ISSN 1061-9348, Journal of Analytical Chemistry, 2007, Vol. 62, No. 1, pp. 58–62. © Pleiades Publishing, Ltd., 2007.

ARTICLES

Determination of Palladium, Platinum, and Rhodium by HPLC with Online Column Enrichment Using 4-Carboxylphenyl-Thiorhodanine As a Precolumn Derivatization Reagent[1]

H. Lin[a], Z. J. Huang[a], Q. Hu[a], G. Yang[a], and G. Zhang[b]

[a] *Department of Chemistry, Yunnan University, Kunming, 650091 China*

[b] *Guangzhou Institute of Geochemistry, China Academy of Sciences, Guangzhou, 510640 China*

e-mail: huqiufena@163.com

Received March 16, 2005; in final form, June 19, 2006

Abstract—In the present work, 4-carboxylphenyl-thiorhodanine (CPTR) was synthesized. A new method for the simultaneous determination of palladium, platinum, and rhodium ions as metal-CPTR chelates was developed using rapid column high-performance liquid chromatography equipped with an online enrichment capability. Palladium, platinum, and rhodium ions were precolumn-derivatized with CPTR to form colored chelates. The Pd-CPTR, Pt-CPTR, and Rh-CPTR chelates can absorbed onto the front of the enrichment column (ZORBAX Stable Bound, 4.6 × 10 mm, 1.8 μm) when they are injected with a buffer solution of 0.05 M sodium acetate-acetic acid (pH 3.5) as mobile phase. After the enrichment had finished, by switching the six-port switching valve, the retained chelates were back-flushed by mobile phase and moved towards the analytical column. The chelate separation on the analytical column (ZORBAX Stable Bound, 4.6 × 50 mm, 1.8 μm) was achieved with 46% acetonitrile (containing 0.05 M of pH 3.5 sodium acetate-acetic acid buffer and 0.01 M tritonX-100) as mobile phase. The palladium, platinum, and rhodium were separated completely within 2 min. The detection limits ($S/N = 3$) of palladium, platinum, and rhodium are 1.4, 1.6, and 2.0 ng/L, respectively. The method was applied to the determination of palladium, platinum, and rhodium in water, urine, and soil samples with good results.

DOI: 10.1134/S1061934807010121

Environmental contamination by the platinum group elements (PGEs), mainly related to automotive catalytic converters, is exponentially increasing, and reliable and accurate quantification is a mandatory task [1–4]. The wide use of palladium, platinum, and rhodium not only in automotive catalytic converters but as a drug (Pt) and in food production (Pd) [5] has led to a more uncontrolled release of those metals in the environment, with respect to the traditional chemical industry. Moreover, the platinum group elements derived from automotive catalytic converters are released as nanocrystallites (particles less than 3 μm in diameter) due to thermal cracking of the catalyzer structure and to mechanical abrasion [6, 7]. These particles are not blocked by the upper respiratory system and can deeply interact with the lungs. Although the bioavailability and toxicology of PGEs is still an open question, the determination of basal concentrations of these metals has a key role because of the increase in their level [8, 9]. 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 in recent years, and most of the advantages and drawbacks have been reviewed [10–20]. In previous work, a high-performance liquid chromatography method for the determination of platinum group metals has been reported. The method has proven to be a favorable and reliable technique [17–23]. However, the routine chromatographic methods need a long separation time (more then 10 min).

In this paper, a new reagent, 4-carboxylphenyl-Thiorhodanine (CPTR), was first synthesized and used as a precolumn derivatization regent for palladium, platinum, and rhodium, and a ZORBAX Stable Bound rapid analysis column (4.6 × 50 mm, 1.8 μm) was used for the separation of Pd-CPTR, Pt-CPTR, and Rh-CPTR chelates on a high-performance liquid chromatograph equipped with an online enrichment capability. Palladium, platinum, and rhodium can form stable color chelates with CPTR at room temperature rapidly, and the metal chelates were separated completely within 2.0 min. The separation time was greatly shortened compared to the routine chromatographic methods. This method can be applied to the determination of the μg/L level of palladium, platinum, and rhodium

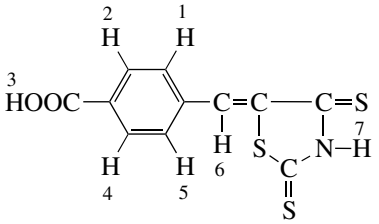
[1] The text was submitted by the authors in English.

ions in water, human urine, and soil samples with good results.

EXPERIMENTAL

Apparatus. The online column enrichment system used is shown in Fig. 1. This system includes a Waters 2690 Alliance quadripump, Waters 515 pump, Waters 996 photodiode array detector, six-port switching valve, large volume injector (containing 10.0 mL samples), and column. The enrichment column is a ZORBAX Stable Bound precolumn (4.6 × 10 mm, 1.8 μm) and the analytical column is a ZORBAX Stable Bound rapid column (4.6 × 50 mm, 1.8 μm). The pH value was determined with a Beckman F-200 pH meter.

Synthesis of CPTR. CPTR was synthesized using the following procedure: 50 mL of acetic acid was added to a sample of 1.5 g of thiorhodanine and 1.9 g of 4-carboxylbenzaldehyde, and the mixture was heated gently to dissolve the thiorhodanine and 1.9 g of 4-carboxylbenzaldehyde completely. The solution was refluxed for about 1.0 h, and 0.5 mL of concentrated sulfuric acid was added dropwise during refluxing. After the color of the solution turned red, the refluxing was stopped and the sample was poured into 150 mL of distilled water. A small amount of aqueous ammonia was added to the solution. Thereafter, the precipitants were separated by filtration and were recrystallized twice with absolute alcohol. The yield was 52%. The structure of CPTR was verified by elemental analysis, IR, ^{1}HNMR and MS. Elemental analysis: $C_{11}H_7NO_2S_3$; calculated (found), 46.95 (46.89%) C, 2.51 (2.64%) H, 4.98 (4.91%) N, 34.19 (34.13%) S. IR (KBr) (cm^{-1}): 3520–2540 (ν_{-COOH}); 3060, 3030 ($\nu_{=C-H}$); 1660 (δ_{N-H}); 1566, 1548, 1515 ($\nu_{-C=C}$); 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): 10.94 (1 H, s, –COOH, H 3); 8.02 (2 H, d, Ar–H, H 2 and H 4); 7.58 (2 H, d, Ar–H, H 1 and H 5); 6.35 (1 H, s, –C=C–H, H 6). MS (El) (*m*/*z*): 281 (M^+). All this shows that CPTR has the following structure.



Chemicals. All of the solutions were prepared with HOOC ultrapure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, United States). Palladium, platinum, and rhodium standard solution (1.0 mg/mL) was obtained from the Chinese Standards Center. A working solution of 0.2 μg/mL was prepared by diluting this standard solution. HPLC grade acetonitrile (Fisher Corporation, United States) and sodium acetate-acetic acid buffer solution (0.5 M, pH 3.5) were used. CPTR solution (2.0×10^{-4} M) was prepared by dissolving CPTR with 95% ethanol. Mobile phase A: 0.05 M pH 3.5 sodium acetate-acetic acid buffer solution. Mobile phase B: 46% acetonitrile (containing 0.05 M of pH 3.5 sodium acetate-acetic acid buffer salt and 0.01 M of Triton X-100). All other reagents used were of analytical reagent grade. The glass and Teflon ware used were soaked in 5% nitric acid for at least 2 h and then thoroughly wash with pure water.

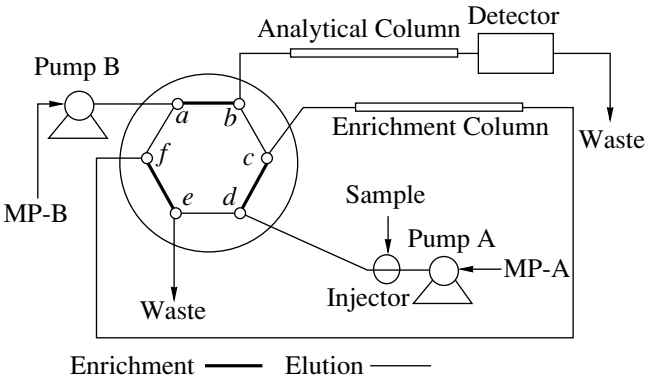


Fig. 1. Online enrichment system using the valve-switching technique. Pump A, Waters 515 Pump. Pump B, Waters 2690 Alliance quadripump. Injector can contain 10 mL of sample. Six-port switching valve (Waters Corporation). Enrichment Column, ZORBAX (4.6 × 50 mm, 1.8 μm). Analytical column, ZORBAX (4.6 × 50 mm, 1.8 μm). Detector, Waters 996 photodiode array detector. MP A, 0.05 M of pH 3.5 sodium acetate-acetic acid buffer solution MP B, 46% acetonitrile (contain 0.05 M sodium acetate-acetic acid buffer pH 3.5 and 0.01 M tritonX-100).

Standard procedure. A 0–15 mL portion of 0.2 μg/mL standard or sample solution was transferred into a 25-mL of volumetric flask. 4.0 mL of 1.0×10^{-4} M CPTR solution, 3.0 mL of 0.5 M sodium acetate-acetic acid buffer solution (pH 3.5), and 1.0 mL of 1% TritonX-100 solution were added. The solution was diluted to volume with water and mixed well. After 10 min, 10.0 mL of solution were introduced into the injector and sent to the enrichment column with mobile phase A at a flow rate of 2.0 mL/min. When the enrichment had finished, by switching the valve of the six-port switching valve, the metal-CPTR chelates, which absorbed onto the foreside of the enrichment column, were eluted by mobile phase B at a flow rate of 2.0 mL/min in the reverse direction and moved towards the analytical column. The chelates were separated on the analytical column. A tridimensional (*X* axis: retention time, *Y* axis: wavelength, *Z* axis: absorbance) chromatogram was recorded at 400 ~ 650 nm with a photodiode array detector; the chromatogram at 510 nm is shown in Fig. 2.

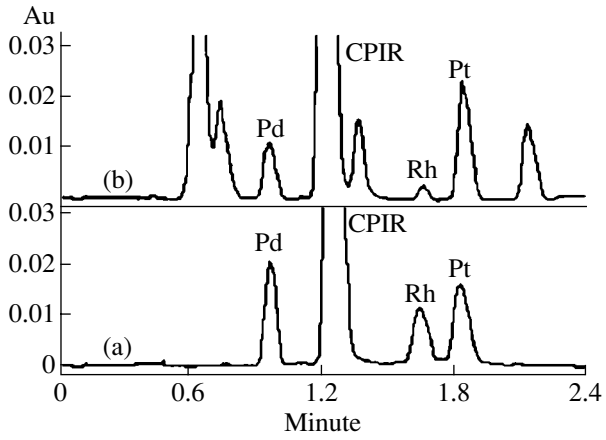


Fig. 2. Chromatogram of the standard sample (a) and occupationally exposed human urine sample (b). The concentration of palladium, platinum, and rhodium is 1.0 μg/L in the standard sample.

RESULTS AND DISCUSSION

Precolumn derivation. The optimal pH value for the CPTR reaction with metal ions is 2.3–5.8 for palladium, 2.1–4.6 for platinum, and 1.2–4.2 for rhodium, so 0.5 M (pH 3.5) sodium acetate-acetic acid buffer solution was recommended to control pH.

It was found that 1.0 mL of 1.0×10^{-4} M CPTR solution was sufficient to complex 5.0 μg of palladium, platinum, and rhodium. However, in real samples, foreign ions such as Hg^{2+}, Pb^{2+}, Cu^{2+}, and Ag^{+} form complexes with CPTR. Therefore, the amount of CPTR must be in excess. In this experiment, 4.0 mL of 1.0×10^{-4} M CPTR solution was recommended.

The experiments show that, in a nonionic surfactant or cationic surfactant medium, the sensitivity of the metal-CPTR chelates was increased markedly. Various nonionic surfactants and cationic surfactants enhance the absorbance in the following sequence: TritonX-100 > Tween-80 > Tween-20 > CTMAB > CPB. Therefore, TritonX-100 was selected as additive in this experiment. The use of 0.5–1.5 mL of TritonX-100 solution gives a constant and maximum absorbance in this experiment. Accordingly, 1.0 mL TritonX-100 solution was recommended.

CPTR can react with Pd(II), Pt(II), and Rh(III) rapidly. The reaction completed within 5 min at room temperature, and the complex was stable for at least 6 h.

Online enrichment. The Pd-CPTR, Pt-CPTR, and Rh-CPTR chelates are stable in an acid medium. To prevent the chelates from decomposing during enrichment, 0.05 M sodium acetate-acetic acid buffer solution of pH 3.5 (mobile phase A) was selected as mobile phase to transfer the chelates to the enrichment column and a ZORBAX Stable Bound precolumn (4.6 × 10 mm, 1.8 μm) with a pH range of 1–11.5 was selected as enrichment column. Experiments showed that the sample injected volume of 10 mL was sensitive enough to determine Pt(II), Pd(II), and Rh(III) in water, urine, and soil samples, so a 10-mL sample injection was recommended.

Spectrophotometric data. The absorption spectrum of metal-CPTR chelates was obtained with a Shimadzu UV-2401 spectrophotometer. Results show that the maximum absorption is at 518 nm for Pd-CPTR chelate, at 512 nm for Pt-CPTR and at 515 nm for Rh-CPTR chelate. Therefore, 515 nm was selected as the detecting wavelength.

Chromatographic separation. The experiments showed that the Pd-CPTR, Pt-CPTR, and Rh-CPTR chelates have a good stability in the presence of an acid buffer solution and the TritonX-100 medium. The pH of mobile phase 2.5–3.8 and 0.008–0.12 M of TritonX-100 help to prevent the metal-chelate from decomposing in the course of separation and provide a good peak shape. Thus, an acetonitrile/water (46/54) mixture (containing 0.05 M pH 3.5 sodium acetate-acetic acid buffer salt and 0.01 M tritonX-100) was selected as mobile phase. To shorten the chromatographic separation time, a ZORBAX Stable Bound rapid analysis column (4.6 × 50 mm, 1.8 μm) was selected in this experiment. With the rapid analysis column, the palladium, platinum, and rhodium chelates were separated completely within 2 min. Compared to the routine chromatographic method, the separation time was shortened by over 80%.

Calibration graphs. Under optimum conditions, regression equations of metal-CPTR chelates were established based on the standard sample injected and its peak areas. The limits of detection are calculated by the signal to noise ratio (S/N=3). The results are shown in Table 1. The reproducibility of this method was also examined for 1.0 μg/L of Pd(II), Pt(II), and Rh(III). The relative standard deviations (n = 10) are also shown in Table 1.

Interference. Under the precolumn derivatization conditions, foreign ions of Cu(II), Hg(II), Pb(II), Tl(III), Bi(III), Ag(I), and Au(III) can react with CPTR

Table 1. Regression equation, coefficient, and detection limit

Component	Regression equation	Linearity range, ng/L	Coefficient r	Detection limit, ng/L	RSD, % (n = 11)
Pd-CPTR	$A = 1.86 \times 10^6 c + 1521$	11–9000	0.9996	1.4	2.2
Pt-CPTR	$A = 1.98 \times 10^6 c - 1436$	8–8000	0.9998	1.6	2.4
Rh-CPTR	$A = 1.72 \times 10^6 c + 1658$	12–9500	0.9993	1.8	2.3

Table 2. Determination Pt, Pd, and Rh (ng/g) in the samples

Samples	Found, ng/g;			ICP-MS Method, ng/g			RSD, % ($n = 5$)			Recovery, % ($n = 5$)		
	Pt	Pd	Rh	Pt	Pd	Rh	Pt	Pd	Rh	Pt	Pd	Rh
Human urine (general population)	0.0287	0.0175	0.0125	0.0296	0.0159	0.0112	3.1	3.2	3.5	93	91	88
Human urine (occupationally exposed)	0.684	0.228	0.113	0.698	0.241	0.106	2.9	2.8	3.1	91	93	89
Planting effluents	0.846	1.852	0.143	0.831	1.839	0.152	3.1	3.4	3.2	94	93	91
River water	0.0532	0.0416	0.0165	0.0518	0.0546	0.0178	2.9	3.2	3.3	89	92	89
Soil (near the highway)	69.3	92.8	51.2	70.2	91.3	52.8	2.8	3.1	3.5	94	95	88
Soil (general)	19.5	28.4	8.32	17.8	27.2	8.18	3.4	3.3	3.7	93	91	86

to form color chelates. To examine the selectivity of the method, the interference of these foreign ions was investigated. When 4.0 mL of 1.0×10^{-4} M CPTR was used, with 10 μg/L of Pd(II), Pt(II), and Rh(III), respectively, the tolerance amount with an error of ±5% was 2500 μg/L for Cu(II), Hg(II), Pb(II), Ag(I) and 600 μg/L for Tl(III), Bi(III), Au(III).

Application to analysis of water and human urine samples. An appropriate volume (planting effluents 20 mL, river water 200 mL, human urine 50 mL) of sample was taken in a 500-mL flask. The samples were concentrated to about 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). 2.0 mL of concentrated nitric acid and 3.0 mL of 30% hydrogen peroxide were 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 digest was evaporated to near dryness. The residue was dissolved with 5 mL of 5% of hydrochloric acid and transferred into a 25-mL calibrated flask quantitatively and was then diluted to volume with 5% hydrochloric acid. The palladium, platinum, and rhodium contents were analyzed by using a proper volume of this solution according to general procedure. The results (deducting the reagents blank) are shown in Table 2.

Application to analysis of soil. A 1.0000 g soil sample was weighed into a 50-mL teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China). 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 30 min. 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 filtered and the undissolved residue was washed with 5% hydrochloric acid two times. The leachate was collected into a 25-mL calibrated flask quantitatively and diluted to volume with 5% hydrochloric acid. The palladium, platinum, and rhodium contents were determined by using a proper volume of this solution according to general procedure. The results (deducted the reagents blank) are shown in Table 2.

CONCLUSIONS

The proposed method has the following features: (1) 4-carboxylphenyl-thiorhodanine was first synthesized and used as precolumn derivatization reagent for Pd, Pt, and Rh ions, and the ZORBAX rapid analysis column was used for the separation of Pt-CPTR, Pd-CPTR, and Rh-Pd-CPTR chelates. CPTR can react with palladium, platinum, and rhodium rapidly at room temperature. The Pt-CPTR, Pd-CPTR, and Rh-Pd-CPTR chelates were separated completely within 2 min. Compared to the routine chromatographic method, the separation time was shortened by more than 85%. (2) Using an online enrichment system, a large volume of sample (10 mL) can be injected, and the sensitivity of the method is greatly improved. This method has high sensitivity and high selectivity for the determination of palladium, platinum, and rhodium.

REFERENCES

1. Farago, M.E., Kavanagh, P., Blanks, R., Kelly, J., Kazantzis, G., Thornton, I., Simpson, P.R., Cook, J.M., Delves, H.T., and Hall, G.E.M., *Analyst*, 1998, vol. 451, p. 123.
2. Wei, C. and Morrison, G.M., *Sci. Total. Environ.*, 1994, vol. 169, p. 146.
3. Lucena, P., Vadillo, J.M., and Laserna, J.J., *Anal. Chem.*, 1999, vol. 71, p. 4385.
4. Helmes, E., *Environ. Sci. Pollut. Res.*, 1997, vol. 4, p. 100.
5. Hu, Q.F., Yang, G.Y., Yang, J.H., and Yin, J.Y., *J. Environ. Monitor.*, 2002, vol. 4, p. 956.
6. Savchenko, V.I., and Makaryan, I.A., *Plat. Metals Rev.*, 1999, vol. 43, p. 74.

7. Hu, Q.F., Chen, X.B., Huang, Z.J., Chen, J., and Yang, G. Y., *Anal. Sci.*, 2006, vol. 22, p. 627.
8. Palacios, M.A., and Gomez, M., *Sci. Total. Environ.*, 2000, vol. 182, p. 1.
9. Hu, Q.F., Yang, X.J., Huang, Z.J., Chen, J., and Yang, G.Y., *J. Chromatogr., A*, 2005, vol. 1094, p. 77.
10. Hu, Q.H., Yang, G. Y, Huang, Z.J., and Yin, J.Y., *Talanta*, 2002, vol. 58, p. 467.
11. Georgieva, M. and Pihlar, B., *Fresenius' J. Anal. Chem.,* 1997, vol. 357, p. 874.
12. Godlewska-Zylkiewicz, B. and Zaleska, M., *Anal. Chim. Acta*, 2002, vol. 462, p. 305.
13. Krachler, M., Alimonti, A., Petrucci, F., Irgolic, K.J., Forastiere, F., and Caroli, S., *Anal. Chim. Acta*, 1998, vol. 363, p. 1.
14. Hu, Q.F., Yang, G.Y., Yao, Y., and Yin, J.Y., *Talanta*, 2002, vol. 57, p. 751.
15. Wollenweber, D., Straaburg, S., and Wunsch, G., *Fresenius' J. Anal. Chem.*, 1999, vol. 364, p. 33.
16. Boulyga, S.F., Dietze, H.J., and Becker, J.S., *Microchim. Acta*, 2001, vol. 137, p. 93.
17. Philippeit, G. and Angerer, J., *J. Chromatogr., B*, 2001, vol. 760, p. 237.
18. Gregurek, D., Reimannb, C., and Stump, E.F., *Environ. Pollut.*, 1998, vol. 102, p. 221.
19. Parent, M., Vanhoe, H., Moens, L., and Dams, R., *Fresenius' J. Anal. Chem.*, 1996, vol. 354, p. 64.
20. Bruzzoniti, M.C., Cavalli, S., Mangia, A., Mucchino, C., Sarzanini, C., and Tarasco, E., *J. Chromatogr., A*, 2003, vol. 997, p. 51.
21. Barefoot, R.R. and Vanloon, J.C., *Anal. Chim. Acta*, 1996, vol. 364, p. 5.
22. Hoshi, S., Higashihara, K., Suzuki, M., and Sakurada, Y., *Talanta*, 1997, vol. 44, p. 571.
23. Wang, H., Zhang, H.S., and Cheng, J. K., *Talanta,* 1999, vol. 48, p. 1.