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Ultrasonic Assisted Liquid Phase Microextraction of Pb^{2+} Based on Deep Eutectic Solvent Followed by Electrothermal Atomic Absorption Spectrometry

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Abstract

This study presents an efficient, rapid, green, and low-cost method for preconcentrating trace levels of Pb^{2+} using ultrasonic-assisted liquid-phase microextraction (UA-LPME) followed by electrothermal atomic absorption spectrometry. We used sulfanilamide as a complexing agent to form a hydrophobic complex with Pb^{2+}, and a mixture of choline chloride-phenol as an extraction solvent. We investigated and optimized several parameters affecting the analyte's extraction recovery, including pH of the sample solution, concentration of the complexing agent, mole ratio of choline chloride phenol, volume of extraction solvent, volume of tetrahydrophoran (as an aprotic solvent), and ultrasonic time. Under the optimized conditions, we found that the proposed method has a linear range of 0.5-10 µg L-1 Pb^{2+} and a limit of detection of 0.16 µg L-1 Pb^{2+} (n=6). The proposed method's accuracy was verified using certified reference material-trace metals in drinking water (CRM-TMDW) samples. We also successfully used the proposed method to determine trace levels of Pb^{2+} in different water samples. In conclusion, our study offers an effective UA-LPME-based method for preconcentrating trace levels of Pb^{2+} that can be applied to environmental monitoring and analysis.

Keywords: Ultrasonic assisted liquid phase microextraction, Lead, Sulfanilamide, Deep eutectic solvent.

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Introduction

Lead (Pb) is one of the most abundant toxic heavy metals that has been used in different industrial activities, such as car batteries, cable sheathing, colors and pigments, weights for lifting and alloys manufacturing [1]. Its exposure from the combustion of fossil fuels for electrical utility or gasoline combustion engines causes to contamination of earth's soil and surface water. Furthermore, due to its high toxicity for humans and animals even at low concentrations, determination of low amounts of Pb^{2+} is very crucial [2]. Electrothermal atomic absorption spectrometry (ETAAS) is the most common analytical tool for determination of heavy metals due to its high sensitivity, selectivity, and ability to use low amounts of analyte [3]. However, in order to obtain accurate results at trace levels of analyte, a sample preparation technique is highly required.

In order to determine ultra-trace levels of Pb^{2+} in different real samples with high accuracy, the application of preconcentration techniques is inevitable. Liquid phase microextraction (LPME) is one of the sample preparation techniques that is widely used for preconcentration of wide ranges of pollutants [4-10]. Ultrasonic assisted liquid phase microextraction (UA-LPME) employed an ultrasonic bath for dispersion of extraction solvent into the fine droplets to increase the surface area ratio [11, 12]. Therefore, extraction of the analyte takes place in a short time.

Deep eutectic solvents (DESs) have recently been introduced and used as extraction solvents in LPME techniques. DESs are generally composed of two or more green and inexpensive components that associate with each other through hydrogen bonds to form eutectic mixture with a melting point lower than that of each individual component [13-15]. DESs are usually obtained by the complexation of choline chloride salt, a quaternary ammonium salt (ChCl) with hydrogen bond donor (HBD) compounds or metal oxides [16, 17]. Due to the many advantages of DESs, such as non-toxicity, biodegradability, ease of synthesis, and low cost, these solvents could be considered as green extraction solvents for LPME methods. Also, these DESs exhibit similar physicochemical properties to the traditionally used ionic liquids (ILs). As compared to ILs, DESs have unique advantages including: (1) convenient synthesis (2) very low price due to their accessible chemicals and (3) low toxicity, especially DESs derived from ChCl and renewable chemicals [18-21].

In the present work, we used DESs for the preconcentration of trace levels of Pb^{2+} followed by its determination with electrothermal atomic absorption (ETAAS). Sulfanilamide (SA) was used as a chelating agent to form a hydrophobic complex with Pb^{2+}. By using choline chloride-phenol (as the extraction solvent) and THF (aprotic solvent), ultrasonic-assisted liquid-phase microextraction (UA-LPME) was used for preconcentration of trace levels of Pb^{2+}. The main parameters affecting the extraction recovery, such as pH, concentration of SA, volume of extraction solvent, volume of THF and the extraction time were completely investigated and optimum conditions were selected.

Finally, the proposed method was used for determination of trace levels of Pb^{2+} in different water samples.

Experimental

Instruments

Perkin Elmer Analyst 700 model 4100 electrothermal atomic absorption spectrometry equipped with deuterium lamp as a background correction system was used for determination of Pb. A lead hollow cathode lamp at a wavelength of 283.3 nm was used as a radiation source. A pyrolytic-coated graphite tube with Lvov platform was used. Table 1 shows the instrumental parameters of ETAAS for determination of Pb. The pH of sample solution was measured with Metrohm 827 pH lab, Switzerland. Phase separation was assisted using the Centurion Scientific Centrifuge (model Andreas Hettich D72, Tuttlingen, Germany).

Reagents

Deionized water was used throughout the analysis. A solution of 1000 mg L^{-1} of lead was prepared in 1% HNO_3 form $Pb(NO_3)_2.H_2O$ (Merck, Darmstadt, Germany). A solution of 0.01 mol L^{-1} SA was prepared by dissolving of 0.0861g of SA (Merck, 99.5%) in 50 mL of deionized water. Choline chloride (a hydrogen bond acceptor) and phenol (a hydrogen bond donor) were purchased from Merck (Darmstadt, Germany). Tetrahydrofuran, an aprotic solvent was purchased from Merck, Germany. Solutions of 0.1 mol L^{-1} HNO_3 and NaOH were used for adjusting the pH values.

Preparation of extraction solvent

6.9 g choline chloride and 9.4 g phenol (mole ratio of 1:2, choline chloride: phenol) were mixed at room temperature and stirred for 15 min. the obtained liquid was used as an extraction solvent in the UA-LPME technique.

Microextraction procedure

Eight milliliters of sample solution containing 5 µg L^{-1} Pb^{2+} and optimum amounts of SA as a complexing agent were transferred into the conical centrifuge tube, followed by adjusting the pH value to 6. Then, 400 µL of choline chloride-phenol (with a mole ratio of 1:2 as the extraction solvent) was added to the sample solution. The resulting mixture was stirred for 1 min, followed by addition of 500 µL tetrahydrofuran to the mixture. By ultarsonication of the mixture for 5 min at 3500 rpm, the collected extraction solvent was diluted to 400 µL with ethanol, and an aliquot of 20 µL of the resulting solution was injected into the ETAAS for quantification of Pb.

Sample preparation

Water sample

Different water samples including tap water (Mashhad and Neyshabur, Iran), spring water (Nowchah, Mashhad, Iran) and river water (Kashaf Rood, Mashhad, Iran) were collected and kept at 4 ˚C before analysis. For analysis of the water samples, an aliquot of each sample was adjusted to desired pH values and analyzed for its Pb^{2+} content according to the preconcentration procedure.

Results and discussions

Optimization of ETAAS

Three main steps in ETAAS including, drying, ashing and atomization were optimized to obtain maximum sensitivity for determination of Pb^{2+}. Two drying steps including 80 ˚C and 120 ˚C, were applied to remove solvent from the graphite tube. The ashing temperature was studied in the range of 400-800 ˚C. The results show that a temperature of 700 ˚C with 15- sec hold time provides the maximum absorbance for determination of lead. The atomization temperature was studied in the range of 1600-2000 ˚C. The results show that a temperature of 1800 ˚C with a hold time of 3- sec provides the maximum absorbance for determination of lead (Table 1).

Table 1. ETAAS instrumental parameter for determination of lead.

Step	Temperature[a]	Ramp time[b]	Hold time[c]	Argon flow rate[d]
Drying 1	80	3	15	300
Drying 2	120	10	20	300
Ashing	700	30	15	300
Atomization	1800	0	3	0
Cleaning	2400	2	3	300

a: °C, b & c: sec and d: mL min^{-1}

Effect of pH

The pH of sample solution is one of the most important parameters affecting the stability of the metal-complexing agent complex; therefore it has an important effect on the extraction recovery of the analyte [22, 23]. The effect of pH on the extraction recovery of Pb^{2+}-SA complex was investigated in the range of 2-9. The results showed that, at pH values higher than 6, the extraction recovery decreases dramatically (Figure 1). Also, at acidic pH values (below 5), due to the instability of the Pb^{2+}-SA complex, the extraction recovery decreases, which clearly show that the resulting complex is stable at a neutral pH value. Therefore, pH 6 was selected as the optimum pH value.

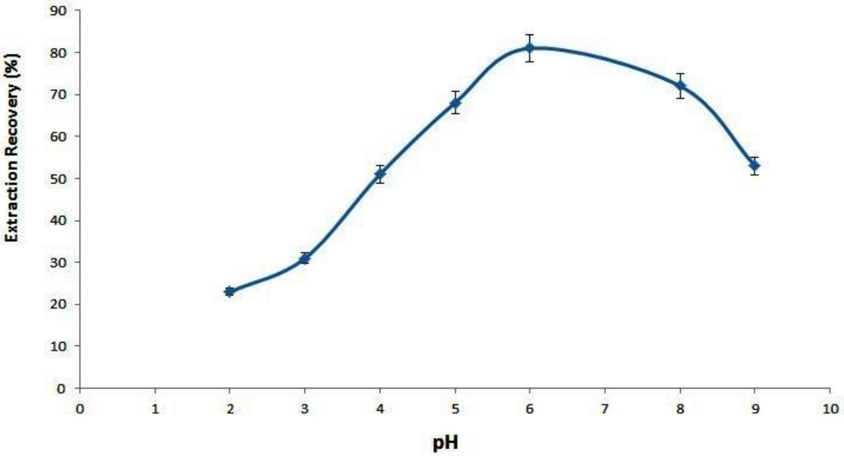

Figure 1. Effect of pH on the extraction recovery of Pb^{2+}. Conditions: 5 µg L^{-1} Pb^{2+}, 2.5×10^{-4} mol L^{-1} SA, 400 µL extraction solvent, 2 min extraction time and 500 µL of THF.

Effect of concentration of complexing agent

The concentration of the complexing agent is an important parameter affecting the extraction recovery of the analyte. In this paper, SA was used as the complexing agent and its effect was studied in the range of 1×10^{-4}-5×10^{-4} mol L^{-1}. The obtained results are presented in Figure 2. According to the results, by increasing of the concentration of SA up to 2.0×10^{-4} mol L^{-1}, the extraction recovery of Pb^{2+} increases, and it remains constant for higher amounts of SA. Therefore, in this experiment, a concentration 2.5×10^{-4} mol L^{-1} SA was selected as the optimum value.

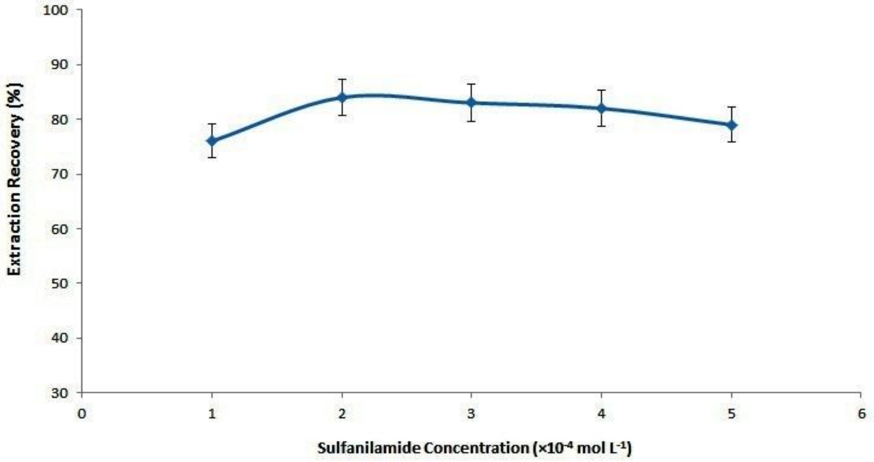

Figure 2. Effect of SA concentration on the extraction recovery of Pb^{2+}. Conditions: 5 µg L^{-1} Pb^{2+}, pH 6, 400 µL extraction solvent, 2 min extraction time and 500 µL of THF.

Effect of mole ratio of extraction solvent

In this paper, a mixture of choline chloride and phenol was used as a green extraction solvent. In order to find the optimum mole ratio of choline chloride-phenol components, different mixtures of choline chloride-phenol including 1:1, 1:2, 1:3, and 1:4, were prepared and used as extraction solvents. Based on the obtained results presented in Figure 3, the mole ratio of 1:2 choline chloride to phenol provides maximum extraction recovery for determination of Pb.

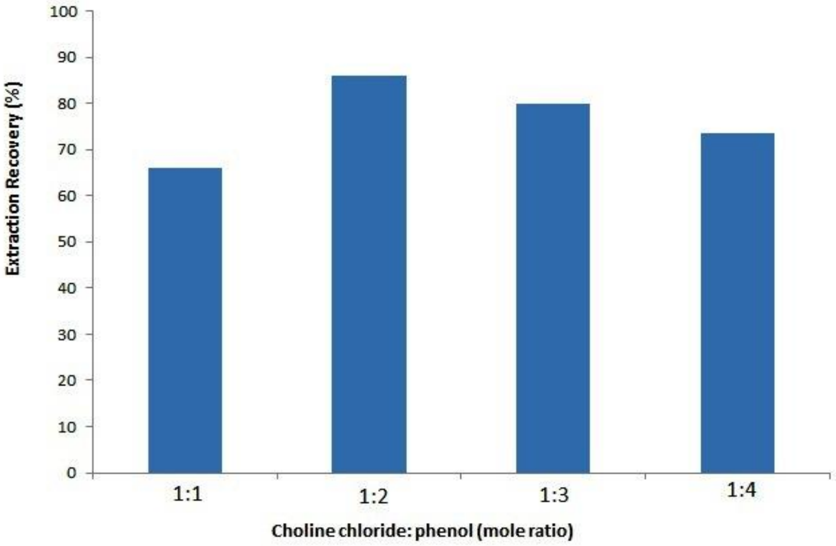

Figure 3. Effect of mole ratio of extraction solvent on the extraction recovery of Pb^{2+}. Conditions: 5 µg L^{-1} Pb^{2+}, pH 6, 400 µL extraction solvent, 2 min extraction time and 500 µL of THF.

Effect of volume of extraction solvent

to optimize the volume of the extraction solvent (choline chloride and phenol) in UA-LPME method, different volumes of extraction solvent in the range of 200 to 500 µL were tested. The results in Figure 4 show that for, 400 µL of the choline chloride and phenol provides maximum extraction recovery of Pb^{2+}-SA complex. The increase in extraction recovery with an increase in the volume of the extraction solvent could be related to the higher surface-to-volume ratio of the extraction solvent in the aqueous solution. Therefore, 400 µL of the extraction solvent was considered as the optimum value.

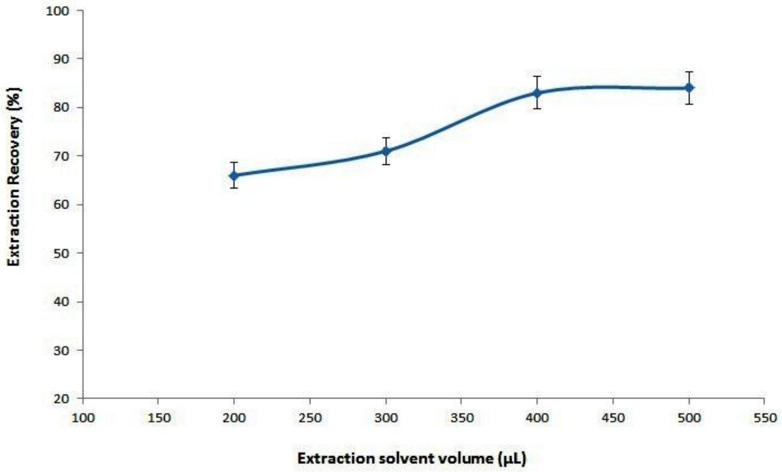

Figure 4. Effect of volume of the extraction solvent on the extraction recovery of Pb^{2+}. Conditions: 5 µg L^{-1} Pb^{2+}, 2.5×10^{-4} mol L^{-1} SA, 2 min extraction time and 500 µL of THF.

Effect of ultrasonic time

Extraction time is also one of the significant parameters affecting the extraction recovery of analyte. It should be optimized critically to ensure that the equilibrium conditions between the acceptor (extraction solvent) and the donor (aqueous) phases are established. In the UA-LPME method, the ultrasonic radiation causes of DES solvent to disperse into the nanosized droplets. Therefore, it could be expected that the extraction recovery of the Pb^{2+}-SA complex in UA-LPME microextraction techniques would reach the maximum value in a short period of time. Figure 5 shows the extraction recovery of the Pb^{2+}-SA complex at different extraction times for the UA-LPME microextraction method. As it can be seen, a 2- min extraction time is adequate to obtain the maximum extraction recovery of Pb^{2+}. Therefore, a 1.5- min extraction time was selected as the optimum value.

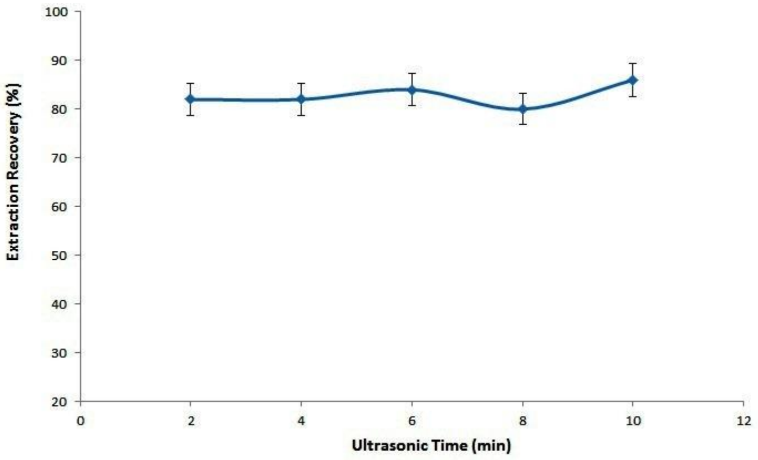

Figure 5. Effect of ultrasonic time on the extraction recovery of Pb^{2+}. Conditions: 5 µg L^{-1} Pb^{2+}, 2.5×10^{-4} mol L^{-1} SA, 400 µL extraction solvent and 500 µL of THF.

Volume of THF

THF was used as an aprotic solvent to reduce the solubility of choline chloride-phenol extraction solvent in the sample solution. The effect of THF on the RP of Pb^{2+}-SA complex was investigated by addition of different volumes of THF in the range of 200-1000 µL. Based on the obtained results presented in Fig 6, by increasing of the volume of THF, the extraction recovery of Pb^{2+} increases, which could be related to the complete aggregation of the extraction solvent, at 500 µL THF, that reaches to the maximum value. Therefore, 500 µL THF was selected as the optimum value.

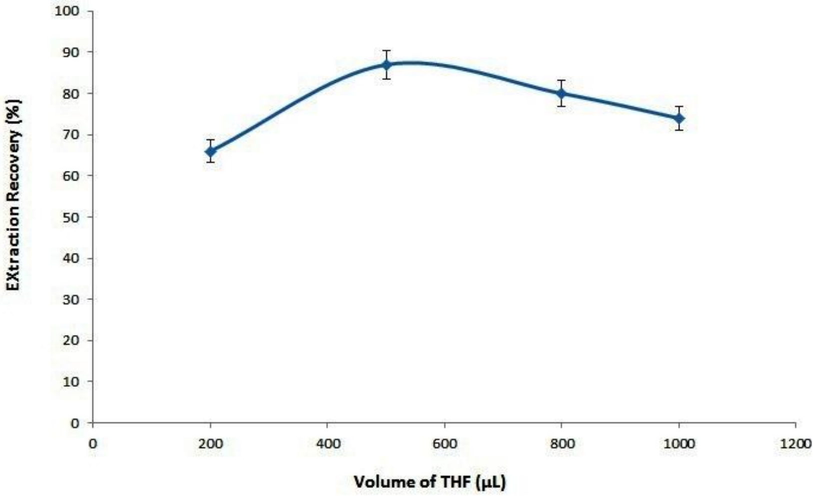

Figure 6. Effect of volume of THF on the extraction recovery of Pb^{2+}. Conditions: 5 µg L^{-1} Pb^{2+}, 2.5×10^{-4} mol L^{-1} SA, 2 min extraction time, 400 µL extraction solvent.

Effect of ionic strength

The effect of ionic strength on the extraction recovery of Pb^{2+} was studied by changing the concentrations of KNO_3 in the range of 0.1 – 0.5 % (w/v). Based on the results (Figure 7) no significant changes were observed in the ER of Pb^{2+} up to 0.4 % (w/v) of KNO_3.

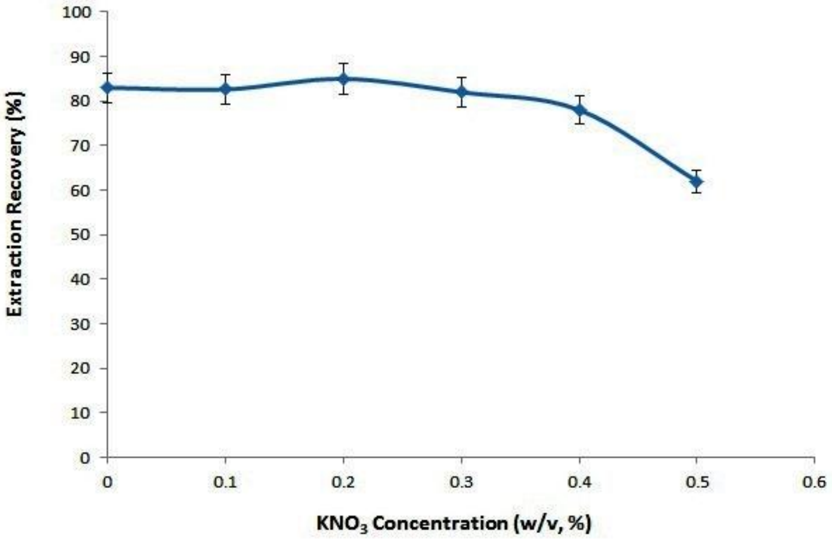

Figure 7. Effect of volume of ionic strength on the extraction recovery of Pb^{2+}. Conditions: 5 µg L^{-1} Pb^{2+}, 2.5×10^{-4} mol L^{-1} SA, 2 min extraction time, 400 µL.

Extraction solvent

Interferences Study

The effect of different cations and anions on the extraction recovery of Pb^{2+} was studied, and the results are shown in Table 2. The tolerance limits of different ions were defined as the concentration that reduces the extraction recovery to less than 95% [24]. As the results shown, no serious interferences were observed for determination of Pb^{2+}. Therefore, the proposed DESs microextraction method could be selectively used for determination of Pb^{2+} in different real samples.

Table 2. Effect of different cations and anions on the extraction recovery of 5 ng mL^{-1} Pb^{2+}.

Interfering ions	Added as	Concentration (ng mL^{-1})	Recovery, %
Mg^{2+}	$Mg(NO_3)_2.9H_2O$	50000	98.0
Zn^{2+}	$Zn(NO_3)_2$	200	99.3
Cu^{2+}	$Cu(NO_3)_2.5H_2O$	200	99.3
Co2+	$Co(NO_3)_2.6H_2O$	200	97.3
Mn^{2+}	$MnSO_4.H_2O$	150	97.6
Ni^{2+}	$Ni(NO_3)_2$	150	95.0
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	150	98.0
Hg^{2+}	$Hg(NO_3)_2.H_2O$	150	96.5
Fe^{3+}	$Fe(SO_4)_2.NH_4.12H_2O$	150	96.3
Al^{3+}	$Al(NO_3)_3.9H_2O$	150	97.5
SO$_4^{2-}$	K_2SO_4	50000	95.7
Cl$^-$	KCl	50000	96.3

Analytical Figures of Merit

Under the optimum experimental conditions, the calibration curve was linear in the range of 0.5 – 10 ng mL^{-1} Pb^{2+} with a correlation coefficient of 0.9981. The equation of calibration curve was A= 0.0636 C_{Pb2+} + 0.0163 (A is the absorbance of lead and C_{Pb2+} was the concentration of lead in ng mL^{-1}). The relative standard deviation based on six replicate analysis of 5 ng mL^{-1} Pb^{2+} was 4.0 % and limit of detection of 0.16 ng mL^{-1}. The preconcentration factor was calculated as the sample solution volume (8 mL) to the desorbed solvent after preconcentration (400 µL) which was 20. The enrichment factor defined as the slope of the calibration curve after preconcentration step to that slope of calibration curve before preconcentration step (A = 0.0041 C_{Pb2+}+ 0.0143) was 15.5.

Analysis of real samples

Different water samples were analyzed for determination of Pb^{2+} according to the proposed method, and the results are shown in Table 3. Also, spike analysis was performed on the samples to check the accuracy of the obtained results. Based on the results, good recoveries were obtained for determination of Pb^{2+}. Additionally, CRM-TMDW certified reference material with known amounts of 40 ng mL^{-1} Pb^{2+} was analyzed and based on the results 39.1 ± 1.9 ng mL^{-1} Pb^{2+} was obtained (95 % confidence interval; n=6).

Table 3. The results of analysis of water samples for determination of Pb^{2+}. (Results: Mean ± standard deviation based on three replicate analysis).

Sample	**Added (ng mL^{-1})**	**Found (ng mL^{-1})**	**Recovery (%)**
Tap Water [a]	-	1.1 ± 0.1	**-**
	5.0	6.4 ± 0.4	**106.0**
Tap Water [b]	-	0.9 ±0.1	**-**
	5.0	5.6 ± 0.4	**94.0**
Spring water [c]	-	N D	**-**
	5.0	4.6 ± 0.3	**92.0**
River Water [d]	-	3.1 ± 0.3	**-**
	5.0	7.7 ± 0.4	**92.0**

a: Obtain from Mashhad, Iran
b: Obtained from Neyshabur, Iran
c: Nowchah, Mashhad, Iran
d: Kashaf Rood, Mashhad, Iran
ND: Not Detected

The proposed UA-LPME-ETAAS method was compared by other techniques (25-30) for liquid phase microextraction of Pb^{2+} and the obtained results are presented in Table 4. According to the results, the proposed method has green view, acceptable RSD and low LOD values for determination of trace levels of Pb^{2+} in different real samples.

Table 4. Comparison of the proposed method with other procedures.

Method	Linear range	RSD[b]	LOD[c]	Ref
Temperature-controlled ionic liquid–LPME-FAAS	10-200	4.4	9.5	25
Deep eutectic solvent based air assisted LPME-ETAAS	0.12-2.5	2.9	0.6	26
Deep utectic solvent ased air assisted LPME-ETAAS	1.0-200.0	2.3-4.4	0.10	27
LPME based on hydrophobic deep eutectic solvents	0.8-350	1.4	0.24	28
LPME based on hydrophobic deep eutectic solvents-UV-Vis	1.0-200.0	< 5	0.23	29
Temperature controlled ionic liquid-dispersive liquid phase microextraction	5.0-20.0	4.3	4.3	30
UA-LPME-ETAAS	0.5-10.0	4.0	0.16	Present work

a :ng mL^{-1} , b: % and c:ng mL^{-1}

Conclusion

The ultrasonic assisted liquid phase microextraction (UA-LPME) technique using sulfanilamide (SA) as a complexing agent and a choline chloride-phenol mixture as an extraction solvent with a mole ratio of 1:2 was found to be an efficient, rapid, green, and low-cost method for preconcentrating trace levels of Pb^{2+}. We optimized the parameters affecting the extraction efficiency and checked the selectivity of the proposed method through analysis of interfering ions.

Our results also demonstrate the successful application of the proposed method for determining Pb^{2+} in real samples.

The proposed method has several advantages, including high efficiency, rapidity, green aspect, and low cost for determining Pb^{2+}. However, some limitations should also be considered, such as the need for specific equipment and a skilled operator. Future research could focus on developing simpler and more user-friendly methods for determining trace levels of Pb^{2+} that can be applied to environmental monitoring and analysis. This could involve exploring different complexing agents and extraction solvents, as well as optimizing the parameters affecting the extraction efficiency. Nonetheless, the proposed method holds great promise for advancing the field of trace metal analysis and environmental monitoring.

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