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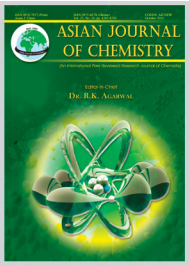

Determination of Palladium and Platinum by Solid Phase Extraction and High Performance Liquid Chromatography

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A new method for the determination of palladium and platinum ions using high performance liquid chromatography equipped with on-line solid phase extraction was developed. The palladium and platinum ions were derivatized with 2-(2-quinolinylazo)-1,3-diaminobenzene (QADAB) to form coloured chelate. The Pd-QADAB and Pt-QADAB chelates were then enriched on an enrichment column using a 0.05 mol L^{-1} of phosphoric acid as mobile phase. After the enrichment was completed, the retained chelates were back-flushed to the analytical column. The separation of chelates on the analytical column [CQUITY UPLC BEH C_{18} (1.7 μm 4.6 × 50 mm)] was satisfactory when 40 % acetonitrile (containing 0.05 mol L^{-1} of phosphoric acid and 0.1 % of triton X-100) was used as mobile phase. The Pt-QADAB and Pd-QADAB chelates were separated completely within 2.5 min. The detection limits (S/N = 3) for palladium and platinum were 1.0 ng L^{-1} and 1.2 ng L^{-1}, respectively. The method was applied to the determination of palladium and platinum in water samples with good results.

Key Words: Palladium, Platinum, 2-(2-Quinolinylazo)-1,3-diaminobenzene, HPLC, On-line enrichment.

INTRODUCTION

In recent years, environmental contamination by platinum group elements (PGEs) was increase markedly due to the widely use of these metal in modern industry[1,2]. Although the bioavailability and toxicology of platinum group elements is still an open question, the determination of low concentrations of those metals has received more and more attention as a result of an increase of their concentration levels in the environment[3,4]. The heterogeneous composition of samples and the low concentration levels of palladium and platinum make their direct measurement in various analytes very difficult[4]. Though the atomic absorption spectrometry[5], inductively coupled plasma-atomic emission spectrometry (ICP-AES)[6,7] and inductively coupled plasma-mass spectrometry (ICP-MS)[8,9] are routinely used for platinum group metals analysis, ICP-AES and ICP-MS require expensive instrumentation and the detection sensitivity of atomic absorption spectrometry and ICP-AES varies considerably according to the metal. The application of high performance liquid chromatography (HPLC) for the separation and determination of metal ions has increased in recent years. This has been proved to be a favourable and reliable technique[10,11]. However, the routine chromatographic methods have some disadvantages because of the stability of chelates and the long separation time. In this paper, 2-(2-quinolinylazo)-1,3-diaminobenzene (QADAB) was used as pre-column derivatization reagent for palladium and platinum and a new method for the determination of palladium and platinum ions using high performance liquid chromatography equipped with on-line solid phase extraction was developed. The new method was applied to the determination of μg L^{-1} (ppb) levels of palladium and platinum ions in water samples with good results.

EXPERIMENTAL

The on-line solid phase extraction system (Waters Corporation, USA) that was used in the experiments is shown in Fig. 1. The system includes a waters 2695 alliance quadripump, a waters 515 pump, a waters 996 photodiode array detector, a six port switching valve, a large volume injector (can handle 5.0 mL samples) and a column. The enrichment column is a CQUITY UPLC BEH C_{18} (1.7 μm 4.6×10 mm) and the analytical column is a CQUITY UPLC BEH C_{18} (1.7 μm 4.6 × 50 mm) (waters corporation, USA). The pH value was determined with a Beckman F-200 pH meter.

All solutions were prepared using ultra-pure water obtained from a Milli-Q50 SP reagent water system (Millipore Corporation, USA). The standard solutions of palladium and platinum (1.0 mg mL^{-1}) were obtained from the Chinese standards center

and a working solution of 0.2 mg mL^{-1} was prepared by diluting the standard solutions. Acetonitrile (HPLC grade) was obtained from Fisher Corporation, USA. TritonX-100 was obtained from Fluka Corporation, Switzerland and Triton X-100 solution (1 %) was prepared by dissolving 5.0 g of Triton X-100 in water and diluting to a volume of 500 mL. A phosphoric acid 0.5 mol L^{-1} was used. QADAB was synthesized according to the literature[12] and a QADAB solution (2.0×10^{-4} mol L^{-1}) was prepared by dissolving QADAB in ethanol. A 0.05 mol L^{-1} of phosphoric acid was used as mobile phase A and a solution of 40 % acetonitrile (containing 0.05 mol L^{-1} of phosphoric acid and 0.1 % of tritonX-100) was used as mobile phase B. All other reagents were of analytical reagent-grade. Glass and Teflon wares were soaked in 5 % of nitric acid for at least 2 h and then thoroughly washed with pure water.

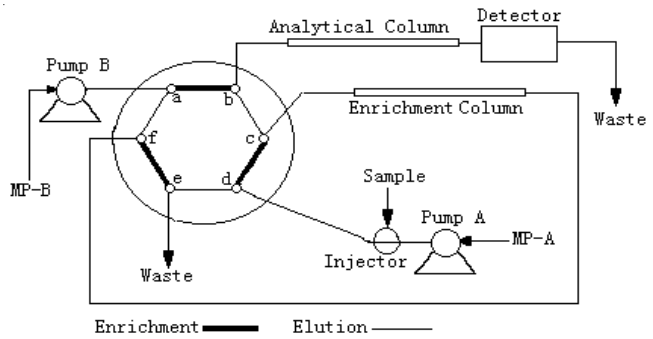

Fig. 1. On-line enrichment system using the valve-switching technique; Pump A, Waters 515 Pump. Pump B, Waters 2690 Alliance quadripump. Injector can contain 5 mL of sample. Six ports switching valve (Waters Corporation). Enrichment Column, CQUITY UPLC BEH C_{18} (1.7 μm 4.6 × 10 mm). Analytical column, CQUITY UPLC BEH C_{18} (1.7 μm 4.6 × 50 mm). Detector, Waters 996 photodiode array detector. MP A, 0.05 mol L^{-1} of phosphoric acid. MP B, 40 % acetonitrile (containing 0.05 mol L^{-1} of phosphoric acid and 0.1 % of tritonX-100)

Sample preparation: An appropriate volume (industrial plant effluents 20 mL, river water 200 mL) of sample in a 500 mL flask were concentrated to about 5 mL by heating on a hot plate and then transferred into a 25 mL teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China). 2.0 mL of concentrated HNO_3 and 3.0 mL of 30 % hydrogen peroxide was added. The bombs were sealed tightly and then positioned in 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 6.0 min. The digested sample was evaporated to near dryness. The residue was dissolved with 5 mL of 5 % of nitric acid and transferred quantitatively into a 25 mL calibrated flask and filled up to the mark with 5 % nitric acid. The palladium and platinum content was analyzed by using an appropriate volume of this solution according to the general procedure. The results (after deduction of the reagents blank) are shown in Table-1. An ICP-MS method as described in the literature[13] was used as a reference method and the results are also shown in Table-1.

Standard procedure: 0-15 mL of a 0.2 mg mL^{-1} standard or sample solution were transfered into a 25 mL volumetric flask, to which 2 mL of 1.0×10^{-4} mol L^{-1} QADAB solution, 2 mL of 0.5 mol L^{-1} phosphoric acid solution and 1 mL of 1 % Triton X-100 solution were added. They were diluted to the mark with deionized water and mixed well. After 15 min, 2.5 mL of that solution were introduced into the injector and transported to the enrichment column using mobile phase A at flow rate of 1 mL min^{-1}. After the enrichment was completed, the six ports switching valve was switched and the metal-QADAB chelates, which adsorbed onto the top of the enrichment column, were eluted with mobile phase B at a flow rate of 1 mL min^{-1} in reverse direction and transported to the analytical column. The chelates were separated on the analytical column. A chromatogram was recorded from 350-600 nm using a photo-diode array detector. The chromatogram at 595 nm is shown in Fig. 2.

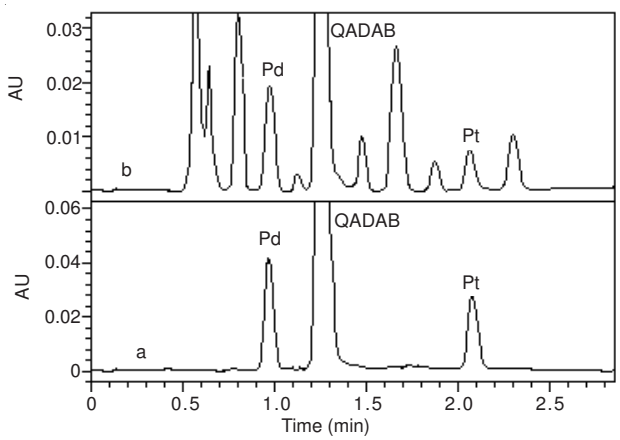

Fig. 2. Chromatogram of standard sample (a) and water sample (b)

RESULTS AND DISCUSSION

Pre-column derivation: The optimum pH for complex formation of QADAB was 0.2-2.6 for palladium and 0.1-2.5 for platinum. Therefore, 2 mL of 0.5 mol L^{-1} phosphoric acid solution was recommended to control the pH. It was found that 0.5 mL of a 1×10^{-4} mol L^{-1} QADAB solution was sufficient to complex 5 mg of palladium and platinum, respectively. In real samples, however, foreign ions such as Co^{2+}, Ni^{2+}, Cu^{2+}, Rh^{3+}, or Ag^{+} form complexes with QADAB and consume reagents. It was therefore necessary to use an excess of QADAB and 2 mL of a 1.0×10^{-4} mol L^{-1} QADAB solution is recommended.

The experiments showed that in the presence of non-ionic or cationic surfactants, the response of the detector to metal-QADAB chelates was markedly increased. Various nonionic or cationic surfactants enhanced the absorbance in the following

TABLE-1
DETERMINATION RESULTS OF THE SAMPLES

Samples	Found (μg L^{-1})		ICP-MS method (μg L^{-1})		RSD (%) (n = 5)		Recovery (%) (n = 5)	
	Pd	Pt	Pd	Pt	Pd	Pt	Pd	Pt
Planting effluents	0.381	0. 215	0.344	0. 248	3.6	3.8	87	93
River water	0.0528	0.0234	0.0547	0.0203	4.2	4.3	91	95

TABLE-2
CALIBRATION CURVE, COEFFICIENTS AND DETECTION LIMITS

Components	Regression equation	Linearity range (ng L^{-1})	Coefficient	Detect limit (ng L^{-1})	RSD (%) (n=11)
Pd-QADAB	$A = 2.64 \times 10^6 C - 2147$	5 - 550	r = 0.9992	1.0	2.3
Pt-QADAB	$A = 2.35 \times 10^6 C + 3182$	8 - 900	r = 0.9991	1.2	2.6

sequence: TritonX-100 > Tween-80 > Tween-20 > CTMAB > CPB. Triton X-100 was therefore selected as additive in this experiment. The use of 0.8-2.0 mL of TritonX-100 solution gave a constant and maximum absorbance. Accordingly, the addition of 1.0 mL of Triton X-100 solution is recommended. QADAB reacted rapidly with Pd(II) and Pt(II) and the reaction was complete after 10 min at room temperature. The formed complexes were both stable for at least 8 h.

On-line enrichment: The on-line enrichment was carried out on an on-line enrichment system as shown in Fig. 1. The flow direction for enrichment is: pump B → a → b → analytical column → detector → waste; pump A → injector → d → c → enrichment column → f → e → waste; for elution: pump B → a → f → enrichment column → c → b → analytical column → detector → waste, pump A → injector → d → e → waste.

Pd-QADAB and Pt-QADAB chelates were stable in acidic medium and to avoid decomposition of the chelates during the enrichment step, a 0.05 mol L^{-1} phosphoric acid solution was selected as mobile phase for transport of the chelates to the enrichment column while a CQUITY UPLC BEH C_{18} pre-column (1.7 μm 4.6 × 50 mm) with a pH range of 0.5-12 was selected as enrichment column.

The aim of the present research was to determine trace metal ions by injecting a large volume of sample. The effect of the injection volume was therefore investigated. An injection volume of 0.1-4 mL was found to be acceptable. The experiment showed that the chromatographic peaks were obviously broadened and the enrichment column would be overloaded when the injection volume was over 4 mL. An injection volume of 2.5 mL was found to be sensitive enough to determine palladium and platinum in all experiments and a injection volume of 2.5 mL is therefore recommended.

Spectrophotometric properties: The absorption spectrum of the metal-QADAB chelates was measured with a Shimidzu UV-2401 spectrophotometer. The results showed that the maximum absorption is found at a wavelength of 580 nm for Pd-QADAB and 610 nm for Pt-QADAB. An intermediate wavelength of 595 nm was therefore selected.

Chromatographic separation: The optimum conditions for chromatographic separation were studied under the on-line model. The experiments showed that the Pd-QADAB and Pt-QADAB have a high stability in acidic buffer solution in the presence of Triton X-100. A 0.05 mol L^{-1} of phosphoric acid and containing 0.05-0.2 % of Triton X-100 prevented the decomposition of the metal complexes during separation and resulted in a good peak shape. acetonitrile/water (40/60) (containing 0.05 mol L^{-1} of phosphoric acid and 0.1 % of Triton X-100) was therefore selected as the mobile phase. To shorten the chromatographic separation time, a CQUITY UPLC BEH C_{18} (1.7 μm 4.6 × 50 mm) was selected in this experiment. This allowed complete separation of the palladium and platinum chelates in 2.5 min, which represents a reduction in separation time of 80 % compared to routine chromatographic methods.

Calibration graphs: Under optimum conditions, calibration curves (peak area analysis) for metal-QADAB chelates were established based on five standard samples of 10-500 ng L^{-1}. The limits of detection are calculated by the ratio of signal to noise (S/N = 3). The results are shown in Table-2. The reproducibility of the method was verified by repeated measurements of a 1.0 mg L^{-1} of Pd(II) and Pt(II) standard. The relative standard deviations (n = 10) are shown in Table-1.

Interference: Under pre-column derivatization conditions foreign ions such as Cu(II), Ni(II), Co(II), Ag(I), Rh(III), Ru(III) can form coloured stable chelate complexes with QADAB. To examine the selectivity of this method possible interference by these foreign ions was investigated. When 2.0 mL of 1.0×10^{-4} mol L^{-1} QADAB was used for samples with 10 mg L^{-1} of Pd(II) and Pt(II) respectively, the tolerance (with an error of ± 5 %) for Cu(II), Ni(II), Co(III) was 2000 mg L^{-1}, for Tl(III), Bi(III), Ir(IV), Ag(I) 500 mg L^{-1} and for Rh(III), Ru(III) 250 mg L^{-1}. The described method is therefore highly selective.

Conclusion

The proposed method has the following characteristics: (**1**) 2-(2-quinolinylazo)-1,3-diaminobenzene was used for the first time as a pre-column derivatization reagent for Pd and Pt ions. The metal complexes were separated completely with a CQUITY UPLC BEH C_{18} (1.7 μm 4.6 × 50 mm) column within 2.5 min at room temperature. This represents a reduction in separation time by 85 % as compared to standard chromatographic methods. (**2**) The use of an on-line enrichment system allowed the injection of large sample volumes (2.5 mL) hereby greatly improving the sensitivity of the method.

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