

Color Reaction of 2-(2-Quinolylazo)-5-Dimethylaminoaniline with Palladium and Its Application

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A new chromogenic reagent, 2-(2-quinolylazo)-5-dimethylaminoaniline (QADMAA) was synthesized. A sensitive, selective and rapid method for the determination of palladium based on the rapid reaction of palladium(II) with QADMAA was developed. In the presence of 0.5-2.5 mol L⁻¹ of hydrochloric acid solution and cetyl trimethylammonium bromide medium QADMAA reacts with palladium to form a violet complex with a molar ratio of 1:2 (palladium to QADMAA). The molar absorptivity of the chelate is $1.35 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 600 nm. Beer's law is obeyed in the range of 0.01 to 0.6 $\mu\text{g mL}^{-1}$. The detection limit is 1.2 $\mu\text{g L}^{-1}$. This method has been applied to the determination of palladium with good results.

Key Words: 2-(2-quinolylazo)-5-dimethylaminoaniline, palladium, spectrophotometry.

Introduction

Palladium is an important element for industry and biological systems¹⁻². Many sensitive instruments, such as spectrofluorimetry, X-ray fluorescence spectrometry, neutron activation analysis, atomic absorption spectrometry and chemiluminescence have been widely applied to the determination of palladium. However, the spectrophotometric method has the advantages of being simple and not requiring expensive or complicated test equipment. For this reason, a wide variety of spectrophotometric reagents, such as azo dyes, rhodanine derivatives, porphyrin ligands, thiourea derivatives, 8-aminoquinoline derivatives and nitroso dye have been developed for the determination of palladium³⁻¹⁰. Each chromogenic system has its advantages and disadvantages with respect to sensitivity, selectivity and convenience. However, the use of 2-quinolylazo derivatives for the determination of palladium has received little attention.

In our previous studies, some 2-quinolylazo-phenol reagents were reported for the determination of metal ions¹¹⁻¹³. This kind of reagent has a higher sensitivity than pyridylazo reagents because of its larger

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conjugated system. However, the 2-quinolylazo-phenol reagent has also the disadvantage of poor selectivity because both the oxygen and nitrogen atoms donate to the metal ions. To select a more sensitive and selective reagent, we synthesized 2-(2-quinolylazo)-5-dimethylaminoaniline (QADMAA) and thoroughly studied the color reaction of QADMAA with palladium. This reagent has a higher selectivity than 2-quinolylazo-phenol reagents because it only donates nitrogen atoms to metal ions. Based on the color reaction of QADMAA with palladium, a highly sensitive, selective and rapid method for the determination of palladium was developed.

Experimental

Apparatus

A UV-160 A spectrophotometer (Shimadzu Corporation, Tokyo) equipped with 1 cm cells was used for all absorbance measurements. The pH values were determined with a Beckman Φ -200 pH meter (Beckman Instruments, Fullerton, CA, USA).

Synthesis of QADMAA

2-Aminoquinoline (6.9 g, 0.048 mol) was dissolved in 500 mL of anhydrous ethanol. To this was added sodamide (2.0 g, 0.051 mol) and the mixture was refluxed in a boiling water bath for 5 h, followed by the addition of isoamyl nitrite (7.4 mL, 0.052 mol). The solution was refluxed for 30 min in a boiling water bath. Then the solution was cooled and placed overnight under 0 °C. The diazo salt was obtained by filtering the precipitates in this solution. The yield is 95%. The diazo salt was dissolved in 200 mL of anhydrous ethanol, followed by the addition of *m*-dimethylaminoaniline (5.7 g; 0.042 mol). Carbon dioxide was ventilated into the solution with stirring until the pH level reached about 8.0. The solution was left for 2 days and evaporated to dryness. The residue was recrystallized with 30% ethanol. QADMAA was obtained with a 36% yield. The structure of QADMAA was verified by elemental analysis, IR, ¹HNMR and MS. IR (KBr) (cm⁻¹): 3300 (ν_{N-H}), 1600, 1560, 1505, 1426 ($\nu_{C=C}$, $N=N$), 1380, 1323 (ν_{C-N}), 2850 (ν_{C-H}), 1465 (ν_{C-H}), 3050, 3015 (ν_{Ar-H}), 1175, 1120, 865, 780, 720 (ν_{Ar-H}). ¹HNMR (solvent: *d*₆-acetone) (δ ppm): 2.28 (s, 6H, N-CH₃), 3.69 (s, 2H, -N-H₂); 6.86 ~ 7.85 (m, 9H, Ar-H). MS: 291 (M⁺). Elemental analysis: C₁₇H₁₇N₅ found (calculated) C 69.82 (70.08), N 23.83 (24.04), H 6.04 (5.88). All these show that the QADMAA has the structure shown in Figure 1.

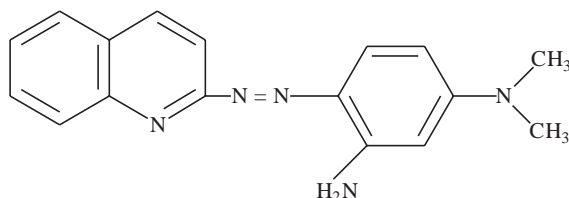


Figure 1. The structure of QADMAA.

Reagents and material

All the solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). A 5×10^{-4} mol L⁻¹ quantity of QADMAA solution was prepared by dissolving

QADMAA with 95% ethanol. A stock standard solution of palladium (1.0 mg mL^{-1}) was obtained from the Chinese Standard Center, and a working solution of $2.0 \mu\text{g mL}^{-1}$ prepared by diluting this solution. 5 mol L^{-1} of hydrochloric acid was used. Cetyl trimethylammonium bromide (CTMAB) solution (1.0% (w/v)) was prepared by dissolving CTMAB with 20% ethanol. All chemicals used were of analytical grade unless otherwise stated.

The river water was collected from the Panglog River, Kunming, P.R. China according to the method described in the literature ¹⁴. The plating effluents were collected from the Yunnan Smelt Factory, Kunming, P.R. China following the method described in the literature ¹⁴. The catalyst for determination was a Chinese certified reference standard material (GBW(E)070029) obtained from the Chinese Standard Material Center. The certified standard palladium value is $0.538\% \pm 0.005\%$.

General procedure

To a standard or sample solution containing no more than $0.25 \sim 15 \mu\text{g}$ of Pd(II) in a 25 mL calibrated flask were added 5 mL of 5 mol L^{-1} hydrochloric acid, 4.0 mL of $5 \times 10^{-4} \text{ mol L}^{-1}$ QADMAA solution and 2.0 mL of 1.0% CTMAB solution. The mixture was diluted to a volume of 25 mL and mixed well. After 10 min, the absorbance was measured in a 1 cm cell at 600 nm against a reagent blank prepared in a similar way without palladium.

Results and Discussion

Absorption Spectra

The absorption spectra of QADMAA and its Pd(II) complex are shown in Figure 2. The absorption peaks of QADMAA and its complex are located at 440 nm and 600 nm.

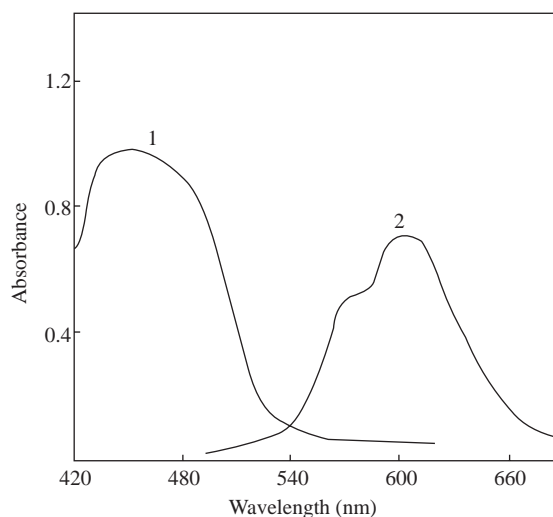


Figure 1. Absorption spectra of QADMAA and its Pd(II) complex. 1 QADMAA-CTMAD complex against reagent blank. The PD(II) concentration is $4.50 \times 10^{-6} \text{ mol L}^{-1}$, the QADMAA concentration is $3.64 \times 10^{-6} \text{ mol L}^{-1}$, and the other conditions are as in the standard procedure.

Effect of acidity

The results showed that the optimal condition for the reaction of Pd(II) with QADMAA is in the an acid medium. Therefore, the effect of hydrochloric acid, sulfuric acid, perchloric acid, phosphoric acid and the like on the color reaction of Pd(II) with QADMAA was studied. The experiments show that hydrochloric acid has the best effect, and the concentration of hydrochloric acid within 0.5-2.5 mol L⁻¹ was found to give a maximum and constant absorbance. Therefore, 5 mL of 5 mol L⁻¹ of hydrochloric acid is recommended.

Effect of surfactants

The effect of surfactants on the Pd(II)-QADMAA chromogenic system was studied. In the presence of cationic surfactant or nonionic surfactant medium, the absorption of the chromogenic system increases markedly. The experiments show that CTMAB is the best additive. The use of 1 ~ 4 mL of 1.0% CTMAB solution gives a constant and maximum absorbance. Accordingly, the use of 2 mL is recommended.

Effect of QADMAA concentration

For up to 15 µg of Pd(II), the use of 3.5 ~ 5 mL of 5 × 10⁻⁴ mol L⁻¹ of QADMAA solution has been found to be sufficient for a complete reaction. Accordingly, 4 mL of QADMAA solution was added in all further measurements.

Stability of the chromogenic system

After mixing the components, the absorbance reaches its maximum within 8 min at room temperature and remains stable for 6 h in aqueous solution. The chelates remain for stable at least 20 h.

Calibration curve and sensitivity

The calibration curve shows that Beer's law is obeyed in the concentration range of 0.01 to 0.6 µg of Pd(II) mL⁻¹, The linear regression equation obtained was $A = 1.294 C(\mu\text{g mL}^{-1}) + 0.0158$ ($r = 0.9996$). The molar absorptivity was calculated to be 1.35 × 10⁵ L.mol⁻¹.cm⁻¹ at 600 nm. The relative standard deviation for the slope of the calibration curve (11 repetitions) was 0.86%. The detection limit, based on 3 times the relative standard deviation of the blank, is 1.2 µg L⁻¹.

Composition of the complex

The composition of the complex was determined by the continuous variation and molar ratio methods. Both showed that the molar ratio of Pd(II) to QADMAA is 1:2.

Interference

The selectivity of the proposed method was investigated by the determination of 5 µg of 25 mL⁻¹ of Pd(II) in the presence of various ions within a relative error of ±5%. The results are given in Table 1 and shows that the Ni(II) and Co(II) have low tolerance limits. However, the Ni(II) and Co(II) can be masked with citric acid. The tolerance limits reaches 1 mg for Co(II) and 0.5 mg for Ni(II) when masked with citric acid. This method is highly selective.

Table 1. Tolerance limits for the determination of 5 μg of Pd(II) with QADEAA (relative error $\pm 5\%$).

Ion added	Tolerance (mg)
NO_3^- , K^+ , borate, Na, Cl^- , Mg^{2+} , SO_4^{2-} , ClO_4^-	200
Li^+ , Al^{3+} , PO_4^{3-} , NO_2^- , ClO_3^-	20
Ca^{2+} , Sr^{2+} , IO_3^- , BrO_3^- , B(III)	10
Mn^{2+} , Ce(IV), Fe^{3+} , Mo(VI), V(V)	5
Ti(IV), Bi(III), Cr(VI), Ba^{2+} W(VI), U(IV), $[\text{Co}^{2+}]^*$	1
Cd^{2+} , Pd^{2+} , Cr^{3+} , La^{3+} , Zn^{2+} , Zr(IV), $[\text{Ni}^{2+}]^*$	0.5
Bi(III), Pb^{2+} , Hg^{2+} , Sb^{3+} , Th(IV), Sn(IV)	0.1
Se(IV), Te(IV), Au^{3+} , Cu^{2+} , Ag^+	0.05
Ni^{2+} , Co^{2+}	0.01

*masked with 2 mL of 10% citric acid.

Application

The proposed method has been successfully applied to the determination of palladium in water and catalyst.

For a water sample, an appropriate volume (plating effluents 20 mL, river water 500 mL) of water sample was placed in a 500 mL flask. The samples were concentrated to about 10 mL by heating on a hot plate. Then 5 mL of concentrated nitric acid and 2 mL of 30% hydrogen peroxide was added to this solution. The mixture was heated on a hot plate and evaporated to near dryness. The residue was dissolved with 5 mL of 5% hydrochloric acid and transferred into a calibrated flask. Then 2 mL of 10% citric acid was added to mask the nickel and cobalt, and the solution was neutralized with sodium hydroxide. The palladium content was analyzed using the general procedure. The recovery of palladium was determined by adding 1.0 μg of palladium to the water samples. A standard method using flame atomic absorption spectrometry together with preconcentration as described in the literature¹⁴ was also used as a reference method. The results are shown in Table 2.

Table 2. Determination of palladium in the water sample.

Samples	AAS method	Found	RSD% (n=5)	Recovery (%) (n=5)
River water	0.0176 ($\mu\text{g mL}^{-1}$)	0.0162 ($\mu\text{g mL}^{-1}$)	2.5	94
Plating effluents	0.248 ($\mu\text{g mL}^{-1}$)	0.237 ($\mu\text{g mL}^{-1}$)	2.1	96
Catalyst	0.532 (%)	0.536 (%)	1.2	101

For the catalyst, 0.1 g of sample was weighed accurately into a Teflon high-pressure microwave acid-digestion bomb (Fei Yue, Analytical Instrument Factory, Shanghai, China) and 3.0 mL of concentrated nitric acid, 2 mL of hydrochloric acid and 5.0 mL of 30% hydrogen peroxide were added. The bombs were sealed tightly and then positioned on the carousel of the microwave oven (Model WL 5001, 1000 W, Fei Yue Analytical Instrument Factory, Shanghai, China). The system was operated at full power for 10 min. The digest was evaporated to near dryness. The residue was dissolved with 10 mL 10% hydrochloric acid, and then transferred into a 50 mL calibrated flask and diluted to volume with 10% hydrochloric acid. Then 5 mL of 10% citric acid was added to mask the nickel and cobalt. The palladium content was analyzed according to the general procedure. The recovery of palladium was carried out using the added 1.0 μg of palladium in sample, and a standard method using flame atomic absorption spectrometry as described in the literature¹⁵ was used as a reference method. The results are shown in Table 2.

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