Talanta 109 (2013) 121–127

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Ferrofluid-based dispersive solid phase extraction of palladium

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ARTICLE INFO

Article history:
Received 22 December 2012
Received in revised form
21 January 2013
Accepted 30 January 2013
Available online 16 February 2013

Keywords:
Ferrofluid
Dispersive solid phase extraction
1-octanol
Palladium
Real samples

ABSTRACT

A new mode of dispersive solid phase extraction based on ferrofluid has been developed. In this method, an appropriate amount of ferrofluid is injected rapidly into the aqueous sample by a syringe. Since the sorbent is highly dispersed in the aqueous phase, extraction can be achieved within a few seconds. The ferrofluid can be attracted by a magnet and no centrifugation step is needed for phase separation. Palladium was used as a model compound in the development and evaluation of the extraction procedure in combination with flame atomic absorption spectrometry. The experimental parameters (pH, DDTC concentration, type and concentration of eluent, the amount of adsorbent, extraction time, and the effect of interfering ions) were investigated in detail. Under the optimized conditions, the calibration graph was linear over the range of 1–100 $\mu g\,L^{-1}$ and relative standard deviation of 3.3% at 0.1 $\mu g\,mL^{-1}$ was obtained ($n=7$). The limit of detection and enrichment factor (EF) was obtained to be 0.35 $\mu g\,L^{-1}$ and 267, respectively. The maximum adsorption capacity of the adsorbent at optimum conditions was found to be 24.6 $mg\,g^{-1}$ for Pd(II). The method was validated using certified reference material, and has been applied for the determination of trace Pd(II) in actual samples with satisfactory results.

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1. Introduction

The importance of the palladium metal has grown in recent years due to characteristics such as the resistance to corrosion and oxidation, high melting points, electrical conductivity, and extraordinary catalytic activity [1]. Palladium and its alloys have an extensive range of applications in the automobile, electronics, metallurgy, catalytic converters, dental and medical prostheses, and jewelry manufacture. Palladium compounds have been regarded as highly toxic and carcinogenic to humans, and easily transported to biological material through plant roots, and ultimately intensified along the food chain. The excessive exposure to palladium causes adverse health effects such as primary skin problems, eye irritations, and substantial degradation of DNA and cell mitochondria. Hence, the separation and determination of palladium is of special interest in environmental analysis. However, the direct determination of these metal ions is often difficult because of low concentration of palladium in industrial and environmental samples and together with complexity of the matrix in real samples. Therefore, preliminary preconcentration of the analyte and matrix separation prior to analysis is often necessary.

Several analytical methods have been employed for separation and preconcentration of Pd(II) prior to its detection, such as coprecipitation, solid phase extraction (SPE), liquid–liquid extraction (LLE), flow injection extraction (FIE), cloud point extraction (CPE) and dispersive liquid–liquid microextraction (DLLME) [2–6].

SPE is more flexible and efficient than LLE in terms of simplicity, low consumption of the organic solvents, flexibility to choose the adsorbent and high enrichment factor. Recently, SPE has been increasingly used for the preconcentration and separation of ultra-trace amounts of inorganic and organic species from complex matrices [1,7]. However, because of the limited interface between the sorbent and the aqueous sample, considerable time is needed for the analyte to be extracted onto the sorbent [8]. Thus, a clear trend in analytical chemistry is miniaturization of extraction time. In the last years, the dispersive liquid–liquid microextraction technique has been developed. In this method, an appropriate mixture of the extraction and disperser solvents is injected into the aqueous sample by a syringe to form an emulsified solution. Since the extractant is highly dispersed in the aqueous phase, extraction can be achieved within a few seconds. Despite the many benefits of this method, the choice of the extraction solvent is its main drawbacks [8]. The different modes of DLLME demonstrate that the convenient retrieval of organic solvents after extraction is of crucial importance in such techniques. It is critical, that the extraction solvent be of higher density than that of water, in order to form a stable cloudy solution capable of being separated by centrifuging. However, solvents with their densities higher than that of water are not often compatible with inductively coupled plasma-optical emission spectrometry (ICP-OES) and reverse phase HPLC. So, several

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0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.01.061

recent works have reported the use of low-density organic solvents in DLLME. But, most of these procedures require additional processing steps, apart from the mandatory centrifugation, including refrigeration to freeze the organic solvent, manually retrieving it to let it thaw, and use of additional materials such as surfactants [9].

These problems can be avoided by the new technique of dispersive-solid phase extraction (D-SPE) based on a ferrofluid. Ferrofluids are suspensions of single-domain magnetic nanoparticles suspended in various carriers such as water, ester and hydrocarbons. Magnetic suspension characteristically has both magnetic and fluid properties [10–12]. The particle volume fraction of the magnetic material in ferrofluid is typically only a few percent [13,14]. Since the concentration of the magnetic particles is low, 3–10%, many properties of the ferrofluid, such as density, vapor pressure, pour point and chemical properties of the liquid are similar to those of the base fluid. Two types of ferrofluids are available: ionic ferrofluid and surface ferrofluid depending on the method used to prevent the particles from aggregating by Vander Waals forces or magnetostatic interactions [15]. Steric repulsion prevents agglomeration of particles in surface ferrofluid while charged repulsion accounts for the stability in ionic ferrofluid. High stability of a ferrofluid is achieved through a combination of thermal motion as well as steric and electrostatic repulsive interactions, both working against Vander Waals and dipolar attractive interactions [16]. Remote control of the fluid flow by an externally applied magnetic field leads to attractive applications in dynamic loudspeakers, computer hard discs, dynamic sealing, electronic packing, mechanical engineering in high-vacuum equipment, laser systems in audio devices, electromagnetic shielding, high density digital storage, and biomedicine and magnetic cell separation such as enzyme and protein immobilization, genes, radiopharmaceuticals, magnetic resonance imaging MRI and diagnostics [17].

In this method, an appropriate amount of ferrofluid is injected rapidly into the aqueous sample by a syringe. The large contact surface between the sample and the sorbent speeds up the mass transference processes. Since the sorbent is highly dispersed in the aqueous phase, extraction can be achieved within a few seconds.

In the present report, for the first time, a new method of dispersive-solid phase extraction (D-SPE) based on a ferrofluid is proposed. The hydrophobic analytes are enriched in the extraction sorbent which is dispersed into the bulk aqueous solution. This technique is easily carried out.

To the best of our knowledge, there is no report on the use of D-SPE for the separation and preconcentration of inorganic or organic species. The present study has developed a quick method for the extraction of Pd(II) by D-SPE and its determination by FAAS. This method is simple, rapid and efficient for the extraction and preconcentration of Pd(II) from various samples. Furthermore, in comparison with solid phase extraction, it is much faster, since the extractant (sorbent) is highly dispersed in the aqueous phase.

2. Experimental

2.1. Apparatus

A Varian model AA-400 atomic absorption spectrometer (http://www.varianinc.com), equipped with an air–acetylene burner and with palladium hollow cathode lamp was used for the determination of palladium. The lamp was operated at 5 mA, using the wavelength at 244.8 nm and slit of 0.2 nm, and the flow rates of air and acetylene were set as recommended by the manufacturer. Background correction has been used with a deuterium lamp. All measurements were carried out in peak height mode. A pH-meter Model 692 from Metrohm (http://www.metrohm-ag.com, Herisau, Switzerland) equipped with a glass combination electrode was used for the pH measurements. In addition, for magnetic separations a strong neodymium–iron–boron ($Nd_2Fe_{12}B$) magnet (1.31 T) was used. A Field emission scanning electron microscope (FESEM), model S-4160 (www.hitachi.com/procurement/network/japan) was used for preparation of SEM images.

2.2. Reagents

All chemicals used were of analytical-reagent grade and all aqueous solutions were prepared using ultrapure water. 1-Octanol, sodium diethyldithiocarbamate trihydrate (DDTC), acetylacetone, acetic acid, tetraethyl orthosilicate (TEOS), and all used salts were purchased from Merck (Darmstadt, Germany). Standard stock solutions of Pd(II) were prepared by dissolving spectral pure grade chemical $PdCl_2$ ($1000\ \mu g\ mL^{-1}$ in 5% HNO_3; Merck, Darmstadt, Germany) in double distilled water with the addition of 5 mL of 12 $mol\ L^{-1}$ nitric acid and further diluted daily prior to use. A solution of $10^{-3}\ mol\ L^{-1}$ DDTC was prepared by dissolving appropriate amount of this reagent in pure ethanol. Nano-Fe_3O_4 was purchased from Sigma-Aldrich (http://www.sigmaaldrich.com, Fe_3O_4 spheres powder, <50 nm, purity $>98\%$). A buffer solution (pH=6.0, 1 $mol\ L^{-1}$) was prepared by mixing 50 mL potassium dihydrogen phosphate (1 $mol\ L^{-1}$) and 5.7 mL of sodium hydroxide (1 $mol\ L^{-1}$). High purity HNO_3 (65%, r ultrapure, Merck, Darmstadt, Germany), and HCl were used for digesting of dust sample throughout this work. The pipettes and vessels were cleaned before use by soaking in 10% nitric acid solution for at least 24 h and then rinsed thoroughly with ultrapure water.

2.3. Preparation of silica-coated magnetite nanoparticles

Fe_3O_4/SiO_2 NPs were synthesized according to the previously reported methods by some modification [18]. Briefly, Fe_3O_4 nanoparticles (2.0 g) were suspended in ethanol (200 mL) under sonication for 1 h. Concentrated ammonia (40 mL), deionized water (35 mL) and TEOS (1 mL) were added in sequence to the suspension. The mixture was sonicated for 1 h followed by vortex mixing for another 8 h. The silica-coated nanoparticles (SCMNPs) were collected by magnetic separation and were thoroughly washed with deionized water three times and then dried, yielding a fine powder. Fig. 1 shows the SEM image of the modified nanoparticles.

2.4. Sample preparation

The reference material GBW-07289 (soil) was employed for testing the accuracy of developed method.

Samples of road dust were collected from three different roadsides with dense traffic in Tehran. An amount of 1.0 g of homogenized dust sample 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 100 mL and pH of solution was adjusted to 6.0. Then 50 mL of this solution was poured into a Falcon tube. The obtained solution was analyzed following the experimental procedure.

2.5. Extraction procedures

2.5.1. Preparation of the ferrofluid

Acetic acid has been used as stabilizing agent. In order to coat SCMNPs with acetic acid 15 mg of the silica-coated magnetic nanoparticles and 100 μL of acetic acid were mixed in a vial and the mixture were heated at 90 °C under continuous stirring for 45 min to allow acetic acid adsorption. Then acetic acid-coated magnetite nanoparticles were dispersed in 200 μL 1-octanol. This suspension was sonicated for 30 min to obtain ferrofluid. The resulting suspension had a magnetite fraction of 9.3%.

2.5.2. Extraction

A schematic view of D-SPE experimental setup is shown in Fig. 2. The sample or standard solution containing Pd(II), DDTC (1×10^{-6} mol L^{-1}), NaNO$_3$ (0.5%, w/v) and buffer (pH=6.0, 1.0 mol L^{-1}) was poured to a 50 mL tube. Then ferrofluid was injected rapidly into the sample solution through a 1.0 mL syringe. Thereupon, ferrofluid was dispersed thoroughly in solution, and the extraction process was completed quickly. Subsequently, a strong magnet was placed at the bottom of the tube to let the ferrofluid settle. After about 2 min, the solution became limpid and supernatant was discarded simply by decanting it. Thereafter, the magnet was removed and 0.75 mL of acetylacetone was introduced to the vial to desorb the Pd(II) complex by sonication. Finally, the obtained mixture was exposed on the magnet and the clear solution of eluent, containing the eluted metal ions, was transferred to the glass tube. The analyte in the eluent were determined by FAAS.

3. Results and discussion

3.1. Organic solvent selection for preparation of the ferrofluid: type and volume

Several criteria in selecting the organic solvent phase should be met. Firstly, the solvent should be immiscible with aqueous solution. Secondly, the solvent should have a low vapor pressure to prevent loss during extraction. According to these criteria, 1-octanol was selected as a carrier to achieve stable ferrofluid. Moreover, it conceivably also has a particular affinity with the silica-coated magnetic particles because of the terminal hydroxyl moiety, so it was firmly confined within the silica-coated particles, preventing them from being lost during extraction.

In the next step, the minimum volume of 1-octanol required for a quantitative extraction of the Pd(II) was determined in the range of 100–400 μL. Accordingly, 200 μL of 1-octanol was enough to preconcentrate the metal ions, at the studied concentrations, using 50 mL of sample. For higher amounts of 1-octanol, the extraction efficiency was almost constant.

3.2. Selection of sorbent

In order to find the best sorbent for the preparation of ferrofluid, Fe$_3$O$_4$, Fe$_3$O$_4$/SiO$_2$, Fe$_3$O$_4$/acetic acid, Fe$_3$O$_4$/SiO$_2$/acetic acid and Fe$_3$O$_4$/SiO$_2$/SDS were examined. The stability of the suspensions was checked by qualitative observations of the sedimentation when the samples were placed on working table. Before this test, the samples were redispersed by ultrasound. The results of these experiments showed that the suspension of bare

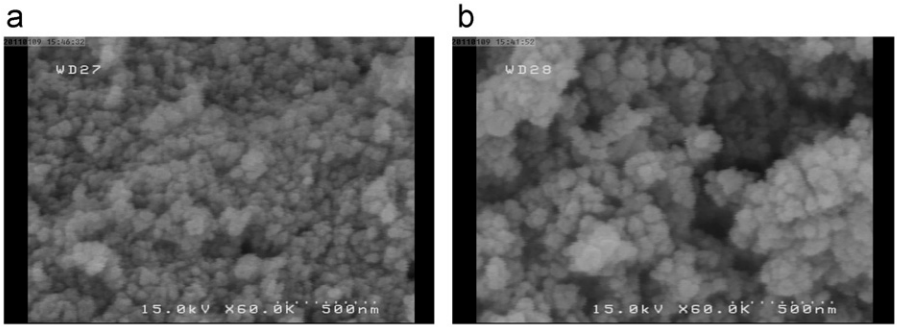

Fig. 1. SEM images of (a) Fe$_3$O$_4$ NPs and (b) silica-coated Fe$_3$O$_4$ NPs.

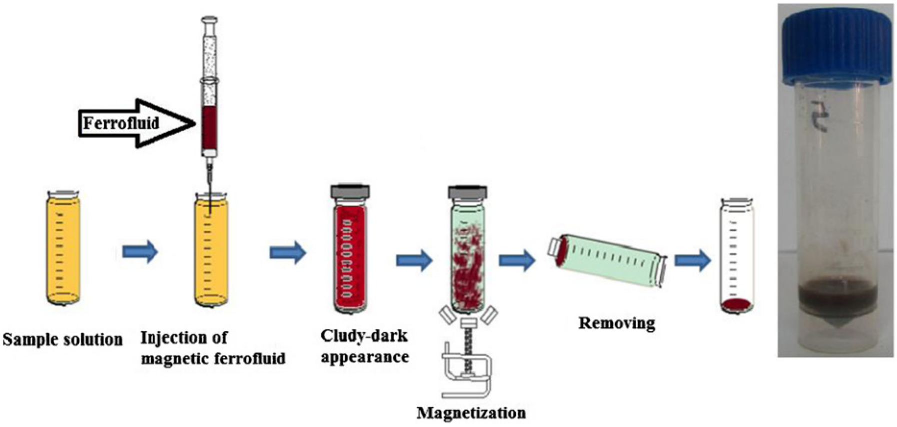

Fig. 2. Schematic view of D-SPE experimental setup.

nanoparticles (Fe_3O_4) was rather unstable. The same phenomena were observed for samples Fe_3O_4/SiO_2 and Fe_3O_4/acetic acid and Fe_3O_4/SiO_2/SDS. Although the sedimentation was a bit slower in this case, the suspension of Fe_3O_4/SiO_2/acetic acid did not exhibit phase separation even after 10 h of application. However, this sample was quickly redispersed by turning the tube upside down, without any remaining compact sediment at the bottom. The first conclusion that can be extracted is the fact that some kind of surface coating is needed to get a stable ferrofluid. In the oil-based ferrofluids, stability is achieved by steric repulsion between the dispersed particles frequently using silica adsorbed on their surface. Acetic acid has been used as stabilizing agent.

3.3. *Effect of pH*

pH plays an unique role on the metal–DDTC chelate formation and its subsequent extraction because the existing form of metal ions and DDTC is pH dependent. DDTC may decompose when the sample pH is too acidic. Thus, the effect of pH on the extraction efficiency of Pd(II) was evaluated in the pH range of 2–9. The results are shown in Fig. 3. As could be seen, the extraction recovery of Pd(II) increased as the pH in the aqueous solution increased from 2 to 6, and then decreased with further increasing pH from 7 to 9. DDTC acts as a bidentate ligand with S as donor atom. With the increase of pH, more negative charge of S in DDTC was beneficial for the formation of Pd–DDTC complex, resulting in the increase of extraction efficiency of metal ions [19]. Therefore, pH 6.0 was selected for subsequent experiments and real sample analysis.

3.4. *Study of the concentration of DDTC*

Palladium being a soft metal can be effectively complexed with ligands having soft donor atoms like ‘S’ and ‘N’ [20]. The influence of the DDTC concentration on the extraction of Pd(II) (0.1 μg mL^{-1}) was evaluated in the concentration range of 0.1–12 × 10^{-6} mol L^{-1} (Fig. 4). As can be seen, the extraction recovery of Pd increased with the increase of DDTC concentration up to 4 × 10^{-6} mol L^{-1}, and then remained constant. Because of some other ions that could be present in real samples and probably react with DDTC, a concentration of 6 × 10^{-6} mol L^{-1} was used in the experiments. The extraction recovery was not affected by the addition of excess ligand.

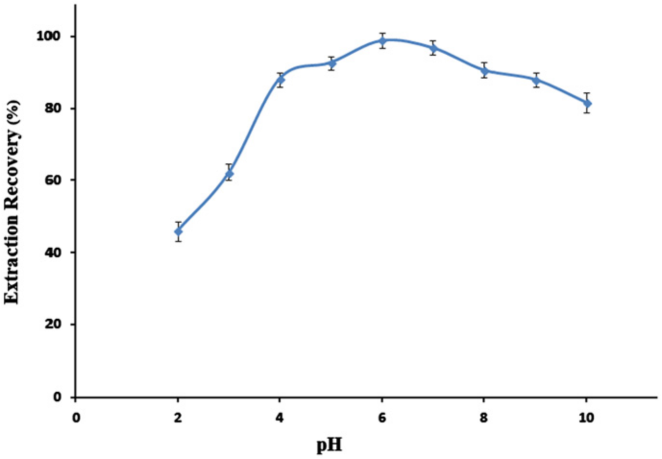

Fig. 3. Effect of pH on the extraction recovery of Pd(II). Sample volume, 50 mL; Pd(II), 0.1 μg mL^{-1}; concentration of DDTC, 6 × 10^{-6} mol L^{-1}; $NaNO_3$, 0.5% (w/v); amount of sorbent, 15 mg; 1-octanol, 200 μL; and eluent volume (acetylacetone), 0.75 mL (n=3).

3.5. *Effect of type and volume of eluent*

In order to find the best eluent for the retained palladium ions, various eluting solutions, such as HCl, HNO_3, thiourea, acetylacetone, ethanol, sodium thiosulfate and acetonitrile were used. As shown in Fig. 5, quantitative recoveries (above 90%) of palladium were obtained using acetylacetone.

The minimum volume of acetylacetone required for a quantitative elution of the retained analyte was 0.75 mL. Desorption times were evaluated in the range of 1–15 min. The results showed that 3 min time is sufficient for quantitative desorption of the palladium ions by 0.75 mL of the acetylacetone.

3.6. *Microextraction time and amount of sorbent*

In this experiment, extraction time means the time interval from the beginning of the dispersion and its end just before using an external magnetic field. The effect of extraction time was examined in the range of 1 s–5 min with the constant experimental conditions. As results clearly show, extraction time has no

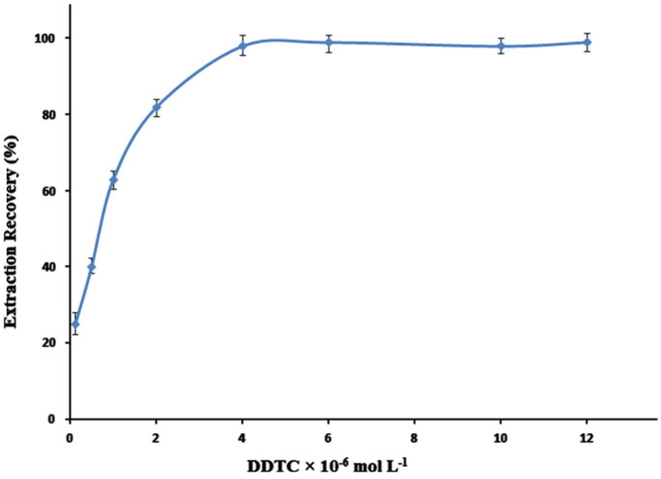

Fig. 4. Effect of DDTC concentration on the extraction recovery of Pd(II). Sample volume, 50 mL; pH of sample solution, 6.0; Pd(II), 0.1 μg mL^{-1}; $NaNO_3$, 0.5% (w/v); amount of sorbent, 15 mg; 1-octanol, 200 μL; and eluent volume (acetylacetone), 0.75 mL (n=3).

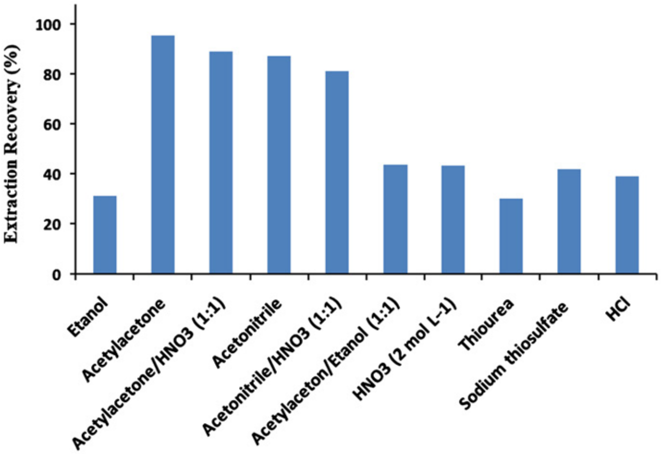

Fig. 5. Effect of type of eluent on the extraction recovery of Pd(II). Sample volume, 50 mL; pH of sample solution, 6.0; Pd(II), 0.1 μg mL^{-1}; $NaNO_3$, 0.5% (w/v); concentration of DDTC, 6 × 10^{-6} mol L^{-1}; amount of sorbent, 15 mg; 1-octanol, 200 μL; and eluent volume, 0.75 mL (n=3).

significant effect on the extraction efficiency, because the rate of extraction was extremely large. After the formation of a cloudy solution, the surface area between the dispersed sorbent and the aqueous phase is very large. Thereby, transition of the complex from the aqueous phase to the dispersed sorbent is fast. Subsequently, the equilibrium state is achieved quickly after injection of the ferrofluid into the sample solution. Thus, the most important advantage of D-SFE is time independence of the method. In the next step, the optimum amount of the sorbent for maximum takeup was determined in the range of 5–100 mg. Accordingly, 15.0 mg of modified magnetite NPs was enough to preconcentrate the metal ions, at the studied concentrations, using 50 mL of sample. For higher amounts of modified magnetic NPs, the extraction efficiency was almost constant.

3.7. *Breakthrough volume*

For this purpose, a series of solutions with increasing sample volumes containing 5.0 μg Pd(II) at pH 6.0 were investigated under the optimized conditions. The amount of Pd(II) was measured after elution by 0.75 mL of acetylacetone. As shown in Fig. 6, quantitative recovery for Pd(II) was obtained up to 200 mL of sample solution. The recovery decreased with increase of the sample volume, caused by the low concentration of metal ion in the solution. Therefore, an enrichment factor (EF) of 267 can be achieved when using 200 mL of the sample and 0.75 mL of the final volume.

3.8. *Effect of ionic strength*

The influence of ionic strength on the extraction of palladium was studied in the sodium nitrate solution with concentration ranged from 0% to 20% (w/v). The rest of the experimental conditions were kept constant. Results have shown that ionic strength has no considerable effect on extraction efficiency up to 5% (w/v) of $NaNO_3$.

3.9. *Sorption capacity*

The maximum palladium sorption capacity was studied using 20 mg of adsorbent, which was equilibrated with excess amounts of metal ion solution (50 ml, 30 mg L^{-1}) for 1 h under optimized conditions. After decantation of the mixture by applying an external magnetic field, the retained metal ions in the supernatant solution were determined by using FAAS. The maximum capacity was found to be 24.6 mg g^{-1} for Pd(II).

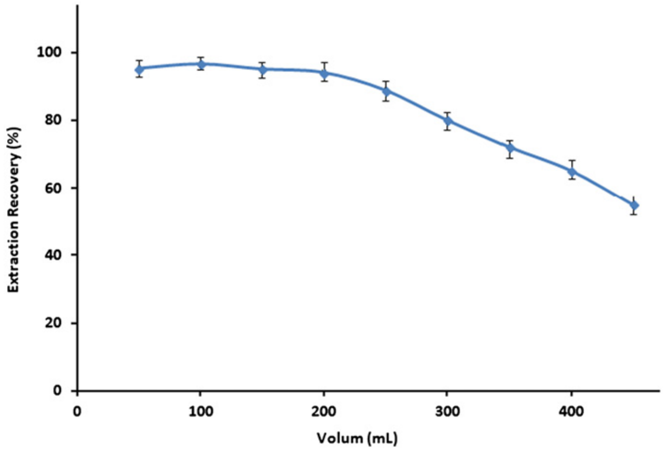

Fig. 6. Effect of sample volume on the extraction recovery of Pd(II). pH of sample solution, 6.0; Pd(II), 5 μg; concentration of DDTC, 6×10^{-6} mol L^{-1}; $NaNO_3$, 0.5 % (w/v); amount of sorbent, 15 mg; 1-octanol, 200 μL; and eluent volume (acetylacetone), 0.75 mL (n=3).

3.10. *Effect of coexisting ions*

The effects of common coexisting ions in the natural water samples on the recovery of Pd(II) were studied by spiking appropriate amounts of interfering ions to 50.0 mL of the solutions containing 0.08 μg mL^{-1} of Pd(II) and excess amounts of DDTC (as chelating agent) and they were treated according to the recommended procedure. The tolerance limits (defined as the ion concentration that produced an error not exceeding 5% causing a relative error of not more than 5%) are given in Table 1, and it was found that many cations and anions had no significant effects on the determination of Pd(II) ions under the optimized conditions. However, some of the species tried such as Al^{3+}, Zn^{2+} and Hg^{2+}, interfered with the determination of ions.

3.11. *Analytical figures of merit*

To evaluate the practical applicability of the proposed D-SFE method several analytical performance characteristics such as limit of detection (LOD), enrichment factor (EF) and linearity along with the relative standard deviation (RSD) were investigated under the optimized conditions. The limit of detection (LOD=0.35 μg L^{-1}) is 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. Linearity was observed over the range of 1–100 ng mL^{-1} with a correlation coefficient (R^2) of 0.9962. The precision of the method was evaluated by analyzing standard solution at 0.35 μg mL^{-1} of Pd for seven times in continuous, and the relative standard deviation (R.S.D) was 3.3%. The enrichment factor, calculated as the ratio of the initial volume to the final, was 267 for 50.0 mL sample solution.

Table 2 compares the characteristic data of the present method with those reported in literature. The proposed method possesses

Table 1
Effect of coexisting ions on recovery of 0.08 μg mL^{-1} Pd(II) (N=3).

Ions	Concentration (μg mL^{-1})	Recovery (%)
Na^+	10,000	98.1 ± 2.0
Li^+	10,000	97.5 ± 1.8
K^+	1000	98.4 ± 1.4
Ni^{2+}	100	101.3 ± 1.6
Co^{2+}	100	101.1 ± 1.7
Al^{3+}	10	98.4 ± 1.4
Al^{3+}[a]	50	96.3 ± 1.3
Pb^{2+}	100	97.1 ± 0.9
Ca^{2+}	1000	98.7 ± 0.6
Ba^{2+}	1000	97.5 ± 1.8
SO_4^{2-}	1000	98.0 ± 2.1
Cr^{3+}	100	102.4 ± 0.7
Zn^{2+}	50	104.0 ± 1.2
Zn^{2+}[a]	100	95.8 ± 1.2
Fe^{3+}	100	98.3 ± 0.9
Cu^{2+}	100	98.3 ± 0.8
Au^{3+}	100	96.7 ± 2.4
Ag^{1+}	100	99.1 ± 2.8
Hg^{2+}	50	101.3 ± 0.9
Hg^{2+}[a]	100	103.3 ± 1.3
Ca^{2+}	1000	102.6 ± 1.1
Mg^{2+}	1000	99.5 ± 1.3
Cl^{1-}	1000	102.9 ± 0.6
CO_3^{2-}	1000	102.2 ± 2.2
PO_4^{3-}	1000	97.8 ± 1.9
NO_3^{1-}	10,000	99.6 ± 0.8

[a] Using higher amounts of DDTC (L/M=50).

Table 2
Comparison of the published preconcentration methods for Pd with the proposed method.

Method	EF[a]	LOD (µg L^{-1})	RSD (%)	Linear range(µg L^{-1})	Sorption capacity(mg g^{-1})	Ref.
SPE–FAAS	75	1.2	1.7		4.06	[21]
SPE-–ICP-OES	10	0.44	2.3	–	7.6	[22]
CPE–FAAS	32[b]	1.6	2.7	–	–	[4]
Coprecipitation	100	0.4	6.3	–	–	[23]
SPE–FAAS	–	17	1.7	0.20–4.00[e]	0.141[f]	[24]
FIA–SPE–FAAS	57[b]	1.7	2.8	0.05–1.0[e]	–	[25]
SPE–FAAS	–	3.9	1.7	0.04–0.4[e]	0.1787[f]	[26]
FIA–SPE–FAAS	80	1.0	2.4	0–200	–	[2]
SPE–ICP-AES	100	0.2	3.2	1–1000	5	[27]
D-DLLME–GFAAS	96[c]	7.6[d]	4.5	0.05–8.0	–	[28]
DLLME–GFAAS	156	2.4[d]	4.3	0.1–5	–	[5]
D-SPE–FAAS	267	0.35	3.3	1–100	24.6	Our work

[a] EF: ratio of the aqueous phase to final volume of eluent phase.
[b] Preconcentration factor.
[c] Enhancement factor.
[d] ng L^{-1}.
[e] µg mL^{-1}.
[f] m mol g^{-1}.

lower limit of detection and higher enrichment factor than those of the reported methods. The sample preparation time is further decreased by the fact that sorbent dispersed in the bulk solution, extraction can be achieved very fast and no centrifugation is required for phase separation. These significant features which were obtained with this method are of key interest for routine trace laboratory analysis.

3.12. *Analytical applications*

The method was validated by analysis of a certified reference material GBW-07289 (soil). The result obtained (2.6 ± 0.1 µg kg^{-1}, n=5) is in good agreement with the certified value (2.3 ± 0.2 µg kg^{-1}). Moreover, the proposed method has been applied for the determination of trace Pd(II) in road dust and river water, lake water and tap water samples. All water samples were filtered through a 0.45 µm membrane filter and analyzed as soon as possible after sampling. The standard addition method was used and a good correlation was obtained between the added and measured amounts. Generally, the recoveries of Pd(II) ions were obtained in the range between 95.6% and 102.6%. The results are listed in Table 3.

4. Conclusions

A method of D-SPE was developed for the determination of trace Pd(II) in dust and environmental water samples. The extraction of Pd(II) was performed by D-SPE using ferrofluid as the extraction solvent and sodium diethyldithiocarbamate sodium trihydrate (DDTC) as the chelating agent. This technique is easily carried out. Furthermore, in comparison with solid phase extraction, it is much faster, because the sorbent is highly dispersed in the aqueous phase and no centrifugation is required for phase separation. In this way, the separation of sorbent from the aqueous bulk was achieved without using conical bottom glass tubes, which are easily damaged and hard to clean. D-SPE is very simple, of low cost and suitable for batch operations, which could greatly shorten the sample preparation time. The precision and accuracy of the method were satisfactory. An enrichment factor of 267 for a 200 mL sample volume was accomplished. The maximum adsorption capacity for Pd(II) was found to be 24.6 mg g^{-1}.

Table 3
Analytical results for Pd(II) determination in different samples.

Sample	Spiked (ng mL^{-1})	Found (ng mL^{-1})[a]	Recovery (%)
Sea water[b]	0	ND	–
	15	14.8 ± 0.6	98.6
	30	29.3 ± 1.1	97.6
River water[c]	0	1.2 ± 0.1	–
	15	15.9 ± 0.7	98.1
	30	31.7 ± 1.4	101.6
Well water	0	ND	–
	15	15.4 ± 0.6	102.6
	30	29.5 ± 1.3	98.3
Road dust	0	0.2 ± 0.1 µg g^{-1}	–
	20	19.3 ± 1.0 µg g^{-1}	95.5

[a] Mean ± SD, (n=5).
[b] Caspian sea water.
[c] From Tajan river.

Acknowledgments

Support of this investigation by the Research Council of University of Tehran through a Grant is gratefully acknowledged.

References

[1] R. Li, Q. He, Z. Hu, S. Zhang, L. Zhang, X. Chang, Anal. Chim. Acta 713 (2012) 136–144.
[2] R.S. Praveen, S. Daniel, T.P. Rao, S. Sampath, K.S. Rao, Talanta 70 (2006) 437–443.
[3] M.V.B. Krishna, M. Ranjit, K. Chandrasekaran, G. Venkateswarlu, D. Karunasagar, Talanta 79 (2009) 1454–1463.
[4] M. Ghaedi, A. Shokrollahi, K. Niknam, E. Niknam, A. Najibi, M. Soylak, J. Hazard. Mater. 168 (2009) 1022–1027.
[5] P. Liang, E. Zhao, F. Li, Talanta 77 (2009) 1854–1857.
[6] B. Gómez, M.A. Palacios, M. Gómez, J.L. Sanchez, G. Morrison, S. Rauch, C. McLeod, R. Ma, S. Caroli, A. Alimonti, F. Petrucci, B. Bocca, P. Schramel, M. Zischka, C. Petterson, U. Wass, Sci. Total Environ. 299 (2002) 1–19.
[7] A. Bagheri, M. Taghizadeh, M. Behbahani, A. Akbar Asgharinezhad, M. Salarian, A. Dehghani, H. Ebrahimzadeh, M.M. Amini, Talanta 99 (2012) 132–139.
[8] H.K.L. Zhi-Guo Shi, Anal. Chem. 82 (2010) 1540–1545.
[9] M. Rezaee, Y. Yamini, A. Khanchi, M. Faraji, A. Saleh, J. Hazard. Mater. 178 (2010) 766–770.
[10] C.-L. Lin, C.-F. Lee, W.-Y. Chiu, J. Colloid Interface Sci. 291 (2005) 411–420.
[11] Y.X. Zhao, L. Zhuang, H. Shen, W. Zhang, Z.J. Shao, J. Magn. Magn. Mater. 321 (2009) 377–381.

[12] Y. Zhai, F. Liu, Q. Zhang, G. Gao, Colloids Surf. A 332 (2009) 98–102.

[13] L. Lin, J. Li, J. Fu, Y. Lin, X. Liu, Mater. Chem. Phys. 134 (2012) 407–411.

[14] J. Li, X. Qiu, Y. Lin, X. Liu, R. Gao, A. Wang, Appl. Surf. Sci. 256 (2010) 6977–6981.

[15] A. Zefczak, J. Magn. Magn. Mater. 321 (2009) 2225–2231.

[16] S.Z. Zhang, R.Y. Hong, Y.P. Han, H.Z. Li, J. Ding, Y. Zheng, Powder Technol. 170 (2006) 1–11.

[17] C. Holm, J.J. Weis, Curr. Opinion Colloid Interface Sci. 10 (2005) 133–140.

[18] L. Zhu, D. Pan, L. Ding, F. Tang, Q. Zhang, Q. Liu, S. Yao, Talanta 80 (2010) 1873–1880.

[19] X. Guo, M. He, B. Chen, B. Hu, Talanta 94 (2012) 70–76.

[20] E. Mladenova, I. Dakova, I. Karadjova, M. Karadjov, Microchem. J. 101 (2012) 59–64.

[21] Ş. Tokalıoğlu, T. Oymak, Ş. Kartal, Anal. Chim. Acta 511 (2004) 255–260.

[22] C. Hang, B. Hu, Z. Jiang, N. Zhang, Talanta 71 (2007) 1239–1245.

[23] N. Ozturk, V.N. Bulut, C. Duran, M. Soylak, Desalination 270 (2011) 130–134.

[24] S. Zhang, Q. Pu, P. Liu, Q. Sun, Z. Su, Anal. Chim. Acta 452 (2002) 223–230.

[25] T. Çetin, Ş. Tokalıoğlu, A. Ülgen, S. Şahan, İ. Özentürk, C. Soykan, Talanta http://dx.doi/org/10.1016/j.talanta.2012.10.054, in press.

[26] X.Z. Wu, P. Liu, Q.S. Pu, Q.Y. Sun, Z.X. Su, Talanta 62 (2004) 918–923.

[27] M.R. Jamali, Y. Assadi, F. Shemirani, M. Salavati-Niasari, Talanta 71 (2007) 1524–1529.

[28] P.L.E. Zhao, Microchim. Acta 174 (2011) 153–158.