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Simultaneous determination of palladium, platinum, rhodium and gold by on-line solid phase extraction and high performance liquid chromatography with 5-(2-hydroxy-5-nitrophenylazo)thiorhodanine as pre-column derivatization regents

Qiufen Hu [a,b,c], Xiangjun Yang [a], Zhangjie Huang [a], Jing Chen [a,c], Guangyu Yang [a,*]

[a] *Department of Chemistry, Yunnan University, Kunming 650091, China*
[b] *Department of Chemistry, Yuxi Teacher's College, Yuxi 653100, China*
[c] *Faculty of Materials and Metallurgical Engineering, Kunming University of Science and Technology, Kunming 650031, China*

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Abstract

In this paper, 5-(2-hydroxy-5-nitrophenylazo)thiorhodanine (HNATR) was synthesized. A new method for the simultaneous determination of palladium, platinum, rhodium and gold ions as metal-HNATR chelates was developed using a rapid analysis column high performance liquid chromatography equipped with on-line solid phase extraction technique. The samples (Water, human urine, geological samples and soil) were digested by microwave acid-digestion. The palladium, platinum, rhodium and gold ions in the digested samples were pre-column derivatized with HNATR to form colored chelates. The Pd-HNATR, Pt-HNATR, Rh-HNATR and Au-HNATR chelates can be absorbed onto the front of the enrichment column when they were injected into the injector and sent to the enrichment column [Zorbax Stable Bound, 10 mm × 4.6 mm, 1.8 μm] with a buffer solution of 0.05 mol L^{-1} phosphoric acid as mobile phase. After the enrichment had finished, by switching the six ports switching valve, the retained chelates were back-flushed by mobile phase and travelling towards the analytical column. These chelates separation on the analytical column [Zorbax Stable Bound, 10 mm × 4.6 mm, 1.8 μm] was satisfactory with 72% acetonitrile (containing 0.05 mol L^{-1} of phosphoric acid and 0.1% of Triton X-100) as mobile phase. The palladium, platinum, rhodium and gold chelates were separated completely within 2.5 min. Compared to the routine chromatographic method, more then 80% of separation time was shortened. By on-line solid phase extraction system, a large volume of sample (10 mL) can be injected, and the sensitivity of the method was greatly improved. The detection limits (S/N = 3, the sample injection volume is 10 mL) of palladium, platinum, rhodium and gold in the original samples reaches 1.4, 1.8, 2.0 and 1.2 ng L^{-1}, respectively. The relative standard deviations for five replicate samples were 2.4–3.6%. The standard recoveries were 88–95%. This method was applied to the determination of palladium, platinum, rhodium and gold in human urine, water and geological samples with good results.

Keywords: Palladium; Platinum; Rhodium; Gold; 5-(2-Hydroxy-5-nitrophenylazo)thiorhodanine; Rapid column high performance liquid chromatography; On-line solid phase extraction

1. Introduction

Environmental contamination by the precious metal, mainly related to electroplating, hydrogenation catalyst, microcontactors in the electronics, hard alloy in dentistry and the three-way catalysts in automobile exhaust gas catalytic beads, is exponentially increasing [1–9]. However, the heterogeneous composition of samples and the low concentration levels of precious metal make the direct measurement of precious metals really difficult. Several analytical techniques have been employed with this matrix in recent

* Corresponding author. Fax: +86 8718316812.
E-mail address: huqiufena@163.com (G. Yang).

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years and most of the advantages and drawbacks have been reviewed [10–20]. In previous work, some high performance liquid chromatography method for the determination of precious metals with derivatization has been reported. This has been proved to be a favorable and reliable technique [17–23]. However, the routine chromatographic methods need a long separation time (more then 10 min is needed).

In this paper, to select a more sensitivity, selectivity and convenience derivatization reagents for palladium, platinum, rhodium and gold, a new reagent, 5-(2-hydroxy-5-nitrophenylazo)thiorhodanine (HNATR) was synthesized and used as pre-column derivatization regents for palladium, platinum, rhodium and gold. To shorten the separation time and improve the sensitivity, a Zorbax Stable Bound rapid analysis column (50 mm × 4.6 mm, 1.8 μm) was used for the separation of Pd-HNATR, Pt-HNATR, Rh-HNATR and Au-HNATR chelates on a high performance liquid chromatography equipped with on-line solid phase extraction technique. The palladium, platinum, rhodium and gold can form stable colored chelates with HNATR at room temperature at least after 8 min, and the metal chelates were separated completely within 2.5 min. The separation time was greatly shortened compared to the routine chromatographic methods. This method can be applied to the determination μg L^{-1} level of palladium, platinum, rhodium and gold ions in water, human urine and geological samples.

2. Experimental

2.1. Apparatus

On line column enrichment system used is shown in Fig. 1. This system includes a Waters quadripump, Waters 515 pump, Waters 996 photodiode array detector, six ports switching valve, large volume injector (can containing 10.0 mL samples) and column. The enrichment column is Zorbax Stable Bound reversed-phase C_{18} pre-column (10 mm × 4.6 mm, 1.8 μm) and the analytical column is Zorbax Stable Bound reversed-phase C_{18} rapid column (50 mm × 4.6 mm, 1.8 μm). The pH value was determined with a Beckman Φ-200 pH meter.

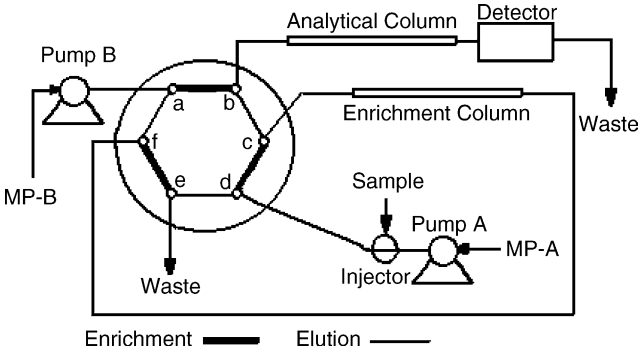

Fig. 1. On-line enrichment system using the valve-switching technique. Pump A: Waters 515 Pump. Pump B: Waters 2690 Alliance quadripump. Injector can contain 10 mL of sample. Six ports switching valve (Waters Corporation). Enrichment column, Zorbax (4.6 mm × 10 mm, 1.8 μm). Analytical column, Zorbax (4.6 mm × 50 mm, 1.8 μm). Detector, Waters 996 photodiode array detector. MP-A, 0.05 mol L^{-1} of phosphoric acid. MP-B, 72% acetonitrile (containing 0.05 mol L^{-1} of phosphoric acid and 0.1% of Triton X-100).

2.2. Synthesis of HNATR

In a 100 mL beaker, a 1.54 g of 4-nitro-2-aminophenol was dissolved in 45 mL of 95% alcohol. To this solution, 12.0 mL of 6.0 mol L^{-1} HCl were add and then cool the solution to 0 °C. After this, 7.0 mL of 10% $NaNO_2$ was added slowly with stiring to obtain a diazotized salt. In another 200 mL beaker, 1.48 g of thiorhodanine and 14 mL of 7.5 mol L^{-1} ammonia were added. After the solution has been cooled to 0 °C, The above diazotized solution was added dropwise and left the mixture overnight. The solution is then acidified to pH 1 with concentrated HCl and the precipitate was isolated by filter. The crude product was re-crystallized with 90% ethanol for three times, and the pure HNATR was obtained with a 62% yield. Its structure was be verified by IR, ^{1}H NMR, MS spectrometry and elemental analysis. Elemental analysis: $C_9H_6N_4O_3S_3$, calculated (found), 34.39 (33.98)% C, 1.92 (2.03)% H, 17.82 (17.64)% N, 30.60 (30.28)% S. IR (KBr) (cm^{-1}): 3600 (ν_{-OH}), 3280 (ν_{-N-H}); 3080, 3050 ($\nu_{=C-H}$); 1565, 1360($\nu_{-N=O}$); 1660 (δ_{N-H}); 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}H NMR (solvent: acetone-d_6) (δ, ppm): 4.85 (1H, s, O–H, H 1); 7.68 (1 H, s, Ar–H, H 2); 7.78 (1 H, d, Ar–H, H 3); 7.25 (1 H, d, Ar–H, H 4); 2.56 (1H, s, –C–H, s, H 5). MS (EI) (m/z): 314 (M^+). All those show that the HNATR has the structure in Fig. 2.

2.3. Chemicals

All of the solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). Palladium, platinum, rhodium and gold standard solution (1.0 mg mL^{-1}) was obtained from Chinese Standards Center, and a working solution of 0.2 μg mL^{-1} was prepared by diluting this standard solution. HPLC grade acetonitrile was obtained from Fisher Corporation, USA. A phosphoric acid solution (2.0 mol L^{-1}) was used. HNATR solution (2.0×10^{-4} mol L^{-1}) was prepared by dissolving HNATR with 95% ethanol. Mobile phase A:

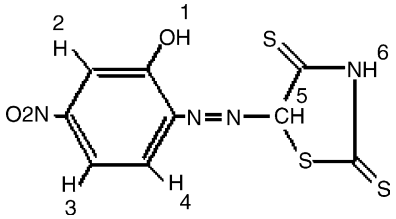

Fig. 2. The structure of HNATR.

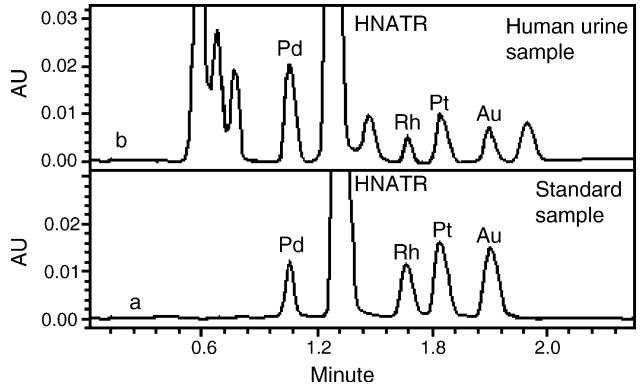

Fig. 3. Chromatogram of standard sample (a) and the human urine sample (b). The concentration of palladium, platinum, rhodium and gold is 1.0 μg L^{-1} in standard sample. The sample injected is 10 mL.

0.05 mol L^{-1} phosphoric acid. Mobile phase B: 72% acetonitrile (containing 0.05 mol L^{-1} of phosphoric acid and 0.1% of Triton X-100). All other reagents used were of analytical reagent-grade. The glass and PTFE ware used were soaked in 5% of nitric acid for at least 2 h, and then thoroughly wash with pure water.

2.4. Standard procedure

An appropriate volume (not more than 20 mL) of standard or sample solution was transfered into a 25 mL of volumetric flask (For the blank test, no standard or sample solution were added). To which, 2.0 mL of 1.0×10^{-4} mol L^{-1} HNATR solution, 2 mL of 2 mol L^{-1} phosphoric acid and 1.0 mL of 1% Triton X-100 solution were added. The solution was diluted to volume with water and mix well. After 10 min, a 10.0 mL of solution was introduced into the injector and sent to enrichment column with mobile phase A at a flow rate of 2.0 mL min^{-1}. When the enrichment had finished, by switching the valve of six ports switching valve, the metal-HNATR chelates, which absorbed onto the foreside of enrichment column, were eluted by mobile phase B at the flow rate of 2.0 mL min^{-1} in reverse direction and traveled towards the analytical column. The chelates were separated on the analytical column. A three-dimensional (*X* axis: retention time, *Y* axis: wavelength, *Z* axis: absorbance) chromatogram was recorded from 400 to 650 nm with photodiode array detector and the chromatogram of 505 nm is shown in Fig. 3.

3. Result and discussion

3.1. Pre-column derivation

The optimal condition for the reaction of Pd(II), Pt(II), Rh(III) and Au(III) with HNATR is in the acid medium. Therefore, the effect of hydrochloric acid, sulfuric acid, perchioric acid, phosphoric acid and the like, on the color reaction of Pd(II), Pt(II), Rh(III) and Au(III) with HNATR was studied. The experiments show that the phosphoric acid has the best effect, and the concentration of phosphoric acid within 0.05–0.5 mol L^{-1} was found to give a maximum and constant absorbance, so 2 mL of 2 mol L^{-1} of phosphoric acid solution was recommended.

It was found that 0.5 mL of 1.0×10^{-4} mol L^{-1} HNATR solution was sufficient to complex 5.0 μg of palladium, platinum, rhodium and gold, respectively. But in real samples, the foreign ions, such as Hg^{2+}, Pb^{2+}, Cu^{2+}, Ag^{+} and the like, form complex with HNATR and consume reagents. Therefore, the amount of HNATR must be in excess. In this experiment, a 2.0 mL of 1.0×10^{-4} mol L^{-1} HNATR solution was recommended.

The experiments show that in the nonionic surfactants or cationic surfactants medium, the sensitivity of the metal-HNATR chelates was increased markedly. Various nonionic surfactants and cationic surfactants enhance the absorbance in the following sequence: Triton X-100 > Tween-80 > Tween-20 > CTMAB > CPB. Therefore, Triton X-100 was selected as additive in this experiment. The use of 0.6–1.4 mL of Triton X-100 solution give a constant and maximum absorbance in this experiment. Accordingly, 1.0 mL Triton X-100 solution was recommended.

The HNATR can react with Pd(II), Pt(II), Rh(III) and Au(III) rapidly. The reaction was complete for 8 min at room temperature, and the complex was stable for at least 6 h.

3.2. On-Line solid phase extraction

The on-line solid phase extraction was carried out on an on-line solid phase extraction 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.

The Pd-HNATR, Pt-HNATR, Rh-HNATR and Au-HNATR chelates were stable in phosphoric acid medium. To avoid decomposition of the chelates during the enrichment step, a 0.05 mol L^{-1} phosphoric acid (mobile phase A) was selected as mobile phase for transport of the chelates to the enrichment column and a Zorbax reversed-phase C_{18} pre-column (10 mm × 4.6 mm, 1.8 μm) with a pH range of 1–11.5 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 0.1–20 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, platinum, rhodium and gold in this experiments and an injection volume of 10 mL is therefore recommended.

3.3. Spectrophotometric properties

The absorption spectrum of metal-HNATR chelates was obtained by measured with a Shimidzu UV-2401 spectrophotometer. The results show that the maximum absorption is 504 nm for Pd-HNATR chelate, 506 nm for Pt-HNATR, 500 nm for Rh-HNATR chelate and 510 nm for Au-HNATR chelate. Therefore, the 505 nm was selected as detecting wavelength. The molar absorptivity was calculated to be 1.28×10^5 L mol^{-1} cm^{-1} for Pt-HNATR chelate, 1.02×10^5 L mol^{-1} cm^{-1} for Pd-HNATR chelate, 1.15×10^5 L mol^{-1} cm^{-1} for Rh-HNATR chelate and 1.34×10^5 L mol^{-1} cm^{-1} for Au-HNATR chelate. The results show that HNATR is a sensitive pre-column derivatization regent for palladium, platinum, rhodium and gold.

3.4. Chromatographic separation

The experiments showed that the Pd-HNATR, Pt-HNATR, Rh-HNATR and Au-HNATR chelates have a good stability in the presence of phosphoric acid solution and Triton X-100 medium. The mobile phase containing a 0.02–0.15 mol L^{-1} of phosphoric acid and 0.05–0.2% of Triton X-100 can avoid the metal-chelate decomposing in the course of separation and get a good peak shape. So acetonitrile/water (72/28) (containing 0.05 mol L^{-1} of phosphoric acid and 0.1% of Triton X-100) was selected as mobile phase. To shorten the chromatographic separation time, a Zorbax Stable Bound rapid analysis column (50 mm × 4.6 mm, 1.8 μm) was selected in this experiment. With rapid analysis column, the palladium, platinum, rhodium and gold chelates were separated completely within 2.5 min. Compared to the routine chromatographic method, more then 80% of separation time was shortened.

3.5. Calibration graphs

Under the optimum conditions, regression equations of metal-HNATR chelates were established based on the standard sample injected and its peak areas, and the linearity defined by Mandel's fitting test. The limits of detection in the original samples are calculated by the ratio of signal to noise (S/N = 3, the sample injection volume is 10 mL). 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), Rh(III) and Au(III). The relative standard deviations (n = 10) were also shown in Table 1.

3.6. Interference

Under the pre-column derivatization conditions, the foreign ions of Cu(II), Hg(II), Pb(II), Tl(III), Bi(III), Ag(I) which can reacts with HNATR to form color chelates. To examine the selectivity of this method, the interference of these foreign ions was investigated. When 2.0 mL of 1.0×10^{-4} mol L^{-1} HNATR was used, with 10 μg L^{-1} of Pd(II), Pt(II), Rh(III), Au(III), respectively, the tolerance amount with an error of ± 5% was 2500 μg L^{-1} for Cu(II), Hg(II), Pb(II), Ag(I) and 600 μg L^{-1} for Tl(III), Bi(III). This method is high selectivity.

3.7. Applied to the water and human urine samples

Taking an appropriate volume (industrial plant effluents 20 mL, human urine and river water 200 mL) of sample 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). To which, 2.0 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 6.0 min. The digest was evaporated to near dryness. The residue was dissolved with 5 mL of 5% of phosphoric acid and transferred into a 25 mL of calibrated flask quantitatively, then diluted the solution to volume with 1% phosphoric acid. The palladium, platinum, rhodium and gold contents were analyzed by using a proper volume of this solution according to general procedure together with the results of a recovery test by adding 0.1 μg of Pt, Pd, Rh and Au in samples according to stanrd addition procedure. The results (deducted the reagents blank) were shown in Table 2, and the chromatogram of 505 nm is shown in Fig. 4. An ICP-MS method was used as a reference method and the result are also shown in Table 2.

3.8. Applied to the geological samples and soil samples

A 20,000 × g of sample was weighed into a 50 mL of teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China). To which, 20 mL of aqua regia was added. The bombs were

Table 1
Regression equation, coefficient and detect limit

Components	Regression equation	Linearity range (ng L^{-1} of metal ions)	Coefficient	Detect limit (ng L^{-1} of metal ions)	RSD% (n = 11)
Pd-HNATR	$A = 2.95 \times 10^6$ C − 1627	5–8500	r = 0.9992	1.4	2.8
Pt-HNATR	$A = 2.87 \times 10^6$ C − 1485	6–7600	r = 0.9989	1.8	2.6
Rh-HNATR	$A = 2.53 \times 10^6$ C + 1762	10–9400	r = 0.9992	2.0	3.0
Au-HNATR	$A = 3.64 \times 10^6$ C + 1.61	4–9400	r = 0.9993	1.2	2.9

Table 2
Determination results of the samples

Samples	Found				ICP-MS method				RSD% ($n=5$)				Recovery (%) ($n=5$)			
	Pt	Pd	Rh	Au	Pt	Pd	Rh	Au	Pt	Pd	Rh	Au	Pt	Pd	Rh	Au
Human urine ($ng\,L^{-1}$)	16.3	23.4	8.67	12.6	14.8	25.6	8.28	11.4	2.8	2.9	3.0	2.9	89	93	94	92
Plant effluents ($ng\,L^{-1}$)	320	218	82.5	520	318	224	80.6	531	2.9	2.6	2.4	3.1	92	94	92	94
River water ($ng\,L^{-1}$)	52.5	41.2	18.6	83.4	54.6	42.3	20.2	81.2	3.1	3.2	3.3	2.8	90	92	95	92
Soil ($ng\,g^{-1}$)	18.6	23.5	8.37	42.3	19.6	24.5	8.43	43.6	2.8	3.1	3.6	3.0	88	93	92	91
Geological sample ($ng\,g^{-1}$)	83.5	56.8	24.2	83.5	85.2	54.1	26.4	86.1	3.1	3.4	3.4	3.2	88	91	93	89

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% phosphoric acid was added and heated close to boiling to leach the residue. After cooled, the residue was filtrated and the undissolved residue was washed with 5% phosphoric acid for two times. The leachate was collected into a 25 mL of calibrated flask quantitatively and diluted to the volume with 1% phosphoric acid. The palladium, platinum, rhodium and gold contents were analyzed by using a proper volume of this solution according to the general procedure together with the results of a recovery test by adding 0.1 μg of Pt, Pd, Rh and Au in samples according to stanrd addition procedure. The results (deducted the reagents blank) were shown in Table 2, and the Chromatogram of 505 nm is shown in Fig. 5. An ICP-MS method was used as a reference method and the result are also shown in Table 2.

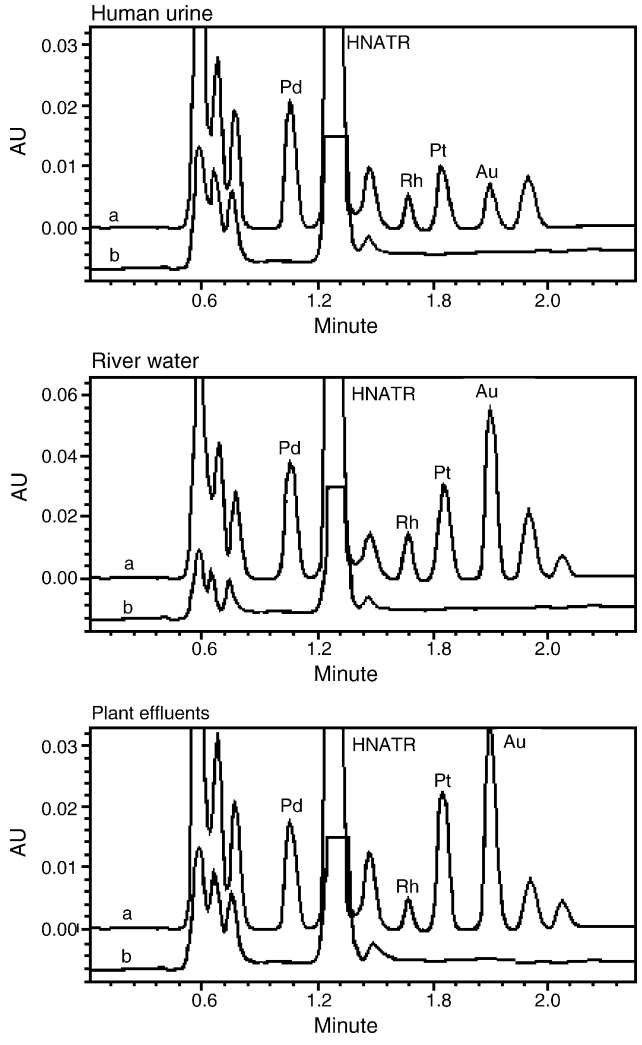

Fig. 4. The Chromatogram of water and human Urine sample. The sample injected is 10 mL: (a) sample; (b) reagent blank. The amounts for the peaks are 2.2 $\mu g\,L^{-1}$ for Pd, 0.32 $\mu g\,L^{-1}$ for Rh, 0.74 $\mu g\,L^{-1}$ for Pt, 0.34 $\mu g\,L^{-1}$ for Au in human urine sample; 5.8 $\mu g\,L^{-1}$ for Pd, 1.7 $\mu g\,L^{-1}$ for Rh, 2.3 $\mu g\,L^{-1}$ for Pt, 6.2 $\mu g\,L^{-1}$ for Au in river water sample; 1.8 $\mu g\,L^{-1}$ for Pd, 0.34 $\mu g\,L^{-1}$ for Rh, 1.2 $\mu g\,L^{-1}$ for Pt, 2.2 $\mu g\,L^{-1}$ for Au in plant efluent sample.

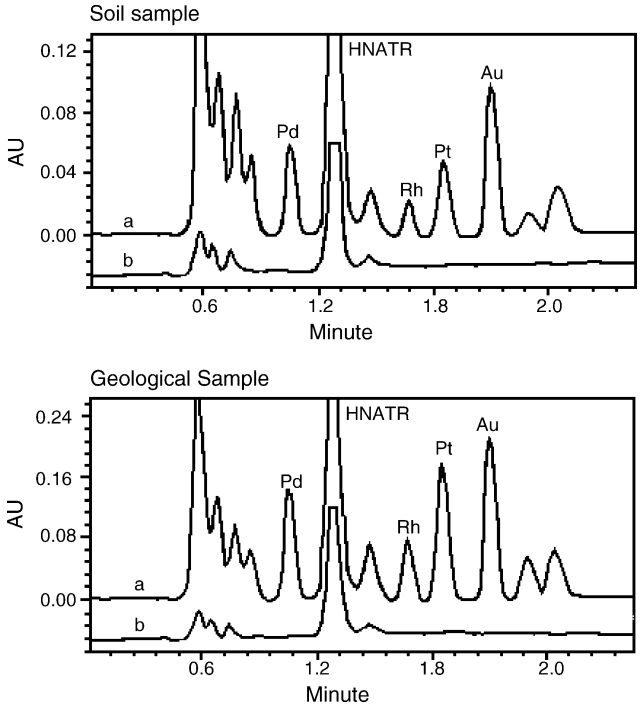

Fig. 5. The chromatogram of soil and the geological sample. The sample injected is 10 mL: (a) sample; (b) reagent blank. The amounts for the peaks are 4.6 $\mu g\,L^{-1}$ for Pd, 1.9 $\mu g\,L^{-1}$ for Rh, 4.8 $\mu g\,L^{-1}$ for Pt, 5.3 $\mu g\,L^{-1}$ for Au in soil sample; 14.1 $\mu g\,L^{-1}$ for Pd, 6.8 $\mu g\,L^{-1}$ for Rh, 11.2 $\mu g\,L^{-1}$ for Pt, 12.6 $\mu g\,L^{-1}$ for Au in geological sample.

4. Conclusion

The proposed method has the following characteristics: (1) HNATR was firstly synthesized and used as pre-column derivatization regents. The palladium, platinum, rhodium and gold ions can form stable color chelates with HNATR at room temperature rapidly. The molar absorptivity was calculated to be 1.28×10^5 L mol^{-1} cm^{-1} for Pt-HNATR chelate, 1.02×10^5 L mol^{-1} cm^{-1} for Pd-HNATR chelate, 1.15×10^5 L mol^{-1} cm^{-1} for Rh-HNATR chelate and 1.34×10^5 L mol^{-1} cm^{-1} for Au-HNATR chelate. This is a sensitive and convenience pre-column derivatization regents for palladium, platinum, rhodium and gold. (2) The Zorbax rapid analysis column was used for the separation of Pt-HNATR, Pd-HNATR and Rh-Pd-HNATR chelates, and the Pt-HNATR, Pd-HNATR and Rh-HNATR chelates were separated completely within 2.5 min. Compared to the routine chromatographic method, more then 80% of separation time was shortened. (3) By on-line solid phase extraction system, a large volume of sample (10 mL) can be injected, and the sensitivity of the method was greatly improved. In a word, for the determination of palladium, platinum, rhodium and gold, this method is high sensitivity and high selectivity.

Acknowledgements

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