



# A highly selective and sensitive ultrasonic assisted dispersive liquid phase microextraction based on deep eutectic solvent for determination of cadmium in food and water samples prior to electrothermal atomic absorption spectrometry



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## ABSTRACT

A simple, fast, green, sensitive and selective ultrasonic assisted deep eutectic solvent liquid-phase microextraction technique was used for preconcentration and extraction of cadmium (Cd) in water and food samples by electrothermal atomic absorption spectrometry (ETAAS). In this technique, a synthesized reagent (Z)-N-(3,5-diphenyl-1H-pyrrol-2-yl)-3,5-diphenyl-2H-pyrrol-2-imine (Azo) was used as a complexing agent for Cd. The main factors effecting the pre-concentration and extraction of Cd such as effect of pH, type and composition of deep eutectic solvent (DES), volume of DES, volume of complexing agent, volume of tetrahydrofuran (THF) and ultrasonication time have been examined in detail. At optimum conditions the value of pH and molar ratio of DES were found to be 6.0 and 1:4 (ChCl:Ph), respectively. The detection limit (LOD), limit of quantification (LOQ), relative standard deviation (RSD) and preconcentration factor (PF) were observed as 0.023 ng L<sup>-1</sup>, 0.161 ng L<sup>-1</sup>, 3.1% and 100, correspondingly. Validation of the developed technique was observed by extraction of Cd in certified reference materials (CRMs) and observed results were successfully compared with certified values. The developed procedure was practiced to various food, beverage and water samples.

## 1. Introduction

Cadmium (Cd) is familiar with its elevated toxicity and bio accumulative nature (Kah, Levy, & Brown, 2012; Luevano & Damodaran, 2014) and is considered as one of the vast contamination in plant foods due to common usage of phosphate fertilizers in agricultural crops (Borges, et al., 2011). Even at small concentration of Cd is extremely toxic to animals and plants as its non-essentiality in living organisms. Food chain is the primary source of cadmium exposure in humans beings (Rizwan et al., 2016). Due to agricultural inputs, industrial pollution, and other causes, it is included among those elements which are well known for exerting their toxicity through food and water (Zhang et al., 2016). Whereas the Joint FAO/WHO Expert Committee on Food Additives (JECFA) recognized the harmless level of Cd intake as provisional tolerable weekly intake (PTWI) of 7 µg kg<sup>-1</sup> bw (Meeting & Organization, 2006).

In these days scientific society is showing a great interest towards analytical techniques, looking for extra competent and non toxic solutions. Usually a number of techniques have been utilized for

preconcentration and extraction of different ultra trace metals from complex matrix, including cloud point extraction (Chen & Teo, 2001), solid phase extraction (Ghaedi, Ahmadi, & Soyak, 2007), liquid phase microextraction (Baliza, Teixeira, & Lemos, 2009), chromatography (King & Fritz, 1987), liquid-liquid extraction (Reza Jamali, Assadi, & Shemirani, 2007), solid phase microextraction (Panhwar et al., 2015), zeolite cation exchange (Qiu & Zheng, 2009) and ion exchange purification (Kholmogorov et al., 1997) are most famous techniques employed for extraction and preconcentration. Dispersive liquid-liquid microextraction (DLLME) method shows great benefits such as rapid, low cost, easy to use, low consumption of organic solvents and high enrichment factors (Andruch, Balogh, Kocúrová, & Šandrejová, 2013; Hu, He, Chen, & Xia, 2013).

For better preconcentration and eco-friendly techniques, the correct choice of eco-friendly and non toxic reagents is usually a difficult target in LPME techniques (Allothman, Habila, Yilmaz, Al-Harbi, & Soyak, 2015). Non toxic solvents are required to reduce the increasing environmental problems related with the usage of traditional toxic solvents. Therefore, to conquer the elevated price and toxicity of ionic

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liquids (ILs), the scientists have searched a new generation of inexpensive, green and environmental friendly extraction solvents and as a result of investigation (Li et al., 2016). To defeat the elevated cost and toxicity of ionic liquids, innovative, non toxic, environmental friendly, and inexpensive extraction deep eutectic solvents (DESs), has been appeared (Abbott, Capper, Davies, McKenzie, & Obi, 2006; Chang et al., 2009). Choline chloride (ChCl) is one of the most widely used component in the synthesis of DESs because it is cheap, biodegradable and non toxic quaternary ammonium salt (Abbott et al., 2006; Abbott, Capper, Davies, Rasheed, & Shikotra, 2005).

DESs have some advantages over ionic liquids that these are easy to synthesize with elevated purity at low cost. Many DESs with high melting points, however, can hamper their uses as non toxic solvents at room temperature compared to the large uses of ILs. Basically these DESs are made up of two or greater than two secure and cheap components having capability to combine with one another through hydrogen bond, to generate eutectic mixture with low melting point than every individual component (Bubalo, Ćurko, Tomašević, Ganić, & Redovniković, 2016; Li et al., 2016). DESs are frequently achieved by means of generating complex of salt named choline chloride (Vitamin B4, ChCl) (e.g. inexpensive, nontoxic and biodegradable) through hydrogen bond donor (HBDs) or a metal salt (e.g. low-cost and green, sugars, glycerol and carboxylic acids). While contrast to ionic liquids (ILs) and organic solvents applied in preconcentration techniques, DESs made up of from ChCl give a lot of benefits like inexpensive, simple to synthesize via just mixing the components, no additional pretreatment required, biologically compatible, biodegradable, and green (Smith, Abbott, & Ryder, 2014). Many instrumental techniques like ETAAS, FAAS, electro analytical and inductive coupled plasma attached through optical emission spectrometry were used in the determination of toxic metal ions in various environmental and biological samples (Ghaedi et al., 2009; Hajiaghbabaei et al., 2012; Kalfa, Yalcinkaya, & Turker, 2012; Turkmen, Turkmen, & Tepe, 2014; Yilmaz, Ozturk, Ozdemir, Eroglu, & Ertas, 2013). Among these LPME technique is one of the most flexible preconcentration and extraction technique to separate analyte of interest from complex matrix (Khajeh, Saravani, Ghaffari-Moghaddam, & Bohloli, 2016).

The aim of our study was to develop a novel, green and highly sensitive method for preconcentration and determination of Cd in different water and food samples by ultrasonic assisted deep eutectic solvent liquid-phase microextraction technique (UA-DES-LPME) coupled with electrothermal atomic absorption spectrometry (ETAAS). According to our literature survey, synthesized reagent (Z)-N-(3,5-diphenyl-1H-pyrrol-2-yl)-3,5-diphenyl-2H-pyrrol-2-imine (Azo) was not used before as complexing reagent in UA-DES-LPME of Cd. This reagent is very sensitive to Cd. Various analytical parameters were also studied and optimized.

## 2. Experimental

### 2.1. Instrumentation

Digestion of all samples was performed by using closed vessel microwave (Milestone Ethos D) (Soriso-Bg Italy) system (temperature maximum 300 °C, pressure maximum 1450 psi). For digestion of samples the conditions of microwave were chosen as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, and ventilation time was 8 min (Naeemullah, Tuzen, & Kazi, 2018). pH values were measured by using Sartorius (Professional Meter PP-15 glass-electrode, Germany) pH meter. Centrifuge machine (Nuve NF 800 Model, Turkey) was employed for phase separation. A fully computer operated Perkin Elmer (Norwalk, CT, USA) Analyst 700 graphite furnace atomic absorption spectrometry was employed for the determination of Cd. The wavelength for Cd was set at 228.8 nm with 7.0 mA current and 0.7 nm of spectral bandwidth.  $Mg(NO_3)_2$  and  $Pd(NO_3)_2$  were employed as modifier and

introduced into the furnace by means of auto sampler (Perkin Elmer AS-800). Highly pure argon with flow rate of  $250 \text{ mL min}^{-1}$  was used during all measurements.

### 2.2. Pyrolysis and atomization conditions

The optimum operating conditions of ETAAS for Cd analysis have five steps: drying 1, drying 2, pyrolysis, atomization and cleaning set as [temperature(°C)/ramp time(s)/hold time(s)] for all steps such as [100/5/20], [140/15/15], [850/10/20], [1600/0/5] and [2600/1/3], respectively.

### 2.3. Reagents and standard solutions

All analytical grade reagents were used with no any extra purification. Double distilled water was utilized for dilution purposes. The standard working solution of cadmium ( $1000 \text{ mg L}^{-1}$ ) was obtained from (Merck, Darmstadt, Germany). The reagent (Z)-N-(3,5-diphenyl-1H-pyrrol-2-yl)-3,5-diphenyl-2H-pyrrol-2-imine (Azo) was synthesized by reported analytical procedure (Gorman, et al., 2004). 0.1% solution of this reagent was prepared by dissolving suitable amount in acetone. In order to decrease the possibility of metal contamination, all glassware were put into  $HNO_3$  (5 M) for 24 h and then washed with double distilled water.

### 2.4. Preparation of DES

Many chemicals are available for the synthesis of different DESs. In present study, four different molar ratios of choline chloride:phenol (ChCl:Ph) deep eutectic solvents were synthesized i.e. 1:2, 1:3, and 1:4. Also four different types of DESs were prepared by mixing choline chloride:urea (ChCl:U), choline chloride:oxalic acid (ChCl:Ox), choline chloride:lactic acid (ChCl:LA), and choline chloride:ethylene glycol (ChCl:EG) at molar ratios 1:2. DESs components were placed in 50 mL polypropylene tubes and vortexed for 3 min for consecutive formation of monophasic phase. These solvents were used for preconcentration and extraction of Cd within water and food samples.

### 2.5. General procedure

In 50 mL standard solution containing  $10 \text{ ng L}^{-1}$  of Cd, 2 mL acetate buffer (pH 6.0), 400  $\mu\text{L}$  of (Z)-N-(3,5-diphenyl-1H-pyrrol-2-yl)-3,5-diphenyl-2H-pyrrol-2-imine (Azo) (0.1% w/v) and 0.5 mL DES were taken into screw capped test tube and then vortexed for 30 s to get homogeneous solution and then THF (600  $\mu\text{L}$ ) was added and mixtures was put into ultrasonication bath for 3 min. As a result, the DES aggregates slowly broken into nano sized due to the effect of ultrasonication. Then solution was centrifuged for 5 min at 4000 rpm to get fast and better separation of two phases. Then glass pipette was employed to take water and DES rich phase was remain in the tube, into which 0.5 mL acidic ethanol was added. Then ETAAS was used for the determination of Cd.

### 2.6. Selection of DES and its volume

The DES as extraction solvent must have some properties such as elevated extraction affinity for analyte, less soluble in aqueous solution and can easily dispersed into water. Therefore the choice of appropriate DES as an extracting solvent is aimed at its water phobic nature, selectivity and electrostatic connections with analyte (García, Rodríguez-Juan, Rodríguez-Gutiérrez, Rios, & Fernández-Bolaños, 2016). The selectivity may be defined as the capability of solvent to extract the targeted constituent in medium as associated to other components. To check the extracting efficiency of Cd, five different DESs were prepared including ChCl:U, ChCl:Ox, ChCl:Ph, ChCl:LA and ChCl:EG with molar ratio of 1:4. The difference in extraction efficiency was observed as

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