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Ultrasonic-assisted dispersive liquid–liquid microextraction based on hydrophilic deep eutectic solvents: Application to lead and cadmium monitoring in water and food samples

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ABSTRACT

A green and innovative ultrasonic-assisted dispersive liquid–liquid microextraction using hydrophilic deep eutectic solvents (UA-HDES-DLLME) was developed for the selective and simultaneous extraction and enrichment of Pb (II) and Cd (II) in water and food samples for flame atomic absorption spectrometry. Several natural deep eutectic solvents (NADES) were used for the preparation of six different HDES and methyl violet was used as chelating reagent. Effective parameters such as pH, sonication time, methyl violet amount, DES type, dispersive solvent types, etc were optimized. Relative standard deviation (RSD) and preconcentration factor (PF) were 4.0% and 80. Low limits of detection (LOD, 1.3 ng mL^{-1} for Pb (II) and 0.33 ng mL^{-1} for Cd (II)) and quantification (LOQ, 4.0 ng mL^{-1} for Pb (II) and 1.0 ng mL^{-1} for Cd (II)) were found. The method accuracy was confirmed with analyses of certified reference materials.

Introduction

In recent years, heavy metal pollution has increased because of industrial activities, traffics, mining, fossil fuels and the use of fertilizers in agricultural areas. Some heavy metals are known as carcinogens and as they are non-biodegradable, they can be bioaccumulated in a biological system (Nyaba and Nomngongo 2020; Xie et al. 2020). The bioaccumulation of cadmium in the human kidney and liver severely damages the urinary and DNA system, leading to cancers, including prostate and lung (Biata et al. 2017; Feist and Sitko 2018; Nyaba and Nomngongo 2020). The maximum recommended concentration of lead and cadmium in drinking water are 10 and 3 μg L^{-1} by WHO (World Health Organization 2008).

Consumption of contaminated food or drinking water with heavy metal ions is the major route for transfer into the human body. Lead and cadmium are among the most toxic heavy metals for the environment according to environmental health agencies declaration (Langston 2018). Lead affects the central nervous system and can cause growth retardation, kidney cancers, intelligence damage and behavioral changes, and it enters our body from air, water, beverage and food samples (Aboufazeli et al. 2013; Huang et al. 2020). Lead and cadmium are found in water, food, and environmental samples at μg L^{-1} or μg kg^{-1} levels (Nordberg et al. 2002; Kumar et al. 2020). Since the concentrations of heavy metals in analyzed samples are usually low, highly selective and sensitive detection techniques or effective sample preparation methods are required. Different instrumental techniques such as inductively coupled plasma equipped with mass spectrometry (ICP-MS) (Ohki et al. 2016; Teran-Baamonde et al. 2018), atomic emission spectrometry (ICP-AES) (Nomngongo and Ngila 2015; Yan et al. 2021), X-ray fluorescence spectrometry (XRF)

(Goodlaxson et al. 2018), graphite furnace atomic absorption spectrometry (Aleluia et al. 2017), high resolution continuum source flame or routine flame atomic absorption spectrometry (FAAS) (Rajabi and Hemmati 2021; Chaikhan et al. 2022) have been applied in trace analysis of heavy metals ions in diverse samples.

Although these instruments have sufficient sensitivity towards heavy metals,sample preparation methods are still significant due to low concentration of analytes than the detection limit of instruments and matrix components of real samples (Altunay et al. 2019; Suo et al. 2019; Sorouraddin et al. 2020). Several enrichment and separation methods, such as supramolecular solvent extraction (Lemes and Tarley 2021), cloud point extraction (Coelho and Arruda 2005), dispersive liquid–liquid microextraction (Sixto et al. 2019; Adhami et al. 2020), solid phase microextraction (Chen et al. 2019; Altunay et al. 2021), deep eutectic solvent microextraction (Shishov et al. 2022), and hydrophobic deep eutectic solvent extraction (Elik et al. 2022) have been developed in order to solve these problems and improve the quality in the analysis of real samples.

Dispersive liquid–liquid microextraction (DLLME) is a significant separation and preconcentration technique. Ultrasonication can accelerate the formation of dispersive mixtures between aqueous and extraction solution, shorten the equilibration time, and significantly improves extraction recovery of analyte ions (Ji et al. 2021). Combination of ultrasonication with DLLME provides several advantages such as rapidity, simplicity, and high recovery, and enhancement factor (Aguirre et al. 2019; Arpa and Arıdaşır 2019).

The objective of this study was to synthesize a green hydrophilic deep eutectic solvent (HDES) composed of methyltriphenylphosphonium bromide (MTPB) and ethylene glycol (EG) as extraction solvent and its use in UA-DLLME for selective and simultaneous separation and preconcentration cadmium and lead ions in water and food samples. Compared with ionic liquids or organic solvents, DES as extraction solvents have advantages such as simplicity of green synthesis, cheap, biocompatibility, and biodegradability (Sadeghi and Davami 2019). HDES are known

as natural deep eutectic solvents (NADES). NADES are more environmentally friendly than DES because of their natural origin (Li and Row 2019) and they generally provide a network of hydrogen bonding among acceptors and donors, thus promoting dissolution of target analytes and also have freezing points much lower than those of the two components (Vanda et al. 2018). According to our literature survey, UA-DLLME-HDES have not been used for selective and simultaneous separation and enrichment of lead and cadmium ions. Critical factors like pH, methyl violet amount, DES type, dispersive solvent type, ultrasonication time and sample volume were optimized.

Materials and methods

Reagents and solutions

The experiments were carried out using ultrapure water (18.2 MΩ cm^{-1}, Millipore, United States), and the material used was previously decontaminated in a bath (1 mol L^{-1} of HNO$_3$). Standard solutions of Pb (II) and Cd (II) were bought from Inorganic Ventures (USA). The working solutions were daily prepared in water. A methyl violet (Merck, Darmstadt, Germany) solution (10^{-4} mol L^{-1}) was prepared in deionized water. Choline chloride (ChCl, Merck), ethylene glycol (EG) (Sigma Aldrich, St. Louis, MO, USA), malonic acid (MalA) (Sigma), N,N-diethylethanolammonium chloride (DAC, Merck), tetrabutylammonium chloride (TBAC, Sigma), benzyltrimethylammonium chloride (BTMAC, Merck), and methyltriphenylphosphonium bromide (MTPB, Merck) were used in the preparation of hydrophilic deep eutectic solvents. Acetone (Sigma), ethanol (Merck), acetonitrile (Merck) and tetrahydrofuran (THF, Sigma) were tested as dispersive solvents. Buffer solutions such as ammonia, borate, acetate and phosphate were used to adjust pH values of the sample solutions.

Instruments

A microwave system (model Star D, Milestone, Italy) was used in microwave-assisted acid digestion. A centrifuge (Universal-320, Hettich, London, England) was applied to separate

supernatants and the agitation was performed using an ultrasonic bath (SK5210LHC model Kudos, Shanghai, China). A digital pH-meter (Metrohm model 654, Herisau, Switzerland) was used for pH measurement purposes. The analysis step was performed using FAAS (Shimadzu AAS-6300 model, Kyoto, Japan). Pb ($\lambda = 217$ nm) and Cd ($\lambda = 228.8$ nm) hollow cathode lamps were utilized as radiation sources.

Sample preparation

Bottled water, mineral water, leek, onion, tomato, eggplant, rice, and black tea were purchased from local markets in Sivas (Turkey). Honey samples were collected from the producers in Erzincan. Tap water samples were collected from the agricultural region of Sivas. Standard reference material (SRM) of the Peach Leaves (NIST 1547) and simulated fresh water-trace elements (NIST 1643e) provided by the National Institute of Standards and Technology (NIST, United States) were used in the evaluation and validation of the proposed method.

About 50 mL of all water samples, passed through 0.45 μm membrane filter, was taken and evaporated on the heating plate until 5 mL remained. Finally, the amounts of lead and cadmium were determined by applying the suggested method to the evaporated water samples. Moreover, the suggested method was applied directly to 5 mL of the certified water sample without any pre-treatment.

Food samples were prepared by the microwave digestion described below. The food samples (0.5 g) and NIST 1547 (0.1 g) were accurately weighed into a PTFE digestion tubes. Next,

concentrated HNO_3 (3 mL) and concentrated H_2O_2 (1 mL) were added to the tubes. After capping the tubes, they were placed in the microwave system. The digestion step was as follows: (1) 900 W at 110 °C for 10 min; (2) 1200 W at 200 °C for 16 min; (3) 1200 W at 240 °C for 25 min; (4) 0 W for 40 min to cool. Blank samples were treated in the same way.

Preparation of hydrophilic DES

The HDES was prepared using a heating bath (Li and Row 2019). The mass of each component for the desired molar ratio and the appropriate volume of water were added in a closed container and homogenized. In the procedure, the mixture was heated in a bath for 60 min at a temperature of 80 °C. The formation of a homogeneous solution indicates that HDES were prepared. After the cooling step, the prepared HDES were tested for microextraction studies. Properties such as composition, abbreviation, density, freezing point of the prepared HDES are presented in Table 1.

HDES based UA-DLLME procedure

The proposed analytical method includes the following experimental steps. First, a solution of the analytes (5 mL at a concentration of 30 ng mL^{-1}) was added to a 15 mL test tube and its pH was adjusted to pH 4.0 by using 1 mL of 0.1 mol L^{-1} acetate buffer. Then, 500 μL of 10^{-4} mol L^{-1} of methyl violet was added into the solution to complex the analyte ions in the mixture. After providing complexation, 700 μL of HDES-6 (at 1:1 molar ratio) as extraction solvent and 300 μL of ethanol as dispersive solvent were injected into

Table 1. Some chemical and physical properties of the prepared hydrophilic DES.

Abbreviation	HBA	HBD	Molar ratio	Appropriate volume of water	Melting point (°C)	Density (kg/m³)
HDES-1	ChCl	EG	1:2	4 mL	−24.5	1.12
HDES-2	ChCl	MalA	1:1	4 mL	10	1.08
HDES-3	DAC	EG	1:3	4 mL	−24.19	1.13
HDES-4	TBAC	EG	1:2	4 mL	−44.93	1.07
HDES-5	BTMAC	glycerol	1:5	4 mL	−1.97	1.22
HDES-6	MTPB	EG	1:1	4 mL	−49.34	1.23

ChCl: choline chloride.
EG: Ethylene glycol.
MalA: Malonic acid.
DAC: N,N-diethylethanolammonium chloride.
N4444–Cl: Tetrabutylammonium chloride.
BTMAC: benzyltrimethylammonium chloride.
MTPB: Methyltriphenylphosphonium bromide.

the sample solution. Next, the tubes were sonicated at room temperature for 5 min. During this step, a turbid mixture resulting from finely dispersed HDES-6 in the aqueous solution was obtained. After centrifugation (2 min, 4000 rpm) the upper aqueous phase (approximately 750 μL) was discarded and the remaining viscous phase was diluted to 1.25 mL with 1 mol L^{-1} HNO_3 in methanol. Finally, the remaining solution was injected into the atomization section of the FAAS and the lead and cadmium contents were determined.

Results and discussion

pH effect

pH is a crucial parameter for complex formation between methyl violet and Pb (II) and Cd (II) ions and it was evaluated by adjusting the solutions at different pHs (2–10). The extraction conditions were 500 μL of 10^{-4} mol L^{-1} of methyl violet solution, 700 μL of HDES-6 (MTPB and EG) at 1:1 molar ratio as extraction solvent, 300 μL of ethanol as dispersive solvent, 5 min sonication time and centrifugation (2 min, 4000 rpm). Quantitative recovery values were found at pH 4 for Pb (II) and Cd(II) ions (Figure 1(a)). For pH lower or higher than 4, there may be insufficient complex formation between Pb (II) and Cd (II) ions and methyl violet solution. After pH 6, the recovery of Pb (II) and Cd (II) ions decreased because of hydrolysis with formation of Mx (OH)y. So, acetate buffer was used thereafter for adjusting the solution pH at 4.

Methyl violet amount

Methyl violet is mainly used as a dye and is known as crystal violet. It has been reported that crystal violet forms complexes with bivalent metal ions (Maslov et al. 2020). A good phase separation of analyte ions relates to the formation of complex between the studied ions and chelating agent. Recovery of analyte ions was found to be 30% without methyl violet chelating reagent. Altering the method efficacy by changing methyl violet amount was evaluated. Recovery values of analyte ions were found quantitative in the range of 500–700 μL for 10^{-4} mol L^{-1} chelating reagent.

So, further studies were performed by using 500 μL of 10^{-4} mol L^{-1} methyl violet solution (Figure 1(b)).

DES type and its composition

Selectivity of the UA-DLLME-HDES method is expressed as the ability of DES to remove Pb (II) and Cd (II) ions under different conditions. Different HBA (MTPB, ChCl, DAC, TBAC, and BTMAC) and HBD (ethylene glycol, malonic acid, and glycerol) species were tested for the formation of effective DES for UA-DLLME-HDES method. In this context, six DESs in diverse molar ratios were prepared and firstly, studies were done with these DES compositions. The analytical data are presented in Table 1. Quantitative recovery values were obtained only by using HDES-6 (MTPB and EG) (Figure 1(c)). Molar ratio of HDES was also critical factor for the extraction and preconcentration of Pb (II) and Cd (II) ions. Different molar ratios of HDES-6 (MTPB and EG) were tested: 3:1, 2:1, 1:1, 1:2, and 1:3. Good recovery of Pb (II) and Cd (II) ions was found by using 1:1 molar ratio of HDES-6 (MTPB and EG). For subsequent studies, MTPB and EG (1:1) molar ratio as extraction solvent was used as HDES-6. The results are shown in Figure 1(d). The volume of HDES solution was also studied considering preconcentration factor and extraction recovery of Pb (II) and Cd (II) ions. The volume of HDES-6 (MTPB and EG) (1:1) molar ratio) was investigated over the range 200 to 800 μL. Recoveries of Pb (II) and Cd (II) ions were found quantitative by using 700 μL of HDES-6. For subsequent studies, 700 μL of HDES-6 (MTPB and EG) (1:1) molar ratio was used as extraction solution in UA-DLLME-HDES method. The type of dispersive solvent is also an important factor. So, various dispersive solvents including acetone, acetonitrile, ethanol and THF were studied (Figure 1(e)). The recovery of analyte ions was found quantitatively by using ethanol as dispersive solvent. Then, the effect of the volume of the dispersive solvent on the recovery of the analyte ions was studied in the volume range of 100-700 μL. The study showed that both analytical recoveries increased up to 300 μL ethanol volume, while at higher
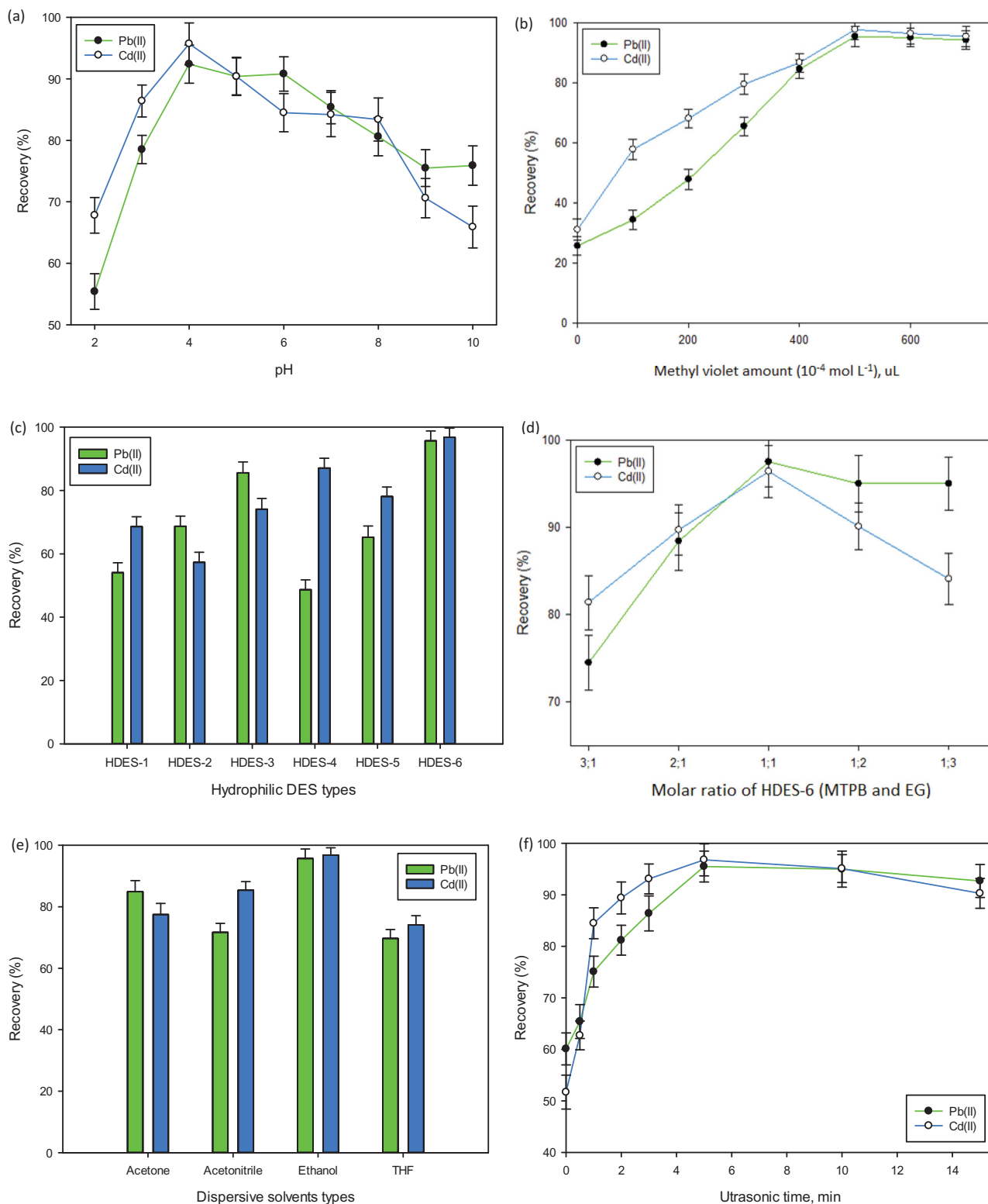
Figure 1. (a–g) The results of the optimization studies. The microextraction conditions were as follows. 5 mL sample solution containing 30 ng mL^{-1} Pb(II) and Cd (II) ions; pH 4; 500 μL of 10^{-4} mol L^{-1} of methyl violet solution; 700 μL of HDES-6 (MTPB and EG) at 1:1 molar ratio as extraction solvent; 300 μL of ethanol as dispersive solvent, 5 min sonication time, 2 min centrifugation at 4000 rpm and 100 mL sample volume.
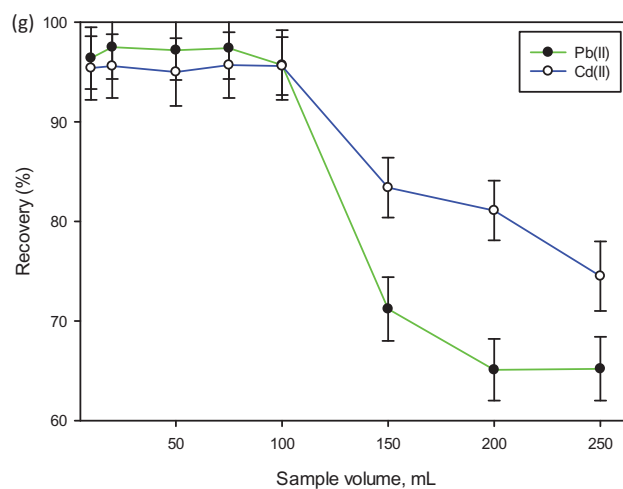
Figure 1 Continued.

ethanol volumes, reductions in the recovery values of the analyte ions were observed. Therefore, the volume of the dispersive solvent was chosen as 300 µL.

Ultrasonication time

Ultrasound energy accelerates the migration of chelated analyte ions from the sample solution through the HDES phase. Ultrasonication time is an important factor for the mass transfer rate of analyte ions from the aqueous phase to the extraction phase. The recovery of Pb (II) and Cd (II) ions was found to be 60% and 50%, respectively, without ultrasonication. Ultrasonication of analyte ions is necessary to shorten the extraction time and increase the phase separation efficiency. The mixture of Pb (II) and Cd (II) ions was sonicated up to 15 min at room temperature in UA-DLLME-HDES method. Recovery values of the ions were found quantitative in the range of 5-10 min ultrasonication time (Figure 1(f)). HDES has been gradually subdivided into the micro and nanoscale due to the application of ultrasonication, which creates temporary cavitation at the interface of HDES species. The resulting complex was transferred into the DES phase containing analyte ions. After centrifugation 2 min at 4000 rpm, the fine droplets of the HDES-6 collapsed to the bottom of the test tubes. The upper aqueous phase was discarded by decantation and

the remaining solution was analyzed by FAAS for the determination of analytes.

Sample volume

Volume of the sample solution is an important parameter to enhance the preconcentration factor (PF). The PF is calculated from the ratio of the initial volume to the measurement volume. Sample volume of UA-DLLME-HDES method was varied in the range of 10–250 mL containing 30 ng mL^{-1} of standard Pb (II) and Cd (II) ions (see Figure 1(g)). For volumes of 100 mL recoveries were quantitative. Due to the dilution effect, recovery values of analytes ions in higher samples volumes were decreased. PF was calculated as 80 by divided 100 mL sample volume to 1.25 mL of final volume.

Interference effects

The tolerance limits of co-extracted ions are defined as the matrix species amount causing a relative error no more than 5% for Pb (II) and Cd (II) ions. Under the given conditions, model solution containing 30 ng mL^{-1} of Pb (II) and Cd (II) ions and the spiked matrix species were applied to UA-DLLME-HDES method. Tolerance limits of co-extracted ions were found high with respect to real samples (Table 2). The results indicate that various anions, cations, and transition metal ions generally existing in water and

Table 2. Effect of matrix ions on the recovery of Pb(II) and Cd(II) ions ($N = 3$).

	Pb(II)			Cd(II)		
Interference ion	Tolerable limit	RSD (%)	Recovery (%)	Tolerable limit	RSD (%)	Recovery (%)
Ca^{2+}	1500	2.9	99 ± 4	1500	2.7	99 ± 3
Na^+	1500	2.7	99 ± 3	1000	2.9	98 ± 3
Cl^-	5000	2.9	95 ± 3	5000	2.5	96 ± 2
PO_4^{3-}	1500	2.6	98 ± 2	1000	3.2	97 ± 2
SO_4^{2-}	1000	2.8	98 ± 4	1500	2.6	99 ± 4
Mg^{2+}	1000	2.9	96 ± 5	1000	3.2	98 ± 3
K^+	1000	3.2	98 ± 5	500	3.4	97 ± 3
Co^{2+}	1000	3.1	97 ± 5	750	3.2	99 ± 2
Se^{4+}	500	3.3	97 ± 3	250	3.5	97 ± 4
As^{3+}	500	3.2	98 ± 2	250	3.7	96 ± 5
Cu^{2+}	500	3.4	97 ± 4	100	3.9	93 ± 5
Mn^{2+}	250	3.6	95 ± 3	250	3.6	95 ± 3
Ni^{2+}	250	3.3	96 ± 5	100	3.9	94 ± 3
Zn^{2+}	100	3.4	96 ± 2	100	3.8	94 ± 2
Fe^{3+}	100	3.7	95 ± 4	500	3.3	97 ± 4
Cr^{3+}	100	3.9	94 ± 5	250	3.5	96 ± 3

Table 3. Validation of the UA-DLLME-HDES method for Pb(II) and Cd(II) with standard reference materials ($N = 5$).

SRMs	Analytes	[a,b]Certified value	[a,b]Obtained value	Recovery (%)	t-value
SRM-1547 Peach Leaves[a]	Pb	0.869 ± 0.018	0.847 ± 0.036	97.5	1.35
	Cd	0.0261 ± 0.0022	0.0258 ± 0.0006	98.9	1.02
SRM-1643e simulated fresh water-trace elements[b]	Pb	19.63 ± 0.21	19.32 ± 0.79	98.4	0.87
	Cd	6.568 ± 0.073	6.437 ± 0.24	98.0	1.21

[a]mg kg^{-1}, [b]ng mL^{-1}

food samples do not interfere with the analysis of Pb (II) and Cd (II) ions under the developed experimental conditions when using FAAS. Relative standard deviation (RSD) was below 4% for concomitant ions.

Analytical data

Analytical data of the UA-DLLME-HDES method was tested under optimal experimental conditions containing 30 ng mL^{-1} of Pb (II) and Cd (II) ions (pH 4500 μL of 10^{-4} mol L^{-1} of methyl violet solution, 700 μL of HDES-6 (MTPB and EG) at 1:1 molar ratio as extraction solvent, 300 μL of ethanol as dispersive solvent, 5 min sonication time, 2 min centrifugation at 4000 rpm, 100 mL sample volume). Calibration curves were depicted by different solutions and the data confirmed that they are linear in the range of 4–550 ng mL^{-1} for Pb(II) and 1–300 ng mL^{-1} for Cd (II), respectively. The linear calibration equations for model solution were found as $A = (0.8389 \pm 0.0058)C + (0.3452 \pm 0.0269)$ (r^2: 0.9978) for Pb (II) and $A = (0.4270 \pm 0.0074)C + (0.0967 \pm 0.0325)$ (r^2: 0.9982) for Cd (II), respectively (A: absorbance, C: concentration, ng mL^{-1}). The limits of detection (LOD) and quantification (LOQ) were

calculated as 1.3 ng mL^{-1} and 4.0 ng mL^{-1} for Pb (II) and 0.33 ng mL^{-1} and 1.0 ng mL^{-1} for Cd (II), respectively, with the help of formulas $3S_{blank}/m$ and $10S_{blank}/m$, respectively. Where S_{blank} is the standard deviation obtained from the ten-replication analysis of blank samples and m is the slope of the calibration graphs. LOQ values for Pb and Cd in solid food samples were found as 2.1 and 8.5 μg kg^{-1}, respectively. The enhancement factor (EF) was calculated as 85 ± 4 for Pb (II) and 96 ± 7 for Cd (II), respectively from the ratio of the correlation coefficient of the analytical curve obtained before and after the UA-DLLME-HDES method. The PF values were 80 for both Pb (II) and Cd (II) ions. The reproducibility and repeatability of UA-DLLME-HDES method for 25 and 100 ng mL^{-1} of Pb(II) and Cd (II) were calculated with relative standard deviation (RSD), which were found to be less than 4%.

Validation and applications of UA-DLLME-HDES method

Accuracy of the UA-DLLME-HDES method was investigated with analysis of SRM-1643e simulated fresh water-trace elements and SRM-1547

Table 4. Recovery obtained from the determination of Pb(II) and Cd(II) in water samples using the UA-DLLME-HDES method ($N = 3$).

Samples	Spiked Pb(II)/Cd(II) (ng mL^{-1})	Pb (ng mL^{-1})			Cd (ng mL^{-1})		
		Obtained	Recovery (%)	RSD (%)	Obtained	Recovery (%)	RSD (%)
Mineral water	–	n.d*	–	–	n.d*	–	–
	50	49.1	98.2	2.4	49.0	98.0	2.8
	250	243.3	97.3	2.7	243.0	97.2	3.1
Tap water-1	–	11.2	–	2.8	27.6	–	3.1
	50	58.2	94.0	3.1	76.3	97.4	3.5
	250	250.2	95.6	3.3	273.1	98.2	3.4
Tap water-2	–	23.8	–	2.2	35.1	–	2.4
	50	72.2	96.8	2.5	83.7	97.2	2.7
	250	267.8	97.6	2.6	279.6	97.8	3.3
Bottled water-1	–	n.d*	–	–	n.d*	–	–
	50	49.4	98.8	2.7	49.7	99.4	2.8
	250	247.5	99.0	3.2	245.5	98.2	3.3
Bottled water-2	–	n.d*	–	–	n.d*	–	–
	50	48.2	96.4	3.1	49.4	98.8	2.4
	250	243.0	97.2	2.8	248.5	99.4	2.9

*Could not be determined.

Table 5. Spiked and obtained amount and recovery values for determination of Pb and Cd in different samples using the UA-DLLME-HDES method ($N = 3$).

Samples	Pb (µg kg^{-1})			Cd (µg kg^{-1})		
	Spiked	Obtained	Recovery (%)	Spiked	Obtained	Recovery (%)
Leek	–	62 ± 3	–	–	89 ± 5	–
	25	85 ± 4	94	100	183 ± 6	94
Onion	–	18 ± 2	–	–	34 ± 3	–
	25	42 ± 3	95	100	130 ± 5	96
Tomato	–	71 ± 4	–	–	47 ± 3	–
	25	95 ± 5	96	100	146 ± 7	99
Eggplant	–	13 ± 2	–	–	26 ± 1	–
	25	36 ± 3	92	100	123 ± 4	97
Honey	–	36 ± 2	–	–	58 ± 3	–
	25	50 ± 3	96	100	151 ± 5	93
Rice	–	41 ± 3	–	–	21 ± 1	–
	25	66 ± 5	100	100	117 ± 5	96
Black tea	–	26 ± 2	–	–	33 ± 2	–
	25	49 ± 3	92	100	127 ± 6	94

peach leaves for Pb(II) and Cd(II) ions. The results of the present method are in agreement with certified values (Table 3). So, good accuracy of the method ($p < 0.01$) was found and the data confirmed that there was no difference at 95% confidence level. Values of $t_{experimental}$ were found to be lower than the $t_{critical}$ values.

The UA-DLLME-HDES method was successfully applied to real samples, such as mineral water, tap water, and bottled drinking water. The standard addition approach was used to test the accuracy in the analysis of real samples. The recoveries and RSD values for Pb (II) and Cd (II) ions were found in the ranges of 94.0–98.8% and 2.2–3.5%, respectively (Table 4).

The UA-DLLME-HDES method was also applied to food samples including leek, onion, tomato, eggplant, honey, rice, and black tea. The standard addition approach was also applied to digested food samples. For this purpose, 25 µg kg^{-1} for Pb(II) and 100 µg kg^{-1} for Cd (II) were added to food samples. Quantitative recovery was calculated in the range of 92–100% for Pb (II) and 93-99% for Cd (II) (Table 5). Lead and cadmium levels were determined in analyzed food samples at µg kg^{-1} levels. The obtained results indicated that the current UA-DLLME-HDES method has high sensitivity and reproducibility, and can be successfully applied to samples containing different matrix media for the determination of lead and cadmium.

Conclusions

A new and green UA-DLLME-HDES method was developed for the selective and simultaneous extraction, preconcentration and determination of lead and cadmium ions in water and food samples by using FAAS. Six different natural and hydrophilic DES with different molar ratio were prepared for the extraction of lead and cadmium ions. All HDES were prepared using combinations of ChCl, malonic acid, ethylene glycol, DAC, TBAC, BTMSC, MTPB, and glycerol. The UA-DLLME-HDES method presented has advantages that include low cost, simple, biodegradable solvents, sensitive, selective, environmentally friendly, good precision, short extraction time and high tolerance limits for the preconcentration, separation, and determination of lead and cadmium in water and food samples. The

Table 6. Analytical performance of the present UA-DLLME-HDES method compared with other methods.

Analyte	Method/techniques	Sample matrix	LOD (ng mL^{-1})	Extraction time (min)	RSD (%)	PF or EF	References
Pb, Cd	dSPME/FAAS	water, vegetables and barbecue samples	0.03	20	2.2	98	(Altunay et al. 2021)
Pb, Cd	EA-SS-LPME/FAAS	canned food samples	6.8–19.5	>10	1.69	1.4–3.3	(Chaikhan et al. 2022)
Pb, Cd	SPE/FAAS	environmental samples	0.20–0.27	>30	2.6–3.8	160	(Kumar et al. 2020)
Cd	SM-DLLME/ FAAS	flaxseed flour samples	0.10	>20	4.61–7.34	8.72	(Lemes and Tarley 2021)
Cd	DLLME/FAAS	honey samples	0.82	5	3.0	–	(Sixto et al. 2019)
Pb, Cd	SPE/GFAAS	soil and food samples	0.011– 0.102	60	4.3–4.5	–	(Xie et al. 2020)
Pb, Cd	DLLME/SWASV	Vegetable oil samples	0.01–0.006	>10	6	36–39	(Shishov et al. 2022)
Pb, Cd	UA-DLLME-HDES/FAAS	water and food samples	0.33–1.3	7	<4	85–96	This study

dSPME: dispersive solid phase microextraction; EA-SS-LPME: effervescent-tablet assisted switchable solvent based liquid phase microextraction; FAAS: flame atomic absorption spectrometry; SPE: solid phase extraction; SM-DLLME: supramolecular solvent-based dispersive liquid–liquid microextraction; DLLME: dispersive liquid–liquid microextraction; GFAAS: graphite furnace atomic absorption spectrometry; SWASV: square-wave anodic stripping voltammetry; UA-DLLME-HDES: ultrasonic-assisted dispersive liquid–liquid microextraction based on hydrophilic deep eutectic solvents; LOD: limit of detection; RSD: relative standard deviation; PF: preconcentration factor; EF: enhancement factor.

comparison of the UA-DLLME-HDESmethod with literature values for lead and cadmium are given in Table 6. Low RSD, low detection limit, short extraction time, high preconcentration and EF were observed. Water and food samples can be analyzed with the present UA-DLLME-HDES method at µg L^{-1}or µg kg^{-1} levels with respect to lead and cadmium content.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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