Spectrophotometric determination of palladium(II) using piperonal thiosemicarbazone

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A simple, rapid, selective and sensitive spectrophotometric method for the determination of palladium is proposed using piperonal thiosemicarbazone (PATS) as a reagent. The reagent forms a 1:2 complex (Pd:Reagent) with palladium. The yellow complex is soluble in 32-40% ethanol and has an absorption maximum at 363 nm. Beer's law is obeyed upto 3.85 ppm of palladium and the optimum concentration range is 0.5-2.45 ppm of Pd. The molar absorptivity and Sandell's sensitivity are 3. 80×10^4 dm^3 mol^{-1} cm^{-1} and 2.8×10^{-3} μg cm^{-2}, respectively. The experimental conditions for complete colour development and the interference from various ions are investigated. The method is used for the determination of palladium in its complexes and synthetic mixtures.

Thiosemicarbazones are important organic analytical reagents. Because of the presence of a thioketo sulphur atom and an azomethine nitrogen atom, they act as good chelating agents, forming stable complexes with various metal ions. A large number of thiosemicarbazones have been reported as spectrophotometric reagents for palladium(II). Some of the important thiosemicarbazones used are phthalimide dithiosemicarbazone[1], glyoxal dithiosemicarbazone[2], furoin thiosemicarbazone[3], quinolin-2-aldehyde thiosemicarbazone[4], 2-furaldehyde thiosemicarbazone[5], 2-methyl-1,4-naphthoquinone thiosemicarbazone[6], p-anisaldehyde thiosemicarbazone[7], phenanthraquinone monothiosemicarbazone[8], methyl glyoxal *bis*(4-phenyl-3-thiosemicarbazone)[9], salicylaldehyde thiosemicarbazone[10], 4-(dimethylamino)benzaldehyde thiosemicarbazone[11], 3-thiophenaldehyde-4-phenyl-3-thiosemicarbazone[12] and nicotinaldehyde-4-phenyl-3-thiosemicarbazone[13]. Some of these methods require either heating[5,8] or considerable time for maximum colour development[6,9], while some others involve extraction[4,10,12,13]. In this paper, the application of piperonal thiosemicarbazone as a selective spectrophotometric reagent in the determination of palladium(II) has been reported. The method, besides being sensitive and reasonably selective, is simple and rapid as it does not require heating or extraction.

Experimental Procedure

A Shimadzu UV-Visible spectrophotometer (UV-160A) with 10 mm fused silica cells was used. All chemicals used were of either AR or chemically pure grade. The stock solution of palladium(II) was prepared by dissolving palladium chloride in minimum amount of conc. HCl, making up to one litre with distilled water and standardised gravimetrically by dimethylglyoximate method[14]. The experimental solutions were prepared by diluting the stock solution to a concentration containing 5 μg per cm^3 of the solution. Piperonal thiosemicarbazone (PATS) was synthesized by refluxing equimolar amounts of piperonal and thiosemicarbazide in methanol for three hours. The crude sample obtained on cooling was recrystallised twice from aqueous dioxan and characterised by elemental analysis. [Found (calcd), % are C = 48.40 (48.43), H = 4.22 (4.04), N = 18.74 (18.83), O = 14.26 (14.35), S = 14.38(14.35)]. A freshly prepared 0.07% solution of PATS in acetone was used. The solutions of various metal ions and anions were prepared by dissolving required amount of appropriate salts in distilled water or in suitable dilute acids and making up to a known volume.

A series of aliquots of the sample solution containing 12.5-61.25 μg of Pd(II) in 25 mL standard flasks were treated with 2 mL of 0.5 M HCl and 2 mL of 0.07% solution of PATS in acetone. After the addition of 10 mL of ethanol, the solutions were finally made upto 25 mL with distilled water and

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shaken well. The reaction mixtures were allowed to stand for 10 min to attain maximum colour intensity. The absorbances of the solutions were measured at 363 nm against the reagent blank. The calibration curve was then obtained by plotting absorbance along the Y-axis and concentration of palladium along the X-axis. The sample solutions containing palladium were treated in the same manner as above and their absorbances measured at 363 nm against the reagent blank. The palladium content in the samples were computed from the standard calibration curve.

Analysis of palladium complexes

Palladium(II) complexes with salicylolyl hydrazide, thiocarbohydrazide, thiosemicarbazide, dimethylglyoxime and 1,2,3-benzotriazole were prepared as per the reported procedures[15,16,17]. A known amount of the complex was decomposed carefully with aqua regia and evaporated to near dryness. The residue was then cooled and dissolved in minimum volume of 2 N HCl and made up to a known volume. The test solutions were prepared by further dilution of the stock solution to the required concentration. The palladium content in the solution was determined as per the recommended procedure.

Results and Discussion

The yellow complex of Pd(II) with PATS shows maximum absorbance at 363 nm. At the same wavelength, the reagent shows negligibly small absorbance. All subsequent studies were, therefore, made at 363 nm.

Effect of the medium

The reagent forms a sparingly soluble yellow complex with Pd(II) in aqueous medium and the complex was found to be completely soluble in 40% ethanol. Preliminary investigations of pH studies using different buffers showed that the complex had a maximum absorbance in acid medium. Therefore, attempts were made to find out suitable acid among HCl, H_2SO_4, HNO_3 and CH_3COOH. These studies revealed that the absorbance of the complex was maximum in hydrochloric acid medium. In order to find out the optimum concentration of hydrochloric acid needed for complete colour development, absorbance measurements were carried out at different concentrations of hydrochloric acid. The constant maximum absorbance was shown in a concentration range of 0.024-0.064 M HCl.

Effect of reagent concentration

The effect of PATS concentration was studied by measuring the absorbance of the solution containing a constant amount of Pd(II) and varying amounts of PATS at 363 nm. It was observed that 12 moles of PATS per mole of Pd was required for maximum colour development. However, the excess amounts of the reagent did not show any substantial change in absorbance.

Stoichiometry of the complex

The stoichiometry of Pd(II)-PATS complex was studied by Job's method of continuous variation[18] and also by the mole ratio method[19]. Both the methods indicated the formation of a 1:2 complex between Pd(II) and PATS. The reagent can act as a bidentate ligand by forming bonds with the metal ion through sulphur and hydrazine nitrogen, resulting in the formation of a five-membered chelate.

Order of addition of reagents, rate of reaction and stability of colour

The order of the addition of the reagent did not have any effect on the absorbance of the complex. The colour reaction between Pd(II) and PATS was found to be fast and colour development took place soon after the mixing of the reagents. However, the reaction mixture was allowed to stand for five min before measuring its absorbance to ensure the maximum colour development. The colour of the solution remained stable for about 70 min.

Adherence to Beer's law, optimum range and sensitivity

The experimental investigations revealed that the method obeys Beer's law up to 3.85 ppm of Pd(II). The optimum concentration range for effective determination of palladium, calculated by Ringbom's plot method[20] is 0.5-2.45 ppm. The molar absorptivity and Sandell's sensitivity of the method are 3.80×10^4 dm^3 mol^{-1} cm^{-1} and 2.8×10^{-3} μg cm^{-2}, respectively.

Accuracy and precission

The absorbance measurements were carried out with a series of solutions having different concentrations of Pd in the optimum range following the above procedure. The standard deviation and coefficient of variation of the method were found to be not exceeding 0.008 and 0.86%, respectively. From these results, it is reasonable to infer that the method is precise and accurate.

Effect of diverse ions

The presence of various diverse ions were examined for their possible interference in the determination of 1.65 ppm Pd. An error of ±2% in the absorbance value was considered as tolerance limit. No interference was observed for the following anions at the amounts shown in ppm: nitrate (5000), sulphate (2000), phosphate (400), fluoride (650), chloride (6000), bromide (4800), iodide (450), thiocyanate (10), dichromate (100), tartarate (3000), acetate (1500), borate (300), oxalate (200), citrate (1600) and EDTA (300). However, the presence of thiosulphate caused interference due to the decrease in the intensity of the colour. It is expected that the complexation of palladium with the reagent is not quantitative as thiosulphate can also form stable complex with palladium[21]. It was also found that the following metal ions did not interfere at the amounts shown in ppm: Mg(II) (200), Ca(II) (200), Zn(II) (800), Cd(II) (1500), Ba(II) (2000), Al(III) (400), Tl(III) (100), Ce(III) (20), U(VI) (300), Ti(IV) (40), Sn(II) (75), Sn(IV) (100), Pb(II) (3000), Cr(III) (25), Mo(VI) (25), Mn(II) (400), Fe(II) (5), Pt(II) (5), Co(II) (1000), Ni(II) (800), Ru(III) (4), Rh(III) (8), Ir(III) (10), Fe(III) (5) and Ce(IV) (8). However, the presence of Cu(II), Hg(II) and Pt(IV) caused severe interference. The interference due to 5 ppm of Cu(II) can be avoided by premasking with EDTA.

Applications

The method was employed for the determination of palladium in palladium complexes and in synthetic mixtures simulating the composition of alloy samples. The results are given in Tables 1 and 2. These results indicate that the method can be conveniently employed for the analysis of palladium complexes and alloys with a fair degree of accuracy.

Comparison with other reagents

The comparison of PATS as a spectrophotometric reagent for Pd with other reported thiosemicarbazones is given in Table 3. It is observed that the proposed method is comparable with other methods and is more sensitive than many of the reported methods as indicated by higher molar absorptivity values.

Table 1—Analysis of palladium complexes

Complex	Palladium present (%)	Palladium found* (%)
$Pd(C_7H_8O_2N_2)_2Cl_2$[a]	22.09	21.99
$Pd(CH_6N_4S)_2Cl_2$[b]	27.31	27.19
$Pd(CH_5N_3S)_2Cl_2$[c]	29.59	29.49
$Pd(C_4H_7O_2N_2)_2$[d]	31.61	31.48
$Pd(C_6H_5N_3)Cl_2$[e]	25.60	25.47

*Average of three determinations
[a] Palladium complex of salicylolylhydrazide
[b] Palladium complex of thiocarbohydrazide
[c] Palladium complex of thiosemicarbazide
[d] Palladium complex of dimethylglyoxime
[e] Palladium complex of 1,2,3-benzotriazole

Table 2—Determination of palladium(II) in synthetic mixtures of metal ions

Palladium Present,(ppm)	Metal ions added (ppm)					Palladium Found,(ppm)
	Ni(II)	Co(II)	Ru(III)	Fe(II)	Rh(III)	
0.55	2.0	-	0.8	-	2.0	0.54
1.10	4.0	2.0	-	-	-	1.10
1.65	2.0	-	-	1.0	-	1.64
2.20	-	6.0	-	2.0	1.6	2.21

Table 3—Comparison of PATS with other thiosemicarbazones

S No	Reagent	λ_{max} (nm)	Range (ppm)	Molar Absorptivity (10^4 dm^3 mol^{-1} cm^{-1})
1	Furoin thiosemicarbazone	360	2-4	1.98
2	p-Anisaldehyde thiosemicarbazone	370	0.1-3.3	2.16
3	Salicylaldehyde thiosemicarbazone	405	1.3-6.5	6.40
4	4-(Dimethylamino) benzaldehyde thiosemicarbazone	405	0.5-1.75	4.59
5	3-Thiophenaldehyde-4-phenyl-3-thiosemicarbazone	355	0.4-6.0	2.50
6	Nicotinaldehyde-4-phenyl-3-thiosemicarbazone	365	0.5-8.0	2.81
7	Phenanthraquinone monothiosemicarbazone	590	3.4-18.2	0.42
8	Methylglyoxal-bis-(4-phenyl-3-thiosemicarbazone)	606	4.0-8.0	0.32
9	Piperonal thiosemicarbazone (PATS)	363	0.5-2.45	3.80

Conclusion

The proposed method offers advantages of simplicity, rapidity, reasonable selectivity and sensitivity without the need for heating or any extraction. The method can be used for the rapid determination of palladium at low concentration ranges.

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