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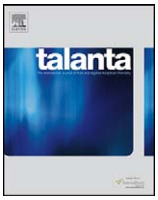

A novel solidified floating organic drop microextraction based on ultrasound-dispersion for separation and preconcentration of palladium in aqueous samples

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This paper is dedicated to the memory of the founder of Kerman University, Mr. Alireza Afzalipour, on the occasion of the centenary of his birth.

Keywords:
Solidified floating organic drop microextraction
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ABSTRACT

A new method of solidified floating organic drop microextraction, based on ultrasound-dispersion prior to flame atomic absorption spectrometry was successfully used for separation and enrichment of trace amounts of palladium in aqueous samples. In this method, palladium (II) was extracted into the fine droplets of 1-undecanol after chelate formation with the water soluble ligand, ammonium pyrrolidinedithiocarbamate. The fine droplets of 1-undecanol were made and dispersed as a cloud in the aqueous sample with the help of ultrasonic waves. Several variable factors that influence the extraction and complex formation, such as pH, concentration of ammonium pyrrolidinedithiocarbamate, sonication time, centrifuging time, type and volume of the extracting solvent were optimized. Under the optimized conditions, a detection limit of 0.60 ng mL^{-1} and a good relative standard deviation of ±2% at 10 ng mL^{-1} were obtained ($n = 7$). The proposed method was applied to well water, tap water, wastewater and synthetic samples and spiked recoveries were in the range of 97–105%. The results showed that solidified floating organic drop microextraction based on ultrasound-dispersion combined with flame atomic absorption spectrometry was a rapid, simple, sensitive, low cost, minimum organic solvent consumption and efficient analytical method for the separation and determination of trace amounts of palladium ion.

1. Introduction

In many analytical procedures, sample preparation is the most time-consuming and cost-determining step. Liquid–liquid extraction (LLE) is a versatile classical sample preparation technique prescribed in many standard analytical methods [1]. However, conventional LLE consumes large amounts of high cost and potentially hazardous organic solvents. In addition, for trace analysis, a large volume of sample is often required and hence can be extremely time-consuming and tedious [2]. LLE also has the tendency for emulsion formation and uses large amount of hazardous and costly organic solvents. So efforts were made to miniaturize the LLE extraction procedure by greatly reducing the solvent to aqueous phase ratio, leading to the development of liquid-phase microextraction (LPME) methodology [3,4]. In LPME, the principles of LLE and the miniaturized nature of solid-phase microextraction are combined to realize the advantages of both techniques. LPME is accomplished either by extraction into small water immiscible drops of organic solvents [5–14] (microdrop) or into small volumes of acceptor solution present inside the lumen of porous hollow fibers [15–19]. LPME may be very effective for analyte enrichment and may result in major reduction in the use of organic solvents [20], and has attracted increasing attention as a novel technique for sample preparation.

Recently, Dadfarnia et al. [21] developed a new liquid–liquid microextraction method based on solidification of floating organic drop, which was successfully used for the separation and preconcentration of lead. Solidified floating organic drop microextraction (SFODME) is a new microextraction technique in which a small volume of an organic solvent with melting point near room temperature (in the range of 10–30 °C) is floated on the surface of aqueous solution. The aqueous phase is stirred for a prescribed period of time, and then the sample is transferred into an ice bath. When the organic solvent is solidified, it is transferred into a small conical vial, and the melted organic solvent is used for analyte determination [22]. SFODME has the advantages of simplicity, low cost, short extraction time, minimum organic solvent consumption and achievement of high enrichment factor [23].

Palladium is a metal, the output and use of which has more than doubled in the past 10 years. It is used in dental appliances, chemical catalysts, electrical appliances and jewellery, but the greatest increase in Pd demand has been in automotive emission control

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catalysts. Studies on Pd concentrations in ancient ice and recent snow samples reflect the increase in mining, smelting and use of palladium in the last decades. An increase of palladium in the environment has been shown in air and dust samples [24]. Thus, because of its increasing use, on the one hand, and the toxicity of Pd (II) compounds for mammals, fish and higher plants, on the other, all environmental analysis should include the determination of the amount of palladium [25].

Several techniques such as complexometry [26], high-performance liquid chromatography [27], inductively coupled plasma [28], atomic absorption spectrometry [29,30], spectrophotometric [31,32], etc., have been used for the determination of palladium in samples.

Our work is a combination of dispersive liquid–liquid microextraction (DLLME) and solidified floating organic drop microextraction, on a cloudy solution and subsequent solidification of extracting solvent. Unlike traditional DLLME, the procedure does not need of organic dispersive solvent. In fact we have introduced a new form of SFODME in which ultrasonic waves play the role of the stirrer bar, decreasing the extraction time still further; i.e. using an ultrasonic water bath we accelerated the formation of a cloudy dispersive extraction mixture instead of floatation of organic solvent drop. Ultrasound assistance is a growing trend in analytical chemistry. From the most basic use for cleaning to facilitating or making possible different steps of the analytical process, particularly those involved in sample preparation [33]. For example it is a powerful aid in the acceleration of various steps in the process of separation and extraction such as homogenizing, emulsion forming, and mass transferring between immiscible phases [34]. Concerning two-phase liquid systems, dispersion of a phase as small droplets into another under ultrasound assistance until the initial heterogeneous liquid–liquid system is made uniform, which is known as "homogenization" or "emulsification", is a well documented process in both the analytical and industrial fields [35]. In this study, the possibility of Pd enrichment by solidified floating organic drop microextraction based on ultrasound-dispersion (SFODME based on USD) was considered. Ammonium pyrrolidinedithiocarbamate (APDC) was selected as the chelating reagent and a new microextraction method combined with flame atomic absorption spectrometry (FAAS) was developed for separation, enrichment and determination of palladium in aqueous samples. Factors affecting the extraction efficiency, such as pH, concentration of chelating reagent, extraction time, and nature of the organic solvent were studied and optimized.

2. Experimental

2.1. Instrumentation

The palladium measurement was performed with a Varian SpectrAA 220 atomic absorption spectrometer (Australia) equipped with a computer processor. A palladium hollow cathode lamp, operated at 5 mA, was utilized as the radiation source. The analytical wavelength (363.5 nm) and slit width (0.1 nm) were used as recommended by manufacturers. The pH values were measured with a metrohm 827 pH meter (Switzerland) supplied with a combined glass electrode. Fine droplets of organic solvent were made by Sonorex RK255 ultrasonic water bath (Germany). An IEC-model HN-S centrifuge was used to accelerate the phase separation.

2.2. Reagents and solutions

All reagents used were of the highest purity available and at least of analytical reagent grade. The stock solution of palladium (II) ($100\ \mu g\ mL^{-1}$) was prepared by dissolving the proper amount of Pd $(CH_3COO)_2$ from Merck (Darmstadt, Germany) in $2\ mol\ L^{-1}$ hydrochloric acid solution. Standard solutions of palladium (II) were prepared daily by appropriate dilution of palladium stock solution. 1-Undecanol (99%) was obtained from Aldrich (Steinheim, Germany) and was used as the extracting solvent. A solution of ammonium pyrrolidinedithiocarbamate (APDC, 0.37%, w/v) was prepared every day by dissolving an appropriate amount of APDC (99%, Merck) in double distilled water. Dimethylformamide (DMF, 99.5%) obtained from Merck, was used for sediment phase dilution before FAAS determination. The vessels used for trace analysis were kept in 10% nitric acid for at least 24 h and subsequently washed three times with double distilled water.

2.3. General procedure

A 15.0 mL of double distilled water containing 2.25 μg of Pd (II) with adjusted pH to 2.0, was placed in a ~40 mL vial. After addition of 5 μL of APDC solution, 35 μL of 1-undecanol were added in and sonicated for 2 min. A cloudy solution, resulting from the dispersion of fine 1-undecanol droplets in the aqueous solution, was formed in the test tube. Then this turbid solution was centrifuged for 8 min at 2500 rpm leading to aggregation of 1-undecanol as a floating drop on the surface of solution. Then, the tube was transferred to a beaker containing crushed ice. After 5 min, the solidified solvent drop was transferred into conical vial where it melted immediately. Thirty microlitres of the organic phase was sediment after centrifugation. This phase was diluted to 300 μL with DMF for FAAS determination.

3. Results and discussion

To demonstrate the applicability of the approach, Pd as a principal environmental pollutant and APDC as the chelating reagent were selected. 1-Undecanol was used as the extracting solvent, because of its low volatility, low water solubility and melting point (near room temperature). Furthermore, to obtain high extraction efficiency, different parameters affecting the complex formation, extraction and analysis process were optimized. In the SFODME based on USD/FAAS method, enrichment factor and percent of extraction are calculated as SFODME [31]:

$$\text{Percent of extraction} = \left(\frac{C_o V_o}{C_{aq} V_{aq}}\right) \times 100 \tag{1}$$

$$\text{Enrichment factor} = \frac{C_o}{C_{aq}} \tag{2}$$

where V and C are the volume and concentration and the suffixes o and aq indicate organic and aqueous phase, respectively. C_o was calculated from the calibration graph of standard solution of interested metal in DMF.

3.1. Effect of pH

It is obvious that pH plays a unique role on the metal-adduct formation and its subsequent extraction. So, the influence of pH on the extraction of hydrophobic chelate of Pd^{2+} with APDC from 15 mL of aqueous phase into 35 μL of 1-undecanol was studied for the pH range of 1.0–6.0. The pH was adjusted by either diluted nitric acid or sodium hydroxide solution. As can be seen in Fig. 1 the absorbance of Pd remained constant for pH from 1.0 to 3.0, and then decreased in the range 3.0–6.0. When pH was higher than 6, nearly no Pd absorbance was detected, indicating that almost no Pd extracted. The reason for higher absorbance at pH range of 1.0–3.0 is that APDC can be protonated in acidic solution, which results in forming stable Pd (II)–APDC complex through its two donor sulphur atoms [36]. So, in the subsequent studies the pH of the solutions was adjusted at 2 by using dihydrogen phosphate buffer.

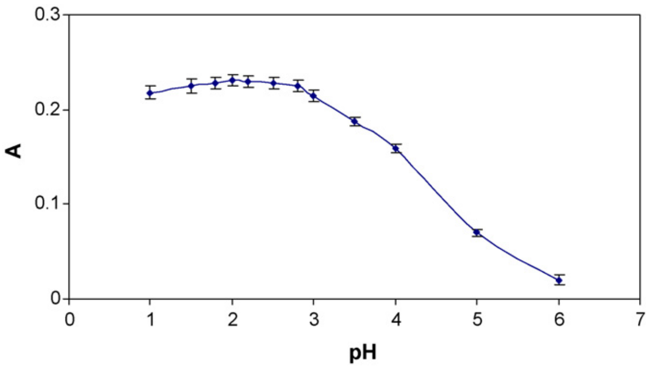

Fig. 1. Effect of pH on the extraction of 2.25 μg of palladium. Extraction conditions: aqueous sample volume, 15 mL; APDC, 0.30% (w/v); extracting solvent volume, 35 μL; sonication time, 5 min; centrifugation time, 8 min.

3.2. *Effect of APDC concentration*

The effect of APDC concentration on the extraction efficiency was evaluated in the range of 0.07–0.5%. The results are shown in Fig. 2. It is obvious that the absorbance of Pd increases with an increase in APDC concentration up to 0.32% (w/v) and is then constant up to 0.5% (w/v). For subsequent experiments a concentration of 0.37% (w/v) of APDC was chosen.

3.3. *Selection of extracting solvent*

The extracting solvent for SFODME based on USD should be able to form a cloudy solution in the aqueous phase. In addition it must have a lower density than water, high extraction capability for the compounds of interest, low volatility, low water solubility and a melting point near room temperature. Several extracting solvents, including 1-undecanol (mp 13–15 °C), 1-hexadecanethiol (mp 18–20 °C) and 2-undecanone (mp 11–13 °C) were investigated. 1-Undecanol was selected because of its sensitivity, stability, lower price, low water solubility and low vapor pressure. It was also found to have the best extraction efficiency. With 2-undecanone, the dispersed drop could not be aggregated completely after centrifugation. With 1-hexadecanethiol, the extraction efficiency was about 31% of 1-undecanol. Thus, 1-undecanol was selected as the extracting solvent.

3.4. *Effect of the volume of extracting solvent*

During SFODME based on USD process, extracting solvent volume was an essential factor which could influence the occurrence of the cloudy state and also determine enrichment performance. To examine the effect of extraction solvent volume, different volumes of 1-undecanol (25, 30, 35, 40, and 45 μL) were subjected to the same SFODME based on USD procedures. The results are shown in Fig. 3. As can be seen, absorbance increased with the increase of 1-undecanol volume in the range of 25–35 μL, and then remained constant when the volume was continuously increased. Therefore, 35 μL of 1-undedanol was selected in order to achieve higher enrichment factor, better repeatability and lower limit of detection.

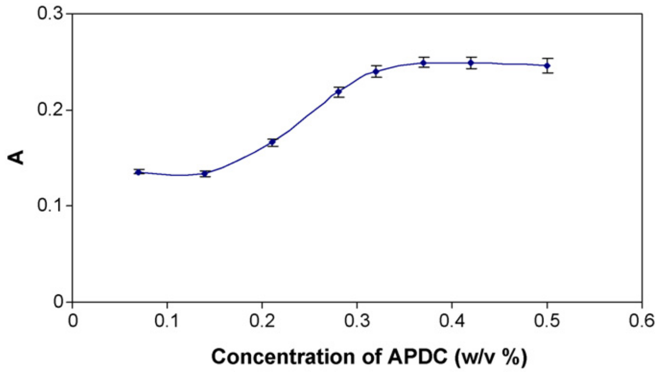

Fig. 2. Effect of APDC concentration on the extraction of 2.25 μg of palladium. Extraction conditions were the same as Fig. 1 except APDC concentration, at pH = 2.

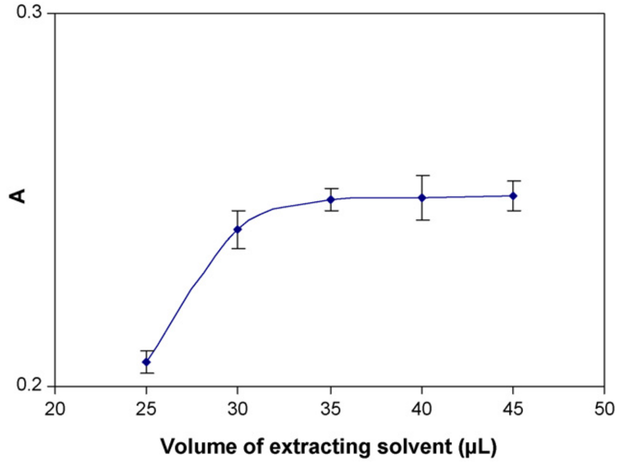

Fig. 3. Effect of extracting solvent volume on the extraction of 2.25 μg of palladium. Extraction conditions were the same as Fig. 1 except extracting solvent volume and APDC concentration (0.37%, w/v).

3.5. *Effect of salt*

Salting-out is a process of addition of electrolytes to an aqueous phase in order to increase the distribution ratio of a particular solute. The term also connotes reduction of mutual miscibility of two liquids by addition of electrolytes. Weak intermolecular forces, e.g., hydrogen bonds, between organic molecules or nonelectrolytes and water are easily disrupted by the hydration of electrolytes [37]. Accordingly, the effect of salt on extraction efficiency was studied by varying the concentration of $NaNO_3$ within the range of 0–5% (w/v). The results showed that the addition of salt has no significant effect on the efficiency of the SFODME based on USD of Pd (II) ion.

Table 1
Effect of interfering ions.

Coexisting ions	Coexisting ion/Pd (II) ratio	Recovery (%)
Mg^{2+}	2000	102
Ca^{2+}	2000	103
ClO_4^-	1120	99
$H_2PO_4^-$	1300	102
SO_4^{2-}	1360	96
CO_3^{2-}	850	97
PO_4^{3-}	1050	100
Cd (II)	750	97
Pb (II)	480	98
Zn (II)	450	101
Co (II)	400	98
Cr (VI)	340	100
Rh (III)	340	95
Mn (II)	260	95
Cu (II)	240	97
Ni (II)	220	99
Fe (III)	50	102

Table 2
Determination of palladium in water and synthetic samples.

Sample	Spiked (ng mL^{-1})	Found (ng mL^{-1})[a]	Recovery (%)
Well water (Shahid Bahonar University)	–	N.D[b]	–
	10.0	9.8 ± 0.2	98
	50.0	51.0 ± 0.9	102
Tap water (Kerman drinking water)	–	N.D	–
	10.0	9.7 ± 0.2	97
	50.0	49.0 ± 0.8	98
Wastewater[c]	–	N.D	–
	10.0	10.5 ± 0.2	105
	50.0	50.4 ± 0.8	100.8
Synthetic sample 1[d]	10.0	9.9 ± 0.2	99
Synthetic sample 2[e]	10.0	10.1 ± 0.1	101

[a] Mean ± SD, $n = 3$.
[b] N.D: not detected.
[c] Recycle water from copper factory.
[d] Zn^{2+}, Cd^{2+}, Ni^{2+}, Rh^{3+}, Co^{2+}, Cu^{2+}, 2000 ng mL^{-1} of each cation.
[e] Zn^{2+}, Cd^{2+}, Ni^{2+}, Rh^{3+}, Co^{2+}, Cu^{2+}, 1300 ng mL^{-1} of each cation.

3.6. *Effect of sonication time*

Dispersion is the key step to determine whether the extraction was successfully carried out or not. Accordingly, sonication time plays an important role in SFODME based on USD procedure. Enough time will make the extracting solvent dispersed more finely into the aqueous solution and result in an excellent cloudy solution. So, the effect of sonication time was evaluated in the range of 0–6 min. It was seen that the analyte signal reached a maximum and was independent of further increase in the time of sonication at a time greater than 2 min. Hence, 2 min was chosen for the dispersive procedure.

3.7. *Effect of centrifuging time*

In SFODME based on USD, ultrasonic agitation disperses the extractant completely in the aqueous phase and forms vast organic vesicles to achieve efficient extraction. Centrifugation was necessary to obtain two distinguishable phases in the extraction tubes. The effect of centrifuging time on the extraction efficiency was evaluated in the range of 2–10 min at 2500 rpm. The extraction performance all reached its peak when the solution was centrifuged at 2500 rmp for 8 min. When the centrifuging time was longer than 8 min, the absorbance remained constant, so 8 min was chosen in the following study.

3.8. *Effect of interfering ions*

Preconcentration methods for trace determination of metals can be strongly affected by the matrix constituents of the samples. In order to demonstrate the selectivity of the developed method for determination of Pd, the extraction efficiency was investigated in presence of different ions. The results of this investigation are given in Table 1. A species that cause a variation of more than 5% in absorbance of Pd was consider as interfering ion. As is shown in the table other ions at the given level show no significant interference in the determination of palladium. In these experiments, solutions containing the interfering ions and 0.75 μg of Pd were treated according to the recommended procedure. These results indicate that the method is applicable to analysis of Pd in different samples.

3.9. *Application to real and synthetic samples*

The proposed method was applied to the determination of palladium in tap water, well water and wastewater. Reliability was checked by spiking the sample. The results along with the recovery for the spiked sample are given in Table 2. As may be seen, the recoveries of the spiked samples are satisfactory. In order to verify the accuracy of the approach, the standard addition method was applied for the determination of palladium in spiked synthetic samples which are mentioned in Table 2. Cations which could compete significantly with Pd for chelate formation were chosen for this purpose. The concentration of Pd in the samples was found to be 9.9 ± 0.2 and 10.1 ± 0.1 and are in good agreement with the certified value of 10.0 for Pd. Thus the method is reliable for determination of Pd in natural water samples.

3.10. *Analytical performance*

Important parameters such as the linear range, calibration graph, precision, detection limit, and enrichment factor were determined to evaluate the method performance. The calibration curve was obtained after the standard series were subjected to the proposed procedure and then determined by FAAS. Linearity was obtained with palladium concentration in the range of 2.0–400 ng mL^{-1}, the linear equation being $A = 0.0016C + 0.0018$ (where A is the absorbance and C is the concentration of palladium (ng mL^{-1}) in aqueous phase) with a correlation coefficient of 0.9996. The enrichment factor calculated as in Eq. (2) was 49.9. The limit of detection and quantification determined as $3S_b/m$ and $10S_b/m$ (S_b is the standard deviation of the blank and m is the slope of the calibration curve after extraction) were 0.60 and 2.0 ng mL^{-1}, respectively. The relative standard deviation (RSD) for seven replicates of 10 ng mL^{-1} of Pd (II) was ±2%.

3.11. *Comparison of SFODME based on USD with other methods*

Determination of palladium in the aqueous samples by solidified floating organic drop microextraction based on Ultrasound-

Table 3
Comparison of the published preconcentration methods for Pd with the proposed method.

Preconcentration/determination method	Aqueous sample volume (mL)	Organic solvent volume (μL)	Enrichment factor	Detection limit (ng mL^{-1})	Linear range (ng mL^{-1})	Ref.
CPE/ICP-OES[a]	10	–	20.2	0.3	0.5–1000	[38]
DLLME/FAAS	5	150	45.7	90	100–2000	[39]
DLLME/GFAAS[b]	5	40	156	2.4 ng L^{-1}	0.1–5	[40]
DLLME/FO-LADS[c]	10	70	162[d]	0.25	2–100	[41]
SFODME based on USD/FAAS	15	35	49.9	0.60	2–400	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 (ratio of slopes).

dispersion compared with the other reported preconcentration methods used for determination of palladium [38–41] and the results are shown in Table 3. The proposed method shows a comparatively low detection limit (0.60 ng mL^{-1}), high enrichment factor (49.9) and good linear range (2–400 ng mL^{-1}) for Pd in a short time (2 min) of extraction. As can be seen, this method has higher enrichment factor than CPE/ICP-OES [38] and DLLME/FAAS [39]. Lower enrichment factor than DLLME/GFAAS [40] and DLLME/FO-LADS [41] could be the result of the determination system and the fact that these methods have no need of dilution. The detection limit of the proposed method is also better than method using FAAS determination [39].

4. Conclusion

As mentioned, ultrasound is a powerful aid in the extraction procedure. However, organic solvents tend to volatilize under the ultrasonic radiation. In this study, solidified organic drop microextraction based on ultrasound-dispersion coupled with flame atomic absorption spectrometry has been developed for separation and sensitive determination of palladium in aqueous samples. An ultrasonic water bath was used to accelerate the formation of a cloudy dispersive extraction mixture in the short time of 2 min while the extracting solvent (1-undecaol) has low volatility. APDC, used as chelating reagent, cannot form colorful chelate with metals, so it is difficult to distinguish the organic phase from the aqueous phase in LPME methods such as DLLME. However since the organic drop containing Pd–APDC chelate becomes white after solidifying when our method is used, we can distinguished between these phases. The sample preparation time and the consumption of organic solvents were minimized with the use of the proposed technique, which is volatile organic solvent-free and has no need for a dispersive solvent compared with the conventional DLLME. Solidified floating organic drop microextraction based on ultrasound-dispersion is a modified solvent microextraction method. It has advantages such as rapidity, high recovery, simplicity of operation, low cost, minimum organic solvent consumption, and achievement of high enrichment factor.

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