Asian Journal of Chemistry Vol. 9, No. 2 (1997), 218–223

Extraction Spectrophotometric Determination of Micro Amounts of Palladium(II) with 2,4-Dihydroxy Acetophenonethiosemicarbazone

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2,4-Dihydroxy acetophenonethiosemicarbazone is used as a chromophoric reagent for the extraction and spectrophotometric determination of palladium(II). Palladium(II) forms 1 : 1 and 1 : 2 complexes with the reagent in acetic acid-sodium acetate buffer of pH 3.5. The 1 : 1 and 1 : 2 complexes have λ_{max} at 375 nm and 390 nm respectively. Palladium(II) is qualitatively extracted from aqueous phase using 4-fold molar excess of reagent and the complex is stable for 48 h. Beer's law is obeyed in the range of 0.7 to 12.0 ppm and molar absorptivity of the complex is 1.3×10^4 lit mol^{-1} cm^{-1}. The effect of various foreign ions is also studied. The method is applied for the estimation of micro amounts of palladium(II) in synthetic mixtures having typical palladium-alloy composition.

INTRODUCTION

Various thiosemicarbazones have been reported in literature for the spectrophotometric determination of palladium(II). But, only a few of these[1–5] have been used in the extractive spectrophotometric determination of palladium(II). 2,4-Dihydroxy acetophenonethiosemicarbazone (DAPT) has been prepared and used as a photometric reagent for the determination of copper and cobalt[6]. This reagent has also been used for the spectrophotometric determination of nickel[7]. Later, DAPT has been used for the sequential extractive spectrophotometric determination of copper and nickel[8] and extractive radiometric determination of cobalt[9] and silver[10, 11]. In the present work, the use of DAPT as an extractant is exploited for the spectrophotometric determination of palladium(II).

EXPERIMENTAL

Absorbance measurements are made on recording spectrophotometer (model Shimadzu UV-240), supplied by Shimadzu Corporation, Japan. A digital pH meter model LI-120 (ELICO) is used for measuring the pH of solutions.

2,4-Dihydroxy acetophenonethiosemicarbazone is prepared by the method reported earlier[6]. Required concentrations of DAPT solutions are prepared using n-butanol as solvent. Stock solution of palladium(II) chloride is prepared by dissolving analytical grade sample in 2N hydrochloric acid and the concentration is determined by using standard method[12]. Further dilutions are made by using double distilled water. The buffer solutions of different pHs from 2.0 to 7.0 are prepared by mixing 1 M hydrochloric acid and 1 M sodium acetate solutions and 1M acetic acid and 1 M sodium acetate solutions. All other chemicals are of AR

grade. Double distilled water is used for the preparation of 1 mg/mL solutions of various interfering radicals.

An aliquot containing 30–300 μg of Pd(II) is transferred to a separating funnel and 10.0 mL of acetic acid-sodium acetate buffer (pH 3.5) is added to the same. The solution is diluted to 20 mL and then extracted with 20.0 mL portion of reagent solution for 1 min. The n-butanol extract is collected and dried with anhydrous sodium sulphate. The extract is then decanted in to 25 mL standard flask and then diluted to the mark with n-butanol washings of the drying agent. The absorbance is measured at 390 nm against a reagent blank

RESULTS AND DISCUSSION

Palladium(II) reacts with DAPT and forms soluble yellow complex in the pH range 2.5–7.0. The complex is extractable into n-butanol. It has maximum absorption at 390 nm and is stable for 48 h. The conditions for effective extraction are established by studying the effects of various factors such as pH, solvent and reagent concentration in order to develop a sensitive and rapid extractive spectrophotometric method for the determination of palladium(II) in microgram level.

Effect of pH: Palladium(II) gives yellow colour in 0.01 to 1 N hydrochloric acid solutions but the colour disappears immediately. Extraction commences from pH 2.5 and the colour of the organic phase remains stable. The absorbance of the organic phase is maximum and remains constant in the pH range 3.0–5.5. Further increase in pH decreases the percent of the metal extracted into the organic phase. Hence, further studies are carried out at pH 4.0.

Choice of Solvent: Among the various solvents used for the extraction of Pd-DAPT complex, only n-butanol and ethyl acetate are found to be better solvents. Butyl acetate extracts only to a negligible extent. Other solvents such as chloroform, carbon tetrachloride, benzene, substituted benzenes etc., do not extract the complex at all.

Effect of Reagent Concentration: While studying the effect of the reagent concentration, it has been found that λ_{max} has shifted from 375 to 390 nm. Quantitative recovery of palladium(II) is possible with only fourfold molar excess of reagent to that of metal concentration. It is proved that Pd(II) forms 1 : 1 complex in lower concentrations of reagent and forms 1 : 2 complex in higher concentrations of reagent. The above compositions of the complex have been arrived at by Vosburgh and Cooper method[13].

Absorption Spectra: The absorption spectra of DAPT and two palladium(II)-DAPT complexes (1 : 1 and 1 : 2) extracted into n-butanol are shown in Fig. 1. The 1 : 1 and 1 : 2 complexes have λ_{max} at 375 and 390 nm respectively. The system adheres to Beer's law over a wide range of palladium(II) concentration (0.7 to 12.0 ppm). The molar absorptivity of the 1 : 2 complex is 1.36×10^4 lit mol^{-1} cm^{-1}.

Composition of the Complex: Job's method of continuous variation is not applied for the determination of the composition of the complex due to the formation of different complexes. Hence slope analysis method is applied to determine the composition of the complex. In view of the shift in the absorption maximum, palladium(II) remaining in the aqueous phase after extraction is

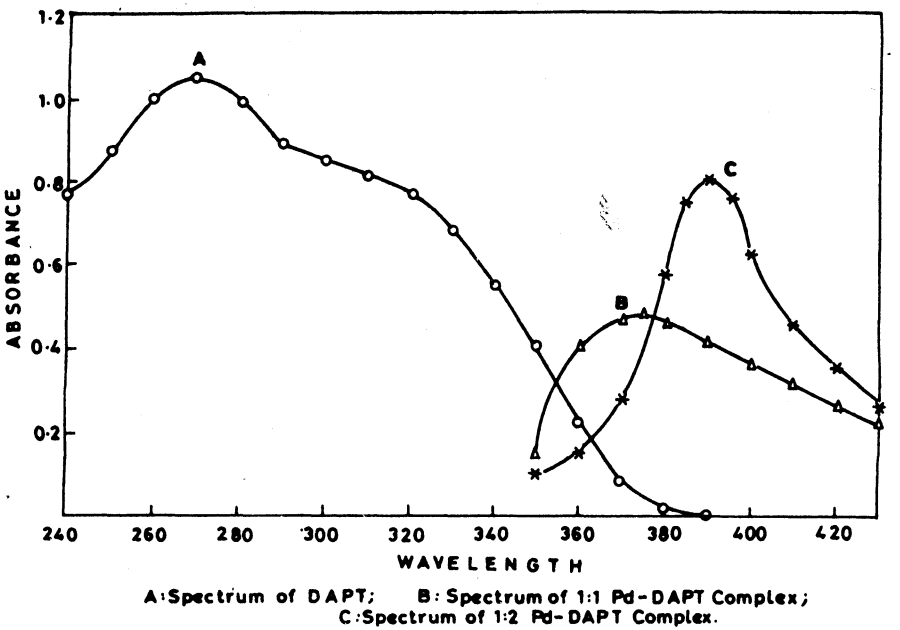

Fig. 1. Absorption spectra of DAPT, 1 : 1 Pd-DAPT and 1 : 2 Pd-DAPT complexes

determined by the standard iodide method[14]. Thus the amounts of metal extracted into the organic phase and thereby 'D' values are calculated. It is proved that palladium(II) is forming complex in 1 : 1 ratio at lower concentrations and in 1 : 2 ratio at higher concentrations of DAPT.

TABLE-1
EFFECT OF FOREIGN IONS ON THE EXTRACTION OF PALLADIUM(II)

Foreign ion	Added as	Tolerance limit (μg)
Ag(I)	$AgNO_3$	None
Cu(II)	$CuSO_4 \cdot 5H_2O$	None
Fe(III)	$NH_4Fe(SO_4)_2 \cdot 12H_2O$	50
Hg(II)	$Hg(NO_3)_2 \cdot xH_2O$	None
Ni(II)	$(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6H_2O$	200
V(V)	NH_4VO_3	None
Pt(IV)	$PtCl_4$	100
Thiocyanate	NH_4SCN	500
Thiourea	$H_2N \cdot CS \cdot NH_2$	500
Thiosulphate	$Na_2S_2O_3 \cdot 5H_2O$	None
Cyanide	KCN	None

Effect of Foreign Ions: The results in Table-1 show the effect of various metal ions on the extraction of 4 μg/mL of palladium(II). The tolerance limit is set at a change of absorbance of ± 0.02 at 390 nm. Excess of large number of cations such as Al(III), Bi(III), Cd(II), Co(II), Mn(II), Mo(VI), Ti(IV), U(VI),

W(VI), Sn(IV), Au(III), Sb(III) and Zn(II) and anions such as bromide, iodide, oxalate, citrate, tartrate, phosphate, fluoride, ascorbate and EDTA do not interfere in the extraction. Ag(I), Hg(II), V(V), Cu(II), thiosulphate and cyanide ions interfere in the determination seriously. Higher amounts of Ni(II). Fe(III), Pt(IV) thiocyanate and thiourea decrease the absorbance.

Analysis of palladium in synthetic mixtures

As the alloys and minerals are not available for analysis, the synthetic mixtures containing palladium(II) and associated metal ions are prepared and they are analysed for palladium by masking interfering radicals with suitable masking agents. The data is reported in Table-2.

TABLE-2
DETERMINATION OF PALLADIUM(II) IN SYNTHETIC MIXTURES

S.No.	Pd(II) taken (μg)	Amounts of foreign metal ions added	Palladium found* (μg)	Relative error (%)	Standard deviation (%)	Remarks
1.	20.0	Cu(II) (2.0 mg) and Sn(II) (2.0 mg)	19.8	1.0	0.10	EDTA is used to mask Cu(II)
2.	20.0	Ni(II) (2.0 mg) Cu(II) (2.0 mg) and Fe(II) (2.0 mg)	19.9	0.5	0.05	EDTA is used to mask Co(II), Ni(II) and Fe(III)
3.	20.0	Cu(II) (2.0 mg) Sn(II) (2.0 mg) and Sb(III) (2.0 mg)	19.9	0.5	0.05	EDTA is used to mask Cu(II)
4.	20.0	Au(III) (2.0 mg) and Pt(IV) (40.0 μg)	19.8	1.0	0.10	—

*Average of six determinations

Similarly the present method has been applied for the determination of palladium in synthetic mixtures corresponding to jewellery alloy (Pd 95.5% and Ru 4.5%) and the data is reported in Table-3.

TABLE-3
DETERMINATION OF PALLADIUM(II) IN SYNTHETIC MIXTURES CORRESPONDING TO JEWELLERY ALLOY

S. No.	Taken (mg)		Found* (mg)	Relative error (%)	Standard deviation (%)
	Pd	Ru	Pd		
1.	9.55	0.45	9.50	0.52	0.039
2.	7.50	0.36	7.56	0.80	0.041
3.	5.00	0.25	4.91	1.80	0.036

*Average of six determinations

Conclusion

The proposed method is compared with the previous thiosemicarbazones in Table-4. This reagent is found to be more sensitive or comparable to other

TABLE-4
RELATIVE MERITS OF THIOSEMICARBAZONES IN THE EXTRACTION OF PALLADIUM(II)

Name of the thiosemicarbazone	λ_{max} nm	molar absorptivity $\times 10^4$ lit mol^{-1} cm^{-1}	Applicability of Beer's law ppm	pH	Composition of the complex	Solvent	Remarks
1. Quinoline-2-aldehyde thiosemicarbazone	510	0.26	2.5–20.0	1.0–3.0 M HCl	1 : 2	MIBK + DMF	Pb(II), Au(III), Cu(II), Sb(III) and Sn(IV) interfere
2. Phenanthraquinone monothiosemicarbazone	600	0.22	2.5–18.0	1.0–3.0 M CH_3COOH	1 : 2	$CHCl_3$+ DMF	Cd(II), Bi(III), Ir(III), Sn(IV), Th(IV), Se(IV), Te(IV) and Pb(II) interfere
3. 3, 5-Dichloro salicylaldehyde-4-phenyl-1-3-thiosemicarbazone	410	1.43	up to 8.0	1 M HCl (pH = 0.0)	—	$CHCl_3$	Pd is determined in Pd-C powder
4. 2-Hydroxy-1-naphthaldehyde-4-phenyl-3-thiosemicarbazone	412	1.42	up to 8.0	0.05 M H_2SO_4	—	$CHCl_3$	Palladium is determined in palladium brazing filter
5. 5-Bromo salicylaldehyde 4-phenyl-3-thiosemicarbazone	412, 437	1.41	up to 8.0	H_2SO_4 Medium	—	$CHCl_3$	Palladium is determined in palladium brazing filter and palladium catalyst samples
6. 2,4-Dihydroxy acetophenone thiosemicarbazone	390	1.36	0.7–12.5	3.0–5.5	1 : 2	n-butanol	Cations like Ag(I), Cu(III), Hg(II), V(V) and large amounts of Ni(II), Fe(II) and Pt(IV) interfere

reagents. In four of the five other methods, chloroform which is toxic is used as a solvent, whereas in the present method, n-butanol is used as a solvent. Though EDTA is known for masking palladium(II), the careful study has revealed that it is not interfering even in high amounts. Hence, the selectivity of the reagent is improved by masking Fe(II), Cu(II) and Ni(II) with EDTA. As Ni(II) interferes above pH 3.5, Pd(II) can be determined in presence of Ni(II) at pH 3.5.

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(*Received*: 27 July 1996; *Accepted*: 16 November 1996) AJC-1184