

Ultrasound-assisted emulsification–solidified floating organic drop microextraction combined with flow injection–flame atomic absorption spectrometry for the determination of palladium in water samples

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Received: 08.12.2012 • Accepted: 07.04.2013 • Published Online: 16.09.2013 • Printed: 21.10.2013

Abstract: The ultrasound-assisted emulsification–solidified floating organic drop microextraction (USAE–SFODME) methodology was combined with flow injection–flame atomic absorption spectrometry (FI–FAAS) for the separation/pre-concentration and determination of palladium at ultratrace level. In this method, the palladium ion in the aqueous solution was complexed with acetylacetone ($6 \times 10^{-3} \text{ mol L}^{-1}$) in the pH range of 1–7 and was extracted into 40 μL of 1-undecanol, which was sonically dispersed in the aqueous phase. The vial was then centrifuged and cooled in an ice bath for 5 min. The solidified extract was melted and diluted to 100 μL with a solution of hydrochloric (1 mol L^{-1}) acid in ethanol, and the concentration of palladium was determined by FI–FAAS. Under the optimum conditions, an enhancement factor of 55 and a good relative standard deviation of $\pm 2.1\%$ at 40 $\mu\text{g L}^{-1}$ were obtained ($n = 7$). The proposed method was successfully applied to the determination of palladium in different types of water samples. Accuracy was assessed through recovery experiments, independent analysis by furnace atomic absorption spectrometry, and analysis of a certified reference ore by the proposed method.

Key words: Acetylacetone, palladium, preconcentration/separation and determination, solidified floating organic drop microextraction, ultrasound–assisted emulsification, flow injection–flame atomic absorption spectrometry (FI–FAAS)

1. Introduction

The abundance of palladium in the earth's crust is about 0.01–0.02 mg mL^{-1} and it exists in various natural minerals including soils and rocks.¹ Nowadays, the use of palladium has grown considerably because of its physical and chemical properties. It is used in different industries, including the electrical industry (30%–40%),² the production of dental and medicinal devices (25%–40%), jewelry (2%–5%), the automotive industry (5%–15%), and the chemical industry (10%–15%).³ Palladium is rather inert and is biologically inactive, but its ionic species are highly toxic and carcinogenic to humans, causing asthma, allergy, and rhino conjunctivitis as well as other serious health problems.⁴ As the concentration of palladium in environmental and biological samples is very low, its direct determination is difficult even with highly sensitive and selective analytical techniques. Therefore, a separation and preconcentration step prior to its determination is required.⁵ Various methods including co-precipitation,⁶ liquid–liquid extraction (LLE),^{7,8} solid phase extraction (SPE),^{9,10} cloud point extraction (CPE),^{11,12} and liquid-phase microextraction (LPME)^{13–18} have been applied for the separation and preconcentration of palladium prior to its determination by atomic spectrometry.

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LPME has emerged as a new powerful tool for preconcentration and matrix separation prior to detection. It is a simple, inexpensive, fast, and effective preconcentration technique. LPME is based on the principle of the LLE technique; however, the volume of the organic solvent is greatly reduced.¹⁹ Since its introduction in 1996,²⁰ LPME has been performed in different modes such as single drop microextraction (SDME),¹⁵ hollow fiber-liquid phase microextraction (HF-LPME),²¹ ultrasound-assisted emulsification-microextraction,^{22,23} dispersive liquid-liquid microextraction (DLLME),^{24,25} and solidification of floating organic drop microextraction (SFODME).²⁶⁻³⁰ SFODME is a simple, fast, and inexpensive technique. The extraction is done upon the addition of a small volume of an extraction solvent with a density lower than that of water and a melting point near to room temperature (10–30 °C) to the aqueous solution containing the analyte. The solution is stirred and after the extraction the organic drop is floated on the aqueous surface, the mixture is put into an ice bath, and the solidified extractant is easily separated with a spatula. SFODME is an equilibrium extraction technique where the concentration of the analyte in the organic solution increases to a certain level, and subsequently the system enters the equilibrium and the analyte concentration in the acceptor phase remains constant versus time. The extraction efficiency in SFODME is dependent on the actual partition coefficient, the volume of the sample, and acceptor phase. In 2008, Leong and Huang³¹ reported a new variation of SFODME. In this mode, a mixed solution of the dispersive and extractant solvent with density lower than that of water and a melting point near to room temperature is rapidly injected into the aqueous phase. This produces a vast contact area between the extractant and the sample, leading to faster mass transfer and better extraction times, but the partition coefficient of the analyte might be lower due to the increase in the solubility of the organic phase in the aqueous phase in the presence of the dispersive solvent. Recently, a new mode of SFODME, which is called ultrasound-assisted emulsification-solidified floating organic drop microextraction (USAE-SFODME) was introduced.³² The ultrasound-assisted emulsification is based on the combination of the microextraction system and ultrasound radiation and has been used for acceleration of the extraction step in the analytical procedure for both solid and liquid samples.^{23,24,33-35} In the USAE-SFODME method, instead of using the organic dispersive solvent or the stirring bar, the extractor vial is put into the ultrasonic water bath where a cloudy emulsion is formed. The ultrasonic wave facilitates the dispersion and emulsification of the organic solvent.³² The advantages of this mode of SFODME are the acceleration of the mass transfer between the 2 immiscible phases without the need for the dispersive solvent and the ease of operation.

In this study, the possibility of palladium extraction by USAE-SFODME was considered. Palladium from natural water samples was complexed with acetylacetone, extracted into 1-undecanol in an ultrasonic bath, and determined by flow injection-flame atomic absorption spectrometry (FI-FAAS).

2. Experimental

2.1. Instrumentation

A Buck Scientific flame atomic absorption spectrometer (Model 210 VGP, USA) furnished with a palladium hollow cathode lamp and air-acetylene flame was used for all the absorption measurements. The absorbance wavelength, lamp current, and spectral band width were set at 244.8 nm, 6.25 mA, and 0.2 nm, respectively. The single line flow injection system consisting a peristaltic pump (Ismatic, MS-REGLO/8-100, Switzerland) with silicone rubber tubing, and a rotary injection valve (Rheodyne, CA, USA) with a loop volume of 80 μ L was used for the sample introduction into the FAAS.

The pH measurements were carried out with a Metrohm pH meter (model 691, Switzerland) equipped with a combined glass calomel electrode. Fine droplets of the organic solvent were made by the STARSONIC18-

35 ultrasonic water bath (Liarre Casalfumanese, Italy). A centrifuge (Pars Azma Company, Iran) was used to accelerate the phase separation.

2.2. Reagents

All the reagents were of analytical reagent grade from Merck (Darmstadt, Germany) and were used as received, while distilled deionized water was used to prepare all the solutions. The stock solution (1000 mg L^{-1}) of palladium was prepared by dissolving the appropriate amount of $\text{Pd}(\text{NO}_3)_2$ in 1% nitric acid solution. The standard solution of palladium(II) was prepared daily from the stock solution by serial dilution with distilled water. 1-Undecanol was used as the extracting solvent. The solution of acetylacetone in 1-undecanol ($5 \times 10^{-3} \text{ mol L}^{-1}$) was prepared by dissolving the appropriate amount of acetylacetone in 1-undecanol. A solution of hydrochloric acid (1 mol L^{-1}) in ethanol was used for dilution of the extract. Sodium chloride solution (1 mol L^{-1}) was prepared by dissolving a sufficient amount of NaCl in distilled water.

2.3. Sample preparation

Water samples were filtered through a $0.45\text{-}\mu\text{m}$ Millipore filter; the pH and the NaCl concentration were adjusted to ~ 1 and 0.01 mol L^{-1} , respectively, and treated according to the given procedure.

Then 0.5 mg of standard reference platinum ore (SARM7) was dissolved in a mixture of concentrated hydrochloric acid and nitric acid in 3:1 ratio. The mixture was filtered into a 50-mL volumetric flask, diluted to the mark with deionized water, and treated according to the given procedure.

2.4. Procedure

The concentration of NaCl and the pH of 10 mL of a sample or standard solution containing palladium were adjusted to 0.01 mol L^{-1} and 1 , respectively. Subsequently, it was transferred into a $\sim 12\text{-mL}$ test tube and $40 \mu\text{L}$ of 1-undecanol containing acetylacetone ($6 \times 10^{-3} \text{ mol L}^{-1}$) as the complexing agent was added. The test tube was immersed into an ultrasonic bath for 5 min , which caused the formation and dispersion of the fine droplets of 1-undecanol in the aqueous solution. At this stage, a cloudy emulsified solution was formed. The mixture was then centrifuged at 2400 rpm for 8 min , leading to disruption of the emulsified solution and the dispersed droplets of 1-undecanol coagulated and floated on the surface of the solution. Then the tube was transferred to an ice water bath until the organic drop was solidified. The solidified extractant was then transferred into a conical vial where it melted immediately, and was diluted to $100 \mu\text{L}$ with a solution of hydrochloric acid (1 mol L^{-1}) in ethanol. Then $80 \mu\text{L}$ of the resultant solution was introduced into the FAAS by the use of a single line flow injection system (Figure 1) and the analyte was measured.

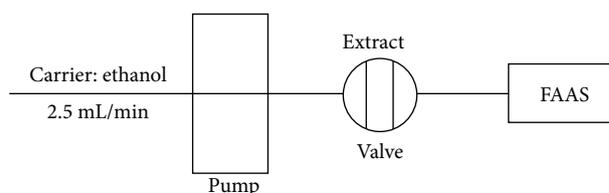


Figure 1. Schematic diagram of the flow injection system coupled to flame atomic absorption spectrometry.

3. Results and discussion

Acetylacetone is a classical β -diketone ligand containing an enolic hydroxyl group whose hydrogen atom can be replaced by a metal. It also has a ketonic oxygen atom in the β -position and the metal can bond to this oxygen atom to give a chelating ring. Acetylacetone is capable of forming complexes with a variety of metal ions. However, its complex with palladium is very strong. The extractabilities of the metal acetylacetone chelates decrease in parallel with their stability constants.³⁶ Therefore, in the present study, it was chosen as a selective chelating agent for palladium. In order to obtain a high enrichment factor, parameters affecting the formation of the complex and extraction were optimized. In USAE-SFODME, the enrichment factor and the percentage of the extraction are calculated as in SFODME¹⁹ using the following equations:

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

$$\text{Enhancement factor} = \frac{C_o}{C_{aq}} \quad (2)$$

where V_o , C_o and V_{aq} , C_{aq} are the volume and the concentration of the analyte in the organic and the initial aqueous phases, respectively. C_o was calculated from the calibration curve of palladium in the solution of hydrochloric acid (1 mol L⁻¹) in ethanol.

3.1. Selection of the extracting solvent

One of the critical factors in the development of an efficient USAE-SFODME procedure is the selection of organic solvent as the physico-chemical properties of the solvent govern the emulsification phenomenon, and consequently the extraction efficiency. The extracting solvent for the USAE-SFODME procedure should form a cloudy, emulsified solution with the aqueous phase. It must have low water solubility, volatility, and toxicity. Its melting point should be close to room temperature (10–30 °C), and it should have high affinity for the target analyte. It must also be compatible with the analytical technique used for the determination of the analyte. Based on these phenomena, several extracting solvents including 1-undecanol (m.p. 13–15 °C), 1-dodecanol (m.p. 22–24 °C), 1,10-dichlorodecane (m.p. 14–16 °C), and n-hexadecane (m.p. 18 °C) were investigated. The n-hexadecane and 1,10-dichlorodecane, which have low polarity, did not disperse well into the aqueous phase; therefore, the recovery was very low (about 10%–15% of 1-undecanol), and so these solvents were ruled out for further consideration. 1-Undecanol was found to give higher recovery. The extraction efficiency was about 94% of 1-undecanol with 1-dodecanol. Thus, in the present study, 1-undecanol was selected as the extracting solvent due to its sensitivity, stability, low water solubility, low vapor pressure, and lower price.

3.2. Effect of pH

The pH of the sample has a considerable effect on the formation of chelate with sufficient hydrophobicity that can be extracted into a small volume of the organic phase. Therefore, the effect of the pH in the range of 0.5–9 on the extraction of 0.5 μ g of Pd²⁺ (0.5 μ g) from 10 mL of aqueous phase into 40 μ L of 1-undecanol containing acetylacetone (3×10^{-2} mol L⁻¹) was investigated. The pH was adjusted by either diluted nitric acid or ammonia solution while the other experimental variables were kept constant. The results are shown in Figure 2 and indicate that the absorbance of palladium is nearly constant in a wide pH range (1–7). In order to have high selectivity, a pH of 1 was selected for the subsequent work and the real sample analysis, because at higher pH acetylacetone can form chelates with other metals.

3.3. Effect of acetylacetone concentration

The formation of the metal chelates and its distribution ratio between the 2 phases affect the efficiency of the analyte extraction. An increase in the ligand concentration up to its solubility limit in the organic phase will increase the value of the distribution ratio and consequently the extraction efficiency.³⁷ Therefore, the influence of acetylacetone concentration in the range of 1.0×10^{-4} to 5.0×10^{-2} mol L⁻¹ on the extraction efficiency was studied. The result of this study is demonstrated in Figure 3 and reveals that the absorbance signal increased with an increase in acetylacetone concentration up to 5.0×10^{-3} mol L⁻¹, and then leveled off at higher concentration of acetylacetone. Thus, a concentration of 6.0×10^{-3} mol L⁻¹ of acetylacetone was selected for the subsequent studies.

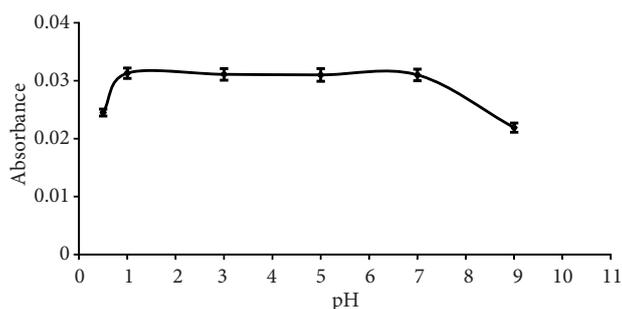


Figure 2. Effect of pH on the extraction of $50 \mu\text{g L}^{-1}$ of palladium. Extraction conditions: aqueous sample volume, 10 mL; extracting solvent, 40 μL of undecanol containing acetylacetone (0.03 mol L^{-1}); sonication time, 5 min; centrifugation time, 8 min, $n = 4$.

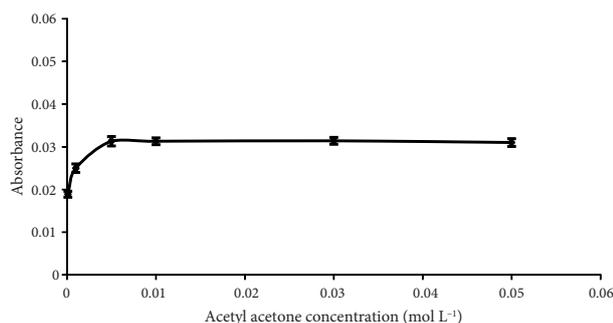


Figure 3. Effect of acetylacetone concentration on the extraction of $50 \mu\text{g L}^{-1}$ of palladium. Extraction conditions: aqueous sample volume, 10 mL; sample pH ~ 1 ; extracting solvent, 40 μL of undecanol containing different concentrations of acetylacetone; sonication time, 5 min; centrifugation time, 8 min, $n = 4$.

3.4. Effect of salt

Increasing the ionic strength of the aqueous phase usually results in the improvement of the extraction efficiency by a process called the salting-out effect. The salting-out effect has been widely applied to LLE and SPME.^{37–39} However, in LPME, some contradictory results have been reported.^{29,40,41} Thus, in some cases a decrease in the extraction efficiency at a high concentration of salt has been reported, which is related to the increase in the sample viscosity and the restriction of the transport of the analyte to the organic phase. Therefore, in order to investigate the effect of salt on the USAE-SFODME performance, several experiments were performed with different NaCl concentrations ($0.0\text{--}0.07 \text{ mol L}^{-1}$) while keeping the other experimental parameters constant. The results (Figure 4) indicated that an increase in salt concentration up to 0.01 mol L^{-1} causes an increase in the absorbance signal and then remains constant with further increase in the salt concentration. Therefore, the method is suitable for the extraction of palladium from saline samples. A salt concentration of 0.01 mol L^{-1} was selected as the optimum for further studies.

3.5. Effect of solvent volume on extraction

The volume of the extracting solvent is an essential factor that affects the appearance of the cloudy state and determines the enrichment factor in USAE-SFODME. The lower the ratio of the volume of organic phase to the aqueous phase, the higher the enrichment factor, but a low volume ratio may reduce the extraction efficiency in a given extraction time. For this purpose, different volumes of 1-undecanol (10, 20, 30, 40, 50, 60, 70 μL) were

subjected to USAE-SFODME under constant conditions of the other variables, the final extract was diluted to 100 μL , and the concentration of palladium was determined by FI-FAAS. The results shown in Figure 5 indicate that by increasing the volume of 1-undecanol up to 20 μL , the extraction efficiency was increased and leveled off at a higher volume of the extracting solvent. Thus, an optimum organic volume of 40 μL was selected for further studies.

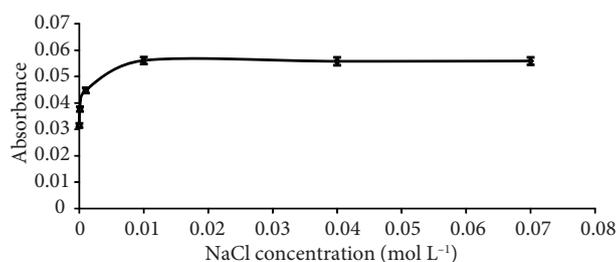


Figure 4. Effect of salt concentration on the extraction of 50 $\mu\text{g L}^{-1}$ of palladium. Extraction conditions: aqueous sample volume, 10 mL; sample pH ~ 1 ; extracting solvent, 40 μL of undecanol containing acetylacetone (6.0×10^{-3} mol L⁻¹); sonication time, 5 min; centrifugation time, 8 min, $n = 4$.

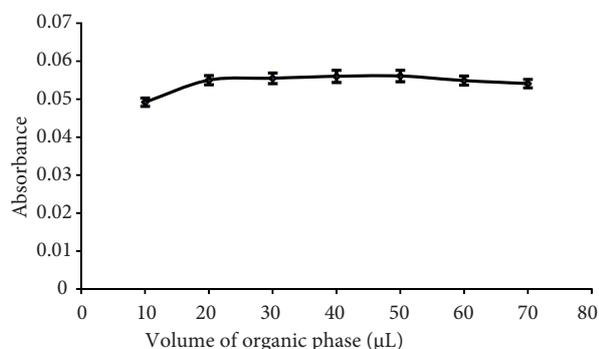


Figure 5. Effect of extracting volume on the extraction of 50 $\mu\text{g L}^{-1}$ of palladium. Extraction conditions: aqueous sample volume, 10 mL; sample pH ~ 1 ; acetylacetone (6×10^{-3} mol L⁻¹); salt concentration (0.01 mol L⁻¹); sonication time, 5 min; centrifugation time, 8 min, $n = 4$.

3.6. Effect of sample volume

In order to demonstrate the capability of the method for the enrichment of low concentration of the analyte from a large sample volume, the effect of sample volume was considered. For this purpose, at optimum conditions, 0.5 μg of palladium was extracted from different volumes (5–60 mL) of the aqueous solution using 40 μL of acetylacetone in 1-undecanol (5×10^{-3} mol L⁻¹) and the appropriate size vial. After the separation of the phases, the extract was diluted to 100 μL with a solution of 1 mol L⁻¹ of hydrochloric acid in ethanol and the analyte was determined by FI-FAAS. The results showed that up to a sample volume of 50 mL the recovery was constant. However, in further study, an aqueous volume of 10 mL was selected as it was more convenient.

3.7. Effect of sonication and centrifuge time

Another important factor that affects the emulsification, the extraction time, the mass transfer phenomena, and consequently the extraction efficiency of the analyte in USAE-SFODME is the sonication time. The effect of the sonication time was studied by varying it in the range of 1–10 min under constant experimental conditions. It was found that by increasing the sonication time up to 5 min the absorbance was increased and reached a plateau at a higher time. Thus, after 5 min, the equilibrium condition was achieved between the 2 phases. Thus, the 5-min sonication was chosen as the optimum extraction time.

The centrifugation time must be optimized for the coagulation of the dispersed fine droplets of the organic solvent. The effect of centrifugation time on extraction efficiency was studied by varying centrifugation time in the range of 3 to 10 min at 2400 rpm. The extraction efficiency reached its maximum and remained constant when the solution was centrifuged for at least 8 min. Therefore, in further experiments, the solutions were centrifuged for 8 min.

3.8. Effect of interfering ion

The effect of the diverse ion usually present in the natural water samples on the preconcentration of palladium by USAE-SFODME was investigated. Various cations and anions were added to the solution containing $0.5 \mu\text{g}$ of Pd at an initial mole ratio of 1000 (ion/palladium). A relative error of less than 5% was considered to be within the range of the experimental error. The results are shown in Table 1 and indicate that the presence of excessive amounts of possible interfering cations and anions has no significant effect on the extraction of palladium and the recoveries are almost constant. In other words, under the optimum conditions of the developed method, acetylacetone acts as a very selective chelating agent for palladium. Thus, the method is suitable for the separation/preconcentration and determination of palladium from various matrices.

Table 1. Effect of diverse ions on the recovery of palladium: concentrated volume 10 mL, Pd(II) at a concentration of $50 \mu\text{g L}^{-1}$.

| Ions | Mole ratio [ion/Pd(II)] | Recovery % | Ions | Mole ratio [ion/Pd(II)] | Recovery % |
|-------------------------------|-------------------------|-------------|-------------------------------|-------------------------|-------------|
| I ⁻ | 1000 | 103.0 ± 2.2 | CO ₃ ²⁻ | 1000 | 100.0 ± 1.8 |
| Mg ²⁺ | 1000 | 104.1 ± 2.3 | SO ₃ ²⁻ | 1000 | 95.1 ± 2.1 |
| Ca ²⁺ | 1000 | 97.3 ± 1.8 | Cl ⁻ | 1000 | 96.7 ± 2.5 |
| SO ₄ ²⁻ | 1000 | 99.0 ± 1.7 | Cr ³⁺ | 1000 | 99.4 ± 2.4 |
| Cd ²⁺ | 1000 | 100.5 ± 2.4 | Co ²⁺ | 1000 | 104.5 ± 2.7 |
| K ⁺ | 1000 | 97.6 ± 2.1 | Cu ²⁺ | 1000 | 97.6 ± 2.3 |
| F ⁻ | 1000 | 95.0 ± 2.9 | Zn ²⁺ | 1000 | 103.2 ± 3.2 |
| Br ⁻ | 1000 | 96.0 ± 2.2 | Fe ³⁺ | 1000 | 101.3 ± 2.7 |
| Sr ²⁺ | 1000 | 100.0 ± 2.5 | Pb ²⁺ | 1000 | 95.1 ± 2.2 |
| SCN ⁻ | 1000 | 103.4 ± 3.0 | Pt ²⁺ | 1000 | 97.4 ± 2.9 |
| Ag ⁺ | 1000 | 97.6 ± 2.1 | Ni ²⁺ | 1000 | 104.5 ± 2.4 |

Results are mean and standard deviation of 3 independent measurements.

3.9. Analytical performance

The analytical characteristics of the developed method such as the linear dynamic range, the enhancement factor, the limit of detection, and the precision as well as the correlation coefficient are summarized in Table 2. The limit of detection and quantification, defined as $3S_b/m$ and $10S_b/m$ (where S_b is the standard deviation of the blank and m is the slope of the calibration graph), were $0.3 \mu\text{g L}^{-1}$ and $1 \mu\text{g L}^{-1}$, respectively. The relative standard deviation (RSD) for 7 replicate measurements at $40 \mu\text{g L}^{-1}$ of palladium was 2.1%. Under the optimized conditions, the calibration graph exhibited linearity over the range of 1.5 to $100 \mu\text{g L}^{-1}$ of palladium. The equation of the calibration curve was $A = 0.0011 C + 0.0018$ (A is the absorbance and C is the concentration of palladium ($\mu\text{g L}^{-1}$) in the aqueous phase) with a correlation coefficient of 0.9998. The enhancement factor, calculated as the ratio of the slopes of the calibration graphs with and without preconcentration,²⁷⁻²⁹ was 55.

3.10. Application

The proposed method was applied to the determination of palladium in tap water, spring water, well water, river water, and rain water samples. The palladium concentration in the tap water, spring water, and well water was determined to be less than the limit of detection (Table 3). The reliability of the method was verified by the recovery experiments and comparing the results with data obtained by electrothermal atomic absorption

spectrometry (ETAAS). The results of this study are given in Table 3 and indicate that the recoveries of the added palladium are good, and at the 95% confidence level there is good agreement between the results of the developed method and the ETAAS analysis. Thus, the method of USAE-SFODME/FI-FAAS is suitable for the determination of palladium in the examined sample type.

Table 2. Analytical characteristics of USAE-SFODME/FI-FAAS for determination of palladium.

| Parameter | Analytical feature |
|---|-----------------------|
| Linear range ($\mu\text{g L}^{-1}$) | 1.5–100 |
| r^2 | 0.9998 |
| Linear equation | $A = 0.011C + 0.0018$ |
| Limit of detection ($\mu\text{g L}^{-1}$) | 0.3 |
| RSD % ($n = 7, 40 \mu\text{g L}^{-1}$) | 2.1 |
| Enhancement factor ^a | 55 |
| Sample volume (mL) | 10 |

^aEnhancement factor is calculated as the ratio of the slopes of calibration graphs with and without preconcentration.

Table 3. Determination of palladium in water samples.

| Sample | Added ($\mu\text{g L}^{-1}$) | Found ($\mu\text{g L}^{-1}$) | Recovery % | GFAAS ($\mu\text{g L}^{-1}$) |
|--------------|--------------------------------|--------------------------------|------------|--------------------------------|
| Tap water | — | ND | — | ND |
| | 40 | 39.2 ± 1.2 | 98.0 | |
| | 60 | 61.2 ± 1.8 | 102.0 | |
| Spring water | — | ND | | 0.90 ± 0.06 |
| | 40 | 39.0 ± 1.3 | 97.5 | |
| | 60 | 59.8 ± 2.7 | 99.7 | |
| Well water | — | ND | | ND |
| | 40 | 38.9 ± 1.4 | 97.2 | |
| | 60 | 57.8 ± 2.2 | 96.3 | |
| River water | — | 2.3 ± 0.1 | | 2.40 ± 0.09 |
| | 40 | 40.9 ± 1.3 | 96.5 | |
| | 60 | 61.3 ± 1.6 | 98.3 | |
| Rain | — | 3.7 ± 0.1 | | 3.91 ± 0.12 |
| | 40 | 42.1 ± 1.1 | 96.0 | |
| | 60 | 61.8 ± 2.3 | 96.8 | |

ND: not detected.

In addition, the above procedure was applied to the determination of palladium in a certified ore sample (SARM 7) (composition ($\mu\text{g g}^{-1}$) Pt = 3.740 ± 0.045 Pd = 1.530 ± 0.032 , Au = 0.310 ± 0.015 , Ag = 0.420 ± 0.040 , Rh = 0.240 ± 0.013 , Re = 0.430 ± 0.057 , Ir = 0.074 ± 0.012 , Os = 0.063 ± 0.006). The concentration of palladium in the sample was found to be $1.50 \pm 0.04 \mu\text{g g}^{-1}$, which is in good agreement with the accepted value of $1.53 \pm 0.03 \mu\text{g g}^{-1}$. Thus, the procedure is reliable for the analysis of a wide range of samples.

3.11. Comparison of the developed method with other methods

The preconcentration and the determination of palladium by the developed USAE-SFODME were compared with those of the other liquid phase microextraction methods reported for the separation and preconcentration

of palladium prior to its determination by atomic spectrometry.^{13–18} The results of this comparison are summarized in Table 4. As can be seen, the enhancement factor of the developed USAE–SFODME is higher. Consequently, its detection limit is lower than that of the other LPME methods in which palladium is determined by FAAS. Furthermore, the selectivity of this method is higher than that of the other reported methods.

Table 4. Comparison of USAE–SFODME/FI–FAAS with other LPME–AS methods for determination of palladium.

| LPME method | Detection technique | Dynamic range ($\mu\text{g L}^{-1}$) | EF ^a | LOD ^b ($\mu\text{g L}^{-1}$) | RSD (%) | Ref. |
|----------------------------------|---------------------|--|-----------------|---|---------|-----------|
| USAE–SFODME | FAAS | 1.5–100 | 55 | 0.3 | 2.1 | This work |
| HFLPME | ICP–MS | — | 24 | 7.9 (ng L^{-1}) | 9.4 | 14 |
| SDME | ICP–MS | — | 40 | 1.5 (ng L^{-1}) | | 15 |
| DLLME | FAAS | 15.0–7000 | — | 1.4 | 1.5 | 16 |
| DLLME | FAAS | 100–2000 | 45.7 | 90 | 0.7 | 17 |
| SFODME based on USD ^c | FAAS | 2–400 | 49.9 | 0.6 | 2 | 18 |

^a Enhancement factor; ^b Limit of detection; ^c solidified floating organic drop microextraction based on ultrasound-dispersion.

4. Conclusions

USAE–SFODME combined with FI–FAAS was proved to be a powerful tool for the separation/determination of ultratrace amounts of palladium in different types of water samples. It also has been shown that acetylacetone can act as a very selective chelating agent for the extraction of palladium under the optimum conditions of the developed method. In addition, it offers an alternative procedure to the techniques such as ETAAS and ICP–AES for the determination of palladium at $\mu\text{g L}^{-1}$ levels in water samples.

The method also has the advantages of speed of analysis, enhancement of FAAS sensitivity, rejection of matrix constituent, low cost, simplicity, high efficiency, and low consumption of the organic solvent.

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