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Determination of Palladium and Gold in Water and Geological Samples by FAAS after Preconcentration

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A new preconcentration and separation flame atomic absorption spectrophotometry (FAAS) method was developed for the determination of trace of palladium and gold ions in water and geological samples. The method was based on sorption of noble metal ions on the porous nano-barium strontium titanate by reversed-phase suspension polymerization (PBST-RSP) and sol-gel method. The possible parameters influencing the enrichment were optimized. In pH range of 6-7, Pd(II) and Au(III) could be quantitatively retained by PBST-RSP. The analytes retained on PBST-RSP were effectively eluted with 0.1 moL/L HNO_3 solution. At optimum conditions, the method detection limits (3σ) of 0.012 µg/L for Pd and 0.019 µg/L for Au along with enrichment factors of 100 were obtained. Finally, established method has been successfully applied for the determination of Pd and Au in water and geological samples with satisfactory results.

Keywords: Palladium, Gold, Porous nano-barium strontium titanate, Solid-phase extraction, Water, Geological samples.

INTRODUCTION

The noble metals, such as the palladium and gold have been widely applied to the electronics, chemical, aerospace industries, gold-plated jewelry, car manufacturing industry and the pharmaceutical industry[1,2]. Determining the presence of these noble metals in water and other samples is typically accomplished by inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), spectrophotometry and atomic absorption spectrometry (AAS)[3]. But the noble metals occur in water and geological materials at trace or ultra-trace levels, the direct determination of ultra-trace Pd and Au in many kinds of samples is still difficult with these detection methods due to insufficient sensitivity and selectivity. Therefore, pretreatment steps in the analytical procedure, such as preconcentration of an analyte and/or its separation from the matrix components, are frequently necessary. At present, the widely used techniques for the preconcentration and separation include solvent extraction[4-6], ion exchange[7,8], co-precipitation[9], HPLC[10], cloud point extraction[11] and solid phase extraction (SPE)[12-16] *etc*.

Amongst these methods, solid phase extraction (SPE) preconcentration and separation has become increasing popular for the determination of trace level of noble metals. The main solid-phase extraction sorbents are chelating resin[11], modified barium-strontium titanate powder[12] and modified silica[13,14], nano-powder[15], *etc*. In our previous published work, we have used the nano-barium strontium titanate in the adsorption of heavy metal ions in water[17]. However, the nano-barium strontium titanate particles are so small that, when used in adsorption of metal ions, it was difficult to recover. Making the nano-barium strontium titanate into porous matter by reversed-phase suspension polymerization (PBST-RSP) and sol-gel method corrects these problems[18]. In this work, The adsorptive potential of PBST-RSP for the preconcentration of trace Pd(II) and Au(III) were assessed using the batch adsorption method. A new method using PBST-RSP as solid phase extraction agent has been developed for the preconcentration of trace Pd(II) and Au(III) in water and geological samples analyses by FAAS.

EXPERIMENTAL

A WYX-9003A atomic absorption spectrometer (Shenyang Yi Tong Analytical Instrument Co., Ltd.). The measurements were done in air-acetylene flame and the operation conditions are summarized in Table-1.

The pH values were measured with a PHS-3C acidometer (Shanghai REX Instrument Factory, Shanghai, China) supplied with a combined electrode. A bath shaker (Jintan Experiment Instrument Factory, Jiangsu China) was used to shaking for adsorption and elution.

Porous nano-barium strontium titanate was prepared by reversed-phase suspension polymerization and sol-gel method was prepared in our laboratory as previously described elsewhere[18].

Standard stock solution of Pd(II) and Au(III) (1000 mg/L) were prepared by dissolving spectroscopically pure palladium

TABLE-1
FAAS OPERATING CONDITIONS

Element	Wavelength (nm)	Spectral band width (nm)	Lamp current (mA)	Burner height (mm)	Acetylene gas consumption (L/min)
Pd	244.8	0.2	7.5	8	8
Au	242.8	0.4	5.0	7	7

and gold powders with aqua regia. And the working standard solutions of Pd(II) and Au(III) were obtained by appropriate dilution of the stock standard solutions.

All the other reagents used were at least of analytical-reagent grade. The water in this study was double-quartz sub-boiling distilled water.

General procedure: A quantity of noble metal solution was added into a 150 mL (or 1000 mL) calibrated Erlenmeyer flask with plug. The pH was adjusted to 5-7 with hydrochloric acid or sodium hydroxide solution. After diluting to the mark of 50 mL (or other volume) with water, 0.1 g of adsorption agent (PBST-RSP) was added. Covered with a plug, the Erlenmeyer flask was shaken for 5 min in the bath shaker. Filter the solution and then the concentrations of Pd(II) and Au(III) in filtrate were determined by FAAS and absorption capacity were calculated. Then the adsorbent was washed with water to remove any unadsorbed Pd(II) and Au(III), the adsorbed Pd(II) and Au(III) were eluted with 5 mL of 0.5 mol/L HNO_3 solution by shaking for 5 min. The concentrations of the Pd(II) and Au(III) in the eluents were determined by FAAS, respectively and the recoveries were calculated.

RESULTS AND DISCUSSION

Effect of pH on adsorption: In order to study the effect of pH on adsorption, the pH was adjusted in the ranges of 1-8 using hydrochloric acid or sodium hydroxide solution and then the adsorption procedure was applied. The results are shown in the Fig. 1. The adsorption percentages of PBST-RSP to Pd(II) and Au(III) were dependent on the pH value of the medium. Increasing the pH resulted in an increase of adsorption capacity. The adsorption of Pd(II) at the pH range of 5-8 and of Au(III) at the pH range of 6-8 were 100 %. In order to preconcentrate Pd(II) and Au(III) simultaneously and to avoid the precipitation of metal ions at high concentration, the pH range of 6-7 was selected as the optimal condition.

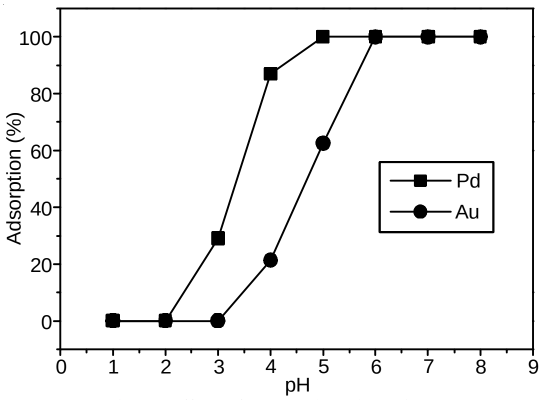

Fig. 1. Effect of pH on the adsorptions

Effect of shaking time on adsorption: To investigate the influence of shaking time on the adsorption of Pd(II) and Au(III) onto PBST-RSP, the adsorption capacity was determined at different shaking time, respectively. The results are showed in Fig. 2. The adsorption capacity increased with an increase in shaking time and reached equilibrium at 10 min for Pd(II) and 15 min for Au(III). The static adsorption capacities of PBST-RSP to Pd(II) and Au(III) at room temperature were 35.9 and 31.6 mg/g, respectively. Therefore, in order to adsorb Pd(II) and Au(III) together, the shaking time was set to 15 min in this study.

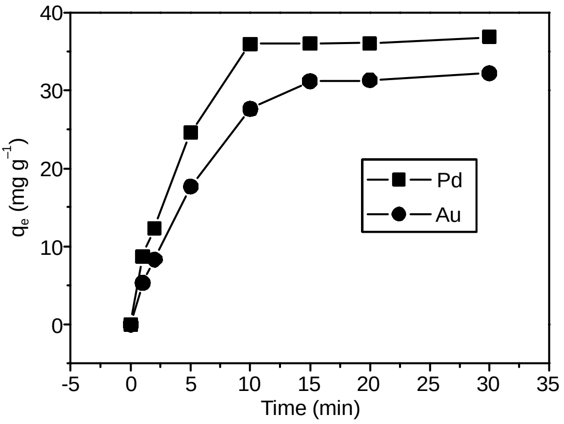

Fig. 2. Effect of contact time on Pd(II) and Au(III) adsorption

Elution: According to Fig. 1, the adsorption of Pd(II) and Au(III) on the PBST-RSP were all zero when pH value no more than 2. For this reason, after adsorption under the optimized adsorption conditions, 5 mL of HNO_3 at different concentration (0.001-1.0 mol/L) were chosen to be eluents in desorption of Pd(II) and Au(III) adsorbed on PBST-RSP by shaking 5 min.

It was found that a concentration of 0.1 mol/L nitric acid (or higher) is required to obtain quantitative elution. Therefore, 5 mL of 0.1 mol/L HNO_3 was chosen.

After elution, the PBST-RSP was dried at 105 ºC and reused 10 times. Its adsorption performance did not decrease, indicating that this adsorption agent was very stable.

Enrichment factor and detection limit: For studied the possibility of enriching low concentrations of Pd(II) and Au(III) from large volumes, 2 µg of Pd(II) and 2 µg of Au(III) were dissolved together in various volume (including 20, 50, 100, 250, 500, 750 and 1000 mL) of water. After shaking and adsorbing for 15 min, the adsorption agents were eluted with 5 mL of 0.1 mol/L HNO_3. The amounts recovered are listed in Table-2.

It is observed that when the solution volume was 500 mL, the recoveries were all above 90 % and the enrichment factor was 100. The detection limits (3σ) were calculated using the concentration of three times standard deviation, calculated from 11 runs of the blank solution with concentrations of Pd(II) and Au(III) at 0.012 and 0.019 µg/L, respectively. The relative standard deviations (RSD) for Pd(II) and Au(III) were 3.4 and 4.2 %, respectively (n = 11, $C_{Pd} = C_{Au} = 10$ µg/L).

TABLE-3
DETERMINATION OF PALLADIUM(II) AND GOLD(III) IN WATER SAMPLES (n = 6)

Samples	Found (µg/L)		RSD (%)		Added (µg/L)		Found (µg/L)		Recovery (%)	
	Pd	Au	Pd	Au	Pd	Au	Pd	Au	Pd	Au
Rivulet water	15.35	12.83	4.17	5.46	10	10	25.36	22.03	100.10	92.00
Tailing pond water	27.56	33.52	3.85	4.78	20	20	46.31	52.77	93.75	96.25

TABLE-4
DETERMINATION OF PALLADIUM(II) AND GOLD(III) IN MINE STONES SAMPLES (n = 6)

Samples	Found (µg/g)		RSD (%)		Added (µg/g)		Found (µg/g)		Recovery (%)		Certified (µg/g)	
	Pd	Au	Pd	Au	Pd	Au	Pd	Au	Pd	Au	Pd	Au
GBW 07291	0.0523	0.0041	6.45	4.66	0.05	0.005	0.0985	0.0089	92.4	96	0.0600	0.0043
GBW 07293	0.5140	0.0430	5.21	6.34	0.5	0.05	0.9968	0.0887	96.56	91.4	0.5680	0.0450
Sample 1	0.0776	0.1973	7.02	3.98	0.1	0.1	0.1801	0.2891	102.5	91.8	0.0769*	0.1994*
Sample 2	0.1104	0.4290	5.21	6.34	0.1	0.1	0.2103	0.5187	99.9	89.7	0.1241*	0.442*

*Certified concentration of the elements were reported by a mining company of Liao Ning.

TABLE-2
PRECONCENTRATION AND RECOVERY OF Pd(II) AND Au(III)

Volume of solution (mL)	Quantity in eluent (µg)		Recovery (%)		Enrichment factor
	Pd(II)	Au(III)	Pd(II)	Au(III)	
20	1.989	1.968	99.45	98.40	4
50	2.041	1.991	102.05	99.55	10
100	1.912	2.021	95.60	101.05	20
250	2.027	1.934	101.35	96.70	50
500	1.868	1.842	93.40	92.10	100
750	1.795	1.683	89.75	84.15	150
1000	1.747	1.625	87.35	81.25	200

Effect of interfering ions: In the view of the high selectivity provided by AAS, the only interferences studied were those related to the enrichment step. To perform this study, various interference ions were added into a 100 mL volumetric flask containing 10 µg of Pd(II) and Au(III). The results showed that recoveries of the Pd(II) and Au(III) remained in 95-105 % even in the presence of ions in the following concentrations: 500 mg/L for Na^+, K^+, NH_4^+ and NO_3^-; 200 mg/L for Ca^{2+}, Mg^{2+} and PO_4^{3-}; 100 mg/L for Cr(III), Al^{3+}, Co^{2+}, Cr(VI) and Cu^{2+}; 20 mg/L for Ni^{2+}, Fe^{3+}, Pt(IV); 1 mg/L for Zn^{2+}, Pb^{2+}, Ag^+ and Cd^{2+}.

Application of the method: The proposed method was applied to real water samples and mine stone. The well water sample was obtained from Huludao City of Liao-ning China. The surface waters were collected from a gold mine tailings and its near rivulet (Chao yang of Liao-ning China). 100 mL of water sample was preconcentrated using proposed method after digestion process with concentrated nitric acid. The results are given in Table-3.

A 5 g amount of finely powdered sample was taken in porcelain dish, roasted at 650 ºC for 0.5 h, transferred into 500 mL PTFE vessel and digested in aqua regia by refluxing the mixture for 12 h. The solution of each sample was filtered. The filtered solution was diluted with concentrated hydrochloric acid up to 25 mL. Finally, 5 mL of concentrated hydrochloric acid was added and the solution was evaporated almost to dryness. The residue was dissolved in 0.1 mol/L HNO_3 and the solution was made up to 50 mL with distilled water after adjustment of pH to 6.0-7.0. The solution was then extracted using the proposed method at the optimal conditions. The obtained results and the associated recovery are shown in Table-4.

The recovery was 89.7-102.5 %, which were excellent for trace analysis. So, the proposed method was demonstrated the suitability of this sorbent for the pre-concentration and determination of trace palladium and gold.

Conclusion

It is concluded that Pd(II) and Au(III) could be quantitatively retained by the PBST-RSP in the pH of 6-7, the adsorption time was 15 min and capabilities of adsorbent agent to Pd(II) and Au(III) were 35.9 and 31.6 mg/g, respectively. The Pd(II) and Au(III) adsorbed on the PBST-RSP could be completely eluated by using 5 mL 0.1 mol/L HNO_3. The enrichment factor was more than 100. The detection limit of this method for Pd(II) and Au(III) were 0.012 and 0.019 µg/L, respectively. The proposed method has been applied to the determination of trace amounts of palladium and gold in water and mine stone samples with satisfactory results.

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