

# Determination of ultra traces of lead in water samples after combined solid-phase extraction–dispersive liquid–liquid microextraction by graphite furnace atomic absorption spectrometry

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**Abstract** A solid-phase extraction coupled with dispersive liquid–liquid microextraction (DLLME) method followed by graphite furnace atomic absorption spectrometry (GFAAS) was developed for the extraction, preconcentration, and determination of ultra trace amounts of lead in water samples. Variables affecting the performance of both steps were thoroughly investigated. Under optimized conditions, 100 mL of lead solution were first concentrated using a solid phase sorbent. The extracts were collected in 1.50 mL of THF and 18  $\mu\text{L}$  of carbon tetrachloride was dissolved in the collecting solvent. Then 5.0 mL pure water was injected rapidly into the mixture of THF and carbon tetrachloride for DLLME, followed by GFAAS determination of lead. The analytical figures of merit of method developed were determined. With an enrichment factor of 1,800, a linear calibration of 3–60  $\text{ng L}^{-1}$  and a limit of detection of 1.0  $\text{ng L}^{-1}$  were obtained. The relative standard deviation for seven replicate measurements of 30  $\text{ng L}^{-1}$  of lead was 5.2 %. The relative recoveries of lead in mineral, tap, well, and river water samples at spiking level of 10 and 20  $\text{ng L}^{-1}$  are in the range 94–106 %.

**Keywords** Dispersive liquid–liquid microextraction · Solid-phase extraction · Graphite furnace atomic absorption spectrometry · Lead · Water analysis

## Introduction

Lead is a highly toxic metal found in the earth's crust. Because of its abundance, low-cost, and physical properties, lead and lead compounds were used in a wide variety of products including paint, ceramics, pipes, solders, gasoline, batteries, and cosmetics. Lead is a serious cumulative body poison and enters our body system through food, water, and air [1]. Lead is a toxic element and can affect almost every organ or system in human body. The main target for lead toxicity is nervous system. It also increases blood pressure and causes weakness in fingers, wrists, and ankles. Moreover, exposure to high level of lead can severely damage kidneys and brain [2]. In recent years, concern has increased over the concentration of lead in drinking and natural waters [3]. The US Environmental Protection Agency has classified lead as a Group B2 (probable) human carcinogen [4]. As a consequence, the World Health Organization (WHO) has established the maximum allowable limit of 10  $\mu\text{g L}^{-1}$  for lead in drinking water [5]. Thus, the determination of lead in environmental samples at ultra trace level is very important.

There are several methods reported for the determination of lead in various samples, including flame atomic absorption spectrometry [6, 7], electrothermal atomic absorption spectrometry [8–10], graphite furnace atomic absorption spectrometry (GFAAS) [11], inductively coupled plasma atomic emission spectrometry [12], and inductively coupled plasma mass spectrometry (ICP-MS) [13]. GFAAS is a good technique for determination of trace of lead in several types of samples in view of its high sensitivity. More recently, ICP-MS has produced a detection limit in the same range with GFAAS. However, the use of ICP-MS often involves a greater cost, higher sample volume requirements, and increased instrumentation

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complexity, limiting its widespread application to routine analytical works. GFAAS is still being used because it combines a fast analysis time, a cheaper cost, a relative simplicity, low sample volume requirements, and low detection limits. However, the determination of lead at very low concentrations is often difficult because of insufficient sensitivity of method as well as the matrix interferences occurring during the real sample analysis. For this reason, a preliminary separation and preconcentration step is often required to enhance the sensitivity of the method.

The most widely used techniques for separation and preconcentration of trace amount of lead include liquid–liquid extraction (LLE) [14], coprecipitation [15], solid-phase extraction (SPE) [16–18], and ion exchange [19]. Each technique has its advantages and disadvantages and should be chosen according to the analytical problem.

Modern trends in analytical chemistry are towards the miniaturization and simplification of sample preparation, as well as the minimization of the used organic solvent. In view of this aspect, several novel microextraction techniques are being developed in order to reduce the analysis step, increase the sample throughput, and to improve the quality and the sensitivity of the analytical methods. Cloud point extraction (CPE) [20, 21], homogeneous LLE [22, 23], solid-phase microextraction [24, 25], liquid-phase microextraction [26–28], and dispersive liquid–liquid microextraction (DLLME) [29–43] are new methods of sample preparation. DLLME is a miniaturized sample pretreatment that utilizes microliter volumes of the extraction solvent. The advantages of DLLME were simplicity, rapidity, low-cost, high recovery, and enrichment factors, however, the applications of DLLME in most cases were limited for water samples.

However, for complex matrices such as highly saline solution, savage, and biological samples DLLME cannot be used successfully. Therefore, in the analysis of these samples, a clean-up step is necessary before DLLME. Combination of SPE and DLLME as a novel sample pretreatment method leads to high enrichment factor (>1,500) and can be used successfully in complex matrices. Until now, this method was successfully applied for the determination of organic compounds such as clenbuterol [37], polybrominated diphenyl ethers [44], selected fungicides [45], organophosphorous pesticides [46], chlorophenols [47], and amide herbicides [48] in different matrices, but the application of this method for determination of heavy metals was not reported.

In this study, for the first time, the combination of SPE and DLLME was employed as a sample-preparation method for GFAAS. The applicability of the method was demonstrated for the rapid determination of ultra trace amounts of lead in water samples using diethyl dithiophosphoric acid (DDTP) as a suitable chelating agent.

Factors that would influence the efficiency of SPE–DLLME extraction and the determination with GFAAS were investigated.

## Experimental

### Reagents and solutions

All solutions were prepared with ultra pure water (six times distilled) was purchased from Shahid Ghazi Pharmaceutical Co. (Tabriz, Iran). Stock standard solution of lead with a concentration of  $1,000 \text{ mg L}^{-1}$  was obtained by dissolving appropriate amount of lead nitrate obtained from Merck (Darmstadt, Germany). Working standard solution was obtained by appropriate dilution of the stock standard solution. The chelating agent, DDTP with the density of  $1.17 \text{ kg L}^{-1}$  was supplied from Merck. Carbon tetrachloride and chloroform (both of analytical grade for determination with dithizone) and carbon disulfide (for spectroscopy) as extraction solvent, methanol (MeOH, for spectroscopy), acetone (AC, HPLC grade), and acetonitrile (AN, HPLC grade) as disperser solvent, NaCl (analytical grade),  $\text{HNO}_3$  (65 %, analytical grade), and HCl (37 %, analytical grade) were obtained from Merck. Tap, river, well, and mineral water samples used for development of the method were collected in PTFE containers from Kermanshah (Iran) and stored in dark at  $4 \text{ }^\circ\text{C}$  and analyzed within 24 h of collection without previous treatment or filtration.

### Instrumentation

All measurements were carried out using a Model nov AA 400 atomic absorption spectrometer (Analytik Jena AG, Jena, Germany), equipped with deuterium background correction, a transversely heated graphite tube atomizer and a MPE 60 auto-sampler. The lead hollow cathode lamp (Analytik Jena, Jena, Germany) was operated at 5 mA, with a spectral bandwidth of 0.8 nm, and the most sensitive analytical line at 283.3 nm was used. Pyrolytic graphite coated graphite tubes with integrated PIN platform (Analytik Jena Part No. 407-A81.026) were used for all measurements. The optimum operating parameters for GFAAS are given in Table 1. Argon (99.999 %) was purchased from Air Products (UK) as purge and protective gas with a flow rate of  $500 \text{ mL min}^{-1}$  during all stages, except during atomization, when the flow was stopped. All measurements were based on the peak height. The Hettich Zentrifugen (EBA20, Tuttlingen, Germany) was used for centrifugations. The pH values were measured with a Metrohm pH-meter (Model: 692, Herisau, Switzerland) supplied with a glass-combined electrode.

**Table 1** Graphite furnace temperature program for lead determination

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon flow rate (mL min <sup>-1</sup> )
Drying	80	1	10	500
Drying	95	1	5	500
Pyrolysis	600	10	15	500
Atomization	2,000	0	3	0
Cleaning	240	0	2	500

### Extraction procedure

Solid-phase extraction cartridge used for the extraction of complexed lead ions from the water samples was 500-mg C<sub>18</sub> sorbent (6 mL syringe barrel, Varian, Harbor City, CA, USA). The sorbent was conditioned with 3.0 mL of THF, water, and water at pH 3, respectively. A 100-mL volume of ultra pure water was placed in a 100 mL volumetric flask and was spiked at the lead concentration of 30 ng L<sup>-1</sup>. 15 µL of DDTP as a chelating agent were added to sample solution and gently shaken for a few minutes. After complexation of lead ions with DDTP, the sample was loaded at a flow rate of about 15 mL min<sup>-1</sup> with the aid of a vacuum pump (Rotavac, Heidolph, Germany). The C<sub>18</sub> cartridges were rinsed with 3 mL of water at pH 3.0 to remove the matrix interferences. After drying the solid phase by passing air through it, the desired lead ions that reacted with DDTP were eluted with 1.50 mL THF and collected into the 10-mL screw cap glass test tubes with conical bottom. Then, 18.0 µL of carbon tetrachloride (extraction solvent) were added to the THF in the test tube. Then, 5.00 mL pure water was rapidly injected into a test tube, using a 5.00-mL syringe (gastight, Hamilton, Reno, NV, USA). A cloudy solution, resulting from the dispersion of the fine carbon tetrachloride droplets in the aqueous solution, was formed in the test tube. In this step, the lead complexes were extracted into the fine droplets of carbon tetrachloride. The mixture was then centrifuged for 2 min at 5,000 rpm, until the dispersed fine particles of the extraction phase settled to the bottom of the conical test tube (25 ± 2 µL). The sedimented phase was completely transferred into conical glass sample cup and 20 µL of this sedimented phase using auto-sampler was injected into the GFAAS and was subjected to the temperature program of Table 1.

### Results and discussion

In this research, a SPE–DLLME method combined with GFAAS was developed and applied to the determination of lead in different water samples. To attain a high enrichment

factor, the influence of different parameters affecting the complex formation and the extraction conditions for SPE and DLLME including flow rates, breakthrough volume, type and volume of elution solvent, type of extraction and disperser solvents and their volume, pH, concentration of chelating agent, extraction time, and salt addition were optimized. Enrichment factor (EF), defined as the ratio of concentration of analyte in the sedimented phase,  $C_{\text{sed}}$ , to concentration of analyte in the aqueous sample,  $C_0$ , was used as:

$$EF = C_{\text{sed}}/C_0 \quad (1)$$

$C_{\text{sed}}$  was calculated from the calibration graph obtained by conventional LLE–GFAAS, with extraction conditions: 3.0 mL from the standard water samples with the Pb concentration range of 10–100 µg L<sup>-1</sup>, 50.0 µL from the aqueous solution of 10 % (v/v) DDTP, and 3.0 mL CCl<sub>4</sub> at pH 2.5.

### Optimization of SPE parameters

#### *Effect of flow rate of sample solution*

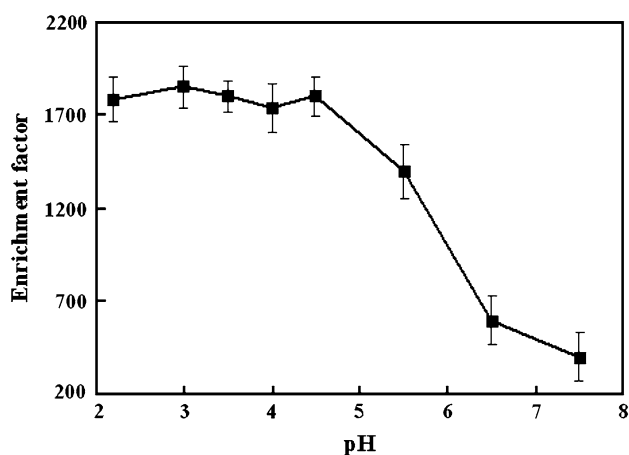
The flow rate of the sample solution must be low enough to perform an effective retention of the complexed lead ions. On the other hand, it must be high enough not to waste time. The effect of the flow rate of sample solution was examined from 5 to 30 mL min<sup>-1</sup>. It was found that the flow rates up to 15 mL min<sup>-1</sup> has no effect on enrichment factor of lead ions while, at higher speeds, the enrichment factor decreased. Thus, a flow rate of 15 mL min<sup>-1</sup> was selected for further studies.

#### *Effect of breakthrough volume*

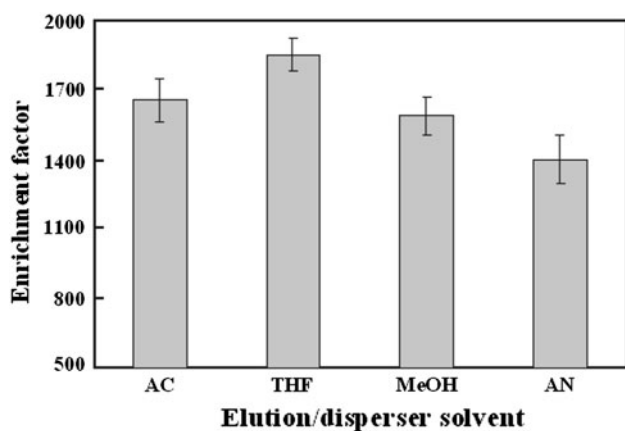
In the analysis of heavy metals, the sample volume is one of the important parameters influencing the enrichment factor. In order to achieve a high enrichment factor for sample with very low analyte concentration, a large volume of samples solution is required. Therefore, the effect of sample volume on the retention of lead ions was investigated. For this purpose, different sample volumes of the sample solutions (i.e., 20, 50, 100, 200, and 300 mL) containing a constant amount of lead ions were pre-concentrated in the C<sub>18</sub> cartridge. The results showed that the different sample volumes did not affect the enrichment factor of lead ions obviously. Considering the analytical time and trace level of lead ions in real water samples, a solution volume of 100 mL was used as the best breakthrough volume.

#### *Effect of sample solution pH*

In the SPE studies, pH is an important factor for the quantitative recoveries of analytes and plays a unique role on

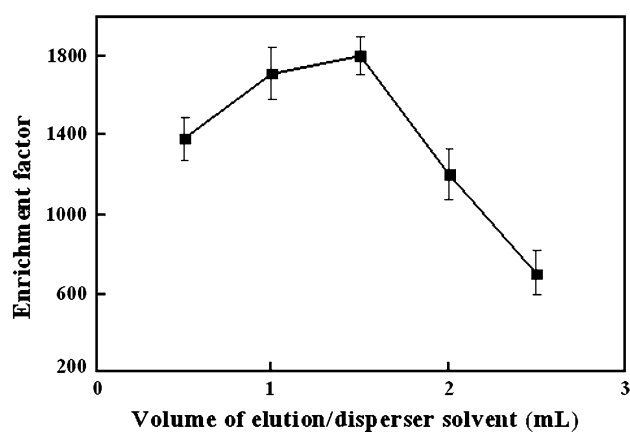


**Fig. 1** Effect of pH on the enrichment factor of lead obtained from SPE–DLLME. Extraction conditions: water sample volume, 100 mL; elution or disperser solvent (THF) volume, 1.50 mL; extraction solvent (carbon tetrachloride) volume, 18  $\mu$ L; concentration of DDTP, 0.015 % (v/v); sedimented phase volume,  $25 \pm 2$   $\mu$ L; room temperature; concentration of lead, 30  $\text{ng L}^{-1}$

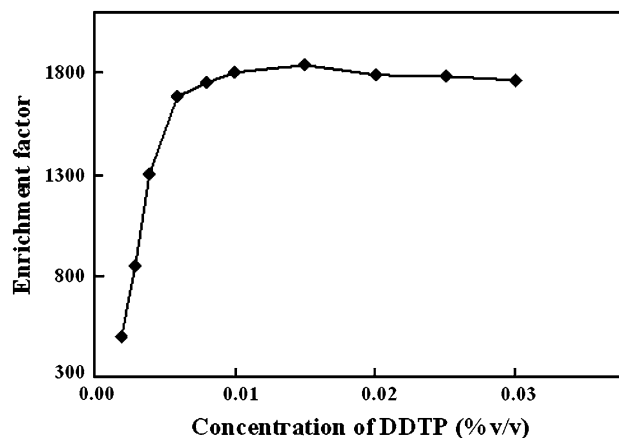


**Fig. 2** Effect of type of elution or disperser solvent on the enrichment factor of lead obtained from SPE–DLLME. Extraction conditions: similar to those in Fig. 1, except for a sample solution pH of 2.5

metal-chelate formation and subsequent extraction. At first, the ammonium salt of diethyl dithiophosphate was prepared from its acid DDTP, upon addition of an equivalent amount of  $\text{NH}_3$ . Then, an appropriate amount of this mixture was added to 100 mL of sample solution of lead ion and the pH adjustment in the range 2.2–7.5, by using HCl,  $\text{CH}_3\text{COOH}$ , and NaOH, was performed. The results shown in Fig. 1 revealed that the enrichment factor of lead remained more or less constant when the sample pH increased from pH 2.2 to 4.5, and decreased significantly at higher pH values. On the other hand, since an aqueous solution of DDTP is nearly acidic, within the optimized pH range (i.e., pH 3.1 in 100 mL aqueous solution), in this work, the use of an acidic solution for the pH adjustment was not needed.



**Fig. 3** Effect of volume of elution or disperser solvent on the enrichment factor of lead obtained from SPE–DLLME. Extraction conditions are similar to those of Fig. 2



**Fig. 4** Effect of concentration of DDTP on the enrichment factor of lead obtained from SPE–DLLME. Extraction conditions are similar to those of Fig. 2

#### *Effect of elution solvent type and volume*

In SPE–DLLME procedure, the elution solvent of SPE should be able to play the role as a disperser solvent in the following DLLME stage. For this purpose, AC, THF, AN, and MeOH, displaying this ability, were examined as the elution solvent. Thus, the  $\text{C}_{18}$  cartridge was eluted using 1.50 mL of each of these elution solvents and the results illustrated in Fig. 2. As seen, the use of THF as elution solvent will result in a higher enrichment factor, as compared with that with other elution solvents and, thus, it was selected for further studies. For obtaining optimized volume of elution solvent, various experiments were performed by using different volumes of THF (i.e., 0.50, 1.00, 1.50, 2.00, and 2.50 mL) and the results are shown in Fig. 3. As seen, enrichment factor increases with increasing volume of eluent up to 1.50 mL, and then decreased drastically at higher volumes, the decreased enrichment factor being due

to increasing volume of the sedimented phase. Thus, a THF volume of 1.5 mL was selected as the optimal volume.

#### Effect of concentration of DDTP

Diethyl dithiophosphoric acid is a well-known chelating agent for lead extraction with the formation of a stable 2:1 complex with  $\text{Pb}^{2+}$  ion. This study was conducted over the DDTP concentration range 0.002–0.030 % (v/v) and the results are shown in Fig. 4. It was found that the enrichment factor was increased with the increasing amount of DDTP from 0.002 to 0.010 % (v/v) and remained constant upon further addition of the ligand concentration and there after no change. Therefore, a concentration of 0.015 % (v/v) DDTP was selected as the best choice to prevent any interference.

#### Effect of salt addition

To investigate the influence of ionic strength of the sample solution on the performance of SPE, various experiments were performed by adding different amounts of NaCl from 0 to 5.0 % (w/v), while other experimental conditions were kept constant. The results showed that salt addition has no significant effect on the enrichment factor. These observations suggest the possibility of using this method for separation of lead from saline solutions such as sea water.

#### Effect of coexisting ions

It is known that DDTP as chelating agent can form complexes with several transition metals and semi-metals in acidic media, but it does not react with alkali and alkaline earth metals and other elements [49–51]. Thus, the effects of common coexisting ions in natural water samples on the recovery of lead were studied. Here, a series of experiments were designed using a standard solution of  $50 \text{ ng L}^{-1}$  lead ion and varying amounts of potential interfering ions under the above optimized conditions. The tolerance level was defined as the maximum concentration of the foreign ion causing a change in the analytical signal not higher than 5 %, compared with the signal of  $50 \text{ ng L}^{-1}$  lead alone. The results are summarized in Table 2. As it is obvious from Table 2, in the case of all cationic and anionic potential interferences studied, the presence of coexisting ions have no measurable effect on the determination of lead at [interferent]/ $[\text{Pb}^{2+}]$  ratios of 200 and (much) larger.

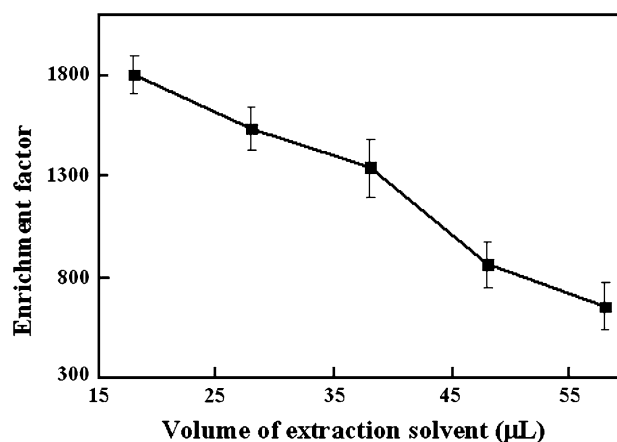
#### Optimization of DLLME parameters

##### Effect of type and volume of extraction solvent

The extraction solvent should possess some special properties, such as higher density than water, high extraction

**Table 2** Effect of potential interferants on the recovery of  $50 \text{ ng L}^{-1}$  Pb(II) in water sample using SPE–DLLME–GFAAS

Interferant	Concentration ( $\mu\text{g L}^{-1}$ )	Interferant/Pb(II) ratio	Pb(II) recovery (%)
$\text{Na}^+$	10,000	200,000	92.4
$\text{K}^+$	1,000	20,000	97.0
$\text{Li}^+$	1,000	20,000	102.5
$\text{Ca}^{2+}$	500	10,000	99.0
$\text{Ba}^{2+}$	500	10,000	95.3
$\text{Mg}^{2+}$	500	10,000	101.0
$\text{Mn}^{2+}$	50	1,000	98.6
$\text{Co}^{2+}$	50	1,000	92.1
$\text{Fe}^{2+}$	50	1,000	99.0
$\text{Ni}^{2+}$	50	1,000	102.4
$\text{Al}^{3+}$	50	1,000	100.5
$\text{Zn}^{2+}$	50	1,000	98.0
$\text{Sn(IV)}$	25	500	93.0
$\text{Cr}^{3+}$	50	1,000	95.5
$\text{Cd}^{2+}$	10	200	97.6
$\text{Cu}^{2+}$	50	1,000	97.4
$\text{Hg}^{2+}$	50	1,000	106.2
$\text{Cl}^-$	10,000	200,000	95.0
$\text{SCN}^-$	500	10,000	94.8
$\text{CH}_3\text{COO}^-$	1,000	20,000	103.1
$\text{SO}_4^{2-}$	500	10,000	101.5
$\text{NO}_3^-$	500	10,000	96.0



**Fig. 5** Effect of the volume of extraction solvent ( $\text{CCl}_4$ ) on the enrichment factor of lead obtained from SPE–DLLME. Extraction conditions are similar to those of Fig. 2

capability of the analytes, and low solubility in water. To investigate the effect of extraction solvent, chloroform, carbon tetrachloride, and carbon disulfide were tested using 1.50 mL THF (as disperser solvent) containing different volumes of extraction solvents to achieve 25.0  $\mu\text{L}$  volume of the sedimented phase. In this experiment, the use of

**Table 3** Analytical characteristics of SPE–DLLME–GFAAS for determination of Pb

Parameter	Analytical feature
Linear range (ng L <sup>-1</sup> )	3–60
$r^2$	0.9986
Limit of detection (ng L <sup>-1</sup> ) ( $3\sigma$ , $n = 7$ )	1
Repeatability (R.S.D <sup>a</sup> , %) ( $n = 7$ )	5.2
Enrichment factor	1,800
Sample volume (mL)	100
Sample preparation time (min)	<15

<sup>a</sup> Pb(II) concentration was 30 ng L<sup>-1</sup> for which R.S.D. was obtained

**Table 4** Determination of Pb(II) content of different water samples

Sample	Concentration of Pb <sup>2+</sup> (ng L <sup>-1</sup> )	Added Pb <sup>2+</sup> (ng L <sup>-1</sup> )	Found Pb <sup>2+</sup> (ng L <sup>-1</sup> )	Relative recovery (%)
Mineral water	Nd	10	9.5 ± 0.3	98
		20	20.6 ± 0.5	103
Tap water	41.3 ± 3.1	5	43.5 ± 2.4	94
		10	49.5 ± 3.3	96
Well water (50 times diluted)	21.5 ± 1.3	10	33.2 ± 1.8	105
		20	40.3 ± 2.2	97
River water (20 times diluted)	18.9 ± 1.2	10	27.4 ± 1.7	95
		20	41.4 ± 2.8	106

chloroform, carbon tetrachloride and carbon disulfide as extraction solvents resulted in enrichment factors of  $1,654 \pm 113$ ,  $1,800 \pm 95$ , and  $1,257 \pm 174$ , respectively. According to these results, carbon tetrachloride was selected as the extraction solvent due to higher enrichment factor and lower standard deviation.

In order to examine the effect of volume of extraction solvent, additional experiments were performed by using 1.50 mL THF containing different volumes of carbon

tetrachloride (i.e., 18.0, 28.0, 38.0, 48.0, and 58.0  $\mu\text{L}$ ). The results clearly indicated the by increasing the volume of carbon tetrachloride from 18.0 to 58.0  $\mu\text{L}$ , the volume of the resulting sedimented phase was increased approximately from 25 to 80  $\mu\text{L}$ . Subsequently, the enrichment factor reduced from 1,800 to 650 with the increasing volume of carbon tetrachloride, as shown in Fig. 5. Thus, according to the results, 18.0  $\mu\text{L}$  of carbon tetrachloride was chosen as the optimum extraction solvent.

#### Effect of type and volume of disperser solvent

In SPE–DLLME, disperser solvent was the solvent used in SPE stage as elution solvent. For this purpose, acetone, THF, acetonitrile, and methanol were used as disperser (elution) solvent. According to the results reported in Sect. 3.1.4, THF was selected as disperser solvent. Since disperser solvent in SPE stage is used as elution solid phase, its volume should be enough to elute the solid phase completely. Meanwhile, the volume of disperser solvent should be low enough not to increase sedimented phase. According to the results in Sect. 3.1.4, a volume 1.5 mL of THF was selected as an optimum volume of disperser solvent.

#### Effect of extraction time

In DLLME, extraction time is defined as the time between injection mixture of disperser and extraction solvent, and starting to centrifuge. The effect of extraction time was examined in the range of 0–60 min with constant experimental conditions. The results indicated that the recovery of lead remained constant when the extraction time was changed from 0 to 30 min and then began to decrease slightly at extraction time was longer than 30 min, most probably because of the adsorption onto the wall of the conical tube. Thus, the extraction procedure was carried out for a time interval of <30 min.

**Table 5** Comparison of the characteristic performance data obtained by using SPE–DLLME–GFAAS with those of other preconcentration techniques for determination of lead in water samples

Method	LOD (ng L <sup>-1</sup> )	R.S.D. (%)	Enrichment factor	Sample volume (mL)	Time (min)	Linear range (ng L <sup>-1</sup> )	References
LLE–GFAAS	1,000	2.7	5	5	20	2,000–30,000	[52]
Co-precipitation–GFAAS	500	4.9	20	200	>20	–	[53]
On-line-SPE–GFAAS	12	3.2	20.5	>3.3	2	100–10,000	[54]
CPE–GFAAS	80	2.8	50	10	30	1,000–30,000	[21]
DLLME–GFAAS	20	2.5	150	5	<3	50–1,000	[51]
IL–DLLME–ETAAS	3	7.3	280	10	<6	10–400	[55]
DLLME–ETAAS	10	2.4	115	5	–	30–1,000	[56]
SPE–DLLME–GFAAS	1	5.2	1,800	100	<15	3–60	This work

### Analytical figures of merit

Analytical characteristics of the optimized method, including linear range, limit of detection, reproducibility, and enrichment factor are listed in Table 3. The calibration graph was linear over the  $\text{Pb}^{2+}$  concentration range 3–60  $\text{ng L}^{-1}$ . The limit of detection, defined as  $C_L = 3S_B/m$  (where  $C_L$ ,  $S_B$ , and  $m$  are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was found to be 1  $\text{ng L}^{-1}$ . The relative standard deviation for seven replicate measurements of 30  $\text{ng L}^{-1}$   $\text{Pb(II)}$  was 5.2 %. A very high enrichment factor of 1,800 was obtained for a 100 mL water sample. The enhancement factor, obtained from the slope ratio of calibration graph after and before extraction, was about 2,400.

### Analysis of real water samples

The proposed SPE–DLLME method combined with GFAAS was applied to the determination of lead in mineral, tap, well and river water samples. River water was collected from Gharaso River (Kermanshah, Iran), tap water was collected from Kermanshah (Iran) and well water sample was collected from Mahidasht (Kermanshah, Iran). The results are summarized in Table 4. It should be noted that the concentration of lead in the well and river water samples was out of the calibration range. Therefore, before SPE–DLLME procedure, the well water sample was diluted for 50 times and river water sample for 10 times. The lead amount in mineral water sample was below the limit of detection (Table 4). The concentration of lead in the tap, well and river water samples were determined as  $43.5 \pm 2.4$ ,  $21.5 \pm 1.3$ , and  $18.9 \pm 1.2$   $\text{ng L}^{-1}$ , respectively (Table 4). The concentration of lead in the well and river water samples without dilution was calculated to be  $1,075 \pm 66$  and  $189 \pm 12$   $\text{ng L}^{-1}$ , respectively. Mineral, tap, well, and river water samples were also spiked with lead standards to assess the matrix effects. The relative recoveries of lead from mineral, tap, well, and river water at spiking levels of 10 and 20  $\text{ng L}^{-1}$  are also listed in Table 4. These results demonstrated that the mineral, tap, well and river water sample matrices had little effect on SPE–DLLME–GFAAS determination of lead.

### Comparison of proposed SPE–DLLME with other methods

Characteristics of the proposed method have also been compared with other methods reported for the preconcentration and determination of lead in water samples [21, 51–56]. Table 5 compares the limit of detection, repeatability,

sample volume, enrichment factor, linear range, and extraction time. As is obvious, the limit of detection of the proposed SPE–DLLME–GFAAS method with a sample volume of 100 mL is much better than the detection limits of the other methods. The enrichment factor in SPE–DLLME–GFAAS is very high and the extraction time is relatively short, compared to the literature reports. Hence, the proposed method would be a good alternative for the determination of ultra traces of lead in water samples.

### Conclusions

This study reports a SPE–DLLME combination followed by GFAAS determination as a highly sensitive, accurate and reliable method for the preconcentration and determination of lead at concentrations of 3–60  $\text{ng L}^{-1}$  in environmental water samples. High enrichment factors up to 1,800 were achieved at an extraction time of <15 min. A comparison with literature revealed that the limit of detection of the proposed method, with a sample volume of 100 mL, is much better than that of the other methods. Also the enrichment factor in SPE–DLLME–GFAAS is very high and the extraction time is relatively short, compared to the literature reports. As the results shown, the combination of SPE and DLLME offers numerous advantages such as simplicity, ease of operation, high preconcentration factor, low limit of detection, and relatively short analysis time. The method is successfully applicable to the determination of ultra traces of lead in environmental and drinking waters.

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