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# In situ formed 1-hexyl-3-methylimidazolium hexafluorophosphate for dispersive liquid-liquid microextraction of Pd(II) prior to electrothermal AAS and spectrophotometry

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1-Hexyl-3-methylimidazolium hexafluorophosphate was prepared in situ and used as extractant in dispersive liquid-liquid microextraction. Ultra-trace amounts of Pd(II) could be accurately determined by electrothermal atomic absorption spectrometry (ETAAS) and spectrophotometry after extraction by the formed micro-droplets of the ionic liquid phase. 1-(2-Pyridylazo)-2-naphthol was used to produce a hydrophobic palladium complex prior to extraction. The effects of concentrations of reagents, reaction and extraction times, and the other parameters were investigated and optimized. Beer's law was obeyed in the ranges of 0.015-0.900 and 1.50-63.0 ng mL<sup>-1</sup> Pd(II) by ETAAS and spectrophotometry, respectively. Under the optimized conditions, the limit of detection (LOD) by ETAAS was 3 ng L<sup>-1</sup> with an enrichment factor of 460. The RSD percent was in the range of 1.3%-4.8% for various standard concentrations of Pd(II) in the range of 0.050-40.0 ng mL<sup>-1</sup>. Most ions did not interfere. The method was successfully applied to the determination of Pd(II) in some water and alloy samples, jewels, and palladium catalysts.

**Key Words:** Palladium, dispersive liquid-liquid microextraction, 1-(2-pyridylazo)-2-naphthol, 1-hexyl-3-methylimidazolium hexafluorophosphate

## Introduction

Palladium (Pd) is a valuable metal and has an increasing importance in today's industries.<sup>1</sup> Pd is extensively applied in the preparation of various important materials due to its catalytic properties, and also is used in

micro-electronics, jewels, and dental alloys. Pd applications have caused pollution of the environment.<sup>2-4</sup> Monitoring of Pd in industrial and environmental samples is of great importance in terms of human health and environmental purposes.

A preconcentration step often increases the sensitivity and selectivity of the determination. Solid phase extraction (SPE) and liquid-based extractions have found widespread applications in the preconcentration-determination of Pd. SPE is flexible in choice of adsorbent but generally needs a back-extraction step. Therefore, SPE produces organic wastes. SPE has been used for the preconcentration of Pd traces prior to determination.<sup>5</sup> Different solid adsorbents such as activated carbon,<sup>6</sup> polyurethane foam,<sup>7</sup> amberlite XAD resins,<sup>8</sup> and modified silica gel<sup>9</sup> have been used for the preconcentration-determination of Pd. Liquid-liquid extraction (LLE),<sup>10</sup> cloud point extraction,<sup>11</sup> and dispersive liquid-liquid microextraction (DLLME)<sup>12</sup> are some liquid-based methods that have been used for the enrichment-determination of Pd.

In recent years, water insoluble ionic liquids (ILs) have been widely used for liquid-liquid microextraction. This new class of liquid extractants is tunable, non-volatile, and green.<sup>13</sup> ILs as extractant are generally dispersed in aqueous samples but sometimes are used as a single drop.<sup>14,15</sup> Various techniques have been used to extract analytes into ILs. Microextraction by ILs is performed using their fine droplets, which are formed often by dispersive solvents,<sup>16-19</sup> cold-induced process,<sup>20</sup> sonication,<sup>21,22</sup> and in situ IL formation.<sup>23-26</sup> DLLME is a simple, fast, and miniaturized extraction method that has been under development for trace determinations. DLLME has been used by various ILs such as 1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim][PF<sub>6</sub>]),<sup>23,24</sup> 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF<sub>6</sub>]),<sup>14,16,20,22</sup> 1-octyl-3-methylimidazolium hexafluorophosphate ([Omim][PF<sub>6</sub>]),<sup>18</sup> 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide,<sup>17</sup> 1-octyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide,<sup>19,21</sup> tetradecyl(trihexyl) phosphonium chloride,<sup>15,27</sup> and 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide<sup>34,35</sup> for trace determination of different analytes.

Generally, an ion exchange process is used to prepare water immiscible 1-alkyl-3-methylimidazolium hexafluorophosphates. The ion exchange process may be performed in situ, prior to DLLME. DLLME by in situ prepared ILs has various advantages over the other IL-based DLLME methods.<sup>23-26</sup>

Pd(II) reacts with 1-(2-pyridylazo)-2-naphthol (PAN) and produces a water-insoluble complex (Pd-PAN). In the present work, the in situ formed [Hmim][PF<sub>6</sub>] was applied for fast and efficient extraction-determination of Pd-PAN. 1-Hexyl-3-methylimidazolium chloride ([Hmim][Cl]) and potassium hexafluorophosphate (KPF<sub>6</sub>) as aqueous solutions were mixed to form fine droplets of [Hmim][PF<sub>6</sub>]. After extraction, the IL-rich phase was used for ETAAS and spectrophotometric determination.

## Experimental

### Reagents

Nitric acid, ethanol, Pd-charcoal (ca. 5.0%), Pd-CaCO<sub>3</sub> (ca. 10.0%), palladium(II) chloride, and PAN were purchased from Merck (Germany). KPF<sub>6</sub> was purchased from Ionic Liquid Technology (Germany) and [Hmim][Cl] was prepared in our laboratory according to the method described by Liu et al.<sup>28</sup>

The stock solution of PAN was prepared as  $8.02 \text{ mmol L}^{-1}$  in ethanol. The stock Pd(II) solution ( $1000 \mu\text{g mL}^{-1}$ ) was prepared by dissolving  $0.1660 \text{ g}$  of palladium(II) chloride in  $10 \text{ mL}$  of aqueous solution containing  $2.0 \text{ mL}$  of concentrated hydrochloric acid and diluting in a  $100.0 \text{ mL}$  volumetric flask. This Pd solution was standardized by a known gravimetric standard method.<sup>29</sup>  $\text{KPF}_6$  solution as  $0.339 \text{ mol L}^{-1}$  and  $[\text{Hmim}][\text{Cl}]$  as  $0.339 \text{ mol L}^{-1}$  were prepared in deionized water.

All of the aqueous working solutions were prepared by appropriate dilution of the stock solutions with deionized water. The working solutions of PAN were prepared by diluting the stock solution of PAN with ethanol.

## Apparatus

Palladium atomic absorbances were measured by an Analytik Jena (Germany) continuum source atomic absorption spectrometer model *contraAA 700*. All UV-Vis spectra and absorbance measurements were performed using a double beam spectrophotometer, Shimadzu model *UV-1650 PC* (Tokyo, Japan), equipped with a  $20 \mu\text{L}$  quartz cell with  $10.0 \text{ mm}$  path length (Hellma, Germany). A pH meter model *744 Metrohm* (Metrohm, Switzerland) was used to measure and control the pH of the solutions. A centrifuge model *CE. 144* (Shimifan company, Iran) was used to settle the IL phases. IL phases were delivered to graphite furnace tube and spectrophotometer cell by using a  $25 \mu\text{L}$  syringe (Hamilton, Switzerland).

## General procedure

To a  $15 \text{ mL}$  screw-cap conical-bottom plastic centrifuge tube were added  $1.0 \text{ mL}$  of  $1.0 \text{ mol L}^{-1}$  nitric acid,  $6.8 \text{ mL}$  of Pd(II) containing sample solution, and  $0.2 \text{ mL}$  of  $1.00 \text{ mmol L}^{-1}$  PAN (dissolved in ethanol). After  $4 \text{ min}$  standing,  $1.0 \text{ mL}$  of  $0.339 \text{ mol L}^{-1}$   $[\text{Hmim}][\text{Cl}]$ , and  $1.0 \text{ mL}$  of  $0.339 \text{ mol L}^{-1}$   $\text{KPF}_6$  were added and the solution was shaken. After  $5 \text{ min}$ , the mixture was centrifuged for  $5 \text{ min}$ .

For analysis by ETAAS,  $15 \mu\text{L}$  of ethanol was transferred to a  $25 \mu\text{L}$  syringe and thereafter  $10 \mu\text{L}$  of  $[\text{Hmim}][\text{PF}_6]$  phase was sampled. The contents of the syringe were directly injected into a platform graphite tube carefully. The thermal program in Table 1 was applied and absorbance was measured for quantification (3 pixels in the center of the photodiode array detector of the ETAAS instrument were used to calculate the absorbance).

For spectrophotometric determination of Pd,  $20 \mu\text{L}$  of the settled  $[\text{Hmim}][\text{PF}_6]$  phase was transferred to a  $20 \mu\text{L}$  cell together with  $20 \mu\text{L}$  of ethanol. The absorption spectrum of the resulting solution was recorded against the same manner prepared blank in the range of  $520\text{-}720 \text{ nm}$ . Absorbance at  $664 \text{ nm}$  and first derivative of absorbance at  $682 \text{ nm}$  ( $\Delta\lambda = 2 \text{ nm}$ ) were also used as analytical signals.

## Results and discussion

Early experiments showed atomic absorbances of Pd and molecular absorbances of Pd-PAN in  $[\text{Hmim}][\text{PF}_6]$  extract were proportional to the aqueous concentration of Pd(II). The author decided to optimize conditions spectrophotometrically.

**Table 1.** Electrothermal AAS operating conditions.

Parameters		Argon purge disposition
Element	Pd	
Wavelength	244.791 nm	
Sample volume	10 $\mu$ L	
Furnace type	Platform	
Modifier	No modifier	
Measurement mode	Peak area	
Drying	90 °C (ramp 6 °C/s, hold 20 s)	Maximum
Drying	120 °C (ramp 10 °C/s, hold 10 s)	Maximum
Pyrolysis	400 °C (ramp 50 °C/s, hold 20 s)	Maximum
Pyrolysis	1000 °C (ramp 300 °C/s, hold 30 s)	Maximum
Gas adaption	1000 °C (ramp 0 °C/s, hold 5 s)	Stop
Atomization	2200 °C (ramp 1500 °C/s, hold 6 s)	Stop
Cleaning	2450 °C (ramp 500 °C/s, hold 5 s)	Maximum
Read Time	5 s	Stop

## Spectrophotometric and first-derivative spectrophotometric spectra

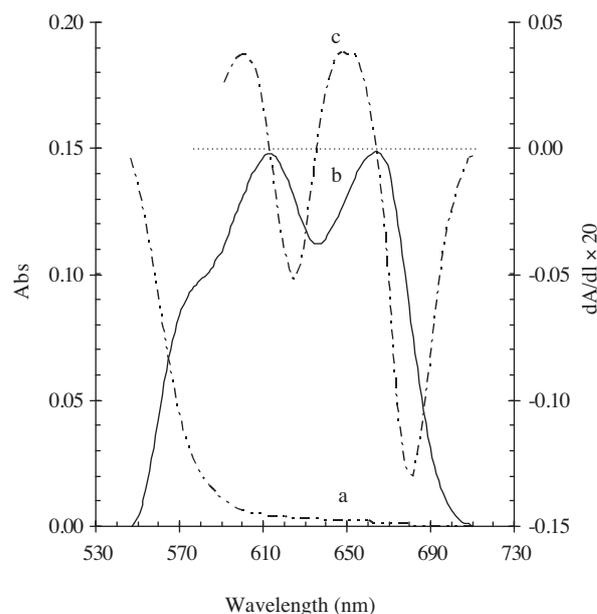
Figure 1 shows zero- and first-derivative spectrophotometric spectra of the IL-ethanol phases. The spectrophotometric spectra of the blank and Pd-PAN are highly distinguishable. The most suitable wavelengths are 664 and 682 nm for zero- and first-derivative spectrophotometric determination of Pd, respectively. The wavelengths were used throughout all of the spectrophotometric detections. The experiments were performed at room temperature.

## ETAAS determination condition

The high viscosity and organic nature of the used IL produced some drawbacks, especially in sample delivery into the furnace tube and pyrolysis of the injected IL phase. The viscous IL phase may produce an uncertainty in the volume of the injected IL phase. To overcome this difficulty, 15  $\mu$ L of pure ethanol was sampled by syringe just before sampling of 10  $\mu$ L of IL phase. Injection of the syringe contents delivered the IL phase into the furnace tube precisely and uniformly.

The initial ETAAS program proposed by the manufacturer was considered and some modifications were performed. The drying and pyrolysis steps are important to avoid spattering the liquids and to ensure uniform deposition of the solid contents of the samples in the graphite furnace tube. A complete pyrolysis and the highest possible analyte response to background are desirable. The second step of the pyrolysis was tested in the range of 800-1200 °C. The results of the experiments showed that low background absorbance and complete pyrolysis were possible for temperatures higher than 800 °C, and a decrease in absorbance was observed for pyrolysis temperatures higher than 1300 °C, which may be attributed to the loss of palladium during the

pyrolysis step. A well shaped and sharp absorbance peak was observed at 2200 °C atomization temperature. Lower temperature caused lower sensitivity because palladium was not completely evaporated.



**Figure 1.** Absorbance spectra of: a) blank, b) Pd-PAN and c) first-derivative spectrum of Pd-PAN. Conditions: 10.0 mL Pd(II) 12.0 ng mL<sup>-1</sup> aqueous solution containing nitric acid 0.10 mol L<sup>-1</sup>, 20.0 μmol L<sup>-1</sup> PAN, [Hmim][Cl] 33.9 mmol L<sup>-1</sup> and KPF<sub>6</sub> 33.9 mmol L<sup>-1</sup> for extraction; and then a mixture containing 20 μL of [Hmim][PF<sub>6</sub>] and 20 μL of ethanol for recording the spectra.

### Optimization of the affecting parameters

The triangular phase diagrams at ambient condition<sup>30</sup> show phase diagrams of three 1-alkyl-3-methylimidazolium hexafluorophosphates in ethanol-water mixtures, when the alkyl group is butyl, hexyl, or octyl. [Bmim][PF<sub>6</sub>] is not dissolved in ethanol in all of the mole fractions, but ethanol dissolves [Hmim][PF<sub>6</sub>] and [Omim][PF<sub>6</sub>] completely. Moreover, small amounts of water are dissolved in the ethanolic solutions of these ILs but large amounts of water are dissolved in these IL-ethanol solutions containing large amounts of ethanol. Composition of the aqueous solution in an IL-based extraction may change the mole fraction of water in the IL-rich phase. This may change the amounts of ethanol required to produce a clear final solution, which is used for spectrophotometric detection. Furthermore, [Bmim][PF<sub>6</sub>] dissolves in water higher than [Hmim][PF<sub>6</sub>] and [Omim][PF<sub>6</sub>].<sup>31</sup> Because of the high ethanol solubility and low water solubility of [Hmim][PF<sub>6</sub>], it was selected as extractant IL. The spectrophotometric measurements of Pd were performed after dilution of the IL phase with ethanol.

Optimization is always necessary for achieving the best sensitivity. A one-at-a-time optimization procedure was evaluated for optimizing the affecting parameters.

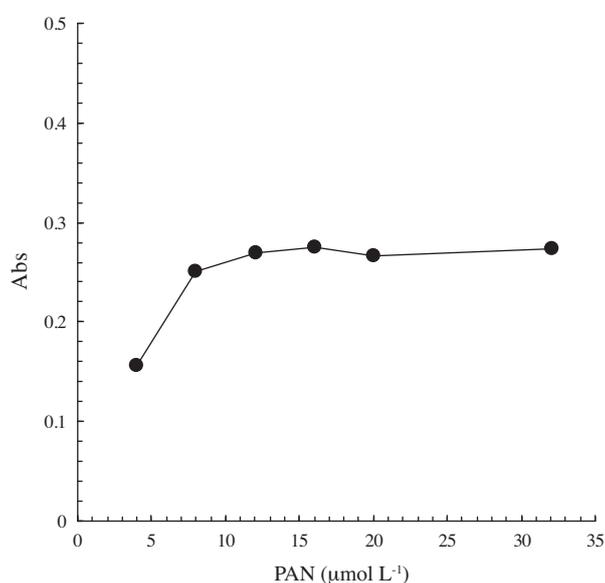
The effects of [Hmim][Cl] and KPF<sub>6</sub> amounts (as equi-molar) were investigated. The settled IL phases (8-43 μL) were completely isolated and were dissolved in 70 μL of ethanol and absorption spectra were obtained.

The obtained results showed that [Hmim][Cl] and  $\text{KPF}_6$  as  $0.339 \text{ mol L}^{-1}$  introduce the best sensitivity (the settled IL phase was about  $21 \mu\text{L}$ ).

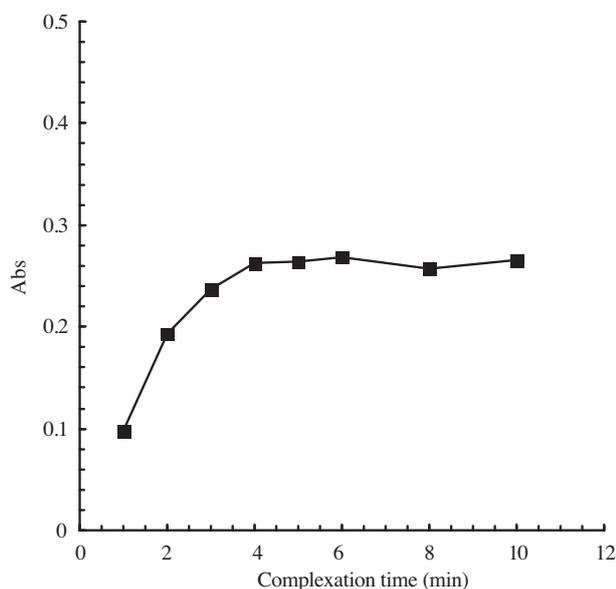
PAN is a general complexing agent but it has been used in various works for selective determination of Pd.<sup>32–34</sup> Various metal ions are present in environmental samples that may interfere in the determination of Pd. Low pHs are preferred for selective determination of Pd. At low pHs, the ions cannot complex with PAN and therefore do not interfere in the determination of Pd.<sup>33</sup> The influence of pH on the sensitivity of the present method was also studied. Nitric acid and acetate buffers were used to prepare pHs in the ranges of 1.4–3.3 and 3.6–4.2, respectively. The sensitivity of Pd determination was constant in the range of pH tested. For further investigations pH equal to 1.4 (nitric acid  $0.10 \text{ mol L}^{-1}$ ) was selected.

To evaluate the effect of PAN concentration on the sensitivity of the introduced method, PAN concentrations up to  $32.1 \mu\text{mol L}^{-1}$  were studied, and the procedure was followed. The obtained results in Figure 2 reveal that the sensitivity increased up to  $12.0 \mu\text{mol L}^{-1}$  and then remained constant. Therefore,  $20.0 \mu\text{mol L}^{-1}$  PAN was used for the subsequent experiments.

The effect of Pd-PAN complexation time was studied in the range of 1–10 min at room temperature according to the procedure (Figure 3). The results showed that the rate of Pd-PAN formation was relatively fast and the reaction was completed after 4 min. Therefore, a reaction time of 4 min was selected for Pd-PAN formation.

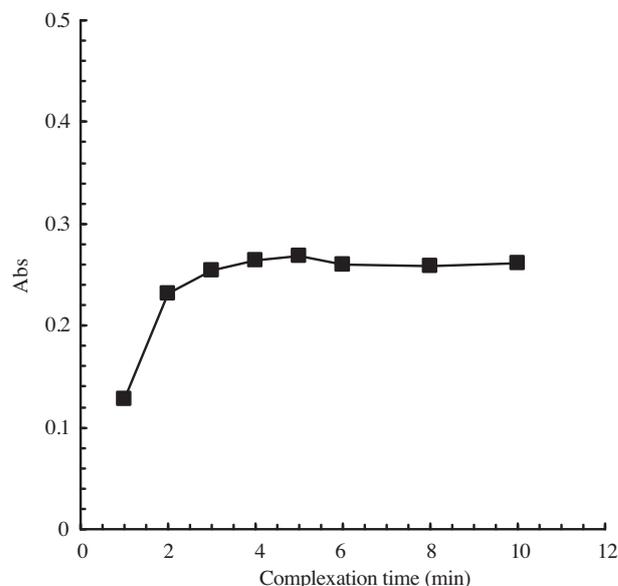


**Figure 2.** Effect of PAN concentration on the sensitivity of the method. Conditions: 10.0 mL Pd(II)  $20.0 \text{ ng mL}^{-1}$  aqueous solution containing nitric acid  $0.10 \text{ mol L}^{-1}$ , [Hmim][Cl]  $33.9 \text{ mmol L}^{-1}$  and  $\text{KPF}_6$   $33.9 \text{ mmol L}^{-1}$  for extraction; and then a mixture containing  $20 \mu\text{L}$  of [Hmim][PF<sub>6</sub>] and  $20 \mu\text{L}$  of ethanol for recording the spectra.



**Figure 3.** Effect of complexation time on the sensitivity. Conditions: 10.0 mL Pd(II)  $20.0 \text{ ng mL}^{-1}$  aqueous solution containing nitric acid  $0.10 \text{ mol L}^{-1}$ ,  $20.0 \mu\text{mol L}^{-1}$  PAN, [Hmim][Cl]  $33.9 \text{ mmol L}^{-1}$  and  $\text{KPF}_6$   $33.9 \text{ mmol L}^{-1}$  for extraction; and then a mixture containing  $20 \mu\text{L}$  of [Hmim][PF<sub>6</sub>] and  $20 \mu\text{L}$  of ethanol for recording the spectra.

The dependence of the sensitivity of the method on the extraction time was also monitored in the range of 1-10 min. The results are given in Figure 4. To achieve satisfactory extraction, extraction times longer than 4 min were sufficient. Therefore a 5 min extraction was selected for additional studies.



**Figure 4.** Effect of extraction time on the sensitivity of the method. Conditions: 10.0 mL Pd(II)  $20.0 \text{ ng mL}^{-1}$  aqueous solution containing nitric acid  $0.10 \text{ mol L}^{-1}$ ,  $20.0 \text{ } \mu\text{mol L}^{-1}$  PAN, [Hmim][Cl]  $33.9 \text{ mmol L}^{-1}$  and  $\text{KPF}_6$   $33.9 \text{ mmol L}^{-1}$  for extraction; and then a mixture containing  $20 \text{ } \mu\text{L}$  of [Hmim][PF<sub>6</sub>] and  $20 \text{ } \mu\text{L}$  of ethanol for recording the spectra.

The solution was centrifuged for different durations to achieve the complete settlement of the IL phase. The study showed that a 5 min centrifugation at 2000 rpm is sufficient to complete precipitation of the IL-rich phase.

### Effect of ionic strength

The effects of ionic strength are complex. Salting out or salting in effects may be observed. On the other hand, high contents of salts in the aqueous phase increase the solubility of ILs.<sup>21,23</sup> The range of ionic strength tested is also important and may show different behaviors. Such behaviors are found extensively. The effect of ionic strength on the sensitivity of the present method was studied by the addition of sodium nitrate in the range of  $0.00\text{-}0.40 \text{ mol L}^{-1}$ . The obtained results showed that the electrolyte concentration had no considerable effects on the sensitivity of the method.

### Calibration, precision, and accuracy

The characteristics of the obtained calibration plots are given in Table 2. One calibration equation by ETAAS and 2 spectrophotometric calibration curves (by zero-derivative and first-derivative spectrophotometry) were

derived. The obtained calibration curves enable determination of Pd in the ranges of 0.015-0.900 and 1.5-63.0 ng mL<sup>-1</sup>.

**Table 2.** Calibrations for determination of Pd.

Method	Calibration equation	Linear range (ng mL <sup>-1</sup> )	Correlation coefficient (R <sup>2</sup> )	LOD (ng mL <sup>-1</sup> )
ET-AAS:	Abs = $4.8 \times 10^{-3} + 7.2 \times 10^{-1} C_{Pd}$	0.015-0.900	0.9979	0.003
Spectrophotometry:				
Zero-derivative	Abs = $-0.007 + 1.35 \times 10^{-2} C_{Pd}$	1.5-46.0	0.9965	0.45
First-derivative	dA/dλ = $8.1 \times 10^{-5} - 5.89 \times 10^{-4} C_{Pd}$	1.5-63.0	0.9991	0.30

The enrichment factor was also calculated as the ratio of the slope of the ETAAS calibration curve for Pd before and after the enrichment. The enrichment factor was found to be about 460.

The limit of detection (LOD) was also measured using 10 times blank analysis by ETAAS and zero- and first-derivative spectrophotometry. LODs were calculated as  $3 \times S_b/m$ , where m and S<sub>b</sub> are the slope of the obtained calibration curve and standard deviation of blank, respectively.

Precision of the method was also examined (Table 3). Four standard solutions were prepared and analyzed according to the procedure (n = 8), and then the analytical responses were changed to Pd concentrations by the calibrations obtained.

**Table 3.** Precision of the method (n = 8).

Method	Concentration of Pd (ng mL <sup>-1</sup> )		RSD (%)
	Taken	Found	
ET-AAS:	0.80	0.78 ± 0.01	1.3
	0.050	0.053 ± 0.002	3.8
Spectrophotometry:			
Zero-derivative	6.0	6.2 ± 0.3	4.8
	40.0	39 ± 1	2.6
First-derivative	6.0	5.9 ± 0.2	3.4
	40.0	39.4 ± 0.9	2.3

± Amounts are standard deviation.

### Effects of foreign ions

In order to evaluate the selectivity of the presented method, the effect of various species on the Pd determination was investigated by adding known concentrations of each ion to a solution containing 10.0 ng mL<sup>-1</sup> of Pd. The tolerance limit was defined as the concentration of each ion where the ion caused an error in ±8% range. The tolerance limits for the tested ions are given in Table 4. The results showed that most of the ions did not interfere up to at least 500-fold. Au(III) and Fe(III) showed only mild interferences.

**Table 4.** Effects of the potentially interfering ions on the determination of Pd by zero-derivative spectrophotometry.

Coexisting ion	Tolerance limit as mass ratio (ion to Pd)
Na(I), Co(II)	5000 <sup>a</sup>
Ba(II), Al(III), Sr(II), Hg(II), Ni(II), Pb(II), Zn(II), Bi(III), Ca(II), NH <sub>4</sub> <sup>+</sup> , Br <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> , SCN <sup>-</sup>	> 500 <sup>b</sup>
Ag(I), Cd(II), Mg(II), Mn(II), Mo(IV), CH <sub>3</sub> COO <sup>-</sup> , I <sup>-</sup> , F <sup>-</sup> , CrO <sub>4</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup>	500
Cu(II), V(V), HPO <sub>4</sub> <sup>2-</sup>	250
Fe(III), Au(III)	50

<sup>a</sup> 5000-fold of the ions were tested and no interferences were observed.

<sup>b</sup> 500-fold of the ions were tested and no interferences were observed.

## Application of the method

Various samples were considered for analysis. Two jewels were analyzed according to the presented procedure. In a beaker containing 0.2510 g of an 18-carat gold sample, 4.0 mL of concentrated hydrochloric acid and 4.0 mL of concentrated nitric acid were added and the mixture was heated at 150 °C until the solution was evaporated to dryness. Then 20 mL of deionized water was added and the mixture was filtered. Four milliliters of nitric acid (1:6) was added to the yellow solid residue, followed by heating to dryness and 4 mL of deionized water was added and the mixture was filtered. The procedure was repeated 4 times to produce a white residue. All filtrates were heated to be evaporated to about 1.0 mL. Then the solution was transferred to a 500.0 mL volumetric flask together with 25.0 mL of a standard 1000 μg mL<sup>-1</sup> Pd solution.<sup>35</sup> Then the flask was adjusted by adding deionized water. After 400-fold dilution, 2.0 mL of the solution was used for analysis.

Analysis of Pd-charcoal was performed as follows: 0.1020 g of Pd-charcoal catalyst was mixed with 50 mL of 1.0 mol L<sup>-1</sup> nitric acid in a beaker. The mixture was heated for about 2 h on a hot plate until dryness. The residue was mixed with 50 mL of deionized water, and then filtered and washed with 5 mL of deionized water 3 times. The filtrate solution was transferred to a 250.0 mL volumetric flask.<sup>36</sup> After appropriate dilution, Pd content of the Pd-charcoal catalyst was analyzed by the presented procedure and nitroso-R method<sup>37</sup> for comparison. To 0.0712 g of the Pd-CaCO<sub>3</sub> catalyst in a 100 mL beaker was added 3 mL of concentrated nitric acid followed by heating on a hot plate to near dryness. The beaker was cooled and 1.3 mL of concentrated nitric acid and 3.7 mL of concentrated hydrochloric acid were added. The beaker was covered by a watch glass and was heated for 30 min. Then the watch glass was removed and the solution was heated to near dryness. The beaker content was washed with 50.0 mL of nitric acid (1:100) and the solution was transferred to a 100.0 mL volumetric flask and its volume was adjusted using deionized water. After appropriate dilution, Pd content in Pd-CaCO<sub>3</sub> catalyst was determined by the proposed preconcentration-ETAAS determination method and a flame AAS standard method.<sup>38</sup>

Two solutions were prepared according to the composition of 2 alloys. Pd concentrations in the 2 synthetic prepared solutions were 734 ng L<sup>-1</sup> and 34.3 μg L<sup>-1</sup>; the solutions were analyzed according to the

**Table 5.** Determination of Pd in some water, catalysts, synthetic jewels, and alloys.

Sample	Pd					Standard method <sup>a</sup>
	Added	Spectrophotometry (n = 5)		ETAAS (n = 4)		
		Zero-derivative	First-derivative	Found	Recovery (%)	
Jewelry 1	25.0 (mg)	23.9 ± 0.6 (mg)	24.4 ± 0.5 (mg)			
Jewelry 2	25.0 (mg)	24.3 ± 0.6 (mg)	25.5 ± 0.6 (mg)			
Pd-charcoal <sup>b</sup>		4.7 ± 0.2 (%)	4.8 ± 0.2 (%)	4.7 ± 0.1 (%)		
Pd-CaCO <sub>3</sub>				9.8 ± 0.2 (%)	96.1	10.2 ± 0.3 (%)
Pd alloy <sup>c</sup>		69.1 ± 2.0 (%)	68.0 ± 1.7 (%)	66.3 ± 1.5 (%)		
Palau <sup>d</sup>		81.3 ± 1.9 (%)	78.5 ± 2.3 (%)	81.6 ± 2.8 (%)		
River water		ND <sup>e</sup>	ND	279 ± 11 (ng L <sup>-1</sup> )		
	200 (ng L <sup>-1</sup> )			466 ± 15 (ng L <sup>-1</sup> )	93.5	
	350 (ng L <sup>-1</sup> )			645 ± 17 (ng L <sup>-1</sup> )	104.6	
	10.0 (μg L <sup>-1</sup> )	9.8 ± 0.3 (μg L <sup>-1</sup> )	9.9 ± 0.3 (μg L <sup>-1</sup> )			
Mineral water		ND	ND	39 ± 2 (ng L <sup>-1</sup> )		
	70 (ng L <sup>-1</sup> )			112 ± 5 (ng L <sup>-1</sup> )	104.3	
	120 (ng L <sup>-1</sup> )			155 ± 5 (ng L <sup>-1</sup> )	96.7	
	20.0 (μg L <sup>-1</sup> )	20.5 ± 0.4 (μg L <sup>-1</sup> )	20.7 ± 0.6 (μg L <sup>-1</sup> )			
Lake water		ND	ND	130 ± 6 (ng L <sup>-1</sup> )		
	90 (ng L <sup>-1</sup> )			224 ± 9 (ng L <sup>-1</sup> )	104.4	
	150 (ng L <sup>-1</sup> )			273 ± 10 (ng L <sup>-1</sup> )	95.3	
	20.0 (μg L <sup>-1</sup> )	20.7 ± 0.5 (μg L <sup>-1</sup> )	19.5 ± 0.5 (μg L <sup>-1</sup> )			
Tap water		ND	ND	178 ± 10 (ng L <sup>-1</sup> )		
	120 (ng L <sup>-1</sup> )			303 ± 12 (ng L <sup>-1</sup> )	104.2	
				386 ± 16 (ng L <sup>-1</sup> )	94.5	
	10.0 (μg L <sup>-1</sup> )	10.2 ± 0.2 (μg L <sup>-1</sup> )	10.4 ± 0.3 (μg L <sup>-1</sup> )			

<sup>a</sup>The standard method was a flame AAS method (n = 6).<sup>38</sup>

<sup>b</sup> Pd-charcoal catalyst was also analyzed by nitroso-R method as a comparative method (n = 5).<sup>37</sup> The obtained Pd amount was 4.8 ± 0.1 (%) by nitroso-R method.

<sup>c</sup> Ag (33.0%), Pd (67.0%).

<sup>d</sup> Au (20.0%), Pd (80.0%).

<sup>e</sup> ND means non-detectable.

± Amounts are standard deviation.

recommended procedure by ETAAS and spectrophotometry, respectively.

Different water samples were also analyzed. Five milliliters of the water samples were analyzed, according to the presented method. Pd standard solutions were also spiked. The results are shown in Table 5. The obtained results clearly revealed the presence of Pd in the samples. Comparison of the spiked amounts of Pd and the found amounts of Pd revealed the complete recoveries of the added Pd. The obtained results showed the success of the presented method in the determination of Pd in these water matrices.

## Comparison with the other methods

The method was compared with some other published Pd determination works. The comparison is given in Table 6. The presented method showed some advantages in terms of selectivity,<sup>5,39</sup> working range,<sup>12,5,33,39-41</sup> and LOD.<sup>12,5,9,33,39-41</sup>

**Table 6.** Comparison of the presented method with the other Pd preconcentration-determination methods.

Preconcentration method	Detection method	Interferent ions	Detection limit (ng mL <sup>-1</sup> )	Linear range (ng mL <sup>-1</sup> )	Ref.
CPE	Spectrophotometry	Hg(II)	0.47	2-50	39
SPE	FAAS	Ag(I)	0.54	2-80	5
SPE	Spectrophotometry	No interferents	0.3	2-90	33
SPE	FAAS	No interferents	0.3	1-200	40
SPE	FAAS	No interferents	1.2	NA	9
SFODME	FAAS	No interferents	0.6	2-400	41
DLLME	FAAS	No interferents	90	100-2000	12
DLLME	ETAAS and spectrophotometry	No interferents	0.003 and 0.3	0.015-0.900 and 1.5-63.0	This work

CPE: cloud point extraction; SPE: solid phase extraction; FAAS: flame atomic absorption spectrometry; SFODME: solidified floating organic drop microextraction; DLLME: dispersive liquid-liquid microextraction.

<sup>a</sup> Non-available.

## Conclusion

In this study, an IL microextraction-based method was developed for sub-nanomolar Pd determination. Two Pd detection techniques were used and compared. PAN was used in a selective manner for microextraction-determination of Pd without any masking agents. ETAAS and spectrophotometric detection showed wide linear dynamic ranges and highly desirable LODs due to a high enrichment factor. Reasonable accuracies and precisions were obtained for different samples. The DLLME procedure consumed low amounts of reagents and eliminated the use of toxic solvents as extractant.

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