 80 µg/mL
Standard deviation	1.789 x 10^{-3}
Coefficient of variation	0.16%

4.3 Nature of extracted species

An attempt was made to find out the probable composition of the extracted species from a plot of log D vs. log C (Cyanex 301) at fixed acid and $SnCl_2$ concentration. The slope of this plot was found to be 2.083 ≈ 2 indicating the complex to be 1:2 with respect to Cyanex 301, thus confirming the oxidation state of Palladium as +2 in the extracted species. (Fig. 7)

5. Effect of diverse ions & binary separation:



5.1 Effect of diverse ions

The extraction of Pd (II) was carried out according to the recommended procedure to examine the effect of interference from various foreign ions. The tolerance limit was set at an amount to cause an error of ± 2% in the recovery of the metal ion. It was observed that, a large number of cations and anions were tolerated (Table. 3)

Table.3: Effect of foreign ions

Tolerance Ratio Pd(II): Diverse ions	Diverse Ions	
	Cation	Anions
Interference	Cu^{+2}, Pb^{+2}, Co^{+2}, Zn^{+2} Pd^{+2}, Rh^{+3}, Ru^{+3}, Hg^{+2} Cd^{+2}, Bi^{+3},	-----
1:10	Mo^{+6}, Zr^{+4}, Ni^{+2}, Th^{+4}, Cd^{+2}	---------
1:15	Co^{+2},La^{+3}, Al^{+3}, Ba^{+2}	
1:20	Be^{+2}, , K^+	F^-,I ,SCN^-,Oxalate
1:25	Sr^{+2}, Sb^{+3},Na^+,Ca^{+2}	SO_3^{2-},CO_3^{-3},Br
1:30	Ti^{+4}, Te^{+2},Mg^{+2} Fe^{+2},Fe^{+3},Mn^{+2} ,Ce^{+4}	,SO_4^{2-} ,NO_3^-

5.2 Binary Separations of Palladium (II)

Ions such as Ti^{+4}, Mg^{+2}, Ce^{+4}, Al^{+3}, Mn^{+2} do not get extracted into Cyanex 301 under optimum extraction conditions for Palladium (II) up to a certain concentration. Hence, it was possible to separate them from their binary mixtures. The unextracted Ti^{+4}, Mg^{+2}, Ce^{+4}, Al^{+3}, Mn^{+2} were determined spectrophotometrically by known methods. (Table. 4)

Table. 4 Binary Separation of Palladium

Composition µg	Recovery of Pd(II)* %	Coefficient of Variation	Recovery of the added ion* %	Coefficient of Variation	Estimation procedure for the added ion and its reference
Pd(II):Ti(IV) 100 : 100	99.99	0.47%	94.36	0.58%	Hydrogen peroxide Method [89]
Pd(II):Mg(II) 100 : 100	99.99	0.32 %	98.65	0.63%	Solochrom Black Method[90]
Pd(II):Ce(IV) 100 : 100	99.99	0.12 %	96.54	0.38%	Carbonate Method[90]
Pd(II):Al(III) 100 : 100	99.99	0.54%	94.32	0.66%	Eriochrome Cyanine R. method.[90]
Pd(II):Mn(II) 100 : 100	99.99	0.29%	97.54	0.77%	Potassium Periodate Method [91]

* Mean of five determinations

6. Analysis of Palladium (II) in real samples:

6.1. 0.1 g of Pd- charcoal was taken in a silica combustion tube and incinerated for 8 hours to ash the carbon completely. The sample was treated with 5 Ml formic acid and dried on hot plate. The resulting residue was dissolved in 6 M HCl and 2 M HNO_3 and evaporated to dryness then the residue was dissolved in distilled water and diluted to100mL with distilled water.2 mL of the sample solution was taken and Pd (II) was extracted and estimated using the proposed method. The results obtained were in close agreement with theoretical values. (Table. 5)

Table. 5

Samples	Amount of Pd (II) certified	Amount of Pd (II) Found with Standard method	Amount of Pd (II) Found with Proposed method	% Found with Standard method	% Found with Proposed method	R.S.D. (%)
Pd-charcoal	5 %	4.48 %	4.46 %	99.99 %	99.98 %	0.45 %

***Average of six determination**

6.2. 0.1 g Pd – $CaCO_3$ catalyst was taken in a beaker with aquaregia and evaporated to dryness. The residue was leached with dilute hydrochloric acid and diluted to 100mL with distilled water. 2 mL of the sample Solution was taken and Pd (II) was extracted and estimated using the proposed method. The results obtained were in close agreement with theoretical values. (Table. 6)

Table. 6

Samples	Amount of Pd (II) certified	Amount of Pd (II) Found with Standard method	Amount of Pd (II) Found with Proposed method	% Found with Standard method	% Found with Proposed method	R.S.D. (%)
Pd – $CaCO_3$ catalyst	4.7 %	4.68 %	4.63 %	99.99 %	99.94 %	0.74 %

***Average of six determination**

6.3. 0.1 g Pd – $BaCO_3$ Catalyst was taken in a beaker with aquaregia and evaporated to dryness. The residue was leached with dilute hydrochloric acid and diluted to 100 mL with distilled water. 2 mL of the sample Solution was taken and Pd (II) was extracted and estimated using the proposed method. The results obtained were in close agreement with theoretical values. (Table.7)

Table. 7

Samples	Amount of Pd (II) certified	Amount of Pd (II) Found with Standard method	Amount of Pd (II) Found with Proposed method	% Found with Standard method	% Found with Proposed method	R.S.D. (%)
Pd – $BaCO_3$ catalyst	4 %	3.99 %	3.95 %	99.99%	99.96 %	0.67 %

***Average of six determination**

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