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Simultaneous Determination of Palladium and Platinum by On-line Enrichment and HPLC with 4-(2-Hydroxy-naphthalene-1-ylmethylene)-thiazolidine-2,5-Dithione as Pre-column Derivatization Reagent

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ABSTRACT

In this paper, a new reagent, 4-(2-hydroxy-naphthalene-1-ylmethylene)-thiazolidine-2,5-dithione (HNMTD) was synthesized. A new method for the simultaneous determination of palladium and platinum ions as metal-HNMTD chelates was developed using high performance liquid chromatography equipped with an on-line enrichment technique. Prior to chromatography the palladium and platinum ions were derivatized with HNMTD to coloured chelate complexes. The Pd-HNMTD and Pt-HNMTD complexes were then enriched on an enrichment column (ZORBAX Reversed Phase Stable Bound C_{18}, 4.6 × 10 mm, 1.8 μm) using a buffer solution of 0.05 mol L^{-1} sodium acetate-acetic acid buffer (pH 3.8) 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 (ZORBAX Reversed Phase Stable Bound C_{18}, 4.6 × 50 mm, 1.8 μm) was satisfactory when 72% methanol (containing 0.05 mol L^{-1} of pH 3.8 sodium acetate-acetic acid buffer salt and 0.1% of TritonX-100) was used as mobile phase. The Pt-HNMTD and Pd-HNMTD chelates were separated completely within 2 min. The detection limits (S/N = 3) for palladium and platinum were 1.2 ng L^{-1} and 1.4 ng L^{-1}, respectively. The method was applied with good results to the determination of palladium and platinum in water and urine samples.

KEYWORDS

Palladium, platinum, 4-(2-hydroxy-naphthalene-1-ylmethylene)-thiazolidine-2,5-dithione, high performance liquid chromatography, on-line enrichment.

1. Introduction

Environmental contamination by platinum group elements (PGEs), mainly from automotive catalytic converters, is exponentially increasing and reliable and accurate quantification is a mandatory task.[1–4] The wide use of palladium and platinum not only in automotive catalytic converters but in medical applications (Pt) and in food production (Pd)[5] has increased the release of these metals into the environment beyond levels attributed to traditional chemical industry. Moreover, the platinum group elements derived from automotive catalytic converters are released as nanocrystallites (particles less than 3 μm in diameter) as a result of thermal cracking of the catalyst and mechanical abrasion.[6–7] Nanoparticles are not blocked by the upper respiratory system and can therefore penetrate deeply into the lungs. Although the bioavailability and toxicology of PGEs 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.[8,9] The heterogeneous composition of samples and the low concentration levels of palladium and platinum make their direct measurement in various analytes very difficult. Several analytical techniques have been employed for the determination of PGEs in recent years and most of their advantages and disadvantages have been reviewed.[10–20] Several methods using high performance liquid chromatography for the determination of platinum group metals have been reported previously and have shown HPLC to be a exact and reliable technique.[17–23] However, previously used routine chromatographic methods require long separation times (more then 10 min is needed).

In this paper, a new reagent, 4-(2-hydroxy-naphthalene-1-ylmethylene)-thiazolidine-2,5-dithione (HNMTD) was used as pre-column derivatization reagent for palladium and platinum to synthesize the respective chelate complexes Pd-HNMTD and Pt-HNMTD, that were then separated by HPLC on a ZORBAX Reversed Phase C_{18} rapid analysis column (4.6 × 50 mm, 1.8 μm) using on-line enrichment. The Pd-HNMTD and Pt-HNMTD chelates were separated completely within 2.0 min. The separation time was greatly shortened compared to routine chromatographic methods. The new method is applicable with good results to the determination of μg L^{-1} (ppb) levels of palladium and platinum ions in water and human urine samples.

2. Experimental Procedures

2.1. Apparatus

The on-line enrichment system (Waters Corporation, USA) that was used in the experiments is shown in Fig. 1. The system includes a Waters 2690 Alliance quadripump, a Waters 515

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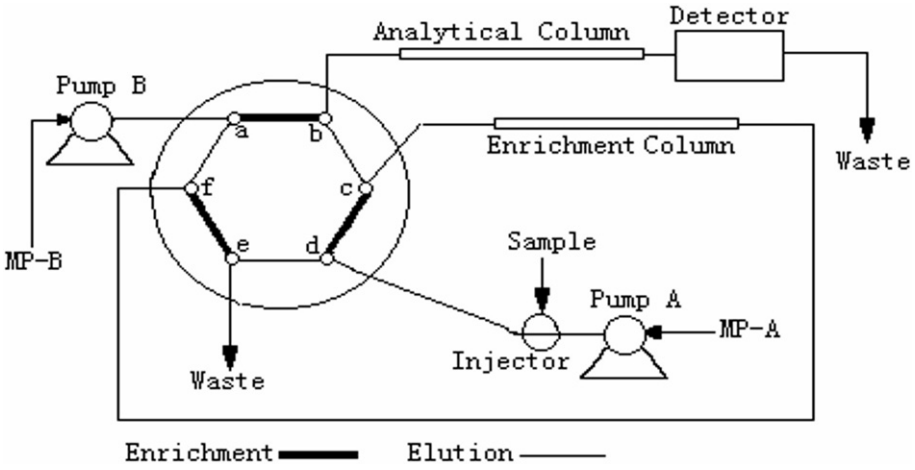
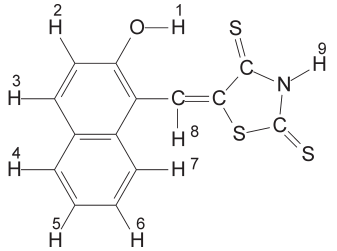


Figure 1 On-line enrichment system using the valve-switching technique. Pump A, Waters 515 Pump. Pump B, Waters 2690 Alliance quadripump. Injector can contain a 10 mL sample. Six-port switching valve (Waters Corporation). Enrichment Column, ZORBAX (4.6 × 10 mm, 1.8 μm). Analytical column, ZORBAX (4.6 × solution. MP B, 72% methanol (containing 0.05 mol L^{-1} of pH = 3.8 sodium acetate-acetic acid buffer salt and 0.1% of triton X-100).

pump, a Waters 996 photodiode array detector, a six-port switching valve, a large-volume injector (can handle 10.0 mL samples) and a column. The enrichment column is a ZORBAX Reversed Phase Silica-Bonded C_{18} pre-column (4.6 × 10 mm, 1.8 μm) and the analytical column is a ZORBAX Reversed Phase Silica-Bonded C_{18} rapid analysis column (4.6 × 50 mm, 1.8 μm) (Agilent Technologies, USA). The pH value was determined with a Beckman Φ-200 pH meter. The synthesis of HNMTD was carried out using a Quest Series chemical synthesis system (Argonaut Corporation, USA).

2.2. Synthesis of HNMTD

The HNMTD was synthesized by the following procedure: 50 mL acetic acid was added to 1.5 g (0.0101 mol) of thiazolidine-2,5-dithione and 1.7 g (0.0099 mol) of 2-hydroxy-1-naphthaldehyde. The mixture was heated gently to completely dissolve the thiazolidine-2,5-dithione and 2-hydroxy-1-naphthaldehyde. The solution was refluxed for about 1.0 h, and 0.5 mL of concentrated H_2SO_4 was added dropwise during refluxing *via* a dropping funnel. After the colour of the solution had turned red the reaction was stopped and the reaction mixture was poured into 150 mL distilled water. To this solution, a small amount of aqueous ammonia was added. The precipitate was isolated by filtration and recrystallized twice with absolute alcohol to give a yield of 46%. The structure of HNMTD was verified by elemental analysis, IR, ^{1}HNMR and MS. Elemental analysis: $C_{14}H_9NOS_3$, calculated (found), 55.42 (55.23)% C, 2.99 (3.15)% H, 4.62 (4.57)% N, 31.70 (30.68)% S. (KBr) (cm^{-1}): 3450 (ν_{-OH}), 3285 (ν_{-N-H}); 3060, 3020 ($\nu_{=C-H}$); 1660 (δ_{N-H}); 1566, 1548, 1515, 1450 ($\nu_{C=C}$); 1292 (ν_{C-N}); 1171, 1215 ($\nu_{C=S}$); 825 (δ_{Ar-H}); 806 ($\delta_{C=C-H}$). ^{1}HNMR (solvent: DMSO-d_6) (δ,ppm): 4.85 (1H, s, C-OH, H 1); 6.95–7.58 (6 H, m, Ar-H, H 2–7); 6.58 (1H, s, -C=C-H, s, H 8); 2.16 (1 H, s, N-H, H 9). MS (EI) (m/z): 303 (M^+). These experimental data are consistent with the shown structure.



2.3. Chemicals

All solutions were prepared using ultra-pure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). Palladium and platinum standard solutions (1.0 mg mL^{-1}) were obtained from the Chinese Standards Center, and a working solution of 0.2 μg mL^{-1} was prepared by diluting the standard solutions. Methanol (HPLC grade) was obtained from Fisher Corporation, USA. TritonX-100 was obtained from Fluka Corporation, Switzerland, and TritonX-100 solution (1%) was prepared by dissolving 5.0 g of TritonX-100 in water and diluting to a volume of 500 mL. A sodium acetate-acetic acid buffer solution (0.5 mol L^{-1}, pH 3.8) was used. A HNMTD solution (2.0×10^{-4} mol L^{-1}) was prepared by dissolving HNMTD in 95% ethanol. A 0.05 mol L^{-1} pH 3.8 sodium acetate-acetic acid buffer solution was used as mobile phase A and a solution of 72% methanol (containing 0.05 mol L^{-1} of pH 3.8 sodium acetate-acetic acid buffer salt 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.

2.4. Sample Preparation

Using an appropriate volume (industrial plant effluents 20 mL, river water 200 mL, human urine 50 mL) of sample in a 500 mL flask the samples 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 on 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% 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 analysed 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[24] was used as a reference method and the results are also shown in Table 1.

Table 1 Comparison of Pd and Pt concentrations ($\mu g\ L^{-1}$) determined by HPLC and ICP-MS. (The samples were prepared according to section 2.4.; palladium and platinum were analysed according to the standard procedure. The ICP-MS analysis was carried out as described in the literature.[24])

Samples	Found ($\mu g\ L^{-1}$)		ICP-MS method ($\mu g\ L^{-1}$)		RSD % ($n = 5$)		Recovery % ($n = 5$)	
	Pd	Pt	Pd	Pt	Pd	Pt	Pd	Pt
Human urine (general population)	0.0263	0.0105	0.0246	0.0128	3.3	3.5	8	92
Human urine (occupationally exposed)	0.518	0.236	0.521	0.245	3.1	3.2	9	89
Planting effluents	0.512	0.278	0.531	0.267	2.6	2.8	88	93
River water	0.0786	0.0515	0.0763	0.0492	3.2	3.3	86	91

2.5. Standard Procedure

0~15 mL of a 0.2 $\mu g\ mL^{-1}$ standard or sample solution were transferred into a 25 mL volumetric flask, to which 4.0 mL of 1.0×10^{-4} mol L^{-1} HNMTD solution, 3 mL of 0.5 mol L^{-1} sodium acetate-acetic acid buffer solution (pH 3.8) and 1.0 mL of 1% TritonX-100 solution were added. They were diluted to the mark with deionized water and mixed well. After 10 min, 10.0 mL of that solution were introduced into the injector and transported to the enrichment column using mobile phase A at a flow rate of 2.0 mL min^{-1}. After the enrichment was completed the six-port switching valve was switched and the metal-HNMTD chelates, which adsorbed onto the top of the enrichment column, were eluted with mobile phase B at a flow rate of 2.0 mL min^{-1} in reverse direction and transported to the analytical column. The chelate complexes were separated on the analytical column. A 3D (*X* axis: retention time, *Y* axis: wavelength, *Z* axis: absorbance) chromatogram was recorded from 350~600 nm using a photodiode array detector. The chromatogram at 535 nm is shown in Fig. 2.

3. Result and Discussion

3.1. Pre-column Derivation

The optimum pH for complex formation of HNMTD with metal ions was 1.8~5.2 for palladium and 1.5~4.6 for platinum. A 0.5 mol L^{-1} sodium acetate-acetic acid buffer solution of pH 3.8 is therefore recommended to control the pH.

It was found that 0.5 mL of a 1.0×10^{-4} mol L^{-1} HNMTD solution was sufficient to complex 5.0 μg of palladium and platinum, respectively. In real samples, however, foreign ions such as Hg^{2+}, Pb^{2+}, Cu^{2+}, Rh^{3+}, or Ag^{+} form complexes with HNMTD and consume reagents. It was therefore necessary to use an excess of HNMTD and 4.0 mL of a 1.0×10^{-4} mol L^{-1} HNMTD solution is recommended.

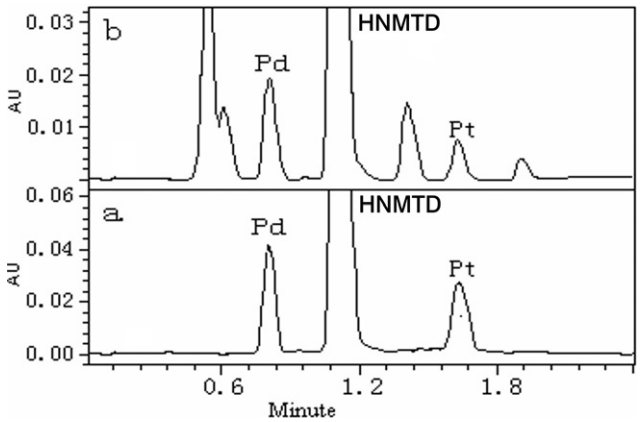


Figure 2 Chromatogram of (**a**) standard sample and (**b**) occupationally exposed human urine samples. The concentration of palladium and platinum is 1.0 $\mu g\ L^{-1}$ in standard sample, and the other conditions are as in the standard procedure.

The experiments showed that in the presence of nonionic or cationic surfactants, the response of the detector to metal-HNMTD chelates was markedly increased. Various nonionic or cationic surfactants enhanced the absorbance in the following sequence: TritonX-100 > Tween-80 > Tween-20 > CTMAB > CPB. TritonX-100 was therefore selected as additive in this experiment. The use of 0.6~2 mL of TritonX-100 solution gave a constant and maximum absorbance. Accordingly, the addition of 1.0 mL of TritonX-100 solution is recommended.

HNMTD reacted rapidly with Pd(II) and Pt(II) and the reaction was complete after 5 min at room temperature. The formed complexes were both stable for at least 8 h.

3.2. 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-HNMTD and Pt-HNMTD chelates were stable in weakly acidic medium and to avoid decomposition of the chelates during the enrichment step, a 0.05 mol L^{-1} sodium acetate-acetic acid buffer solution of pH 3.8 (mobile phase A) was selected as mobile phase for transport of the chelates to the enrichment column while a ZORBAX Reversed Phase C_{18} pre-column (4.6 × 10 mm, 1.8 μm) with a pH range of 2~11.5 was selected as enrichment column.

The aim of the present research was to determine trace metal ions by injecting a large-volume sample. The effect of the injection volume was therefore investigated. An injection volume of 0.1~20 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 20 mL. An injection volume of 10 mL was found to be sensitive enough to determine palladium and platinum in all experiments and a injection volume of 10 mL is therefore recommended.

3.3. Spectrophotometric Properties

The absorption spectrum of the metal-HNMTD chelates was measured with a Shimidzu UV-2401 spectrophotometer. The

Table 2 Calibration curve, Coefficients And Detection limits. [The calibration curve was obtained from the peak areas of standard samples concentrations of 2~10000 ng × L^{-1}. The detect limits were obtained form the signal to noise ratio (S/N = 3). The RSD was obtained from 11 measurements of 1.0 μg L^{-1} of Pd(II) and Pt(II).]

Components	Regression equation	Linearity range (ng L^{-1})	Coefficient	Detect limit (ng L^{-1})	RSD % (n = 11)
Pd-HNMTD	$A = 2.86 \times 10^6 C - 1842$	6~8200	r = 0.9992	1.2	2.3
Pt-HNMTD	$A = 2.47 \times 10^6 C + 1251$	8~9500	r = 0.9991	1.4	2.6

results showed that the maximum absorption is found at a wavelength of 530 nm for Pd-HNMTD and 538 nm for Pt-HNMTD. An intermediate wavelength of 535 nm was therefore selected.

3.4. Chromatographic Separation

The optimum conditions for chromatographic separation were studied using the on-line model. The experiments showed that the Pd-HNMTD and Pt-HNMTD have a high stability in weakly acidic buffer solution in the presence of TritonX-100. A pH of the mobile phase in a range of 1.8~4.5 and containing 0.05~0.2% of TritonX-100 prevented the decomposition of the metal complexes during separation and resulted in a good peak shape. Methanol/water (72/28) (containing 0.05 mol L^{-1} of pH 3.8 sodium acetate-acetic acid buffer salt and 0.1% of TritonX-100) was therefore selected as the mobile phase. To shorten the chromatographic separation time, a ZORBAX Reversed Phase C_{18} column (4.6 × 50 mm, 1.8 μm) was selected in this experiment. This allowed complete separation of the palladium and platinum chelates in 2 min, which represents a reduction in separation time of 85% compared to routine chromatographic methods.

3.5. Calibration Graphs

Under optimum conditions, calibration curves (peak area analysis) for metal-HNMTD chelates were established based on five standard samples of 10 ng L^{-1}, 50 ng L^{-1}, 250 ng L^{-1}, 1250 ng $L^{-1}$and 6250 ng L^{-1}. The limits of detection were calculated from the signal to noise ratio (S/N = 3). The results are shown in Table 2. The reproducibility of the method was verified by repeated measurements of a 1.0 μg L^{-1} of Pd(II) and Pt(II) standard. The relative standard deviations (n = 10) are shown in Table 1.

3.6. Interference

Under pre-column derivatization conditions foreign ions such as Cu(II), Hg(II), Pb(II), Tl(III), Bi(III), Ag(I), Au(III), Rh(III), Ru(III) can form coloured stable chelate complexes with HNMTD. To examine the selectivity of this method, possible interference by these foreign ions was investigated. When 4.0 mL of 1.0 × 10^{-4} mol L^{-1} HNMTD was used for samples with 10 μg L^{-1} of Pd(II) and Pt(II), respectively, the tolerance (with an error of ±5%) for Cu(II), Hg(II), Pb(II), Ag(I) was 2000 μg L^{-1}, for Tl(III), Bi(III), Ir(IV), Au(III) 500 μg L^{-1} and for Rh(III), Ru(III) 200 μg L^{-1}. The described method is therefore highly selective.

4. Conclusion

The proposed method has the following characteristics: (1) 4-(2-hydroxy-naphthalene-1-ylmethylene)-thiazolidine-2,5-dithione 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 ZORBAX rapid analysis column within 2 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 (10 mL) thereby greatly improving the sensitivity of the method.

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