A Novel and Sensitive Catalytic Method for the Determination of Trace Amounts of Palladium Using High-Performance Liquid Chromatography with Ultraviolet Detection

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Abstract

The experiments show that Pd(II) has a strong catalytic effect on the slowly decolored reaction between malachite green and NaH_2PO_2 in acetate buffer solution (pH 4.4) at 100°C. The catalytic reaction system is investigated using high-performance liquid chromatography (HPLC) with ultraviolet detection at 625 nm. A novel HPLC method for the determination of 0.6–50 ng/mL Pd with a detection limit of 0.2 ng/mL is described. Palladium in real samples is analyzed using this catalytic HPLC method.

Introduction

The rapid development of high-performance liquid chromatography (HPLC) in recent years has considerably expanded the area of its application in scientific, technological, and industrial fields. In addition to the traditional fields, such as the monitoring of environmental pollution and the separation and determination of organic compounds and biologically active substances, HPLC is widely employed in inorganic systems for the separation and determination of metals in the ionic state and in the form of orgametallic and complex compounds (1–3). Several HPLC methods for the determination of palladium that are based on the formation of Pd compexes have been proposed (4–9). The chelates include 1-(Z-pyridylazo)-2-naphthol (4), 2-(5-bromine-2-pyridylazo)-5-diethylaminophenol (5), 1-(2-triazolylazo)-2-naphtholates (6), diethyldithiocarbamate (7), dithiocarbamate (8), and 2-(6-methyl-2-bezothiazolylazo)-5-diethlaminlphenol (9). Catalytic methods with spectrophotometric and voltammetric detection for palladium have been reported; the detection limit is 10^{-8} to 10^{-9} g/mL Pd (10–12). However, the combination of a catalytic reaction with a chromatographic analysis of palladium does not seem to have been reported to date (13–16). This paper reports a study of the chromatographic properties of the catalytic system of Pd(II)–malachite green–NaH_2PO_2 and the development of a novel HPLC method for the determination of trace amounts of Pd.

Experimental

Apparatus

Liquid chromatographic measurement was performed using a Waters model 501 HPLC instrument with a model UV-481 ultraviolet (UV) detector and a model 745 recorder. A model pHS-2 pH meter (Shanghai Analytical Instrument Factory, Shanghai, China) and a Nucleosil (Dalian Institute of Physical Chemistry, Academia Sinica, Dalian, China) C_{18} column (150 mm × 4.6-mm i.d.) with a particle size of 10 μm were also used. The mobile phase was methanol–water (80:20, v/v). The flow rate was 0.6 mL/min. Malachite green was detected at the 625-nm wavelength and quantitated by peak area.

Reagents

A stock solution of Pd(II) (1 mg/mL) in 1.0 mol/L hydrochloric acid was prepared from $PdCl_2$. Working solutions were diluted with double-distilled water before use. Malachite green (1.00×10^{-4} mol/L), NaH_2PO_2 (0.50 mol/L), and an acetate buffer solution (1.0 mol/L, pH 4.4) were used.

Procedure

Three milliliters of the buffer solution (pH 4.4) and 0.4 mL of 1.00×10^{-4} mol/L malachite green were combined in a 10-mL test tube, diluted by filling the tube with water to the 10-mL mark, mixed well, and heated for 10 min in a water bath at 100°C. After cooling with tap water, 10 μL of the solution was injected into the column. The peak area (A_i) at retention time 2.8 min was recorded (Figure 1).

Three milliliters of the buffer solution (pH 4.4), 0.4 mL of

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1.00×10^{-4} mol/L malachite green, 0.6 mL of 0.5 mol/L hypophosphate, and Pd(II) were transferred into a 10-mL test tube, diluted by filling the tube with water, and mixed well. The tube was heated for 10 min in a water bath (100°C). After cooling, 10 µL of the solution was injected into the column. The peak area (A_c) was recorded, and the $\log(A_i/A_c)$ value was obtained. The peak area (A_b) for the uncatalyzed (blank) reaction was measured in a similar manner and the $\log(A_i/A_b)$ value (blank value) was obtained.

The $\log(A_b/A_c)$ values over a range of Pd concentrations were plotted as a function of Pd concentration, and a calibration graph was prepared.

Results and Discussion

Malachite green is a commonly used tribenzomethane dye that has been employed for the catalytic determination of Mn (17,18), Ru (19), and Ir (20) with spectrophotmetric or voltametric detection. In the acetate buffer solution (pH 4.4) at 100°C, trace Pd(II) has a catalytic effect on the slowly decolored reaction between hypophosphate and malachite green (Figure 2).

According to Jiang (20), the following formula can be deduced:

$$\log(C_i/C_b) = K_b \cdot t \qquad \text{Eq 1}$$

$$\log(C_i/C_c) = (K_b + K_c \cdot C_{Pd})t \qquad \text{Eq 2}$$

where C_i is the initial concentration of malachite green and C_b and C_c are malachite green concentrations of the uncatalytic and catalytic systems at t min, respectively. K_b and K_c are the rate constants of the non-catalytic and catalytic reactions, respectively, for use with a fixed concentration of hypophosphate and pH. Because malachite green can be measured by HPLC–UV, and $A = K'C$, where K' is a constant, Eq 1 and 2 may be rewritten as

$$\log(A_i/A_b) = K_b \cdot t \qquad \text{Eq 3}$$

$$\log(A_i/A_c) = (K_b + K_c C_{Pd})t \qquad \text{Eq 4}$$

$$\log(A_b/A_c) = K_c \cdot C_{Pd} \cdot t \qquad \text{Eq 5}$$

Eq 5 shows that the logarithmic term is proportional to the Pd concentration, with the other variables held constant for the given system.

Effects of variables

The effects of hypophosphate and malachite green concentrations, pH, reaction temperature, and time on $\log(A_i/A_b)$ and log (A_i/A_c) values were considered. In general, the effect of each
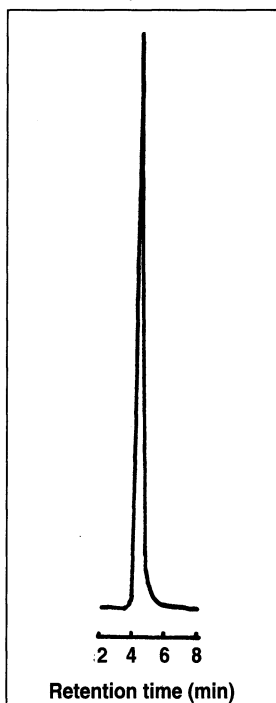
factor leads to higher $\log(A_i/A_c)$ values and lower $\log(A_i/A_b)$ values, which is recommended.

The reaction media, including phosphoric acid, hydrochloric acid, sulfuric acid, and acetate buffer solution, were tested. The results (Figure 3) show that acetate buffer solution (pH 4.4) gives a larger $\log(A_i/A_c)$ value and a lower blank value than the others; therefore, it was chosen for use.

The effects of the variation of hypophosphate concentration on the logarithmic terms is shown in Figure 4. The $\log(A_i/A_b)$ increases slowly with pypophosphate concentration, but the $\log(A_i/A_c)$ increases substantially with hypophosphate concentration (less than 0.025 mol/L), and the logarithmic value reaches a limiting value that is not affected by hypophosphate concentration (more than 0.025 mol/L). A concentration of 0.03 mol/L hypophosphate, which gave the largest $\log(A_b/A_c)$ value, was chosen for use.

Figure 5 shows the relationship between the logarithmic terms and the malachite green concentration (the indicator component). The $\log(A_i/A_c)$ value decreases with the malachite green
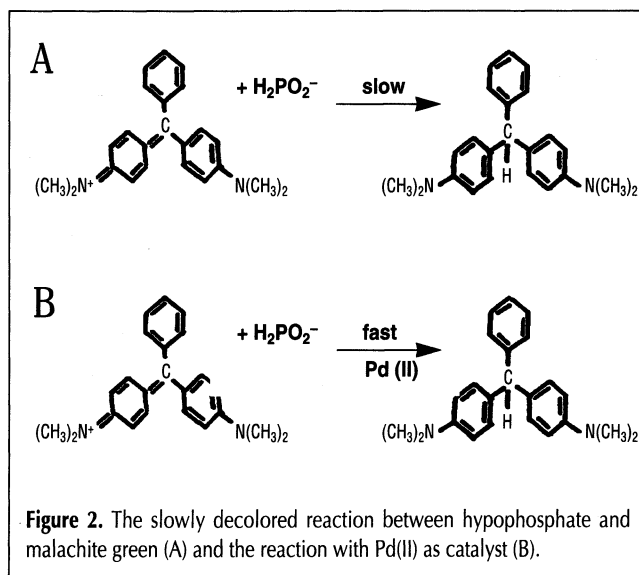
Figure 2. The slowly decolored reaction between hypophosphate and malachite green (A) and the reaction with Pd(II) as catalyst (B).
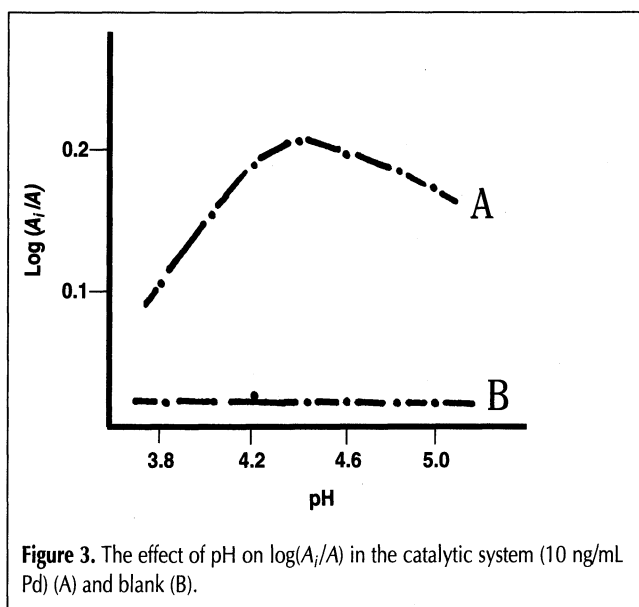
Figure 1. The chromatographic peak of malachite green.

Figure 3. The effect of pH on $\log(A_i/A)$ in the catalytic system (10 ng/mL Pd) (A) and blank (B).
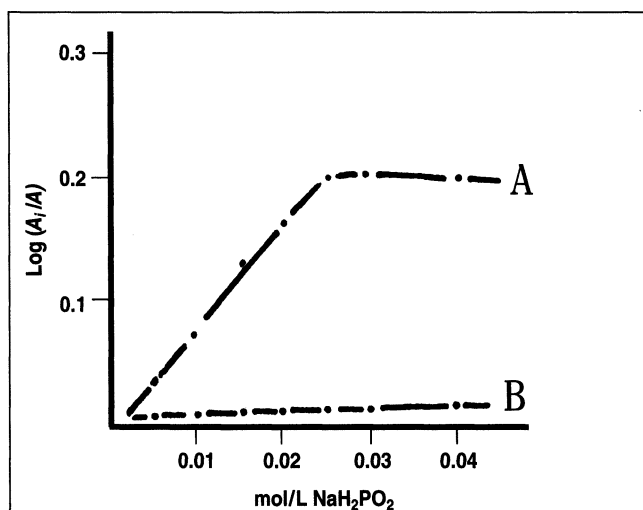
Figure 4. The effect of Na_2PO_2 concentration on $\log(A_i/A)$ in the catalytic system (10 ng/mL Pd) (A) and blank (B).
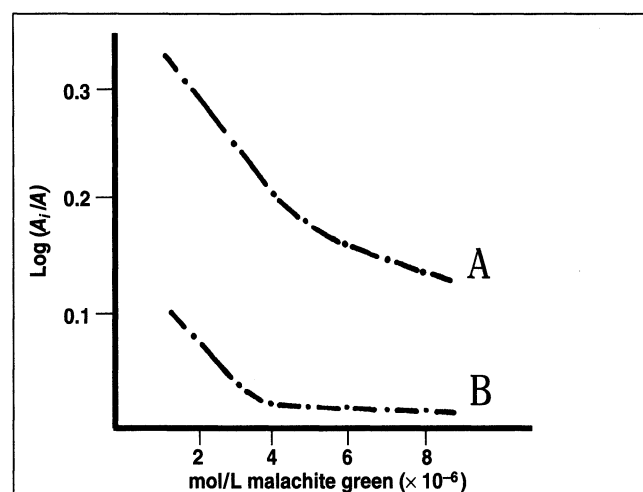

Figure 5. The effect of malachite green concentration on $\log(A_i/A)$ in the catalytic system (10 ng/mL Pd) (A) and blank (B).
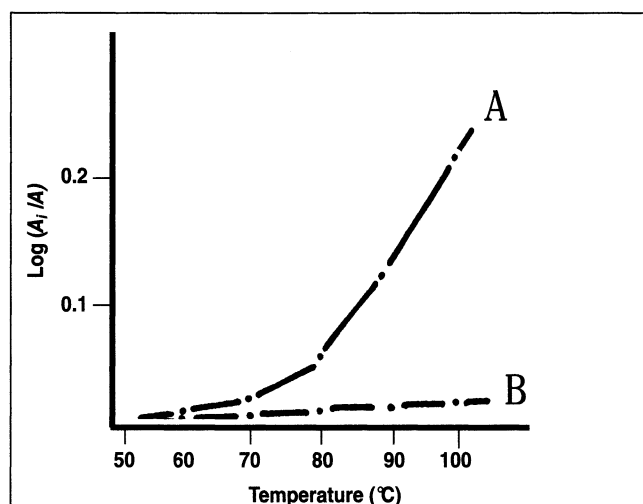

Figure 6. The effect of reaction temperature on $\log(A_i/A)$ in the catalytic system (10 ng/mL Pd) (A) and blank (B).

concentration. The $\log(A_i/A_b)$ value increases for concentrations less than 3.0×10^{-6} mol/L. A malachite green concentration of 4.0×10^{-6} mol/L was chosen because it gave a lower blank.

Figure 6 shows that the $\log(A_i/A_c)$ increases substantially with the reaction temperature, and the blank value increases slowly with the temperature. A reaction temperature of 100°C was selected to achieve high sensitivity. A fixed reaction time of 10 min was chosen as a good compromise between high sensitivity and short analysis time.

Effect of foreign ions

The influence of 28 foreign ions on the catalytic determination of 10 ng/mL Pd was examined. The results are listed in Table I. The tolerance limit was that giving not more than ± 5% error. Most common ions did not interfere with the catalytic determination of Pd. The metal ions Au(III) and Cu(II) have catalytic effects on the indicator reaction when they exceed their tolerance limits by 20- and 10-fold, respectively. Table I indicates that this catalytic method for Pd has good selectivity.

Calibration graph

There are three procedures (fixed time, fixed concentration, and initial rate) in kinetic analysis. Under the reaction temperature of 100°C, the initial rate and fixed concentration procedures were not suitable for the catalytic system; the fixed time procedure is convenient and was chosen for use in this experiment. Under optimal experimental conditions, a calibration graph from 0.6 to 50 µg/L Pd was obtained using the fixed time procedure. The relative standard deviation of the method for 10 and 30 µg/L Pd was 1.6% and 1.0% (10 replications), respectively. The detection limit is 0.2 µg/L Pd. It is one of the most sensitive HPLC methods for Pd.

Analysis of sample

The sample solutions were prepared as follows (12): a 10-mg sample of PdC catalyst was placed in a 100-mL beaker, and 3 mL concentrated H_2SO_4 and 3 mL $HClO_4$ were added. The solution was heated to dissolve the sample and then vaporized to dryness. Three milliliters of concentrated HCl was added, and the solution was transferred into a 50-mL volumetric flask

Table I. Influence of Foreign Ions

Tolerance limit (ion/Pd)	Ion added
1×10^5	PO_4^{3-}, SO_4^{2-}, NO_3^-, SiO_3^{2-}, Ca(II), Al(III)
6×10^4	F-, Ag(I), Bi(III)
1×10^4	SO_3^{2-}, Br-, Ni(II), Zn(II)
1×10^3	Cd(II), V(V), Te(IV), Fe(II)
500	Mn(II), Pt(IV), Fe(III), Cr(III)
200	Ir(IV), Rh(III)
100	O_s(IV)
20	Au(II)*
10	Cu(II)*

* Excess also has a catalytic effect on the reaction.

Table II. Analysis of Pd in Catalyst

Sample	Single determination values (%)			Mean value (%)	RSD (%)	Oscillopolarography (%)
PdC catalyst	2.43	2.45	2.48	2.45	1.0	2.50
PdAl catalyst	0.0266	0.0270	0.0275	0.0270	1.7	0.0272

and diluted further with water as necessary. A 10-mg sample of PdAl catalyst was placed in a 100-mL beaker, and 3 mL of mixed acid (V_{HCl}–V_{HNO_3}, 3:1) was added. The solution was heated to dissolve the sample and then vaporized to dryness. The residue was dissolved with 4 mL of 0.1 mol/L HCl, transferred into a 100-mL volumetric flask, and diluted to 100 mL with water.

The catalytic method was applied to the analysis of Pd in the catalysts. The results are given in Table II and are in good agreement with those obtained by oscillopolarography.

Conclusion

A new catalytic method that utilizes HPLC–UV was developed for the determination of Pd in catalyst samples. The method has a low detection limit of 0.2 µg/L Pd and good selectivity. It is one of the most sensitive methods among catalytic or HPLC methods for Pd.

Acknowledgments

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