Extractive Spectrophotometric Determination of Palladium(II) Using Mixed Ligand Complex Formation with Pyridine/α-Picoline/β-Picoline/γ-Picoline/2, 4, 6-Collidine & Iodide

T K THOKDAR, A SARKAR, P K PARIA* & S K MAJUM-
DAR

Department of Chemistry, North Bengal University, Darjeeling
734 430

Palladium(II) forms complexes with pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine in presence of potassium iodide. These are extractable into chloroform and absorb at 354-360 nm. The molar absorptivities of the complexes are in the range 1.6-1.9×10^4 $1 \, mol^{-1} cm^{-1}$. The formation of these complexes has been utilized to propose an extractive spectrophotometric method of determination of palladium. The notable metal interference is due to mercury. Use of other common organic solvents provides no special advantages.

There are reports on extraction of iodide complexes of platinum metals with tributylphosphate in hexane as the coordinating solvent, and using this method the platinum metals have been separated from each other[1,2]. It has been noted that palladium(II) iodide forms complexes with pyridine or its methyl substituted derivatives in aqueous solution. These mixed ligand complexes are extractable into chloroform. These systems have been studied now to develop a simple spectrophotometric method for the determination of palladium. Apart from pyridine, other bases used are α-picoline, β-picoline, γ-picoline and 2, 6-collidine.

Absorbance measurements were made with a Shimadzu PR1 model spectrophotometer with stoppered quartz cells of 10 mm optical path length. An ECL 5651 digital pH meter was used to measure the acidities of the aqueous solutions.

Palladium(II) chloride (Johnson & Matthey) (1g) was dissolved in 1 ml hot conc. HCl and diluted to 250 ml with distilled water followed by standardisation by dimethylglyoxime[3]. A working solution (41.75 ppm Pd) was prepared by dilution.

Chloroform (E. Merck), pyridine (BDH), α-picoline (Reidel), β-picoline (BDH), γ-picoline (Fluka) and 2, 4, 6-collidine (BDH) were distilled before use. Potassium iodide (BDH) and all the other reagents used were of analytical reagent grade. Stock solutions of desired diverse ions were prepared from their nitrates, chlorides or sulphates by dissolving pure samples in dilute acid or pure water. Sodium/ammonium salts were used in the case of anions. The metal contents were determined by standard methods[3].

General procedure

To an aliquot containing 10-100 µg of palladium was added 1 ml of 0.015 M aqueous potassium iodide and 0.02 ml of pyridine/α-picoline/β-picoline/γ-picoline/2, 4, 6-collidine followed by addition of adequate amount of distilled water to make up the volume upto 10 ml. The mixture thus obtained was equilibrated with 10 ml of chloroform for 30 sec. The two layers were allowed to settle for 1 min. The separated organic layer was shaken with anhydrous sodium sulphate to remove any retained water droplets. pH of the aqueous solution, after extraction, was measured. Finally the absorbance of the chloroform extract was measured at the λ_{max} of the complex against a reagent blank. Amount of palladium(II) was determined from a previously prepared calibration curve.

The absorption spectra of palladium(II) complexes in chloroform, extracted as above, exhibit maxima as indicated in Table 1. The reagent blanks show insignificant absorbances from 300 nm onwards. Beer's law is obeyed at the respective absorption maxima. All the absorption measurements were carried out against respective reagent blanks. The systems are stable for at least 48 hr.

The liquid-liquid extraction behaviour of Pd(II)-complexes was investigated in the pH range 0-14.0. After extraction, pH of the aqueous solution was measured in each case. In presence of pyridine bases, quantitative extraction of palladium(II) was found to be achieved in the pH range 3.5-10.0. From the graph $pH_{1/2}$ values were evaluated to be 1.6 & 10.7.

The optimum reagent concentrations were found to be 1 ml of 0.015 M KI and 0.02 ml of pyridine/α-picoline/β-picoline/γ-picoline/2, 4, 6-collidine for quantitative extraction of 41.75 µg of palladium. Higher concentrations of the reagents (upto 4 ml of 0.015 M KI and 0.1 ml of pyridine bases) had no adverse effects on the extraction behaviour.

Apart from chloroform, other common organic solvents such as carbon tetrachloride, benzene and ethyl acetate were tested as extracting solvents. The molar absorptivities of the palladium(II) complexes (on the basis of Pd content) at the respective absorption maxima in various solvents are shown in Table 1. It has been found that use of other organic solvents of-

Table 1—Details of Extractive Methods

Parameter	Base employed				
	Pyridine	α-Picoline	β-Picoline	γ-Picoline	2,4,6-Collidine
λ_{max}(nm)	359[a]	355[a]	356[a]	356[a]	354[a]
	366[b]	360[b]	365[b]	363[b]	360[b]
	365[c]	360[c]	362[c]	361[c]	360[c]
	355[d]	355[d]	356[d]	356[d]	359[d]
Molar absorptivity* ($mol^{-1}cm^{-1}$)	1.68×10^{4a}	1.79×10^{4a}	1.70×10^{4a}	1.75×10^{4a}	1.98×10^{4a}
	1.63×10^{4b}	1.94×10^{4b}	1.78×10^{4b}	1.88×10^{4b}	1.78×10^{4b}
	1.78×10^{4c}	2.19×10^{4c}	1.73×10^{4c}	1.98×10^{4c}	1.83×10^{4c}
	1.78×10^{4d}	2.04×10^{4d}	2.08×10^{4d}	1.88×10^{4d}	1.83×10^{4d}

Extracting solvents: a-chloroform, b-carbon tetrachloride, c-benzene & d-ethyl acetate.
* Measured at corresponding absorption maxima

fers no special advantages. Chloroform was used as the extracting solvent in the present investigation.

Different amounts of palladium were extracted by the general procedure and the absorbance of the chloroform extracts was measured at the respective absorption maxima. In all the cases Beer's law was found to be valid over the concentration range 1-10 µg Pd/ml.

Effect of diverse ions—In order to study the effect of diverse ions on the extraction behaviour, a definite amount of palladium(II) was extracted and determined according to the general procedure in presence of the respective foreign ions. All the bases i.e., pyridine, α-picoline, β-picoline, γ-picoline and 2, 4, 6-collidine showed similar behaviour towards the extraction of palladium. In each case an average of three determinations was taken. An ion was considered to interfere if the recovery of Pd(II) differed by more than ± 3% from the actual amount taken.

It was found that 41.75 µg of palladium could easily be determined without any interference in presence of the following cations and anions, the amounts (mg) taken being mentioned in parentheses: Co(II) (5.1), Ni(II) (5.3), Cd(II) (4.9), Zn(II) (6.7), V(V) (5.2), Rh(III) (2.4), Zr(IV) (1.2), U(VI) (5.1), Mn(II) (3.9), Cr(III) (4.8), La(III) (4.2), Al(III) (3.9), Th(IV) (4.1), Be(II)(6.9), Pb(II)(1.3) and Bi(III)(1.1). Iron(III)(1.2) and Cu(II) (0.2) were kept in the aqueous phase by masking them with ammonium hydrogen fluoride

Table 2—Reproducibility of the Method Using 2,4,6-Collidine

Palladium taken (µg)	Palladium found (µg)	Relative mean deviation (%)
10.44	10.5	3.8
20.88	20.7	1.7
41.75	41.9	1.2
62.62	62.1	0.77
83.50	83.3	0.91

and citrate respectively. All attempts to remove the interference due to Hg(II) failed. Pt(IV) interfered in all cases except in the 2, 4, 6-collidine system where the interference was avoided by extracting Pd at pH 10.0. Among the anions tested the following (10 mg each) did not interfere: EDTA, borate, phosphate, tartrate, citrate, fluoride, bromide, ascorbate, phthalate. However, thiocyanate and thiosulphate, even in trace amounts interfered seriously.

Among the based used, 2, 4, 6-collidine is found to be most sensitive. With this reagent the precision and accuracy of the method were tested (Table 2) by analysing solutions containing a known amount of Pd following the recommended procedure. Average of six determinations was taken in each case.

References
1 Faye G H & Inman W R, *Analyt Chem*, **35** (1963) 985.
2 Berg E W & Lau E Y, *Analyt chim Acta*, **27** (1962) 248.
3 Vogel A I, *A textbook of quantitative inorganic analysis* (ELBS, London), 1962.