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Extractive Spectrophotometric Determination of Palladium(II) Using 2-Hydroxy-1-naphthalenecarboxaldehyde Hydrazine Carboxamide as an Analytical Reagent

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A spectrophotometric method has been developed for the determination of Pd(II) using 2-hydroxy-1-naphthalene carboxaldehyde hydrazine carboxamide as an analytical reagent. The reagent forms an orange-coloured complex with Pd(II), which can be quantitatively extracted into ethyl acetate at pH 4.2 having absorption maxima at 410 nm. Beer's law is obeyed over the range of 0.55 g/mL to 2.50 μg/mL of palladium. The molar absorptivity is 0.4×10^3 L mol^{-1} cm^{-1} and Sandell's sensitivity is 1.50×10^{-5} μg cm^{-2}. The stoichiometric ratio of the complex was found to be 1 : 2. The proposed method has been applied to determine palladium in silver alloy, palladium complexes and palladium catalysts.

Key Words: Spectrophotometric determination, Pd(II), 2-Hydroxy-1-naphthalene carboxaldehyde hydrazine carboxamide.

INTRODUCTION

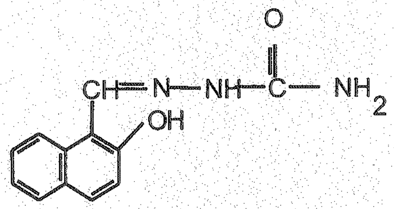
Analytical separation and recovery of palladium are necessary from the variety of matrices. Solvent extraction procedure is an efficient method for its extraction and separation from other metals. Pd(II) forms chelate complexes with many organic reagents which are bonded through N, O and/or sulphur atom. These complexes are widely used for the separation and/or spectrophotometric determination of Pd(II).

The colorimetric reagents known for palladium are numerous[1]. The literature survey revealed the facts that 2-hydroxy-1-naphthalene carboxaldehyde hydrazine carboxamide (HNCHC) have not been used earlier for the determination of palladium. The proposed method has been applied for the spectrophotometric determination of palladium at trace levels for alloy, ore and catalyst samples and synthetic mixtures.

EXPERIMENTAL

A Shimadzu UV-Visible spectrophotometer with 10 mm fused silica cells was used. All chemicals used for the work were of analytical reagent grade. The stock solution of palladium(II) was prepared by dissolving palladium chloride in minimum amount of concentrated HCl, making up to one litre with distilled water and standardized gravimetrically by dimethylglyoximate method[2]. The pH measurements were carried out using buffer solutions. The characterization of the product was carried out using conventional techniques.

2-Hydroxy-1-naphthalene carboxaldehyde hydrazine carboxamide (HNCHC) was prepared by refluxing 2-hydroxy-1-napthaldehyde with semicarbazide hydrochloride using ethanol as a solvent for 60–80 min. The mixture was poured on ice and was recrystalized from methanol and used for further studies. The melting point recorded was 197°C.



2-Hydroxy-1-naphthalene carboxaldehyde hydrazine carboxamide

The extraction was performed by shaking the appropriate organic and aqueous solutions at O/A phase ratio of 1. HNCHC extractant formed a complex with Pd(II) which was transferred to a separating funnel; it was extracted in ethyl acetate and then transferred to a 10 mL volumetric flask containing some amount of sodium sulfate. The amount of Pd(II) in organic phase was calculated by spectrophotometric method at 410 nm.

Procedure for determination of palladium in silver alloy

0.5 gm of alloy was dissolved in 10 mL nitric acid (1 : 1) and the solution was evaporated to dryness. The residue was dissolved in 10–15 mL of distilled water and silver was precipitated as AgBr by adding KBr solution. The precipitate was removed by filtration, washed with dilute nitric acid and finally with water. The filtrate was concentrated to 2–3 mL and diluted to 25 mL with water. An aliquot (1 mL) of this solution was used for the estimation of palladium by the procedure as described above.

Procedure for determination of palladium in catalysts

1. 0.1 g of palladium charcoal was taken in a silica combustion tube and incinerated for 8 h to ash the carbon completely. The sample was treated with 5 mL of formic acid and dried on a hot plate. The resulting compound was dissolved in 6 M HCl and 2 M nitric acid, then diluted to 100 mL with distilled water.
2. 0.1 gm of Pd-calcium carbonate catalyst was taken in a beaker, treated with aqua regia and evaporated to dryness. The residue was leached with water. Hydrochloric acid was added and diluted to 100 mL with distilled water. Aliquots of these samples were analyzed by the proposed method and the results obtained were found to be in good agreement with the theoretical values.

RESULTS AND DISCUSSION

Effect of pH on the extraction of Pd(II): The extraction of palladium with HNCHC was studied over the pH range 1–12. The percentage extraction of Pd(II) with HNCHC increased from 4.0 and maximum extraction was observed at 4.2 pH and further the percentage extraction of the complex decreased.

Absorption spectrum: The absorption spectrum of Pd : HNCHC in ethyl acetate shows an intense absorption peak at 410 nm and the absorbance due to the reagent is negligible at this wavelength. Hence, the absorption measurement were taken at this wavelength using a reagent blank.

Effect of solvent or influence of diluents: The value of percentage extraction of palladium gives the following order of the organic solvent used:

Ethyl acetate > ethyl methyl ketone > diethyl ether > chloroform = toluene
> carbon tetrachloride > hexane = nitrobenzene = *n*-butanol = xylene

Ethyl acetate, being the most satisfactory solvent, has been selected for the subsequent experimental work.

Effect of salting out agents: The presence of 0.1 M salts of alkali and alkaline metals such as Na, K, Mg, Ca and Ba does not show any improvement over the absorbance value of Pd : HNCHC extract. Hence these salts are not added in the aqueous phase before extraction of further studies.

Effect of reagent concentration: The study of change in colour intensity of palladium extract with varying concentration of HNCHC in aqueous phase was studied. The experimental data show that 1 mL of HNCHC (1%) in aqueous solution is sufficient for quantitative extraction of palladium and full colour development due to 25 μg of palladium solution in aqueous phase. Therefore, 1.0 mL of 1% reagent was chosen for the quantitative determination of the metal (Table-1).

TABLE-1
EFFECT OF REAGENT (HNCHC) CONCENTRATION ON THE ABSORBANCE OF Pd(II) IN ETHYL ACETATE

Total amount of iron taken: 25.0 μg; Wavelength: 410; pH: 4.2
Aqueous phase: 10.0 mL containing 1.0 mL HNCHC (0.1%) in methanol.

S.No.	% HNCHC in aqueous phase	Absorbance	S.No.	% HNCHC in aqueous phase	Absorbance
1	0.1	0.073	8	0.8	0.588
2	0.2	0.147	9	0.9	0.590
3	0.3	0.220	10	1.0	0.599
4	0.4	0.294	11	1.2	0.599
5	0.5	0.367	12	1.4	0.599
6	0.6	0.441	13	1.6	0.599
7	0.7	0.514	14	2.0	0.600

Effect of equilibration time: The study of change in absorbance with variation in equilibration time for the extraction of palladium shows that equilibration time of 30 s is sufficient for the quantitative extraction of Pd(II).

Effect of the stability of the complex with time: The study of stability of the extracted colour species with time shows that the absorbance of the extracted species is stable up to 48.0 h. Throughout the experiment, for the reason of practical convenience, the absorbance measurement have been carried out with in 1 h of the extraction of palladium.

Calibration curve: The calibration plot of absorbance against concentration of Pd(II) gives a linear reproducible graph in the concentration range 0.5–2.50 μg/mL of palladium (Fig. 1) indicating that the Beer's law is obeyed in this range. The molar absorptivity and Sandell sensitivity were calculated to be 0.4×10^3 L mol^{-1} cm^{-1} and 1.50×10^{-5} μg cm^{-2} respectively.

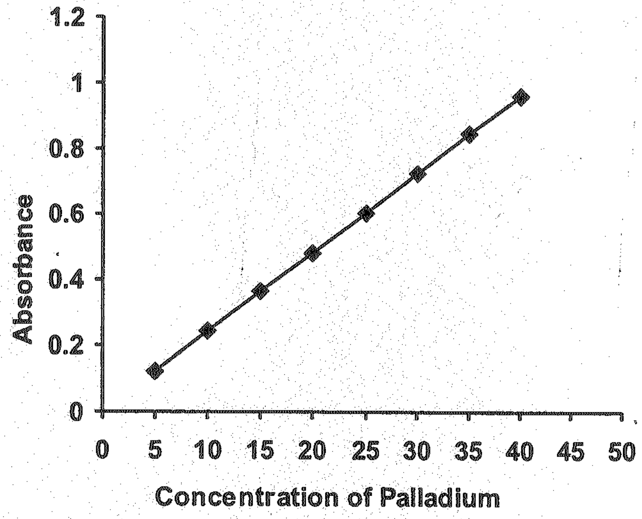


Fig. 1. Calibration plot of Pd(II) with HNCHC

Nature of extracted species: The composition of extracted species has been determined by Job's continuous variation method[3], slope ratio method (Fig. 2)

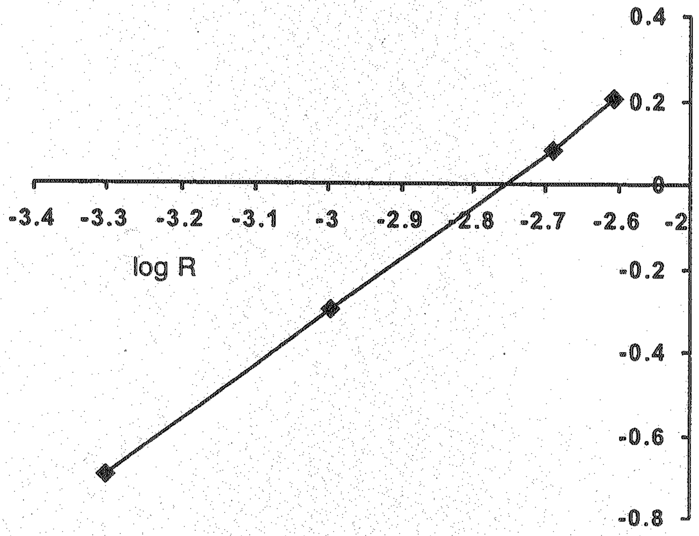


Fig. 2. Stoichiometric ratio of metal to reagent complex of Pd(II) with HNCHC in ethyl acetate from aqueous media

and mole ratio method[4]. It shows that the composition of Pd (II) : HNCHC complex is 1 : 2.

Precision and Accuracy of the method: The precision and accuracy of the spectrophotometric method have been tested by analyzing five solutions containing 25 μg of palladium(II) in 10 mL aqueous solution (Table-2).

TABLE-2
PRECISION AND ACCURACY OF THE METHOD

Aqueous phase: 25 μg of Pd(II) + 1.0 mL of HNCHC (0.1%) in methanol
Organic phase: 10.0 mL (2 × 5) of ethyl acetate
Wavelength: 410 nm; pH: 4.2

Obs. No.	Absorbance (nm)	Amount of Pd(II) in μg	$\overline{X}$	$D = \lvert X_i - \overline{X} \rvert$	$D^2 = (X_i - \overline{X})^2$
1.	5.597	24.75	25.04	0.29	0.0841
2.	0.602	25.15		0.11	0.0121
3.	0.599	25.00		0.04	0.0016
4.	0.605	25.30		0.26	0.0676
5.	0.599	25.00		0.04	0.0016

Standard deviation: 0.0913. Confidence limit: 25.04 ± 0.105 (at 95%).

Applications

The proposed method has been applied to determine palladium in silver alloy, palladium complexes and palladium catalysts. The results of the analysis are comparable with dimethyl glyoxime method. The results are shown in Tables 3–5.

TABLE-3
BINARY SEPARATION OF Pd(II) WITH HNCHC IN ETHYL ACETATE FROM AQUEOUS MEDIA

S. No.	Binary mixtures[a] Metal taken (ppm)	Palladium found (ppm)*	
		Present method†	Standard method
1.	Pd (5) + Fe (5)	4.99	5.0
2.	Pd (6) + Cu (4)	5.98	3.99
3.	Pd (6) + Ni (6)	6.01	6.00
4.	Pd (4) + Zn (6)	4.00	6.00
5.	Pd (6) + V (4)	5.98	4.02
6.	Pd (5) + Co (6)	5.01	6.02
7.	Pd (5) + Zr (5)	4.99	5.01

*An average of three determinations. †Dimethyl glyoxime method

TABLE-4
DETERMINATION OF Pd(II) FROM REAL SAMPLES

S. No.	Standard samples	Palladium found (%)*	
		Present method	Standard method
1.	Silver alloy	0.098	0.099
2.	Pd-Charcoal catalyst	9.990	10.010
3.	Pd-$BaSO_4$ Catalyst	0.892	0.879
4.	Pd-$CaCO_3$	4.445	4.449

*An average of three determinations.

TABLE-5
DETERMINATION OF Pd(II) FROM PALLADIUM COMPLEXES

S. No.	Complex	Palladium found (%)*	
		Present method	Standard method
1.	$Pd(C_7H_8O_2N_2)_2Cl_2^a$	22.08	21.98
2.	$Pd(CH_6N_4S)_2Cl_2^b$	27.30	27.17
3.	$Pd(CH_5N_3S)_2Cl_2^c$	29.58	29.46
4.	$Pd(C_4H_7O_2N_2)_2^d$	31.60	31.49
5.	$Pd(C_6H_5N_3)Cl_2^e$	25.61	25.46

*Average of three determinations.

[a]Pd complex of salicylolylhydrazide.

[b]Pd complex of thiocarbohydrazide.

[c]Pd complex of thiosemicarbazide.

[d]Pd complex of dimethylglyoxime.

[e]Pd complex of 1,2,3-benzotriazole.

Conclusion

The results obtained show that the HNCHC in ethyl acetate can be effectively used for quantitative extraction of Pd(II) from aqueous media. The proposed method is quick and requires less amount of organic solvent. The equilibrium time required is very little, *i.e.*, only 30 sec, and the complex is stable for 48 h. The method has a detectable range from 0.5–2.50 μg for palladium. The results show good agreement with the standard method. The method is found to be very precise.

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