Ionic Liquid Based Dispersive Liquid Liquid Microextraction and Enhanced Determination of the Palladium in Water, Soil and Vegetable Samples by FAAS

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ABSTRACT: *In this study, we combined Ionic Liquid-based Dispersive Liquid Liquid Micro Extraction (IL-DLLME) with FAAS for determining the palladium in different real samples at the trace level. 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF$_6$] ionic liquid and 1-(2-pyridylazo) 2-naphthol (PAN), were chosen as the extraction solvent and the chelating agent, respectively. The hydrophobic Pd–PAN complex was extracted into the [Hmim][PF$_6$] and separated from the aqueous phase. Then, the concentration of the enriched palladium in the sediment phase was determined by FAAS. Some effective parameters that would influence the FAAS signals and the microextraction efficiency, such as concentration of the chelating agent, pH, amount of the ionic liquid, type of disperser solvent and diluting agent, ionic strength, extraction and centrifugation times were investigated and optimized. Under optimum experimental conditions, the detection limit (3 s) and enhancement factor were 3.2 μg/L and 16.2, respectively. The Relative Standard Deviation (RSD) was 1.2% at a concentration of 50 μg/L. The developed method was successfully applied for determining trace amounts of the palladium in the water, soil and vegetable samples.*

KEY WORDS: *Palladium, Ionic liquid, Dispersive liquid liquid microextraction, Flame atomic absorption spectroscopy.*

INTRODUCTION

Some metal ions such as palladium are the most dangerous pollutants due to their acute toxicity and carcinogenecity. These metal ions are cumulative poisons, capable of being assimilated in the tissues of organisms, causing noticeable adverse physiological effects [1]. Exposure to high concentrations of these metal ions causes lung, nasal and throat cancers.

Therefore, interest and demand are increasing for metal level determination in biological and environmental samples [2]. The direct determination of Pd in environmental samples by atomic spectrometric techniques is usually difficult and an initial sample pretreatment, such as preconcentration of the analyte and matrix separation, is often necessary [3]. There are several research studies

that deal with separation and preconcentration of pd by coprecipitation [4], Liquid Liquid Extraction (LLE) [5], Solid Phase Extraction (SPE) [6-8], and Cloud Point Extraction (CPE) [9]; ion imprinted polymer [10]; but these methods are time-consuming, have unsatisfactory enrichment factors and use large organic solvents which limit their applications.

Dispersive Liquid Liquid MicroExtraction (DLLME) is a novel liquid-liquid extraction protocol based on ternary component solvent systems [11]. DLLME method has the advantages of simplicity of operation, rapidity, low cost, high recovery and enrichment factors, and has been proved to be a suitable preconcentration procedure for various metal ions [12,13]. In recent years, the application of Ionic Liquids (ILs) as solvents instead of organic solvents, in combination with various techniques, has attracted considerable attention in the field of analytical chemistry [14]. Ionic liquids are liquid salts with melting points near or below room temperature. They are generally considered to be environmentally friendlier than common organic solvents and have unique chemical and physical properties such as negligible vapor pressure, non-flammability, good extractability for various organic compounds and metal ions as neutral or charged complexes, as well as tunable viscosity and miscibility with water and organic solvents [15].

The present study applied a new approach to optimize IL-DLLME-FAAS conditions for the separation and determination of palladium ion in water, soil and vegetable samples by using 1-(2-pyridylazo) 2-naphthol as a chelating reagent.

EXPERIMENTAL SECTION
Apparatus

The measurement was performed with a Shimadzu atomic absorption/flame emission spectrometer (AA-670) equipped with a computer processor. A palladium hollow cathode lamp operated at 5 mA was utilized as the radiation source. The analytical wavelength (244.8 nm) and slit width (0.3 nm) were used as recommended by manufacturers. Air-acetylene flame was used with a fuel-oxidant ratio of 1.6:8. The pH values were measured with a metrohm E-691 pH/mV meter (Switzerland). A laboratory centrifuge (Heraeus, Labofuge 400 model, Germany) was used to accelerate the phase separation.

Reagents and standard solution

All reagents and solvents used such as $PdCl_2$, 1-(2-pyridylazo) 2-naphthol (PAN), methanol, ethanol, acetone, acetonitrile (ACN), sodium nitrate, nitric acid were highly purified reagents produced by Merck Co. (Darmstadt, Germany). The 1-Hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF$_6$] ionic liquid was produced by Kimiaexir (Iran). Double distilled water was used during the whole procedure. Stock standard solutions of Pd(II) at a concentration 1000 µg/mL were prepared by the dissolution of the proper amount of $PdCl_2$ in 3:1 HCl/HNO$_3$ (V/V). Solutions of lower concentrations were prepared daily by a suitable dilution of the stock solution with distilled water. A buffer solution (0.01 mol/L) was prepared by dissolving the appropriate amount of sodium dihydrogen phosphate (NaH$_2$PO$_4$.2H$_2$O) (Merck) in the double distilled water and adjusted to pH 3.0 by adding the diluted HCl solution. The solution of PAN was prepared by dissolving the appropriate amount of PAN in the ethanol. Vessels in the experiments were kept in 10% nitric acid for at least 24 h and subsequently washed with the double distilled water.

Dispersive liquid-liquid microextraction procedure based on ionic liquid

In a typical experiment, 5.0 mL of aqueous solution containing 50 µg/L Pd(II) in a 10-mL test tube with conical bottom, 1 mL phosphate buffer (0.01 mol/L, pH 3) and 0.5 mL of 10^{-4} mol/L PAN solution were mixed. Then, by using a 5-mL syringe, 1 mL ethanol containing 100 µL [Hmim][PF$_6$] was added to the above mentioned solution. The mixture was centrifuged for 5 min at 3000 rpm. The volume of the sedimented phase was determined by use of a 100-µL Hamilton syringe. The sedimented phase (ionic liquid) was transferred to another test tube and allowed to evaporate at room temperature. Finally, the residue was dissolved into 0.5 mL ethanol and the Pd(II) ion concentration was determined by flame atomic absorption spectrometry. Pd(II) standard solutions (0.2-2.2 µg/mL), obtained by the serial dilutions of the stock solution with double distilled water, were prepared daily and their absorbances were read along with the samples.

Preparation of soil sample

Analysis for soil sample was carried out by the acid digestion method [16]. A portion of 1 g of dried soil sample was weighed and placed in a beaker and 10 mL 1:1 nitric acid was added. The beaker was covered with a watch glass and heated on a hot plate under boiling point for 15 min. The mixture was agitated several times during heating in order to assist the extraction and mixing. After cooling down the mixture, 10mL of concentrated nitric acid was added with 30 min of heating under boiling point. The concentrated nitric acid was added sequentially until no brown fume was emitted. The sample volume was allowed to reduce to below 5 mL and cooled down to room temperature before reaching the 2 mL water mark. Then 3 mL 30% hydrogen peroxide was added, followed by heating at under boiling point. The additional hydrogen peroxide was added until effervescence ceased. The process was continued for 2 h until the volume of sample was reduced to below 5 mL, then 10 mL HCl was added and followed by heating for 15 min. The digestate was then cooled down to room temperature and filtered through a Whatman filter and diluted to 50 mL with water. Aliquotes of 5mL sample solution were preconcentrated and determined by following the procedure described later.

Preparation of vegetable sample

One gram of the sample was placed in a 100 mL beaker, and 10 mL of concentrated HNO_3 (65% w/w) was added to the beaker. The mixture was evaporated on a hot plate at about 130 °C for 4 h. After cooling down to room temperature, 3 mL of concentrated hydrogen peroxide (30%, w/w) was added. The mixture was again evaporated near to dryness. This solution was diluted to 25 mL with the distilled water [17]. The filtration procedure was made for some vegetable samples which were not completely dissolved. The dispersive liquid liquid microextraction procedure described was applied to the sample solutions.

Preparation of water samples

Water samples such as tap water and dam water were chosen for the analysis. These samples were collected from Mahabad city in PTFE container. Aliquotes of 5mL from each sample solution were analyzed without previous treatment or filtration.

RESULTS AND DISCUSSION

In this research, IL-based DLLME method was combined with flame atomic absorption spectroscopy to evaluate the concentration of palladium ion in different real samples at trace levels. For this purpose, the effect of several factors influencing the extraction conditions were investigated and optimized.

Selection of diluting agent

Based on FAAS, the solvent should have good nebulization and burning characteristics, not have a very low-boiling point and compatibility with direct injection into FAAS. To dilute the settled IL-phase at the bottom of the tubes, 500 μL of nitric acid (0.1 mol/L), ethanol, acetone and acetonitrile were studied. The nitric acid could not dissolve the settled IL-phase. Ethanol and acetone had higher absorption than acetonitrile. However, ethanol was preferred to acetone due to major compatibility of ethanol with flame atomic absorption spectrometer.

Effect of type and volume of the dispersive solvent

A dispersive solvent was chosen based on immiscibility between IL phase and aqueous sample. Thus acetone, methanol and ethanol were particularly evaluated. Recovery efficiency was evaluated using 1 mL of each dispersive solvent and 100 μL [Hmim][PF$_6$]. The results showed that there was no significant difference between the absorbance obtained by these solvents. Because of the lower toxicity of ethanol, it was selected as a dispersive solvent in subsequent experiments. On the other hand, the volume of dispersive directly affected IL solubility in the aqueous phase which significantly determined the volume of the final phase, and thus influenced the efficiency of the microextraction technique. Terefore, ethanol volumes ranging within 250-2500 μL were assayed (Fig. 1). Using low volume of ethanol (<500 μL), the cloudy state of solution was not formed completely. At high volumes of ethanol (>1000 μL), the solubility of complexes in water increased and the extraction efficiency decreased. Thereby, at high volume of ethanol the absorbance of Pd decreased. Thus, a volume of 1000 μL of ethanol was used in subsequent experiments.

Effect of IL solvent volume

Effect of ionic liquid volume of [Hmim][PF$_6$] was studied at the range of 20-350 μL. In all studies, the amount of dispersive solvent (ethanol) was 1000 μL.
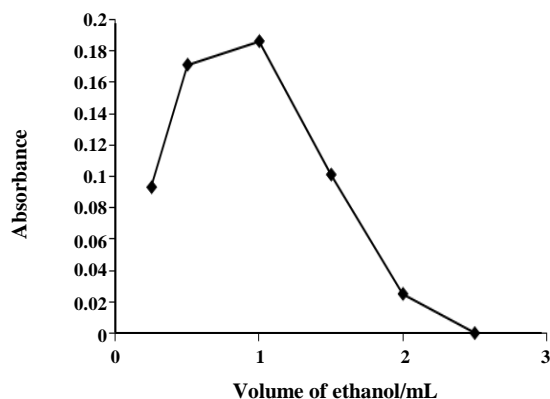
Fig. 1: Effect of volume of dispersive solvent (ethanol) on the absorbance. Conditions: sample volume: 5 mL, [Hmim][PF₆]: 100 μL, PAN concentration: 0. 5 × 10⁻⁵ mol/L, concentration of Pd: 50 μg/L, pH: 3.0, diluting agent: 0.5 mL.

Fig. 2: Effect of amount of [Hmim][PF₆] on the absorbance. Conditions: sample volume: 5 mL, PAN concentration: 0. 5 × 10⁻⁵ mol/L, dispersive solvent (ethanol): 1 mL, concentration of Pd: 50 μg/L, pH: 3.0, diluting agent: 0.5 mL.

The minimum $[Hmim][PF_6]$ amount required for the formation of cloudy solution was 50 μL. By increasing the $[Hmim][PF_6]$ amount, the absorbance of Pd initially increased up to about 100 μL of $[Hmim][PF_6]$ and then began to decrease (Fig. 2) because of an increase in the volume of settled IL-phase. By increasing the volume of settled IL-phase, viscosity of the IL-ethanol mixture increases. When the viscosity of solution aspirated into the flame of the atomic absorption spectrometer is high, the nebulizer uptake rate and therefore the absorbance decreases. Therefore, 100 μL of $[Hmim][PF_6]$ was chosen as the optimum value.

Effect of pH and chelating agent concentration

Separation of metal ions by IL-DLLME involved prior complex formation with a sufficient hydrophobicity to be extracted into a small volume of the IL phase, whereby the desired preconcentration was obtained. The pH plays a distinctive role in the metal-chelate formation and subsequent extraction into IL phase. The effect of pH on the Pd-PAN complex extraction was studied at the range of 1.0–11.0 by adding hydrochloric acid and sodium hydroxide. The absorbance of the system in IL-rich phase was studied against a reagent blank. The results illustrated in Fig. 3 reveal that the absorbance was initially increased by raising pH level to 3.0 and after pH 3.0, the absorbance started to decrease. The decrease in the extraction of palladium at high pH values may be due to the hydrolysis of palladium ions and at the lower pH values may be due to the competition
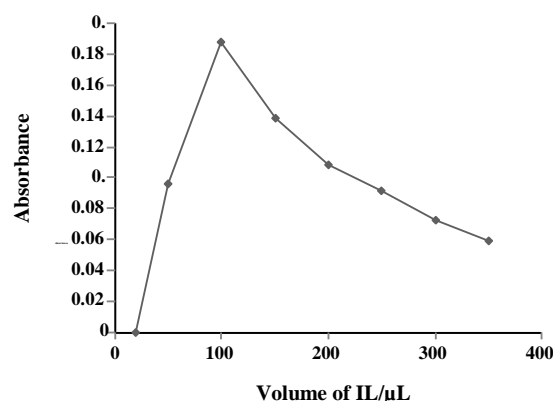
palladium ions with hydrogen ions. Accordingly, pH 3.0 seemed to be a proper choice for both complexation and extraction.

The concentration effect of PAN was also investigated at a range of 5×10^{-5} to 1×10^{-2} mol/L. The result showed that the absorbance of Pd increased by increasing the PAN concentration up to 1×10^{-4} mol/L and then remained constant up to 1×10^{-2} mol/L. A concentration of 1×10^{-4} mol/L of PAN was chosen for subsequent experiments.

Influence of salt concentration

In this experiment, the effect of salt concentration on the extraction efficiency was evaluated by adding different amounts of $NaNO_3$ from 0% to 20% (w/v), while other experimental conditions were kept constant. As shown in Fig. 4, the addition of $NaNO_3$ up to 5% (w/v) has no considerable effect on the absorbance while with a higher salt content the absorbance was reduced because of the solubility of ILs in the aqueous solution. Thus, the subsequent experiments were carried out without salt.

Effect of centrifuge time

The effect of centrifugation time on the absorbance was studied at 3-15 min time ranges. The optimum centrifugation time was considered to be at five minutes because complete separation occurred at this time and no appreciable improvements were observed for longer times.

Table 1: Effects of foreign ions on the recovery of 50 µg/L of Pd from aqueous solutions.

Coexisting ions	Added as	Tolerance ratio (C_{ion}/C_{Pd})
Cu^{2+}	$Cu(NO_3),3H_2O$	1^b
Co^{2+}	$Co(NO_3)_2,6H_2O$	10^b
Cd^{2+}	$Cd(NO_3)_2,4H_2O$	10000^b
Pb^{2+}	$Pb(NO_3)_2$	1000^b
Hg^{2+}	$Hg(NO_3)_2,H_2O$	1000^b
Ba^{2+}	$Ba(NO_3)_2$	10000^b
Fe^{3+}	$Fe(NO_3)_3,9H_2O$	1^b
Ni^{2+}	$Ni(NO_3)_2$	10^b
Zn^{2+}	$Zn(NO_3)_2,6H_2O$	10000^b
K^+	KNO_3	10000^a
Br^-	KBr	10000^a
HSO_4^-	$KHSO_4$	10000^b
CH_3COO^-	CH_3COOK	10000^b

a) At this ratio no interfering effect was observed.
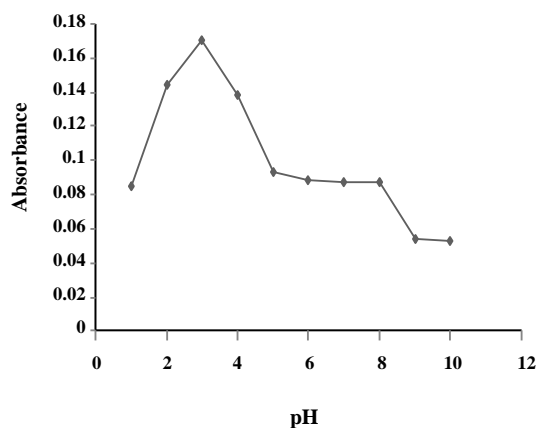*b) At this ratio interfering effect was observed.*

Fig. 3: Effect of pH on the absorbance of Pd complex. Conditions: sample volume: 5 mL, [Hmim][PF₆]: 100 µL, PAN concentration: 0.5×10^{-5} mol/L, dispersive solvent (ethanol): 1 mL, concentration of Pd: 50 µg/L, diluting agent: 0.5 mL.

Fig. 4: Effect of NaNO₃ on the absorbance of Pd–PAN complex in the range of 0–20% (w/v). . Conditions: sample volume: 5 mL, [Hmim][PF₆]: 100 µL, PAN concentration: 0.5×10^{-5} mol/L, dispersive solvent (ethanol): 1 mL, concentration of Pd: 50 µg/L, diluting agent: 0.5 mL.

Selectivity of the method

Under the optimum conditions cited above and with 50 µg/L of palladium, a systematic study of the effect of foreign ions was undertaken. The results are summarized in Table 1. The tolerance limit of ions was fixed as the maximum amount causing an error which was not greater than 5% in the absorbance. As illustrated, most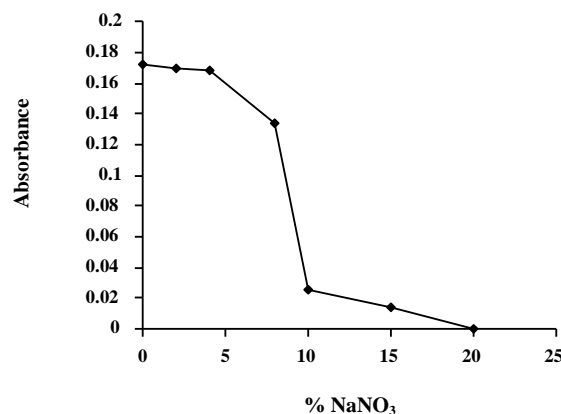 of the substances did not have any interference on the determination of palladium. Cu(II), Fe(III), Co(II) and Ni(II) interfered at 1 and 10 times concentration of palladium, respectively. The interference of Cu(II) and Fe(III) up to tolerance ratio of 100 was eliminated in the presence of 2×10^{-3} mol/L thiourea and interference of Co(II) and Ni(II) was eliminated up to tolerance ratio of 500 using 2×10^{-3} mol/L thiocyanate.

Table 2: Comparison of the published methods with the proposed method.

Method	Enrichment factor	Detection limit (ng/m[1])	Linear range (ng/mL)	Reference
CPE/ICP-OES[a]	20.2	0.3	0.5-1000	[10]
DLLME/FAAS	45.7	90	100-2000	[18]
DLLME/GFAAS[b]	156	0.0024	0.1-5	[19]
DLLME/FO-LADS[c]	162[d]	0.25	2-100	[20]
SFODME-FAAS	49.9	0.60	2-400	[21]
M-CIAME /UV	97[d]	0.2	0.6-100	[22]
IL-DLLME-FAAS	16.2[d]	3.2	10-200	This work

a) Inductively coupled plasma-optical emission spectrometry.   b) Graphite furnace atomic absorption spectrometry.
c) Fiber optic-linear array detection spectrophotometry.   d) Enhancement factor

Table 3: Determination of palladium in real sample.

Sample	Concentration	Added	Found Pd(II), mean±SD[a]	Relative recovery %
Tap water[b]	nd	50 µg/L	48.4 ± 0.63 µg/L	97
Dam water[c]	nd	50 µg/L	47.4 ± 1.3 µg/L	95
Vegetable	nd	1.25 µg/g	1.2 ± 0.7 µg/g	96.6
Soil[d]	0.87 ± 0.16 µg/g	5 µg/g	5.92 ± 0.8 µg/g	100.9

a) Standard deviation (n=3).   b) From drinking water of Mahabad, Iran
c) From dam water of Mahabad, Iran   d) From gavashan mineral, Iran

Evaluation of method performance

Calibration graph was obtained by the use of 5 mL of the standard solution of Pd ion buffered at pH 3 and contained 100 µL [Hmim][PF$_6$] at optimal conditions. The findings of this study showed that the calibration curve was linear in the concentration range of 10-200 µg/L Pd with correlation coefficient (R^2) 0.999. The Relative Standard Deviation (RSD) obtained from the analysis of five replicates of the 5mL solution containing 50 µg/L Pd was 1.2%. The limit of detection (LOD) based on a Signal-to-Noise (S/N) ratio of 3, was 3.2 ng/mL. The enhancement factor (16.2) was obtained from the slope ratio of the calibration curve after and before the preconcentration.

As shown in Table 2, the characteristic data of the present method were compared with those reported in the literature review. Generally, the detection limit and enhancement factor obtained by the present method were comparable to those reported methods.

Analysis of real samples

In order to validate the proposed method, it was applied to the determination of palladium in tap water, dam water, and soil sample. For this purpose, 5 mL of each prepared sample was preconcentrated using IL-DLLME after complex formation with PAN. The results are shown in Table 3. In all cases, the spike recoveries confirmed the reliability of the proposed method. Furthermore, the calibration curve method was applied for determining the palladium level in soil samples of Gavashan mineral (Iran) which is mentioned in Table 4. As can be seen, recoveries between 95% and 100.9% were obtained, which confirmed the accuracy of the proposed method. The results showed that the proposed method is accurate and free from systematic errors.

CONCLUSIONS

In this study, an ionic liquid-based dispersive liquid liquid microextraction method (IL-DLLME) was developed for the preconcentration of palladium from water, soil and vegetable samples as a prior step to its enhanced determination by FAAS. PAN reagent was employed as the complexing agent to assess the extraction procedure. Some advantages of this method were that it was simple, rapid, low cost, and safe method for the preconcentration and separation of trace palladium

in aqueous solutions. IL-DLLME provided high recovery and had low toxicity since only very small amounts of IL as a "green extraction solvent" was used.

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