# Emulsification liquid–liquid microextraction method based on a deep eutectic solvent for separation and preconcentration of lead from environmental water samples

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## ABSTRACT

In this paper, a novel emulsification liquid–liquid microextraction method based on deep eutectic solvents (DESs) for the preconcentration of lead from water samples and its determination by flame atomic absorption spectrometry is described. Purpurin was used as complexing ligand and the Pb(II)-purpurin complexes were extracted and preconcentrated from the aqueous phase using a choline chloride/2-chlorophenol (at a 1:2 molar ratio) based DES as a water-miscible extraction solvent and tetrahydrofuran as an emulsifier solvent. Some analytical parameters affecting the extraction yield were investigated and optimized. Using a 20 mL aqueous sample, the limit of detection and preconcentration factor of the method were 5.93 $\mu g\,L^{-1}$ and 20, respectively. The accuracy of the method was assessed through the analysis of certified reference surface water (SPS-SW2 Batch 127) and spiked water samples. The certified and obtained values were statistically in good agreement at 95% confidence level. The recovery values of spiked water samples were between 102% and 105%.

**Key words** | deep eutectic solvent, emulsification liquid–liquid microextraction, lead, preconcentration, waters

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## INTRODUCTION

Lead is a highly toxic heavy metal which can cause health problems such as damage to kidney and liver, memory loss, reproductive disorder, cancer, nausea and convulsions (Mo *et al.* 2017; Zhang *et al.* 2017). Lead contamination in soil and water can eventually impact human health through the food chain. Recently there has been an increased concern over the content of lead in natural and potable water (Mohammadi *et al.* 2014). The World Health Organization (WHO) gives the permissible limit of lead in drinking waters as 10 $\mu g\,L^{-1}$ (WHO 1996). Therefore, it is very important to develop accurate and sensitive methods for the determination of Pb in natural water samples.

Flame atomic absorption spectrometry (FAAS) is one of the most popular spectroscopic techniques for routine metal determinations, because of the relatively simple and inexpensive equipment required. However, direct determination of metals at trace levels by FAAS is restricted due to their very low concentrations and matrix effects (Tokalıoğlu *et al.* 2017). Therefore, a separation/preconcentration step is necessary before determination of trace elements. Several preconcentration methods such as solid phase extraction (SPE) (Dos Santos *et al.* 2004; Tokalıoğlu *et al.* 2017), cloud point extraction (Soylak *et al.* 2012; Mohammadi *et al.* 2016), dispersive liquid–liquid microextraction (DLLME) (Naseri *et al.* 2008; Mandlate *et al.* 2017), and ionic liquid-based dispersive liquid–liquid microextraction (IL-DLLME) (Soylak & Yilmaz 2011; Mohammadi *et al.* 2014) have been used for the separation and preconcentration of Pb from

environmental samples. Recently, deep eutectic solvents (DESs) have emerged as a new generation of green solvents instead of ionic liquids (ILs). The physical and chemical properties of DESs are similar to those of ILs. They both have high thermal and chemical stability, low vapour pressure, high viscosity, tunable miscibility, and low toxicity (Karimi et al. 2015; Farajzadeh et al. 2016b; Tan et al. 2016). In comparison with ILs, DESs have several advantages like their easy synthesis, relative cheapness, biodegradability, and biocompatibility (Farajzadeh et al. 2016a, 2016b; Tan et al. 2016; Bağda et al. 2017). For these reasons, DESs are now highly popular. A DES is formed by mixing two or more components that are capable of associating with each other through hydrogen bonds. The obtained DES has a melting point lower than that of each individual component (Farajzadeh et al. 2016b; Yilmaz & Soylak 2016). A number of DESs are prepared by simply mixing and heating organic halide salts such as choline chloride (e.g. cheap, non-toxic and biodegradable) as the hydrogen bond acceptor with urea, organic acids, alcohols, amines or amides as the hydrogen bond donor (Karimi et al. 2015; Yilmaz & Soylak 2016).

The emulsification liquid–liquid microextraction method based on deep eutectic solvent (ELLME-DES) is based on self-aggregation and emulsification of DESs in aqueous sample solution. In this extraction procedure, DESs are separated from aqueous solution by adding aprotic solvents such as tetrahydrofuran (THF), 1,4-dioxane or acetone (Khezeli et al. 2015). So far, a few studies have focused on the use of DESs in the preconcentration process. For instance, Farajzadeh et al. preconcentrated polycyclic aromatic hydrocarbons from aqueous samples (Farajzadeh et al. 2016b) and some pesticides from fruit juices and vegetable (Farajzadeh et al. 2016a). Tan et al. extracted plant growth regulators in edible vegetable oils (Tan et al. 2016). Khezeli et al. extracted benzene, toluene, ethylbenzene and seven polycyclic aromatic hydrocarbons from water samples (Khezeli et al. 2015). Aydin et al. reported the preconcentration of malachite green in farmed and ornamental aquarium fish water samples (Aydin et al. 2017). As well as organic compounds, inorganic ions can also be preconcentrated such as chromium from water samples (Yilmaz & Soylak 2016), selenium species (IV) and (VI) from water and food samples (Panhwar et al. 2017), arsenic from water and environmental samples (Zounr et al. 2017) and cobalt after

chelation with 1-nitroso-2-naphthol in pharmaceutical supplement and tea samples (Arain et al. 2016).

In this paper, an emulsification liquid–liquid microextraction method based on deep eutectic solvent (ELLME-DES) was developed for the preconcentration of Pb(II) prior to FAAS determination. The analytical parameters (e.g. sample pH, concentrations of ligand and NaCl and volumes of DES, THF and sample) that affect the extraction yield were investigated in detail. The developed method was successfully applied to the determination of Pb(II) in environmental water samples such as tap, river and seawater. The accuracy of the developed method was verified by analysing SPS-SW2 Batch 127 certified reference surface water.

## METHOD

### Instruments

Determination of Pb(II) in standard and sample solutions was performed using a PerkinElmer model AAnalyst 200 (Shelton, CT, USA) flame atomic absorption spectrometer equipped with deuterium background correction and an air-acetylene burner. A lead hollow cathode lamp was the radiation source operating at a wavelength of 283.31 nm and with a lamp current of 10 mA. The air-acetylene flame rates were adjusted to $10.0/2.3$ L min$^{-1}$. pH adjustments of sample solutions were monitored using a Hanna Instruments model 221 (Cluj-Napoca, Romania) digital pH-meter. A Hettich Rotofix 32 A model centrifuge (Germany) was used for phase separation.

### Reagents and solutions

All the reagents used were analytical grade and water purified by a reverse osmosis system (AquaTurk Reverse Osmosis System, HSC ARITIM, Istanbul, Turkey) was used to prepare all the solutions. Sodium dihydrogen phosphate, phosphoric acid, ammonium acetate, ammonium chloride, ethanol, purpurin, choline chloride (ChCl), and 2-chlorophenol were supplied by Sigma-Aldrich (St Louis, MO, USA). Nitric acid, ammonia and acetic acid were purchased from Riedel-de Haen (Sigma-Aldrich, St Louis, MO,

USA). The laboratory glassware used was kept in 10% (v/v) nitric acid overnight and rinsed with deionized water before use. Working standard solutions of Pb were prepared by dilution from 1,000 mg L$^{-1}$ stock standard solutions (VHG Labs). The solution of purpurin (0.03% w/v) was daily prepared by dissolving appropriate amounts of the reagent in ethanol. The sodium dihydrogen phosphate/phosphoric acid buffer solution for pH 3, sodium acetate/acetic acid buffer solution for pH 4 and 5, ammonium acetate/acetic acid solution for pH 6 and 7 and ammonium chloride/ ammonia buffer solution for pH 8–10 were used to adjust the pH of the sample solutions. The certified reference material SPS-SW2 level 2 Batch 127 surface water was obtained from Spectrapure Standards AS (Oslo, Norway).

## Preparation of the DES

ChCl (4.17 g) and 2-chlorophenol (7.68 g) were added into a 50 mL polyethylene tube. After closing its lid, it was placed into a shaking water bath at 80 °C for approximately 20 minutes until a homogeneous liquid was formed.

## ELLME-DES procedure

Aliquots (10 or 20 mL) of the sample or standard solution containing Pb(II) ions were adjusted to pH 8.0 using ammonia buffer solution in a 50 mL polyethylene centrifuge tube. 0.5 mL of 0.03% (w/v) purpurin solution and 150 μL of DES (water-miscible extraction solvent) were added to this solution. Then the mixture was manually shaken for 5–6 sec and a homogeneous solution was obtained. 0.75 mL (for 10 mL of sample volume) or 1.5 mL (for 20 of mL sample volume) of THF as emulsifier solvent was added to this sample solution which was then manually shaken for 2 min. Then, the turbid solution was centrifuged at 4,000 rpm for 5 min for the separation of aqueous phase and DES rich phase. The DES phase was situated at the bottom of the tube. The aqueous phase was removed with a Pasteur pipette and the DES rich phase was diluted to 1.0 mL with 0.5 mol L$^{-1}$ HNO$_3$ in ethanol. The final solution was aspirated directly into the FAAS instrument. The ELLME-DES procedure described above was also applied to the blank and calibration standards.

## Applications to real samples

The certified reference surface water (SPS-SW2 level 2 Batch 127) was analysed to verify the accuracy of the developed method. The proposed method was also applied to tap water, river water and seawater samples. Tap water, river water and seawater were collected from Balıkesir University, Küçük Bostancı (Balıkesir) and The Aegean Sea near the Edremit Coast, respectively. The river water and seawater samples were filtered through a cellulose membrane filter of 0.45 μm pore size, acidified to pH 2 with HNO$_3$ and stored in pre-cleaned polyethylene containers. The pH of the samples (20 mL) was adjusted to 8.0 and the analytical procedure given above was applied.

## RESULTS AND DISCUSSION

### Optimization of the experimental conditions

Several experimental conditions that affect the performance of the ELLME-DES method, such as sample pH, concentration of ligand and NaCl and volumes of DES and THF, were optimized to get the highest extraction efficiency. 10 mL of standard solution containing 5 μg of Pb(II) was employed in these optimization experiments.

The effect of pH on the extraction efficiency was investigated over the range of 3.0–10.0. The purpurin concentration (0.05% w/v), DES volume (150 μL), and THF volume (1.0 mL) were used to investigate the effect of pH on the extraction of Pb(II). The results presented in Figure 1(a) indicate that the extraction recovery of Pb(II) increased with increasing pH from 3.0 to 8.0, and reached quantitative recoveries (103–104%) at pH ranges 8.0–9.0. Above pH 9.0, the recovery of the analyte decreased. Hence, pH 8.0 was chosen for all subsequent experiments.

The extraction solvent volume is an important parameter that can change the efficiency of the extraction method (Farajzadeh *et al.* 2016a). The effect of DES volume on the recovery of the analyte was examined between 70 and 200 μL. The sample pH (8.0), purpurin concentration (0.05% w/v), and THF volume (1.0 mL) were kept constant during the optimization of the extraction solvent volume. As shown in Figure 1(b), quantitative
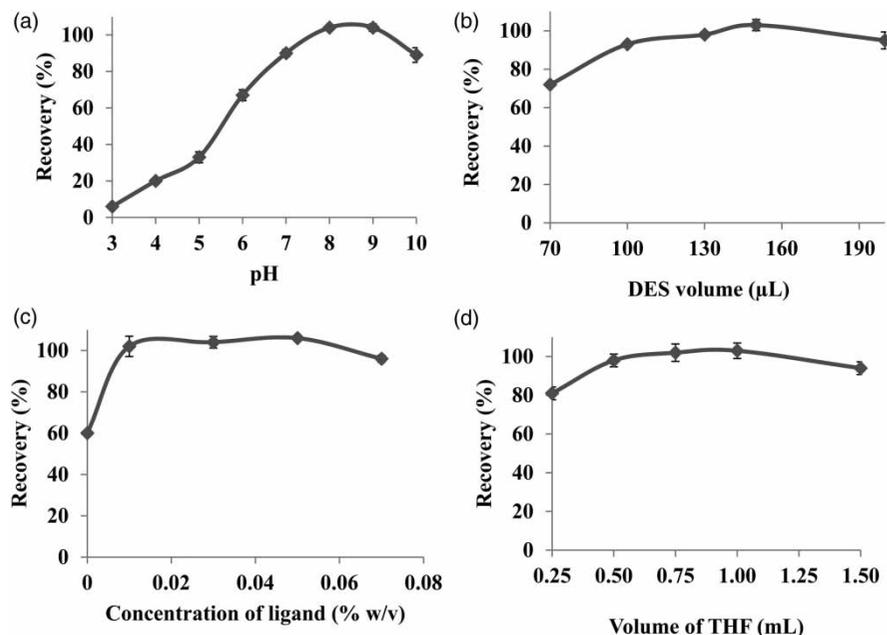
**Figure 1** │ (a) Effect of pH on the recovery of Pb(II), (b) effect of DES volume on the recovery of Pb(II), (c) effect of ligand concentration on the recovery of Pb(II), (d) effect of THF volume on the recovery of Pb(II).

recoveries (95–103%) were obtained between 130 μL and 200 μL of DES. Therefore, 150 μL of DES was used for further studies.

The effect of the purpurin concentration was evaluated in the concentration range of 0–0.07% (w/v). Sample pH (8.0), DES volume (150 μL), and THF volume (1.0 mL) were used to investigate the effect of the purpurin concentration on the extraction of Pb(II). The results are shown in Figure 1(c). The percentage recovery values increased by increasing the ligand concentration up to 0.01% and then remained nearly constant. Quantitative recoveries (96–106%) were obtained for the ligand concentration range of 0.01–0.07% (w/v). A purpurin concentration of 0.03% (w/v) was chosen for further experiments.

The developed method is based on emulsification and self-aggregation of DES in aqueous solution (Arain *et al.* 2016). In the ELLME-DES method, an aprotic solvent which separates DES phase from aqueous phase should be used. For this purpose, THF was used as an aprotic solvent in this work. The effect of THF volume on the extraction efficiency was studied over the range of 0.25–1.5 mL. The other experimental variables were kept constant at their optimal values. The results are shown in Figure 1(d). Maximum

recoveries (98–103%) were obtained between 0.5 and 1.0 mL. At higher THF volume, the percentage recovery value of Pb(II) slightly decreased to 94%.

The effect of NaCl concentration on the extraction efficiency was evaluated over the range of 0.0–0.4 mol $L^{-1}$ using the same ELLME-DES procedure. According to the results, salt addition has no significant effect on the recovery of Pb(II). Therefore, all the extraction experiments were carried out without adding salt.

## Effect of the volume of sample solutions

In order to acquire a high preconcentration factor, the sample volume is a key factor. To investigate the influence of sample volume, 10 and 20 mL of sample solutions containing 5 μg of Pb(II) were used as sample size and the ELLME-DES procedure was performed using 150 μL of DES and 0.75 mL (for 10 mL of sample volume) or 1.5 mL (for 20 mL of sample volume) of THF. When 0.75 mL of THF was used for a 20 mL sample volume, the DES phase was not formed. The recoveries of the Pb(II) were found to be 102 ± 3% for 10 mL of sample solution and 101 ± 4% for 20 mL of sample solution.

## Effect of matrix ions

The interference effects of some common matrix ions in real samples were tested. In this experiment, 10 mL of solution containing 5 μg of Pb(II), as well as interfering ions at a concentration of 10,000 mg $L^{-1}$ $Na^+$, 1,000 mg $L^{-1}$ $Mg^{2+}$, $Ca^{2+}$, and $K^+$, and 10 mg $L^{-1}$ $Fe^{3+}$, $Ni^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Cr^{3+}$, $Al^{3+}$, $Mn^{2+}$, $Zn^{2+}$, and $Cd^{2+}$, had no significant effect on the recovery of Pb(II). The results indicate that this method can be applied for the extraction and preconcentration of Pb(II) from water samples prior to its determination using FAAS.

## Analytical characteristics of the method and comparison with other methods

Under the optimized experimental conditions, a calibration curve was prepared by analysing 20 mL of the standard solutions containing known amounts of Pb(II) over the concentration range of 12.5–2,000 μg $L^{-1}$ using the recommended procedure. The calibration equation was $A = 3.37 \times 10^{-4}$ C$+ 6.34 \times 10^{-4}$ with a correlation coefficient (R) of 0.9997, where A is absorbance and C is the concentration of Pb(II) (μg $L^{-1}$) in the solution. To determine the limit of detection (LOD), the proposed method was also applied for ten independent repeat analyses of 20 mL of blank solutions. The LOD was calculated to be 5.93 μg $L^{-1}$ using the equation of $3S_b/m$. Where $S_b$ is the standard deviation of ten replicate blank signals and m is the slope of the calibration curve. The preconcentration factor was 20 when the sample and final volumes were 20 mL and 1 mL, respectively.

For comparative purposes, the performance of the developed method and the other reported preconcentration methods (Zhang *et al.* 2011; Alothman *et al.* 2013; Bahadır *et al.* 2014; Habila *et al.* 2014; Mohammadi *et al.* 2014; Mohammadi *et al.* 2016; Satti *et al.* 2016; Tuzen *et al.* 2016) are given in Table 1. As seen from the table, the LOD of the method is better than or comparable to those obtained with other methods (Alothman *et al.* 2013; Habila *et al.* 2014; Mohammadi *et al.* 2014; Mohammadi *et al.* 2016). Although some of these methods have better detection limits or higher preconcentration factors, they need large sample volumes and longer preconcentration time per sample (Bahadır *et al.* 2014; Satti *et al.* 2016; Tuzen *et al.* 2016).

## Analysis of certified sample

In order to assess the accuracy of the developed method, the method was applied to the determination of Pb in the

**Table 1** | The comparison between the proposed method and other methods for the determination of lead by FAAS

| Method[a] | Sample type | Detection limit (LOD) (μg $L^{-1}$) | Preconcentration factor | Sample volume (mL) | Time of analysis (min) | Reference |
|---|---|---|---|---|---|---|
| ELLME-DES | Water samples | 5.93 | 20 | 20 | 7 | This paper |
| IL-DLLME | Water samples | 5.9 | 35 | 35 | 9 | Mohammadi *et al.* (2014) |
| CPE | Biological and water samples | 5.27 | 30 | 15 | at least 20 | Mohammadi *et al.* (2016) |
| SPE | Water and food samples | 1.05 | 100 | 600 | 130 | Tuzen *et al.* (2016) |
| Coacervate-based extraction | Water samples | 3.2 | 100 | 50 | 31 | Satti *et al.* (2016) |
| NPU-DLLME | Water and food samples | 5.7 | 37.5 | 15 | 16 | Habila *et al.* (2014) |
| DLLME-SFO | Water samples | 2.53 | 20 | 10 | 5 | Zhang *et al.* (2011) |
| Coprecipitation | Water, black tea and tobacco samples | 0.86 | 50 | 250 | 20 | Bahadır *et al.* (2014) |
| TC-IL-ME | Hair samples | 5.8 | 30 | 15 | at least 14 | Alothman *et al.* (2013) |

[a]IL-DLLME, Ionic liquid dispersive liquid–liquid microextraction; CPE, Cloud point extraction; SPE, Solid phase extraction; NPU-DLLME, Nanoparticles ultrasound assisted dispersive liquid–liquid microextraction; DLLME-SFO, Dispersive liquid–liquid microextraction based on the solidification of a floating organic drop; TC-IL-ME, Temperature controlled ionic liquid based microextraction.

**Table 2** | The results of the water samples

| Sample | Added ($\mu$g L$^{-1}$) | Found$^a$ ($\mu$g L$^{-1}$) | Recovery (%) | R.S.D (%) |
|---|---|---|---|---|
| Tap water | – | <LOD | – | – |
|  | 50 | 52.4 ± 1.4 | 105 | 2.7 |
| River water | – | <LOD | – | – |
|  | 50 | 51.6 ± 1.7 | 103 | 3.3 |
| Seawater | – | <LOD | – | – |
|  | 50 | 52.4 ± 1.7 | 105 | 3.2 |

$^a$Mean value ± standard deviation based on three replicate determinations.

SPS-SW2 Batch 127 certified reference surface water. The certified value of Pb is 25.0 ± 0.1 $\mu$g L$^{-1}$. The value obtained using the proposed method was 24.8 ± 1.4 $\mu$g L$^{-1}$ (N = 3). The accuracy of the method was evaluated by Student's t-test. The t value was calculated as 0.25 using the equation $t = (|\mu - \bar{x}|\sqrt{N})/s$. The critical t value for 2 degrees of freedom at the 95% confidence level is 4.30. The calculated t value is smaller than the critical t value at the 95% confidence level, confirming that there is no significant difference between the value obtained by the proposed method and the certified value.

### Application of the method to real samples

The feasibility of the improved method was evaluated by the extraction and preconcentration of Pb(II) from tap water, seawater and river water samples. In order to investigate the reliability of the method, the recovery experiments were performed and the water samples were spiked with a concentration of 50 $\mu$g L$^{-1}$ of Pb(II). The results are given in Table 2. The recoveries of the analyte were 105% for tap water, 103% for river water, and 105% for seawater. These results indicate that the method is reliable for the preconcentraion of Pb(II) from natural waters.

### CONCLUSIONS

In the present study, an ELLME-DES method was improved for the preconcentration of Pb(II) from natural waters prior to FAAS detection. The proposed method is simple, accurate, easy to use and economic. The method requires nearly 7 minutes of sample preparation time per sample.

However, eight samples can be centrifuged for analysis simultaneously. The developed method shows high tolerance to many potentially foreign ions. In addition, the analytical performance of the method is comparable with other methods reported in the literature. The method could be combined with other detection techniques, such as ETAAS, ICP-OES and ICP-MS in order to acquire a lower detection limit. Had ETAAS been used for the detection of Pb, no dilution would be required and so the preconcentration factor could have been far higher.

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