



## Surface Modified Nanomagnetite-Assisted Hollow Fiber Solid/ Liquid Phase Microextraction for Pre-concentration and Determination of Palladium in Water Samples by Differential Pulse Voltammetry

Zarrin Es'haghi<sup>\*</sup>, Fatemeh Moeinpour

<sup>\*</sup>*Department of Chemistry, Payame Noor University, P.O. Box 19395-4697, Tehran, Iran*

<sup>\*</sup> E-mail: [eshaghi@pnu.ac.ir](mailto:eshaghi@pnu.ac.ir)

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### ABSTRACT

An efficient separation-preconcentration procedure namely hollow fiber solid/liquid phase microextraction (HF-SLPME) was developed for determination of trace amounts of palladium in water samples by differential pulse voltammetry. In this method, a hybrid sorbent utilizing functionalized nanoparticles incorporated in an organic solvent was used as the extractor phase. The nanoparticle dispersed in the organic solvent is held in the pores and lumen of a porous polypropylene hollow fiber. It is in contact directly with the aqueous donor phase. The influence of the various analytical parameters such as pH, kind and amounts of nanoparticle and matrix effects, sample volume, extraction time, etc. were studied for the quantitative recoveries of the analyte ions. Under the optimized experimental conditions, the calibration curves for Pd (II) was linear from 0.1 to 500 ng/mL. The relative standard deviation for seven replicate determinations of 0.1 mg/mL palladium in the standard solutions was 3.95 %. The detection limit based on  $3S_b$  for Pd (II) in the standard solutions was 0.01 ng/mL. The proposed method has been applied for determination of trace amounts of palladium in the real water samples and satisfactory results were obtained.

**KEYWORDS:** Palladium; Nanomagnetite; Hollow Fiber Solid/Liquid Phase Microextraction; Differential Pulse Voltammetry.

### 1. INTRODUCTION

Palladium, together with rhodium, ruthenium, osmium, iridium and platinum form a group of elements referred to as the platinum group metals (PGM). Palladium itself has been used as a precious metal in jewelry since 1939, as an alternative to platinum for making white gold [1].

Palladium is regarded as of low toxicity, being poorly adsorbed by the body when ingested. It may cause skin, eye or respiratory tract irritation and should be regarded as highly toxic and as carcinogenic. Although, there is only little information available on the carcinogenic potential of palladium. But there are reports that; mice given palladium (II) chloride at 5 mg Pd(II) /liter in drinking-water (corresponding to about 1.2 mg Pd(II)/kg body weight per day by assuming a body weight of (0.03) kg and a daily water uptake of (7.0 mL) over a lifetime (from weaning to natural death) developed tumors in mice. Cytotoxic effects of palladium (II) chloride has been proved too [2].

Due to palladium increasing use and the toxicity of Pd(II) compound to living organisms, determination of palladium is necessary in environmental samples. On the other hand, owing to low concentration of Pd in industrial and environmental samples and complexity of the matrix sample, application of sample enrichment

procedures is necessary before detection of the analyte. Since different extraction methods have been used for palladium preconcentration. The following methods can be noted. Dispersive liquid-liquid microextraction [3-5] solid phase extraction [6-9] cloud point extraction [10-11]; solid phase microextraction [12].

The purpose of this work is to prepare a small microextraction device for improving the extraction performance of liquid phase and solid phase microextraction techniques.

Recently, our group provided a new method namely hollow fiber solid-liquid phase microextraction (HF-SLPME) in which we have combined hollow fiber liquid phase microextraction with solid phase extraction and benefited from the advantages of both [13-14].

In this technique, incorporation of chemically surface modified nanoparticles in organic solvent that was supported by a piece of polypropylene hollow fiber improved microextraction performance. Nanoparticles incorporated in the membrane system could act as a nanoscale solid phase extractant with high surface area. It has provided high enrichment factor of analyte. HF-SLPME is used in two-phase and three-phase modes. This research describes the implementation of a two phase HF-SLPME mode consisting of an aqueous phase (donor phase) and organic solvent/surface modi-

fied nanoparticles (acceptor phase) operated in direct immersion sampling mode.

It is a sample preparation method developed to solve some of the analytical challenges of liquid phase and solid phase sample preparation methods. Since its development, the utilization of HF-SLPME has addressed the need to facilitate rapid sample preparation and integrate sampling, extraction, concentration method. This achievement resulted in fast adoption of the technique in many fields of analytical chemistry and successful hyphenation to continuously developing sophisticated separation and detection systems. However, the facilitation of high-quality analytical methods in combination with HF-SLPME requires optimization of the parameters that affect the extraction efficiency of this sample preparation method. Therefore, the objective of the current work is to provide a detailed sequence of SLPME optimization steps that can be applied toward development of LPME and SPME methods for a wide range of analytical applications.

## 2. EXPERIMENTAL

### 2.1. Chemical and reagents

Sodium and potassium chloride, palladium chloride and other used chemicals were purchased from Merck (Darmstadt, Germany). Stock solution of 500 mg/L of Pd(II) ion, were prepared by dissolving appropriate amount of palladium chloride in de-ionized water. Working standard solutions were prepared daily by dilution of the stock solutions and stored in the dark at 20°C.

Buffer solutions; pH 2.0, 2.5 and 3.4 were prepared by mixing 0.1M sodium hydroxide and 0.01M nitric acid solutions in suitable ratio. 0.1 M NaClO<sub>4</sub> was used as supporting electrolyte. All the glass wares were cleaned by soaking in 3M HNO<sub>3</sub> solution and then rinsed with distilled water prior to use. All reagents used were of analytical grade.

The accrual Q3/2 polypropylene hollow fiber membrane used here was obtained from Membrana (Wuppertal, Germany). The wall thickness of the fiber was 200 μm, the inner diameter was 600 μm and the pore size was 0.2 μm. The MWCNTs with 10–40 nm diameters, 1–25 μm length, core diameter 5–10 nm, BET surface area (SBET) 40–600 m<sup>2</sup>g<sup>-1</sup>, V total 0.9 cm<sup>3</sup> g/L, bulk density 0.1 g/cm<sup>3</sup>, true density 2.1 g/cm<sup>3</sup> and with 98% < purity were purchased from Research Institute of the Petroleum Industry (Tehran, Iran). Nanomagnetite (NMG) was synthesized, purified and functionalized in our laboratory.

### 2.2. Electrochemical Measurements

All the differential pulse voltammetry (DPV) measurements were done by Metrohm (Herisau, Switzerland) autolab potentiostats/galvanostats (Model PGSTAT-128N) using a standard cell with three electrodes. The working electrode was a graphite electrode. The reference electrode was the Ag/AgCl/3M KCl electrode and the auxiliary electrode was a platinum wire. The analyzed samples were deoxygenated prior

to measurements by purging with nitrogen (99.999%), saturated with water for 300 s. All voltammograms carried out by DP mode.

To measure the pH values of the solutions, a 827 Metrohm pH meter was used. All experiments were carried out at room temperature.

### 2.3. Activation of carbon nanotubes

Based on our previous experiences, MWCNT were dispersed in H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> (70:30, v/v) and was refluxed for 3h to introduced oxygen groups (COOH, C=O, OH) on the MWCNT surface. After that, the functionalized MWCNTs were filtered through cellulose membrane filter (Millipore) of 0.45 μm pore size. The filtrate was washed with deionized water to remove remaining oxidant until a pH of 7.0 was reached. Finally, Functionalized MWCNTs dried at 70°C for 1h.

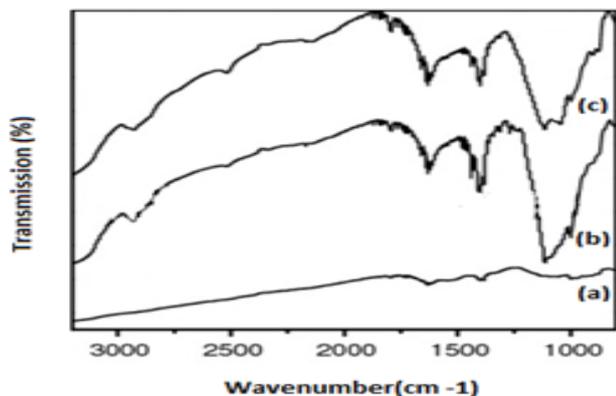
### 2.4. Synthesis and surface modification of nanomagnetite

First of all, Fe<sub>3</sub>O<sub>4</sub> nanomagnetites are synthesized by co-precipitation method from aqueous FeCl<sub>3</sub>/FeCl<sub>2</sub> salt solution by addition of base under inert atmosphere at room temperature. The modification of these MNPS With a suitable coating has proven to be one of the most efficient ways. Therefore, functionalization of particles with suitable reagents which have functional group for selective extraction or removal of organic or inorganic pollutant is a requirement for future applications. The modified sorbent Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> were synthesized via two steps. First, a magnetic silica support was prepared using nanomagnetite as the core and tetraethoxysilane (TEOS) as silica source. Second, the anatase nano TiO<sub>2</sub> was coated on the SiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> particle surface using tetrabutyltitanate (TBOT) as titanium source. TiO<sub>2</sub>/SiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> were used for extraction and determination of Pd(II) in aqueous solutions. The details are as follow:

0.1 g of obtained Fe<sub>3</sub>O<sub>4</sub> (nanomagnetite) particles was dispersed into the mixture solution of 80 mL of ethanol and 20 mL of de-ionized water and 1.0 mL of concentrated ammonia aqueous solution (28 wt%). After this, the mixture solution was homogenized by ultrasonic for 30 min to form a uniform dispersion. Subsequently, certain of tetraethoxysilane (TEOS) was added drop wise into solution with vigorous stirring. After stirred at room temperature for 6 h, the product was separated with a permanent magnet, washed with deionized water for 3 times and dried in vacuum at 50 °C for 12 h. Synthesized SiO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> was used in the next step for further modification.

The above SiO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> particles were dispersed in 40 mL of ethanol and homogenized by ultrasonic for 30 min. After that, an appropriate amount of tetrabutyltitanate (TBOT) and glacial acetic acid (volume ratio 45:1) were orderly introduced to the solution under vigorous mechanical stirring. After stirred at room temperature for 4 h, 15 mL of ethanol and 3.0 mL of deionized water were added to the system, and then the solution was heated at 45°C. The final product was dried in vacuum at 50 °C and calcined under nitrogen

at 500°C for 3 h.  $\text{TiO}_2/\text{SiO}_2\text{-Fe}_3\text{O}_4$  particles were prepared and used in the extraction section (see Fig. 1).



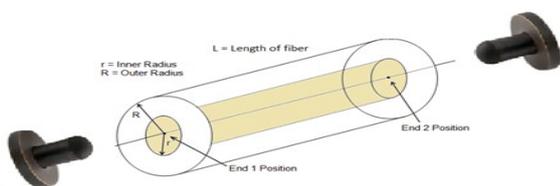
**Fig. 1.** FT-IR spectra of (a)  $\text{Fe}_3\text{O}_4$ , (b)  $\text{SiO}_2/\text{Fe}_3\text{O}_4$ , (c)  $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ .

As our experiences by using layer-by-layer chemical technique, a core-shell structure of  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  composite was prepared by coating magnetite core particles with silica and titania. Direct deposition of titania onto the surface of magnetic iron oxide would decrease the efficiency due to the dissolution of magnetite and the transfer of electrons-holes from  $\text{TiO}_2$  to core particle. Thus, an intermediate passive  $\text{SiO}_2$  layer between magnetite and titania is required to prevent the dissolution.  $\text{TiO}_2$  particles were deposited on silica coated  $\text{Fe}_2\text{O}_3$  by mixing them and followed by calcination.

### 2.5. Fiber treatment

The polypropylene hollow fibers were cut into segments of 2 cm. These segments were soaked in acetone for thirty minutes, for remove impurities and then dried in air directly.

The appropriate amount of functionalized nanoparticles was dispersed in 2.0 mL n-octanol and ultrasonicated to obtain a homogeneous mixture. It was injected into lumen of cleaned hollow fiber segments (8  $\mu\text{L}$ ). Then two sides the polypropylene tube sealed at both ends by magnetic stoppers. The devices were washed with de-ionized-water and then dried in air directly. The fibers were placed into the sample solution and operated as a pseudo-stir bar device. A simple scheme of the HF-SLPME device is presented in Fig. 2.



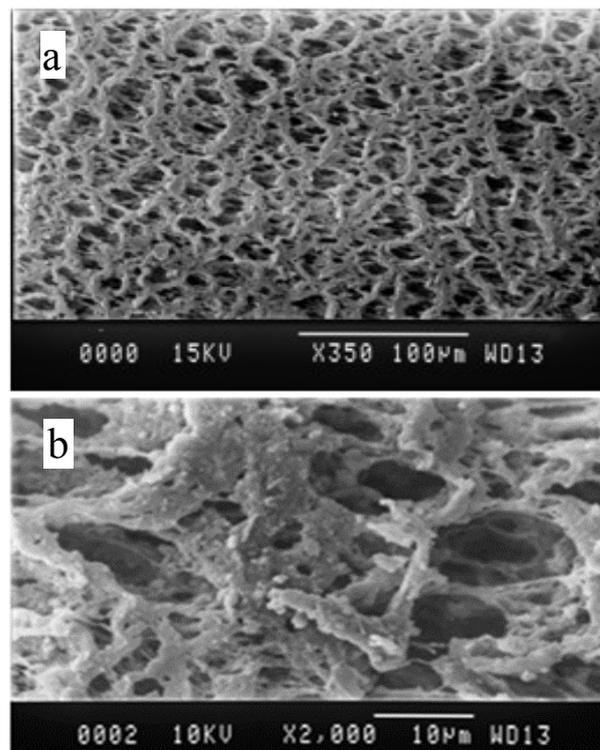
**Fig. 2.** Simple scheme of pseudo stir bar device. L: 2.0 cm; r: 300  $\mu\text{m}$ ; R: 500  $\mu\text{m}$ , inner fiber volume: 6.0  $\mu\text{L}$  (The fiber and stoppers are not shown to scale).

### 2.6. Extraction and pre-concentration of palladium (II) procedure

HF-SLPME that was used in this research is a two-phase microextraction technique consisting of an

aqueous donor phase and n-octanol reinforced with nano-particles as the extractor phase. The extractor phase was supported by a piece of polypropylene hollow fiber membrane which operated in direct immersion sampling mode. The functionalized nanomagnetite (or MWCNTs) dispersed in the 2.0 mL of n-octanol was held into the lumen of fiber and pores of porous fiber wall supported by sonification. It was in contact with aqueous donor phase. The analyte from the aqueous sample diffused through the fiber pores into n-octanol and on the functionalized nanomagnetite surface, which was dispersed in n-octanol. The analyte was trapped on a solid sorbent and in an organic solvent simultaneously.

All microextraction experiments in this research were performed using a polypropylene hollow fiber membrane. The scanning electron microscopy of a polypropylene hollow fiber, before and after filling with n-octanol/nanomagnetite was shown in Fig. 3 (a) and (b). For the HF-SLPME extraction, an aliquot of 5.0 mL of a solution containing, Pd(II) in optimized pH was added to an appropriate volumetric flask. The fiber after treatment was placed into the sample solution present in the vial and it was operated as a pseudo-stir bar sorption. The samples were stirred at 400 rpm for 30 min. After that two fiber stoppers were ejected and hollow fiber placed into a vial containing 3.0 mL, 2M  $\text{HNO}_3$  and shaken at 600 rpm for 15 minutes. Extracted transferred into a voltammetry cell and was brought to volume of 15.0 mL with  $\text{NaClO}_4$  0.01 M as the supporting electrolyte, until then be prepared for differential pulse voltammetry analysis.



**Fig. 3.** Scanning electron microscopy; (a) polypropylene hollow fiber, (b) polypropylene hollow fiber filled with n-octanol/F-MWCNTs mixture.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of donor phase pH

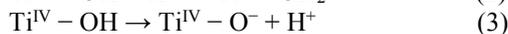
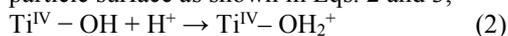
Metal ion adsorption on all adsorbents is pH-dependent [15-16]. The pH of the feed solution affects the solubility of metal ions and the surface characteristics of sorbents [17].

The effects of the initial pH on palladium removal at pH 2.0–4.0 are shown in Fig. 4. Fluctuations above the pH value of 4 were observed that might be justified by the formation of insoluble metal hydroxide in the solution. Thus, studies beyond pH 5.0 were not attempted as the precipitation of the ions as hydroxides would have occurred. The adsorbed palladium by surface modified nanomagnetite increased when the solution pH increased from 2.0 and reached the maximum value at pH 2.5. On the other hand the pH dependency of removal efficiency could be explained by the functional groups involved in the metal uptake. At low pH values, the protons of hydroxyl functional groups are very difficult to dissociate, which increases the protonation of these groups on the surface. On the other hand, a large number of  $H^+$  the solution competed with Pd(II) for the adsorption sites [18]. When the pH values increased, the negatively charged density on the sorbent surface increased because of the de-protonation of the metal-binding sites. Therefore, the uptake of metal ions (positive charge) increased.

From another perspective, the surface of  $Fe_3O_4/SiO_2/TiO_2$  nanoparticles dispersed in water is generally covered by hydroxyl group as shown in Eq. 1,

$$Ti^{IV} + H_2O \rightarrow Ti^{IV} - OH + H^+ \quad (1)$$

The surface charge of titanium is a function of solution pH, which is affected by the reactions that occur on the particle surface as shown in Eqs. 2 and 3,



The pH at which the surface of titania is neutral is point of zero charge or isoelectric point. When pH is less than  $pH_{PZC}$  ( $pH_{IEP}$ ), Eq. 2 results in creation of the positive surface charge. When pH is larger than  $pH_{PZC}$  ( $pH_{IEP}$ ), Eq. 3 results in creation of the negative surface charge [19].

Increase in particle surface charge (zeta potential) can enhance the electrostatic repulsive force, suppress the agglomeration and increase the effective surface area of nanoparticle. According to the results optimum pH was 2.5 for palladium (II) uptake.

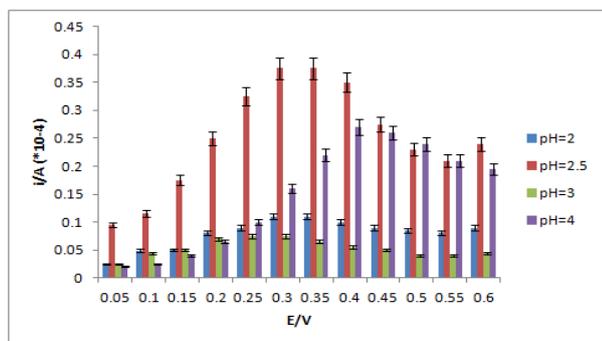


Fig. 4. pH effect on the Pd(II) extraction.

#### 3.2. Effect of nanomagnetite concentration

In the beginning based on our previous researches, we used of multiwalled carbon nanotube. For this purpose we examined adding varied amount of functionalized MWCNTs per 2.0 mL of n-octanol (40, 50 and 60 mg). The results were reasonably good. But as a novel experience, we prefer to use a new nanoparticle. So we used the coated surface nanomagnetite. The good results obtained in this case too.

The second factor studied was the concentration of nanoparticle. Varied amount of  $Fe_3O_4/SiO_2/TiO_2$ , 40 to 60 mg per 2.0 mL n-octanol, were examined at feed solution pH 2.5. The results are obvious in Fig. 5. The optimal was 60.0 mg/2.0 mL n-octanol, but according to the high concentration of the mixture and the problems caused by its injection into the fiber, preferably the amount of 50 mg  $Fe_3O_4/SiO_2/TiO_2$  was used in other experiments.

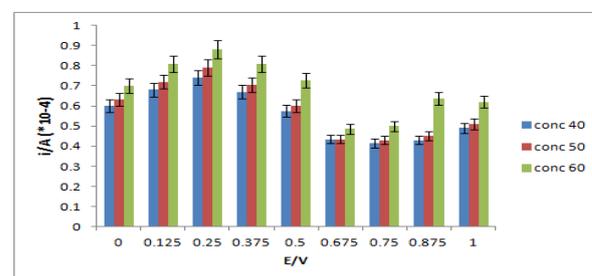


Fig. 5. Effect of  $Fe_3O_4/SiO_2/TiO_2$  amount in the extraction of Pd(II).

#### 3.3. Effect of donor phase volume

HF-SLPME is a type of equilibrium extraction and there exist equilibrium in this system: the equilibrium of an analyte in the donor solution and the acceptor phase (n-octanol/nano  $Fe_3O_4/SiO_2/TiO_2$ ). So, increase the volume of the feed will lead to increased analyte pre-concentration factor [20-21].

As show in Fig. 6, up to 15 mL, with increasing donor phase volume increase pre-concentration factor of palladium, but no obvious increase was obtained for feed volumes of 20.0 mL. Hence, feed volume of 15.0 mL was applied to subsequent experiments.

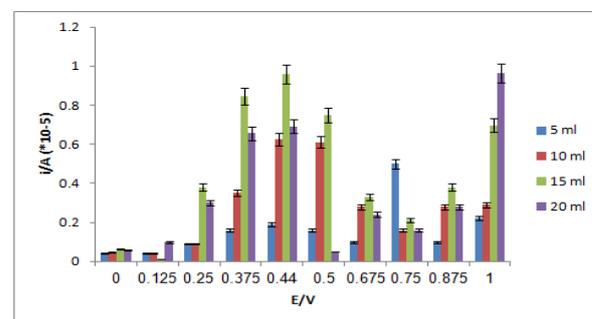


Fig. 6. Effect of volume of the donor solution on the extraction efficiency.

#### 3.4. Salt effect

It is well known that phase separation occurs from phases of aqueous solution and organic solvent/non-absorbent upon the addition of electrolytes to the sys-

tem. The salting-out is due to the decreased solubility of analyte in water in the presence of electrolytes. In this work NaCl was added to donor phase at 1%, 2%, 5% and 10% w/v. Pre-concentration factor of palladium increased up to 4 times in 10% w/v NaCl.

### 3.5. Selection of desorption solvent

The desorption solvent plays important role at solid phase microextraction. The influence of desorption solvent and amount on extraction recovery of palladium (II) was investigated by changing kind and concentration of the solvents and keeping other variables constant. We examined nitric acid, methanol and their mixture as the analyte recovery solvent according to the previous works. In the separation experiments 0.5 to 3.0 mL desorption solvent that was included methanol and nitric acid 2 mol/L. The results shown methanol doesn't have positive effect on extraction, actually with increasing volume percent of methanol in desorption solvent, pre-concentration factor decreased rapidly. Thus the nitric acid was used as the recovery solvent. The concentrations 0.5 to 4.0 molL<sup>-1</sup> HNO<sub>3</sub> examined. It has been found that at HNO<sub>3</sub> concentration higher than at concentrations lower than 0.5 mol/L, solvent capacity was insufficient to analyte recovery. 3.0 mol/L no significant variations in the extraction yield occurs and better result obtained at 3.0 mL, 3 mol/L HNO<sub>3</sub> with curve slope R<sup>2</sup>: 0.9505 and equation Y=0.0183X+0.0453. For method development we examined effect of some ligands such as benzythiosemicarbazone and diphenylglyoxim, but no significant increase in the extraction yield occurs. Thus, 3.0 mL of 3.0 mol/L concentration of HNO<sub>3</sub> solution was chosen as optimal to achieve higher efficiency.

### 3.6. Effect of other salts on the palladium extraction

In this work, analyte extraction efficiency has been tested in the presence of some cations and anions. For detection interferences, the influence of several ions was tested. The effect of interfering ions at different concentrations on the signal of a solution containing 1 µg l<sup>-1</sup> of palladium was studied. An ion was considered to interfere when its presence produced a variation in the current of the sample of more than 5%. Among the interfering ions tested, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, Li<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup> (Ion/Pd (II) (w/w) = 1000) did not interfere at palladium determination.

### 3.7. Figures of merit

Under the optimized conditions, the analytical performance of the HF-SLPME/DPV technique was evaluated. The detection limits (calculated as three times the standard deviation (3σ) of the blank signal), limit of quantification (10σ), relative standard deviations (RSD%) and pre-concentration factor were determined and are listed in Table 1. The pre-concentration factor that is ratio of concentration between acceptor phase and initial donor phase aqueous solution for palladium was determined. For determination of this factor, peak currents after extraction of analyte should be divided to

peak currents before extraction at the same concentration and conditions. For doing this, after extraction of analyte onto the sorbent. It was desorbed with 3.0 mL of HNO<sub>3</sub> solution (3.0 mol/L).

**Table 1.** Performance of the method.

PF*	LOD µg L <sup>-1</sup>	LOQ µg L <sup>-1</sup>	Linear rang µg L <sup>-1</sup>	R <sup>2</sup>	RSD% n=5
4583	0.01	0.02	0.1-500	0.943	3.95

\*Pre-concentration Factor

Then the 1.0 mL of this solution was diluted with supporting electrolyte up to 10 mL. Thus peak current after extraction divided to peak current before extraction multiple by dilution factor. The volume of donor phase was 15.0 mL and 8 µL of the mixture containing 50 mg Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> per 2.0 mL octanol was the acceptor phase volume.

### 3.8. Real sample analysis

The accuracy and applicability of the proposed method has been applied to the determination of palladium in environmental water samples. Thus, for accessing the capability of the method for real samples with different matrices, the method was applied to pre-concentration and determination of palladium of water samples. Samples were collected in clean, plastic bottles that have been rinsed three times prior to use. Sampling from distribution systems was done after the lines have been flushed sufficiently to ensure that the sample is representative of the supply. Due to the problems of absorption or precipitation, the samples, were acidified to pH <2 as soon as possible after collection. All real water samples were filtered before reflected by the extraction process. According to the results, the concentration of palladium in analyzed water samples was below the LOD of the method. The suitability of the proposed method for the analysis of natural water samples was checked by spiking samples with 0.1 µg l<sup>-1</sup> of palladium. Good recoveries (85%) were achieved for all analyzed samples. The data obtained with the proposed method were presented in Table 2.

## 4. CONCLUSIONS

Hollow fiber solid liquid phase microextraction combined with differential pulse voltammetry (HF-SLPME/DPV) measure easily palladium (II) at µg/L level in real water samples. Many advantages obtained such as; high sensitivity, little sample solution, simplicity, high linear range and limit of detection at µg/L. In desorption stage, the pore structure of the polypropylene fiber allows rapid exit of the analyte from the sorbent in the enriched solvent. The disposable nature of the hollow fiber completely eliminates the possibility of sample carry-over and ensures high reproducibility. In addition, the small pore size prevents large molecules in the matrix and unsolved particles in the donor solution from entering the acceptor phase, thus yielding a very clean extract. A review of selected methods which used in the determination of palladium in real samples is shown in Table 3.

**Table 2.** Relative Recovery of palladium in real water samples by differential pulse voltammetry.

Analyte	Concentration <sup>a</sup> ( $\mu\text{g/L}$ )	Relative recovery %					
		Tap water	Lab.1 waste water	Lab. 2 waste water	Dam Golestan <sup>b</sup> water	Torghabe <sup>c</sup> stream water	Mashhad <sup>d</sup> Sewage
Palladium	0.1	80 $\pm$ 2.88	81 $\pm$ 4.2	95 $\pm$ 3.1	83 $\pm$ 5.6	92 $\pm$ 5.5	81 $\pm$ 7.1

<sup>a</sup> Spiked amount of analytes.<sup>b&c</sup> The country side around the Mashhad<sup>d</sup> One of the great cities in north eastern of Iran**Table 3.** Comparison between methods of determination of palladium in real samples.

No	Date	Matrix	Extraction Method	Detection Method	LOD	DLR	RSD%	Ref
1	2010	Water samples	LL-DLLME <sup>a</sup>	F-AAS	1.4 ng/mL	15ng/L -7 $\mu\text{g/L}$	1.5	[3]
2	2009	Real water samples	D-LLME <sup>b</sup>	F-AAS	90 $\mu\text{g/L}$	100-2000 $\mu\text{g/L}$	0.7	[4]
3	2010	Water samples	Modified organonano clay	F-AAS	0.1 ng/mL	0.5-8 $\mu\text{g/mL}$	2.1	[22]
4	2010	Food additive	M-clame <sup>c</sup>	UV-VIS	0.2 ng/mL	-	1.7	[23]
5	2011	Saline solutions	M-clame	UV-VIS	0.4 ng/mL	-	2.23	[24]
6	2012	Water samples	IP-SAME <sup>d</sup> ICD-OES <sup>e</sup>	ICP	0.2 $\mu\text{g/L}$	-	4.1	[25]
7	2012	Real water samples	HF-SLPME <sup>f</sup>	PPP	0.01 $\mu\text{g/L}$	0.1-500 $\mu\text{g/L}$	3.95	Present work

<sup>a</sup> LL-DLLME: Ligandless dispersive liquid-liquid microextraction<sup>b</sup> D-LLME: dispersive liquid-liquid microextraction<sup>c</sup> M-CIAME: Modified cold-induced aggregation microextraction<sup>d</sup> IP-SAME: ion pair based surfactant-assisted microextraction<sup>e</sup> ICP-OES: inductively coupled plasma-optical detection<sup>f</sup> HF-SLPME: hollow fiber solid/liquid phase microextraction

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