

Direct and derivative spectrophotometric determination of palladium with 2-aminoacetophenone isonicotinoyl hydrazone (2-AAINH)

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Manuscript received 20 June 2005, revised 2 August 2006, accepted 2 August 2006

Abstract : 2-Aminoacetophenone isonicotinoyl hydrazone (2-AAINH) has been proposed as a sensitive and selective reagent for the spectrophotometric determination of palladium(II) in alloy samples. The palladium ion forms an intense orange red coloured soluble complex with 2-aminoacetophenone isonicotinoyl hydrazone (2-AAINH) in the acidic pH medium. The orange red color of Pd^{II}-2-AAINH solution exhibits maximum absorbance at 500 nm in the pH range 3-5. Beer's law is obeyed in the range 0.30-3.00 µg/ml of Pd^{II} at pH 4.0. The molar absorptivity and Sandell's sensitivity of the colored solution are found to be $3.00 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0035 \text{ µg cm}^{-2}$ respectively. The absorbance is found to increase linearly with increase in concentration of Pd^{II}, which is corroborated by the calculated correlation coefficient value (0.9998). The effect of foreign ions absorbance of the colored solution has been studied. The composition of the complex is calculated as 1 : 2 {Pd^{II}-2-AAINH}. The first derivative spectrum shows a peak at 540 nm with a zero cross at 494 nm. The second derivative spectrum shows a maximum at 560 nm and a minimum at 500 nm with a zero cross at 537 nm. Thus, sensitive first and second derivative spectrophotometric methods for the determination of Pd^{II} are also proposed.

Keywords : Palladium, hydrazone, spectrophotometry.

In our laboratories, isonicotinoyl hydrazones are being extensively used as spectrophotometric reagents for the determination of number of metal ions¹. In the course of our studies with isonicotinic acid hydrazide derivatives, we have observed that palladium reacts with 2-AAINH in sodium acetate-acetic acid buffer solutions giving a highly intense orange red colouration which is quite stable. Hence spectrophotometric investigations are made on this colour reaction to develop a sensitive method for the determination of Pd^{II} in microgram quantities.

The derivative methods are used to eliminate interference during spectrophotometric analysis². It has been widely used in pharmaceutical analysis, amino acid and protein analysis, clinical industry, environmental analysis³ etc. but less often in inorganic analysis⁴. For determining the concentrations of components in mixtures with overlapping spectra, derivative spectrophotometry is a very useful approach as it eliminates much of the interference.

In this paper, direct, first and second order derivative spectrophotometric methods are described for the determination of Pd^{II} in which the interference from foreign ions observed in zero-order method is eliminated by the first and second order derivative plots. The methods are

applied for the determination of Pd^{II} in alloy samples.

Experimental

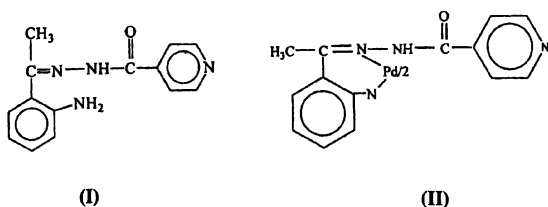
A Shimadzu UV visible spectrophotometer model UV-160A equipped with 1 cm quartz cells and Elico pH meter model LI 120 were used for absorbance and pH measurements respectively. Suitable settings for first and second order derivative were as follows. Spectral band length 2 nm, wavelength readability 0.1 nm increment, scan speed nearly 2400 nm min^{-1} ; wavelength accuracy $\pm 0.5 \text{ nm}$ with automatic wavelength correction, recorder, computer controlled thermal graphic printer with cathode ray tube and with 9 degrees of freedom. Zero-order spectrum of each solution was recorded in the wavelength range 350-600 nm against the reagent blank prepared under identical conditions.

Reagents : The 2-amino acetophenone isonicotinoyl hydrazone was prepared by condensing purified samples of 2-amino acetophenone and isonicotinic acid hydrazide in aqueous methanol in the presence of sodium hydroxide using general procedure⁵. The yellow product is recrystallised from ethanol in the presence of norit (m.p. 183-185 °C). The structure of the product obtained is ascertained from IR and NMR spectral studies. The infrared (IR) spectrum of the compound is recorded in KBr

pellet. The peaks observed at 3406 and 3286 cm^{-1} are due to symmetric and asymmetric -N-H- stretching frequency of primary amino group. The following peaks are assigned as below : 1664 cm^{-1} to C=O stretching frequency of amide (band I); 1545, 1245 cm^{-1} to amide II band; 1604–1432 cm^{-1} to C=C of benzene ring and C=N of pyridine ring. 748 and 701 cm^{-1} to C-H out of plane bending of pyridine ring.

NMR spectral studies⁶ : The peak observed at 11.2 (singlet) is characteristic of enolic -OH group. The peaks found at δ values 8.8 and 7.8 (doublets) are due to the pyridine ring protons, 7.4, 7.0, 6.75, 6.45 (two doublets and two triplets) are due to -NH amide linkage. The peak observed at δ value 2.3 is due to -CH₃ group and 2.5 may be assigned to -NH₂ protons. The spectral data confirm the structure of 2-AAINH as shown below (I).

The composition and stability constant of the complex were determined by the Job's and mole ratio methods and found to be 1 : 2 (Pd^{II} : 2-AAINH) and 3.53×10^{11} respectively which give the possible structure of the complex (II).



A freshly prepared 0.01 *M* solution of this reagent in dimethylformamide (DMF) was used in the present studies.

1 g of palladium chloride (A.R., Loba) is dissolved in doubly distilled water in 100 ml standard flask and standardized⁷. The working solutions were prepared daily diluting the stock solution to an appropriate volume. All other chemicals used were of analytical grade.

Buffer solutions : Buffer solutions, 1 *M* hydrochloric acid and 1 *M* sodium acetate (pH 1.0 to 3.0) and 0.2 *M* acetic acid and 0.2 *M* sodium acetate (pH 3.2 to 7.0) were used.

Direct spectrophotometry : In a series of 10 ml volumetric flasks, 5 ml of buffer solution (pH 4.0), varying amounts of Pd^{II} (0.30–3.00 $\mu\text{g ml}^{-1}$), 1 ml of 2-AAINH (1×10^{-3} *M*) and 1 ml of DMF were mixed and diluted to the volume with doubly distilled water. The absorbance of the resultant solutions was measured at 500 nm against the reagent blank and plotted against the amount of Pd^{II}.

The calibration plot follows the equation :

$$A = 0.2783c + 0.0016.$$

First and second derivative spectrophotometry : The first and second order derivative spectra were recorded with a fast scan speed of nearly 2400 nm/min. Slit width of 1 nm, with 9 degrees of freedom, in the wavelength range from 350–600 nm. With test solution the first derivative peak amplitude at 540 nm and the peak to valley amplitude (500–560 nm) for the second order derivative were measured. The peak height was plotted against the amount of palladium(II) to obtain the calibration curve.

The calibration graph follows the straight line equation $y = mx + b$, where x is the concentration of the solution, y is the measured absorbance or peak height, and m and b are constants. By substituting the corresponding experimental data into the above equation, calibration equations were calculated as $y = 0.2783c + 0.0016$; $y = 0.1121c + 0.0033$ and $y = 0.2005c + 0.0016$ for the zero-order, first order and second order data respectively.

Results and discussion

The absorption spectra of the reagent and the complex were recorded in the wavelength range 350–600 nm at pH 4.0 against the buffer solution and reagent blanks respectively (Fig. 1). The complex shows an absorption maximum at 500 nm where the reagent has negligible absorbance. It is observed that the orange red color forms instantaneously between Pd^{II} and 2-AAINH showing con-

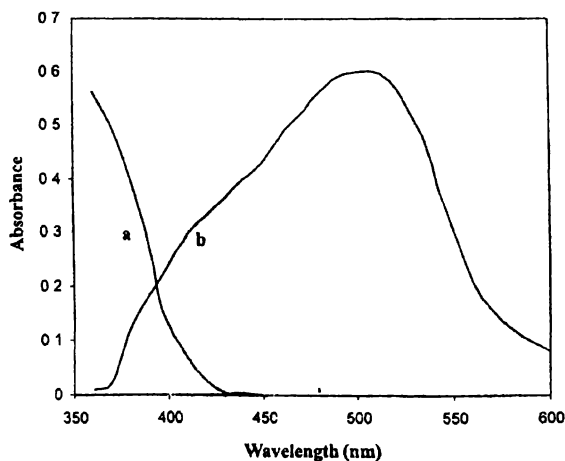


Fig. 1. Absorption spectrum of (a) 2-AAINH vs buffer blank, (b) Pd^{II}-2-AAINH system vs reagent blank [Pd^{II}] = 2×10^{-5} *M*, [2-AAINH] = 1×10^{-3} *M*, pH = 4.0

stant and maximum absorbance in the pH range 3–5. Hence further studies are carried out at pH 4.0. The studies revealed that a 10-fold molar excess of 2-AAINH is sufficient to attain maximum absorbance. Presence of excess reagent has no effect on the absorbance of the complex. The absorbance of the Pd^{II}-2-AAINH complex at various volume percentages of DMF is studied. The studies indicated that a minimum of 20% (v/v) of DMF has to be maintained in the experimental solution to retain the metal complex completely in solution and to get maximum absorbance. The colour formation between Pd^{II} and 2-AAINH is instantaneous at room temperature and is stable for 24 h.

Beer's law is obeyed in the concentration range 0.30 to 3.00 µg ml⁻¹ of Pd^{II}. According to Ringbom's plot, the optimal concentration range of determination is found to be 0.60 to 2.50 µg ml⁻¹. The molar absorptivity and Sandell's sensitivity are determined from the calibration plot and are found to be 3.00 × 10⁴ L mol⁻¹ cm⁻¹ and 0.0035 µg cm⁻² respectively. The statistical results obtained for the present experimental data are presented in Table 1, which conform the validity of the present method.

Table 1. Statistical data for the determination of Pd^{II} with 2-AAINH

Parameter	Zero-order method	First derivative method
Angular coefficient (<i>m</i>)	0.2783	0.1121
Y-intercept (<i>b</i>)	0.0016	0.0033
Correlation coefficient (<i>r</i>)	0.9998	0.9998
Standard deviation (<i>s</i>)	0.0055	0.0052

(*n* = 10).

The effect of various diverse ions on the determination of Pd^{II} was studied to find out the tolerance levels of these diverse ions in the present method. The tolerance limit of a foreign ion is taken as the amount that causes an error in the absorbance value by ±2%. The data are presented in Table 2. Large numbers of commonly associated cations and anions do not interfere in the determination of Pd^{II}.

Determination of palladium(II) by first and second order derivative spectrophotometry : The first order derivative spectra of the Pd^{II}-2-AAINH complex at different concentrations of Pd^{II} recorded and are presented in Fig. 2. The peak zero (h) method is followed for the prepara-

Table 2. Tolerance limits of foreign ions
Amount of Pd^{II} = 1.28 µg ml⁻¹; pH = 4.0

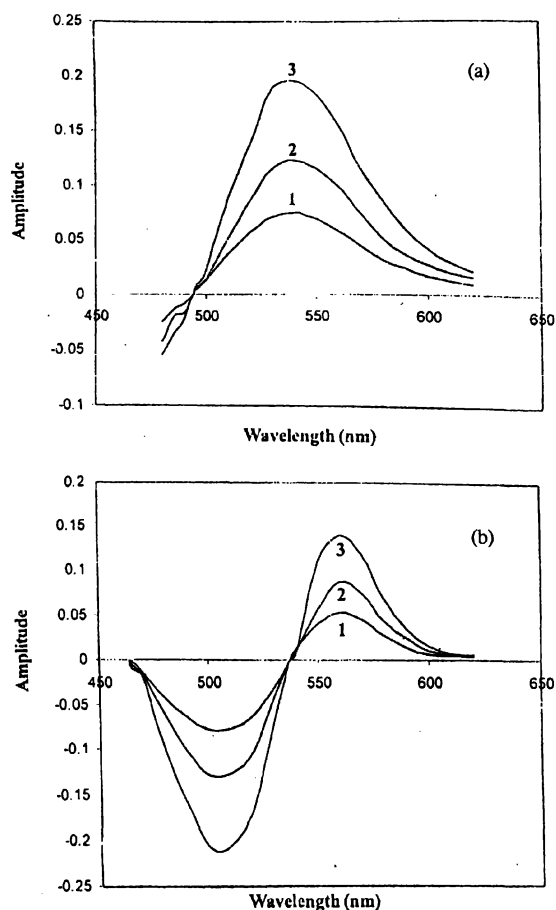
Foreign ion	Tolerance limit (µg ml ⁻¹)	Foreign ion	Tolerance limit (µg ml ⁻¹)
Thiourea	304	V ^V	5
			102 ^a
Thiocyanate	348	Fe ^{III}	11
			1100 ^a
Chloride	425	Cu ^{II}	127
EDTA	446	Pt ^{IV}	132
Oxalate	528	Al ^{III}	166
Sulphate	576	Mn ^{II}	175
Iodide	761	Co ^{II}	176
Fluoride	850	Sn ^{II}	236
Citrate	1134	Pb ^{II}	250
Phosphate	1164	Ba ^{II}	275
Nitrate	1488	Ce ^{IV}	280
Tartrate	1776	Th ^{IV}	280
Ascorbic acid	2100	Cr ^{III}	310
		Cd ^{II}	335
		Ni ^{II}	350
		Ca ^{II}	408
		Mg ^{II}	480
		Au ^{III}	590
		Zn ^{II}	780

^aIn presence of 500 µg ml⁻¹ of fluoride.

tion of analytical calibration plot. The maximum peak is at 540 nm. The second derivative spectra of the Pd^{II}-2-AAINH complex at different concentrations of Pd^{II} are presented in Fig. 2b. The valley peak method is followed for the preparation of calibration plot. The valley peak amplitude (540–560 nm) is observed for the second order derivative method. Other statistical data derived for the present method are as follow : The standard deviation of the method for 10 determinations of 1.28 µg ml⁻¹ of Pd^{II} is 0.0052 and 0.0047 respectively for first and second derivative methods. The correlation coefficient (*γ*) for both the methods is 0.9998. The effect of various cations and anions on the derivative amplitudes is studied, all the ions that do not interfere in the zero-order determination of Pd^{II} (cf. Table 2) also do not interfere in the first and second order derivative spectrophotometric determination of Pd^{II}. If the second order determination is carried out by peak-zero method at 560 nm, the method is highly selective in the sense that no cation that is commonly

Table 3. Determination of palladium(II) in alloy samples

Alloy sample and its composition	Amount of Pd ^{II} ($\mu\text{g ml}^{-1}$)				Error (%)	
	Zero-order		Second derivative		Zero-order	Second derivative
	Certified	Found ^a	Certified	Found ^a		
Co-Pd alloy 95% Co, 5% Pd	5.00	5.09	5.00	5.05	1.8	0.99
Ni-Pt-V-Pd (Okay alloy)						
(i) 60% Ni; 120% Pt; 9.5% V; 10.5% Pd	10.50	10.62	10.50	10.43	1.1	-0.07
(ii) 60% Ni; 30.2% Pt; 7.3% V; 2.5% Pd	2.50	2.46	2.50	2.52	-1.6	-0.79

^aAverage of six determinations.**Fig. 2.** (a) First; (b) Second order derivative spectra of Pd^{II}-2-AAINH system vs reagent blank. Pd^{II} ($\mu\text{g ml}^{-1}$) = (1) 0.638; (2) 1.064; (3) 1.701.associated with Pd^{II} interferes in the determination.

Application : The present method is applied for the determination of Pd^{II} in some alloy samples. To a 10 ml volumetric flask containing 5 ml of buffer (pH 4.0) solution, 1 ml DMF, 1 ml of 2-AAINH (1×10^{-2} M) solution and 0.5 ml of fluoride (1×10^{-1} M) solution is added an aliquot of the alloy sample and made up to the mark with distilled water. The amount of palladium is determined from pre-determined calibration plots by applying zero-order and second order derivative methods. The results are presented in Table 3.

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