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In-situ differential pulse anodic stripping voltammetry combined with hollow fiber-based liquid-three phase micro extraction for determination of mercury using Au-nanoparticles sol–gel modified Pt-wire

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ABSTRACT

A new method has been proposed based on hollow fiber-based liquid three-phase micro extraction and in-situ differential pulse anodic stripping voltammetry (DPASV) for the micro extraction and quantification of mercury(II) ions. Different factors affecting the liquid-three phases micro extraction, including organic solvent, pH of the donor and acceptor phases, concentration of the complexing agent, extraction time, and stirring rate were investigated and the optimal extraction conditions were established. Three microelectrodes designed and constructed for this study were inserted into the two ends of a hollow fiber inside the acceptor solution, and then voltammetric analysis was performed in-situ during the extraction time. After 1600 s, final stable signal was used for the analytical applications. Under the optimized conditions, an enrichment factor of 277 was achieved and the relative standard deviation (R.S.D.) of the method was 6.2% ($n=5$). The calibration curve was obtained in the range of 0.2–30.0 nmol L^{-1} Hg(II) with a reasonable linearity ($R^2 > 0.9880$) and a limit of detection of 0.06 nmol L^{-1}. Finally, the applicability of the proposed method was evaluated by extraction and determination of mercury in real samples such as fish and rice.

1. Introduction

Heavy metals are persistent environmental contaminants. They cannot be metabolized by the body and are not stable and bioaccumulative. These toxic metals are sometimes passed up the food chain to humans. They have toxic effects on the environment and life in aquatic system at trace level too. Among the toxic trace metals, mercury ion is one of the most hazardous environmental pollutants that can affect the nervous system. It is found as an industrial waste because of its growing area in production of some batteries, thermometers, cameras, mercury vapor lamps, calculators, and has been used as a catalyst in the production of urethane polymers for plastics. Thus, it is very important to determine mercury at trace levels in different samples.

Various common methods are used to determine mercury ions such as potentiometry [1,2], spectrophotometry [3], atomic absorption spectrometry [4–6], inductively coupled plasma [7,8], atomic fluorescence spectrometry [9], X-ray fluorescence [10], voltammetry [11–14], liquid–liquid extraction [15], and complexometry [16]. Among these techniques, electrochemical methods are interesting because of simplicity, environmental friendly and sometimes good sensitivity.

Anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV) have received very much attention for metal ions determination owing to their intrinsic sensitivity [13,17–19]. It occurs because in stripping analysis, a preconcentration step is combined with a stripping step, thereby enhancing the sensitivity [20,21]. Leakage in selectivity is an essential problem of ASV, especially in analyzing complex real samples. In fact, it often happens that different species undergo redox reactions at potential values that are very close to each other. Prevalent experimental manipulations, such as changing the supporting electrolyte pH or using modified electrodes and chemometrics methods, offer efficient options to overcome the problem of overlapping signals [22]. Moreover, the application of sample preparation techniques could be an effective alternative for elimination of interferences encountered in electrochemical analysis of complex matrices such as food, blood and wastewater.

Hollow fiber-based liquid three-phase micro extraction (HF-LPME) method has been a powerful preparation method in recent years [23–27]. This technique can provide preconcentration and clean up of analytes simultaneously. In this method, analytes of interest are extracted from aqueous samples (donor solution) through the thin layer of an organic solvent, which is immobilized within the pores of a porous hollow fiber and then back-extracted

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into an acceptor solution inside the lumen of the hollow fiber. The fibers, being typically disposable, contribute to the elimination of sample carryover. The pores in the walls of the hollow fiber cause it to display some selectivity by preventing the extraction of macromolecules such as proteins and particles from the sample matrix. Selecting the suitable organic solvent, changing the type of hollow fiber and optimizing micro extraction conditions could obtain the required selectivity for the analytes considered [28,29]. The application of HF-LPME for micro extraction of metals has been a new concept in recent years [28].

Combining HF-LPME, as a sample preparation method, with anodic stripping voltammetry can increase selectivity and sensitivity in the quantification of trace heavy metals. However, type and shape of working electrode in voltammetric analysis have a significant effect on the results. The use of bare electrodes for analysis have several limitations such as lack of reproducibility and electrode fouling, sluggish electron transfer, high overpotential, and low selectivity and sensitivity [30–32]. Therefore, modification of electrode surface with suitable compounds is an important objective in this field.

Different substances and methods have been used for the modification of electrodes [33,34]. For the modification of a bare electrode, using sol–gel decorated Au-nano particles is an attractive method qualified with high preconcentration factor [35–40]. A typical procedure involves mixing an alkoxysilane (i.e., tetrametoxysilane) with water, alcohol, and a catalyst, such as HCl or NH_3.The silane is hydrolyzed and condensed. The sol–gel process provides a versatile method of preconcentration techniques different from the traditional ones and used for the electrochemical analysis. On the other hand, Au nanoparticles with high surface area have very interesting physicochemical properties as good sorbents for mercury, because amalgamation between gold and mercury occurs with a high ratio [41,42].

The aim of the present study is combining HF-LPME technique with differential pulse anodic stripping voltammetry, using a modified electrode. This combination can improve selectivity and sensitivity for the determination of mercury ions in complex matrixes such as food and wastewater samples. The selection of a suitable working microelectrode is a key step because internal diameter of hollow fiber is usually 0.6 mm and there are a few proper cases. So in this research, Au-nanoparticles sol–gel modified platinum wire was used as a working electrode. In order to extract Hg(II) ions to organic solvent, inside the hollow fiber wall, a ligand (typically PAN) as a complexing agent was carried out. An enrichment factor of 277 was achieved and Hg(II) as low as 0.06 nmol L^{-1} could be detected.

2. Experimental

2.1. Reagents

Milli-Q water (resistance $> 18\ m\Omega\ cm^{-1}$) was used through the experiments. Q3/2 Accurel polypropylene hollow fiber membrane (with a pore size of 0.2 μm, an internal diameter of 600 μm, and a wall thickness of 200 μm) was obtained from Membrana (Wuppertal, Germany). Sodium hydroxide, potassium chloride, hydrochloric acid (37%, w/w), 1-(2-pyridylazo)-2-naphthol (PAN), trimethyelbenzene, undodecane, propyl benzoate and dibenzyl ether were obtained from Merck (Darmstadt, Germany). 3-Trimethoxysilyl-1-propanethiol (TPS) (95%) was prepared from Aldrich (St. Louis, USA). Other reagents were of analytical grade and obtained from Merck (Darmstadt, Germany).

Stock standard solution of mercury(II) (0.001 mol L^{-1}) was prepared by dissolving a proper amount of mercury nitrate in milli-Q water (in the presence of 1 mL 0.1 mol L^{-1} HNO_3), which was subsequently diluted with water to reach a secondary mixed stock solution with a concentration of 1.0 μmol L^{-1}. All working standard solutions were freshly prepared by diluting standard solution with water to the required concentration.

2.2. Apparatus

All electrochemical measurements were performed using a Metrohm potentiostat/galvanostat connected to a three-electrode cell, Metrohm, Model 797 VA computrace, linked to a computer (Pentium IV, 1200 MHz) with the 797 VA computrace 1.2 Metrodata software installed.

A pH-meter (Corning, Model 140) with a double junction glass electrode was used to check the pH of the solutions.

Atomic force microscopy was performed in ambient conditions using Bruker Nanosinstrument (Germany), operating in contact mode.

2.3. Preparation of the microelectrodes

An Ag/AgCl reference microelectrode was constructed according to the previous work [24]. A slight shift was observed in the potential of the reference microelectrode towards that of the conventional reference electrode. However, the electrode was very stable and reproducible during the analysis.

A piece of platinum wire (0.25 mm o.d.) was used as a counter electrode. Another piece of platinum wire modified with sol–gel and decorated with gold nanoparticles was used as a working electrode. The gold decorated sol–gel was prepared by a method catalyzed under acidic conditions. A sol–gel solution was prepared as follows: first, for initial hydrolysis, 0.3 mL of TPS, 0.3 mL hydrochloric acid solution (0.1 mol L^{-1} as acidic catalyst) and 0.45 mL ethanol were added into a polypropylene microcentrifuge vial. The mixture was stirred and heated at 50 °C for 15–20 min until turbidity appeared. Immediately, the coating process of the platinum-wire electrode was performed by dipping 1.5 cm of a Pt-wire into the solution mixture for 10 s. After coating, the electrode was washed with 5 mL of water. Then, the electrode was put into the electrochemical cell, which typically contained 2.0 mL of $HAuCl_4$ solution (0.1%). The potential was adjusted in −200 mV to the working electrode for a period of 60 s [43]. First, Au-nanoparticles were prepared and then, chemically bonded to –SH functional group of sol–gel on the surface of the Pt-wire. A length of about 10 mm of the modified platinum electrode was in contact with the acceptor solution inside the hollow fiber. A simple assembly was designed for carrying out a robust micro extraction and in-situ voltammetry. This assembly is exhibited in Fig. 1A. It contains a thin circle polymeric sheet in which in one side, there is reference and counter electrodes. In addition, in the other side, there is a conical polypropylene tube as a needle guide for syringe and working electrode. A polymeric rod was set up in the center of the sheet as a handle. Hollow fiber was easily connected to assembly. Acceptor solution was injected into it and then, the working electrode was inserted into hollow fiber. After that, the extraction started with the immersion of assembly into the sample solution.

2.4. HF-LPME procedure

The experimental setup for the HF-LPME is illustrated in Fig. 1B and C. The extraction was performed according to the following procedure: 8.0 mL of the sample solution (phosphate buffer, pH 7.0) was filled into a 10 mL vial. The vial was placed on a magnetic stirrer. The Q3/2 Accurel polypropylene tubular membrane with a wall thickness of 200 μm (pore size, 0.2 μm) and an internal diameter of 600 μm was cut into 5 cm segments

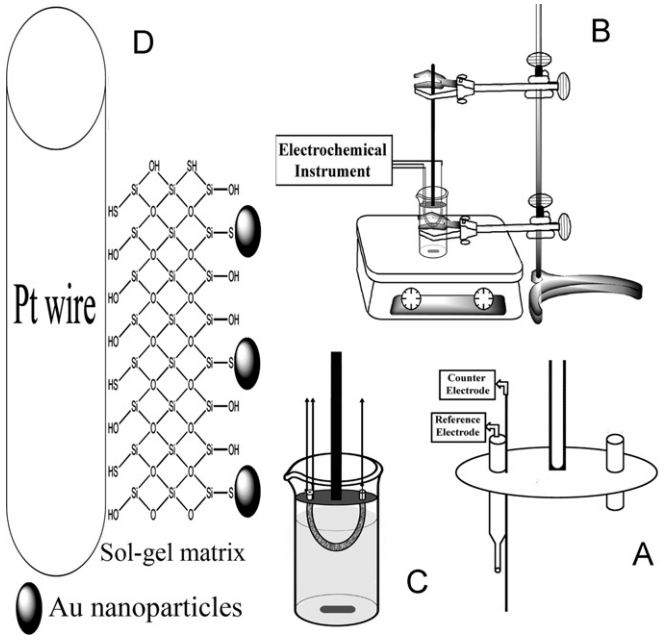

Fig. 1. (A) Designed assembly for robust microextraction and in-situ voltammetric procedure; (B) and (C) schematic of the equipment used for HF-LPME and in-situ DPASV, respectively; and (D) schematic of the working electrode.

for LPME experiments. Each piece of the fiber was employed only once to avoid any possibility of carryover. The hollow fiber segments were sonicated for 2 min in HPLC-grade acetone to remove any contaminants in the fiber. After sonication, the fibers were removed from acetone and the solvent was allowed to evaporate completely. The hollow fiber was then immersed into an organic solvent containing the ligand (typically propyl benzoate as solvent and PAN as ligand) for 30 s to impregnate its pores. After impregnation, air was flushed through the hollow fiber with a 5-mL syringe to remove the excess organic solvent from inside the fiber. For each extraction, a U-shaped hollow fiber was used. Hollow fiber was easily connected to the assembly and the acceptor solution was injected into it using the polymeric tube. Then, the working electrode was inserted into the hollow fiber. After that, the assembly was immersed into the sample solution for the extraction. Care was taken to keep the acceptor phase free of air bubbles to avoid breakage of the electrical connection between counter and working electrodes. The approximate volume of the acceptor solution inside the hollow fiber was 10 μL. During the extraction, the sample solution was continuously stirred (700 rpm) at room temperature for 1600 s and in-situ voltammetric analysis was performed.

2.5. Voltammetric analysis

Once the extraction-electrochemical cell had been set up and the electrical connections checked, DPASV was selected as the detection technique. Differential pulse voltammogram was recorded in the potential range of 0.40–0.70 V at a sweep rate of 20 mV s^{-1}, pulse time of 0.04 s, pulse amplitude of 50 mV, deposition potential of 0.37 V, and deposition time of 90 s. The peak current at initial extraction was measured and recorded as a blank signal (I_b) and after 1600 s, the final signal was measured and recorded as a sample signal (I_s). The difference in the currents ($\Delta I = I_s - I_b$) was considered as a net signal (ΔI) for each concentration. Calibration graph was prepared by plotting net peak currents vs. analyte concentrations in the solutions.

2.6. Real samples preparation

Farmed fish was prepared from lake around Mobarake Steel Complex (Isfahan, Iran) and fresh fish was kept in ice-chest of a refrigerator. 0.500 g of fish tissue was weighed accurately and placed at the bottom of a clean and dry screw cap 5 mL glass vial, which is closed with screw and cap fitted with a septum. The sample was digested with 1.0 mL nitric acid. It was allowed to sit for 3 h before heating. Then, the sample was slowly heated to 90 °C and held within this temperature for 3 h. After heating, the sample was allowed to cool and 0.5 mL 30% H_2O_2 was added drop wise and the sample was carefully heated again and held to 90 °C for 1 h to destroy excess hydrogen peroxide. The tissue was completely dissolved giving a clear solution. The pH of the digested sample was adjusted to 7.0 and then, was quantitatively transferred into 10-mL volumetric flask and diluted to volume. 8.0 mL of the sample solution was used for the extraction step [44].

Rice grain samples were washed with deionized water and allowed to dry at room temperature. A weighed sample of 0.500 g dried rice was placed into a screw cap 5-mL glass vial and reacted with 2 mL of concentrated nitric acid overnight at 80 °C. After digestion, the sample was allowed to cool to room temperature. The clear solution was transferred to 10-mL volumetric flask after adjusting its pH to 7.0; then, it was diluted with water. 8.0 mL of the sample solution was carried out for the extraction [45].

Water samples were collected by a routine technique, preserved by acidification of the sample with HNO_3, and stored in polyethylene bottles and analyzed within 12 h of the collection. Each sample was analyzed in triplicate, using the proposed method by standard addition method.

2.7. Calculations

The enrichment factor (*EF*) of the mercury content was calculated using the following equations:

$$EF = \frac{C_{AP,final}}{C_{DP,initial}}$$

where $C_{AP,final}$ and $C_{DP,initial}$ are the final and initial concentrations of mercury(II) in the acceptor and donor phases, respectively. $C_{AP,final}$ was obtained from the calibration curve. For real sample analysis, recovery was calculated using the following equation:

$$R\% = \frac{C_{DP,detection}}{C_{DP,initial}} \times 100$$

$C_{DP,detection}$ and $C_{DP,initial}$ are measured and initial concentrations of the analyte in the donor phase, respectively.

3. Results and discussion

3.1. Method development

HF-LPME was applied for the extraction and preconcentration of mercury from aqueous samples. The analyte was extracted from the donor phase into the organic solvent and ligand (impregnated in the pores of a porous polypropylene hollow fiber) to be finally back extracted into a smaller volume of the aqueous acceptor phase. In order to achieve maximum sensitivity, all parameters affecting extraction efficiency were optimized and each experiment was repeated at least in three replicates. The peak current of DPASV was used to evaluate extraction efficiency under different conditions.

3.2. Selection of a proper ligand

Dithizone and oxine have been widely accepted as important extracting agents for metals ions, but many other heavy metal ions interfere with these reagents in determinations. The reaction of Hg(II) with PAN is extremely sensitive and quite selective so that many commonly associated ions could not interfere and the reaction can be applied to the solvent extraction [46]. So, PAN was selected as a suitable ligand for the purpose of this investigation.

3.3. Selection of organic solvent

Selection of a suitable organic solvent in HF-LPME is of great importance for efficient analyte preconcentration. The criteria for the selection of a suitable organic solvent in HF-LPME include capability to be easily immobilized in the hollow fiber pores, nonvolatility to prevent solvent loss during extraction, and immiscibility with water because it serves as a barrier between the two donor and acceptor aqueous phases.

Considering the above criteria, four organic solvents including trimethylbenzene, undecane, propyl benzoate, and dibenzyl ether were evaluated for the extraction of mercury by HF-LPME under identical conditions. The evaluations were accomplished with extraction of 5.0 nmol L^{-1} mercury solution (from 8.0 mL of an aqueous solution, phosphate buffer pH 7.0, 0.1 mol L^{-1}, from the donor phase). The U-shaped hollow fibers impregnated with the organic solvent and PAN (0.1%), filled with the acceptor phase (1.0 mol L^{-1} H_2SO_4, 0.6 mol L^{-1} KNO_3, and 0.01 mol L^{-1} EDTA) were inserted into the vial and 20 min was allowed for the extraction to complete. As shown in Fig. 2, among the organic solvents tested, trimethyelbenzene exhibited the highest current peak height for the target analyte. However, propyl benzoate was selected as the most suitable solvent for subsequent experiments because it made the hollow fiber transparent so that it would be visible inside. This allowed the electrodes to be easily positioned inside the fiber and the air bubbles were formed that had to be controlled and eliminated.

3.4. Basicity and acidity of the donor and acceptor phases

pH levels of the donor and acceptor phases play important roles in HF-LPME. According to this method, the analyte from the donor phase must be transferred into the organic phase. The pH of the donor solution plus the influence of H_2SO_4 concentration on the acceptor phase were investigated (Fig. 3). The concentrations of H_2SO_4 varied between 0.002 and 2.0 mol L^{-1} in the acceptor phase. Based on these results, the extraction efficiency increased

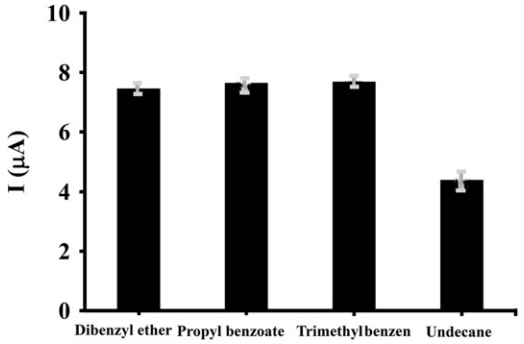

Fig. 2. Influence of organic solvent as a liquid membrane; conditions: Hg(II), 5.0 nmol L^{-1}; pH, 7.0 (phosphate buffer 0.1 mol L^{-1}); sample volume, 8.0 mL; PAN concentration, 0.10%; acceptor phase, 1.0 mol L^{-1} H_2SO_4, 0.60 mol L^{-1} KNO_3, and 0.010 mol L^{-1} EDTA; stirring rate, 700 rpm at room temperature; extraction time, 20 min (number of replications=3).

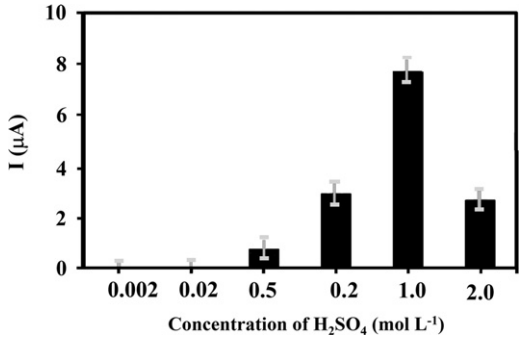

Fig. 3. Influence of sulfuric acid concentration of the acceptor phase on the extraction efficiency; conditions: organic phase, propyl benzoate; donor phase, pH 7.0 (phosphate buffer 0.10 mol L^{-1}); PAN concentration, 0.10%; stirring speed, 700 rpm; extraction time, 20 min; Hg(II), 5.0 nmol L^{-1} (number of replications=3).

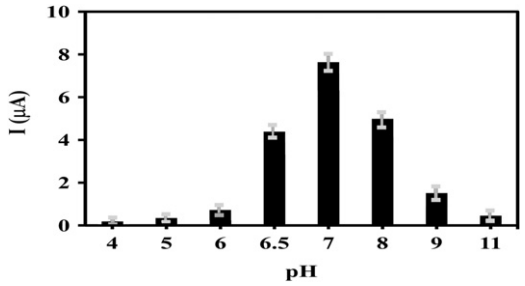

Fig. 4. Influence of donor pH value on the extraction efficiency; conditions: organic phase, propyl benzoate; PAN concentration, 0.10%; stirring speed, 700 rpm; extraction time, 20 min. Acceptor phase, 1.0 mol L^{-1} H_2SO_4, 0.60 mol L^{-1} KNO_3, and 0.010 mol L^{-1} EDTA; Hg(II), 5.0 nmol L^{-1}, (number of replications=3).

with increasing concentration of H_2SO_4 in the acceptor phase and then it decreased in 2.0 mol L^{-1}. It seems that the surface of modified electrode was destructed in the higher concentration of H_2SO_4. Thus, 1.0 mol L^{-1} of H_2SO_4 was selected as an optimum acceptor phase solution. The sample solution pH (in the donor phase) varied between 4.0 and 11.0 (Fig. 4). The best extraction efficiency appeared in pH 7.0. The lower peak current at higher pH may be due to the precipitation of the analyte in more basic solutions. Therefore, pH 7.0 was selected for the sample solution in future study.

3.5. Effect of EDTA

The releasing agent has a significant effect on the back-extraction section of the analyte and affects the enrichment factors and the limit of detection. Here, the effect of EDTA concentration was investigated as an assistance agent for back-extraction of the analyte from the organic phase into the acceptor phase. The results revealed that the peak current was (sensitivity) enhanced with increasing the concentration of EDTA up to 0.010 mol L^{-1}, and it was leveled off in higher concentration of EDTA (Fig. 5). Therefore, 0.010 mol L^{-1} was considered as an optimum concentration for future experiments.

3.6. Effect of stirring speed

Stirring of the donor phase solution increases the rate of the mass transfer into the organic and thus, into the acceptor phase. It reduces the extraction time by increasing the diffusion rate of the analyte from the donor into the acceptor phase. It also reduces the time needed to reach the equilibrium. Therefore, the highest speed of the magnetic stirrer should be selected as the stirring

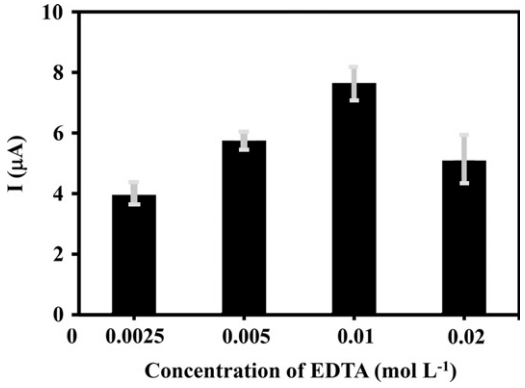

Fig. 5. Influence of EDTA concentration on the back-extraction efficiency; conditions: organic phase, propyl benzoate; stirring speed, 700 rpm; extraction time, 20 min. Hg(II), 5.0 nmol L^{-1} (number of replications = 3).

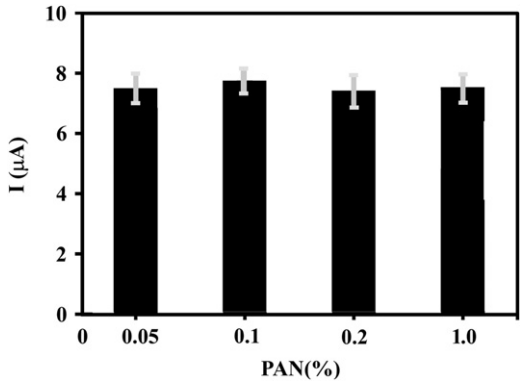

Fig. 6. Influence of PAN percentage on the extraction efficiency. Conditions: Hg(II), 5.0 nmol L^{-1}; pH, 7.0 (phosphate buffer 0.1 mol L^{-1}); sample volume, 8.0 mL; acceptor phase, 10.0 μL of 1.0 mol L^{-1} H_2SO_4, 0.60 mol L^{-1} KNO_3, and 0.010 mol L^{-1} EDTA; stirring rate, 700 rpm at room temperature; extraction time, 20 min (number of replications = 3).

speed. However, at high stirring speeds, air bubbles formed on the surface of the hollow fiber prevent the transfer of the analyte into the fiber and decrease extraction efficiency. In order to avoid this situation, a 700 rpm stirring rate was selected for the rest of the experiments.

3.7. Effect of the ligand concentration

The influence of the amount of PAN on the extraction capacity was examined using PAN concentration at 0%, 0.05%, 0.10%, 0.20%, and 1.0%, respectively. The obtained results showed that increasing PAN percentage had a positive effect on the extracted efficiency of Hg(II) ions and thus, the peak currents were increased by adding PAN concentration up to 0.10%. In addition, for the higher concentration of PAN, the signal amplitude was leveled off (Fig. 6). The optimal concentration of PAN was obtained at 0.1%.

3.8. Effect of the extraction time

As extraction is an equilibrium process, it needs sufficient time to allow partitioning of the analyte between the donor and acceptor phases. In general, to study the extraction time in HF-LPME, a series of experiments are carried out at different times under constant experimental conditions. However, in this work, due to the nature of in-situ analysis, the signal (peak current) is obtained every 30 s during a run. Therefore, the effect of extraction time on the performance of the method was investigated in a single run (Fig. 7). The results indicate that the equilibrium

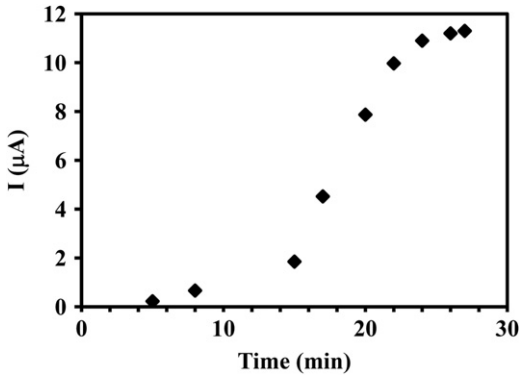

Fig. 7. Effect of extraction time on the extraction efficiency; conditions: Hg(II), 5.0 nmol L^{-1}; pH, 7.0 (phosphate buffer 0.1 mol L^{-1}); sample volume, 8.0 mL; acceptor phase, 10.0 μL of 1.0 mol L^{-1} H_2SO_4, 0.60 mol L^{-1} KNO_3 and 0.010 mol L^{-1} EDTA; stirring rate, 700 rpm at room temperature (number of replications = 3).

between both phases is reached after 1600 s. So, this time was selected for subsequent experiments.

3.9. Working electrode

AFM pictures were captured to get the detailed information of the surface structure such as thickness and roughness of the working electrode. Fig. 8 shows an AFM topology of the surface of the modified electrode (Fig. 8a_2 and b_2), and Pt-electrode (Fig. 8a_1 and b_1) corresponding to 2D and 3D images recorded over an area of $10 \times 10\ \mu m^2$. It can be seen that a dense layer was obtained and the height average of the gold nanoparticles is less than 7 nm. In addition, the roughness (thus the actual surface area) of the modified electrode (Fig. 8a_2 and b_2) is much more when compared it with the unmodified electrode. This is helping us to have a small size of the electrode with more surface area. It is worth mentioning that the size of a single nanoparticle cannot be determined by AFM from the lateral scale due to the high density of the particles that does not allow the AFM tip to penetrate in between the particles.

4. Analytical performance

The figures of merit of the proposed HF-LPME method including the enrichment factor, linear dynamic range and limit of detection (LOD) were investigated for the extraction of mercury from aqueous solutions under the optimum conditions. The results are summarized in Table 1. The calibration curves were obtained by plotting the peaks current height against the concentrations of mercury in the aqueous sample (Fig. 9).

The reproducibility of the proposed method, expressed as relative standard deviation (RSD), was evaluated by extracting the analyte from 5 aliquots of the same vial of water samples (spiked at 5.0 nmol L^{-1}) and the RSD value was found to be 6.2%. The limit of detection (LOD), being 0.06 nmol L^{-1}, was estimated based on a three signal-to-noise ratio criteria. Finally, a high enrichment factor of 277 was obtained for the analyte.

5. Interference study

In order to evaluate the overall selectivity of the method under the optimized experimental conditions described above, the effects of several inorganic and organic compounds, which may be present in real sample, were studied. To evaluate the effect of interferences substances in the determination of mercury(II), standard solutions of the analyte (5.0 nmol L^{-1} in the donor

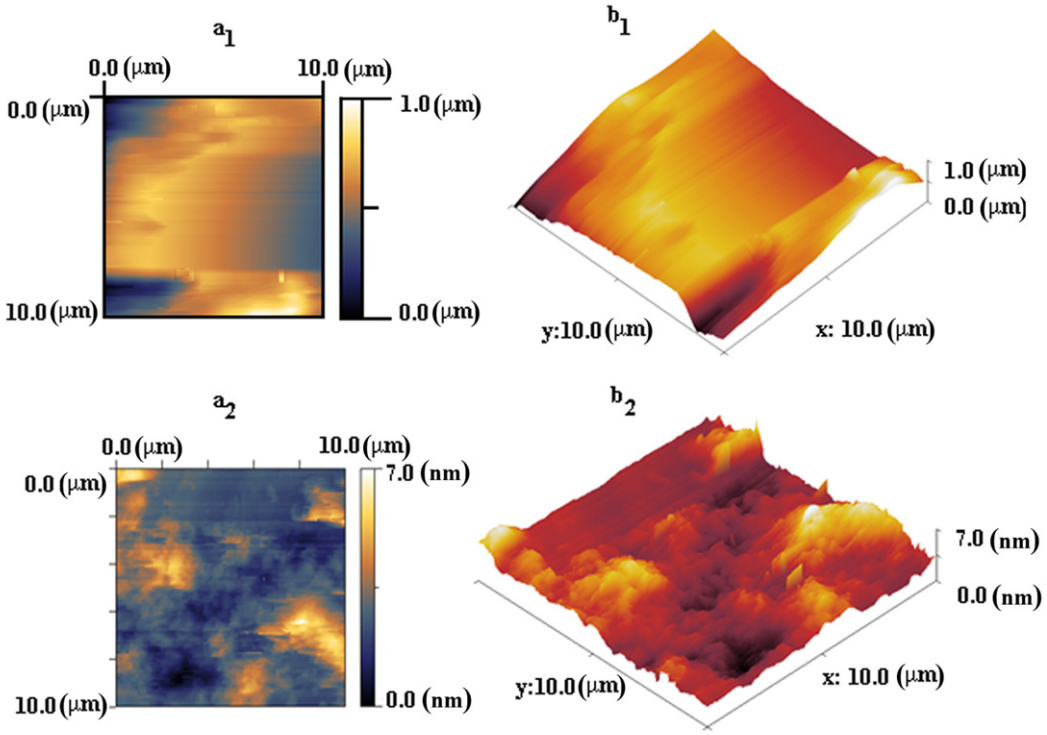

Fig. 8. AFM pictures of (a_1) 2D Pt-wire, (b_1) 3D Pt-wire, (a_2) 2D Pt/sol–gel/nano gold, and (b_1) 3D Pt/sol–gel/nano gold AFM topology of the surface.

Table 1
Limit of detection, enrichment factor, linear dynamic range, squared correlation coefficient and relative recovery for HF-LPME in–situ DPASV in distilled water, fish and rice.

Sample	Limit of detection (nmol L^{-1})	Enrichment factor	Dynamic range (nmol L^{-1})	R^2	Recovery (%)
Water	0.06	277($\pm$4.5)	0.2–30.0	0.9849	98
Fish	0.19	257($\pm$5.4)	0.6–30.0	0.9819	87
Rice	0.15	273($\pm$7.3)	0.5–30.0	0.9825	93

phase) containing different compounds such as organic compounds and inorganic cations and anions at different concentration levels were tested. The tolerance limit was defined as the maximum concentration of the substance that caused an error of less than 3% in the mercury determination [26]. The results are given in Table 2. These results indicate that the studied compounds (i.e., organic compounds, and inorganic cations and anions) have no effect on the selectivity of the mercury determination. In addition, cationic and anionic surfactants such as N-cetyl-N,N,N-trimethyl ammonium bromide, sodium dodecyl sulfate have no effect on the selectivity. However, nonionic surfactants such as Triton X-100 interfers at more than 75-fold to Hg(II) concentration. Therefore, as a routine procedure, for the analysis of environmental samples, it is better to have UV-digestion before the analysis to destroy any surfactants.

6. Real sample analysis

In order to assess the applicability of the newly developed method for the analysis of mercury(II) ions in complex matrices real samples, fish and rice samples were selected and analyzed to obtain the Hg(II) contents under the optimum conditions. 50 ± 1 nmol kg^{-1} (0.01 ± 0.002 mg kg^{-1}) of mercury in fish

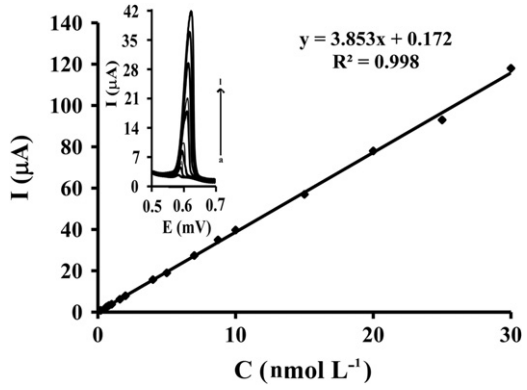

Fig. 9. Calibration curve for Hg(II); Inset: differential pulse anodic stripping voltammograms of Hg(II) standard solution after extraction under the optimized conditions at different concentration levels of: (a) 0.2; (b) 0.6; (c) 0.7; (d) 0.8; (e) 1.0; (f) 1.6; (g) 2.0; (h) 4.0; (i) 5.0; (j) 7.0; (k) 8.7 and 10.0 nmol L^{-1} Hg(II). Conditions: Hg(II), 5.0 nmol L^{-1}; pH, 7.0 (phosphate buffer 0.1 mol L^{-1}); sample volume, 8.0 mL; acceptor phase, 10.0 μL of 1.0 mol L^{-1} H_2SO_4, 0.60 mol L^{-1} KNO_3 and 0.010 mol L^{-1} EDTA; extraction time, 1600 s; stirring rate, 700 rpm at room temperature (number of replications=3).

sample was found and there was no detection in rice sample. Fish and rice samples were spiked with Hg(II) at 1.0 nmol L^{-1} (in the donor phase). As can be seen from Table 1, the recoveries were 87 and 93 for fish meat and rice samples, respectively. To further demonstrate the practicality of the present electrode, it was evaluated by measuring Hg(II) ions in tap water, wastewater, and river water samples. A river water sample was collected from Zayandehrood river (Isfahan, Iran) and treated through a standard 0.45 μm filter. All water samples were spiked with Hg(II) at different concentration levels and then analyzed with the proposed method (summarized in Table 3). The accuracy of the method was also assessed by comparing the electrochemical results with those obtained by standard inductively coupled

Table 2
Interferences study for the determination of 5.0 nmol L^{-1} Hg^{2+} under the optimized conditions.

Species	Tolerance limit
NO_2^-, Ni^{2+}, Zn^{2+}, Sb^{5+}, Cs^+, Mn^{2+}, NO_3^-, Ca^{2+}, Cd^{2+}, Mg^{2+}, Cl^-, CO_3^{2-}, Pb^{2+}, N-cetyl-trimethyl ammonium bromide, sodium dodecyl sulfate, Trimethylamine, Amoxicilin, Methyprednisolone, Phenazopyridine, Isobuthyl phenyl propionicacid, DNA	1000[a]
Lucine, Chloroamine-T hydrate	100
Triton X-100	75

[a] Maximum concentration of substances tested in the donor phase.

Table 3
Recovery of mercury ions from different water sample ($n=3$).

Sample	Hg(II))nmol L^{-1}(		Recovery (%)	Standard method[a] (nmol L^{-1})
	Added	Found		
Tap water	–	0.20(± 0.08)	–	0.20(± 0.31)
Tap water	0.30	0.50(± 0.08)	99.8	–
Tap water	0.62	0.81(± 0.07)	99.0	–
River water (Zayandehrood)	–	2.20(± 0.09)	–	2.10(± 0.21)
River water (Zayandehrood)	3.00	5.07(± 0.06)	97.5	–
River water (Zayandehrood)	6.00	8.24(± 0.04)	100.5	–
Wastewater	–	4.40(± 0.10)	–	4.90(± 0.50)
Wastewater	99.6	7.42(± 0.12)	3.05	–
Wastewater	96.9	9.11(± 0.90)	5.00	–

± Values are RSDs based on three replicate analyses.

[a] Water samples were analyzed by ICP after 100-fold preconcentration, using distillation method.

plasma optical emission spectroscopy (ICP). The results are given in Table 3. The results indicate that the matrices of the real samples do not have obvious effects on the proposed HF-LPME–in-situ DPV method for the determination of Hg(II) in water, fish, and rice samples.

7. Conclusion

In the present study, combination of HF-LPME with in-situ DPASV was successfully applied to the analysis of ultra-trace amounts of Hg(II) in real samples. Mercury was extracted from real samples into the acceptor phase inside the hollow fiber and analyzed in-situ using DPASV. The results indicated that HF-LPME could be used as an in-situ pretreatment procedure before electroanalytical analysis. Combination of HF-LPME and electrochemical techniques enhanced both selectivity and sensitivity for quantitative analysis. Complex matrices such as wastewater, fish, and rice were successfully analyzed using the proposed method.

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