

Study on Solid Phase Extraction and Spectrophotometric Determination of Palladium with MCI GEL CHP 20Y as Sorbent

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In this paper, a new method for the determination of palladium based on the rapid reaction of palladium with 2-(3,5-dichlor-pyridylazo)-5-dimethylaminoaniline (3,5-diCl-PADMA) and the solid phase extraction of the coloured chelate with a reversed phase MCI GEL CHP 20Y resin has been developed. In the presence of 0.05-0.50 mol L⁻¹ of hydrochloric acid solution and cetyltrimethylammonium bromide (CTMAB) medium, 3,5-diCl-PADMA reacts with palladium to form a purple chelate of a molar ratio 1:3 (palladium to 3,5-diCl-PADMA). This chelate was enriched by the solid phase extraction with a MCI GEL CHP 20Y cartridge and eluted the retained chelate from the cartridge with ethanol. The enrichment factor of 100 was achieved. Beer's law is obeyed in the range of 0.01 to 3.0 µg mL⁻¹ in the measured solution. The relative standard deviation for 11 replicates sample of 0.5 µg L⁻¹ level is 3.2 %. The detection limit, based on the three times of standard deviation is 0.05 µg L⁻¹ in the original sample. This method was applied to the determination of palladium with good results.

Key Words: 2-(3,5-Dichlor-pyridylazo)-5-dimethylaminoaniline, Palladium, MCI GEL CHP 20Y resin, Solid phase extraction, Spectrophotometry.

INTRODUCTION

Noble metals, particularly palladium, affects the environment to an increasing degree as a new pollutant, especially by the technical use of catalysts containing active palladium metal^{1,2}. Therefore, simple, sensitive and selective method is required for the determination of trace palladium. Several sophisticated techniques, such as ICP-MS, ICP-AES, electrochemical, spectrofluorimetry and neutron activation analysis are available in literature for determination of palladium³⁻¹⁰. Spectrophotometric method still has the advantages in respect of simplicity and low operating costs⁴⁻¹⁰. However, the routine spectrophotometric methods are often not sensitive enough to determine low concentration of palladium ion. Consequently, a preconcentration step is usually required.

Solid phase extraction is an attractive technique because of its notable advantages¹¹⁻¹³. In our previous works, the determination of some trace metal ions by solid phase extraction with reserved phase cartridge was studied¹⁴⁻¹⁷. However, the chromogenic systems in acidic or alkaline medium not fit the routine reserved phase cartridge because of its narrow pH range. To meet the need of metal chelate enrichment by solid phase extraction in acid medium, in this paper, the solid phase extraction of Pd-(3,5-diCl-PADMA) chelate with a reversed

phase MCI GEL CHP 20Y cartridge was studied. The MCI GEL CHP 20Y is an aromatic type adsorbent based on crosslinked polystyrenic matrix. It is a reversed-phase resin provides a broad range of solvent choices^{18,19} and a pH range from 0-14. By using the MCI GEL CHP 20Y resin, the Pd-(3,5-diCl-PADMA) chelate was enriched by solid phase extraction in hydrochloric acid medium and the enrichment factor of 100 was achieved. Based on this, a highly sensitive, selective and rapid method for the determination of palladium was developed.

EXPERIMENTAL

A UV-160 A spectrophotometer (Shimadzu 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 cartridge packed with MCI GEL CHP 20Y was used. The particle size is 30 µm and surface area is 560 m² g⁻¹.

All solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). HPLC grade ethanol (Fisher Corporation, USA) was used. The 2-(3,5-dichlor-pyridylazo)-5-dimethylaminoaniline (3,5-diCl-PADMA) was synthesized in our

laboratory according to the literature^{20,21} and a 4.0×10^{-4} mol L⁻¹ of 3,5-diCl-PADMA solution was prepared by dissolving 3,5-diCl-PADMA in ethanol. A stock standard solution of palladium (1.0 mg mL^{-1}) was obtained from Chinese Standard Material Center and a work solution of $0.5 \text{ } \mu\text{g mL}^{-1}$ was prepared by diluting this solution. A 5.0 mol L^{-1} of hydrochloric acid was used. Cetyltrimethylammonium bromide (CTMAB) solution [2.0 % (v/v)] was prepared by dissolving CTMAB with water. All chemical used were of analytical grade unless otherwise stated.

Sample preparation: For clean water sample, the samples were acidified with hydrochloric acid, then filtrated by $0.45 \text{ } \mu\text{m}$ filter and prepared for the following determination. If there were organics in water interfere the determination, the sample was digested as following procedure: Taking an appropriate volume of sample in a 500 mL flask and concentrated the sample to about 20 mL by heating on a hot plate. To this solution, 5 mL of concentrated nitric acid, 2 mL of concentrated hydrochloric acid and 5 mL of 30 % hydrogen peroxide were added. The mixture was heated on hot plate till evaporated to near dryness. The residue was dissolved with 20 mL of 5 % of hydrochloric acid and prepared for the following determination.

General procedure: To a standard or sample solution containing *ca.* 3 μg of Pd(II) in a 100 mL of calibrated flask, 5 mL of 5 mol L^{-1} of hydrochloric acid solution, 5 mL of $4 \times 10^{-4} \text{ mol L}^{-1}$ 3,5-diCl-PADMA solution and 3 mL of 2 % CTMAB solution were added. The mixture was diluted to volume of 100 mL and mixed well. After 10 min, the solution was passed through the MCI GEL CHP 20Y cartridge at a flow rate of 20 mL min^{-1} . After the enrichment was finished, the retained chelate is eluted from the cartridge at a flow rate of 5 mL min^{-1} with 1 mL of ethanol in the reverse direction. The eluent was adjusted to the accurate volume of 1 mL. The absorbance of this solution was measured at 620 nm in a 1 cm microcells (0.5 mL) against a reagent blank prepared in a similar way without palladium.

RESULTS AND DISCUSSION

Absorption spectra: The absorption spectra of 3,5-diCl-PADMA and its Pd(II) chelate were measured with spectrophotometer. The results (Fig. 1) show that the absorption peaks of 3,5-diCl-PADMA and its complex in ethanol medium are located at 450 and 620 nm.

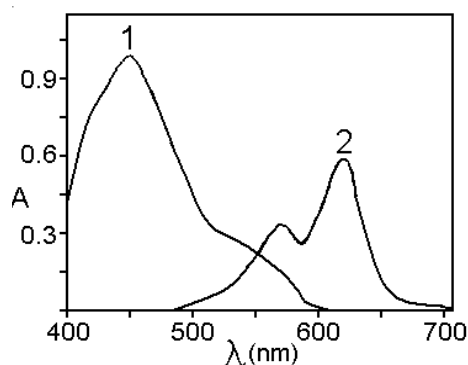


Fig. 1. Absorption spectra of 3,5-diCl-PADMA and its Pd(II) complex: (1) 3,5-diCl-PADMA-CTMAB blank against water; (2) 3,5-diCl-PADMA-CTMAB-Pd(II) complex against reagent blank

Effect of acidity: Results showed that the optimal condition for the reaction of Pd(II) with 3,5-diCl-PADMA is in the acid medium. Therefore, the effect of hydrochloric acid, sulfuric acid, perchloric acid, phosphoric acid and the like, on the colour reaction of Pd(II) with 3,5-diCl-PADMA was studied. The results shows that hydrochloric acid has the best effect and the concentration of hydrochloric acid within a $0.05\text{-}0.5 \text{ mol L}^{-1}$ was found to give a maximum and constant absorbance, so 5 mL of 5.0 mol L^{-1} hydrochloric acid was recommended to control the pH.

Effect of surfactants: The effects of surfactants on Pd(II)-(3,5-diCl-PADMA) system were studied. The results show that in the presence of cationic surfactants or nonionic surfactants medium, the absorption of the chromogenic system increases markedly. Various of surfactants enhance the absorbance in the following sequence: CTMAB > CPB > emulsifier-OP > Tween-80. Accordingly, the CTMAB was the best additive and the use of 2-5 mL of solution give a constant and maximum absorbance. Consequently, the use of 3.0 mL was recommended.

Effect of 3,5-diCl-PADMA concentration: For up to 3 μg of Pd(II), the use of 5 mL of $4 \times 10^{-4} \text{ mol L}^{-1}$ of 3,5-diCl-PADMA solution was found to be sufficient for a complete reaction. Accordingly, 5 mL of 3,5-diCl-PADMA solution were added in all further measurement.

Stability of the chromogenic system: After mixing the components, the absorbance reaches its maximum within 10 min at room temperature and remains stable for at least 6 h. After having been extracted into the ethanol medium, the chelate was stable for at least 10 h.

Solid phase extraction: In this study, 3,5-diCl-PADMA reacts 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 cartridge packed with MCI GEL CHP 20Y resin (pH range 0-14) was used.

Both the enrichment and the elution were carried out on a Waters SPE device (the device can prepare 20 samples simultaneously). The flow rate was set to 20 mL min^{-1} when enrichment and 5 mL min^{-1} when elution. Some experiments were carried out in order to investigate the retention of 3,5-diCl-PADMA and its Pd(II) chelate on the cartridge. It was found that the 3,5-diCl-PADMA 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 22 mg for Pd(II)-(3,5-diCl-PADMA) chelate in a 100 mL of solution. In this experiment, the maximum amount of palladium is only 3 μg . Therefore, the cartridge has adequate capacity to enrich the Pd(II)-(3,5-diCl-PADMA) chelate. In order to choose a proper eluant for the retained 3,5-diCl-PADMA and its Pd(II) chelate. Various organic solvents were studied. For eluting the Pd(II)-(3,5-diCl-PADMA) chelates from the cartridge, the results showed that all the polar organic solvents (ethanol, isopentyl alcohol, acetone, acetonitrile and methanol) can elute the chelate from the cartridge completely. So the ethanol was selected as eluant in this study. The experiment shows that it was easier to elute the retained 3,5-diCl-PADMA and its Pd(II) chelate in reverse direction than in forward direction, so it is necessary to upturned cartridge when

elution. 1 mL of ethanol was sufficient to elute the 3,5-diCl-PADMA and its Pd(II) chelate from cartridge at a flow rate of 5 mL min⁻¹. The volume of 1 mL was selected.

Calibration curve and sensitivity: The calibration curve showed that Beer's law is obeyed in the concentration range of 0.01-3.0 µg Pd(II) per mL in the measured solution. The linear regression equation obtained was $A = 0.648 C (\mu\text{g mL}^{-1}) + 0.0126$ ($r = 0.9992$). The relative standard deviation at a concentration level of 0.5 µg L⁻¹ of Pd(II) (11 repeats determination) was 3.2 %. The detection limit, based on the three times of standard deviation is 0.05 µg L⁻¹ in the original sample.

Interference: The selectivity of the proposed method was investigated by the determination of 0.5 µg 100 mL⁻¹ of Pd(II) in the presence of various ions within a relative error of $\pm 5\%$ are given in Table-1. The result shows that most routine ions do not interfere with the determination. This method is highly selective.

Ion added	Tolerate (mg)
NO ₃ ⁻ , K ⁺ , borate, Na ⁺ , PO ₄ ³⁻ , SO ₄ ²⁻	10
Li ⁺ , Al ³⁺ , NO ₂ ⁻ , Ca ²⁺ , Mg ²⁺ , Mn ²⁺	5
SO ₃ ²⁻ , Sr ²⁺ , Ba ²⁺ , IO ₃ ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , Fe ²⁺	2
Ce(IV), W(VI), Mo(VI), U(IV), I ⁻	1
Ti(IV), Bi(III), V(V), Cr(VI), Zr(IV), F ⁻ , Br ⁻ , Sn(IV)	0.5
Ru(III), Bi(III), Pb ²⁺ , Sb ³⁺ , Th(IV), Os(VIII), Cu ²⁺ , Au(III)	0.2
Cd ²⁺ , Cr ³⁺ , La ³⁺ , Zr(IV), Co ²⁺ , Fe ³⁺ , Zn ²⁺	0.1
Se(IV), Te(IV), S ₂ O ₃ ²⁻ , Ag ⁺ , Ni ²⁺	0.05
Ir(IV), Rh(III), Hg ²⁺	0.01
Pt(IV), Ru(III)	0.005

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 3,5-diCl-PADMA is 1:3.

Application: This method was applied to the determination of palladium in water samples. For the prepared samples, the palladium contents were analyzed according to general procedure. The results (deducted the reagents blank) are shown in Table-2. An ICP-MS method was used as a reference method and the result are shown in Table-2.

Samples	ICP-MS method (µg L ⁻¹)	Proposed method (µg L ⁻¹)	RSD % (n = 5)	Recovery (%)
River water	2.18	2.36	3.5	85
Planting effluents	12.8	13.6	3.1	93

Conclusion

In this method, a sensitive and selective spectrophotometric reagent for palladium, 2-(3,5-dichlor-pyridylazo)-5-dimethyl-aminoaniline (3,5-diCl-PADMA) was used. Most foreign ions do not interfere with the determination. The MCI GEL CHP 20Y resin was used as solid phase extraction sorbent. By this sorbent, the Pd-3,5-diCl-PADMA chelate was enriched in hydrochloric acid medium and the enrichment fact of 100 was achieved. The detection limit reaches 0.05 µg L⁻¹ in the original samples and µg L⁻¹ level of palladium can be determined with good results.

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