

Solid Phase Extraction and Graphite furnace Atomic Absorption Spectrometry for the Determination of Palladium

ZHANGJIE HUANG*, JUN CHANG, SHAOPING FENG and ZHONGQI YANG
Department of Chemistry, Yunnan University, Kunming 650091, P.R. China
Fax: (86)(871)5032180; Tel: (86)(871)6688875; E-mail: zhjhuang@ynu.edu.cn

A solid phase extraction and graphite furnace atomic absorption spectrometry (GFAAS) for the determination of palladium with Diaion SP700 resin as sorbent was studied. Palladium complexed with hexyl benzimidazolyl sulfide (HBMS) was preconcentrated on a nonpolar resin Diaion SP700 and ethanol was used as eluent. The effect 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 palladium in 100 mL solution can be concentrated to 1.0 mL, representing an enrichment factor of 100 was achieved. The detection limit and quantification limit of the method were found to be 0.008 and 0.2 $\mu\text{g L}^{-1}$, respectively. The analytical results for the certified reference samples (GBW07290 and GBW07291) were in a good agreement with the certified value. The relative standard deviation for 10 replicate measurements of 0.50 $\mu\text{g L}^{-1}$ palladium was 4.3 %. The method was successfully applied to the determination of trace amount palladium in environmental samples.

Key Words: Solid phase extraction, Palladium, Hexyl benzimidazolyl sulfide, Graphite furnace atomic absorption spectrometry.

INTRODUCTION

Palladium is an element of increasing importance in today's industries. Due to the catalytic properties, it is widely used in the synthesis of many materials, from polymers to pharmaceuticals. In addition to this, its emission from the automotive catalytic converters has resulted in an increase in the concentration of palladium in the environment^{1,2}.

Some of the palladium compounds have been reported as potential health risks to humans, causing asthma, allergy, rhino conjunctivitis and other serious health problems³. The available evidence indicates that the platinum group metals, especially palladium, are transported to biological materials through deposition in roots by way of binding to sulphur-rich, low molecular weight species in plants. A number of studies have reported the dispersion and accumulation of palladium in various environmental compartments⁴.

The monitoring of palladium in environmental samples has great importance with respect to estimation of the future risk of the human health and the ecosystem. Palladium analysis requires analytical methods of high sensitivity, selectivity and the control of interference effects. The most widely used methods for determination

of palladium in environmental samples include graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma mass spectrometry (ICP-MS) and adsorptive stripping voltammetry (ASV). However, the determination of 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 palladium (ng mL^{-1} levels) together with the high concentration of interfering matrix components often requires an enrichment step combined with a matrix separation⁵. Several methods have been reported for the separation and preconcentration of palladium, such as co-precipitation⁶, liquid-liquid extraction (LLE)⁷, solid-phase extraction (SPE)⁸⁻¹⁴ and cloud point extraction (CPE)^{15,16}. Among these techniques, SPE 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 in on-line or off-line mode.

Palladium, according to Pearson theory, belongs to the group of soft acids, thus forms complexes with ligands containing nitrogen, sulfur and oxygen donor atoms. Non-polar sorbents based on a hydrophobic polymeric phase are capable of extracting low-polarity palladium complexes from aqueous solutions through reverse phase sorption. Hexyl benzimidazolyl sulfide owing to its nitrogen functional group can be utilized as effective complexing agents for palladium.

The aim of this work is to combine solid-phase extraction with GFAAS and develop a new method for the determination of palladium. In this method hexyl benzimidazolyl sulfide (HBMS), which reacts with Pd(II) forming a stable Pd(II)-HBMS complex. Subsequently, water sample containing Pd(II)-HBMS complex was passed through Diaion SP700 cartridge. Palladium complexed with HBMS were preconcentrated on a nonpolar resin Diaion SP700. The Pd(II)-HBMS complex adsorbed on Diaion SP700 cartridge was eluted with ethanol. 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 palladium on Diaion SP700 adsorption resin were investigated.

EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-Technologies Corporation, Japan) was used in the studies. Hitachi hollow cathode lamps (HCL) were used for the determination of Pd (247.6 nm) operated at 10 mA. High-purity argon (99.999 %, Messer Chemical Corporation, Kunming, China) was used as the purge and sheath gas throughout at a flow rate of 200 mL min^{-1} . The output signals were collected and processed with peak-height mode. Other operating conditions were carried out according to the recommendations of manufacturer. The pH values were measured with a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China).

Stock standard solution (1000 mg L^{-1}) of Pd was obtained from the National Institute of Standards (Beijing, China). Working standard solutions were obtained by appropriate dilution of the stock standard solution. Hexyl benzimidazolyl sulfide (Fig. 1) was synthesized by our laboratory as literature¹⁷ and a 0.2 % (w/v) solution of HBMS was prepared by dissolving appropriate amount of HBMS in ethanol. All other reagents used were of the highest available purity and of at least analytical reagent grade. Doubly distilled water was used throughout. Pipettes and vessels in the experiments were kept in 10 % nitric acid for at least 24 h and subsequently washed 4 times with double distilled water.

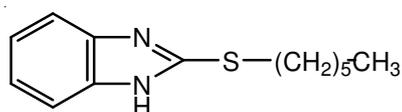


Fig. 1. Structure of hexyl benzimidazolyl sulfide (HBMS)

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 $1200 \text{ m}^2 \text{ g}^{-1}$. Diaion SP700 is widely used in different industrial fields¹⁸. It was washed successively with methanol, water, $1.0 \text{ mol L}^{-1} \text{ HNO}_3$ in acetone, water, $1.0 \text{ mol L}^{-1} \text{ NaOH}$ and water, sequentially.

Preconcentration procedure: An off-line column procedure was applied for the preconcentration process. The Teflon column was 3.5 cm long and 0.8 cm in diameter. The $2.0 \mu\text{m}$ of sieve plate was placed to prevent loss of the resin beads during sample loading. Then, 500 mg of Diaion SP700 resin was poured into the column. The resin bed was washed with plenty of distilled water until neutral pH and subsequently reused. The method was tested with model solutions before its application to real samples. 100 mL of solutions containing 2-90 ng palladium, 10 mL of 1 mol L^{-1} hydrochloride acid solution and 2.0 mL of 0.2 % HBMS was passed through the column at a flow rate of 10 mL min^{-1} using a vacuum aspirator. The retained palladium ions were eluted from the column by 1 mL ethanol and the concentrations of palladium ions were determined by GFAAS. A blank solution was also run under the same conditions without adding the analytes.

Sample preparation: For ore samples, 10.0 g of geological standard reference materials (GBW07290 or GBW07291 peridotite, provided by the Chinese Standard Material Center) was transferred into a porcelain crucible and roasted for 2 h in a muffle furnace at $650 \text{ }^\circ\text{C}$. After roasting, the sample was transferred to 250 mL glass beaker and 40 mL of freshly prepared aqua regia was added to sample. 1.0 g of NaCl was added to stabilize the palladium 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 4 h and enough aqua regia was added at regular intervals to maintain the free acid level at about one centimeter above the sample level. The watch glass was removed and the content was evaporated slowly until

the residue became nearly dry. Then, 40 mL of 3 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 250 mL with distilled water. Finally, palladium in ore sample was determined by the proposed method.

The onion and lettuce sample were collected from a urban vegetable garden in Kunming. The sample was washed with tap water and distilled water. Then, dried at 110 °C. 10.0 g of sample was weighted in a beaker and 50 mL of concentrated nitric acid was added. The mixture was gently heated on a hot plate for at least 2 h and enough concentrated nitric acid was added at regular intervals. After cooling to room temperature, 10 mL of concentrated H₂O₂ was added into the beaker. The mixture was again evaporated near to dryness. Then, 5 mL of 6 mol HCl was added and the mixture was heated to dryness. This last step was repeated twice to ensure total elimination of HNO₃. The solid residue was filtered using Whatman no. 1 filter paper (pore size, 11 µm). The final residue was discarded and the filtrate was then diluted to 100 mL with distilled water.

For water samples, river water sample was collected from Tanglang chuan river (Kumming, P.R. China). Lake water sample was collected from Diangchi lake (Kumming, P.R. China). Tap water sample was freshly collected from our laboratory. All water 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.

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 3 times and the obtained signals were averaged.

TABLE-1
SETTING OF ANALYTICAL CONDITIONS

Analytical condition	Palladium	Analytical condition	Palladium
Calculation mode	Peak height	Ash start/end temp (°C)	700/700
Wavelength (nm)	247.6	Ash ramp/hold time(s)	5/0
Slit width (nm)	0.4	Atomize start/end temp (°C)	2400/2400
Time constant (s)	0.1	Atomize ramp/hold time (s)	0/3
Lamp current (mA)	10 mA	Clean start/end temp (°C)	2500/2500
Cuvette type	Pyro tube HR	Clean ramp/hold time (s)	0/4
Dry start/end temp (°C)	80/110	Gas flow in atomization (mL min ⁻¹)	0
Dry ramp/hold time (s)	30/10	Sample injection volume (µL)	20

RESULTS AND DISCUSSION

Effect of acidity: The acidity of the sample solution is one of the important factors affecting the formation of Pd(II)-complex and the subsequent solid phase extraction. The palladium coordination compounds in aqueous solutions have different stability and kinetic properties. Palladium is usually present in solutions as $\text{Pd}(\text{H}_2\text{O})_4^{2+}$. The formation of PdOH^+ and $\text{Pd}(\text{OH})_2$ starts at pH above 1 and insoluble $\text{Pd}(\text{OH})_2$ precipitates from diluted nitric acid solutions. The evidence of formation of PdNO_3^+ , $\text{Pd}(\text{NO}_3)_2$ and $\text{Pd}(\text{OH})\text{NO}_3$ in nitric acid has been also shown¹⁹. The palladium chloride complexes are more stable than nitrate complexes. According to the results (Fig. 2), quantitative recoveries (> 95 %) for analytes were obtained in the presence of HCl in the concentration range: 0.1-2.0 mol L⁻¹. Thus 10 mL of 1 mol L⁻¹ HCl solutions was recommended to control acidity.

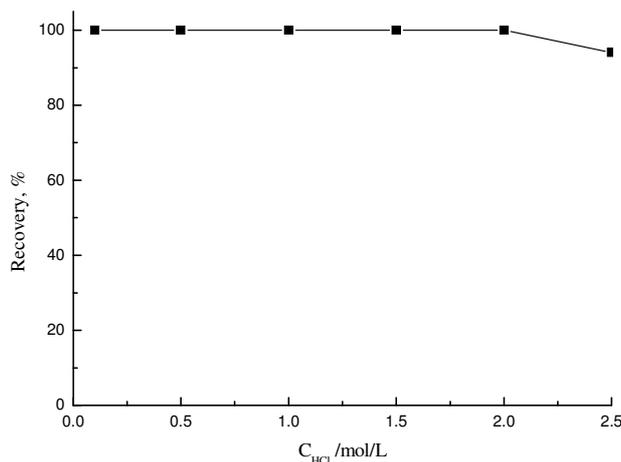


Fig. 2. Influences of acidity on the recovery of palladium; Conditions: Sample volume: 100 mL; Flow rate: 10 mL min⁻¹; Amount of the resin: 500 mg

Influences of ligand amount: In order to determine the amounts of HBMS required for quantitative recovery for palladium(II), the proposed method was applied. Changing the HBMS amounts (0.2 % solution) in the range of 0.5-4 mL. The results showed that the recovery values of the analyte palladium(II) were increased with increasing amounts of HBMS added. The recovery reaches a constant value with at least 1.0 mL of 0.2 % HBMS solution used. On this basis, studies were carried out at HBMS amounts of 2.0 mL. This amount of HBMS is enough for the separation and preconcentration procedure because of the low level of the investigated palladium(II) concentrations in real samples.

Effects of the 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 complexes^{20,21}. The effect of the amount of Diaion SP700 on the sorption of metal ions was examined in the range of 200-800 mg. The results

demonstrated that, quantitative recoveries (> 95 %) of palladium was observed in the range of 400-600 mg. Above 700 mg the recoveries were below 95 % with 1.0 mL of the eluent. Therefore, in the proposed procedure, 500 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 palladium(II)-HBMS complex was also studied. Flow rate in the range of 1-15 mL min⁻¹ had no significant effect on the recoveries of palladium(II). Therefore, in the proposed procedure, 10 mL min⁻¹ flow rate is recommended.

Among several media investigated as eluent (HNO₃, ethanol, methanol, acetone, pentanol, NH₃, thiourea, ethyl acetate), only ethanol showed satisfactory elution characteristics. 1.0 mL ethanol provided quantitative recovery (> 95 %) and reproducibility. The elution was performed in the opposite direction to avoid the clogging of the column. The palladium in 100 mL solution can be concentrated to 1.0 mL, representing an enrichment factor of 100 was achieved.

The flow rate of eluent solution was examined in the range of 0.5-2.0 mL min⁻¹. Maximum recoveries for palladium was obtained in the range of 0.5-1.5 mL min⁻¹. The flow rate of 1.0 mL min⁻¹ was chosen as optimum value.

Effect of interfering ions on recovery: Most common matrix constituents of real samples such as alkali and alkaline earth elements do not react with HBMS because of its selectivity. The effects of common coexisting ions in natural water samples on the extraction recovery of palladium were studied. In these experiments, 100 mL solutions contains 0.5 µg L⁻¹ of palladium and various amounts of interfering ions were treated according to the recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery of Pd less than 95 %. The results obtained are given in Table-2.

TABLE-2
TOLERANCE OF FOREIGN IONS IN
THE DETERMINATION OF 0.50 µg L⁻¹ PALLADIUM

Interferent	Concentration (µg L ⁻¹)	Interferent (Pd ratio)	Recovery (%)
K ⁺	250,000	500,000	98.50
PO ₄ ³⁻	250,000	500,000	96.80
Ca ²⁺	200,000	400,000	102.50
Mg ²⁺	200,000	400,000	105.60
Ba ²⁺	100,000	200,000	97.60
Al ³⁺	80,000	160,000	95.80
Co ²⁺	60,000	120,000	96.50
Fe ³⁺	60,000	120,000	98.10
Cu ²⁺	50,000	100,000	95.10
Zn ²⁺	50,000	100,000	97.30
Ni ²⁺	50,000	100,000	102.80
Pb ²⁺	8,000	16,000	103.50
Rh ³⁺	2,000	4,000	95.80
Pt ⁴⁺	500	1,000	101.50

Loading capacity: To 0.1 g resin was placed in the conical flasks. Stock solution of Pd(II) and HBMS were added to the flask. Acidity of the solution was adjusted to pH 1.0 using 1.0 mol L⁻¹ HCl solution. After shaking for 4 h, the mixture was filtered. Concentration of Pd(II) was measured by ICP-MS. The loading capacity of Diaion SP700 was 45 µg g⁻¹ for palladium.

Composition of the complex: The crystal structure of the Pd(II)-HBMS complex was determined by our laboratory as literature²². The crystal structure of the Pd(II)-HBMS complex showed that the molar ratio of Pd(II) to HBMS is 1:2. The Pd(II)-HBMS complex as a whole is in complete symmetry with palladium atom at the symmetry center of the square-planar complex.

Calibration curve and detection limit: Using the optimized conditions of preconcentration, calibration curve was prepared for Pd(II). The limit of detection (LOD) value (blank + 3 σ) and limit of quantification (LOQ) value (blank + 10 σ)²³⁻²⁶, where σ is standard deviation of blank determination (n = 12), were found to be 0.008-0.2 µg L⁻¹, respectively. The results were also shown in Table-3. Diaion SP700 resin can be reused at least 200 times.

TABLE-3
ANALYTICAL CHARACTERISTICS OF THE PROPOSED METHOD

Parameter	Analytical feature
Regression equation (C _{pd} in µg L ⁻¹) ^a	A = 0.004186 C _{pd} + 0.001889
Linear range (µg L ⁻¹) ^a	2.00-90.00
Correlation coefficient	0.9998
Enrichment factor	100
The relative standard deviation (0.50 µg L ⁻¹ , n = 10) ^b	4.3
Detection limit (µg L ⁻¹) ^b (LOD = bland + 3σ, n = 12)	0.008
Quantification limit (µg L ⁻¹) ^b (LOQ = bland + 10σ, n = 12)	0.02

^aIn the preconcentrated solution, ^bIn the original samples before applying the preconcentration procedure.

Table-4 compares the characteristic data of the proposed method with other preconcentration methods for Pd reported in literatures. As can be seen, the proposed method possesses lower limit of detection and higher enrichment factor than the reported methods.

TABLE-4
COMPARISON OF THE PUBLISHED PRECONCENTRATION
METHODS FOR PALLADIUM WITH THE PROPOSED METHOD

Preconcentration method	Detection method	Enrichment factor	Detection limit (µg L ⁻¹)	Reference
Coprecipitation	FAAS	25	2.1	6
LLE	Spectrophotometry	–	7	7
SPE	GFAAS	8.7	2.0	8
SPE	GFAAS	20	0.39	9
SPE	FAAS	60	1.5	12
SPE	FAAS	–	17	13
SPE	FAAS	–	9.0	14
CPE	ICP-AES	20	0.3	15
CPE	Spectrophotometry	50	0.47	16
Proposed method	GFAAS	100	0.008	This work

Applications of the presented procedure: In order to establish the validity of the proposed procedure, the method has been applied to the determination of palladium in geological standard reference materials (GBW07290 and GBW07291 peridotite). The results are given in Table-5.

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

Sample	Certified value (ng g^{-1})	Present value (ng g^{-1})
GBW07290	4.6 ± 0.6	4.5 ± 0.4
GBW07291	60 ± 9	59 ± 6

The proposed method was applied to determine palladium in water and biological samples. The results for water samples are given in Table-6 and biological samples are given in Table-7. The results indicate that the recoveries in the range of 96-104 % are reasonable well for trace analysis.

TABLE-6
DETERMINATION OF PALLADIUM ($\mu\text{g L}^{-1}$) IN WATER SAMPLES (n = 5)

Samples	Added	Found ^a by present method	Recovery (%)
River water	0	0.7 ± 0.1	–
	5	5.6 ± 0.2	98 ± 4
	10	10.4 ± 0.3	97 ± 3
Lake water	0	0.9 ± 0.1	–
	5	6.0 ± 0.2	102 ± 4
	10	10.7 ± 0.4	98 ± 4
Tap water	0	BDL	–
	5	5.2 ± 0.2	104 ± 4
	10	9.6 ± 0.3	96 ± 3

–, not determined; BDL, below the detection limit; ^aMean \pm SD.

TABLE-7
DETERMINATION OF PALLADIUM (ng g^{-1}) IN BIOLOGICAL SAMPLES (n=5)

Samples	Added	Found ^a by present method	Recovery (%)
Onion	0	16.2 ± 0.2	–
	10	26.4 ± 0.3	102 ± 3
Lettuce	0	11.4 ± 0.3	–
	10	21.1 ± 0.4	97 ± 4

–, not determined; ^aMean \pm SD.

Conclusion

The described method using the Diaion SP700 resin combined with hexyl benzimidazolyl sulfide has a good potential for the enrichment and separation of palladium ions from the water, lettuce and onion samples and their determinations by GFAAS. The method is a simple, sensitive, precise, reliable and accurate technique.

The advantages of this method is its selective adsorption in a wide range of sample acidity (0.1-2.0 M HCl). The method is also low cost. Instead of the use of fresh solvent as an extracting phase for each sample, the reusability of Diaion SP700 was as high as greater than 200 cycles without any loss in its sorption behaviour. The tolerance limits of interfering ions on the recovery of 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 and higher enrichment factor than other reported preconcentration methods for palladium (Table-4), which makes it suitable for the determination of trace amount of palladium in environmental samples.

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