Talanta 82 (2010) 1588–1593

Contents lists available at ScienceDirect

Talanta

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

Combined hollow fiber-based liquid–liquid–liquid microextraction and in-situ differential pulse voltammetry to improve selectivity, sensitivity, and interference elimination in electrochemical analysis

Mohammad Saraji*, Bahman Farajmand, Ali A. Ensafi, Ali R. Allafchian, Zohreh Mirahmdi Zare

Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran

ARTICLE INFO

Article history:
Received 7 April 2010
Received in revised form 25 July 2010
Accepted 27 July 2010
Available online 3 August 2010

Keywords:
Hollow fiber-based liquid three-phase microextraction
Differential pulse voltammetry
Desipramine

ABSTRACT

In this paper, a combined hollow fiber-based liquid three-phase microextraction and voltammetric method are applied for the first time as a highly selective and sensitive method of electrochemical analysis. Desipramine, used as a model compound was extracted from 8 mL aqueous solution (donor phase, 0.10 mol L^{-1} NaOH) through a thin phase of propyl benzoate inside the pores of a polypropylene hollow fiber and finally into a 10 μL acidic acceptor solution inside the hollow fiber. Three microelectrodes designed and constructed for the purposes of this study were placed into the two ends of the hollow fiber inside the acceptor solution, and voltammetric analysis was performed in-situ during the extraction. After 15 min, the final stable signal was used for analytical applications. Under the optimized conditions, an enrichment factor of 301 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 5–5000 nmol L^{-1} with a reasonable linearity ($R^2 > 0.988$) and the limit of detection (LOD) was found to be 0.8 nmol L^{-1}. Finally, the applicability of the proposed method was evaluated by extraction and determination of desipramine in plasma and urine samples without any dilutions.

1. Introduction

An essential limitation of electroanalytical techniques in analyzing complex real samples is their lack of selectivity. In fact, it often happens that different species undergo redox reactions at potential values that are very close to each other. In the case of differential pulse voltammetry, serious overlapping occurs when the difference in peak potentials is less than 0.10 V divided by the number of electrons involved in the electrode charge transfer. Prevalent experimental manipulations, such as changing the supporting electrolyte pH or using modified electrodes and chemometric methods, offer efficient options to overcome the problem of overlapping signals [1]. Moreover, the application of pretreatment techniques could be an alternative for the elimination of the interferences encountered in the electrochemical analysis of complex matrices such as urine and plasma.

Hollow fiber-based liquid–liquid–liquid microextraction (HF-LLLME) is a sample preparation technique. Originally introduced by Pedersen-Bjergaard and Rasmussen [2] in 1999 with its basic principles clearly described elsewhere [3–6], it is based on the use of disposable and porous hollow fibers made of polypropylene. HF-LLLME combines extraction, preconcentration and sample clean-up in one step. In the three-phase mode, analyte extraction occurs through three liquid phases, including: (1) the sample solution (donor phase), where pH is adjusted to keep compounds neutrally charged; (2) the organic extracting phase, which is immobilized in fiber pores; and (3) the receiving aqueous phase (acceptor phase), with a pH that is adjusted to ionize the analytes. Compounds in their non-ionized form are extracted into the organic solvent and subsequently back extracted into the acceptor phase, which can be directly analyzed via high performance liquid chromatography (HPLC) [7–9]. Additional advantages of HF-LLLME are its tolerance to a wide pH range and applications in assays that are not suitable for SPE or SPME. Sample carryover can be avoided because the hollow fiber used in HF-LLLME is cheap, making it affordable to dispose after a single use [10].

The aim of the present study is to combine the hollow fiber-based liquid–liquid–liquid microextraction (HF-LLLME) technique with differential pulse voltammetry in order to improve selectivity and sensitivity in electrochemical analysis. To the best of our knowledge, this is the first time the combined HF-LLLME and differential pulse voltammetry employed for in-situ analysis is reported. Desipramine hydrochloride, used as a model compound, is a tricyclic antidepressant prescribed to elevate mood and to promote recovery of a normal range of emotions in patients with depressive

* Corresponding author at: Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran. Tel.: +98 311 3913248; fax: +98 311 3912350.
E-mail address: saraji@cc.iut.ac.ir (M. Saraji).

0039-9140/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2010.07.072

disorders. It has also been used in a number of other psychiatric and medical conditions. Several procedures have been reported in the literature for the analysis of desipramine hydrochloride [11] that include spectrophotometry [12,13], HPLC [14,15], electrophoresis [16], voltammetry [17], gas chromatography [18], and ion-selective electrode [19].

2. Experimental

2.1. Reagents

Water was deionized and passed through a Milli-Q water purification system (resistance > 18 MΩ/cm). 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), *n*-dodecane, propyl benzoate, isoamyl benzoate, hexyl acetate and dibenzyl ether were obtained from Merck Company (Darmstadt, Germany). Other reagents were of analytical grade and obtained from Merck.

The stock standard solution of desipramine (1 mmol L^{-1}) was prepared separately by dissolving a proper amount of desipramine hydrochloride in milli-Q water, which was subsequently diluted with water to reach a secondary mixed stock solution with a concentration of 1 μmol L^{-1}. All the working standard solutions were freshly prepared by diluting the mixed standard solution with purified water to the required concentration.

2.2. Preparation of microelectrodes

An Ag/AgCl reference microelectrode was constructed according to the following procedure: one end of a piece of polyethylene tube (length: 40 mm, o.d.: 3 mm and i.d.: 1.5 mm) was tapered on a flame. The tapered end was inserted into a warm and fresh agarose gel (including 0.030 g agar, 0.30 g KCl, and 1.0 mL water) to allow the gel to enter into the tube. After 3 min, a few microliters of a saturated KCl solution were injected into the polyethylene tube. Then, an Ag-wire (i.d.: 0.5 mm) covered by a thin film of AgCl was inserted into the KCl solution inside the polyethylene tube while the other end was soldered to a braided wire before the wire was fixed at the end of the polyethylene tube. This reference microelectrode was placed into the saturated KCl solution for 15 min until the solution penetrated into the agarose gel. A slight shift was observed in the potential of the reference microelectrode toward 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 applied as the counter electrode. A graphite pencil lead (0.35 mm o.d., HB, Rotring, Germany) was used as the working electrode. To connect the working electrode to the hollow fiber tightly, a polypropylene micropipette tip was used as a holder for the pencil lead (Fig. 1). A length of about 10 mm of the graphite and platinum electrodes were in contact with the solution inside the fiber.

2.3. Apparatus

All electrochemical measurements were performed using a Metrohm potentiostat/galvanostat connected to a Metrohm three-electrode cell, 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.

2.4. HF-LLLME procedure

The experimental setup for the HF-LLLME is illustrated in Fig. 1. Extraction was performed according to the following procedure: 8 mL of the sample solution (0.10 mol L^{-1} NaOH) was filled into a 10-mL vial. The vial was placed on a magnetic stirrer. The hollow fiber was cut into 5-cm segments 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 (typically propyl benzoate) 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. The reference and counter microelectrodes were inserted into one end of the hollow fiber. Then, the acceptor solution was injected into the hollow fiber using a 25-μL syringe until the acceptor phase filled the hollow fiber. 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 surface of the pencil graphite electrode was washed with purified water and acetone before being inserted into the other end of the hollow fiber. The approximate volume of the acceptor solution inside the hollow fiber was 10 μL. The U-shaped hollow fiber was immersed into a 10-mL vial. During extraction, the sample solution was continuously stirred (700 rpm) at room temperature for 15 min 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, differential pulse voltammetry (DPV) was selected as the detection technique. Differential pulse voltammogram was recorded in the potential range of +0.50 to +1.00 V at a sweep rate of 0.0834 V s^{-1}, pulse time of 0.04 s and pulse amplitude of 50 mV. The peak current at initial extraction was measured and recorded as a blank signal (I_b) and after 15 min; the final signal was measured and recorded as a sample signal (I_s). The difference in the currents ($I_{p_s} - I_{p_b}$) was considered as a net signal (ΔI_p) for each concentration. Calibration graph was prepared by plotting net peak currents vs. analyte concentrations in the solutions.

2.6. Calculations

The enrichment factor (EF) and extraction percent of desipramine were calculated using the following equations:

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

$$\mathrm{Extraction\%} = \mathrm{EF} \times \frac{V_{\mathrm{AP}}}{V_{\mathrm{DP}}} \times 100$$

where $C_{\mathrm{AP,final}}$ and $C_{\mathrm{DP,initial}}$ are the final and initial concentrations of desipramine in the acceptor and donor phases, respectively. $C_{\mathrm{AP,final}}$ was obtained from the calibration curve. V_{AP} and V_{DP} are the volumes of the acceptor and donor phases, respectively. For real sample analysis, relative recovery was calculated using the following equation:

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

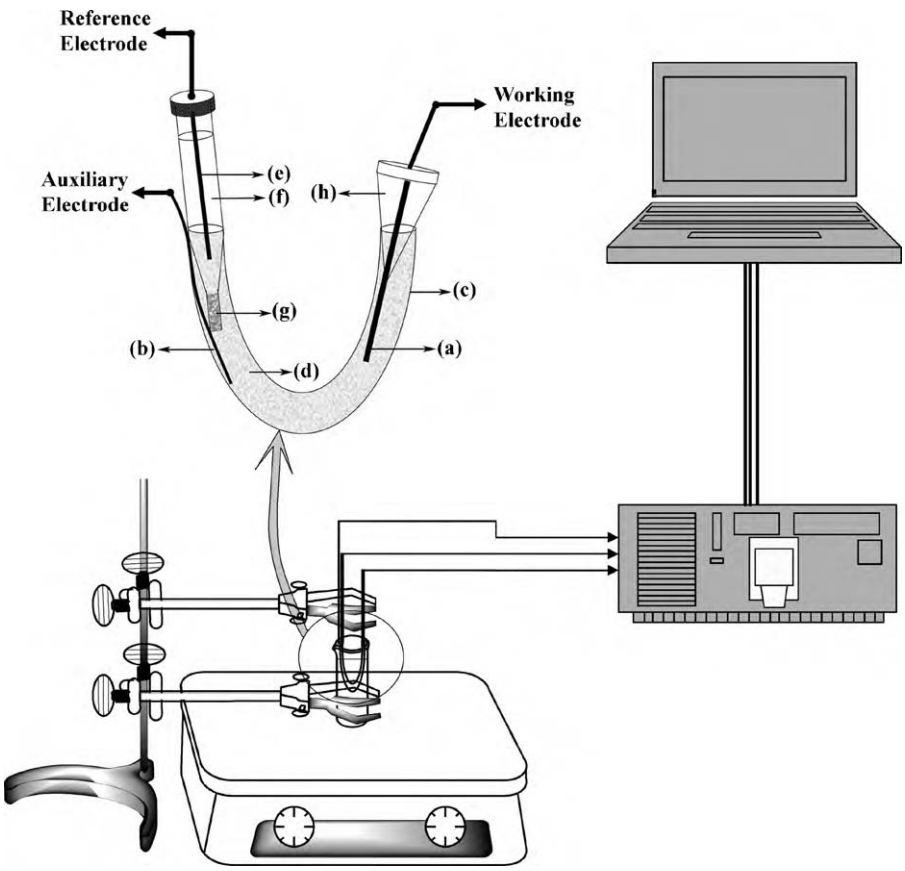

Fig. 1. Schematic of the equipment used for HF-LLLME and in-situ differential pulse voltammetry: (a) graphite pencil electrode; (b) platinum wire microelectrode; (c) polypropylene hollow fiber; (d) acceptor phase; (e) Ag-wire coated with an AgCl thin film; (f) saturated KCl/AgCl solution; (g) agarose gel; (h) 10-μL polypropylene micropipette.

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

3. Results and discussion

3.1. Electrochemical behavior

The sensitivity of the electrochemically active dibenzazepine tricyclic antidepressant compounds (e.g. desipramine) is probably due, at least in part, to the presence of the ring nitrogen. The mechanism of electrochemical oxidation of these compounds could be best described by a two-step, three-electron ECE process [20]. The first step involves the transfer of one electron to form a radical followed by dimerization. This compound is then oxidized further by an overall two-electron process at a more negative potential. Therefore, desipramine indicates two peaks at 0.70 and 0.90 V vs. an Ag/AgCl electrode. The second peak belonged to the first irreversible electrochemical reaction and the first one to the second reversible electrochemical reaction.

3.2. Method development

HF-LLLME was applied for the extraction and preconcentration of desipramine as a model compound from aqueous samples. The analyte was extracted from the donor phase into the organic solvent (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 the parameters affecting extraction efficiency were optimized and each experiment was repeated in at least three replicates. The peak current of DPV was used to evaluate extraction efficiency under different conditions.

3.2.1. Organic solvent selection

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, six organic solvents including *n*-octanol, *n*-dodecane, hexyl acetate, isoamyl benzoate, propyl benzoate and dibenzyl ether were evaluated for the extraction of desipramine by HF-LPME under identical conditions. Evaluations were accomplished with the extraction of 0.1 μmol L^{-1} desipramine solution from 8 mL of an aqueous solution (including 0.10 mol L^{-1} NaOH). The U-shaped hollow fiber impregnated with the organic solvent and filled with the acceptor phase (1.0 mol L^{-1} HCl and 0.10 mol L^{-1} KCl) was inserted into the vial and allowed to complete for 15 min for extraction. Although *n*-octanol is one of the most commonly used extraction solvents in SDME and LPME techniques [21–23], surprisingly no signal was observed when this solvent was used. More investigation is required to clarify the reason.

As can be seen in Fig. 2, among the organic solvents tested, *n*-dodecane 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

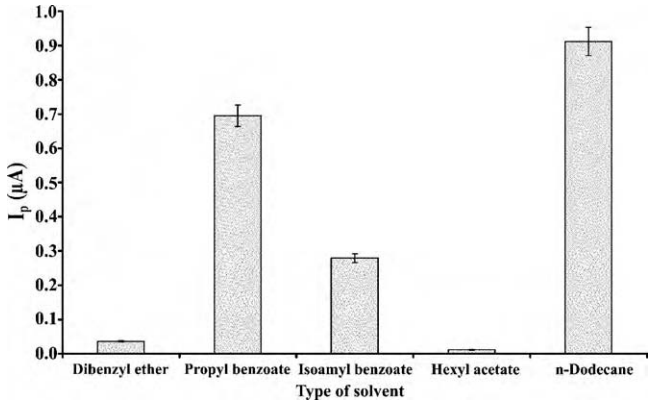

Fig. 2. Effects of different extraction solvents on HF-LLLME. Extraction conditions: concentration of desipramine, 0.1 μmol L^{-1}; sample volume, 8.0 mL; acceptor phase, 10.0 μL of 1 mol L^{-1} HCl and 0.1 mol L^{-1} KCl; salt addition, no NaCl added; stirring rate, 700 rpm at room temperature; extraction time, 15 min (number of replications = 3).

allowed the electrodes to be easily positioned inside the fiber and the air bubbles formed to be controlled and eliminated.

3.2.2. Basicity and acidity of the donor and acceptor phases

pH levels of the donor and acceptor phases play important roles in LLLME. According to this method, the analyte must be transferred into the organic phase in its neutral form in the donor phase. On the other hand, in the acceptor phase, the analyte should be in its ionized form and, therefore, it cannot be back extracted into the organic phase. In the case of basic analytes, the donor phase should be sufficiently basic to maintain the neutrality of the analyte and, consequently, to reduce its solubility within the donor phase. In addition, the acceptor phase should be acidic in order to promote the dissolution of the basic analyte. The effects of NaOH concentration in the donor and HCl concentration in the acceptor solutions were investigated (Fig. 3A and B). The concentrations of HCl and NaOH varied between 0.00001 and 1.0 mol L^{-1} in the donor and acceptor phases, respectively. Based on these results, extraction efficiency increased with increasing the concentration of HCl in the acceptor phase. The effects of higher concentrations of HCl were not checked due to the risk of damaging the syringe used to transfer the acceptor solution into the hollow fiber. On the other hand, extraction efficiency appeared to reach a maximum at a NaOH concentration of 0.1 mol L^{-1} for the acceptor phase, which subsequently declined at 1.0 mol L^{-1}. The lower peak current at 1.0 mol L^{-1} NaOH concentration may be due to the decomposition of the analyte in more basic solutions and/or to the reduced mass transfer rate resulting from increasing sample viscosity. Therefore, 1.0 mol L^{-1} HCl and 0.10 mol L^{-1} NaOH solutions were selected for the acceptor and donor phases, respectively.

3.2.3. Effect of stirring speed

Stirring of the donor phase solution increases the rate of mass transfer into the acceptor phase. It also reduces the time needed to reach equilibrium whereby it reduces the extraction time by raising the diffusion rate of the analyte from the donor into the acceptor. It follows, therefore, that the highest speed of the magnetic stirrer should be selected as the stirring speed. However, at high stirring speeds, air bubbles produced on the surface of the hollow fiber hinder 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.

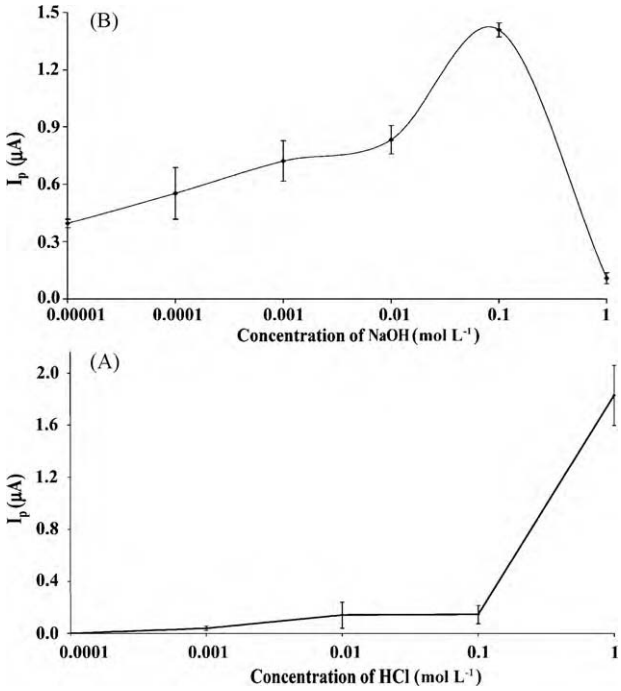

Fig. 3. Optimization of acidity and basicity of the acceptor (A) and donor (B) phases for HF-LLLME and in-situ voltammetry. Conditions: organic phase, propyl benzoate; stirring speed, 700 rpm; extraction time, 15 min. Desipramine concentration was 0.1 μmol L^{-1} (number of replications = 3).

3.2.4. Effect of ionic strength

Many researchers have reported that the addition of ionic strength to the samples is beneficial for enhancing extraction efficiency of many compounds in LLE [24] and SPME [25]. Experiments were designed in this study to evaluate the effect of ionic strength on the peak current by adding different amounts of NaCl into the samples in the range of 0–0.3 g mL^{-1}. It was observed that salt addition did not improve analyte extraction and maximum peak current was observed in the absence of sodium chloride in the solution. Hence, no salt was added in subsequent experiments.

3.2.5. Effect of extraction time

Because extraction is an equilibrium process, sufficient time is required to allow partitioning of the analyte between the donor and acceptor phases. In general, to study the extraction time in LLLME, 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. 4). Voltammograms are a little noisy, which is due to stirring the solution during the analysis. The results indicate that the equilibrium between both phases is reached after 900 s. So, this time was selected for subsequent experiments.

3.3. Analytical performance

The figures of merit of the proposed HF-LPME method including the enrichment factor, extraction percent, linear dynamic range and limit of detection (LOD) were investigated for extraction of desipramine from aqueous solutions under optimum conditions. The results are summarized in Table 1. The calibration curves were obtained by plotting the peaks current height against the concentrations of desipramine in the aqueous sample (Fig. 5). As can be seen, two linearly distinguished regions can be plotted.

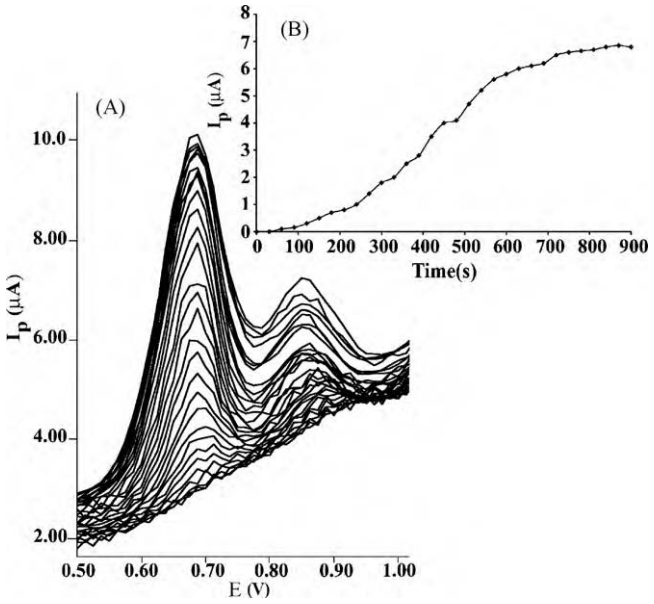

Fig. 4. (A) Time profile of a single extraction, voltammograms obtained at 30 s intervals; (B) effect of extraction time on peak current height. Conditions: donor phase, 1 μmol L^{-1} desipramine solution with 0.1 mol L^{-1} NaOH; organic extraction solvent, propyl benzoate; acceptor phase, 1 mol L^{-1} HCl and 0.1 mol L^{-1} KCl; stirring speed, 700 rpm.

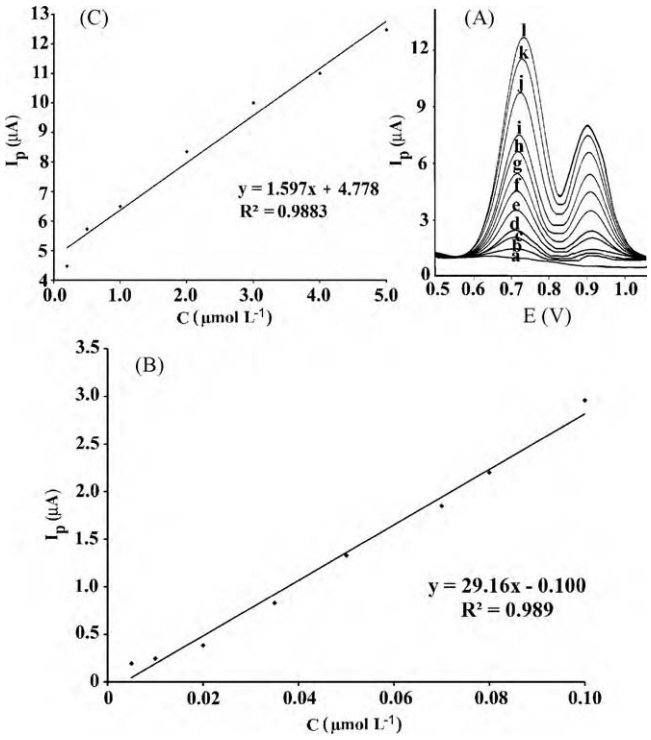

Fig. 5. (A) Differential pulse voltammograms of desipramine standard solution after LLLME under optimized conditions at different concentration levels: (a) blank, (b) 0.02 μmol L^{-1}, (c) 0.035 μmol L^{-1}, (d) 0.05 μmol L^{-1}, (e) 0.07 μmol L^{-1}, (f) 0.1 μmol L^{-1}, (g) 0.2 μmol L^{-1}, (h) 0.5 μmol L^{-1}, (i) 1 μmol L^{-1}, (j) 2 μmol L^{-1}, (k) 3 μmol L^{-1}, (l) 5 μmol L^{-1}. (B) Calibration curve between 0.005 and 0.1 μmol L^{-1}. (C) calibration curve between 0.2 and 5 μmol L^{-1}.

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 0.1 μmol L^{-1}) and RSD value was found to be 10%. The limit of detection (LOD) was estimated based on a three signal-to-noise ratio criteria, being 0.8 nmol L^{-1}. Finally, a high enrichment factor (301) was obtained for the analyte.

3.4. Interference study

In order to evaluate the overall selectivity of the method, under the optimized experimental conditions described above, the effects of some inorganic and organic compounds which may be present in biological media and drugs were studied. To evaluate the effect of interferences in the determination of desipramine, standard solutions of the analyte (1 μmol L^{-1}) containing compounds such as amino acids, drugs, organic acids 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 desipramine determination [26]. The results are reported in Table 2. These results indicate that the compounds studied have no effects on the analysis at concentrations up to 1000 times higher than desipramine. On the other hand, quantification using direct DPV may be seriously affected when the solution contains the above interfering compounds at concentrations even 10 times that of desipramine.

3.5. Real sample analysis

In order to assess the applicability of the newly developed method in the analysis of the drug in real samples with complex matrices, urine and plasma samples were extracted and analyzed under the optimum conditions. Urine and plasma samples were spiked with the analyte at 0.1 μmol L^{-1}. The results showed that the samples analyzed were either free of desipramine or had concentrations below the detection limits. As be seen from Table 1, the relative recoveries are 78 and 89 for plasma and urine, respectively. RSDs are below 9%. These results indicate that the matrices of the real samples do not have obvious effects on the proposed DLLME-in-situ DPV method for the determination of the analyte from urine and plasma samples.

Fig. 6 shows typical voltammograms of the spiked and non-spiked urine samples. The oxidation peak at 0.7 V (Fig. 6A) is probably due to oxidation of uric acid. As can be seen in the figure, the interference of uric acid peak with high background signal of the urine matrix can cause a difficult problem in the quantification of desipramine. Fig. 6B shows that HF-LLLME technique has excellent capability to eliminate the urine matrix. The real sample analysis showed that the proposed method exhibited good selectivity for the determination of desipramine in urine samples.

Table 1
Limit of detection, enrichment factor, extraction percent, linear dynamic range, squared correlation coefficient and relative recovery for LLLME-in-situ DPV in milli-Q water, urine and plasma.

Sample	LOD (nmol L^{-1})	EF	Extraction (%)	Dynamic range (nmol L^{-1})	R^2	Relative recovery (%)
Distillated water	0.8	301(10)[a]	52	200–5000 5–100	0.988, 0.989	–
Plasma	–	234(7)	41	–	–	78
Urine	–	278(9)	48	–	–	89

[a] % Relative standard deviation (RSD), $n = 5$.

Table 2
Interferences study for the determination of 1.0 μmol L^{-1} desipramine under the optimized conditions.

Method	Limit of interfering	Species			
		Inorganic ions	Amino acids	Drugs	Other compounds
LLLME-in-situ DPV	1000	K^+, Na^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, NH_4^+, Cl^-, I^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}	Leucine, glycine, cystine, systeine, tryptophane, valine	Epinephrine, dibucaine, thioguanine, captopril, vitamin B_2	Ascorbic acid, uric acid, fulick acid, DNA
	100	–	–	Dopamine	–
Direct determination (DPV)	1000	K^+, Na^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, NH_4^+, Cl^-, I^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}	–	–	–
	100	–	–	–	–
	10	–	Leucine, glycine, cystine, systeine, tryptophane, valine	Epinephrine, dibucaine, thioguanine dopamine, captopril, vitamin B_2	Ascorbic acid, fulick acid, uric acid, DNA

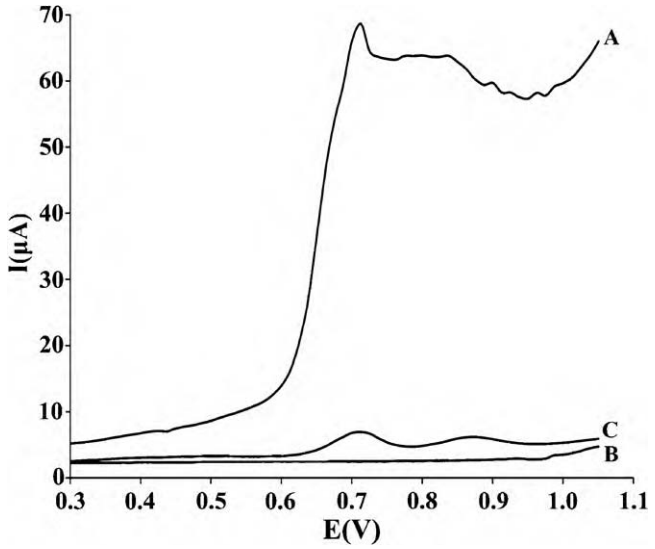

Fig. 6. Obtained votammograms of (A) direct DPV (without extraction) of non-spiked urine sample, (B) LLLME-in-situ DPV of non-spiked urine sample, (C) LLLME-in-situ DPV of spiked urine sample with desipramine (0.1 μmol L^{-1}).

4. Conclusion

In the present study, the combined HF-LLLME and in-situ differential pulse voltammetry was successfully used to analyze samples. Desipramine was extracted from biological samples into the acceptor phase inside the hollow fiber and analyzed in-situ using differential pulse voltammetry. The results indicated that HF-LLLME could be used as an in-situ pretreatment procedure before electroanalytical analysis. Combining HF-LLLME and electrochemical techniques enhanced both selectivity and sensitivity of the method. Complex biological matrices such as plasma and urine were successfully analyzed using the proposed method without any dilution of the sample.

Acknowledgments

The authors are grateful to the Research Council of Isfahan University of Technology (IUT) and Center of Excellence for Sensor and Green Chemistry for their support of this project.

References

[1] M. Cocchia, H. de-Cisneros, Talanta 59 (2003) 735.
[2] S. Pedersen-Bjergaard, K.E. Rasmussen, Anal. Chem. 71 (1999) 2650.
[3] E. Psillakis, N. Kalogerakis, Trends Anal. Chem. 22 (2003) 565.
[4] K.E. Rasmussen, S. Pedersen-Bjergaard, Trends Anal. Chem. 23 (2004) 1.
[5] S. Pedersen-Bjergaard, K.E. Rasmussen, J. Chromatogr. B 817 (2005) 3.
[6] S. Pedersen-Bjergaard, K.E. Rasmussen, J. Chromatogr. A 1184 (2008) 132.
[7] C. Yang, L. Guo, X. Liu, H. Zhang, M. Liu, J. Chromatogr. A 1164 (2007) 56.
[8] F.J.M. De Santana, P.S. Bonato, Anal. Chim. Acta 606 (2008) 80.
[9] I.R.S. Magalhles, P.S. Bonato, J. Pharm. Biomed. Anal. 46 (2008) 929.
[10] S.M. Richoll, I. Colon, J. Chromatogr. A 1127 (2006) 147.
[11] L. Brunton, K. Parker, D. Blumenthal, I. Buxton, Goodman and Gilman's Manual of Pharmacology and Therapeutics, McGraw-Hill Professional, New York, 2007.
[12] A. Syeda, H.R.K. Mahesh, A.A. Syed, Farmaco 60 (2004) 47.
[13] W. Misiuk, Anal. Lett. 35 (2002) 1163.
[14] H. Yoshida, K. Hidaka, J. Ishida, K. Yoshikuni, H. Nohta, M. Yamaguchi, Anal. Chim. Acta 413 (2000) 137.
[15] A.G. Chen, Y.K. Wing, H. Chiu, S. Lee, C.N. Chen, K. Chan, J. Chromatogr. B: Biomed. Sci. Appl. 693 (1997) 153.
[16] H.-S. Kou, C.-C. Chen, Y.-H. Huang, W.-K. Ko, H.-L. Wu, S.-M. Wu, Anal. Chim. Acta 525 (2004) 23.
[17] J. Wang, M. Bonakdar, C. Morgan, Anal. Chem. 58 (1986) 1024.
[18] S. Paterson, R. Cordero, S. Burlinson, J. Chromatogr. B 813 (2004) 323.
[19] J.A. Ortuno, J. Hernandez, C. Sanchez-Pedreno, Sens. Actuators B 119 (2006) 282.
[20] S.N. Frank, A.J. Bard, J. Electrochem. Soc. 122 (1975) 898.
[21] L. Hou, H.K. Lee, Anal. Chem. 75 (2003) 2784.
[22] S. Müller, M. Möder, S. Schrader, P. Popp, J. Chromatogr. A 985 (2003) 99.
[23] X. Wen, C. Tu, H.K. Lee, Anal. Chem. 76 (2004) 228.
[24] Z. Marczenko, Separation and Spectrophotometric Determination of Elements, Ellis Harwood Limited, Chichester, 1986.
[25] A. Mohammadi, Y. Yamini, N. Alizadeh, J. Chromatogr. A 1063 (2005) 1.
[26] E. Mirmomtaz, A.A. Ensafi, S. Soleimanian-Zad, Electrochim. Acta 59 (2009) 1141.