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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

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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

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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.

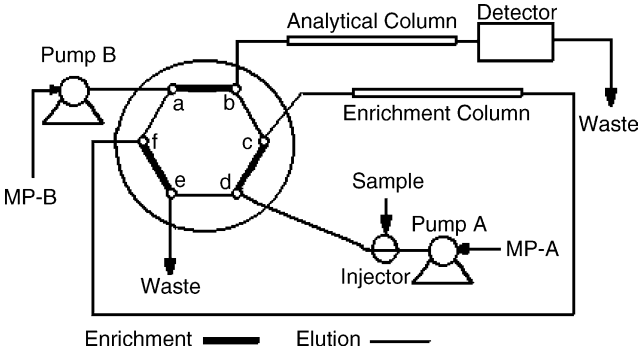

Fig. 1. On-line enrichment system using the valve-switching technique. Pump A: Waters 515 Pump. Pump B: Waters 2690 Alliance quadripump. Injector can contain 10 mL of sample. Six ports switching valve (Waters Corporation). Enrichment column, Zorbax (4.6 mm × 10 mm, 1.8 μm). Analytical column, Zorbax (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:

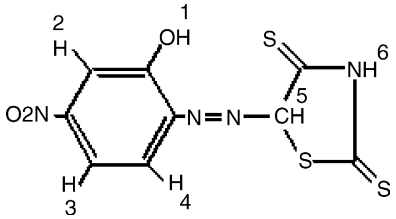

Fig. 2. The structure of HNATR.