Hollow fiber based-liquid phase microextraction using ionic liquid solvent for preconcentration of lead and nickel from environmental and biological samples prior to determination by electrothermal atomic absorption spectrometry

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ABSTRACT

A simple and effective hollow fiber based-liquid phase microextraction (HF–LPME) technique by using ionic liquid, 1-hexyl-3-methylimidazolium hexafluorophosphate, $[C_6MIM][PF_6]$, coupled with electrothermal atomic absorption spectrometry (ETAAS) was developed for the determination of lead and nickel in environmental and biological samples. Ammonium pyrroldinedithiocarbamate (APDC) was used as chelating agent. Several factors that influence the microextraction efficiency and ETAAS signal, such as pH, APDC concentration extraction time, amounts of ionic liquid, stirring rate, pyrolysis and atomization temperature were investigated and the microextraction conditions were established. In the optimum experimental conditions, the detection limits (3 s) of the method were 0.03 and 0.02 μg L^{-1}, for Ni and Pb, respectively and corresponding relative standard deviations (0.5 μg L^{-1}, $n=6$) were 4.2% and 5%. The developed method was validated by the analysis of certified reference materials and applied to the determination of lead and nickel in real samples.

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1. Introduction

The determination of trace metal concentration in environmental and biological samples is getting increasingly important in contamination monitoring studies. In spite of great improvements in the sensitivity and selectivity of modern instrumental analysis such as ICP-MS, ICP-AES and electrothermal atomic absorption spectrometry (ETAAS), difficulties still lie in the analysis of trace heavy metals because of both their low abundance levels in the samples and the high complexity of the sample matrices [1–5]. Therefore, a preconcentration/separation step is often required. The main objective of a sample preparation step is to isolate and concentrate the analytes of interest, and to convert the analytes to a medium compatible with the instrument for the final analytical measurement. In the vast majority of cases, liquid–liquid extraction (LLE) has been the primary sample preparation method to achieve this objective, and is still very popular. However, some disadvantages such as the emulsion formation, the use of large sample volumes and toxic organic solvents and hence, the generation of large amounts of pollutants makes LLE expensive, time-consuming and environmentally unfriendly [6]. The efforts to overcome these limitations have led to the development of microextraction in analytical chemistry [7]. Miniaturized LLE or LPME (liquid phase

microextraction) was introduced in 1996 [8,9]. In LPME, extraction normally takes place into a small amount of water-immiscible solvent (sometimes referred to as the acceptor phase) from an aqueous sample containing analytes (donor phase). The volume of the extracting phase involved in LPME is normally at the microliter level [10]. Basically LPME can be carried out in two forms. If the extraction medium is in the form of a single drop affixed to the tip of a syringe needle, this type of LPME is known as single-drop microextraction (SDME) [11,12]. SDME is a simple, inexpensive, fast, effective and virtually solvent-free sample pretreatment technique. However, it is not very robust, and the droplets may be lost from the needle tip of the microsyringe during extraction. This is especially the case when samples are stirred vigorously to speed up the extraction process. In order to overcome these drawbacks, Pedersen-Bjergaard and Rasmussen [13] introduced the use of a hollow fiber membrane (HF) to stabilize the extracting phase. In hollow fiber LPME, analytes are extracted from an aqueous sample, into the organic solvent immobilized as a supported liquid membrane and into the acceptor solvent placed inside the lumen of the hollow fiber. Subsequently, the acceptor phase is removed by a microsyringe and transferred to final chemical analysis. HF-LPME allows extraction and preconcentration of analytes from complex samples in both a simple and inexpensive way. Usually, two extraction modes including two-phase extraction and three-phase extraction (extraction/back extraction) are used for HF-LPME [14–16]. For both extraction modes, the selection of an appropriate extraction solvent is of major importance to achieve efficient

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extraction. Selection of a solvent is based on the proper immobilization of pores of fiber, immiscibility of the solvent with water, low volatility, and good extraction efficiency of analytes. Several reports have appeared in which hollow fiber has successfully been utilized for extraction of metal ions as chelate. However, in these procedures, toxic organic solvents such as tetrachloromethane and toluene have been used [17–19].

Room temperature ionic liquids (RTILs) are salts that are liquid over a wide temperature range including room temperature and result from combination of organic cations with various anions. They have recently attracted special interest as environmentally friendly solvents to replace traditional volatile organic solvents in various area of chemistry. RTILs based on alkyl imidazolium hexafluorophosphate have been used by many researchers for developing green processes. However, it should be noted that these compounds may be potentially toxic due to the instability of the $[PF_6]^-$ anion towards hydrolysis in contact with moisture, which results in forming some volatile species including HF and POF3 [20]. RTILs have some unique physicochemical properties such as negligible vapor pressure, non-flammability as well as good extractability for various organic compounds and metal ions, which make them very useful for LLE and LPME [21,22]. The attempt of our research group has currently been focused on the application of RTILs in LPME of metal ions with direct injection into the graphite furnace [23,24]. The objective of this work was the application of ionic liquids as efficient and environmentally friendly solvents for the preconcentration of lead and nickel as ammonium pyrroldinedithiocarbamate (APDC) complexes by the aid of HF-LPME technique. A hollow fiber membrane was used for supporting ionic liquid extracting phase in order to eliminate the problem of drop stableness in the SDME method. To the best of our knowledge, this is the first attempt to apply RTILs in HF-LPME of metal ions with direct injection into the graphite furnace.

2. Experimental

2.1. Apparatus

A Shimadzu (Kyoto, Japan) Model AA-670G atomic absorption spectrometer equipped with a GFA-4A graphite furnace atomizer and deuterium lamp background correction was employed. Lead and nickel hollow cathode lamps (Hamamatsu photonics K.K., Japan) were used as the radiation sources. The operating conditions of the hollow cathode lamps were those recommended by the manufacturer. Pyrolytically coated graphite tubes were used throughout. Argon 99.999% (Roham gas Co., Tehran, Iran), with $1.5 \, L \, min^{-1}$ flow rate, was used as a protective and purge gas. The detailed graphite furnace temperature programs used for the determination of lead and nickel are shown in Table 1. A 10 μL microsyringe (Hamilton) was employed to introduce 8 μL ionic liquid extracting phase to the solution and to inject it into the graphite furnace. Q 3/2 Accurel polypropylene hollow fiber membrane (600 μm I.D., 200 μm wall thickness, 0.2 μm pore size) from Membrane, Wuppertal, Germany was utilized. A Metrohm model 654 pH meter was used for pH measurements.

2.2. Standard solutions and reagents

All chemicals used were of analytical-reagent grade and all solutions were prepared with doubly distilled deionized water (obtained from Ghazi Serum Co., Tabriz, Iran). 1-hexyl-3-methylimidazolium hexafluorophosphate, $[C_6MIM][PF_6]$, and 1-butyl-3-methylimidazolium hexafluorophosphate, $[C_4MIM][PF_6]$ were purchased from Acros (NJ, USA) and Merck (Darmstadt, Germany), respectively and used as obtained. A stock standard solution

Table 1
Optimum ETAAS operating conditions for the determination of nickel and lead.

	Nickel	Lead
Wavelength (nm)	232	217
Lamp current (mA)	7	7
Background correction	Deuterium	Deuterium
Drying temperature (°C)	150 (ramp 60 s)	120 (ramp 20 s)
Pyrolysis temperature (°C)	1000 (hold 40 s)	600 (hold 40 s)
Atomization temperature (°C)	2400 (hold 4 s, gas stop)	1300 (hold 3 s, gas stop)
Cleaning temperature (°C)	3000 (hold 2 s)	2000 (hold 2 s)
Argon purge gas flow rate (L min⁻¹)	1.5	1.5
Determination mode	Peak height	Peak height

of lead and nickel was prepared by dissolving an appropriate amount of $Pb(NO_3)_2$ and $Ni(NO_3)_2.6H_2O$ (Merck) into a 100 mL flask and diluting to the mark with distilled water. The working solutions of lead and nickel were made by suitable dilution of the stock solutions with doubly distilled water. A 1% (w/v) solution of ammonium pyrrolidinedithiocarbamate (APDC) was prepared by dissolving appropriate amount of APDC, (Fluka, Buchs, Switzerland), in water. A 0.1% (w/v) chemical modifier solution was prepared by diluting $Pd(NO_3)_2$ stock solution ($10 \, g \, L^{-1}$, Merck (Darmstadt, Germany)). Solutions of $1.0 \, mol \, L^{-1}$ hydrochloric acid and sodium hydroxide were used for pH adjustment.
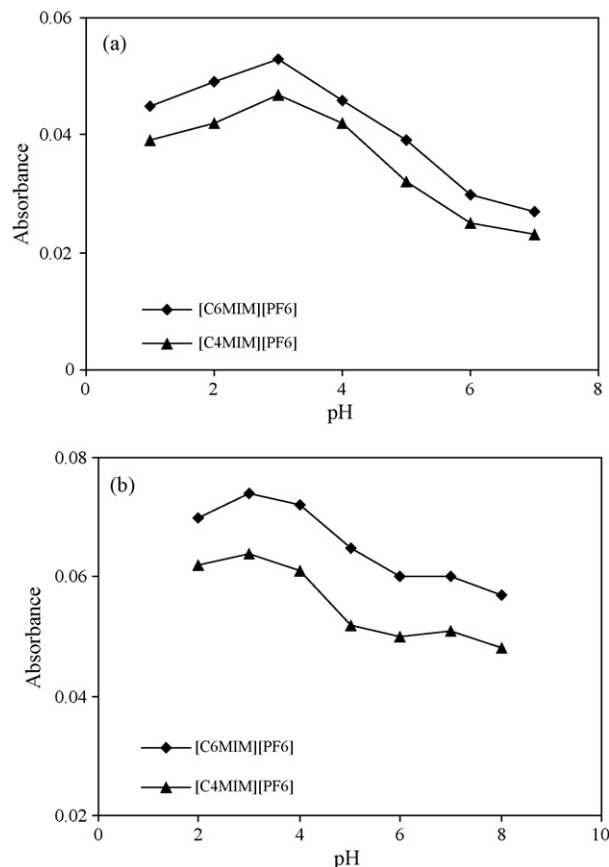

Fig. 1. Effect of pH and type of ionic liquid on the absorbance of (A) nickel and (B) lead. Conditions: lead, $0.2 \, \mu g \, L^{-1}$; nickel, $0.5 \, \mu g \, L^{-1}$; APDC, 0.1%; stirring rate, 1100 rpm; extraction time, 15 min for Pb and 12 min for Ni; ionic liquid volume, 8 μL. Graphite furnace programs are given in Table 1.
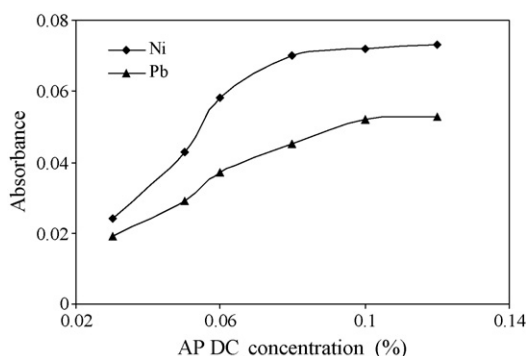
Fig. 2. Effect of APDC concentration on the absorbance of nickel and lead at pH 3.0. Other conditions are as Fig. 1.

Fig. 4. Effect of stirring rate on the absorbance of nickel and lead. Conditions are as Fig. 2.

2.3. Sample preparation

Water samples including river, underground, subterranean canal and tap waters were collected from local sources. After sampling, they were filtered through Rund filter paper (blue band, no. 300210) to remove suspended particulate matter. Aliquots of 3 mL from each sample solution were used for the analysis after adjusting their pH to 3 with 1.0 mol L^{-1} HCl and NaOH solutions.

Two Standard reference materials were used for validation of the method;

(1) NIST SRM 1643e (Trace Elements in Water): A suitable aliquot of this sample was diluted 50-fold and its pH was adjusted to 3 with 1.0 mol L^{-1} HCl and NaOH solutions.
(2) NIST SRM 1566b (Oyster Tissue): An accurately measured amount of the sample was placed in a 100 ml beaker and 30 mL concentrated HNO$_3$ and 8 ml concentrated HClO$_4$ was added, covered with a watch glass. The beaker was heated on an oil bath of 100 °C for 45 min. Then the heating process was continued for 45 min at 150 °C. The watch glass was removed and the acid evaporated to dryness at 200 °C [25]. The white residue obtained was dissolved in about 50 mL distilled water and after adjusting its pH to 3 with 1.0 mol L^{-1} HCl and NaOH, the solution was diluted to the mark in a 100 mL volumetric flask.

2.4. Extraction procedure

The polypropylene hollow fiber that was cut manually and carefully into 3.0 cm length was immersed in [C$_6$MIM][PF$_6$] ionic liquid for 10 s to immobilize the ionic liquid in the pores of the hollow fiber. The approximate internal volume of this segment was 9.0 μL. The hollow fiber was taken out and its outside was washed with water. Then it was mounted onto the needle tip of the microsy-

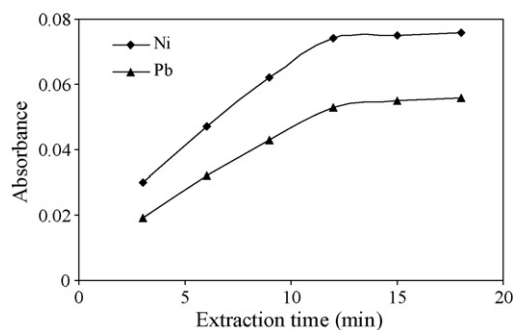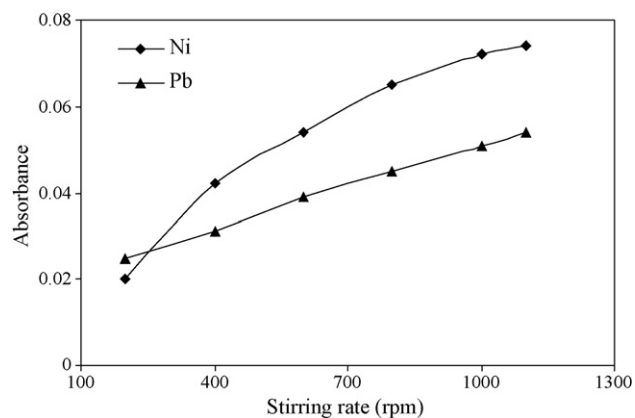**Fig. 3.** Effect of extraction time on the absorbance of nickel and lead. Conditions are as Fig. 2.

ringe holding 8.0 μL acceptor solution (ionic liquid). Thereafter, the plunger of the microsyringe was depressed to flush out 8.0 μL ionic liquid to fill the lumen of the hollow fiber without any air bubbles. Then, the other end of the fiber was sealed with heated tweezers. A 3.0 ml of sample was placed in a 5 ml capacity vial containing stir bar and 300 μL 1% APDC solution was added. The vial was placed on a magnetic stirrer with a stirring rate of 1100 rpm and the prepared hollow fiber with the microsyringe was immersed into the sample solution. The magnetic stirrer was turned on to start the extraction. After stirring for a prescribed time, the hollow fiber was taken out from the aqueous solution. The sealed end was cut open and the acceptor solution was withdrawn into the microsyringe and injected manually into the graphite furnace. Ten microliters of palladium modifier (0.1%) was also injected into the furnace and the temperature program was followed according to Table 1. Before each extraction, microsyringe was rinsed with ethanol to avoid formation of air bubbles and the carryover of compounds between extractions. Calibrations were performed using aqueous calibration solutions submitted to the same HF-LPME procedure described above.

3. Results and discussion

3.1. Optimization of ETAAS conditions

Preliminary experiments indicated that the time and temperature program suggested by the manufacturer could not be efficient in this method. Therefore, the effects of pyrolysis and atomization temperatures and the holding time on the determination of Ni and Pb were investigated. In APDC-[C$_6$MIM][PF$_6$] medium, the analytical signals were low while the background signals were rather large. For improving these conditions, the addition of a chemical modifier was found to be necessary. We used Pd(NO$_3$)$_2$ as a common chemical modifier. Palladium is known to stabilize volatile elements and/or their volatile compounds and to permit the use of higher pyrolysis temperature [26,27]. This higher pyrolysis temperature allows effective charring of organic matrices prior to the analyte volatilization, which leads to a lower background. We found that the pyrolysis temperature reached a maximum at 1000 °C for Ni, and at 600 °C for Pb. The effect of pyrolysis time on the absorbance of Ni and Pb was also investigated. The results showed that the absorbance signals of both elements were increased with increasing pyrolysis time up to 40 s and no appreciable improvements were observed for longer times. As a result, a pyrolysis time of 40 s was chosen.

Using the chosen pyrolysis temperatures and times, the effect of the atomization temperature, on analytical signal of Ni and Pb was

Table 2
Analytical characteristics of the proposed method for determination of Ni and Pb.

Parameter	Ni	Pb
Linear range ($\mu g\,L^{-1}$)	0.08–2.0	0.04–1.0
Slope (±SD)	0.133 (±0.0025)	0.259 (±0.0042)
Intercept (±SD)	0.0045 (±0.0026)	0.0014 (±0.0021)
Number of points	9	9
Correlation coefficient (R^2)	0.9975	0.9981
Enhancement factor[a]	60	76
Limit of detection ($\mu g\,L^{-1}$)	0.03	0.02
RSD% ($n=6$)	4.2	5.0

[a] Calculated as the slope ratio of the calibration graphs obtained with preconcentration of 3 mL solution and without preconcentration.

studied. It was found that the signal intensity of Ni and Pb increased with the increase of atomization temperature. The maximum signal intensities of Ni and Pb were obtained at 2400 °C and 1300 °C, respectively. The results showed that the atomization time had little effect on atomic signals. Therefore, the recommended times by the manufacturer were used as shown in Table 1.

3.2. Optimization of HF-LPME conditions

To develop an ionic liquid-based HF-LPME method for preconcentration of Ni and Pb, several important parameters such as, the type of ionic liquid, pH, APDC concentration, stirring rate and extraction time were assessed.

The type of solvent used in HF-LPME is an essential consideration for efficient preconcentration. The solvent should have a low solubility in water and should be non-volatile to prevent its loss during extraction. For these reasons, we chose two common ionic liquids, [C_4MIM][PF_6] and [C_6MIM][PF_6], as extraction solvents and their extraction performances were compared. According to Fig. 1, the ionic liquids with a longer chain, [C_6MIM][PF_6], showed the higher extraction efficiency and improved preconcentration factor in the LPME techniques.

Extraction of metal ions into RTILs may be accomplished by using a neutral or anionic ligand. In the former case ion-pair formation between ionic complex and the constituent ions of RTILs is believed to be responsible for extraction. However, the use of anionic ligands to form neutral or low-charged metal complexes seems to be preferred in the extraction using RTILs [28]. In this work APDC was chosen as a widely used chelating agent for the microextraction of lead and nickel since it is soluble in aqueous solution and can form extractable complex with target ions in acidic conditions, which is compatible with acid digested samples.

The pH of sample solution is one of the most important factors affecting the formation of complexes and subsequent extraction. Fig. 1 depicts the effect of pH on the absorbance signals of Ni and Pb

Table 4
Tolerance limits of interfering ions in the determination of 0.5 $\mu g\,L^{-1}$ Ni and Pb. Foreign ion to analyte ratio.

Coexisting ions	Analyte to interferent ratio	
	Ni	Pb
Na^+, K^+, Ca^{2+}, Mg^{2+}, I^-, CO_3^{2-}, F^-	50,000[a]	50,000[a]
Li^+, SO_4^{2-}, CH_3COO^-, NO_3^-	15,000	10,000
Al^{3+}, Ba^{2+},	5000	5000
Hg^{2+}, Ag^+,	2500	5000
Cr(VI), Mn^{2+}	1000	500
Cr^{3+}, Zn^{2+}	250	500
V(V)	250	100
Pb^{2+}	250	–
Co^{2+}, As(III)	125	100
Cd^{2+}	125	50
Ni^{2+}	–	100
Fe^{2+}, Fe^{3+}, Cu^{2+}	100	50

[a] Maximum ratio tested.

using APDC as complexing reagent and ionic liquids as the extraction solvents. It could be seen that the absorbance signal for Ni and Pb are relatively constant in the range of 1–3 and diminish at higher pHs. Therefore, a pH value of 3.0 was selected for further studies. This pH was adjusted by using 1.0 mol L^{-1} HCl and NaOH solutions.

The influence of the amount of APDC on the extraction efficiency of Ni and Pb were studied and the experimental results are shown in Fig. 2. The absorbance of Ni and Pb were increased with the increase of APDC amount from 0.03 to 0.12% (w/v) as a result of the high extraction efficiency of the complexes to ionic liquid phase and then remained constant with the further increase of APDC amount. The value of 0.1% was chosen as the optimum amount of APDC.

Extraction time is another important factor influencing the extraction efficiency. Maximum efficiency is obtained when the system is at equilibrium. Since RTILs have higher viscosities than conventional organic solvents, the diffusion of target species through the membrane and so the extraction rate will slightly be slower compared to the cases where organic solvents are used [18,29]. The range of extraction times investigated here was between 4 and 20 min. Fig. 3 shows that the analytical signals increase quickly with the extraction time until 12 and 15 min for Ni and Pb respectively. No significant increase was obtained with additional extraction time. Therefore, 12 and 15 min were chosen in the following studies.

The effect of stirring speed on the extraction efficiency was also examined. Higher stirring rate causes an increase in the mass transfer process and also the kinetic rates. To evaluate the effect of sample stirring, various stirring rates were tested. The results in Fig. 4 indicated that agitation of the sample greatly improves extraction efficiency. High stirring rate caused many bubbles to

Table 3
Comparison of the proposed method with other preconcentration-ETAAS methods.

Preconcentration technique	EF[a]		LOD ($\mu g\,L^{-1}$)		Sample volume (mL)		Ref
	Ni	Pb	Ni	Pb	Ni	Pb	
DLLME	200	78	0.033	0.039	5	5	[30,31]
SPE-SI-LOV	32	27	0.02	0.07	1.8	1.8	[32]
CPE	27	–	0.12	–	10	–	[33]
CPE	–	50	–	0.08	–	10	[34]
Flotation	–	–	0.007[b]	9[b]	15	15	[35]
Emulsion	–	100	0.01	–	100	–	[36]
SPE-FAAS	50	–	1.03	–	250	–	[37]
SPE-FAAS	1000	1000	0.01	1.52	2000	2000	[38]
HF-IL- LPME	60	75	0.03	0.02	3	3	This work

DLLME: dispersive liquid–liquid microextraction, SPE-SI-LOV: solid phase extraction-sequential injection lab-on-valve, CPE: cloud point extraction, HF-IL-LPME: hollow fiber based ionic liquid–liquid-phase-microextraction.

[a] Enhancement or enrichment factor.

[b] $\mu g\,g^{-1}$.

Table 5
Results of determination of Ni and Pb in certified reference materials.

Sample	Certified value	Found value[a]
NIST 1643e		
Ni	62.41 ± 0.69 (μg L^{-1})	62.15 ± 0.01 (μg L^{-1})
Pb	19.63 ± 0.21 (μg L^{-1})	18.86 ± 0.06 (μg L^{-1})
NIST SRM 1566b		
Ni	1.04 ± 0.09 (mg kg^{-1})	1.03 ± 0.045 (mg kg^{-1})
Pb	0.31 ± 0.009 (mg kg^{-1})	0.32 ± 0.007 (mg kg^{-1})

[a] Mean of three determinations ± standard deviation.

attach on the surface of the hollow fiber, which impeded the transfer of the analyte. Therefore, a stirring rate of 1100 rpm was selected in this work.

3.3. Analytical figures of merit

Under the optimized temperature program and extraction conditions, calibration graphs for Ni and Pb were constructed by preconcentrating a series of standard solutions (with volumes of 3 mL) for each analyte. Calibration graph exhibited linearity over the range of 0.08–2.0 μg L^{-1} for Ni and 0.04–1.0 μg L^{-1} for Pb. The analytical characteristics of the methods are summarized in Table 2. Comparison of analytical features of this method with those of some other preconcentration-ETAAS techniques (Table 3) indicates that the enhancement factor and LOD of the proposed method are better than or comparable with the most of other methods.

Table 6
Determination of Ni and Pb in real samples and relative recoveries of spiked samples.

Sample	Added (μg L^{-1})	Found (μg L^{-1})[a]	Recovery (%)
Tap water[b]			
Ni	0	0.34 ± 0.03	
	0.20	0.53 ± 0.04	95
	0.40	0.73 ± 0.06	97.5
Pb	0	0.2 ± 0.01	
	0.20	0.40 ± 0.02	100
	0.40	0.57 ± 0.03	95
Subterranean canal water[c]			
Ni	0	0.36 ± 0.01	
	0.20	0.57 ± 0.008	105
	0.40	0.77 ± 0.03	102.5
Pb	0	0.08 ± 0.008	
	0.20	0.27 ± 0.01	95
	0.40	0.46 ± 0.03	95
River water[d]			
Ni	0	0.20 ± 0.02	
	0.20	0.41 ± 0.01	105
	0.40	0.61 ± 0.03	102.5
Pb	0	0.17 ± 0.03	
	0.20	0.36 ± 0.01	95
	0.40	0.56 ± 0.03	97.5
Underground water[e]			
Ni	0	0.16 ± 0.04	
	0.20	0.35 ± 0.03	95
	0.40	0.54 ± 0.05	95
Pb	0	0.22 ± 0.03	
	0.20	0.43 ± 0.04	105
	0.40	0.62 ± 0.03	102.5

[a] Mean of three determinations ± standard deviation.
[b] From drinking water system of Tabriz, Iran.
[c] Obtained from Tasooj, Iran.
[d] From Almas river, Iran.
[e] Obtained from Sharafkhaneh, Iran.

3.4. Study of interferences

In order to assess the possible analytical application of the procedure presented, the effects of some foreign ions, which often accompany analyte ions in various real samples and may interfere with the methods, were examined in the optimized conditions at above. For this purpose, solution of 0.5 μg L^{-1} of studied analyte containing the corresponding interfering ions were prepared and operated according to the recommended procedure. An ion was considered to interfere when its presence produced a variation of more than 5% in the absorbance of the sample. The results are shown in Table 4. All studied ions were found not to affect Ni and Pb signals in the HF-LPME-ETAAS system when they are present in 100-fold excess. Higher concentrations of alkali and alkaline earth metals can be tolerated. As shown later, these results permit the application of the proposed system for interference-free determination of ultra-trace nickel and lead in water and biological samples.

3.5. Analysis of real samples

In order to verify the accuracy of the proposed procedure, the method was first applied to the determination of nickel and lead in two standard reference materials, NIST SRM 1643e Trace elements in water, and NIST SRM 1566b Oyster Tissue. The obtained values for nickel and lead by using the proposed HF-LPME-ETAAS method were given in Table 5, which are in good agreements with the certified concentrations. It can be concluded that the proposed method is accurate and free from systematic errors.

The proposed method was also applied to the determination of Ni and Pb in four natural water samples. Table 6 shows the obtained results.

4. Conclusion

A new method of hollow fiber based-liquid phase microextraction using ionic liquid solvent for the determination of lead and nickel in environmental and biological samples was demonstrated in this study. The proposed method is simple and effective and has eliminated the difficulty of maintaining the drop in the single-drop microextraction (SDME). Moreover, by using ionic liquids as extraction phase, the need for using toxic organic solvents was eliminated. It can be concluded that our simple supported liquid hollow fiber membrane microextraction has a great potential for the analysis of Ni and Pb in water and biological samples.

Acknowledgment

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