



Study on Solid-Phase Extraction and Graphite Furnace Atomic Absorption Spectrometer (GF-AAS) for the Determination of Platinum, Palladium and Gold

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In this work, a new sorbent was prepared by immobilization of 3-methyl-2,6-diaminopyridine (MDMP) on MCI-GEL resin and then used as a solid phase extraction sorbent for trace platinum, palladium and gold ions. The parameter for solid phase extraction (effects of pH, the sample flow rate and volume, the elution condition and the potentially interfering ions) were carefully investigated. In the desorbed medium, the platinum, palladium and gold were determination by graphite furnace atomic absorption spectrometer (GFAAS). The effect on the atomic signal was eliminated by selecting proper pyrolysis and atomization temperatures for all analysts. This method was applied to the determination of trace platinum, palladium and gold in the geological samples. The relative standard derivation were 3.6-4.8 %. The standard recoveries (three different concentrations of markers: 0.02, 0.04 and 0.08 μg) were ranged from 92-107 %. The results are satisfactory.

Key Words: Precious metals, MCI GEL resin, Solid phase extraction, Graphite furnace atomic absorption spectrometer.

INTRODUCTION

The precious metals have interesting physical and chemical properties beside their low abundance on the earth and their high economic value. However, the precious metals also affect the environment to an increasing degree as a new pollutant, especially by the technical use of catalysts containing active platinum and palladium metal^{1,2}. From an environmental and economical point of view, there remains a need to design more selective and effective analytical method for determination of trace precious metals. In recent years, highly sensitive and selective modern instruments such as atomic absorption spectrometer (AAS) in both flame (FAAS) and electrothermal atomic absorption spectrometer (ETAAS) modes, inductively coupled plasma-atomic emission spectrometer (ICP-AES) and inductively coupled plasma-mass spectrometer (ICP-MS) have been used for the determination of precious metals at trace levels³⁻⁸. The detection limits of these instruments are, however, still not sufficient because precious metals are present in trace amounts and in different complex matrices. Partially, this problematic situation has been resolved recently with new instrumental methods and their applications for the analysis of precious metals in a variety of matrices⁹⁻¹¹. Consequently, a preconcentration step is usually required.

Solid phase extraction is an attractive technique because of its notable advantages¹²⁻¹⁴. In recent years, polymeric sorbents have been studied for the recovery, separation and preconcentration of metal ions either in natural inorganic or organic and synthetic polymeric materials¹⁵⁻¹⁸. The MCI GEL CHP 20Y is an aromatic type adsorbent based on crosslinked polystyrenic matrix. It is a reversed-phase resin provides a broad range of solvent choices and a pH range from 0-14^{18,19}. In this manuscript, a new sorbent was prepared by immobilization of 3-methyl-2,6-diaminopyridine on MCI-GEL resin and then used as a solid-phase sorbent for the solid phase extraction of trace platinum, palladium and gold and a new method for the determination of platinum, palladium and gold by graphite furnace atomic absorption spectrometer were studied. The experimental results show this method is highly sensitive and selective.

EXPERIMENTAL

Standard stock solutions of Au(III), Pd(II) and Pt(IV) (1 mg mL⁻¹ were obtained from Chinese Standard Material Center) and the work solutions used were prepared by the diluting of these stock solutions.

MCI GEL CHP 20Y was purchased from Mitsubishi Chemical Corporation. (Tokyo, Japan). MCI GEL CHP 20Y

is an aromatic type adsorbent is the standard grade and is based on crosslinked polystyrenic matrix. Its, particle size is 30 μm and surface area is 560 $\text{m}^2 \text{g}^{-1}$. 4-Methyl-2,6-diaminopyridine (MDAP) was obtained from Shanghai Institute of Fine Chemicals Retrocession (Shanghai, China). Hydrochloric acid (Merck, Darmstadt, Germany) and Thiourea (Merck, Darmstadt, Germany) was used as desorption agent. Deionized water of 18.2 $\text{M}\Omega \text{cm}$ resistivity obtained from a Milli Q-water purification system (Millipore, Bedford, MA USA) used for the preparation of all solutions.

A Perkin-Elmer Analyst 800 Atomic Absorption Spectrometer (Boston, USA), equipped with Zeeman background correction was employed. Hollow cathode lamp of gold, platinum and palladium (Cathodeon Ltd., Nuffield Road, Cambridge, UK) were used. Pyrolytic coated graphite furnaces (Perkin-Elmer, Boston, USA) were used for analyses and the atomization was direct from the wall of pyrolytic coated graphite furnace. Operating parameters of graphite furnace for the determination of palladium, platinum and gold by graphite furnace atomic absorption spectrometer (GFAAS) and working conditions of hollow cathode lamps for all studied elements are given in Table-1.

	Au	Pt	Pd
Lamp settings Wavelength (nm)	242.2	265.9	248.6
Spectral band width (nm)	0.7	0.7	0.2
Lamp current (mA)	8	30	20
Furnace temperature ($^{\circ}\text{C}$)			
Drying (ramp 10 s, hold 40 s)	120	140	120
Ashing (ramp 10 s, hold 25 s)	820	1300	900
Atomizing (ramp 0 s, hold 4 s)	2550	2550	2600
Clean-up (ramp 1 s, hold 5 s)	2650	2650	2650
Gas flow was set to 0 mL min^{-1} for the third step and 250 mL min^{-1} for the other three steps.			

Optimum working conditions were established before analyzing of the precious metal ions in GFAAS system in order to reach high sensitivity and high precision for GFAAS in the presence of thiourea and high HCl concentration by changing the pyrolysis and atomization temperatures for all studied metal ions. For these set of experiments, the pyrolysis temperature was set constant (800°C) and atomization temperature was changed from 2100 to 2500 $^{\circ}\text{C}$ for 20 $\mu\text{g L}^{-1}$ concentration of each precious metal ion solution (20 mL) to get maximum signal. The similar experiments were repeated setting the atomization temperature constant (2500°C) and changing the pyrolysis temperature from 650 to 1000 $^{\circ}\text{C}$ for the same standard solutions. No additional chemical modifiers were used to increase pyrolysis temperature.

Preparation of solid phase extraction cartridge: 2.5 g of 4-methyl-2,6-diaminopyridine (MDAP) was dissolved in 50 mL of ethanol solution, to which, 10 g of MCI-GEL resin was added. The ethanol was evaporated with stirred. The residues were dried and the modified sorbent was obtained. The modified sorbent (0.28 g) was packed into Teflon cartridge (10 mm long and 0.5 mm in diameter) as literature¹⁸ to afford the solid phase extraction cartridge.

Solid phase extraction: The standard or sample solution (containing no more than 0.2 μg of Au(III), 0.25 μg of Pd(II)

and 0.25 μg of Pt(IV)) were adjusted to pH 1.0. The solution was passed through the MDAP modified cartridge at a flow rate of 5.0 mL min^{-1} . After the enrichment was finished, the bound metal ions were stripped off from the cartridge with 1.0 mL of eluent (0.05 mol L^{-1} HCl and 5 % thiourea) a flow rate of 1.0 mL min^{-1} . The analytes in the elution were determined by GFAAS.

RESULTS AND DISCUSSION

Influences of pH on sorption: For solid phase extraction of the precious metal ions, the pH of the aqueous solution is one of the main factors for quantitative recoveries of the analytes. Due to this important point, the influences of pH were investigated. Keeping the other parameters constant, the recovery values of the analyte metals with the change of pH were shown in Fig. 1. When pH at *ca.* 0.5, only Au(III) could be adsorbed quantitatively and when pH at the range of 1.0-3.5, the recovery of Au(III), Pt(IV) and Pd(II) obtained 95 %. Higher pH values (> 6) were not tested because of the possibility of the hydrolysis of the noble metal. Therefore, pH range of 1.0 was selected as the enrichment acidity for further study.

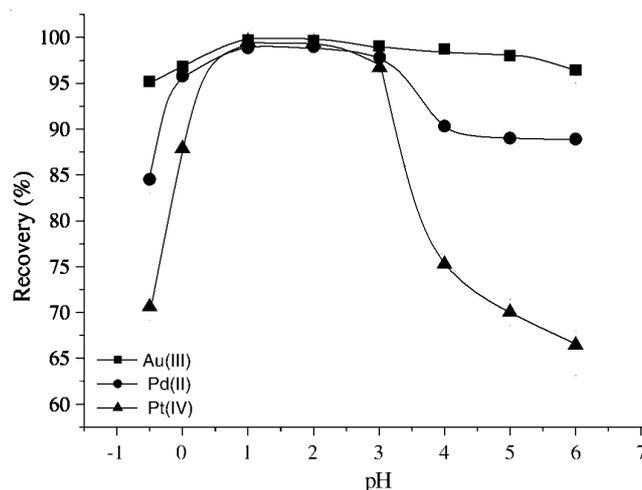


Fig. 1. Influences of pH on sorption of Au(III), Pd (II) and Pt (IV)

Effect of flow rate: Flow rate affects the retention time of analytes on the sorbent. 100 mL of sample solution was flowed through the cartridge with a peristaltic pump which can adjust the flow rate to ranging from 2.5 to 10 mL min^{-1} . The results showed that the recoveries of the studied ions decrease when the flow rate reach 6 mL min^{-1} , due to the Au(III), Pd (II) and Pt(IV) and the sorbent have not sufficient contact time to reach equilibrium. So flow of 5 mL min^{-1} was chose to be the best one in this experiment.

Desorption of Au(III), Pd(II) and Pt(IV) from cartridge: The desorption of the retained analyte precious metal ions from cartridge was examined using various elution solutions. The quantitative recoveries ($> 95\%$) were obtained for the investigated elements with 1 mL 1 mol L^{-1} HCl (contains 0.5 mol L^{-1} thiourea), 2 mL of 1 mol L^{-1} HNO_3 and 3 mL of 1 mol L^{-1} H_2SO_4 . The maximum enrichment factor was achieved when 1 mol L^{-1} HCl (contains 0.5 mol L^{-1} thiourea) used as eluent. Therefore, 1 mol L^{-1} HCl and 0.5 mol L^{-1} thiourea was selected as eluent in this experiment.

TABLE-2
REGRESSION EQUATION AND DETECTION LIMIT

Metal ions	Regression equation*	Linearity range ($\mu\text{g/L}$)*	Coefficient	Detection limit (ng L^{-1})**
Au	$A = 0.0578 C (\mu\text{g/L}) + 0.0184$	1.2-200	$r = 0.9995$	3.5
Ag	$A = 0.0472 (\mu\text{g/L}) - 0.0106$	2.5-250	$r = 0.9993$	8.0
Pb	$A = 0.0518 (\mu\text{g/L}) + 0.0129$	2.5-250	$r = 0.9996$	8.0

*In the preconcentrated solution; **In the original samples before applying the preconcentration procedure.

TABLE-3
DETERMINATION RESULTS OF THE SAMPLES

Metal ions	Samples (ng/g)				%	
	PYJS-21	PYJS-38	PYJS-41	PYJS-53		
Au	5.16	2.79	8.47	14.2	3.6	92-98
Pt	6.21	1.97	1.08	8.74	4.7	91-107
Pd	8.52	3.47	15.2	6.32	4.8	93-102

*Three different concentrations of markers: 0.02, 0.04 and 0.08 μg .

Experiments have shown that it is easier to elute the retained metal ions in the reverse direction in comparison to the forward direction (Only 1 mL of eluant was needed when eluted in reverse direction. However, 2.5 mL of eluant was needed when eluted in forward direction). Thus, it is also recommended to invert the cartridge before elution.

The stability of the cartridge: Through the eluting, regeneration was also investigated. When the cartridge repeated 20 times, the recoveries of Au(III), Pd(II) and Pt(IV) reached 95 %, too. Over 20 times, the recovery is not very satisfactory. So the repeat times of usage of the cartridge are 20 times.

Effect of the sample volume: The effect of the sample solution volume was studied by passing 20-500 mL sample solution through MCI GEL CHP 20Y cartridge at a 5 mL min^{-1} flow rate. The results were show that the adsorption of the metal ions was not affected by sample volume when the volume below 300 mL. However, the percent of analytes sorption decrease when the volume above 300 mL. The recoveries of analytes decrease probably due to the excess analytes loaded over the cartridge capacity with increasing sample volume above 300 mL.

Adsorption capacities: The adsorption capacity is also an important factor because it determines how much adsorbent is utilized to quantitatively adsorb a specific amount of metal ions from the solution²⁰. The capacity study was adopted from the paper recommended by Maquieira *et al.*²¹. The capacity of one gram of modified sorbent was found to be 21 mg for Au(III), 25 mg for Pd(II) and 28 mg for Pt(IV). The result told us that modified sorbent had a high adsorption capacity for the three ions and it is satisfactory for the trace analysis.

Effect of potentially interfering ions: In diversified realistic samples, metal ions always exist together. Therefore, it is necessary to explore the adsorbed properties on the condition that other interfering ions accompanied with it. The tolerance limit was set as the amount of ions causing recoveries of the examined elements to be less than 95 %. The experimental data revealed that 2000 $\mu\text{g mL}^{-1}$ of K^+ , Na^+ , NO_3^- , SO_4^{2-} , PO_4^{3-} ; 500 $\mu\text{g mL}^{-1}$ of Ca^{2+} , Mg^{2+} , 200 $\mu\text{g mL}^{-1}$ of Fe^{3+} , Al^{3+} , Sb^{3+} , Bi^{3+} , Cr^{3+} , 50 $\mu\text{g mL}^{-1}$, Rh^{3+} , Ru^{4+} and Ir^{4+} did not significantly interfere with the determination of the analytes under the selected conditions.

Calibration graphs and detection limits: Under the GFAAS analysis conditions, regression equations of metal ions

were established based on the standard samples injected and their absorption signals. The results were shown in Table-2. The detection limits in the original samples (before applying the preconcentration procedure) were obtained based on three times the standard deviations of the blank. The results were also shown in Table-2.

Recovery of spikes from the samples: In order to estimate the accuracy of the procedure, different amounts of the investigated metal ions were spiked in samples. The resulting solutions were submitted to the preconcentration procedure. Good agreement was obtained between the added and found analyte content using the recommended procedure. The recovery values for the analyte ions were in the range of 91-107 % (Table-3). These values were quantitative and it shows that the presented method can be applied for the separation/preconcentration of analyte ions. The relative standard deviation for the analyte ions (7 repeat determinations) were below 4.8 %.

Sample preparation: For the decomposition of the geological samples, 10 g of each geological sample was dried and mechanically ground to obtain average 50 μm particle size and then dried in the vacuum oven at 110 $^{\circ}\text{C}$ overnight. A 5 g portion of the dry powdered sample was accurately weighted and heated in a muffle furnace at 550 $^{\circ}\text{C}$ for 6 h to remove all organic matrices from the samples. The sample was there after transferred into a 100 mL beaker and heated on a hot plate with 50 mL aqua regia and 1.0 mL Br_2 , evaporating each time to dryness. The heating process was repeated three times and the final residue was heated up to 80 $^{\circ}\text{C}$ with 50 mL of 1.0 mol L^{-1} HCl and then filtered into a 100 mL beaker using filter paper. Filter paper and beaker was washed with water and combined the washings with the filtrate. The pH was adjusted to 1.0 and the final volume was completed to 100 mL exactly with water. This solution was afforded to solid phase extraction and GF-AAS determination. The results are show in Table-3.

Conclusion

The developed method is successfully employed for analysis of geological materials after successful validation. The developed method have the follow advantages: The method is economic. Instead of the use of fresh solvent as an extracting phase for each sample, the reusability of modified

sorbent was as high as greater than 20 cycles without any loss in its sorption behaviour. The elution was easily performed with 1.0 of eluent (contains 0.05 mol L⁻¹ HCl and 5 % thiourea) and the metal ions in 100 mL solution can be concentrated to 1.0 mL, representing an enrichment factor of 100 was achieved. The analytical performance of the method is comparable with other separation and preconcentration methods. The limits of detection of analyte ions are superior to those of some preconcentration/separation techniques for analyses. The matrix effects with the method were reasonably tolerable. The method is relatively rapid as compared with previously reported procedures for the enrichment of traces precious metal ions.

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