

Studies on the Solid Phase Extraction and Spectrophotometric Determination of Palladium with 2-(2-Quinolylazo)-5-Dimethylaminoaniline as Chromogenic Reagent

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A sensitive, selective and rapid method for the determination of palladium with 2-(2-quinolylazo)-5-dimethylaminoaniline (QADMAA) as chromogenic reagent and the solid phase extraction of the Pd(II)-QADMAA chelate with a reversed phase polymer-based C₁₈ cartridge was developed. In the presence of 0.05-0.5 mol/L of hydrochloric acid solution and cetyl trimethylammonium bromide (CTMAB), QADMAA reacts with palladium(II) to form a violet complex of a molar ratio 1:2. This chelate was enriched by the solid phase extraction with a polymer-based C₁₈ cartridge. The enrichment factor of 200 was obtained by elution of the chelates from the cartridge with minimal amount of isopentyl alcohol. In the isopentyl alcohol medium, the molar absorptivity of the chelate is $1.41 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 618 nm. Beer's law is obeyed in the range of 0.01-1.2 $\mu\text{g/mL}$. The relative standard deviation for eleven replicate sample of 0.2 $\mu\text{g/L}$ level is 2.05 %. The detection limit reaches 0.02 $\mu\text{g/L}$ in the original samples. This method had been applied to the determination of palladium in environmental samples with good precision.

Key Words: 2-(2-Quinolylazo)-5-dimethylaminoaniline, Palladium, Spectrophotometry, Solid phase extraction.

INTRODUCTION

Palladium has been applied in various ways as a hydrogenation catalyst, microcontactors in the electronics, hard alloy in dentistry and as a component in the three-way catalysts in automobile exhaustgas catalytic beads. Due to the introduction of palladium, platinum and rhodium for use in catalytic converters in motor vehicles, the emission by plants has led to polluted soil. Palladium is thought to be one of the strongest allergens from a health hazard viewpoint^{1,2}. For these reasons, rapid and accurate Pd determination methods for process, quality and pollution control are

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valuable. Many sensitive instruments, such as spectrofluorimetry, X-ray fluorescence spectrometry, neutron activation analysis, atomic absorption spectrometry, chemiluminescence have been applied to the determination of palladium. But the spectrophotometric method still 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, nitroso dye, *etc.* 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 routine spectrophotometric methods are often not sensitive enough to determine low concentration of palladium ion in environmental samples, the palladium concentration only $\mu\text{g/L}$ or ng/L level.

Solid phase extraction is an attractive technique because of notable advantages. In our previous works, the determination of some trace metal ions by solid phase extraction with reversed phase silica-bond C_{18} cartridge was studied¹¹⁻¹⁵. However, the routine reserved phase silica-bond C_{18} cartridge only can use in pH range of 2-8. To meet the need of metal chelate enrichment by solid phase extraction in acid medium, in this paper, the colour reaction of 2-(2-quinolinylazo)-5-dimethylaminoaniline (QADMAA) with palladium and the solid phase extraction of Pd-QADMAA chelate with a reversed phase polymer-based C_{18} cartridge have been reported. The polymer-based C_{18} is manufactured from a hydrophilic methacrylate polymer, which is functionalized with C_{18} ligands. It is a reversed-phase solid phase cartridge provides a broad range of solvents choices and a pH range from 0-14. By using the polymer-based C_{18} cartridge, the Pd-QADMAA chelate was enriched by solid phase extraction in hydrochloric acid medium and the enrichment fact of 200 was achieved. Base on this, a highly sensitive, selective and rapid method for the determination of palladium in environmental samples was developed.

EXPERIMENTAL

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 of QADMAA solution was prepared by dissolving QADMAA with 95 % of ethanol. A stock standard solution of palladium (0.1 mg/mL) was obtained from Chinese Standard Center and a work solution of $2.0 \mu\text{g/mL}$ was prepared by diluting this solution. A 5 mol/L 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. A UV-160 A spectrophotometer (Shimidzu Corporation, Tokyo, Japan) equipped with

1 cm microcells (0.5 mL) was used for all absorbance measurements. The pH values were determined with a Beckman Φ -200 pH meter (Beckman Instruments, Fullerton, CA, USA). The extraction was performed on water solid phase extraction (SPE) device (It can prepare twenty samples simultaneously) and a Polymer C18™ polymer-based C₁₈ cartridge (Beijing Genosys Technologies, P.R. China) was used.

Synthesis of QADMAA¹⁴: 2-Aminoquinoline (7.2 g) was dissolved in a 500 mL anhydrous ethanol, to which sodamide (2.0 g) was added and the solution was refluxed for 5 h in boiling water bath and then isoamyl nitrite (7.4 mL) was added. The solution was refluxed for 0.5 h in boiling water bath. The solution was cooled and placed over night at 0°C. The diazo salt was obtained by filtering this solution with a yield of 95 %. The diazo salt was dissolved in 200 mL anhydrous ethanol and *m*-dimethylaminoaniline (5.4 g) was added. The carbon dioxide was flushed into the solution with stirring until the pH reached about 8.0. The solution was placed for two days, then diluted the solution with 400 mL water and extracted with chloroform. The chloroform was evaporated and recrystallized the residue with 35% ethanol. QADMAA (Fig. 1) was obtained with a yield of 32 %.

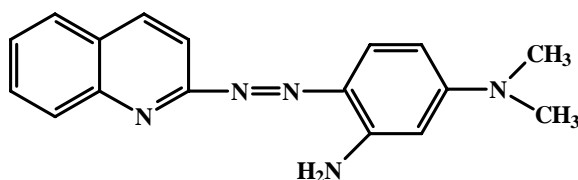


Fig. 1. Structure of 2-(2-quinolyldiazo)-5-dimethylaminoaniline

General procedure: To a standard or sample solution containing less than 1.2 μg of Pd(II) in a 200 mL of calibrated flask, 5 mol/L hydrochloric acid (5 mL), 5×10^{-4} mol/L QADMAA solution (6 mL) and 1 % CTMAB solution (5.0 mL) were added. The mixture was diluted to the volume of 200 mL and mixed well. After 10 min, the solution was passed through the C₁₈ cartridge at a flow rate of 20 mL/min. The retained chelates were eluted from the cartridge with 1 mL of isopentyl alcohol at a flow rate of 5 mL/min. The absorbance of the eluant was measured in a 1 cm cell at 618 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 Fig. 2. The absorption peaks of QADMAA and its complex are located at 440 and 618 nm.

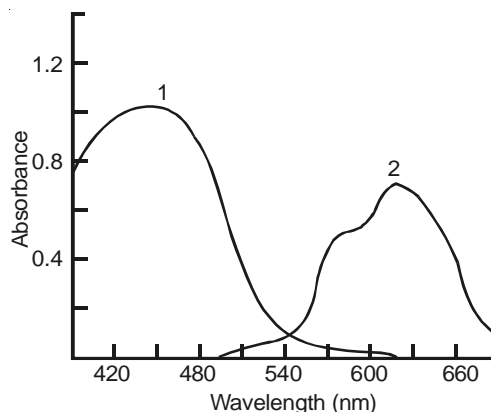


Fig.2 Absorption spectra of QADMAA and its Pd(II) complex, 1) QADMAA-CTMAB blank against water; 2) QADMAA-Pd(II)-CTMAB complex against water

Effect of acidity: The results showed that the optimal condition for the reaction of Pd(II) with QADMAA is in the acid medium. Therefore, the effect of hydrochloric acid, sulfuric acid, perchloric acid and phosphoric acid, on the colour reaction of Pd(II) with QADMAA was studied. Experiment shows that hydrochloric acid has the best effect and the concentration of hydrochloric acid within 0.05-0.5 mol/L was found to give a maximum and constant absorbance. So 5 mL of mol/L of hydrochloric acid was recommended.

Effect of QADMAA concentration: For up to 1.2 μg of Pd(II), the use of about 5-8 mL of 5×10^{-4} mol/L of QADMAA solution has been found to be sufficient for a complete reaction. Accordingly, 6 mL of QADMAA solution was added in all further measurement.

Solid phase extraction: In this study, QADMAA can react with Pd(II) and form stable chelates in acid medium. To meet the need of metal chelate enrichment by solid phase extraction in acid medium, a reversed phase polymer-based C_{18} cartridge with pH range 0-14 was selected. The polymer-based C_{18} is manufactured from a hydrophilic methacrylate polymer, which is functionalized with C_{18} ligands. It is a reversed-phase solid phase cartridge provides a broad range of solvent choices and a pH range from 0-14.

Both the enrichment and the elution were carried out to investigate the retention of QADMAA and its Pd(II) chelate on the cartridge. It was found that the QADMAA and its Pd(II) chelate was retained on the cartridge quantitatively when they pass the cartridge as hydrochloric acid medium. The capacity of the cartridge was determined as 32 mg for Pd(II)-QADMAA chelate in a 200 mL of solution. In this experiment, the maximum amount palladium is only 1.2 μg . Therefore, the cartridge has adequate capacity to enrich the Pd(II)-QADMAA chelate.

In order to choose a proper eluant for the retained QADMAA and its Pd(II) chelate various organic solvents were studied. For eluting the Pd-QADMAA chelates from the cartridge, 0.8 mL of isopentyl alcohol, 1.2 mL of acetone, 1.4 mL of acetonitrile, 2.0 mL of ethanol and 2.2 mL of methanol are required. The maximal enrichment was achieved when isopentyl alcohol was selected as eluant. So the isopentyl alcohol was selected as eluant. The experiment show that it was easier to elute the retained QADMAA and its Pd(II) chelate in reverse direction than in forward direction, so it is necessary to upturned cartridge when elution. 1.0 mL of isopentyl alcohol was sufficient to elute the QADMAA and its Pd(II) chelate from cartridge at a flow rate of 5 mL/min. The volume of 1.0 mL was selected.

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. After extraction of Pd-chelate the isopentyl alcohol medium, the chelate was stable for at least 12 h.

Calibration curve and sensitivity: The calibration curve shows that Beer's law is obeyed in the concentration range of 0.01-1.2 $\mu\text{g Pd(II)}$ per mL in the measured solution. The linear regression equation obtained was: $A = 1.328 C (\mu\text{g/mL}) + 0.0315$, ($r = 0.9993$). The molar absorptivity was calculated to be $1.41 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 618 nm. The detection limit, based on 3 times the relative standard deviation of the blank is 0.02 $\mu\text{g/L}$ in the original samples. The relative standard deviation at a concentration level of 0.2 $\mu\text{g/L}$ (11 repeat determination) was 2.05%.

Composition of the complex: The composition of the complex was determined by continuous variation and molar ratio method. 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 1.0 $\mu\text{g}/200 \text{ mL}$ of Pd(II) in the presence of various ions within a relative error of $\pm 5\%$ are given in Table-1. The results shows that the Ni^{2+} and Co^{2+} have a low tolerance limits. However, the Ni^{2+} and Co^{2+} can masked with citric acid. The tolerance limits reaches 0.2 mg for Co^{2+} and 0.1 mg for Ni^{2+} when masked with citric acid. This method is high selectivity.

Applied to the water sample: For water sample, the samples were acidified with hydrochloric acid and filtrated by 0.45 μm filter. The palladium contents were analyzed according to the general procedure. The results (deducted the reagents blank) are shown in Table-2. An ICP-MS method as described in the literature¹⁶ was used as a reference method and the result are shown in Table-2.

TABLE-1
TOLERANCE LIMITS FOR THE DETERMINATION OF 1.0 µg OF
Pd(II) WITH QADMAA (RELATIVE ERROR ± 5%)

Ion added	Tolerate (mg)
NO ₃ ⁻ , K ⁺ , BO ₃ ³⁻ , Na ⁺ , Cl ⁻ , Mg ²⁺ , SO ₄ ²⁻ , ClO ₄ ⁻	10.000
Li ⁺ , Al ³⁺ , PO ₄ ³⁻ , NO ₂ ⁻ , ClO ₃ ⁻	2.000
Ca ²⁺ , Sr ²⁺ , IO ₃ ⁻ , BrO ₃ ⁻ , B ³⁺	0.500
Mn ²⁺ , Ce ⁴⁺ , Fe ³⁺ , Mn ⁶⁺ , V ⁵⁺	0.300
Ti ⁴⁺ , Bi ³⁺ , Cr ⁶⁺ , Ba ²⁺ , W ⁶⁺ , U ⁴⁺ , [Co ²⁺]*	0.100
Cd ²⁺ , Pd ²⁺ , Cr ³⁺ , La ³⁺ , Zn ²⁺ , Zr ⁴⁺ , [Ni ²⁺]*	0.050
Bi ³⁺ , Pb ²⁺ , Hg ²⁺ , Sb ³⁺ , Th ⁴⁺ , Sn ⁴⁺	0.030
Se ⁴⁺ , Te ⁴⁺ , Au ³⁺ , Cu ²⁺ , Ag ⁺	0.020
Ni ²⁺ , Co ²⁺	0.001

*masked with 2 mL of 10% citric acid

TABLE-2
DETERMINATION OF PALLADIUM IN THE WATER
AND SOIL SAMPLES

Samples	ICP-MS method	Found	RSD% (n-5)	Recover (%) (n-5)
River water	4.65 (µg/L)	4.71 (µg/L)	3.2	88
Planting effluents	21.6 (µg/L)	20.20 (µg/L)	3.4	93
Soil (Near highway)	132 (ng/g)	128.00 (ng/g)	3.3	94
Soil (General)	35.2 (ng/g)	36.30 (ng/g)	2.6	91

Analysis of soil: A 5.0 g of soil sample is weighed into a 250 mL of teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China). To which, 50 mL of aqua regia was added. The bombs were sealed tightly and then kept in a microwave oven (Model WL 5001, 1000 W, Fei Yue Analytical Instrument Factory, Shanghai, China). The system was operated at full power for 0.5 h. The digested material was evaporated to incipient dryness. Then, 5 % hydrochloric acid (50 mL) was added and heated close to boiling to leach the residue. After cooling to room temperature, the residue was filtered and the undissolved residue was washed with 5% hydrochloric acid for two times. The leachate was collected into a 200 mL of calibrated flask quantitatively and the palladium contents were analyzed according to the general procedure. The results were also shown in Table-2. An ICP-MS method as described in the literature¹⁶ was used as a reference method and the result are also shown in Table-2.

Conclusion

This method has been found highly selective and sensitive. 2-(2-Quinolylazo)-5-dimethylaminoaniline (QADMAA) is one of the sensitive and selective spectrophotometric reagents for palladium. The molar absorptivity of the chelate reaches $1.41 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ in measured solution. Most foreign ions do not interfere with the determination when masked with citric acid. By solid phase extraction with C₁₈ cartridge, the QADMAA-Pd(II) chelate in 200 mL solution can be concentrated to 1.0 mL, the enrichment factor of 200 was achieved. The detection limit reaches 0.02 µg/L in original samples and µg/L level of palladium in environmental samples can be determined with good results.

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