

*Full Paper*

## **Simultaneous Determination of Zn, Pb and Cd Ions by Ultrasound-assisted Liquid Phase Micro-Extraction and FFT Voltammetry**

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**Abstract-** In this study, several heavy metal ions ( $Zn^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$ ) were extracted and online determined in water samples by ultrasound-assisted hollow fiber liquid phase micro-extraction (HF-LPME) coupled with stripping fast Fourier transform continuous cyclic voltammetry (SFFTCCV) as a novel electroanalytical technique. Initially, the heavy metal ions were extracted through a polypropylene membrane soaked in xylene and bis(2-ethylhexyl)phosphoric acid (DEHPA), into an acceptor solution located in the lumen of a hollow fiber (HF). The analytes were then determined through an electrochemical approach using a micro carbon paste electrode (micro-CPE) as a working electrode placed into the upper end of the HF. The optimum conditions for the proposed method were reached at scan rate of  $6\text{ V s}^{-1}$ , stripping potential: 200 mV, stripping time: 5 s, the sample solution pH: 5, the acceptor solution pH: 4, extraction time under the ultrasound irradiation: 60 min, membrane composition: 0.5 M DEHPA in xylene. Limit of detection (LOD) and limit of quantification (LOQ) were determined to be in the range of 0.1-1 and 1-5  $ng.mL^{-1}$ . Furthermore, the recovery percentages of 87%, 62% and 41% were obtained for  $Zn^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$  ions, respectively. Based on the results, the method presented adequate potential to be used for the simultaneous determination of the stated analytes in the sea, river and well water samples, under optimal conditions.

**Keywords-** Heavy metals, Ultrasonic irradiation, Hollow fibers, Fast Fourier transform voltammetry, Water samples

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## 1. INTRODUCTION

In today's life, toxic heavy metals are count as serious critical threats for the living organisms due to their determinative role in the biological cycling [1,2] and being non-bio-degradable as well. Zinc (Zn), cadmium (Cd) and lead (Pb) that commonly exist in various environmental samples, are considered as essential set of pollutants of the aquatic life, thus they are classified as highly important members of heavy metal group [3,4].

However, some of these elements have nutritional significance despite others being toxic. Zinc, for instance, is an essential trace element for general body health and its deficiency may interrupt the body main functions, while this element can be toxic at high concentrations [5].

In another point of view, cadmium and lead are available heavy metals with high degree of toxicity even at low concentrations, since they can ruin several biochemical interactions. Due to heavy metals rising industrial applications and their noteworthy environmental effects[6], it would be desired to design novel, sensitive and selective methods for trace analysis of these components in complex matrices .

Among recent applied methods for heavy metals determination; UV-vis spectrometry [7], surface enhanced Raman spectrometry (SERS) [8], atomic absorption spectrometry (AAS) [9, 10], atomic fluorescence spectrometry [11], ion chromatography [12] , inductively coupled plasma mass spectrometry (ICP-MS) [13] and inductively coupled plasma optical emission spectrometry (ICP-OES) [14] can be implied. In addition, there are some other records indicating techniques such as ICP-OES, recommends multi-element analysis have been used for simultaneous determination of heavy metal ions. However, most of these kinds of technique are not yet broadly used because of high implementation and maintenance costs [15].

At this point, electroanalytical techniques offer advantages including considerable sensitivity and selectivity with the capability for the low cost and simultaneous multi-elemental analysis hence, they could have the potential to overcome the probable drawbacks [16].

Furthermore, using fast Fourier transform (FFT) combined with an electrochemical method has led to excellent sensitivity for trace detection of analytes. On this approach, the voltammetric and the background signals are separated in frequency domain by means of discrete FFT technique consequently; some of unavoidable environmental noises would be digitally filtered, which could improve the detection limits. Besides, the signal intensity can be amplified, over a selected potential range and time window of the signal, using two-dimensional integration of the electrode response [17,18].

Despite the stated advantages, these methods mainly suffer from matrix effect, especially when the analyte concentration is very low. Designing an efficient pretreatment and cleanup technique, prior to the detection session, appears to be an appropriate solution. Among the sample pretreatment procedures, micro-extraction techniques with low volume consumption of organic solvents such as liquid phase micro-extraction (LPME) [19-21] and solid phase micro-extraction (SPME) [22-24] , have triggered intense interest.

Recently, hollow-fiber liquid-phase micro-extraction (HF-LPME), an innovative miniaturized format of liquid liquid extraction, was used for extraction and preconcentration of the analytes. Several parameters affect the extraction speed in HF-LPME such as the partition coefficient between the donor solution and the organic solvent, the donor and the acceptor solution volumes and the surface of the liquid membrane. Despite the various advantageous of HF-LPME, in this method the analysis process is relatively slow and time consuming [25,26].

In contrast, the ultrasound-assisted micro-extraction techniques have attracted growing interest, since it is a favorable method for the rapid extraction of compounds with high extraction efficiency. The application of ultrasound energy for the extraction and detection heavy metal ions, from various matrixes, such as natural waters [27], biological samples [28], sediments, and vegetable oils [29] has been reported recently.

Herein, in-situ and simultaneous determination of zinc, lead and cadmium ions was performed using ultrasound assisted HF-LPME coupled with fast Fourier transform stripping continuous cyclic voltammetry (FFTSCCV). All steps of the extraction; pre-concentration and ultra-trace determination of ions were accomplished in a single extraction cell, consequently, the time of analysis is considerably reduced. In addition, due to the application of ultrasound energy in combination with HF-LPME, the extraction process accelerated. The sample solutions were directly conducted into the extraction cell and their concentrations were monitored with no additional pretreatment. Based on the obtained results in optimized conditions, LOD and LOQ were calculated and the designed method presented acceptable capability for determination of the ions in some real samples.

## 2. EXPERIMENTAL

### 2.1. Apparatus

The employed setup was a three-micro-electrode arrangement composed of a handmade micro Ag/AgCl electrode as the reference electrode [30], a 500  $\mu\text{m}$  gold wire as the auxiliary electrode and a micro carbon paste ( $\mu\text{CP}$ ) as the working electrode.

An ultrasonic bath (Elmasonic S. Germany) at 60 Hz of frequency was used for the ultrasound-assisted extraction process. All the electrochemical measurements were carried out using a homemade ultra-voltammetry system (UVS), which was designed at the center of excellence electrochemistry (CEE) at University of Tehran.

### 2.2. Reagents and materials

All used nitrate salts;  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Cd}(\text{NO}_3)_2$ , the analytical graded solvents including dichloromethane, dichloroethane, carbon tetrachloride, chloroform, tetrahydrofuran, xylene, dimethylformamide, dimethylsulfoxide, cyclohexane, ethylacetate, dibutylphthalate, and

also orthophosphoric acid (85%, w/w) and sodium hydroxide (98%) were purchased from Merck company (Darmstadt, Germany).

### 2.3. The electrode preparation

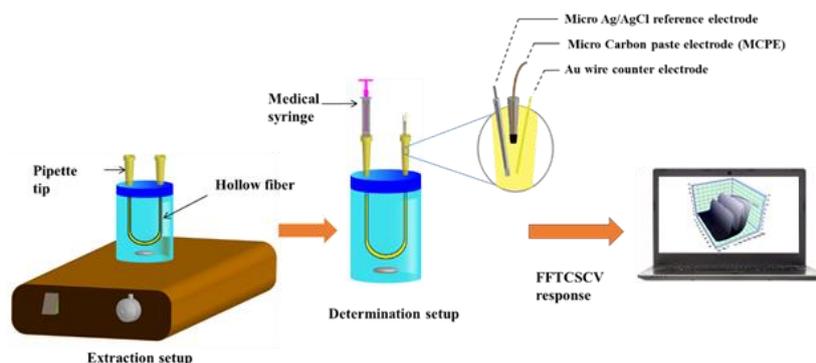
The working electrode ( $\mu$ CP) was prepared as a paste made through a mixture of paraffin oil and graphite powder (30/70 w/w), then being packed into a polyethylene tube, while avoiding the formation of air gaps within the tube. A copper wire was inserted into the paste from the opposite side of the tube in order to make the electrical contact. The surface of the resulting electrode was renewed by being polished on a soft clean paper after each run. Finally, the reference, auxiliary and working electrodes were put together as shown in Fig.1 and placed into the upper tip of a micropipette.

### 2.4. Sample preparation

Stock solutions of the metal ions ( $100 \mu\text{g}\cdot\text{mL}^{-1}$ ) were prepared by dissolving suitable quantities of the corresponding nitrate salts in double distilled water, under sonication in the bath for 5 min. The following solutions were made through diluting the stock solutions with acetate buffer solution (ABS) 0.1 M (pH=4.0). The donor solution was directly fed into the prepared set up after adjusting the pH value at 4.

### 2.5. Extraction and in-situ determination of the analytes

The developed ultrasonic assisted HF-LPME setup is schematically illustrated in Fig. 1. Typically, the donor compartment was filled up by 15-mL of the sample solution containing  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in ABS (pH=4). A polypropylene HF (Membrana, Wuppertal, Germany) with inner diameter of 1200  $\mu\text{m}$ , wall thickness of 200  $\mu\text{m}$  and pore size of 0.2  $\mu\text{m}$  was used as the membrane. In order to form the SLM (supported liquid membrane), a 10 cm piece of the HF was soaked in the mixture of bis(2-ethylhexyl)phosphoric acid (DEHPA) and xylene for 30 minutes. Tips of two micropipettes were used to hold the HF during the electrochemical determinations. Formerly, the acceptor phase containing ABS (pH=4.0), was introduced into the HF, afterward both ends of the HF were connected to the tips of the micropipette in the door of the compartment. Further, the extraction step was assisted by ultrasound irradiation. Eventually, using a syringe (Fig. 1), the acceptor solution was moved to the end of the micropipette tip and with the aid of the miniaturized microelectrode system the heavy metal ion concentrations were monitored.



**Fig. 1.** The schematic image of the HF-LPME and the employed electrochemical setup

### 3. RESULT AND DISCUSSION

#### 3.1. Optimization of electrochemical determination of ions

##### 3.1.1. Voltammetric behavior of the heavy metal ions

Initially, the electrochemical behaviors of all three ions simultaneously in 10, 100 and 1000 ng/mL solutions prepared by 0.1 mol.L<sup>-1</sup> ABS (pH 4.0) was examined using FFT cyclic voltammetry (CV) on the prepared  $\mu$ CPE surface. As can be seen in Fig. 2A, no peak was observed in the absence of the ions (using a blank sample). In the case of adding three ions to the buffer solution, three distinct voltammetric peaks appeared at -814, -561 and -275 mV for Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>, respectively.

Then, the FFTSCCV studies were carried out in the potential range of -1200 to 400 mV. Fig. 2B illustrates the FFTSCCV responses observed before and after adding 18 mL of 1000 ng/mL solutions containing Zn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> in the ABS (pH 4.0). In comparison with the conventional CV studies, FFTSCCV results, also included a time axis representing the number of CVs recorded at the given time window. The demonstrated voltammograms in the Fig. 2B were gathered from a potential waveform continuously applied to the working electrode. As the figure clearly shows, three considerable peak appeared in the CVs indicating the current integrated after addition of the ion mixture.

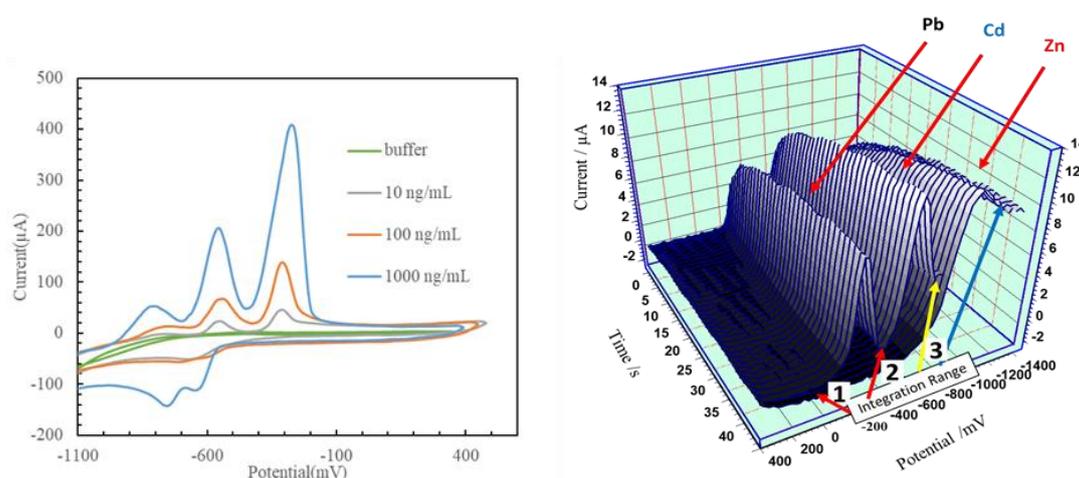
On this approach, the response signal could be the calculated charge change ( $\Delta Q$ ) obtained from a selected potential range in the recorded voltammogram;  $E_1$  to  $E_2$  respect to a reference voltammogram that can be simplified as follows:

$$\Delta Q = Q - Q_r \quad (3)$$

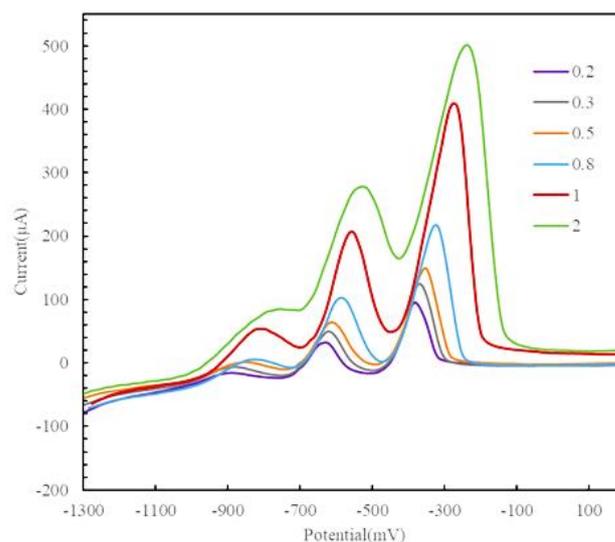
$$\Delta Q (s\tau) = \Delta t \left[ \sum_{E=E_1}^{E=E_2} |i(s, E) - i(s_r, E)| \right] \quad (4)$$

Where  $Q_r$  represents the calculated charge for the reference voltammogram considering the average of 3 CVs at the beginning of the test, prior to adding the ions [31-35];  $Q$  is the charge

at the specified potential range,  $s$  displays the number of scans,  $\tau$  is the period of time between two subsequent voltammogram,  $\Delta t$  is the time difference between the two recorded currents  $i(s, E)$  in the voltammogram, and  $i(s_r, E)$  is the reference current.  $E_1$  and  $E_2$  signify the initial and the final potential limits, for the current integration. A noteworthy advantage of the technique is the capability for determination of the electrode signal for each ion separately, by selecting the proper values for  $E_1$  and  $E_2$ .



**Fig. 2. A)** FFT-CVs obtained using the  $\mu$ CPE in 10, 100 and 1000  $\text{ng.mL}^{-1}$  solution of  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in ABS (pH=4.0) at scan rate of  $1 \text{ V.s}^{-1}$ ; **B)** 3D voltammograms obtained for 10  $\text{ng.mL}^{-1}$  metal ions through FFTSCCV for the bare electrode in  $0.1 \text{ mol.L}^{-1}$  ABS pH 4.0



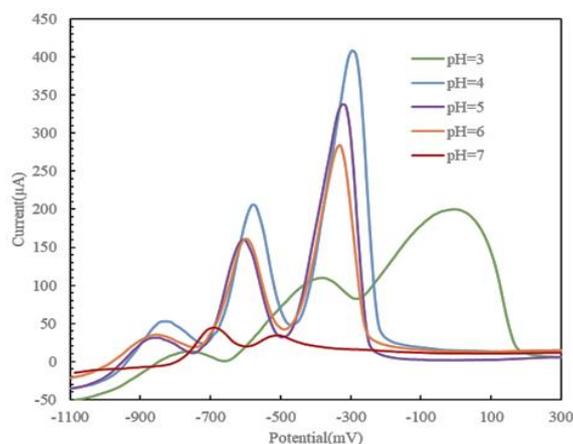
**Fig. 3.** The scan rate effect on the  $\mu$ CPE FFT-SCV response for  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  1000  $\text{ng.mL}^{-1}$  solution in ABS, pH=4

### 3.1.2. Effect of sweep rate

Sweep rate is one the most critical factors that can influence the electrochemical response. The effect of the sweep rate on the electrode response was investigated within the range of 0.1 to 10  $\text{V}\cdot\text{s}^{-1}$  using 1000  $\text{ng}\cdot\text{mL}^{-1}$   $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ion solution. The results (Fig. 3) indicates that the highest sensitivity (i.e. signal to noise ratio, (S/N)) was observed at the sweep rate of 5  $\text{V}\cdot\text{s}^{-1}$ .

### 3.1.3. Effect of stripping potential and time

The effects of the stripping potential ( $E_s$ ) and time ( $t_s$ ), on the FFTSCCV responses were examined. The effect of  $E_s$  on the FFTSCCV responses was evaluated by altering this value in the range of -1000-1000 mV. It was observed that the ion FFTSCCV responses reached a maximum value at -400 mV, and then it decreased, which could be related to the positive charge of the ions existing in the ABS. Similarly, the effect of stripping time was evaluated. The obtained results revealed that the response enhanced by increasing  $t_s$  value up to 10 s, where it remained almost at a steady value after augment the time up to 60 s. This reflects the fact that beyond that time, the surface of the electrode could be saturated by the ions and the adsorption process reaches to the equilibrium. Thus, the optimal stripping time was concluded to be 10 s before each potential scan.



**Fig. 4.** The ABS pH effect on the CPE FFT-SCVs obtained for  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  1000  $\text{ng}\cdot\text{mL}^{-1}$ , pH=4 and scan rate of 1  $\text{mV}\cdot\text{s}^{-1}$

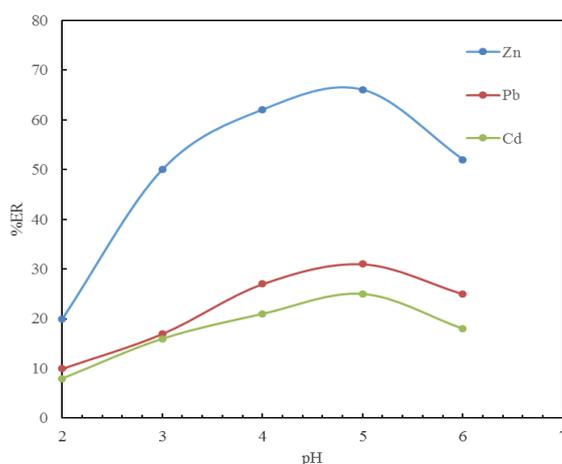
### 3.1.4. Effect of pH

PH was the next factor which was evaluated. For this purpose, the electrochemical behavior of the heavy metal ions (1000  $\text{ng}\cdot\text{mL}^{-1}$  in ABS 0.1 M) was studied while the pH values were differentiated from 2 to 10 and the changes in the response were monitored. As shown in Fig. 4, increasing of the pH amounts led to a shift in the peak potential to less positive amounts, which reflects the participation of  $\text{H}^+$  ions in the interactions at the electrode surface. The

maximum peak current was achieved at a pH 4 that was chosen as the optimal pH value for the upcoming experiments.

### 3.2. Optimizing the HF-LPME

Various parameters have the potential to affect the extraction efficiency which is considered as a principal factor in heavy metal ions analysis. It includes the organic solvent in membrane, the extraction time, DEHPA concentration and the sample solutions pH. In order to reach the maximal extraction recoveries, the stated parameters were optimized for the next steps.



**Fig. 5.** The donor phase pH effect on the extraction efficiency of  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$   $1000 \text{ ng.mL}^{-1}$  solution, 1M DEHPA in xylene, and extraction time of 60 min

#### 3.2.1 The Aqueous phase pH

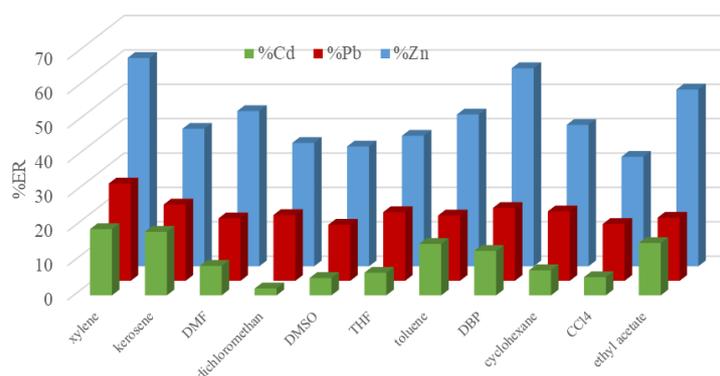
The enrichment factors and extraction recoveries observed in the HF-LPME is highly dependent to the source and receiving phases composition. Consequently, the extraction efficiency is strongly related to the aqueous and donor phase pH. Here, DEHPA was used as an acidic extractant and the extraction reaction occurred through a cation exchange mechanism. On this purpose, the donor phase pH values were alternated from 2 to 6. The results are shown in Fig. 5. The highest extraction efficiency was observed at pH 5. Consequently, the pH value of 5 was chosen for next steps. As mentioned before, the acceptor phase pH was evaluated for electrochemical determination of ions in the receiving phase.

#### 3.2.2. Effect of the solvent type

Since the membrane solvent can be easily immobilized in the HF existing pores, it probably can act as a barrier between the two phases, and also dissolve large amounts of the carrier used for the formation of target ion/carrier pairs. The solvent is desired to have low vapor pressure

to avoid solvent loss during the extraction procedure, and low viscosity to promote ions transfer between the aqueous sample and receiving phase.

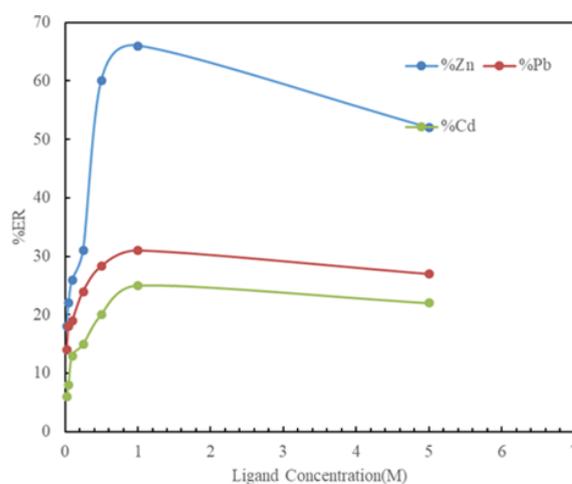
For this goal, various solvents such as dichloromethane, dichloroethane, carbon tetrachloride, chloroform, tetrahydrofuran, xylene, dimethylformamide, dimethylsulfoxide, cyclohexane, ethylacetate and dibutylphthalate were being used for the extraction step under same other stated conditions. It was observed that the most adequate performance of the HF-LPME was obtained through using xylene as the organic phase membrane.



**Fig. 6.** The organic solvent type effect on the extraction efficiency  $Zn^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$  of a  $1000\text{ ng.mL}^{-1}$ ,  $1\text{ M DEHPA}$  and extraction time of  $60\text{ min}$

### 3.2.3. The ligand Concentration

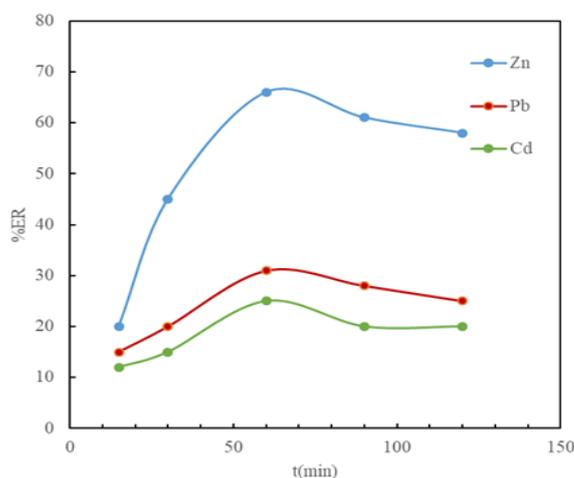
To monitor the effect of DEHPA concentration as the ligand on the target ions extraction recoveries, DEHPA solutions in the range of  $0.025\text{--}5\text{ M}$  in xylene were prepared. According to the results,  $1\text{ M}$  of DEHPA solution in xylene provided the highest extraction efficiency. Over this concentration, the flux of the analytes from the donor phase to the acceptor phase decreased, because of the increased viscosity of the organic s.



**Fig. 7.** The effect of the ligand concentration on the extraction efficiency for  $Zn^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$   $1000\text{ ng.mL}^{-1}$ , DEHPA  $1\text{ M}$  in xylene and extraction time of  $60\text{ min}$

### 3.2.4. Time dependency of the process

It is known that HF-LPME involves two liquid-liquid interfaces including the source/organic phase and the organic/receiving phase interfaces; hence it is supposed that the analyte species might require a long time to pass through these two interfaces.



**Fig. 8.** Time dependency of the extraction efficiency of  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  1000  $\text{ng}\cdot\text{mL}^{-1}$  solution, 1M DEHPA in xylene

The maximum sensitivity could be reached at the equilibrium conditions, since LPME is not an exhaustive extraction technique. Nevertheless, to enhance the precision and sensitivity of LPME and also reach the equilibrium between the phases, it would be required to find the optimal exposure time. On this purpose, the same experiments were run at different extraction times 15-120 minutes and the results are depicted in Fig. 8. This figure clearly indicates that the extraction efficiencies rapidly improved with the extraction time up to 60 min, and after that a relative reduction was observed. Thus, the time of 60 min was chosen and used as the optimal extraction time.

## 3.3. The method Validation

### 3.3.1. The analytical performance

To evaluate the applicability of the introduced method, the limit of detection (LOD), limit of quantification (LOQ), the preconcentration factor (PF), repeatability (i.e. intra-day precision), reproducibility (i.e. inter-day precision) and the extraction recovery (ER) were determined. The LOD was determined by lowering the analyte concentration until the ultrasound assisted HF-LPME-FFTSCCV response led to signals-to-noise ratio (S/N) of 3.

The lowest concentration in the obtained linear range in the calibration curve was considered as the LOQ. The method validation factors were calculated based on five replicate

runs for the ions determination in 1 day (for the repeatability test), as well as five replicate runs over a period of 7 days (to determine the reproducibility). The other determinative parameter known as the extraction recovery (ER %), is the ratio of the extracted analyte value to initial present prior extraction in the donor phase:

$$ER\% = \frac{V_{f,a}}{V_{i,s}} PF \times 100 \quad (1)$$

Where  $V_{f,a}$  and  $V_{i,s}$  are considered as the volumes of the acceptor and donor phases. Additionally, the ratio between the final analyte concentration in the acceptor phase ( $C_{f,a}$ ) to the initial concentration of the analyte in the donor phase ( $C_{i,s}$ ) is identified as the (PF) in which  $C_{f,a}$  is determined from the calibration curves plotted for the direct electrochemical measurements.

$$PF = \frac{C_{f,a}}{C_{i,s}} \quad (2)$$

Under the obtained optimized conditions (donor phase pH=5, acceptor phase pH=4, organic membrane: xylene, DEHPA concentration: 1 M, extraction time: 60 min), the FFTSCCV responses for the ions extracted by ultrasound assisted HF-LPME method, were recorded. For each level, three replicate extractions were performed and the analytical performance of the method are concise in Table 1.

**Table 1.** Validation results for ultrasound assisted HF-LPME-FFTSCCV of  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$  ions

Evaluation parameter <sup>b</sup>	ions		
	Zinc	Lead	Cadmium
Limit of detection (LOD)	0.1	1	0.25
Limit of quantification (LOQ)	1	5	3
Dynamic linear range (DLR)	1-2000	5-1000	3-1500
Determination coefficient ( $R^2$ )	0.99	0.99	0.99
Preconcentration factor (PF)	217.5	155	102.5
Extraction recovery % (ER %)	87	62	41
repeatability	4.5	3.9	3.5
reproducibility	6.2	5.3	4.9

<sup>a</sup>All concentration are based ng/mL

### 3.3.2. The real sample analysis

Three various types of water samples were used to demonstrate the feasibility of the ultrasound assisted carrier-mediated HF-LPME-FFTSCCV. Table 2 shows the gathered results

for three replicate analyses of each real sample spiked with specified analytes amounts. An adequate agreement between the added and measured analyte values was gained. These results confirmed the method validity. Moreover, the coupled method could be used successfully for the extraction, preconcentration and ultra-trace determination of cadmium, lead, zinc ions in the spiked water samples.

**Table 2.** The application of the presented procedure for natural water samples (N=3)

ion	added	River water		Well water		Sea water	
		found	%RR	found	%RR	found	%RR
Zn	-	7.4	-	8.2	-	4.9	-
	25	33.8	104.3	31.6	95.2	30.5	102.0
	50	55.6	96.9	59	101.4	54.1	98.5
Pb	-	5.4	-	5.8	-	3.3	-
	25	28.5	93.8	28.5	92.5	27.3	96.5
	50	56	101.1	60	103.1	51.7	97.0
Cd	-	1.5	-	2.5	-	1.2	-
	25	25.9	97.7	26	94.5	25.3	96.6
	50	49.3	95.7	50.8	96.8	49.8	97.3

### 3.4. Comparison of the results with other methods

Furthermore, the research results were compared with the formerly reported methods employed for the extraction and determination of  $Zn^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$  and the outcome is displayed as Table 3. As it can be seen, the proposed method provided higher sensitivity (i.e. lower LODs) and more wide linear ranges compared with the other reports. In addition to the above advantages, it should be noted that the developed method is simple, easy operated.

**Table 3.** Comparison of ultrasound assisted HF-LPME-FFTSCCV of  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$  ions with other reported extraction techniques

ions	Method <sup>a</sup>	Linearity <sup>b</sup>	LOD <sup>b</sup>	Correlation coefficient	Ref.
Pb, Zn	SPE-FAAS	20-150	8.7-378	0.992	[36]
Pb, Zn, Cd	DPASV	1-130	0.6-0.85	0.998	[37]
Pb, Zn, Cd	SPE-FAAS	20-1000	0.16-0.60	0.999	[38]
Pb, Zn, Cd	CPE- ICP OES	15-5000	4-40	0.999	[39]
Pb, Zn, Cd	SM- $\mu$ -SPE- FAAS	-	0.15-0.7	0.998	[40]
Pb, Cd	SWASV	5-1000	0.2-0.7	0.997	[41]
Pb, Zn, Cd	HF-LPME - FFTSCCV	1-2000	0.1-1	0.99	This work

#### 4. CONCLUSION

In the present paper, a new ultrasonic-assisted HF-LPME mediated with DEHPA as a carrier, was introduced for the extraction and ultra-trace determination of  $Zn^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$  ions using FFTSCCV. It can be concluded that the application of the extraction procedure prior to the electrochemical detection, helped to overcome the existing obstacles. Moreover, the achieved results revealed that the proposed method had the potential to be successfully used for online determination of the analytes in sea water, river and tap water. On the other hand, by combining the ultrasound power with the detection method the time of analysis decreased and also the extraction recoveries of the heavy metal ions enhanced significantly. The best performance of the coupled method was obtained at; donor phase pH=5, acceptor phase pH=4, organic membrane: xylene, DEHPA 1 M, extraction time of 60 min as the optimized circumstances. In a nut shell, the developed coupled method provided lower limit of detection, efficient sample cleanup, short time of analysis and easy operation procedure.

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