Solid Phase Extraction and Graphite Furnace Atomic Absorption Spectrometry for Determination of Silver and Palladium with Diaion SP700 as Sorbent

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A solid phase extraction and graphite furnace atomic absorption spectrometry (GFAAS) for the determination of silver and palladium with Diaion SP700 resin as sorbent was studied. Silver and palladium were reacted with diisopentyl sulfoxide followed by adsorption onto Diaion SP700 solid phase extraction column and 1 mol L^{-1} HNO$_3$ was used as eluent. The effects of various parameters such as acidity, flow rate of sample and eluent, type of eluent, amount of adsorbent and interfering ions have been studied. The silver and palladium in 250 mL solution can be concentrated to 1 mL, representing an enrichment factor of 250 was achieved. When detected with graphite furnace atomic absorption spectrometry, the detection limits in the original samples were 0.0013 µg L^{-1} for Ag(I) and 0.0027 µg L^{-1} for Pd(II). The relative standard deviations for ten replicate measurements were 3.8 % for 0.2 µg L^{-1} silver and 3.6 % for 0.2 µg L^{-1} palladium, respectively. The presented procedure was applied to the determination of silver and palladium in biological, ore and water samples with good results (recoveries range from 94 to 106 %).

Keywords: Solid phase extraction, Silver, Palladium, Diisopentyl sulfoxide, Graphite furnace atomic absorption spectrometry.

INTRODUCTION

Silver has been recognized as a toxic element for biological systems. For human beings, silver accumulation in the body leads to a grayish blue discoloration of skin and a disturbance of the dark adaptation of eyes. Low level exposure to silver compounds is widespread owing to the use of soluble compounds to disinfect water for drinking and recreation purposes[1-3]. Palladium has been used in different areas of science and technology including electrical equipments, corrosion-resistant chemical wares, crucibles for high temperature reactions and catalytic chemical reaction. Palladium also enters the environment through industrial wastes because of the increasing use of palladium compounds in industry. Owing to the toxicity of palladium to mammals, fishes and aquatic organisms even at low concentrations, the serious environmental problems may occur[4].

The most widely used methods for determination of silver and palladium in environmental samples include electrothermal atomic absorption spectrometry (ETAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and spectrophotometric methods[5-11]. However, the determination of silver and palladium in environmental samples by spectrometric techniques is strongly hampered by numerous spectral and non-spectral interferences arising from a complicated sample matrix.

In environmental samples, the low concentration of silver and palladium (ng mL^{-1} levels) together with the high concentration of interfering matrix components often requires an enrichment step combined with a matrix separation. Several methods have been reported for the separation and preconcentration of silver and palladium, such as dispersive liquid-liquid microextraction extraction (DLLME), cloud point extraction (CPE), high-performance liquid chromatography (HPLC) and solid-phase extraction (SPE)[12-19]. Among these techniques, solid-phase extraction is one of the most important preconcentration methodologies because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability to combine with different detection techniques by on-line or off-line mode.

The aim of this work is to combine solid-phase extraction with graphite furnace atomic absorption spectrometry (GFAAS) and develop a new method for the determination of silver and palladium. In this method diisopentyl sulfoxide (DISO), reacts with silver and palladium forming a stable metal-diisopentyl sulfoxide chelates. Subsequently, water sample containing metal-diisopentyl sulfoxide chelates was passed through Diaion SP700 cartridge. The metal-diisopentyl sulfoxide chelates were preconcentrated on a nonpolar resin Diaion SP700. The metal-diisopentyl sulfoxide chelates adsorbed on Diaion SP700 cartridge was eluted with HNO$_3$. The levels

of analyte ions in the samples were determined by the graphite furnace atomic absorption spectrometry. The optimum analytical conditions for the quantitative recoveries of silver and palladium on Diaion SP700 adsorption resin were investigated.

EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High- Technologies Corpotation, Japan) was used in the studies. Hitachi hollow cathode lamps (HCL) were used for the determination of Ag (328.1 nm) and Pd (247.6 nm). High-purity argon (99.999 %, Messer Chemical Corpotation, Kunming, China) was used as the purge and sheath gas throughout at a flow rate of 30 mL min^{-1}. The output signals were collected and processed with peak-height mode. Other operating conditions were carried out according recommendations of manufacturer.

A peristaltic pump mode FIA-3110 (Titan Instruments Co., Ltd. Beijing, China) was used in the solid phase extraction process. A WX-4000 closed vessel microwave system (Preekem Scientific Instruments Co., Ltd. Shanghai, China. maximum pressure 35 atm, maximum temperature 235 ℃).

The certified standard reference materials (ore GBW07290 and biological GBW07603) were obtained from Chinese Standards Center (Beijing, China). Working standard solutions were obtained by appropriate dilution of the stock standard solution.

0.5 % (w/v) solution of diisopentyl sulfoxide was prepared by dissolving appropriate amount of diisopentyl sulfoxide in ethanol. Ultra-pure water was used throughout. All the glass wares used in the experiments were kept in 10% nitric acid for at least 24 h and subsequently washed four times with ultra-pure water. All other reagents used were of the highest available purity and of at least analytical reagent grade. Ultra-pure water of resistivity 18 MΩ cm obtained from a UPHW purification device (Ulupure Co. Shanghai, China) was used to prepare all the solutions.

Diisopentyl sulfoxide was obtained from Yunnan Gold Group Co. Diaion SP700 was purchased from Mitsubishi Chemical Corporation (Tokyo, Japan). Diaion SP700 resin is an aromatic type adsorbent. It is based on crosslinked polystyrenic matrix. Its surface area is 1200 m^2 g^{-1}. It was washed successively with methanol, water, 1 mol L^{-1} HNO$_3$ in acetone, water, 1 mol L^{-1} NaOH and water, sequentially.

Preconcentration procedure: An off-line column procedure was applied for the preconcentration process. The Teflon column was 3 cm long and 1 cm in diameter. The 2 μm of sieve plate was placed to prevent loss of the resin beads during sample loading. Then, 800 mg of Diaion SP700 resin was poured into the column. The resin bed was washed with plenty of ultra-pure water until neutral pH and subsequently reused. The method was tested with model solutions before its application to real samples. 250 mL of solutions containing 1-80 ng of analyte ions, 5 mL of 12 mol L^{-1} hydrochloric acid solution and 8 mL of 0.5 % diisopentyl sulfoxide was passed through the column at a flow rate of 10 mL min^{-1} using a vacuum aspirator. The retained silver and palladium ions were eluted from the column by 1 mL of 1 mol L^{-1} HNO$_3$ and the concentrations of silver and palladium ions were determined

by GFAAS. A blank solution was also run under the same conditions without adding the analyte ions.

Sample preparation: The developed method has been successfully applied to the determination of silver and palladium ions in the certified standard reference materials (ore GBW07290 and biological GBW07603).

For ore reference materials samples, the 10 g of ore reference materials were transferred into a porcelain crucible and roasted for 1.5 h in a muffle furnace at 610 °C. After roasting, the sample was transferred to 400 mL glass beaker and 80 mL of freshly prepared aqua regia was added to sample. 1 g of NaCl was added to stabilize the analyte ions chloride complex during evaporation on a hot plate. The beaker was covered with a watch glass and heated on a hot plate. Heating was continued for at least 3 h and enough aqua regia was added at regular intervals to maintain the free acid level at about 1 cm above the sample level. The watch glass was removed and the content was evaporated slowly until the residue became nearly dry. Then, 30 mL of 6 mol L^{-1} HCl was added to the beaker and the solution was warmed until clear solution was obtained. Afterwards, sample solution was cooled and filtered using whatman No.1 filter paper (pore size,11 μm). The residue was washed with minimum amounts of 0.1 mol L^{-1} HCl. The final residue was discarded and the filtrate was then dissolved and diluted to 100 mL with distilled water. Finally, analyte ions in ore sample were determined by the proposed method.

For biological samples, the sample was mixed with concentrated nitric acid and 30 % hydrogen peroxide in microwave digestion system. The bombs were sealed tightly and then positioned in the carousel of the microwave oven. Digestion conditions for microwave system of the samples were applied as 5 min for 400 W. Blanks were prepared in the same way as the sample. After cooling, the preconcentration procedure given above was applied.

For water samples, the samples were immediately acidified by adding several drops of nitric acid and filtrated with 0.45 μm filter. Then the preconcentration procedure given above was applied to the samples. River water sample was collected from Xiaoqing river (Dongchuang, P.R. China). Lake water sample was collected from Qilu lake (Yuxi, P.R. China). Tap water sample was freshly collected from our laboratory.

GFAAS analysis: The GFAAS analysis condition is listed in Table-1. For samples analysis, a 20 μL aliquot of the samples or standard solution was injected into the graphite cuvette for the GFAAS determination. The atomic absorption signals were measured with the Zeeman background corrector in operation. The measurement was repeated three times and the obtained signals were averaged.

RESULTS AND DISCUSSION

Effect of acidity: The acidity of the sample solution is one of the important factors for quantitative recoveries of the analyte ions. According to the results (Fig. 1), quantitative recoveries (> 95 %) for analyte ions were obtained in the presence of HCl in the concentration range: 0.1-0.5 mol L^{-1}. Thus 5 mL 12 mol L^{-1} HCl solutions was recommended to control acidity.

| TABLE-1 SETTING OF ANALYTICAL CONDITIONS		
Analytical condition	Ag	Pd
Calculation mode	Peak height	Peak height
Wavelength (nm)	328.1	247.6
Slit width (nm)	1.3	0.4
Time constant (s)	0.1	0.1
Lamp current (mA)	7 mA	10 mA
Cuvette type	Pyro tube HR	Pyro tube HR
Dry start/end temp. (°C)	80/140	80/140
Dry ramp time (S)	40	40
Ash start/end temp. (°C)	500/500	700/700
Ash ramp time (S)	20	20
Atomize start/end temp. (°C)	2200/2200	2400/2400
Atomize hold time (S)	5	5
Clean start/end temp. (°C)	2500/2500	2500/2500
Clean hold time (S)	4	4
Gas flow (mL min^{-1})	30	30
Sample injection volume (µL)	20	20
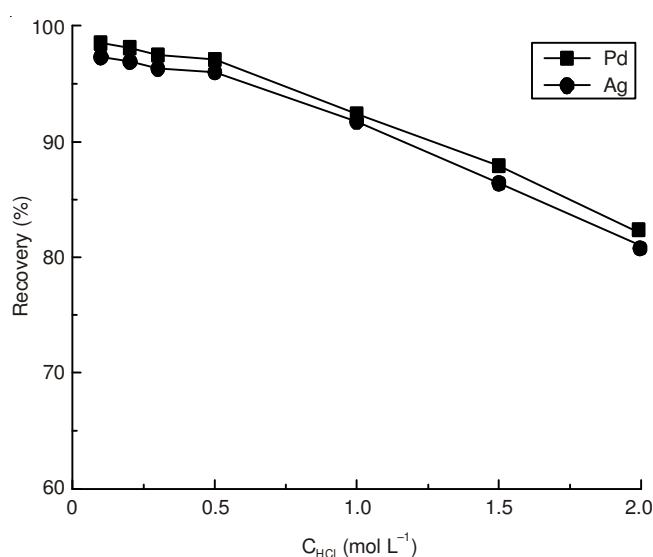
Fig. 1. Influences of acidity on the recovery of silver and palladium. Conditions: Sample volume: 250 mL; flow rate: 10 mL min^{-1}; amount of the resin: 800 mg

Influences of diisopentyl sulfoxide amount: In order to determine the amounts of diisopentyl sulfoxide required for quantitative recovery for silver and palladium, the proposed method was applied. Changing the diisopentyl sulfoxide amounts (0.5 % solution) at the range of 1-10 mL. The results showed that the recovery values of silver and palladium were increased with increasing amounts of diisopentyl sulfoxide added. The recovery reaches a constant value with at least 5 mL of 0.5 % diisopentyl sulfoxide solution used. On this basis, studies were carried out at 8 mL of diisopentyl sulfoxide. This amount of diisopentyl sulfoxide is enough for the separation and preconcentration procedure because of the very low level of the investigated silver and palladium concentrations in real samples.

Effects of amount of resin: Also the amounts of solid phase extraction material are another important factor on the column studies for the quantitative recoveries of metal-diisopentyl sulfoxide chelates. The effect of the amount of Diaion SP700 on the sorption of metal ions was examined in the range of 300-1000 mg. The results demonstrated that,

quantitative recoveries (> 95 %) of silver and palladium were observed in the range of 600-900 mg. Above 900 mg the recoveries were below 95 % with 1 mL of the eluent. Therefore, in the proposed procedure, 800 mg of Diaion SP700 resin is recommended.

Effect of flow rate of sample solution and eluent: The influence of flow rate on the adsorption of metal-diisopentyl sulfoxide chelates was also studied. Flow rate in the range of 8-12 mL min^{-1} had no significant effect on the recoveries of silver and palladium. Therefore, in the proposed procedure, 10 mL min^{-1} flow rate is recommended.

Among several media investigated as eluent (*e.g.*, H$_2$O, HNO$_3$, ethanol, methanol, acetone, NH$_3$ and thiourea), only HNO$_3$ showed satisfactory elution characteristics. 1 mL of 1 mol L^{-1} HNO$_3$ provided quantitative recovery (> 95 %) and reproducibility. The elution was performed in the opposite direction to avoid the clogging of the column.

The flow rate of eluent solution was examined in the range of 0.5-2 mL min^{-1}. Maximum recoveries for the analyte ions were obtained in the range of 0.5-1 mL min^{-1}. The flow rate of 1 mL min^{-1} was chosen as optimum value.

Effect of sample volume: The effect of the sample solution volume on the metal sorption on Diaion SP700 was studied by passing 50-500 mL volumes through Diaion SP700 column at a 10 mL min^{-1} flow rate. The results were given in Fig. 2. The adsorption of the metal ions was not affected by sample volume when the volume is below 250 mL. However, the percent of analytes sorption decrease when the volume is above 250 mL. The recoveries of analytes decrease probably due to the excess analytes loaded over the column capacity with increasing sample volume above 250 mL. The adsorbed metals can be eluted with 1 mL of 1 mol L^{-1} HNO$_3$ representing an enrichment factor of 250 was achieved by this technique.
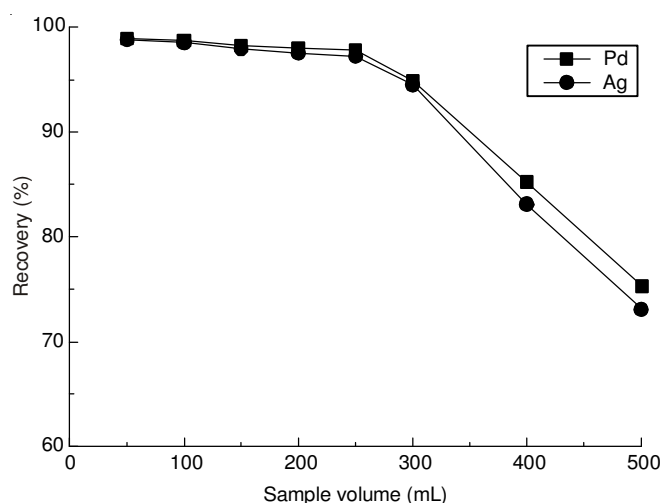

Fig. 2. Effect of the sample volume on the recoveries of silver and palladium. Conditions: HCl in the concentration range: 0.1-0.5 mol L^{-1}; flow rate: 10 mL min^{-1}; amount of the resin: 800 mg

Effect of interfering ions on recovery: In order to evaluate the possibility of selective recovery of silver and palladium ions in the presence of alkaline, earth alkaline metals and major anions of the real samples, the procedure has been performed with 250 mL solutions containing such ions. Quantitative

recoveries (> 95 %) for 1500 mg L^{-1} of NaCl, for 800 mgL^{-1} of Ca^{2+}, for 600 mg L^{-1} of K^+, Fe^{3+}, 300 mg L^{-1} for Zn^{2+}, Cu^{2+}, 100 mg L^{-1} for Al^{3+}, Ni^{2+} were obtained. These tolerable levels of foreign ions were enough for the quantitative separation of silver and palladium ions from the matrix of the real samples.

Loading capacity: In order to study the adsorptive capacity of Diaion SP700 resin, batch method was used. To 0.1 g Diaion SP700 resin was placed in the conical flasks. Stock solution of Ag(I) and Pd(II) were added to the flask, respectively. Acidity of the solution was adjusted to 0.1-0.5 mol L^{-1} using 12 mol L^{-1} HCl solution. After shaking for 3 h, the mixture was filtered. Concentration of silver and palladium ions were measured by GFAAS. The loading capacity of Diaion SP700 was 17 mg g^{-1} for Ag(I) and 11 mg g^{-1} for Pd(II), respectively.

Calibration curve and detection limit: Using the optimized conditions of preconcentration, calibration curve was prepared for Ag(I) and Pd(II). The limit of detection(LOD) value (blank + 3 s) were found to be 0.0013 µg L^{-1} for Ag(I) and 0.0027 µg L^{-1} for Pd(II), respectively. The results were also shown in Table-2. Diaion SP700 resin can be reused at least 50 times.

TABLE-2
ANALYTICAL CHARACTERISTICS OF THE PROPOSED METHOD

Parameter	Analytical feature	
	Palladium	Silver
Regression equation (C in µg L^{-1})[a]	A = 5.16 × 10^{-3} C + 2.16 × 10^{-3}	A = 9.85 × 10^{-3} C + 1.86 × 10^{-3}
Linear range (µg L^{-1})[a]	2-80	1-70
Correlation coefficient	0.9994	0.9993
Enrichment factor	250	250
The relative standard deviation	3.6 (0.2 µg L^{-1}, n = 10)[b]	3.8 (0.2 µg L^{-1}, n = 10)[b]
Detection limit (µg L^{-1})[b] (LOD = bland + 3σ, n = 12)	0.0027	0.0013
Quantification limit (µg L^{-1})[b] (LOQ = bland + 10σ, n = 12)	0.008	0.004

[a]In the preconcentrated solution; [b] In the original samples before applying the preconcentration procedure

Applications of the presented procedure: In order to establish the validity of the proposed procedure, the method has been applied to the determination of silver and palladium in the certified standard reference materials samples (GBW07290 and GBW07603). The results were given in Table-3.

TABLE-3
DETERMINATION OF SILVER AND PALLADIUM (ng g^{-1}) IN THE CERTIFIED REFERENCE MATERIALS AFTER APPLICATION OF THE PRESENTED PROCEDURE (n = 5)

Sample	Certified value (ng g^{-1})	Our value (ng g^{-1})
GBW07603	Ag (49 ± 7)	Ag(48 ± 9)
GBW07290	Pd (4.6 ± 0.6)	Pd(4.5 ± 0.7)

The proposed method was applied to determine silver and palladium in the water samples. The results for the water samples were given in Table-4. The results indicate that the recoveries of silver and palladium ions were in the range of 94-106 %.

TABLE-4
DETERMINATION OF SILVER AND PALLADIUM (µg L^{-1}) IN WATER SAMPLES (n = 5)

Samples	Added		Found[a] by present method		Recovery (%)	
	Ag	Pd	Ag	Pd	Ag	Pd
Lake water	0	0	0.8±0.1	BDL	-	-
	5	5	5.7±0.2	5.1±0.1	98±4	102±2
	10	10	10.9±0.3	9.6±0.2	101±3	96±2
Tap water	0	0	BDL	BDL	-	-
	5	5	5.2±0.1	4.9±0.2	104±2	98±4
	10	10	10.2±0.3	9.9±0.5	102±3	99±5
River water	0	0	0.6±0.1	0.9±0.1	-	-
	5	5	5.5±0.2	6.0±0.2	98±4	102±4
	10	10	10.8±0.4	11.3±0.2	102±4	104±2

-Not determined; [a]Mean ± S.D.

Table-5 compares the characteristic data of the proposed method with other preconcentration methods for silver and palladium reported in literatures. Generally, the detection limit and enhancement factor obtained by the present method are comparable to those reported methods and the enrichment factor has been greatly improved.

TABLE-5
COMPARISON OF THE PRESENT METHOD WITH OTHER SYSTEM

Enrichment method	Detection Method	Metal ions	Limit of detection (ng L^{-1})	Enrichment factor	Ref.
DLLME	GFAAS	Ag	12	132	3
DLLME	GFAAS	Ag	20	72	5
CPE	ETAAS	Ag	12	60	7
SPE	FAAS	Ag, Pd	Ag(1800), Pd(4200)	110	4
DLLME	GFAAS	Pd	2.4	156	8
SPE	GFAAS	Pd	2000	8.7	9
SPE	ICP-AES	Pd	0.2	100	10
CPE	Spectrophotometry	Pd	0.47	50	11
SPE	GFAAS	Ag, Pd	Ag(1.3),Pd(2.7)	250	This work

Conclusion

The described method using the Diaion SP700 resin combined with diisopentyl sulfoxide has a good potential for the enrichment and separation of silver and palladium ions from the biological samples, ore and water samples and their determinations by GFAAS. The method is a simple, sensitive, precise, reliable and accurate technique. Instead of the use of fresh solvent as an extracting phase for each sample, the reusability of Diaion SP700 was greater than 50 cycles without any loss in its sorption behaviour. The elution was easily performed with 1 mol L^{-1} HNO_3 and the metal ions in 250 mL solution can be concentrated to 1 mL, representing an enrichment factor of 250 was achieved. The tolerance limits of interfering ions on the recovery of silver and palladium ions are quite high. The results acquired from the analyses of the two standard reference materials confirmed the reliability of the method. The proposed method possesses lower limit of detection. Enrichment factor are superior to those reported methods. The matrix effects with the method were reasonably tolerable, which makes it suitable for the determination of trace amount of silver and palladium ions in environmental samples.

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