

Kinetic-Catalytic-Spectrophotometric Determination of Ultra Trace Amounts of Palladium(II) by Its Catalytic Effect on The Oxidation of Naphthol Green B by Metaperiodate

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A new, simple, sensitive and selective catalytic spectrophotometric method was developed for the determination of ultra trace amounts of Pd(II). The method is based on the catalytic effect of palladium on the oxidation of Naphthol green B by metaperiodate. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of Naphthol green B at 710 nm with a fixed-time method. The decrease in the absorbance of Naphthol green B is proportional to the concentration of Pd(II) in concentration range 5.0-80.0 ng/mL, with a fixed time of 0.5-3.0 min from initiation of the reaction. The limit of detection is found to be 2.2 ng/mL Pd(II). The relative standard deviation of 20.0 and 60.0 ng/mL Pd(II) was 2.1 and 2.6 %, respectively. The proposed method was applied to the determination of palladium in water and synthetic samples.

Key Words: Palladium, Catalytic, Naphthol green B, Metaperiodate.

INTRODUCTION

The platinum group metals are elements the lowest abundance in earth's crust. Palladium is extensively used in the manufacturing of electronic equipment and as a catalyst in the chemical industry. One of the most important industrial uses of palladium is as a catalyst for hydrogenation reactions, the electronic industry, in dental alloys and in the last few years, as a component of three-way catalysts in automobile exhaust-gas catalysis¹.

Among the methods for the determination of palladium, spectrophotometric methods based on complex formation and extraction procedures have been gained a growing interest²⁻⁹. However, most of them suffer from with interferences of other platinum groups and transition metals and used organic solvents or have high limit detection or a long consuming time procedure.

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Kinetic-catalytic based methods have also been used for determination of palladium¹⁰⁻¹³. But many of these methods are not selective¹⁰⁻¹², low precision^{10,13} and high limit of detection¹¹⁻¹³. Recently, more sensitive methods can be utilized by AAA, NAA, graphite furnace AA, ICP-AES and ICP-MS¹⁴⁻¹⁹, although these instruments are highly expensive, day-to-day maintenance is high and the methods are not free from various types of inherent interferences. The aim of the present study was to develop a new simple, lower cost and high sensitive kinetic spectrophotometric method for determination of ultra trace amounts of Pd(II) based on its catalytic effect on the oxidation of Naphthol Green B (NGB) by metaperiodate at 710 nm.

EXPERIMENTAL

Double distilled water and analytical reagent grade chemicals were used during all of the experimental studies. All glassware were cleaned with detergent solution, rinsed with tap water, soaked in dilute HNO₃ solution (2 % v/v) and dried.

Absorption spectra were recorded with a Cary model 100 spectrophotometer with a 1.0 cm quartz cell. A model 2501 CECIL spectrophotometer with 1.0 cm glass cuvettes as used to measure the absorbance at a fixed wavelength of 710 nm. A thermostate water bath was used to keep the reaction temperature at 30°C.

Naphthol green B solution 4.6×10^{-4} M was prepared by dissolving 0.040 g of the compound (Merck) in water and solution was diluted to 100 mL volumetric flask.

Metaperiodate stock solution 0.010 M, was prepared by dissolving 0.5750 g of potassium metaperiodate (Merck) in water and dilute to 250 mL in 250 mL volumetric flask.

Standard stock palladium(II) solution (100.0 µg/mL) was prepared by dissolving 0.0250 g Pd(NO₃)₂·2H₂O (MW = 266.44) in 0.5 M HNO₃ and dilute to 100 mL volumetric flask. Working solutions was prepared daily by appropriate dilution with water.

Stock solution (1000 µg/mL) of interfering ions were prepared by dissolving suitable salts in water, HCl or NaOH solution.

Recommended procedure: All the solutions and distilled water were kept in a thermostated water bath at 30°C for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 50-800 ng/mL Pd(II) was transferred into a 10 mL volumetric flask and then 0.60 mL of buffer solution (pH = 3, acetate 0.2 M) and 0.20 mL of metaperiodate (0.001 M) were added to the flask. The solution was diluted to *ca.* 7 mL with water. Then, 2.0 mL of Naphthol Green B (4.6×10^{-4} M) was added and the solution was diluted to the mark with water. The solution

was mixed and a portion of the solution was transferred to the spectrophotometer cell. The reaction was followed by measuring the decrease in absorbance of the solution against water at 710 nm for 0.5-3.0 min from initiation of the reaction. This signal (sample signal) was labelled as ΔA_s . The same procedure was repeated without addition of Pd(II) solution and the signal (blank signal) was labelled as ΔA_b . Time was measured just after the addition of last drop of Naphthol green B.

RESULTS AND DISCUSSION

Naphthol green B undergoes a oxidation reaction with metaperiodate in acidic medium to form a colourless product at very slow rate. This reaction rate is found to be sharply increased by addition of trace amount of Pd(II).

Several methods, such as fixed-time, initial rate, rate constant and variable time methods for measuring the catalytic species. Among these, the fixed-time method is the most conventional and simplest, involving the measurement of ΔA at 710 nm. Fig. 1 shows the relationship between A and reaction time. It was found that the rate of reaction is proportional to the Pd(II) concentration. This process was monitored spectrophotometrically by measuring the decrease in absorbance of the characteristic band of Naphthol green B (710 nm) (Fig. 1). Therefore, by measuring the decrease in absorbance of Naphthol green B for a fixed time of 0.5-3.0 min initiation of the reaction, the Pd(II) contents in the sample can be measured.

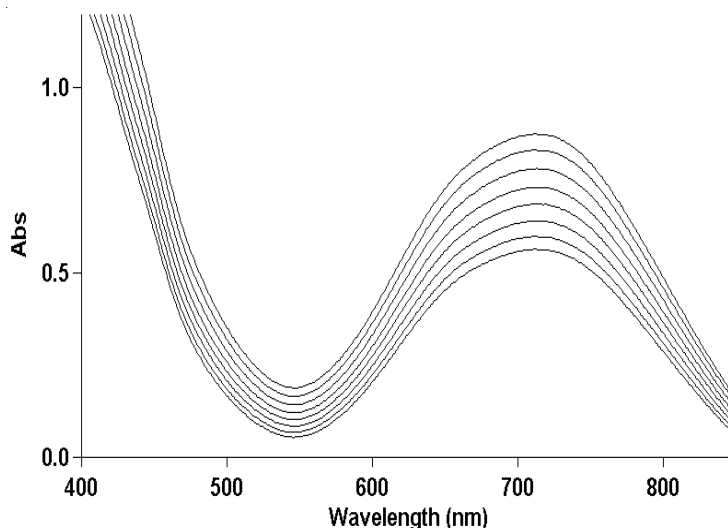
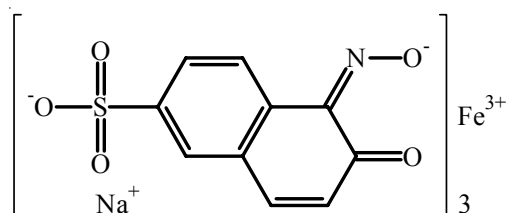


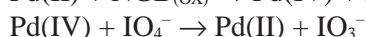
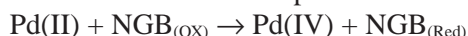
Fig. 1. Variation of the Naphthol green B- IO_4^- -Pd(II) with time.
pH 3; Naphthol green B 9.2×10^{-5} M; IO_4^- 2×10^{-5} M ; Pd(II)
10.0 ng/mL; temperature 30°C

Naphthol green B (NGB) is a complex of Fe^{3+} that have three chelates ligand with fused heteroaromatic rings structure (**Scheme-I**). Therefore catalytic oxidation mechanism of NGB-IO_4^- -Pd(II) may be similar to salicylaldehyde furfural-hydrazone (SAFH)- KBrO_3 -Pd(II) that the Pd(II) catalytic oxidation system²⁰.

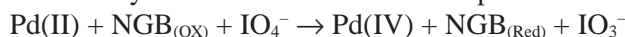


Scheme-I. Structure of Naphthol green B

This mechanism could be represented as follows:



The total catalytic reaction then could be expressed as follows:



The mechanism led to the rate law as:

$$R = -d[\text{NGB}]/dt = k[\text{Pd(II)}][\text{periodate}][\text{NGB}] \quad (1)$$

Assuming that the rate of the uncatalytic reactions was very slow and $[\text{Pd(IV)}]$ was equal to $[\text{Pd(II)}]$. Also assumed that NGB and KIO_4 were present in such excess that their concentration could be regarded as constant, the reaction became pseudo first-order for Pd(II) and the rate equation was further simplified as:

$$R = k'[\text{Pd(II)}] \quad (2)$$

The eqn. 2 was the quantitative basis for the determination of trace Pd(II) by the proposed methods.

Influence of variables

In order to optimize the reaction to get the best sensitivity, the variables affect the sensitivity such as pH, metaperiodate concentration, Naphthol green B concentration and temperature on the rate of catalyzed reaction (with Pd(II)) and uncatalyzed reaction (without Pd(II)) was studied.

The effect of pH on the sensitivity was studied in the range of 2.5-5.0 (Fig. 2). The results show that the net reaction rate increases with pH up to 3 and decreases at higher pH values. Therefore, a pH of 3 (buffer acetate, 0.2 M) was selected as the optimum pH value.

The influence of metaperiodate concentrations on the reaction rate was studied in the concentration range of 6.0×10^{-6} – 8.0×10^{-5} M (Fig. 3). The

results show that the net reaction rate increases with increasing metaperiodate concentration up to 2.0×10^{-5} M and decreases at higher concentrations. This means that the rate of uncatalyzed reaction increases with metaperiodate concentration ($> 2.0 \times 10^{-5}$ M) to a greater extent than the catalyzed reaction and the difference between the rates of catalyzed and uncatalyzed reactions ($\Delta A_s - \Delta A_b$) diminishes at higher metaperiodate concentrations. Therefore, a metaperiodate concentration of 2.0×10^{-5} M was selected for further study.

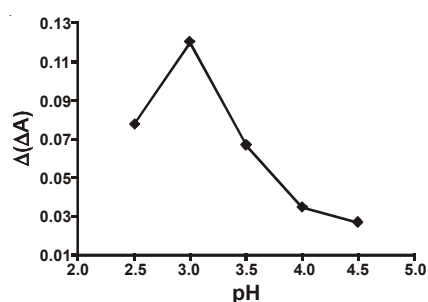


Fig. 2. Influence of pH on the sensitivity, conditions: Pd(II) 40.0 ng/mL; IO_4^- 6×10^{-5} M; Naphthol Green B 9.2×10^{-5} M; temperature 30°C , in fixed time of 0.5-2.0 min from initiation of reaction

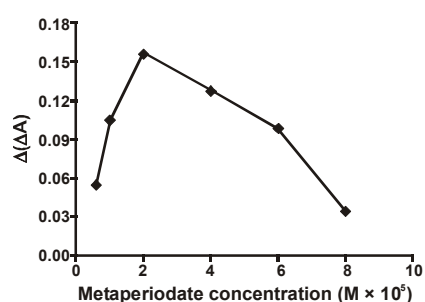


Fig. 3. Effect of metaperiodate concentration on the sensitivity, conditions: pH 3; Pd(II) 40.0 ng/mL; Naphthol green B 9.2×10^{-5} M; temperature 30°C , in fixed time of 0.5-2.0 min from initiation of reaction

Fig. 4 shows the effect of the Naphthol green B concentration on the sensitivity for the range of 5.52×10^{-5} – 1.20×10^{-4} M. This sensitivity (net reaction rate) increases with increasing Naphthol green B concentration up to 9.2×10^{-5} M and decreases at higher concentrations. This may be due to the aggregation of the dye at higher concentrations. Therefore, a final concentration of 9.2×10^{-5} M of Naphthol green B was selected as the optimum concentration.

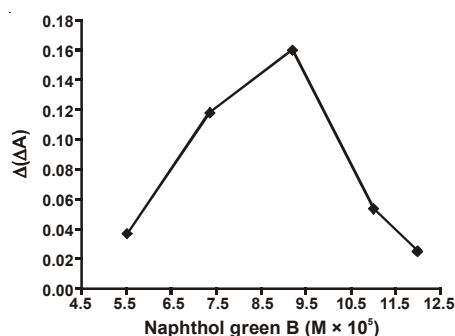


Fig. 4. Effect of Naphthol green B concentration on the reaction rate. Conditions: pH 3; Pd(II) 40.0 ng/mL; IO_4^- 2×10^{-5} M; Naphthol green B 9.2×10^{-5} M; temperature 30°C , in fixed time of 0.5-2.0 min from initiation of reaction

The effect of the temperature on the sensitivity was studied in the range 20-45°C with the optimum of the reagents concentrations. The results showed that, as the temperature increases up to 30°C, the net reaction rate increases, whereas higher temperature values decrease the sensitivity ($\Delta A = \Delta A_s - \Delta A_b$). This means that the rate of uncatalyzed reaction increases with temperature to a greater extent than the rate of the catalyzed reaction and the difference between the rate of the catalyzed and uncatalyzed reaction ($\Delta A = \Delta A_s - \Delta A_b$) diminished at high temperature, therefore, 30°C was selected for further study.

Calibration graph, precision and limit of detection

Calibration graphs were obtained using the fixed-time method. This method was applied to the change in absorbance over an interval of 0.5-3.0 min from initiation of the reaction because it provided the best regression and sensitivity. Under the optimum conditions described above, a linear calibration range 5.0-80.0 ng/mL of Pd(II).

The equation of the calibration graph is $\Delta A = 0.2591 + 3.01CPd$ ($n = 7$, $r = 0.9998$) where ΔA is change in absorbance for the sample reaction for 0.5-3.0 min from initiation of the reaction (catalytic reaction) and C is Pd(II) concentration in ng/mL. The limit of detection from $Y_{LOD} = Y_b + 3S_b$ is 2.2 ng/mL, where, Y_{LOD} is signal for limit of detection, Y_b is average blank signal ($n = 10$) and S_b is standard deviation of blank signal ($n = 10$, uncatalyzed reaction). The relative standard deviation for six replicate determination of 20.0 and 60.0 ng/mL Pd(II) was 2.1 and 2.6 %, respectively.

Interference study: In order to assess the application of the proposed method to synthetic samples, the effect of various ions on the determination of 10.0 ng/mL Pd(II) was studied. The tolerance limit was defined as the concentration of a added ions causing a relative error less than 3 % the results are summarized in Table-1. Many ions did not interfere, even when they were present in 100-fold excess over Pd(II). The results show that method is relatively selective for palladium determination.

TABLE-1
EFFECT OF FOREIGN IONS ON THE DETERMINATION
OF 10 ng/mL Pd(II)

Species	Tolerance limit [$w_{ion}/w_{Pd(II)}$]
Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ , Rb ⁺ , Pb ²⁺ , Zn ²⁺ , Ba ²⁺ , Co ²⁺ , Ni ²⁺ , Te ⁴⁺ , Se ⁴⁺ , C ₂ O ₄ ²⁻ , HSO ₄ ⁻ , ClO ₃ ⁻ , CO ₃ ²⁻ , NO ₃ ⁻ , Tatarate, Borate, Cl ⁻ , Ag ⁺	1000
Rh ³⁺ , Os ⁸⁺ , Br ⁻	800
S ₂ O ₈ ²⁻ , ClO ₃ ⁻	500
Cu ²⁺	200
Fe ²⁺ , I ⁻ , Mn ²⁺	20
Hg ²⁺ , SCN ⁻	5

Sample analysis: In order to evaluate the applicability of the proposed method, water samples and synthetic water samples were analyzed to determine Pd(II) contents with developed method and atomic absorption spectrometry as a reference method¹⁶ (Table-2). The t-test is used directly to the comparison of the means of two methods ($n = 5$) at the confidence level of 95 %. The results show good significant between proposed and reference methods. The recoveries with precise results show good reproducibility and accuracy of the method.

TABLE-2
DETERMINATION OF Pd(II) IN SYNTHETIC SAMPLES

Sample	Pd ²⁺ added (ng/mL)	Pd ²⁺ found (ng/mL) (reference method)	Pd ²⁺ found (ng/mL) (proposed method)	Recovery (%) (proposed method)
River water	–	Less than detection limit	Less than detection limit	–
River water	20.0	19.5 (0.51)*	19.0 (0.42)	95.0
Drinking water	40.0	41.0 (0.87)	41.7 (0.79)	104.3
Drinking water + Rh ³⁺ (10.0 µg/mL) + Os ⁸⁺ (10.0 µg/mL)	20.0	20.9 (0.59)	21.2 (0.51)	106.0

*Standard deviation for five replicated determinations.

Conclusion

The catalytic-spectrophotometric method developed for the determination of Pd(II) is inexpensive, uses readily available reagents, allows rapid determination at low operating costs. With this method, it is possible to determine palladium at levels as low as 2.2 ng/mL without the need for any preconcentration step. Most of ions that have the same property with palladium and often may be found in real samples with palladium and have interferences on the most proposed spectrophotometric methods (such as, Rb⁺, Pb(II), Ag⁺, Rh(III), Os(VIII)) have not interfering on the determination of palladium by developed methods.

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