

Full Length Research Paper

Simple and simultaneous spectrophotometric determination of Pd (II) in alloys using hydrazone compounds

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A highly selective, reproducible and rapid spectrophotometric method for the determination of palladium (II) is developed based on the reaction of Pd (II) with 2,4-dihydroxyl acetophenone-p-hydroxylbenzoylhydrazone [RPPHBH] in the pH range 5 to 6 which forms a stable pale green complex. The complex shows absorbance maximum at 375 nm at pH of 5.5. Beer's law is obeyed in the range 1.06 to 8.51 µg/ml of Pd (II). The molar absorptivity and Sandell's sensitivity of the complex are $0.85 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0126 \mu\text{g cm}^{-2}$ respectively. Au (III) also reacts with RPPHBH at pH 5.5 to form a violet coloured complex. This complex shows an absorbance maximum at 590 nm. Thus, Pd (II) and Au (III) are simultaneously determined at pH of 5.5. The molar absorptivity of Pd (II) and Au (III) complexes of RPPHBH at 375 nm are $0.85 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.42 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ respectively. Pd (II): RPPHBH complex has no absorbance at 590 nm. The molar absorptivity of the gold complex at 590 nm is $0.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. This fact is successfully exploited for the simultaneous determination of palladium (II) and Au (III) in alloys.

Key words: 2, 4-dihydroxylacetophenone-p-hydroxylbenzoylhydrazone (RPPHBH), palladium (II), Au (III), alloy samples, UV- Vis, spectrophotometry.

INTRODUCTION

Palladium is used in industry as a catalyst. It is also used in cosmetic and jewelry industries. With the increasing use of palladium in jewelry and cosmetic industry, a need arose for the development of rapid and effective methods for the determination of palladium (II) in real samples. Pd (II) had strong corrosion resistance in the presence of acids (except nitric acid) at ordinary temperatures. It always occurred naturally with platinum group metals and was found in native metallic state. It had great affinity to absorb hydrogen on its surface. For higher density, it is alloyed with Ag, Au and Cu and used in the manufacture of watch bearings, springs and balance wheels and also for mirrors in scientific instruments. Palladium salts are widely employed in making special photographic printing paper.

Palladium is one of the strongest allergens from a health hazard view point. Hence, a rapid and accurate

method for the determination of palladium is necessary. For the determination of palladium at micro levels, there are several analytical techniques such as X-ray fluorescence spectroscopy, atomic absorption spectrophotometry, spectrofluorimetry and other techniques. Among these, UV-Visible spectrophotometric methods are preferred because they are cheaper, easy to handle and highly sensitive. Though numerous spectrophotometric methods are available for the determination of palladium (II), the literature survey revealed that they are not sensitive enough (Gaurav et al., 2010; Janardhana et al., 2008; Lakshmi et al., 2007; Nain et al., 2006; Pourreza and Elhami, 2006; Roa et al., 1992; Rajeshet al., 1999; Sanke et al., 1981; Sarma et al., 2002; SreeVani et al., 2007).

This method is found to be rapid, sensitive, selective, reproducible and free from interference of a large number of common metal ions. Very few reports on direct spectrophotometric method for the simultaneous determination of Pd (II) and Au (III) are there in the literature (Donglan et al., 2010). However, a third

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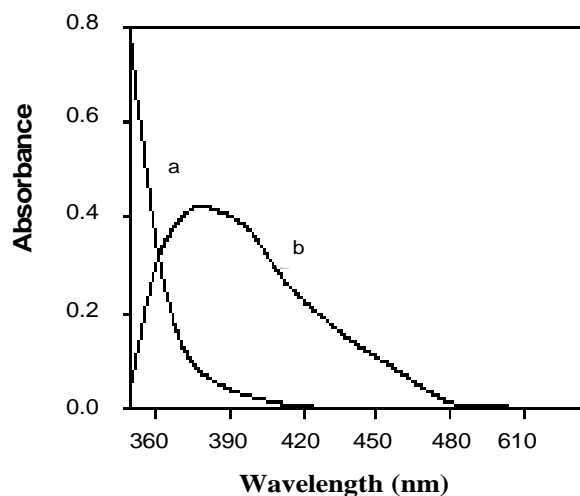


Figure 1. Absorption spectra of (a) RPPHBH Vs buffer blank; (b) [Pd (II)]: RPPHBH Vs reagent blank. Pd (II): 2, 4-dihydroxyacetophenone-p-hydroxybenzoylhydrazone a pale green colored highly water soluble complex is formed within 10 min and has $\lambda_{\text{max}} = 375 \text{ nm}$ (Figure 1), where reagent has low absorbance. It is stable for 3 h.

derivative spectrophotometric method was reported for the simultaneous determination of Pd (II) and Au (III) in the synthetic mixtures but was not applied for real samples like alloys (Vojkovic et al., 2003).

EXPERIMENTAL

Schimidzo (UV-160 A) spectrophotometer, (Koyoto in Japan) is used for absorbance measurements. pH meter (ELICO) was used for measuring pH of buffer solutions. All chemicals and solvents used were of analytical grade. RPPHBH is synthesized by refluxing equimolar quantities of 2, 4-dihydroxyacetophenone and p-hydroxybenzoylhydrazine in aqueous alcoholic medium in presence of small amount of CH_3COONa . The pale yellow coloured product obtained was recrystallised from hot ethanol in presence of charcoal. Its melting point is 248 to 252°C. The structure of RPPHBH was determined from IR, ^1H NMR, Mass spectral studies and the purity was checked by HPLC. 1×10^{-2} M solution of RPPHBH was prepared by dissolving 0.777 g of RPPHBH in dimethylformamide (DMF) in a 25 ml volumetric flask and diluted up to the mark with DMF. Fresh reagent solution is prepared every day before use.

Stock solution of PdCl_2

One gram of palladium chloride was dissolved in distilled water after adding a few drops dilute HCl and diluted up to the mark in 100 ml volumetric flask. It was standardized.

Stock solution of chloroauric acid

One gram of AuCl_3 was dissolved in distilled water after adding a few drops of dilute HCl and made up to the mark with distilled water in a 100 ml volumetric flask and standardized. All the stock solutions were suitably diluted whenever necessary.

Method for simultaneous determination

One milliliter of 4×10^{-4} M solutions of each of Pd (II) and Au (III) were mixed in a 10 ml volumetric flask containing 5 ml buffer solution of pH 5.5. 0.6 ml of RPPHBH solution of 4×10^{-2} M was added and made up to the mark with distilled water. The absorbance of the solution was measured at 375 nm and 590 nm against reagent blank (5 ml of buffer solution and 0.6 ml of RPPHBH solution diluted up to the mark with distilled water).

Preparation of alloy sample

0.1 to 0.5 g of the sample was dissolved in a mixture of 2 ml HCl and 10 ml HNO_3 . The resulting solution is evaporated to a small volume and mixed with 5 ml of 1:1 $\text{H}_2\text{O} : \text{H}_2\text{SO}_4$ mixture, and evaporated to dryness. The residue was dissolved in 15 ml of distilled water and filtered through Whatman filter paper No.41. The filtrate was collected in a 100 ml volumetric flask and made up to the mark with distilled water. The solution was further diluted as required.

RESULTS AND DISCUSSION

[Pd (II)]: RPPHBH] complex

0.5 milliliter of 1×10^{-4} M palladium solution and 1.5 ml of 1×10^{-2} M reagent solution along with 5 ml of pH 5.5, buffer solution are taken in 10 ml volumetric flask and diluted up to the mark with distilled water. The spectrum of [Pd (II) - RPPHBH], a pale green coloured complex, was recorded over the range 300 to 600 nm against a reagent blank. It shows maximum absorbance at 375 nm and is shown in Figure 1. The effect of pH on the absorbance of the complex is shown in Figure 2. The

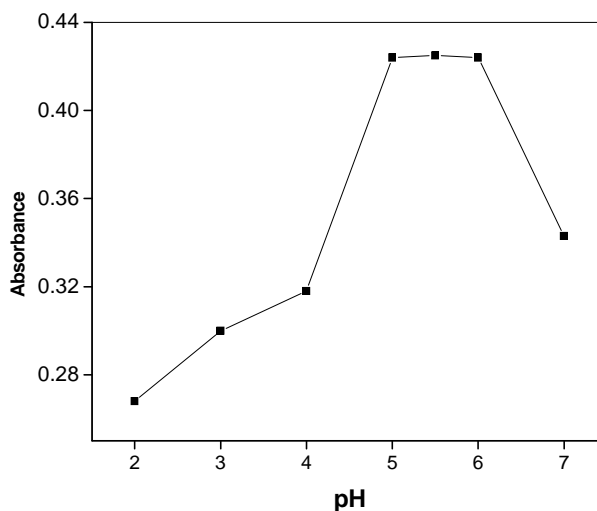


Figure 2. Effect of pH on absorbance of Pb (II). RPPHBH system. $[Pb(II)] = 5.0 \times 10^{-5} M$; $RPPHBH = 1.5 \times 10^{-2} M$. Wave length = 375 nm.

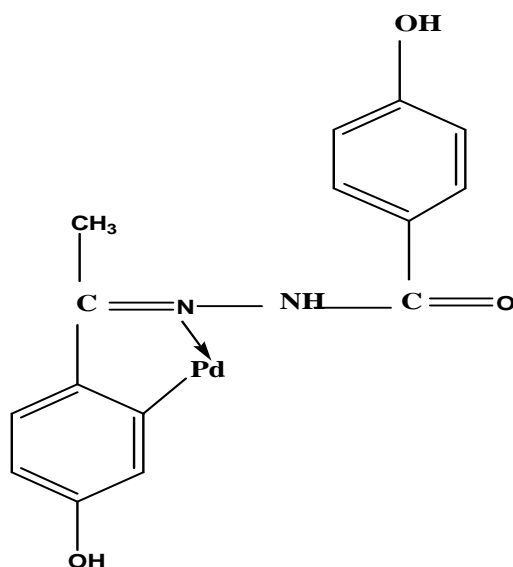


Figure 3. Structure of Pb (II): RPPHBH complex.

absorbance is maximum and constant in the range of pH 5 to 6, therefore pH 5.5 is selected. Fifteen fold excess of the reagent is necessary to get maximum absorbance. Beer's law was obeyed in the range 1.06 to 8.51 $\mu\text{g/ml}$ of Pd (II).

Analysis of the results of Pd (II) – RPPHBH gave linear plots corresponding to $A = 0.0783C + 0.0061$. The optimal concentration range of determination of Pd (II) is found to be 2.12 to 7.45 $\mu\text{g/ml}$ from Ringbom's plot. The molar absorptivity and Sandell's sensitivity are found to be $0.85 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 0.0126 $\mu\text{g cm}^{-2}$ respectively. The standard deviation in the determination

of 5.32 $\mu\text{g/ml}$ of Pd (II) was 0.0069. The composition of the complex was established as 1:1 [Pd (II): RPPHBH] from Job's continuous variation method and molar ratio method. The stability constant of the complex from Job's method was determined as 3.10×10^6 . The possible structure of the complex is shown in Figure 3.

Au (III): RPPHBH complex

Au (III) reacts with RPPHBH solution to form a violet colored water soluble complex. It has maximum intensity

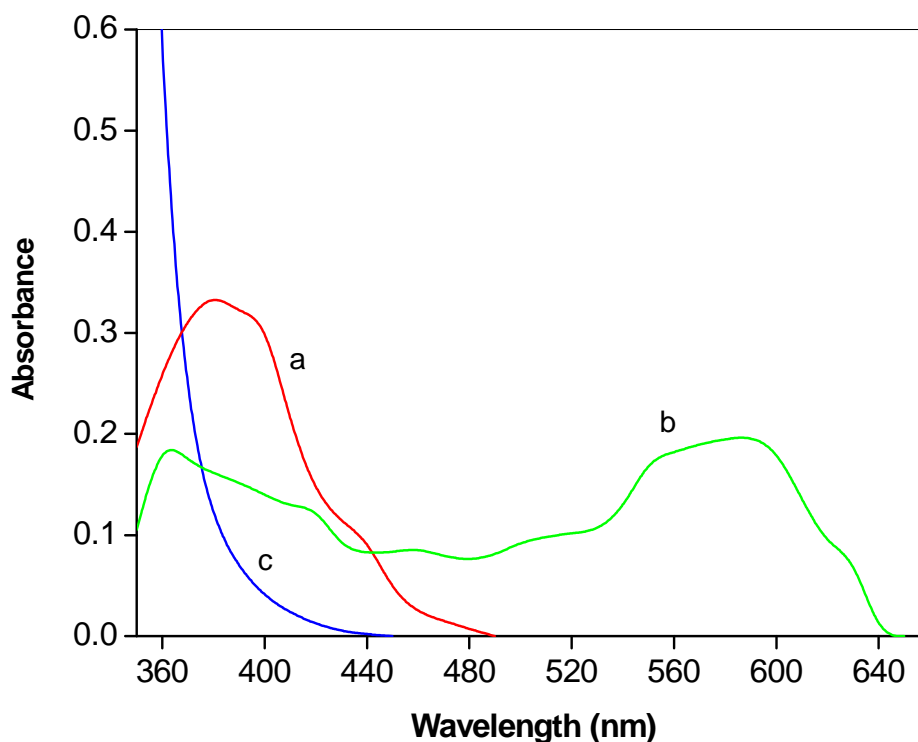


Figure 4. (a) Absorbance spectrum of Pb (II): RPPHBH Vs reagent blank. (b) Absorbance spectrum of Au (III): RPPHBH Vs reagent blank. (c) Absorbance spectrum of RPPHBH Vs buffer solution. Simultaneous spectra of Pd (II): RPPHBH and Au (III): RPPHBH complexes.

in the pH range 4.0 to 7.0. The complex shows maximum absorbance at 590 nm. A 10 fold excess of RPPHBH solution is necessary to attain maximum absorbance.

Simultaneous determination of Pd (II) and Au (III)

Pd (II) and Au (III) complexes of RPPHBH have maximum absorbances at pH 5.5. The advantage of this system is that Pd (II): RPPHBH complex shows maximum absorbance at 375 nm and it had practically no absorbance after 480 nm (Figure 4). It is observed that the total absorbance of the solutions containing a mixture of Au (III) and Pd (II) complex species at 375 nm is equal to the sum of the absorbance values due to individual Pd (II) and Au (III) species. Thus, it is possible to determine simultaneously Au (III) and Pd (II) using RPPHBH at pH 5.5. The absorbance of the Au (III) and Pd (II) complexes in the sample are measured at 590 nm and 375 nm.

Analytical features

Au (III): RPPHBH complex obeys Beer's law in the range 3.94 to 27.50 $\mu\text{g/ml}$ at 375 nm and in the range 1.96 to 19.70 $\mu\text{g/ml}$ at 590 nm. Pd (II) system obeys Beer's law in the range 1.06 to 8.15 $\mu\text{g/ml}$ of Pd (II) at 375 nm. The

molar absorptivities for Au (III) and Pd (II) species at 375 nm are $4.20 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.85 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively. The molar absorptivity of Au (III) at 590 nm was $0.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. The absorbance of Au (III) species at 375 nm is found to be 0.83 times its absorbance at 590 nm. The absorbance due to Pd (II) at 375 nm is obtained by subtracting the absorbance contribution due to Au (III) at this wavelength which is 0.83 times its absorbance at 590 nm, where Au (III) alone absorbs. It was calculated by using the equation.

$$\text{Pd(II)} = \frac{A_{375} - (A_{590} \times 0.83)}{\epsilon_{375}^{\text{Pd(II)}}} \times 106.42 \times 10^3$$

Where at A_{375} and A_{590} nm were the absorbance values of the solution mixture at 375 nm and 590 nm respectively. $\epsilon_{375}^{\text{Pd(II)}}$ is the molar absorptivity of Pd (II) at 375 nm. 106.42×10^3 is the factor to convert the concentration of Pd (II) into amount.

Effect of foreign ions

The interference of other associated ions in the determination of Pd (II) was studied using 3.192 $\mu\text{g/ml}$ of palladium. Most of the ions do not interfere except

Table 1. Tolerance limit of foreign ions.

Foreign ion	Tolerance limit ($\mu\text{g/ml}$)
Ti(IV)	Interferes
Mn(II)	44
Se (IV)	40
Zr(II)	66
Ca (II)	407
Au (III)	20
Mg(II)	243
Pb (II)	84
Cd(II)	68
Co(II)	25
Zn(II)	320
Mo(VI)	29
V (V)	Interferes
Ru(III)	10
Cu(II)	Interferes
Cr(VI)	60
Th (IV)	60
Fe(III) ^a	220
Al (III)	42
Ce(IV)	84

Most of the anions do not interfere except thiocyanate, thiourea, EDTA and thiosulphate anions. These interfering ions used as a masking agent.

Table 2. Simultaneous determination of Au (III) and Pd (II) in synthetic mixture.

Amount taken ($\mu\text{g/ml}$)		Amount found ($\mu\text{g/ml}$)		Relative error (%)	
Au (III)	Pd (II)	Au (III)	Pd (II)	Au (III)	Pd (II)
1.97	4.26	1.97	4.24	-0.50	-0.47
3.94	4.26	3.92	4.24	0.50	-0.47
7.88	4.26	7.85	4.29	-0.38	0.70
9.85	4.26	9.89	4.25	0.41	-0.23
11.80	4.26	11.75	4.23	-0.42	-0.70
7.88	2.12	7.85	2.11	-0.38	-0.85
7.88	3.19	7.93	3.16	0.63	-0.94
7.88	4.26	7.83	4.29	-0.63	0.70
7.88	5.35	7.92	5.33	0.51	-0.37
7.88	6.38	7.81	6.39	-0.89	0.16

*Average of seven determinations.

copper, titanium, vanadium and iron. These ions were masked with suitable anions to avoid their interference during the determination of palladium (Table 1).

APPLICATION

The method is applied for the determination of palladium in certain synthetic mixtures corresponding to its alloys

and also for real alloy samples. The results are presented in Tables 2 and 3.

Conclusion

The proposed spectrophotometric method for the determination of Pd (II) using RPPHBH as a spectrophotometric reagent is sensitive, rapid and selective at pH 5.5. A direct spectrophotometric method

Table 3. Analysis of alloy samples.

Sample	Found (%)	
	Pd (II)	Au (III)
P 30; B 50TF198, [30.5 Pd, 56.55 Ni, 10.5 Cr, 2.45 B]	30.2	-
Pd 72%, Ag 26%, and Ni 2%.	70.9	-
Pd 60%, Au 40%.	60.3	39.7
Pd 34 %, Au 10%, Co 22%, Ni 34%.	34.2	9.8
Au 75%, Pd 10%, Ni 10%, Zn 5%.	10.2	74.9

The results in the table were average of seven determinations.

for the simultaneous determination of Pd (II) and Au (III) in alloys is developed for the first time.

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