Spectrophotometric Determination of Palladium after Solid-liquid Extraction with 4-(2-Pyridylazo)-resorcinol at 90°C

Yanjie Dong[*] and Ke Gai

Department of Chemistry, Longdong University, Qingyang City, Gansu, 745000, China. [*]E-mail: huaxx@ldxy.com.cn
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An effective spectrophotometric determination of palladium with 4-(2-pyridylazo)-resorcinol (PAR) using molten naphthalene as a diluent has been studied. A red complex of palladium with PAR is formed at 90 °C. In the range of pH 9.0-11.0, the complex is quantitatively extracted into molten naphthalene. The organic phase is anhydrously dissolved in $CHCl_3$ to be determined spectrophotometrically at 520 nm against the reagent blank. Beer's law is obeyed over the concentration range of 0.1-2 $\mu g \cdot mL^{-1}$. The molar absorptivity and Sandell's sensitivity are 8.0×10^5 $L \cdot mol^{-1} \cdot cm^{-1}$ and 0.49 $\mu g \cdot cm^{-2}$ respectively. From the results of tolerance limits, it was found that there was no interferences were observed for most of the ions examined and those somewhat high interferences by Co(II), Fe(II) and Bi(III) could be effectively masked by EDTA.

Key Words : Molten naphthalene, Palladium, Solid-liquid extraction, Spectrophotometric

Introduction

Extraction is a very useful separating method.[1,2] Solvent extraction of precious metals is widely employed in chemistry and industry for many years.[3] Normally, it is difficult for metals such as palladium, platinum, rhodium, etc. to form complex with extratent at the room temperature, while at a high temperature the water-insoluble complex can form easily and rapidly. In 1969, Fujinaga *et al.* developed a method involving the extraction of the complex at high temperature followed by the solid-liquid separation at room temperature. In recent years, Jin-zhang Gao did much work on the solid-liquid extraction.[3-6] In this technique, organic substances, which are solid at room temperature such as naphthalene and paraffin waxes, are used as diluents. The water-insoluble complex is extracted into the molten diluents at the high temperature to achieve distribution equilibrium. The phase separation is obtained by cooling the extraction system to room temperature. This technique is also applied for the concentration and separation of precious metals. Solid-liquid extraction spectrophotometric determination of palladium, platinum, rhodium, osmium and ruthenium are reported.[3] The organic extractants used are mainly focused on 8-hydroxyquinolines, oximes and dioximes, cuprals and xanthates.

For the solid-liquid extraction spectrophotometric analysis of platinum group metals, there are some shortages. The sensitivities of some system are low and molar absorptivities are usually at around 10^3 level, others have a relatively high sensitivities, but are not suitable to be extracted and detected for a wider acidity.[3]

As a highly sensitive and selective indicator of polydentate organic reagents, PAR forms intensively colored and water-insoluble complexes with many metals which can be extracted into an organic solvent. However, there is no application of PAR for solid-liquid extraction of platinum group metals at a high temperature. The liquid-liquid extraction of palladium with PAR into $CHCl_3$ has been reported,[7] but it has a narrow pH range for the determination and is time consuming.

In this paper, PAR is first used for the solid-liquid extraction of palladium into molten naphthalene. High sensitivity of detection and a wider pH range of extraction are obtained. Time consumption is decreased and procedures are more convenient.

Experimental Section

Apparatus. A model 7530 ultra-visible spectrophotometer (Shanghai, China). A Model pHS-10A digital acidity ion meter (Xiaoshan, China) and Model CS501 super thermostatic water bath (Shanghai, China) were used in this study.

Reagents.

A standard platinum solution: A standard palladium solution was prepared by dissolving 0.08866 g of palladium chloride in 10 mL of concentrated hydrochloric acid and diluting to 500 mL with water. The content of palladium was also standardized gravimetrically by the method reported elsewhere.[5] The solution contains 106.4 $\mu g \cdot mL^{-1}$ of palladium. Solutions of lower concentration required were prepared by diluting standard solution.

4-(2-Pyridylazo)-resorcinol solution (PAR): A 1.0×10^{-3} $mo \cdot L^{-1}$ solution in acetone is prepared by dissolving 0.02152 g PAR in 100 mL pure acetone and stored in an amber bottle.

Buffer solution: 0.1 M of solution ammonium chloride-ammonia is used for the experiment.

Naphthalene (m.p. 80-82 °C): The purity of naphthalene is checked spectrophotometrically before use in the range 300-700 nm.

Solid-liquid extraction device: All solid-liquid extraction experiments were carried out with the device below (see Fig. 1).

General procedure. All solid-liquid extraction were

A: Water jacket
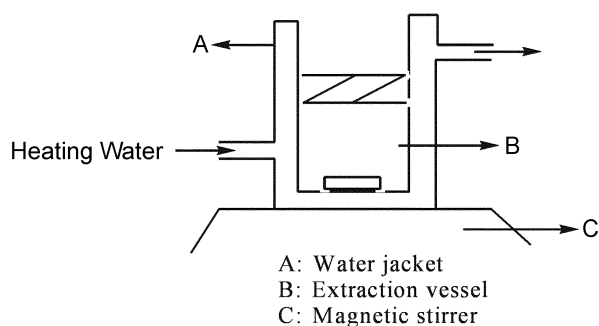B: Extraction vessel
C: Magnetic stirrer

Figure 1. Solid-liquid extraction device.

carried out at 90 ± 0.1 °C as follows: A certain amount of standard palladium solution was pipetted into a 250 mL Erlenmeyer flask. 50 mL of NH_4Cl-NH_3 buffer solution and 1.0 mL of 1.0×10^{-3} $mo \cdot L^{-1}$ PAR-acetone solution were added sequentially. The total volume of the aqueous phase was diluted to 20 mL with water bath of 90 ± 0.1 °C for 4 min after addition of 1.0 g of naphthalene and continued to be warmed until naphthalene melted completely. The flask was shaken vigorously for 30 s, cooled to room temperature until naphthalene coagulated completely. The solid phase was collected, dried at 50 °C, dissolved in 10 mL chloroform. Palladium was determined by spectrophotometry at 520 nm against a reagent blank.

Results and Discussion

Absorption spectra. The absorption spectra of the palladium complex in naphthalene-chloroform are measured against a reagent blank, that of the reagent treated in a similar manner against a chloroform-naphthalene blank (Fig. 2). The palladium complex has one absorbance peaks at 520 nm. The absorbance of the reagent is negligible. The intensity of the peak at 520 nm is most. Therefore, the following determinations performed at 520 nm.

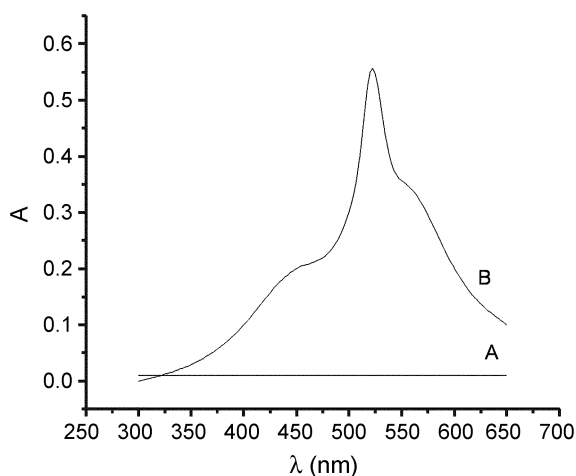**Effect of pH value.** The effect of pH value in aqueous

Figure 2. Absorption spectra of PAR-Pd(II) complex and PAR in naphthalene-chloroform solution. (A) reagent against naphthalene-chloroform; (B) PAR-Pd(II) complex against reagent.
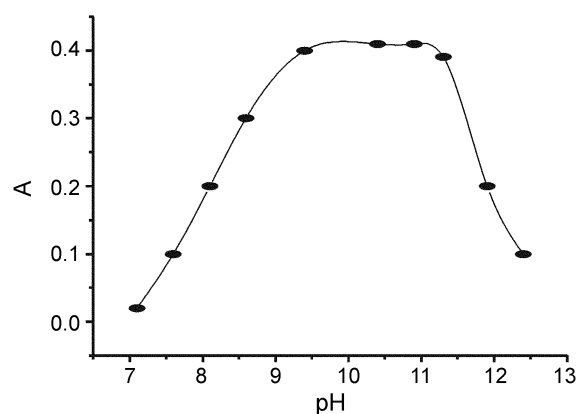

Figure 3. Effect of pH on the extraction Pd(II): 21.28 μg. PAR (1.0 $\times 10^{-3}$ $mo \cdot L^{-1}$): 0.5 mL. V_{aq}: 20 mL. naphthalene: 1.0 g (1.3 mL). I = 0.1 $mo \cdot L^{-1}$ $NaClO_4$.

phase on the absorbance is examined and showed in Figure 3. In the pH value range from 9.0-11.0, quantitative extraction of palladium occurs and the absorbance is found to be constant. Although PAR in the aqueous solution displays different colors at different acidity, no interference is found for the measurement. An NH_4Cl-NH_3 buffer of pH 10.40 is employed for the following experiments.

Effect of volume of the aqueous phase and naphthalene. When the volume of the aqueous phase is varied from 10-150 mL, the absorbance remains constant from 10 mL to 45 mL. Above this volume, it begins to decrease due to excessive ratio of two phases and in completed extraction of palladium occurs. Thus, in the following experiments a volume of 20 mL was maintained. It was found that the absorbance has a slight increase when the amount of naphthalene was varied from 0.2-2.0 g. Excessive naphthalene was detrimental to the determination of palladium because of its low solubility in chloroform and volatilization. An optimum of 1.0 g of naphthalene is employed for this work.

Effect of heating, shaking and standing times. The extraction system is heated about 4-5 min at the temperature of the experiment. After naphthalene is completely molten, 30 s of vigorous shaking can achieve extraction equilibrium. The absorbance of the palladium complex in naphthalene-chloroform solution is constant for more than 24 h.

Mechanism of extraction. As PAR is a weak organic acid, its dissociation degree increases with decreasing acidity in the aqueous phase. At the given acidity, the metal ion Pd(II) reacts with PAR (H_2L) in the presence of anion A^-, giving an uncharged chelate which is distributed between two phase according to the equation:

$$Pd^{2+} + nH_2L_{(O)} + 2nA^- \rightleftharpoons PdL_nA_{2n(O)} + 2nH^+ \qquad (1)$$
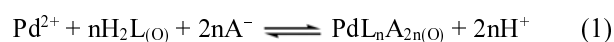
The equilibrium constant of the above reaction is defined as:

$$K_{ex} = [PdL_nA_{2n}][H^+]^{2n} / [Pd^{2+}][H_2L]^n[A^-]^{2n} \qquad (2)$$

Assuming that the species of Pd(II) in the aqueous phase and PdL_nA_{2n} in the organic phase mainly exist respectively, there
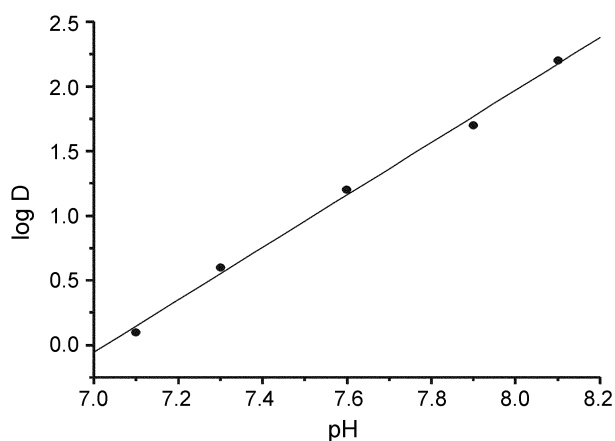
Figure 4. Relationship between log D and pH value: conditions shown are the same as in Figure 2.

is:

$$K_{ex} = D[H^+]^{2n} / [H_2L]^n[A^-]^{2n} \qquad (3)$$

where D is the distribution ratio of the palladium between two phases as defined by Eq. (4).

$$D = [\,PdL_nA_{2n}\,] / [\,Pd^{2+}\,] \qquad (4)$$

Expressing Eq. (3) in the equivalent logarithmic form, there is called:

$$logD = logK_{ex} + 2npH + nlog[H_2L]_{(O)} + 2nlog[A^-] \qquad (5)$$

Under the conditions of experiments, the relationship between the distribution ratio D and absorbance A is expressed as:

$$D = [A_i / (A_{max} - A_i)](V_{aq} / V_o) \qquad (6)$$

Eq. (6) may be simplified into the form:

$$D = [A_i / (A_{max} - A_i)] \times r$$
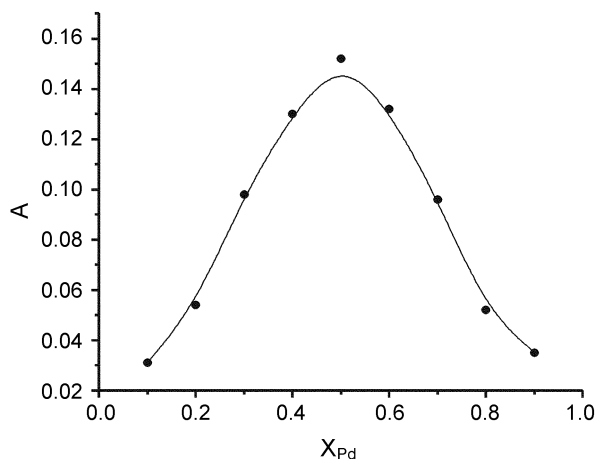
where A_{max} denotes the mean maximum absorbance of

Figure 5. Plot of composition of extracted species by Job's continuous variation method. Pd(II): 1.0×10^{-4} mo·L^{-1}, PAR: 1.0×10^{-4} mo·L^{-1}. pH: 10.40. total content Pd(II) and PAR: 0.4×10^{-6} mol. V_{aq}: 20 mL. Naphthalene: 1.0 g (1.3 mL). I = 0.1 mo·L^{-1} NaClO$_4$.

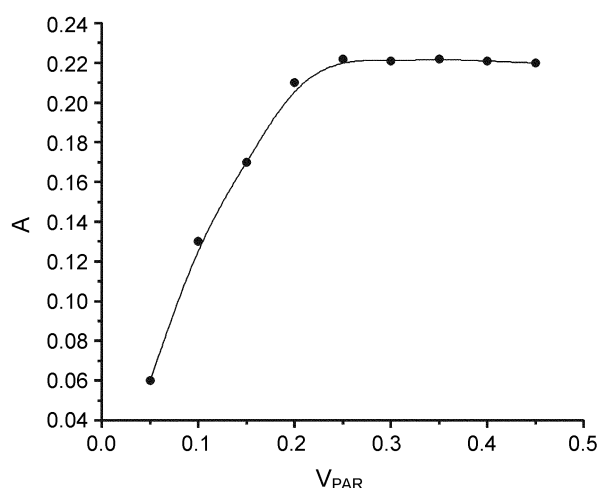**Figure 6**. Plot of composition of the extracted species by Molar ratio method. Pd(II): 21.28 μg, PAR: 1.0×10^{-4} mo·L^{-1}. pH: 10.40. V_{aq}: 20 mL. Naphthalene: 1.0 g (1.3 mL). I = 0.1 mo·L^{-1} NaClO$_4$.
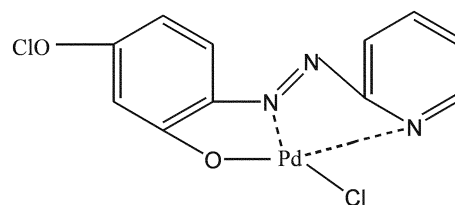

Figure 7. A suggested structure of palladium complex.

determination, A_i denotes the absorbance of single determination; r denotes the ratio of phase.

logD at different pH values keeping $[H_2L]_{(o)}$ and $[A^-]$ constant are obtained. The plot logD versus pH (Fig. 4) gives a straight line with a slop of 2. *i.e.*, n = 1. Two protons are released in the extraction reaction.

The composition of the extraction species is studied by means of Job's method (Fig. 5) and the Molar Ratio method (Fig. 6). The results show that the molar ratio of Pd(II) to PAR in the extracted species is 1 : 1. The palladium and PAR in the extracted species is demonstrated to be [Pd(PAR)Cl]Cl in the presence of large amount of Cl$^-$. Figure 7 shows a possible structure. Therefore, the extraction reaction can be rewritten as follow:

$$PAR_{(O)} + Pd^{2+} + 2Cl^- \xrightarrow{436K} [Pd(PAR)Cl]Cl_{(O)} + 2H^+$$
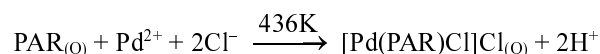
Beer's law and sensitivity. Under the optimum conditions described above. Beer's law is obeyed over the concentration range from 0.1-2 ppm. The molar absorptivity and Sandell's sensitivity are 8.0×10^5 L·mol^{-1}·cm^{-1} and 0.00049 μg·cm^{-2}, respectively.

Effect of coexisting ions. Tolerance limits of various cations and anions were investigated on the extraction of palladium. In the experiment, a certain amount of standard palladium solution, coexisting ion solution and masking agent (or absence of masking agent) were added. The results are listed in Table 1. It is found that large amount of NO$_3^-$,

Table 2. Determination of Pd(II) in synthetic mixtures

Samples	Composition of mixture (μg)	Pd(II) found by present method (μg)	Average (μg)	RSD
1	Pd(II)(21.3), Pt(IV)(19.5), Au(III)(20)	21.3, 21.4, 21.4, 21.2, 21.3	21.32	0.084
2	Pd(II)(21.3), Pt(IV)(19.5), Rh(III)(20)	21.4, 21.3, 21.4, 21.2, 21.2	21.30	0.100
3	Pd(II)(21.3), Pt(IV)(19.5), Ir(III)(20)	21.2, 21.3, 21.4, 21.4, 21.3	21.32	0.062

Table 1. Effect of coexisting ions (Added amount of Pd(II): 21.28 μg)

Coexisting ions	Addition (mg)	Amount of Pd(II) found (μg)	Recovery without masking agent (%)	Recovery of with masking agent (%)
NO_3^-	25.0	21.28	100.0	
Cl^-	25.0	21.28	100.0	
CO_3^{2-}	25.0	21.28	100.0	
SO_4^{2-}	23.0	21.40	100.5	
$C_2O_4^{2-}$	22.0	21.28	100.0	
I^-	25.0	21.50	102.6	
SCN^-	25.0	21.50	102.6	
EDTA-Na$_2$	1.0	21.40	100.5	
Pt(IV)	1.0	21.28	100.0	100.1
Rh(III)	1.0	21.40	100.5	100.2
Au(III)	0.5	21.40	100.5	100.0
Ag(I)	1.0	21.40	100.5	100.0
Ir(III)	1.0	21.40	100.5	
Al(III)	1.0	21.28	100.0	
Ga(III)	1.0	21.28	100.0	
In(III)	1.0	21.28	100.0	
Tl(III)	1.0	21.30	100.1	
Ba(II)	1.0	21.30	100.1	
Zn(II)	1.0	21.30	100.1	
Cd(II)	1.0	21.30	100.1	
As(III)	1.0	21.30	100.1	
Mo(V)	1.0	21.30	100.1	
V(V)	1.0	21.30	100.1	
Mn(II)	1.0	21.30	100.1	
Ni(II)	1.0	21.30	100.1	
Cr(III)	1.0	21.30	100.1	
Sn(II)	0.1	21.28	100.0	
Ti(IV)	0.1	21.28	100.0	
La(III)	0.1	21.28	100.0	
Fe(III)	0.1	21.28	100.0	
Cu(II)	0.1	21.28	100.0	
Hg(II)	0.1	21.28	100.0	
Ru(III)	0.1	21.28	100.0	
Bi(III)	0.1	23.40	110.0	99.8
Fe(II)	0.1	22.50	105.7	100.1
Co(II)	0.1	22.60	100.5	100.2

Cl^-, CO_3^{2-}, SO_4^{2-}, $C_2O_4^{2-}$ do not interfere in the determination. I^-, SCN^- has positive effects on the absorbance. This implies that sensitivity can be improved by choosing I^-

or SCN^- in a suitable system. But the reducibility I^- and chelation of SCN^- also produce disadvantageous at the same time.

Comparing in the presence/absence of masking agents EDTA tested cations. It is found that Pt(IV), Rh(III), Au(III), Ag(I), do not interfere. Co(II), Fe(II), Bi(III) interfere seriously. However, their interferences are masked efficiently by addition of 1.0 mL of 0.1 mo·L^{-1} EDTA.

Applications. The propose method was applied to the determination of palladium in synthetic mixtures. A synthetic mixture was analyzed by the procedure described above and the results displayed in Table 2.

Conclusions

An effective spectrophotometric determination of palladium with 4-(2-pyridylazo)-resorcinol (PAR) using molten naphthalene as a diluent has been established. The composing of complex of palladium with PAR demonstrated to be [Pd(PAR)Cl]Cl in the presence of large amount of Cl$^-$. The extraction reaction can be rewritten as follows:
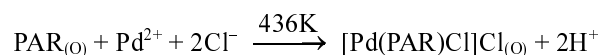
$$PAR_{(O)} + Pd^{2+} + 2Cl^- \xrightarrow{436K} [Pd(PAR)Cl]Cl_{(O)} + 2H^+$$

Beer's law is obeyed over the concentration range of 0.1-2 μg·mL^{-1}. The molar absorptivity and Sandell's sensitivity are 8.0×10^5 L·mol^{-1}·cm^{-1} and 0.49 μg·cm^{-2} respectively.

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