Preconcentration/Separation of Palladium in Geological and Environmental Samples Based on Ionic Liquid Prior to the Determination by Flame Atomic Absorption Spectrometry

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INTRODUCTION

Palladium (Pd) is widely used in medicine, chemical catalysts, the electrical industry, and for alloys. The main application of palladium compounds is as automotive catalyst. The high increase in palladium demand for the automotive emission control catalyst will definitely result in more palladium-containing particles released into our environment in the future. An increase in the palladium levels has been found in road dust and soil samples (1-3), which indicates that wide usage of palladium compounds may pose some environmental problems. Although palladium has not been reported as a serious environmental pollutant such as the toxic heavy metals of mercury and lead, the long-term exposure to palladium can cause adverse health effects in living beings (4). Thus, it is important to determine the trace amounts of palladium in our environment.

It is well known that palladium [Pd(II)] can be determined by various techniques including liquid chromatography and spectrophotometry (4-13). However, Pd(II) concentrations in environmental matrices are usually at trace levels, and detection is difficult because of the presence of interfering metals (14). Atomic absorption spectrometry (AAS) is regarded as the most popular and convenient instrument employed for the determination of Pd(II) despite problems caused

ABSTRACT

A simple and environmentally friendly method was developed for the preconcentration, separation, and determination of palladium (Pd(II)) in geological and environmental samples. Room temperature ionic liquid (RTIL), 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$), was used for Pd(II) preconcentration and diethyldithiocarbamate (DDTC) was used as the chelating agent for extraction. The DDTC complex was extracted into the ionic liquid phase. Subsequently, Pd(II) was back-extracted from the organic phase into 1 mL of 6M nitric acid solution and analyzed by flame atomic absorption spectrometry (FAAS). The parameters influencing the extraction and determination of Pd(II), such as pH, concentration of chelating agent, extraction time and temperature, amount of ionic liquid, ionic strength, and coexisting ions were investigated and optimized.

Under the optimized experimental conditions, an enhancement factor of 29 was achieved with a 30-mL sample. The limit of detection (3σ) was 2.2 ng mL^{-1} , and the relative standard deviation (RSD) was 3.7% for 7 replicates. The method was successfully validated by analyzing palladium in the certified reference material and in environmental samples with satisfactory results.

by the presence of matrix spectral interferences (5-9). However, the real concentrations of Pd(II) in most environmental samples at

trace and ultratrace levels are beyond the scope of atomic absorption spectrometry (AAS). Separation and preconcentration steps are always required prior to determination by AAS in order not only to enrich the sensitivity but also to minimize the interferences caused by the matrix (5-9,15). On the other hand, separation and preconcentration is also a key step in the development of techniques for the recovery of palladium from waste materials (16,17).

Ionic liquids (ILs) have recently attracted special interest as environmentally friendly solvents to replace traditional toxic and volatile organic solvents (18-21). They also have negligible vapor pressure, good thermal stability, tuneable water miscibility, and are non-toxic. The application of ILs for the preconcentration and separation of analytes in analytical chemistry includes not only organic pollutants but also inorganic metals (22-28). Although ILs have in recent years been widely studied for liquid-liquid microextraction, few experiments have been carried out for palladium preconcentration (29, 30). Papaiconomou et al. (29) studied the extraction performance of several metals by hydrophobic ionic liquid without a chelating reagent. Shemirani et al. (30) extracted and determined trace levels of palladium in food additives, seawater, tea, and biological samples by using the ionic liquid 1-hexyl-3-methylimidazolium tetrafluoroborate $[Hmim][BF_4]$ as the extractant and a UV-Vis spectrometer as the detector. These recent

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studies indicate that ionic liquids can be applied to preconcentrate and separate palladium from complex matrices effectively. However, to the best of our knowledge, there is no report about preconcentration and determination of Pd(II) in geological samples using ionic liquids and flame atomic absorption spectrometry (FAAS). Considering that FAAS is one of the most popular instruments for Pd(II) determination, it is very interesting and useful to establish a preconcentration method based on using ionic liquid prior to FAAS analysis.

Therefore, the aim of this study was to establish a new preconcentration and separation method based on using IL for the determination of palladium at trace levels by FAAS. Diethyldithiocarbamate (DDTC) was selected as the chelating reagent by forming the Pd-DDTC complex. The complex was extracted with the IL 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$). The extracted palladium in IL was then back-extracted into a micro-volume of 6M HNO_3 and determined by flame atomic absorption spectrometry.

The present method was successfully applied to the determination of palladium in ore (reference material GBW 07342), fly ash, road dust, and soil samples. The advantages of this method are simplicity of operation, speed, environmental impact, and low cost with good performance.

EXPERIMENTAL

Instrumentation

An atomic absorption spectrometer (Shimadzu AA-6800, Kyoto, Japan) with a palladium hollow cathode lamp and an air-acetylene flame was used for the determination of palladium. The operating parameters were set as recommended by the manufacturer. The pH measurements were taken with a pH

meter using a combined glass calomel electrode. All measurements were performed in peak height mode. A centrifuge was used to accelerate the phase separation.

Reagents and Standard Solution

All chemicals used throughout this study were at least analytical reagent grade. The standard stock solution of palladium (1000 mg L^{-1}) was purchased from the National Research Center for Certified Reference Materials, Beijing, P.R. China. Working solutions were prepared daily by appropriate dilution of the stock solution. Deionized water ($18.2\text{ M}\Omega$) was used throughout for sample preparation. The IL 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$) was purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, P.R. China. The DDTC solution (1%, w/v) was prepared by dissolving appropriate amounts of DDTC (Jinke Chemistry Reagent Company, Tianjin, P.R. China) in ethanol.

Sample Collection and Preparation

The geological standard reference material (GBW 07342, Ore) was purchased from the Institute of Geophysical and Geochemical Prospecting, Langfang, P.R. China. The road dust samples were collected from two sites with usually heavy traffic in Baoding, P.R. China. The fly ash samples were

collected from a power plant in Baoding and the soil samples were also collected from sites near the power plant.

The ore, soil, and fly ash samples were roasted at $600\text{ }^\circ\text{C}$ for 1 hour. After cooling, they were ground, passed through an 80-mesh sieve, and then homogenized, respectively. A 2.0-g specimen of each sample was weighed into a 100-mL beaker. A 10-mL amount of *aqua regia* was added to the beaker, and the mixture heated to moisten the residue. Then, another 10 mL of *aqua regia* was added to the residue and the mixture evaporated to near dryness. The insoluble part was filtered through a filter paper and washed with 1M HNO_3 . The filtered solution was then diluted to 100 mL with deionized water in a marked flask.

Preconcentration and Separation Procedure

The pH of the sample or standard solution was adjusted to the optimized value (6.5) using 1.0M HNO_3 or 1.0M NaOH before extraction. A 0.5 mL amount of $[C_4MIM][PF_6]$ was added to a 50-mL plastic conical tube with 30 mL of the sample. Then, 0.5 mL 1% (w/v) DDTC solution was added to the sample.

For the optimization procedures, a 30-mL amount of $1.0\text{ }\mu\text{g mL}^{-1}$ Pd(II) standard solution was used instead of a sample. The tube was shaken with a vortex stirrer for 10 minutes and put into a water bath at $50\text{ }^\circ\text{C}$ for 5 minutes.

The Pd(II) in the sample or standard solution was complexed with the complexing reagent and extracted into the IL phase. To accelerate separation of the phases, the mixture was centrifuged at 4000 rpm for 15 minutes after cooling. The upper aqueous phase was manually removed. The Pd(II) remained in the upper aqueous phase and was determined by FAAS for the optimization of the extraction conditions. For calibration and

TABLE I
FAAS Instrumental
Operating Parameters

Parameters	
Wavelength	247.6 nm
Lamp current	10 mA
Spectral band width	0.5 nm
Air-acetylene flow rate	1.8 L min^{-1}
Measurement mode	Peak area
Measurement time	5 s

sample analysis, the Pd(II) in the IL phase was back-extracted into 1.0 mL of 6M HNO₃ solution and then determined by FAAS.

RESULTS AND DISCUSSION

Effect of pH on Extraction

One of the most important parameters influencing the efficiency of the complex formation is the pH of the sample. In our experiment, the influence of sample pH on the pre-concentration of the palladium ions was investigated in the range of 2.0-12.0. The pH of the sample solution was adjusted with 1.0M HNO₃ and 1.0M NaOH. As can be seen in Figure 1, the quantitative recovery of Pd(II) is achieved in the pH range of 5.0-8.0. The progressive decrease in extraction of palladium at a pH lower than 4.0 is possibly due to competition of the hydrogen ion with Pd(II) for reaction with DDTC. The decrease in extraction efficiency at a pH higher than 8.0 is probably due to the partial solubility of the IL phase under a high pH. Based on the results, the pH of 6.5 was chosen for subsequent study, which is about the same pH value of deionized water.

Effect of DDTC Concentration on Extraction

In order to investigate the influence of DDTC concentration on the extraction of Pd(II), 1% (w/v) DDTC solution was added to the sample solutions in volumes varying from 0.05 to 1.0 mL and the pH was adjusted to 6.5. After performing the extraction procedure, the extraction efficiency of Pd(II) was found to be quantitative and complete when 0.5-1.0 mL of DDTC was added (Figure 2). For subsequent experiments, the DDTC solution volume of 0.5 mL was used.

Effect of IL Amount on Extraction

To examine the effect of the extraction solvent volume, different volumes of IL within the 0.1-1.0 mL

range were used. The results indicate that extraction can be affected by the amount of IL used (Figure 3). When 0.1 mL of IL was used, the extraction efficiency was low and the repetition was poor due to the difficulty of phase separation and collection of IL. Quantitative extraction can be obtained for an IL amount higher than 0.5 mL. No obvious changes occurred on the extraction efficiency for higher amounts of IL. The extraction efficiency keeps constant when the volume of IL added was from 0.5 to 1.0 mL. Thus, 0.5 mL was selected as optimum for our experiment.

Effect of Ionic Strength

Different concentrations of NaNO₃ solution ranging from 0 to 1.0% (w/v) were applied to evaluate the effects of different ionic strengths on the extraction. As can be seen in Figure 4, the extraction efficiency of Pd(II) decreases with an increase in ionic strength when the concentration of NaNO₃ is higher than 0.2%. The results demonstrate that the sodium ion in solution competes with the palladium ions for complexation reaction and partly increases the solubility of IL.

Influence of Temperature, Extraction Time, and Centrifuge Conditions

Temperature

Temperature can influence the transfer rate of the analyte between different phases and plays an important role in extraction. The possible influence of temperature on extraction was also investigated in the temperature range of 5 to 80 °C. The sample solutions were put into a water bath for 5 minutes at different temperatures, each time after shaking. The results in Figure 5 show that an increase in temperature from 5 to 60 °C slightly benefits the extraction process. The extraction efficiency is constant in the temperature range of 40 to 60 °C. However, recovery decreases obviously when the temperature increases from 60 °C up to 80 °C, probably owing in part to the solubility of the IL phase. Therefore, the extraction was performed at 50 °C to ensure good extraction efficiency.

Extraction Time

The study of shaking time indicate that 10 minutes is enough for the extraction of Pd(II). So, a 10-minute shaking time was applied for this experiment.

Fig. 1. Effect of pH on extraction ($n=3$). Other conditions: 30 mL of 1.0 $\mu\text{g mL}^{-1}$ d(II), 0.5 mL of 1% (w/v) DDTC, 0.5 mL RTIL, 10 min agitation time, 50 °C for extraction.

Fig. 2. Effect of DDTC concentrations on extraction ($n=3$). Other conditions: 30 mL of $1.0 \mu\text{g mL}^{-1}$ Pd(II), pH=6.5, 0.5 mL RTIL, 10 min agitation time, 50 °C for extraction.

Fig. 3. Effect of amounts of IL on extraction ($n=3$). Other conditions: 30 mL of $1.0 \mu\text{g mL}^{-1}$ Pd(II), 0.5 mL of 1% (w/v) DDTC, pH=6.5, 10 min agitation time, 50 °C for extraction.

Fig. 4. Effect of ion strength on extraction ($n=3$). Other conditions: 30 mL of $1.0 \mu\text{g mL}^{-1}$ Pd(II), 0.5 mL of 1% (w/v) DDTC, 0.5 mL RTIL, pH=6.5, 10 min agitation time, 50 °C for extraction.

Fig. 5. Effect of temperature on extraction ($n=3$). Other conditions: 30 mL of $1.0 \mu\text{g mL}^{-1}$ Pd(II), pH=6.5, 0.5 mL of 1% (w/v) DDTC, 0.5 mL RTIL, 10 min agitation time.

Centrifugation Rate and Time

The effect of centrifugation rate on the recovery was studied from 1000–5000 rpm. It was found that over the rate of 4000 rpm, the phases can be separated completely. The results of recovery indicate that a 15 minute centrifugation rate was enough to achieve complete transfer of the room temperature ionic liquid (RTIL) phase to the bot-

tom of the centrifuge tube. For this experiment, 4000 rpm and 15 minutes were chosen for subsequent experiments.

Optimization of Back-Extraction

To apply this preconcentration and separation method to the determination of Pd(II) in samples by FAAS analysis, different back-extraction processes were evaluated. Due

to the high viscosity of IL, it is not possible to directly inject the IL phase into the FAAS for analysis. Therefore, one approach to back-extraction of Pd(II) from the IL phase to the aqueous phase has to be used. Decreasing the pH of the media can lead to dissociation of the Pd-DDTC complex and further release palladium ions from the IL phase into the aqueous phase. Dif-

ferent mineral acids and other solutions at different levels were tested for Pd(II) back-extraction. The recoveries of back-extraction were achieved by using different solutions which are listed in Table II. Our study shows that 6M HNO₃ can quantitatively extract Pd(II) from the IL phase. Therefore, 1.0 mL of 6M HNO₃ was selected as the best choice.

In addition, the effects of temperature on back-extraction were investigated. Before shaking the solutions, the samples were kept in water baths at various temperatures for 5 minutes. The results show that the recovery increases as temperature increases from 5 to 60 °C. Thus, 60 °C was selected for back-extraction.

Agitation time can also affect quantitative back-extraction of Pd(II) from the IL phase into the aqueous phase. The effect of agitation time on back-extraction was studied by varying the time from 0.5 to 10 minutes. It was found that the analyte in IL can be recovered completely in 3 minutes. To minimize the deviation of extraction efficiency between different batches, 5 minutes was chosen as the optimum agitation time.

TABLE II
Evaluation of Different Back-Extraction Processes for Releasing Pd(II) From the IL Phase

Back-Extraction Process ^a	Recovery (%)
0.1M Na ₂ S ₂ O ₃	26±5
0.2M Na ₂ S ₂ O ₃	39±4
0.5M Na ₂ S ₂ O ₃	57±5
1M Na ₂ S ₂ O ₃	61±6
1% Thiourea solution (w/v)	65±4
3% Thiourea solution (w/v)	69±8
2M HCl	21±5
6M HCl	47±7
2M HNO ₃	63±3
6M HNO ₃	97±4

^a The volume of the back-extraction solvent is 1.0 mL.

Interferences Study

The effect of coexisting ions on the extraction of Pd(II) was investigated by keeping the concentration of Pd(II) at 1.0 µg mL⁻¹. The concentrations of commonly coexisting ions were in the 500 ng mL⁻¹ to 2000 µg mL⁻¹ range. Preconcentration was carried out according to the recommended procedure. The tolerance limit of coexisting ions is defined as the largest amount causing variations of less than 5% in the recovery of the analyte (26). The results are given in Table III. It can be concluded that all anions and cations tested did not result in significant interferences. The results also indicate that Pd(II) can be effectively separated from these ions by the recommended separation and preconcentration procedure. The tolerance of coexisting ions enabled us to apply the method to real sample analysis.

Analytical Performances

A calibration graph was constructed under the optimum extraction conditions. A 0.5-mL amount of IL and 30 mL of standard solutions at different concentrations were used. The extracted Pd(II) in the IL phase was back-extracted into 1.0 mL of 6M HNO₃. Then, Pd(II) in the back-extraction solution was determined by FAAS. Table IV summarizes the analytical characteristics of the preconcentration method. The linear concentration ranged from 10.0 to 500 ng mL⁻¹. The calibration function was Y=0.0005C+0.0003, where Y was the peak height of the FAAS signal and C was the concentration of palladium in ng mL⁻¹. A satisfactory correlation coefficient (r²=0.9923) and deviations (RSD =3.7%) were obtained with a limit of detection (3σ) of 2.2 ng mL⁻¹. The enhancement factor, which was calculated

TABLE III
Tolerance of Concentration of Coexisting Ions in the Extraction of Pd(II)^a

Coexisting Ion	Concentration (ng mL ⁻¹)
NO ₃ ⁻	2000*
Cl ⁻	100*
CO ₃ ²⁻	10*
SO ₄ ²⁻	10*
Mg ²⁺	1000
Mn ²⁺	1000
Fe ³⁺	1000
Fe ²⁺	1000
Cu ²⁺	1000
Zn ²⁺	1000
Al ³⁺	1000
Cd ²⁺	500
Co ²⁺	500
Ni ²⁺	500
Pb ²⁺	500
Cr ³⁺	500
Au ³⁺	500

^a Tolerance limit means that the concentration of the coexisting ions added causes changes in Pd extraction by less than 5%.

* Unit: µg mL⁻¹

as the ratio of the slope of preconcentrated samples to that obtained without preconcentration, was 29.

Analytical Application and Method Validation

In order to examine the accuracy and precision of the proposed method, the extraction procedure was applied to the determination of palladium in the ore standard reference material (GBW07342). The content of palladium in the SRM was $1.67 \pm 0.13 \mu\text{g g}^{-1}$. Using the method developed in this work, the palladium content found was $1.54 \pm 0.10 \mu\text{g g}^{-1}$ ($n=3$) and the recovery 92.2%. The results showed good agreement with the certified values and the proposed method was confirmed to be feasible for the preconcentration of Pd(II) in samples with complicated matrices.

The developed method was also applied to the palladium determination in fly ash, road dust, and soil samples and satisfactory results were obtained (see Table V). The good recoveries of the standard spiked analysis demonstrate that the method is practical and reliable enough for real sample analysis.

Comparison of the RTIL Extraction with Other Methods

The determination of palladium by the IL-based micro-extraction method was compared with other reported preconcentration methods for palladium determination and are listed in Table VI. It can be seen that the proposed method has a comparatively low detection limit, a high enrichment factor, and good linear range.

CONCLUSION

A simple and environmentally friendly method was developed for the preconcentration, separation, and determination of palladium (Pd(II)) in geological and environmental samples. Under optimized experimental conditions, an enhancement factor of 29 was achieved with a 30-mL sample. The limit of detection (3σ) was 2.2 ng mL^{-1} and the relative standard deviation (RSD) was 3.7%.

The novel use of ionic liquid (IL)-based micro-extraction for the preconcentration, separation, and determination of palladium by flame atomic absorption spectrometry (FAAS) is for the first time reported in this study. It can be concluded that IL $[\text{C}_4\text{MIM}][\text{PF}_6]$ is a good and green extraction solvent for palladium preconcentration and separation. Under the optimized experimental conditions, an enhancement factor of 29 was achieved with a 30-mL sample. The limit of detection (3σ) was 2.2 ng mL^{-1} , and the relative standard deviation (RSD) was 3.7% for 7 replicates.

The method was successfully applied to the determination of palladium at low concentrations in digested geological and environmental samples. The performance of the method indicates that the separation and preconcentration procedure is simple, environmentally friendly, rapid, and effective with good accuracy and precision.

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TABLE IV
Analytical Characteristics of the Method^a

	Without LLME ^d	With LLME ^d
Concentration range (ng mL^{-1})	500-2000	10-500
Slope	2×10^{-5}	5×10^{-4}
Correlation coefficient (R^2)	0.9998	0.9923
Detection limit ^b (ng mL^{-1})	64	2.2
Relative standard deviation (% , $n=5$)	1.9	3.7
Enhancement factor ^c	–	29

^a Sample volume was 30 mL.

^b Determined as $3\sigma/S$ (σ and S = the standard deviation of the blank signal and the slope of the calibration, respectively).

^c Calculated as the slope ratio of the calibration obtained with and without preconcentration.

^d Liquid-liquid micro-extraction by the present method.

Table V
Analysis of the Real and Spiked Samples by the Present Method
(Sample Solution, ng mL^{-1} , $n=3$)

Sample	Measured ^a	Spiked	Found ^a	Recovery ^b (%)	Content (ng g^{-1}) ^c
Fly ash	10.3 ± 0.7	20.0	31.7 ± 4.9	107	516.7
Road dust	3.7 ± 0.5	10.0	13.7 ± 0.9	100	186.1
Soil	ND	10.0	8.6 ± 0.6	86	ND

^a Mean $\pm$ standard deviation.

^b $100 \times [(\text{found} - \text{measured}) / \text{spiked}]$.

^c Calculated content of Pd in the original solid samples.

TABLE VI
Comparison of the Present Method with Other Preconcentration Methods by FAAS

Preconcentration Method	Detection Limit (ng mL ⁻¹)	RSD (%)	Sample Volume (mL)	Calibration Range (ng mL ⁻¹)	Enhancement Factor	Ref.
Amidinothioureido-silica gel-SPE ^a	17	1.7	4.5	200–4000	–	(31)
Polyamine metalfix-chelamine resin-SPE	9	3.2	4.7	0.2–2000	20	(32)
Octadecyl silica membrane disks modified by thioridazine·HCl-SPE	12	1.2	1000	–	100	(33)
Activated carbon-SPE	14	<10	200	–	–	(5)
Chloroform-DLLME ^b	90	0.7	5.0	100–2000	45.7	(34)
Solidified floating organic drop microextraction	0.6	2	15	2.0–400	49.9	(6)
[C ₄ MIM][PF ₆]-LLME ^c	2.2	3.7	30	10–500	29	This work

^a SPE = solid phase extraction; ^b DLLME = dispersive liquid-liquid microextraction; ^c LLME = liquid-liquid microextraction.

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