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Study on the Separation and Determination of Palladium, Platinum and Rhodium by Solid Phase Extraction and Ultra Performance Liquid Chromatography

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In this paper, a new method for the simultaneous determination of palladium, platinum and rhodium ions by solid phase extraction and ultra performance liquid chromatography was studied. The palladium, platinum and rhodium ions were pre-column derivatized with *p*-rhodanine azobenzoic acid (RBA) to form coloured chelates. The Pb-RBA, Pt-RBA and Rh-RBA chelates were enriched by solid phase extraction with C_{18} cartridge. The separation of these chelates on ACQUITY UPLC BEH C_{18} (1.7 μm 2.1 mm × 50 mm) column was satisfactory with 38 % acetonitrile (containing 0.05 mol L^{-1} of phosphoric acid) as mobile phase. Palladium, platinum and rhodium were separated completely within 2.5 min. The detection limits (S/N = 3) of palladium, platinum and rhodium reaches 12, 18 and 20 ng L^{-1}, respectively. This method was applied to the determination of palladium, platinum and rhodium in water, urine and soil samples with satisfactory results.

Key Words: Palladium, Platinum, Rhodium, *p*-Rhodanine azobenzoic acid, Ultra performance liquid chromatography.

INTRODUCTION

In recent years, the release of palladium, platinum and rhodium into the environment was increase markedly due to the widely use of these metal in modern industry[1,2]. Although the bioavailability and toxicology of palladium, platinum and rhodium is still an open question, the determination of basal concentrations of those metals has a key role since an increase of their level[3-5].

The heterogeneous composition of samples and the low concentration levels of palladium, platinum and rhodium involved make the direct measurement of analytes really difficult. Several analytical techniques have been employed with this matrix in recent years and most of the advantages and drawbacks have been reviewed[6-14]. In previous work, some high performance liquid chromatography method for the determination of platinum group metals with derivatization has been reported[14-18]. This has been proved to be a favorable and reliable technique. However, the routine chromatographic methods have some disadvantages because of long separation time is needed.

The ultra performance liquid chromatography (UPLC) technology takes full advantage of chromatographic principles to run separations using columns packed with smaller particles and/or higher flow rates for increased speed, with superior resolution and sensitivity[19,20]. However, the application of ultra performance liquid chromatography for the determination of platinum group elements had not been reported yet. In this paper, the simultaneous determination of palladium, platinum and rhodium ions by solid phase extraction and ultra performance liquid chromatography using *p*-rhodanine azobenzoic acid (RBA) as pre-column derivatization reagent was studied. The palladium, platinum and rhodium can form stable colour chelates with *p*-rhodanine azobenzoic acid at room temperature rapidly and the metal chelates were separated completely within 2.5 min. The separation time was shortened compared to the routine chromatographic methods[14-18]. This method can be applied to the determination μg L^{-1} level of palladium, platinum and rhodium ions in water, human urine and soil samples with satisfactory results.

EXPERIMENTAL

The ultra performance liquid chromatographic determination was performed on a ACQUITY Ultra Performance LC™ Systems equipped with photodiode array detector. The pH value was determined with a Beckman Φ-200 pH meter.

The solid phase extraction cartridge used is Water extra RP18 solid phase extraction cartridge (1 cc/50 mg, 30 μm) (Waters Corporation, USA). The column used is Waters ACQUITY UPLC BEH C_{18} (1.7 μm 2.1 mm × 50 mm).

All of the solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). Palladium, platinum and rhodium standard solution (1 mg mL^{-1}) were obtained from Chinese Standards Center and a working solution of 0.5 μg mL^{-1} was prepared by diluting this standard solution. HPLC grade acetonitrile was obtained from Fisher Corporation, USA. A phosphoric acid solution (2 mol L^{-1}) was used. The *p*-rhodanine azobenzoic acid was synthesized by our laboratory according to our previous literature[21] and *p*-rhodanine azobenzoic acid solution (2.0×10^{-4} mol L^{-1}) was prepared by dissolving *p*-rhodanine azobenzoic acid with 95 % ethanol. The mobile phase used is 38 % acetonitrile (containing 0.05 mol L^{-1} of phosphoric acid) and the flow rate of mobile phase is 0.4 mL min^{-1}. The glass and Teflon ware used were soaked in 5 % of nitric acid for at least 2 h and then thoroughly wash with pure water.

Standard procedure: An appropriate volume of standard or the sample was transferred into a 50 mL of volumetric flask. To which, 2.5 mL of *p*-rhodanine azobenzoic acid solution and 2 mL of phosphoric acid solution were added. The solution was diluted to 50 mL with water and mixed well. The mixture was placed for 5 min at room temperature. Then the solution was passed through the C_{18} cartridge at a flow rate of 10 mL/min. After the enrichment had finished, the retained chelates were eluted from the cartridge with 1 mL of acetonitrile at a flow rate of 5 mL min^{-1} in an opposite direction. The solution was filtered with 0.45 μm of filters and adjusted to the volume of 1 mL. 2 μL of sample was injected for HPLC analysis. The chromatogram of 455 nm is shown in Fig. 1.

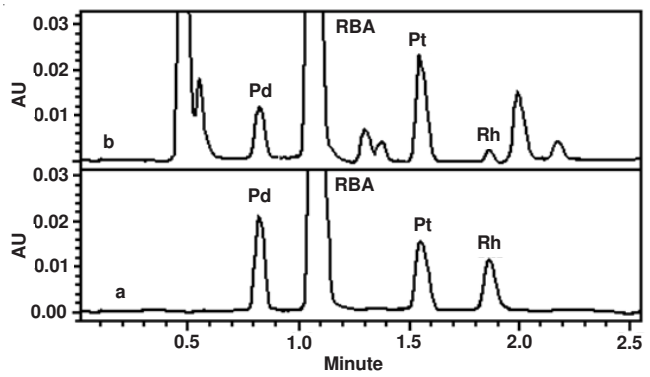

Fig. 1. Chromatogram of standard (a) and real sample (b)

RESULTS AND DISCUSSION

Precolumn derivation: The optimal pH for the *p*-rhodanine azobenzoic acid reacts with metal ions is 0.2-3.8 for palladium, 0.2-2.2 for platinum and 0.1-4.0 for rhodium, so a 2.0 mL of 2.0 mol L^{-1} of phosphoric acid was recommended to control pH.

It was found that 0.5 mL of 1×10^{-4} mol L^{-1} *p*-rhodanine azobenzoic acid solution was sufficient to complex 10 μg of palladium, platinum and rhodium, respectively. But in real samples, the foreign ions, such as Hg^{2+}, Pb^{2+}, Cu^{2+}, Ag^{+} form complex with *p*-rhodanine azobenzoic acid and consume reagents. Therefore, the amount of *p*-rhodanine azobenzoic acid must be in excess. In this experiment, a 2.5 mL of 1×10^{-4} mol L^{-1} *p*-rhodanine azobenzoic acid solution was used.

The *p*-rhodanine azobenzoic acid can reacts with Pd(II), Pt(II) and Rh(III) rapidly at room temperature. The reaction was completed after 5 min and the complex was stable for at least 6 h.

Solid phase extraction: Some experiments were carried out in order to investigate the retention of metal-*p*-rhodanine azobenzoic acid chelates on the cartridge. It was found that the Pd-RBA, Pt-RBA and Rh-RBA chelates could be retained on the cartridge quantitatively when they pass the cartridge as aqueous solution. The capacity of the cartridge for metal-T_4-APP chelates was 18 mg in a 50 mL of solution. In this experiment, the cartridge has adequate capacity to enrich the metal-*p*-rhodanine azobenzoic acid chelates.

In order to choose a proper eluant for the retained *p*-rhodanine azobenzoic acid and its metal-chelates, various organic solvents were studied. It was found that the tetrahydrofuran, isopentyl alcohol, acetonitrile, acetone, ethanol and methanol could elute the metal-*p*-rhodanine azobenzoic acid chelates from cartridge quantitatively. Acetonitrile was selected in this experiment. Experiment showed that it was easier to elute the retained *p*-rhodanine azobenzoic acid and its metal-chelate on cartridge in reverse direction than in forward direction, so it was necessary to upturned the cartridge when elution. 1 mL of acetonitrile was sufficient for eluted the metal-*p*-rhodanine azobenzoic acid chelate from cartridge quantitatively at a flow rate of 5 mL/min. The volume of 1 mL eluant was selected.

Spectrophotometric properties: The absorption spectrum of metal-*p*-rhodanine azobenzoic acid chelates was obtained with photodiode array detector. The results show that the maximum absorption is at 448 nm for Pd-RBA chelate, 452 nm for Pt-RBA and 456 nm for Rh-RBA chelate. Therefore, the 455 nm was selected as detecting wavelength. The molar absorptivity was calculated to be 1.37×10^5 L mol^{-1} cm^{-1} for Pt-RBA chelate, 1.21×10^5 L mol^{-1} cm^{-1} for Pd-RBA chelate, 1.40×10^5 L mol^{-1} cm^{-1} for Rh-RBA chelate. The results show that *p*-rhodanine azobenzoic acid is a sensitive pre-column derivatization regent for palladium, platinum and rhodium.

Chromatographic separation: The experiments showed that the Pd-RBA, Pt-RBA and Rh-RBA chelates have a good stability in the presence of acid solution. The pH of mobile phase within 0.2-2.8 can avoid the metal-chelate decomposing in the course of separation and get a good peak shape. So acetonitrile/water (54/36) (containing 0.05 mol L^{-1} of phosphoric acid) was selected as mobile phase. With this mobile phase, the palladium, platinum and rhodium chelates were separated completely within 2.5 min. Compared to the routine chromatographic method, more then 75 % of separation time was shortened.

Calibration graphs: Under optimum conditions, regression equations of metal-*p*-rhodanine azobenzoic acid chelates were established based on the standard sample injected and its peak areas. The limits of detection are calculated by the ratio of signal to noise (S/N = 3). The results were shown in Table-1. The reproducibility of this method was also examined for 1.0 μg L^{-1} of Pd(II), Pt(II) and Rh(III). The relative standard deviations (n = 9) were also shown in Table-1.

Interference: The experiment show that under the pre-column derivatization conditions, the foreign ions of Cu(II),

TABLE-1
REGRESSION EQUATION, COEFFICIENT AND DETECT LIMIT

Components	Regression equation	Linearity range (μg L^{-1})	Coefficient	Detect limit (ng L^{-1})	RSD % (n = 11)
Pd-RBA	$A = 2.81 \times 10^6 C + 874$	0.10-100	r = 0.9995	12	3.0
Pt-RBA	$A = 2.55 \times 10^6 C - 1121$	0.12-120	r = 0.9993	18	2.9
Rh-RBA	$A = 2.62 \times 10^6 C - 963$	0.15-150	r = 0.9990	20	3.5

TABLE-2
DETERMINATION RESULTS (ng g^{-1}) OF THE SAMPLES

Samples	Found (ng g^{-1})			RSD % (n = 5)			Recovery % (n = 5)		
	Pt	Pd	Rh	Pt	Pd	Rh	Pt	Pd	Rh
Human urine (occupationally exposed)	0.71	0.284	0.182	2.5	3.0	3.2	92.4	93.6	91.5
Planting effluents	0.980	1.50	0.334	3.5	3.7	3.2	95.5	92.0	88.6
River water	0.061	0.072	0.028	3.3	2.5	3.2	91.3	90.5	92.4
Soil (nearby the highway)	72.13	93.0	45.2	2.8	2.5	2.6	93.0	92.6	90.5

Hg(II), Pb(II), Tl(III), Bi(III), Ag(I), Au(III) which can reacts with *p*-rhodanine azobenzoic acid to form colour chelates. However, the Pb-RBA, Tl-RBA, Bi-RBA chelates have not obvious absorbance at 455 nm and do not show peak in the chromatogram of 455 nm. The Cu-RBA, Hg-RBA, Ag-RBA, Au-RBA chelates have obvious absorbance at 510 nm and show peak in the chromatogram of 455 nm (Fig. 3). However, these chelate can be completely separated with Pt-RBA, Pd-RBA, Rh-RBA chelate and do not interfere the determination. This method is high selectivity.

Applied to the water and human urine samples: Taking an appropriate volume (planting effluents 20 mL, river water 200 mL, human urine 50 mL) of sample in a 500 mL flask. The samples were concentrated to *ca.* 5 mL by heating on a hot plate and were transferred into the 25 mL Teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China). To which, 2 mL of concentrated nitric acid 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 min. The digest was evaporated to near dryness. The residue was dissolved with 5 mL of 5 % of hydrochloric acid and transferred into a 50 mL of calibrated flask quantitatively. Then the palladium, platinum and rhodium contents were analyzed according to general procedure together with the results of a recovery test by adding 0.1 μg of Pt, Pd and Rh in samples according to standard addition procedure. The results (deducted the reagents blank) were shown in Table-2.

Applied to the soil: One g of soil sample was weighed into a 50 mL of Teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China). To which, 10 mL of aqua regia 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 0.5 h. The digested material was evaporated to incipient dryness. Then, 10 mL of 5 % hydrochloric acid was added and heated close to boiling to leach the residue. After cooled, the residue was filtrated and the undissolved residures was washed with 5 % hydrochloric acid two times. The leachate was collected into a 50 mL of calibrated flask quantitatively and the palladium, platinum and rhodium contents were analyzed according to general procedure together with the results of a recovery test by adding 0.1 μg of Pt, Pd and Rh in samples according to stanrd addition procedure. The results (deducted the reagents blank) were shown in Table-2.

Conclusion

The proposed method has the following characteristic:

(1) *p*-rhodanine azobenzoic acid is a sensitive and convenience pre-column derivatization regents for palladium, platinum and rhodium. The palladium, platinum and rhodium ions can form stable colour chelates with *p*-rhodanine azobenzoic acid at room temperature rapidly and the molar absorptivity was calculated to be 1.37×10^5 L mol^{-1} cm^{-1} for Pt-RBA chelate, 1.21×10^5 L mol^{-1} cm^{-1} for Pd-RBA chelate, 1.40×10^5 mol^{-1} cm^{-1} for Rh-RBA chelate.

(2) The ultra performance liquid chromatography (UPLC) was used. This technology takes full advantage of chromatographic principles to run separations using columns packed with smaller particles and/or higher flow rates for increased speed, with superior resolution and sensitivity. The Pt-RBA, Pd-RBA and Rh-RBA chelates were separated completely within 2.5 min. Compared to the routine chromatographic method, more then 80 % of separation time was shortened.

(3) By solid phase extraction, high enrichment factor of was achieved. The detection limits of palladium, platinum and rhodium reaches 12, 18 and 20 ng L^{-1}, respectively. Finally, for the determination of palladium, platinum and rhodium, this method is high sensitivity and high selectivity.

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