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Use of Cyanex 923 for Estimation of Pd(II)

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A detailed study of extraction of palladium was carried out using Cyanex 923 in chloroform as an extractant. The Pd(II) content in the extracted pink coloured complex can be estimated using direct spectrophotometric method. Various parameters for extraction of palladium were studied in detail, including the effects of HCl, $SnCl_2$, reagent concentrations, various diluents and equilibration period. These conditions were optimized to obtain quantitative extraction. The probable nature of the extracted species was found out by a plot of log D *vs.* log C. The spectroscopic analysis of the complex was also done using IR, ^1H NMR and ^{31}P NMR techniques. Interference of foreign ions on extraction of Pd(II) was studied. The method can be used to separate Pd(II) from Mn(II), Ni(II), Co(II) and Fe(III) in their binary mixtures.

Key Words: Extraction, Cyanex 923, Palladium(II), Binary separations.

INTRODUCTION

Palladium is generally found in association with the other platinum metals and is the most abundant among them. The placer deposits of Urals and Pestamo deposits of Kola peninsula are known to contain minerals with palladium like Braggite (Pt, Pd, Ni)S and Michenitrite ($PdBi_3$). During electrolysis, palladium electrodes absorb hydrogen in large amounts. This property is used for purification of hydrogen. Palladium is used extensively in the electronics industry in capacitors, as a dental alloy and in jewellery. It is also used as a catalyst in many chemical reactions such as: oxidation of fuels, including methane, methanol and hydrogen as it has the ability to activate H_2, O_2, carbon-hydrogen and oxygen-hydrogen bonds. Thus, owing to its importance in all spheres, it was thought worthwhile to develop a method for estimation of palladium.

Literature reveals an extensive study of palladium using various extractants. These include use of neutral, acidic and basic extractants. The methods suffer from drawbacks such as longer shaking time[1-10], large number of intereferences[11-14] and use of carcinogenic solvents[15-19] for solvent extraction, *etc*.

In the present study, a neutral organophosphorus extractant Cyanex 923 was used for the extraction study of Pd(II) from chloride media. The various parameters studied were effects of HCl concentration, reagent concentration, $SnCl_2$ concentration, various diluents and equilibration period on the extraction.

EXPERIMENTAL

All the chemicals used were of analytical grade and purchased from E. Merck (India). The stock solution Pd(II) was prepared by dissolving 0.1666 g of palladium chloride in a 100 mL standard measuring flask with double distilled water containing about 5 mL conc. HCl. The solution was standardized gravimetrically by a standard method[20] and the working standard solutions were prepared by suitable dilution of the stock solution. A 8×10^{-2} M solution of Cyanex 923 (m.w. 348) was prepared by pipetting out 3.17 mL of Cyanex 923 in a 100 mL standard measuring flask and diluting it up to the mark with chloroform.

A 'Spectronic Genesis 8' UV-Visible spectrophotometer was used for absorbance measurements.

General extraction procedure: To an aliquot of the aqueous solution containing palladium(II) was added 0.75 mL of 1 M $SnCl_2$ to which was added 1 M hydrochloric acid to make it to a total volume of 15 mL. The solution was transferred into a 125 mL separatory funnel and shaken for 1 min with 15 mL of 0.08 M Cyanex 923 solution in chloroform. After allowing the two phases to separate, the organic phase was collected in a 25 mL standard measuring flask and diluted upto the mark with chloroform. A small quantity of anhydrous sodium sulphate was added to all the 25 mL flasks to absorb all the moisture. The absorbance of the extract was measured at 290 nm against the reagent blank prepared analogously.

Palladium was extracted in the presence of $SnCl_2$, which was used as a labilizing agent and quantitative extraction was possible. When tin was added to the solution, palladium got activated. This may be due to the reduction of Pd(II) to Pd(I) with $SnCl_2$ and thus making the complex very easily extractable into Cyanex 923. In the absence of $SnCl_2$, palladium does not get extracted into Cyanex 923 using the recommended procedure.

RESULTS AND DISCUSSION

Extraction conditions: The absorption of palladium(II) complex was studied over a wavelength range of 250-350 nm. This pink coloured complex exhibited absorption maxima at 290 nm. At this wavelength the absorption of the reagent was negligible. Therefore, the wavelength of 290 nm was chosen for all further measurements.

The conditions for quantitative extraction of Pd(II) were established by varying parameters like concentration of HCl (0.2-3.0 M), concentration of $SnCl_2$ (0.03-0.20 M), Cyanex 923 concentration (3.0- 10.0 × 10^{-2} M), diluents and shaking period. It was observed that Pd(II) is quantitatively extracted from 1 M HCl, 0.05 M $SnCl_2$ with 15 cm^3 of 8 × 10^{-2} M Cyanex 923 dissolved in chloroform.

The study showed that shaking period of 1 min is enough for complete transfer of Pd(II) into the organic phase. Prolonged shaking, however, had no adverse effect on the extraction.

The suitability of various solvents was investigated for the proposed system. It was observed that, extraction was quantitative with chloroform but decreased with toluene, xylene, benzene and carbon tetrachloride. Hence chloroform was chosen as a diluent. Besides, it gave a clear phase separation and the lower organic layer was easier to remove. The optimum extraction conditions are shown in Table-1 and in Figs. 1-5.

TABLE-1
OPTIMUM CONDITIONS FOR EXTRACTION OF PALLADIUM

Parameters	Optimum conditions
Palladium(II) (μg)	10 to 110
Hydrochloric concentration (M)	1
$SnCl_2$ concentration (M)	0.05
Cyanex 923 concentration (M)	8 × 10^{-2}
Shaking Time (s)	60
Diluent	Chloroform

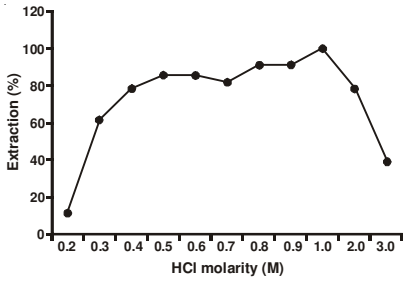

Fig. 1. Extraction behaviour of Pd(II) into Cyanex 923 as a function of the molarity of HCl

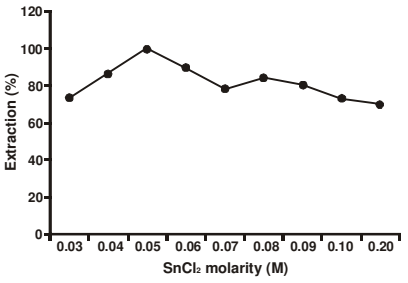

Fig. 2. Extraction behaviour of Pd(II) into Cyanex 923 as a function of the molarity of $SnCl_2$

Spectral characteristics: Palladium(II) was extracted with Cyanex 923 in concentration ranging from 10-120 μg. It was found that, a linear plot was obtained in the concentration range of 10-110 μg of the organic phase. Beyond 110 μg of palladium(II), the slope of the plot changes. The

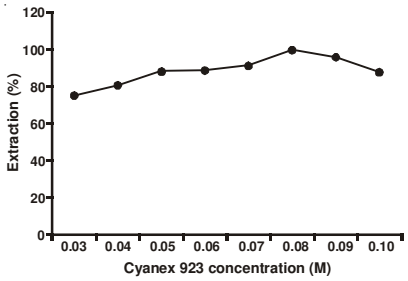

Fig. 3. Extraction behaviour of Pd(II) into Cyanex 923 as a function of Cyanex 923 concentration

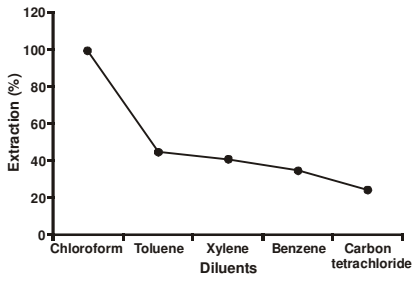

Fig. 4. Extraction behaviour of Pd(II) into Cyanex 923 as a function of different diluents

complex is stable for more than 24 h. The Sandell's sensitivity and the molar absorptivity was found to be 3.4782×10^{-3} μg mL^{-1} cm^{-2} and 30596.49 L mol^{-1} cm^{-1}, respectively. The coefficient of variation was 0.11 % for 50 μg of palladium(II).

The spectrophotometric data for the determination of 50 μg of palladium(II) after extraction with Cyanex 923 is given in Table-2.

TABLE-2
SPECTROPHOTOMETRIC DATA FOR THE DETERMINATION OF PALLADIUM AFTER EXTRACTION WITH CYANEX 923
Pd(II) = 50 μg, $SnCl_2$ = 0.05 M, HCl = 1 M, Extraction solution = 15 mL of 8×10^{-2} M Cyanex 923 in chloroform

Molar absorptivity	3.596.49 L mol^{-1} cm^{-1}
Sandell's sensitivity	3.4782×10^{-3} μg mL^{-1} cm^{-2}
Mean absorbance of 6 determinations	0.575
Beer's law range	10-110 μg
Standard deviation	6.324×10^{-4}
Coefficient of variation	0.11%

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 923) at fixed acid concentration. The slope of this plot was found to be $1.39 \approx 1$ indicating the complex to be 1:1 with respect to Cyanex 923, thus confirming the oxidation state of palladium as +1 in the extracted species (Fig. 6).

An attempt was made to ascertain the nature of the complex spectroscopically. As mentioned earlier, complexation is between Pd in +1 oxidation state and Cyanex 923. Cyanex 923 is available in a pure form from "Cytec Industries", Canada and is composed of four trialkyl phosphine oxides.

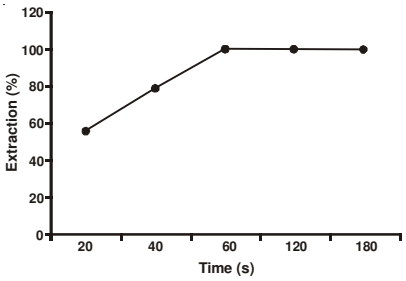

Fig. 5. Extraction behaviour of Pd(II) into Cyanex 923 as a function of shaking time

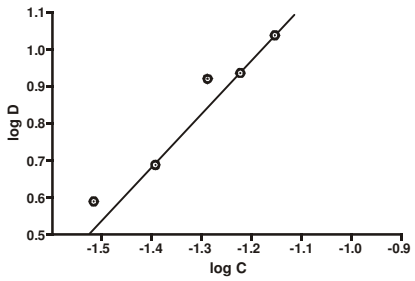

Fig. 6. Distribution ratio of Pd(II) as a function of Cyanex 923 concentration at 0.05 M $SnCl_2$ and 1 M HCl molarity

[$R_3{}^1P{=}O$ (8 %), $R_3P{=}O$ (14 %), $R_2{}^1RP{=}O$ (31 %) and $R_2R^1P{=}O$ (42 %), where R = hexyl and R^1 = octyl].

The complex absorbs in the UV region at 290 nm. An IR spectrum of the complex was taken. However, due to the complexity of the reagent itself, it was not possible to derive any conclusion out of it.

A ^1H NMR and ^{31}P NMR study was also undertaken. The ^{31}P NMR spectra of Cyanex 923 alone showed a mixture of peaks at 47.9 ppm which can be attributed to the 4 types of 'P' which are very similar in chemical environment around the phosphorus group of the phosphines.

A similar ^{31}P NMR spectrum of the complex showed a separation of the mixture into basically 3 peaks due to the paramagnetic shift seen in Pd complex. One of these peaks may actually contain 2 compounds of Cyanex 923 which probably is the peak around 54 ppm from the integral values. Apart from these 3 peaks, the other small peaks are multiplets of phosphorus coupling to either the metal or protons. Thus it is possible to confirm the involvement of 'P' in the complex formation.

A ^1H NMR of the reagent was extremely complex due to the various groups present and also due to 'H-P' coupling. The ^1H NMR of the complex however does not show a major change in the NMR signal.

Thus, in conclusion from spectral data one can although confirm the formation of the complex between Pd and Cyanex 923. it was not possible to know as to which out of the 4 phosphine oxides was actually involved in the complexation.

Effect of foreign ions: The extraction of palladium(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. The results are shown in Table-3. It reveals that a large number of cations and anions are tolerated. However ions such as, Rh(III), Zr(II), Th(II), V(V), Cu(II), Pb(II) and Cd(II) interfere in the extraction of palladium and hence must be absent during the extraction.

TABLE-3
EFFECT OF THE INTEREFERENCE BY FOREIGN IONS ON THE EXTRACTION OF 100 µg OF PALLADIUM(II)*

Tolerance limit (µg)	Foreign ions
100	Co(II), Sr(II), Ce(IV), Nitrate, Phosphate and EDTA
50	Mn(II), Mg(II), Ni(II), Zn(II), Al(II), Ca(II), Fe(III), Cr(IV) and Bromide.
Ions not tolerated	Cu(II), Pb(II), Cd(II), Rh(III), Zr(IV), Th(IV) and V(V)

*Spectrophotometric estimation.

Binary separations of palladium(II) from manganese(II), nickel(II), cobalt(II) and iron(II): Ions such as manganese(II), cobalt(II), nickel(II) and iron(III) are not extracted into Cyanex 923 under optimum conditions for palladium(II). Hence, it is possible to separate them from their binary mixtures. The unextracted manganese(II), cobalt(II), nickel(II) and iron(III) were determined spectrophotometrically[20]. The results of these binary mixtures are given in Table-4.

TABLE-4
BINARY SEPARATIONS OF PALLADIUM

Composition (µg)	Recovery of Pd(II)* (%)	Coefficient of variation (%)	Recovery of the added ion* (%)	Coefficient of variation (%)	Estimated procedure for the added ion and its reference
Pd(II):Mn(II) 50:50	99.99	0.52	97.29	0.40	Spectrophotometrically with periodate[20]
Pd(II):Co(II) 50:50	99.99	0.58	98.21	0.15	Spectrophotometrically with nitroso-R-salt[20]
Pd(II):Ni(II) 50:50	99.99	0.65	95.97	0.45	Spectrophotometrically with DMG[20]
Pd(II):Fe(III) 50:50	99.99	0.62	96.52	0.49	Spectrophotometrically with salicylate method[20]

*Mean of five determinations.

Conclusion

(1) The method is simple and rapid. (2) The method has good precision which is indicated by the low value of RSD. (3) The method had been successfully applied for the separation and determination of palladium(II) in its binary mixtures with Mn(II), Co(II), Ni(II) and Fe(III). (4) The spectroscopic study of the complex with respect to the reagent confirms the formation of the complex.

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