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Solvent-based de-emulsification dispersive liquid–liquid microextraction of palladium in environmental samples and determination by electrothermal atomic absorption spectrometry

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ABSTRACT

A new simple, rapid and efficient sample pretreatment technique for simultaneous extraction and preconcentration was developed. In this study, solvent-based de-emulsification dispersive liquid–liquid microextraction (SD-DLLME) was developed for preconcentration and highly sensitive determination of Pd(II) using the electrothermal atomic absorption spectrometry. The extraction of Pd(II) was performed in the presence of Thio-Michler's ketone (TMK) as the complexing agent. After dispersing, when an aliquot of acetonitrile was introduced as a chemical demulsifier into the aqueous bulk, the obtained emulsion cleared into two phases quickly. Therefore, an extra centrifugation step is not needed for phase separation. Several factors that influence the microextraction efficiency and ETAAS signal, such as pH, TMK concentration, counter ion, extraction time, disperser, de-emulsifier solvents and extraction solvents, stirring rate, pyrolysis and atomization temperature were investigated. Under the optimized conditions, the calibration graph was linear over the range of 0.025–0.500 $\mu g\,L^{-1}$ and relative standard deviation of 3.68% at 0.1 $\mu g\,L^{-1}$ was obtained ($n = 7$). The limit of detection and the enrichment factor (EF) were obtained 0.007 $\mu g\,L^{-1}$ and 231, respectively. The obtained results indicated that the developed method is an excellent alternative for the routine analysis in the environmental field.

1. Introduction

Palladium is a metal of economic importance due to its extensive use in metallurgy, various chemical syntheses, production of medicinal devices and jewellery manufacturing. Since the introduction of catalytic converters into modern automobiles, the determination of palladium has received increasing attention due to its release into the environment [1].

Some palladium compounds have been reported as potential health risks to humans, causing asthma, allergy, rhino conjunctivitis and other serious health problems [2].

Different kinds of conventional analytical techniques, such as flame atomic absorption spectroscopy (FAAS) [3–5], electrothermal atomic absorption spectrometry (ETAAS) [6–8], inductively coupled plasma atomic emission spectrometry (ICP-AES) [9,10], neutron activation analysis (NAA) [11], inductively coupled plasma mass spectrometry (ICP-MS) [12,13] and ultraviolet–visible spectrometry (UV–Vis) [14–16] have been used for determination of palladium. ETAAS is one of the most extensively used techniques for the determination of trace amounts of palladium. The low concentration level of palladium in water is lower than the detection limits of these techniques. Under these circumstances, a separation and enrichment step prior to its determination is mandatory.

Modern trends in analytical chemistry are toward the simplification and miniaturization of sample preparation procedures as well as the minimization of solvent and reagent consumption [17]. Several methods have been reported for the separation and preconcentration of metal ions, such as coprecipitation [18], liquid–liquid extraction (LLE) [19,20], solid-phase extraction (SPE) [21,22] and cloud point extraction (CPE) [9,23], but disadvantages such as large organic solvents, unsatisfactory enrichment factors (EF), secondary waste and being time-consuming limit their applications. In order to overcome these problems, a novel modality of liquid phase microextraction (LPME) termed dispersive liquid–liquid microextraction (DLLME), was proposed [24,25].

However, when performed in manual mode, DLLME is limited to a small number of extraction solvents (carbon tetrachloride, chlorobenzene and chloroform). It is critical for the extraction solvent to be higher density than water, in order to form stable cloudy solution capable of being separated by centrifuging [17]. In addition, the phase separation by centrifugation needs additional instrument and requires extra time. This time consuming procedure, leads to low precision and makes microextraction

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technique difficult to be automated. Moreover, its difficult to handle large volume centrifugation. This time-consuming step can be avoided by the recently introduced alternative of "solvent-based de-emulsification" (SD-DLLME) [26,27]. In this method, the extraction is ended by the addition of a second portion of the disperser solvent that acts as a de-emulsifier and promotes physical phase separation without centrifugation. The stability of the tiny extraction droplets in the dispersed system depends on the nature of the emulsion interface, surface electrical charge, van der Waals forces, etc. Factors such as the speed of agitation, temperature, bulk viscosity and presence of an impurity can play an important role in the effectiveness of demulsification [26,28].

To best of our knowledge, there is no report on the use of SD-DLLME for the analysis of inorganic species. The present study aims to develop a quick and sensitive method for the extraction of Pd(II) by SD-DLLME and its determination by ETAAS.

In this work, acetone, ethanol and acetonitrile, usually used as disperser solvents in DLLME, were introduced as chemical demulsifiers because of their characteristics of low surface tension and high surface activity. After addition of demulsifier solvent, the emulsion is cleared into two phases quickly. In this way, the separation of organic phase from the aqueous bulk was achieved without using conical bottom glass tubes, which are easily damaged and hard to clean, also high extraction recovery was achieved in less than 2 min.

2. Experimental

2.1. Apparatus

The determination of palladium was carried out using a Varian Spectra AA-400, equipped with a graphite furnace atomizer GTA-110 and an auto sampler (ASC-6100). A palladium hollow cathode lamp and pyrolytic graphite coated graphite tubes were used. Aliquots containing 20 μL of the resulting solution were used for the ETAAS analysis.

A palladium hollow-cathode lamp operated at 2.0 mA was used as radiation source. Measurements were carried out in the integrated absorbance (peak area) mode at 247.6 nm, using a spectral bandwidth of 0.4 nm. The heating program employed for palladium determination was given as follow: the drying temperature was 120 °C, ramp 15 s, hold 10 s; the pyrolysis temperature was 700 °C, ramp 10 s, hold 10 s; the atomization temperature was 1800 °C, hold 3 s; the clean temperature was 2100 °C, hold 4 s. The optimal pyrolysis and atomization temperatures of 700 °C and 1800 °C were chosen, respectively. No modifier was used because considerable analyte stabilization was provided by the medium itself. Argon 99.995% (from Roham Gas Co., Tehran, Iran) was used as protective and purge gas. The good graphite wetting by the organic solvents promoted its penetration by the extracts, probably giving rise to the signals of the complicated shapes. To prevent this undesirable effect, the organic extracts were placed at the graphite furnace atomizer, heated at the drying temperature, preventing the sample from spreading over the atomizer surface [29]. Therefore 20 μL of the extraction phase was introduced into the graphite furnace 10 s after starting the drying step in all experiments. A lambda 25 UV-Vis spectrometer (Perkin-Elmer, Waltham, MA, USA) was used for recording the spectra.

2.2. Reagents

All reagents used were of analytical grade. 4,4′-bis(dimethylamino)thiobenzophenone (Thio-Michler's ketone, TMK), 1-propanol, hexane, xylene, toluene, 1-octanol, acetone, ethanol and acetic acid were obtained from Merck (Darmstadt, Germany). A solution of 2×10^{-4} mol L^{-1} TMK was prepared by dissolving appropriate amount of this reagent in 1-propanol and was then kept far from light. Pd(II) stock solution (1000 mg L^{-1}) was prepared by dissolution of the proper amount of $PdCl_2$ (Merck, Darmstadt, Germany) in 3:1, HCl/HNO_3 (v/v) according to the standard methods and then diluted with double distilled water. The working standard solutions were prepared by appropriate step by step dilution of the stock standard solutions. A buffer solution (pH 4, 4 mol L^{-1}) was prepared by mixing of 82 mL acetic acid (4 mol L^{-1}) and 18 mL of sodium acetate (4 mol L^{-1}). The pipettes and vessels used were kept in 20% (v/v) nitric acid for at least 24 h and then washed with ultra pure water.

2.3. SD-DLLME procedure

An aliquot of 10 mL water sample solution containing Pd(II), TMK (10^{-7} mol L^{-1}), NaCl (0.05 mol L^{-1}) and acetate/acetic acid buffer (pH 4, 0.2 mol L^{-1}) was placed in a 15 mL home-made flask with a long neck and kept under continuous stirring at 150 rpm. A mixture of 75 μL organic solvent (1-octanol) and 750 μL disperser solvent was injected rapidly into the sample solution through the 1.00 mL syringe. An emulsion (water, extraction solvent, disperser solvent) was formed in the flask. After a setting time, another 750 μL of disperser solvent, used as the demulsifier, was injected into the top surface of the aqueous bulk to break up the emulsion. Then the emulsion cleared into two phases quickly. The upper organic layer was collected immediately and 20 μL of it injected into ETAAS for analysis. The EF was defined as the ratio of the analyte concentration in the organic phase (C_{org}) after extraction and the initial concentration of analyte (C_{aq}) in the aqueous sample:

$$EF = \frac{C_{org}}{C_{aq}} \tag{1}$$

C_{org} was calculated from the calibration graph obtained by the conventional LLE-ETAAS (extraction conditions: 2.0 mL standard aqueous solution containing Pd in the concentration range of 10–100 μg L^{-1}, 10^{-5} mol L^{-1} TMK, pH 4 into 2.0 mL 1-octanol).

These experiments excluded the usage of typical Teflon-coated stirring bar, as large amounts of the organic micro droplets stuck to the bar due to their good affinity with Teflon. Such behavior would certainly lead to low recoveries and loss in precision. To overcome this potential problem, a glass-coated magnetic stirring bar was used throughout this study.

2.4. Preparation of road dust sample

20 mg of homogenized dust sample (collected from busy streets of Tehran) was weighed accurately and digested with 3:1 HCl/HNO_3 in a 200 mL beaker by refluxing the mixture for 5 h. The solution of each sample was centrifuged and filtered. The filtered solution was diluted with distillated water up to 20 mL. Finally, 5.0 mL of this solution was poured into Falcon tubes and after addition of sodium acetate and adjustment of pH, the volume of solution was adjusted to 10 mL.

3. Results and discussion

3.1. Formation and extractability of the complex

In order to obtain quantitative information on the complexes formed, spectrophotometric measurements were carried out. The absorption maximum of the TMK is at 455 nm and that of complex is at 560 nm. The molar absorptivity is 2.12×10^5 L mol^{-1} cm^{-1}, and the reaction between Pd(II) and TMK is extremely fast. The reaction between TMK and palladium ion is through the sulfur bonding [30,31]. Job's method of continuous variation was used to determine the stoichiometric ratio of palladium–TMK in the complex.

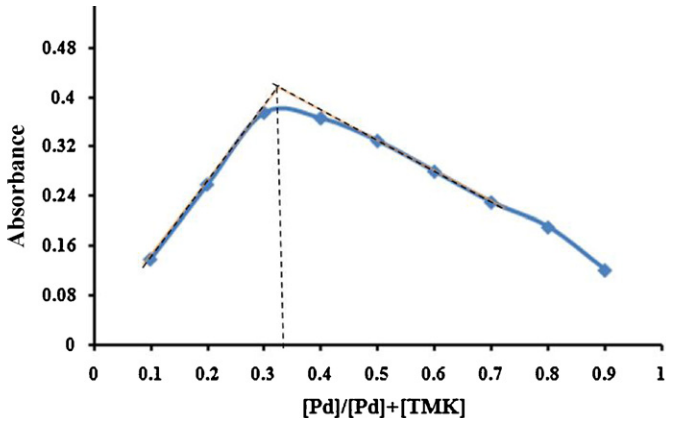

Fig. 1. Continuous variations plot. Concentration of Pd(II) and TMK, 6×10^{-6} mol L^{-1}; pH of sample solution, 4.

Equimolar solution of TMK and Pd (6×10^{-6} mol L^{-1}) having different volumes (1–9 mL) were contacted to obtain the different ratio of TMK and Pd(II). As shown in Fig. 1, the ratio of metal to ligand in the complex is found to be 1:2 but the composition of the extracting species is found to be 1:2:2 for Pd(II):TMK:Cl. The third and fourth coordination site of Pd(II) would therefore be occupied by chloride ions to form a 1:2:2 uncharged complex. The complex species exist as $[Pd(TMK)_2(Cl)_2]$ with Cl^- as the counter ion. This neutral complex is extracted into organic phase. The calculations of the experimental data of Job's curve gave the formation constant of ($\beta_{2Pd(TMK)2}$) 4.8×10^{13}.

In acidic solutions of Pd in the presence of 0.01 mol L^{-1} chloride ions the predominant Pd species are $PdCl_4{}^{2-}$ [32], and stability constants of the chloro complexes of pd(II) are: $\beta_1 = 5.01 \times 10^4$, $\beta_2 = 5.01 \times 10^7$, $\beta_3 = 2.00 \times 10^{10}$, $\beta_4 = 7.94 \times 10^{11}$.

The extraction equilibrium and equilibrium constant can be written as follows:

$$[PdCl_4]^{2-} + 2TMK \rightleftarrows [Pd(TMK)_2Cl_2]_{aq} + 2Cl^- \tag{2}$$

Equilibrium constant = $\beta_{2Pd(TMK)2} \times \beta_{2PdC12}/\beta_{4PdC14} = 3 \times 10^9$.

Thus, it seems that the $2Cl^-$ could be replaced by 2TMKs. $[Pd(TMK)_2Cl_2]_{aq}$ formed in aqueous solution, and extracted as:

$$[Pd(TMK)_2Cl_2]_{aq} \rightleftarrows [Pd(TMK)_2Cl_2]_{org} \tag{3}$$

At equilibrium, the partition coefficient for the analyte in the two-phase system is:

$$K_{o/aq} = \frac{C_{o:eq}}{C_{a:eq}} \tag{4}$$

where $C_{o:eq}$ is the equilibrium concentration of analyte in the organic phase and $C_{a:eq}$ is the equilibrium concentration of analyte in the aqueous phase. According to the mass balance relationship:

$$C_t \cdot V_a = (C_{o:eq} \cdot V_o + C_{a:eq} \cdot V_a) \tag{5}$$

where C_t is the original concentration of analytes, V_o is the volume of the organic solvent, and V_a is the volume of the aqueous sample. LPME is an equilibrium process and can be very effective for analyte enrichment because of the increase in the volume ratio of donor solution and acceptor phase. EF can be calculated from Eqs. (4) and (5).

$$EF = \frac{1}{(V_o/V_a) + (1/K)} \tag{6}$$

Eq. (6) shows that in order to obtain high EF, a low V_o/V_a ratio and high partition coefficient are required. The major factor affecting EF is the partition coefficient. Partition coefficient ($K_{o/aq}$) for this equilibrium was 3039.

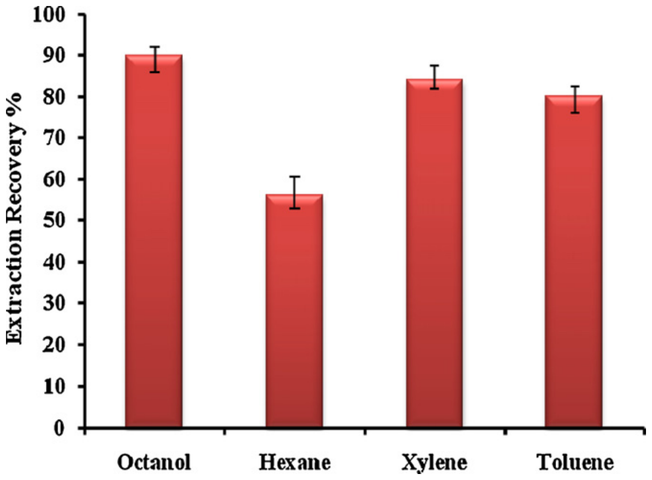

Fig. 2. Effect of the type of the extraction solvent on the extraction recovery. Sample volume, 10 mL; pH of sample solution, 4; disperser/de-emulsifier solvent, acetonitrile (750 + 750) μL; Pd(II), 0.3 μg L^{-1}; concentration of TMK, 10^{-7} mol L^{-1}; NaCl, 0.05 mol L^{-1}; stirring rate, 150 rpm ($n = 3$); 80, 85, 78 and 82 μL volumes of 1-octanol, hexane, xylene and toluene were selected.

3.2. Investigation of the type and volume of the extraction solvent

Selecting a suitable extraction solvent is crucial in this method. It should have low solubility in water, high affinity to analytes and lower density than water. In this work, the exploitation of lower density extraction solvent (e.g. 1-octanol, hexane, xylene, toluene) offers a simple and convenient protocol from a handling point of view without sacrificing sensitivity and efficiency.

A series of sample solutions was studied by using (750 + 750 μL) of acetonitrile, as both disperser and de-emulsifier, containing different volumes of extraction solvent to achieve a final volume of 45 ± 1 μL. Thereby, 80, 85, 78 and 82 μL volumes of 1-octanol, hexane, xylene and toluene were selected, respectively. As it can be seen in Fig. 2, the best extraction recovery was obtained when using 1-octanol. Additionally, the selected solvent is significantly less toxic compared to other typical extraction solvents used in DLLME.

The effect of 1-octanol volumes on the extraction performance was studied in the range of 30–150 μL and the results were shown in Fig. 3. According to the results obtained, by increasing the volume of 1-octanol, the enrichment factor found to decrease significantly. It was found that the best quantitative recovery (>90%)

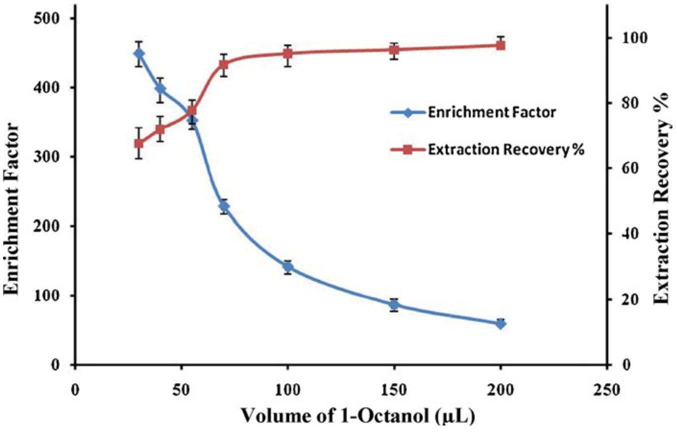

Fig. 3. Effect of the 1-octanol volume on the enrichment factor and extraction recovery. Sample volume, 10 mL; pH of sample solution, 4; disperser/de-emulsifier solvent, acetonitrile (750 + 750) μL; Pd(II), 0.3 μg L^{-1}; concentration of TMK, 10^{-7} mol L^{-1}; NaCl, 0.05 mol L^{-1}; stirring rate, 150 rpm ($n = 3$).

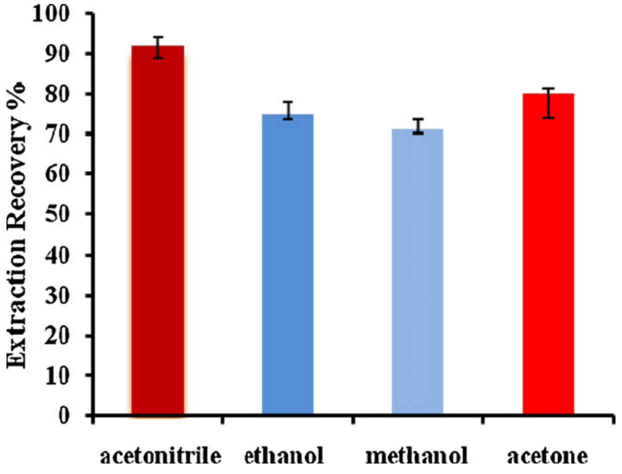

Fig. 4. Effect of the type of disperser and de-emulsifier solvent on the extraction recovery. Sample volume, 10 mL; pH of sample solution, 4; total volume of disperser and de-emulsifier solvent, 1.5 mL; extraction solvent, 75 μL of 1-octanol; Pd, 0.3 μg L^{-1}; concentration of TMK, 10^{-7} mol L^{-1}; NaCl, 0.05 mol L^{-1}; stirring rate, 150 rpm (n = 3).

was obtained when the 1-octanol volume was more than 75 μL. The use of less extractant might lead to the higher EF, but the sampling of the extraction solvent was difficult to carry out when 1-octanol volume was less than 30 μL. Consequently, to obtain a higher EF and extraction recovery value, 75 μL of the extraction solvent was used as the optimal volume in subsequent experiments. The volume of the extractant phase was 40 ± 1 μL after extraction.

3.3. *Investigation of type and volume of disperser/de-emulsifier solvent*

The effectiveness of the emulsification/de-emulsification of oil-in-water emulsions depends on the type of the disperser/de-emulsifier solvent [28,33]. Miscibility of the disperser solvent with extraction solvent and sample solution is the most important point for selection of disperser solvent. A series of sample solutions containing Pd(II)–TMK complex were extracted using 75 μL of 1-octanol using acetone, acetonitrile and methanol as candidates for disperser solvent and demulsifier to break up the emulsion (Fig. 4). The results revealed that acetonitrile provided slightly higher extraction recoveries compared to the other solvents. Based on these findings, acetonitrile was adopted for subsequent experiments.

To simplify the process of selection, the tested solvent was divided into two equal parts. One was used as disperser which mixed with the extraction solvent and was injected into the aqueous sample. After certain minutes, the other part, serving as de-emulsifier solvent, was injected into the dispersed system for phase separation. The effect of the volume of disperser/de-emulsifier on the extraction recovery was also studied.

Fig. 5 shows that the total acetonitrile volume varied between 1000 and 3000 μL at equal disperser/de-emulsifier volumes. It was observed that the emulsion first enhanced with the addition of the de-emulsifier solvent and then separated quickly into two layers in 10–15 s. A volume of acetonitrile of 1500 μL (750 + 750) was finally chosen. Under the selected extraction conditions, the final volume of the 1-octanol was 40 (±1) μL.

3.4. *Effect of pH and TMK concentration*

The solutions of TMK and its complexes are light sensitive, but 1-propanol solution of TMK can be kept for 40 days in a dark place at room temperature, so TMK reagent was prepared in 1-propanol.

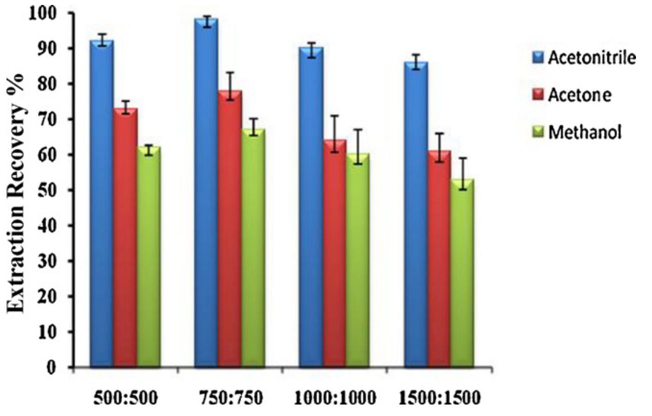

Fig. 5. Effect of the disperser/de-emulsifier volume on the extraction recovery. Sample volume, 10 mL; pH of sample solution, 4; extraction solvent (1-octanol) volume, 75 μL; Pd(II), 0.3 μg L^{-1}; concentration of TMK, 10^{-7} mol L^{-1}; NaCl, 0.05 mol L^{-1}; stirring rate, 150 rpm (n = 3).

TMK forms a selective color complex with Pd(II). The effect of pH on the extraction recovery for Pd(II) was studied between the pH ranges of 2–9, the results was shown in Fig. 6. Based on the obtained results, the extraction recovery of Pd(II), increased as the pH in the aqueous solution was increased from 2 to 3, then it decreased when the pH increased from 5 to 9. Therefore, the optimum pH was laid within the range of 3–5 pH. At lower pH values, ligand is protonated, so recoveries are decreased. However, increase in pH facilities the palladium ion to hydrolyse which decreases the extraction recovery. Therefore, pH 4 was chosen for further extractions.

The influence of the TMK concentration on the SD-DLLME extraction of Pd(II) (2.8×10^{-9} mol L^{-1}) was evaluated in the concentration range of $(0.1–10) \times 10^{-8}$ mol L^{-1}. The results were shown in Fig. 7. As it can be seen, the extraction recovery of Pd increased with the increase of TMK concentration up to 2×10^{-8} mol L^{-1}, and then remained constant. Because of some other ions that could be present in natural water samples and probably react with TMK, a concentration of 10^{-7} mol L^{-1} was used in experiments. The extraction recovery was not affected by the addition of ligand excess.

3.5. *Effect of rate and time of sample agitation*

Due to the formation of the microdroplets in DLLME, the large surface of contact between both phases leads to a very fast mass

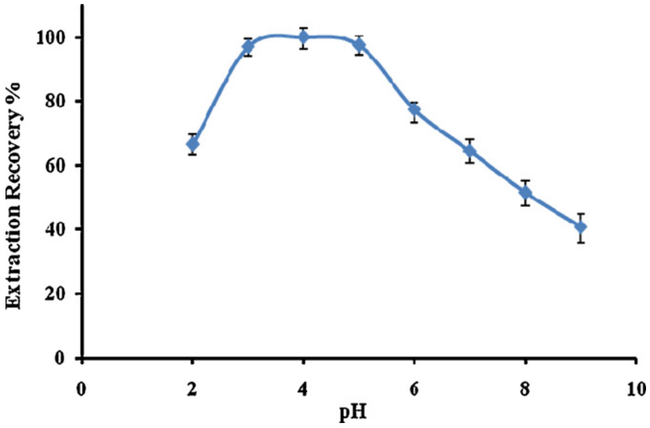

Fig. 6. Effect of sample pH on the extraction recovery of palladium after SD-DLLME. Sample volume, 10 mL; disperser/de-emulsifier solvent, acetonitrile (750 + 750) μL; extraction solvent (1-octanol) volume,75 μL; Pd(II), 0.1 μg L^{-1}; concentration of TMK, 10^{-7} mol L^{-1}; NaCl, 0.05 mol L^{-1}; stirring rate, 150 rpm (n = 3).

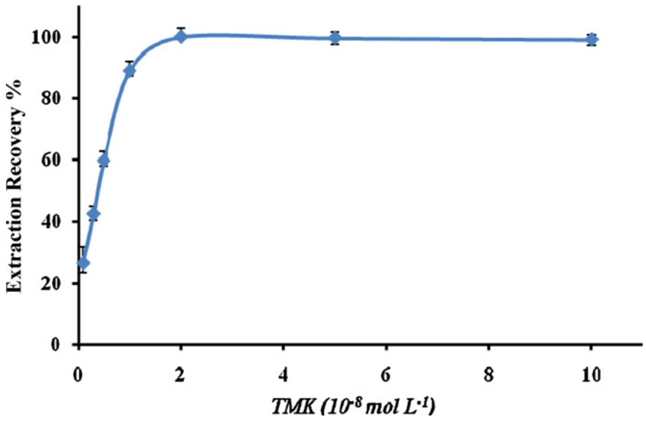

Fig. 7. Effect of TMK concentration on the extraction recovery of palladium ion in SD-DLLME. Sample volume, 10 mL; pH of sample solution, 4; extraction solvent (1-octanol) volume, 75 μL; Pd(II), 0.3 μg L^{-1} (2.8×10^{-9} mol L^{-1}); NaCl, 0.05 mol L^{-1}; stirring rate, 150 rpm ($n = 3$).

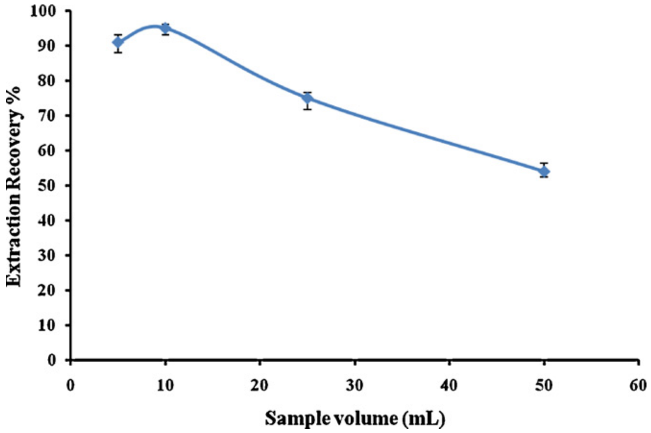

Fig. 8. Effect of sample volume on extraction recovery. pH of sample solution, 4; disperser/de-emulsifier solvent, acetonitrile (750 + 750) μL; extraction solvent (1-octanol) volume, 75 μL; concentration of TMK, 10^{-7} mol L^{-1}; Pd(II), 0.3 μg L^{-1}; NaCl, 0.05 mol L^{-1}; stirring rate, 150 rpm.

transfer process and generally offers a fast extraction protocol. In SD-DLLME, sample agitation in a crucial parameter in determining the extraction recovery of the system, as it can improve the rate of mass transfer of analyte and speed up the de-emulsification process. Thus, the optimum values for agitation rate and agitation duration for the proposed method was studied, as follows.

The extraction recovery was investigated by varying the stirring rate in the range of 100–400 rpm. The recoveries were slightly enhanced up to 150 rpm but remained unaffected at higher rates. Meanwhile, at stirring rates higher than 400 rpm air bubbles were created resulting in lower reproducibility. Finally, a stirring rate of 150 rpm was chosen.

In the next step, the extraction recovery was studied at time intervals between 1 and 10 min using a stirring rate of 150 rpm. The results showed that the agitation time had no significant impact of the extraction recovery and, therefore, a practical time of 2 min was selected for further studies.

3.6. *Effect of sample volume and counter ion*

In order to obtain reliable and reproducible analytical results and a high EF, sample volume is an another important parameter that should be considered for SD-DLLME. In this experiment, the influence of the volumes of sample solution containing 0.3 μg L^{-1} of Pd(II) on the recovery was investigated in the range of 5–50 mL, the experimental results are shown in Fig. 8. When the volume of sample was more than 10 mL, the observed decrease in the extraction recovery is most possibly due to the incomplete formation of cloudy state. Meanwhile, as observed, the solubility of 1-octanol in the aqueous sample increased, thus the volume of the upper phase and the extraction abilities decreased. Hence, a sample volume of 10 mL was selected as the ideal volume for trace analysis of Pd(II) in water samples.

Since TMK forms a cationic complex, to achieve electroneutrality which is necessary for extraction, some anion should accompany the cationic complex into the organic phase. The effect of chloride ion concentration was investigated in the range of 10^{-3} mol L^{-1} to 0.1 mol L^{-1}. Fig. 9 shows that the extraction of palladium was quantitative above 10^{-2} mol L^{-1} of Cl^- and the extraction recovery was not changed by increasing the concentration of NaCl. It was observed that in the excess of NaCl, the volume of extractant phase increases slightly, leading to decrease in EF. Meanwhile, as expected, the salting out effect increases the opposite phenomena practically resulted in no significant effect on recovery and EF of the SD-DLLME [34,35]. A concentration of 5×10^{-2} mol L^{-1} NaCl was selected for subsequent experiments in order to neutral $[Pd(TMK)_2Cl_2]$ would phase transfer into the organic.

3.7. *Effect of coexisting ions*

Effects of common coexisting ions in the natural water samples on the recovery of Pd(II) were studied by spiking appropriate amounts of the relative ions to 10.0 mL of the solutions containing 0.1 μg L^{-1} of Pd(II) (9.4×10^{-10} mol L^{-1}) and 2×10^{-8} mol L^{-1} of TMK (as chelating agent) and they were treated according to the recommended procedure.

An ion was considered to interfere when its presence produced a variation in the absorbance of the sample higher than 5%. The tolerance limits of different cations are shown in Table 1. The findings showed that a 50-fold of Cu^{2+} and 10-fold of Ag^+, Au^{3+} and Hg^{2+} do not reduce the extraction recovery of Pd(II) obviously when $L/M = 20$. However, by using 10^{-7} mol L^{-1} of TMK ($L/M = 100$) the interference effect of them on the extraction of Pd(II) was decreased.

The concentrations of the studied metal ions founding on natural water samples are usually lower than the tolerance limits reported for them.

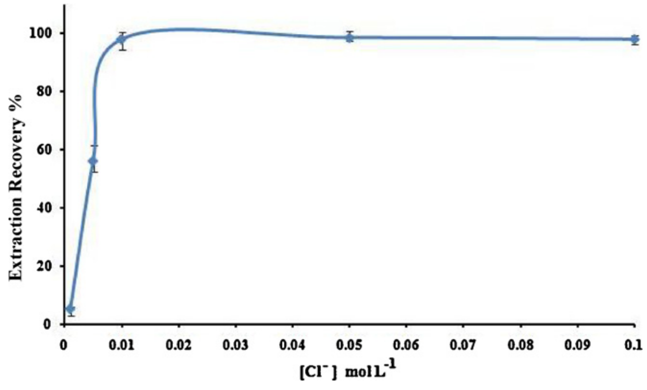

Fig. 9. Effect of counter ion on extraction recovery. pH of sample solution, 4; disperser/de-emulsifier solvent, acetonitrile (750 + 750) μL; extraction solvent (1-octanol) volume, 75 μL; concentration of TMK, 10^{-7} mol L^{-1}; Pd(II), 0.3 μg L^{-1}; stirring rate, 150 rpm.

Table 1
Tolerance limits of coexisting ions on the determination of palladium ion (0.1 μg L^{-1}).

Coexisting ions	Ratio [coexisting ions]/[Pd]
Li^+, Na^+	100,000
Ba^{2+}, Ca^{2+}	10,000
Pb^{2+}, Cd^{2+}, Al^{3+}, Co^{2+}, Zn^{2+}, Mg^{2+}, Ni^{2+}, Cr^{3+}, Mn^{2+}, Bi^{3+}, Sb^{3+}, Fe^{3+}	1000
Cu^{2+}	50
Cu^{2+}	500[a]
Ag^+, Hg^{2+}, Au^{3+}	10
Ag^+, Hg^{2+}, Au^{3+}	100[a]
NO_3^-	100,000
PO_4^{3-}, SO_4^{2-}	10,000
I^-	100

[a] Using higher amounts of TMK ($L/M = 100$).

Table 4
Analytical results for Pd(II) determination in different samples.

Sample	Added (μg L^{-1})	Founded[a] (μg L^{-1})	Recovery (%)
Sea water[b]	0	0.12 ± 0.02	–
	0.1	0.21 ± 0.03	94
River water[c]	0	0.35 ± 0.05	–
	0.1	0.44 ± 0.04	96
Mineral water[d]	0	0.06 ± 0.01	–
	0.2	0.27 ± 0.02	106.5
Road dust	0	170 ± 20 ng g^{-1}	–
	20	188 ± 24 ng g^{-1}	90

[a] Mean ± S.D., $n = 5$.
[b] Caspian sea water.
[c] From Zarineh river.
[d] From Abali mineral water.

Table 2
Analytical characteristics of SD-DLLME method for determination of palladium ion.

Parameter	Analytical feature
%RSD ($n = 7$)[a]	3.68 (0.1 μg L^{-1})
Regression equation	$A = 1.85\,C\,(\mu g\,L^{-1}) + 0.026$
Correlation coefficient (R^2)	0.994
Limit of detection (μg L^{-1})	0.007
Enrichment factor	231
Linear range	0.025–0.500 μg L^{-1}

[a] Values in parentheses are the Pd concentration for which the RSD was obtained.

3.8. *Analytical figures of merit*

To evaluate the practical applicability of the proposed SD-DLLME technique for determination of Pd(II) several analytical performance characteristics such as EF, linearity, limit of detection (LOD) and repeatability were investigated under the optimized conditions. Table 2 summarizes the analytical characteristics of the optimized method. The limit of detection, defined as LOD = 3 s_b/m, where s_b is the standard deviation of seven replicates of blank signals and m is the slope of the calibration curve after preconcentration, was found to be 0.007 μg L^{-1}.

Table 3 compares the characteristic data of the present method with those reported in literature. As can be seen from Table 3, it is evident that high EF, low LOD and RSD are achieved in less than 2 min. The sample preparation time is further decreased by the fact that no centrifugation is required for phase separation and collection. These significant features which obtained with the SD-DLLME-ETAAS are comparable to or even better than some of other methods which use very sensitive detection method such as ICP-MS. These characteristics are of key interest for routine trace metal ion laboratory analysis.

3.9. *Analytical applications*

For accessing the capability of the method for samples with different matrices containing varying amounts of diverse ions, the method was applied to separation, preconcentration and determination of palladium from 10 mL of sea, river and mineral water samples the results were summarized in Table 4. All water samples were filtered through a 0.45 μm membrane filter and analyzed as soon as possible after sampling. The suitability of the proposed method for the analysis of natural water samples was checked by spiking samples at 0.1 μg L^{-1} of palladium. The method was also applied to the determination of palladium content of, as well as recovery of some added Pd to, a road dust sample and the results were also included in Table 4. Palladium of the automobile catalyst origin is introduced into roadside soil in an artificial way. The content of palladium was strongly correlated to the density of traffic [8,13,21,34,36,37]. Our result for palladium content in the dust samples (collected from busy streets of Tehran) was 170 ng g^{-1}. It was higher than that of previous work, which was carried out in Arak city [34].

The results indicated that the proposed method can be reliably used for the determination of palladium in various matrices.

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

Method	LOD (ng mL^{-1})	Enrichment factor	Sample volume (mL)	Process time (min)	Reference
SPE–ETAAS	1.2	75	75	>40	[7]
SPE-FAAS	3.9	–	6	3	[3]
SPE-ICP-AES	0.2	100	10	5	[22]
CPE-ICP-OES[a]	0.3	20.2	10	23	[9]
FIA-SPE-ICP-MS	0.0028	71	3	–	[12]
FO-LADS-DLLME[b]	0.25	165	10	>5	[24]
FIA-SPE-FAAS	1.0	80	8	80	[21]
CIAME Spectrophotometry[c]	0.2	97	10	19	[16]
DLLME-ETAAS	0.0024	156	5	>5	[25]
DLLME-ETAAS	0.007	350[d]	10	>3	[34]
SD-DLLME-ETAAS	0.007	231	10	2	Present work

[a] Cloud point extraction – inductively coupled plasma-optical emission spectrometry.
[b] Fiber optic-linear array detection spectrophotometry and dispersive liquid–liquid microextraction.
[c] Cold-induced aggregation microextraction.
[d] Enhancement factor (calculated as the ratio of the slopes of the calibration graphs with and without preconcentration).

4. Conclusion

One of the main trends followed in sample preparation is the integration of different steps. Thus, SD-DLLME may be considered as the most advanced approach in which separation, preconcentration and derivatization are performed in a single step and does not require any further clean-up. DLLME allows an efficient miniaturization and simplification of the sample pre-treatment, although its automation is clearly difficult. This difficulty arises from the unavoidable centrifugation step which is a typical off-line process. This effort is made to avoid this step in order to open up a new horizon in DLLME automation.

In this method sample preparation time were minimized by the fact that no centrifugation is required for phase separation and collection, and no toxic chlorinated solvents are used without affecting the sensitivity of the method. The developed method is convenient for the usage of low-density extraction solvents such as toluene, xylene, hexane and 1-octanol in DLLME. A high extraction recovery and a high preconcentration factor was obtained in less than 2 min and a detection limit at a 0.007 $\mu g\, L^{-1}$ level was achieved with only 10.0 mL of aqueous sample.

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