

Solid Phase Extraction and Spectrophotometric Determination of Palladium Using 2-Methyl-5-(4-carboxylphenylazo)-8-hydroxyquinoline as a Chromogenic Reagent

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Synthesis and application of 2-methyl-5-(4-carboxylphenylazo)-8-hydroxyquinoline (MCPAHQ) as a new chromogenic reagent for the determination of palladium has been described. Highly sensitive, selective and fast method for determination of palladium based on its rapid reaction with MCPAHQ and solid phase extraction of the coloured chelate on the CLEAN-UP® C₁₂ cartridge has been developed. In the presence of pH 3.2 citric acid-sodium citrate buffer solution and emulsifier-OP medium, MCPAHQ reacted with palladium to form coloured chelate of palladium-to-MCPAHQ molar ratio of 1:2. This chelate was enriched by the solid phase extraction with a reversed phase C₁₂ cartridge. The enrichment factor of 50 was obtained by elution of the chelates from the cartridge with minimal amount of ethanol. In ethanol medium, the molar absorptivity of the chelate was $2.15 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 510 nm. Beer's law is obeyed in the range of 0.01-0.6 µg/mL. The relative standard deviation for eleven replicate sample of 0.8 µg/L level was 2.2 %. In the original sample detection limit was 0.1 µg/L. The proposed method was applied to the determination of trace palladium in automobile exhaust gas converter catalysts with good results.

Key Words: 2-Methyl-5-(4-carboxylphenylazo)-8-hydroxyquinoline, Palladium, Solid phase extraction, Spectrophotometry.

INTRODUCTION

Palladium is one of the most important noble metals due to its wide application both in chemical industry and in instrument production. Palladium plays a decisive role in the performance of exhaust systems and is worldwide applied in vehicles and in some household utensils to reduce the emission of carbon monoxide, nitrogen oxides and hydrocarbons. Recently emission of palladium from the abrasion of automotive catalytic converters to the environment has significantly increased¹. In addition, an increased uptake of palladium by plants has led to soil pollution. Palladium is thought to be one of the strongest allergens from a health hazard viewpoint². For these reasons, establishing sensitivity and accurate methods for the determination of palladium during industrial processes and quality and pollution control is important.

Several sophisticated techniques, such as total reflection X-ray fluorescence spectrometry (TXRF), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), electrochemical, spectrofluorimetry and atomic absorption spectrometry have been widely applied to the determination of palladium³⁻⁵. However, some factors such as instrumentation costs, technical know-how and consumables and costly maintenance of the equipment restrict the wider applicability of these techniques, particularly in the fieldwork and in laboratories with limited budgets in developing countries. The development of a simple, sensitive and selective method for determination of trace amounts of palladium is therefore desirable.

Spectrophotometric methods are essential in trace analysis due to their simplicity and low operating costs. Usually they involve the use of chromogenic agents. Already reported chromogenic systems for the determination of palladium have specific advantages and disadvantages with respect to sensitivity, selectivity and rapidity⁶⁻⁸. Standard spectrophotometric methods are, however, often not enough sensitive to determine palladium ions at low concentrations (at a $\mu\text{g/L}$ level). Determination of such low concentrations of palladium usually requires a pre-concentration step. For this purpose, one may utilize solid phase extraction due to its apparent advantages⁹⁻¹¹. Various materials like synthetic resins including amberlite XAD, chromosorb, ambersorb, diaion resins and natural adsorbents including activated carbon, alumina and wool have been used in solid phase extraction of trace metal ions¹²⁻¹⁶. In this paper, colour reaction of 2-methyl-5-(4-carboxylphenylazo)-8-hydroxyquinoline (MCPAHQ) with palladium and solid phase extraction of Pd(II)-MCPAHQ chelate on the CLEAN-UP[®] C₁₂ cartridge has been described. Based on this, a highly sensitive, selective and fast method for the determination of palladium in automobile exhaust gas converter catalysts has been developed.

EXPERIMENTAL

All the solutions were prepared with ultra-pure water obtained from a UPHW-1-90 reagent water system (Ulupure corporation, China). A 5.0×10^{-3} mol/L 2-methyl-5-(4-carboxylphenylazo)-8-hydroxyquinoline (MCPAHQ) solution was prepared by dissolving MCPAHQ with 95 % ethanol. A stock standard solution of palladium (1.0 mg/mL) was obtained from Chinese Standard Material Center and a work solution of 0.2 $\mu\text{g/mL}$ was prepared by diluting this solution. 0.1 mol/L of pH 3.2 citric acid-sodium citrate buffer solution was used. Emulsifier-OP solution (2.0 %, w/v) was prepared by dissolving emulsifier-OP with water. All reagents were of the highest available purity (at least analytical grade).

A UV-1800 spectrophotometer (Shimadzu, Japan) equipped with 1 cm microcells (0.5 mL) was used for all absorbance measurements. The pH values were determined with a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China). The extraction was performed on water solid phase extraction (SPE) device (it can prepare 20 samples simultaneously) and a reversed phase

CLEAN-UP[®] C₁₂ cartridge (Unite Chemical Technologies Corporation, United States). Teflon high-pressure microwave acid-digestion bomb (Sineo corporation, Shanghai, China) used in present studies. The carousel of the microwave oven obtained from MDS-8,1200W, Sineo corporation, Shanghai, China. Maximum operating pressure: 1500 psi, maximum operating temperature: 300 °C.

Synthesis of MCPAHQ: 1.37 g (0.01 mol) of 4-aminobenzoic acid was dissolved in 15 mL of ice-cold concentrated hydrochloric acid and slowly diazotized with solution of 0.72 g of sodium nitrite in 10 mL of water. The diazotized solution was then added dropwise with stirring to an ice-cold solution of 2-methyl-8-hydroxyquinoline (1.59 g) in 10 mL of 6.0 mol/L hydrochloric acid and leave the mixture overnight. Neutralized with 7.5 mol/L aqueous ammonia and filtered. The precipitate was re-crystallized three times from 95 % ethanol to give a yield of 70 % with a melting point of 252-254 °C. Its structure (Fig. 1) was verified by IR, ¹H NMR and elemental analysis.

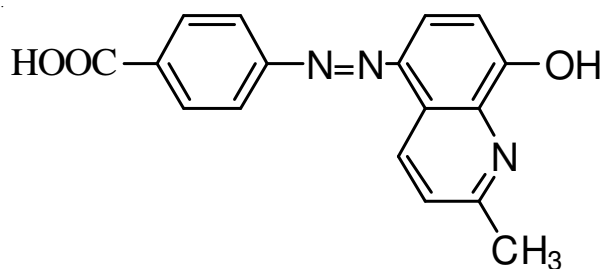


Fig. 1. Structure of 2-methyl-5-(4-carboxylphenylazo)-8-hydroxyquinoline

Elemental analysis: C₁₇H₁₃N₃O₃, calculated (found) (%), C 66.45 (66.32), H 4.23 (4.20), N 13.68 (13.71). IR (KBr, cm⁻¹): 3406 ν(OH), 3051 ν(Ar-H); 1710 δ(-C=O); 1635, 1595, 1530, 1462 ν(-C=C-; -N=N-); 1363 δ(C-N); 1212, 1103, 850, 799, 765 δ(Ar-H). ¹H NMR (500 MHz, CDCl₃) δ: 2.10 (s, 3H); 6.10-7.60 (m, 8H) ppm.

General procedure: To either standard or sample solution containing *ca.* 0.6 μg of Pd(II) in a 50 mL calibrated flask, 4.0 mL of citric acid-sodium citrate buffer solution, 4.0 mL of 5.0 × 10⁻³ mol/L MCPAHQ solution and 5.0 mL of 2.0 % emulsifier-OP solution were added. The mixture was diluted to the mark and mixed well. After 5 min the solution was passed through the CLEAN-UP[®] C₁₂ cartridge at a flow rate of 10 mL/min. After the enrichment step was completed, the retained chelate was eluted from the cartridge with 1.0 mL of ethanol at a flow rate of 1 mL/min in reverse direction. The volume of the eluent was adjusted to 1.0 mL in a 1.0 mL calibrated flask by adding microamount of ethanol with a 200 μL syringes. The absorbance of this solution was measured at 510 nm in a 1 cm microcell (0.5 mL) against a reagent blank prepared in a similar way without palladium.

RESULTS AND DISCUSSION

Absorption spectra: Absorption spectra of MCPAHQ and Pd(II)-MCPAHQ chelate were recorded. Maximum absorbance of MCPAHQ and Pd(II)-MCPAHQ chelate were measured at 410 and 510 nm, respectively. The wavelength of 510 nm was selected for further quantitative analysis (Fig. 2).

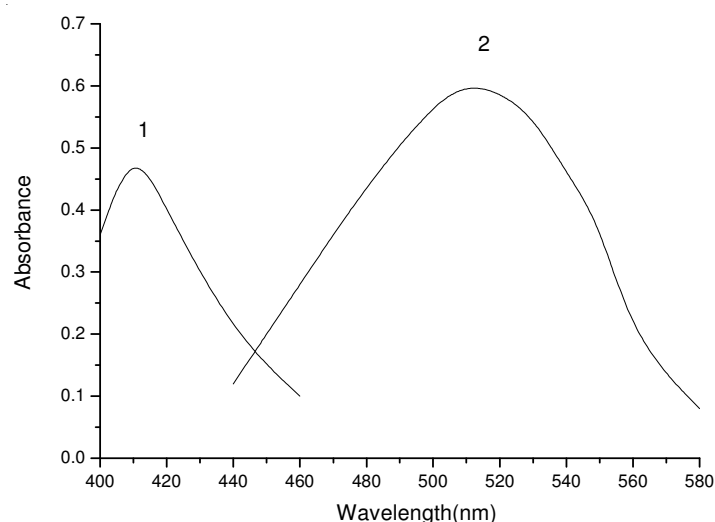


Fig. 2. Absorption spectra of MCPAHQ and its Pd(II) chelate. (1) MCPAHQ-emulsifier-OP blank against water; (2) MCPAHQ-emulsifier-OP-Pd(II) chelate against reagent blank

Effect of acidity: Previous experiments showed that the optimal pH for the reaction of Pd(II) with MCPAHQ is 2.0-4.0. A citric acid-sodium citrate buffer solution of pH 3.2 was recommended to control pH. As the use of 3.0-6.0 mL of the buffer solution (pH 3.2) per 50mL of final solution was found to give the best results in terms of absorbance reproducibility. The use of 4.0 mL buffer solution was recommended.

Effect of surfactants: The Pd(II)-MCPAHQ chelate was poorly soluble in aqueous solution. To enhance its solubility it is required to add a suitable amount of surfactants. The experiments have showed that all type of surfactants: anionic, non-ionic and cationic surfactants enhance solubility of the chelate. Moreover non-ionic surfactants improved sensitivity of determination of Pd(II)-MCPAHQ chelate (Table-1).

TABLE-1
EFFECT OF SURFACTANTS ON THE Pd(II)-MCPAHQ CHROMOGENIC SYSTEM

Surfactant	Absence	Emulsifier- OP	Tween- 80	Tween- 60	Tween- 20	CTMAB	CPB	SDS	SLS
λ_{\max} (nm)	485	510	510	505	505	500	500	490	490
$\epsilon(\times 10^4)$ L mol ⁻¹ cm ⁻¹	5.25	21.5	10.1	9.32	9.19	5.42	5.52	5.27	5.12

It appears from the data in Table-1 that polyoxyethylene nonylphenol ether (emulsifier-OP) is the most appropriate surfactant. Emulsifier-OP is a non-ionic surfactant, which molecule contains both hydrophobic tail (nonylphenol part) and hydrophilic polar head groups (ethoxy chain part) and which thus tends to dissolve in both aqueous and oil phase and reduces the surface tension of liquids. Emulsifier-OP does not dissociate in aqueous solutions, unlike anionic surfactants with negatively charged molecules and cationic surfactants of positively charged molecules in aqueous solution. Emulsifier-OP is non-ionic in solutions, so that its molecules have no electric charge. Thus, it can be successively used in hard water at low temperatures and is stable in acidic and alkaline solutions. Emulsifier-OP shows excellent solvency and chemical stability. Emulsifier-OP is more widely used as a solubilizer than as ionic surfactants. 0.12-0.24 % of emulsifier-OP solution provided constant and maximum absorbance in present studies. In further investigations 0.2 % of emulsifier-OP solution was used.

Effect of MCPAHQ concentration: For up to 0.6 μg of Pd(II), the use of about 3-6 mL of 5.0×10^{-3} mol/L of MCPAHQ solution has been found to be sufficient for a complete reaction. Accordingly, 4.0 mL of MCPAHQ solution was added in all further measurement.

Stability of the chromogenic system: After mixing the components, the absorbance reaches its maximum within 5 min at room temperature and remains stable for 8 h in aqueous solution. After extraction of Pd(II)-chelate the ethanol medium, the chelate was stable for at least 10 h.

Solid phase extraction: It has been shown that MCPAHQ forms stable chelate with Pd(II) in the acid medium. To meet the requirement of metal chelate enrichment by solid phase extraction in the acid medium, the CLEAN-UP[®] C₁₂ cartridge was used. Both enrichment and elution were carried out on an UCT SPE device. The flow rate was set to 10 mL/min during enrichment and to 1 mL/min during elution. It has been found experimentally that MCPAHQ and its Pd(II) chelate are quantitatively retained on the cartridge in the acid medium.

0.2 g of the CLEAN-UP[®] C₁₂ sorbent was placed in the conical flasks (one cartridge of the CLEAN-UP[®] C₁₂ contained 1 g of the sorbent). Stock solution of Pd, emulsifier-OP and MCPAHQ were added to the flask. Acidity of the solution was adjusted to pH 3.2 using citric acid-sodium citrate buffer solution. The solutions were mixed thoroughly in a mechanical shaker. Concentration of Pd(II) was measured by ICP-MS as soon as the equilibrium was reached. The maximum adsorption capacity of the CLEAN-UP[®] C₁₂ cartridge was 6.78×10^{-4} mol/g for Pd(II).

Since the maximum amount of palladium in the performed experiments was only 5.64×10^{-9} mol, the cartridge (1 g) had more than enough capacity to enrich the Pd(II)-MCPAHQ chelate.

In order to choose an appropriate eluent for the retained Pd(II)-MCPAHQ chelate, after extraction of 5.64×10^{-9} mol of palladium from the solution, palladium ions were eluted with different eluting agents, such as ethanol, methanol, acetonitrile,

isopentyl alcohol or acetone. Their elution efficiency decreased in the following sequence: ethanol > methanol > acetonitrile > isopentyl alcohol > acetone. Finally, ethanol was selected as the appropriate eluent. Quantitative recovery (> 98 %) was obtained using 1.0 mL of ethanol at the flow rate of 1 mL/min. In the subsequent experiments, 1.0 mL of ethanol was used as the eluent to desorb the Pd(II)-MCPAHQ chelate.

Calibration curve and sensitivity: The calibration curve shows that Beer's law is obeyed in the concentration range of 0.01-0.6 $\mu\text{g Pd(II)}$ per mL in the measured solution. The corresponding linear regression equation is $A = 2.01 C (\mu\text{g/mL}) + 0.0124$ ($r = 0.9992$). Molar absorptivity was $2.15 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 510 nm. Limit of detection, based on 3 times the relative standard deviation of the blank is 0.1 $\mu\text{g/L}$ in the original samples. The relative standard deviation at the concentration level of 0.8 $\mu\text{g/L Pd(II)}$ (11 replicate determinations) was 2.2 %.

Interference: The selectivity of the proposed method was investigated by the determination 0.5 $\mu\text{g/50 mL}$ of Pd(II) in the presence of various ions with a relative error of $\pm 5 \%$ are given in Table-2. The results shows that most common ions do not interfere with the determination. Selective determination of Pd(II) has been achieved due to the solid phase extraction procedure.

TABLE-2
TOLERANCE LIMITS FOR THE DETERMINATION OF 0.5 μg
OF Pd(II) WITH MCPAHQ (RELATIVE ERROR $\pm 5 \%$)

Ion added	Tolerance (mg)
SO_4^{2-} , Si^{4+} , F^- , Cl^- , NO_3^-	10.000
Na^+ , Fe^{3+} , Pb^{2+} , Cu^{2+} , Zn^{2+}	4.000
Ba^{2+} , K^+ , SO_3^{2-}	2.000
Al^{3+} , PO_4^{3-} , NO_2^- , $\text{S}_2\text{O}_3^{2-}$, ClO_4^-	1.000
Ca^{2+} , Mg^{2+} , Sr^{2+} , V^{5+} , Cd^{2+} , IO_3^- , BrO_3^- , ClO_3^-	0.500
Mn^{2+} , Li^+ , Ce^{4+} , W^{6+} , Mo^{6+} , Co^{2+}	0.200
Ti^{4+} , Bi^{3+} , Cr^{6+} , Zr^{4+} , Fe^{2+}	0.100
Hg^{2+} , Cr^{3+} , La^{3+} , Ag^+ , Sn^{4+} , U^{4+} , Ni^{2+}	0.080
Ru^{3+} , Bi^{3+} , Sb^{3+} , Th^{4+} , Br^- , Os^{8+} , I^-	0.050
Se^{4+} , Ir^{4+} , Rh^{3+} , Te^{4+}	0.020
Au^{3+}	0.010

Application to the catalyst sample: The proposed method has been successfully applied to the determination of microamounts of palladium in automobile exhaust gas converter catalysts.

A 1.000 g of the catalyst samples was weighted accurately into a the Teflon high-pressure microwave acid-digestion bomb. To which, 50 mL of aqua regia was added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven (MDS-8,1200W, Sineo corporation, Shanghai, China). The system

was operated at full power for 0.5 h. The digested material was evaporated to incipient dryness. Then, 30 mL of 10 % hydrochloric acid 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 three times. The filtrate was collected into a 100 mL of calibrated flask quantitatively and the palladium contents were analyzed according to the general procedure. The results were shown in Table-3. An ICP-MS method as described in the literature¹⁷ was used as a reference method and the result are also shown in Table-3.

TABLE-3
DETERMINATION OF PALLADIUM IN AUTOMOBILE CATALYSTS (AC)

Samples	ICP-MS method ($\mu\text{g/g}$)	Proposed method ($\mu\text{g/g}$)	RSD (%) (n = 5)	Recovery (%) (n = 5)
AC-1	0.95	0.93	3.5	94
AC-2	1.48	1.45	3.1	96
AC-3	1.87	1.90	3.2	98
AC-4	2.08	2.05	2.9	97

Conclusion

2-Methyl-5-(4-carboxylphenylazo)-8-hydroxyquinoline (MCPAHQ) has been proven a sensitive and selective spectrophotometric reagent for determination of palladium. Molar absorptivity of the Pd(II)-MCPAHQ chelate was $2.15 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$. Most of the foreign ions did not interfere with the determination. The proposed method is especially selective with respect to noble metals, which commonly seriously interfere with the determination of palladium performed by literature methods. The proposed method can be successfully applied to the direct determination of traces of palladium in automobile exhaust gas converter catalysts samples

Pd(II)-MCPAHQ chelate in 50 mL the solution can be concentrated to 1.0 mL representing enrichment factor of 50, if solid phase extraction on the CLEAN-UP[®] C₁₂ cartridge is applied. Detection limit is 0.1 $\mu\text{g/L}$ in original samples and palladium can be determined at a $\mu\text{g/L}$ level with good results.

2-Methyl-5-(4-carboxylphenylazo)-8-hydroxyquinoline (MCPAHQ) is cheap and can be easily synthesized. Therefore, proposed method can be utilized in the routine analysis.

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