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Ultrasound assisted-deep eutectic solvent based on emulsification liquid phase microextraction combined with microsample injection flame atomic absorption spectrometry for valence speciation of chromium(III/VI) in environmental samples[☆]

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ABSTRACT

A new type of deep eutectic solvents (DESs) have been prepared and used as extraction solvents for ultrasound assisted-deep eutectic solvent based emulsification liquid phase microextraction method (UA-DES-ELPME) for the determination and speciation of total chromium, chromium(III) and chromium (VI). The chromium concentration in DES rich phase (extraction phase) was determined by using microsample injection flame atomic absorption spectrometer (FAAS). The detection limit (LOD), the quantification limit (LOQ), preconcentration factor and relative standard deviation were found as 5.5 μg L^{-1}, 18.2 μg L^{-1}, 20 and 6%, respectively. The accuracy of the developed method was evaluated by the analysis of water the certified reference materials (TMDA-53.3 Fortified environmental water and TMDA-54.4 Fortified Lake Water) and addition-recovery tests for water samples.

1. Introduction

Cr(III) is considered as an essential trace element for mammals metabolism, whereas Cr(VI) can be toxic and carcinogenic for living organisms because of the its oxidizing potential and easy permeating of biological membranes [1,2]. Water-soluble Cr(VI) compounds are also more extremely irritating and toxic to human body tissue [3]. Because of the difference in toxicity of Cr(III) and Cr(V) species to aquatic biota, Today there is an increasing demand to found a simple, accurate and reliable method for the speciation of these two oxidation states in water samples [4,5].

In the determination of chromium species in water samples, sample preparation and/or extraction techniques are necessity prior to detection steps such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), ultraviolet visible absorption spectrometry (UV–vis), high performance liquid phase chromatography (HPLC), gas chromatography (GC) and inductively coupled plasma optical emission spectrometry (ICP-OES) [6–10]. Of these methods, FAAS is a very common and popular measurement technique and has a variety of advantages including simple operation, low cost and good selectivity [11,12]. However, FAAS technique can only measure total concentration of chromium and the direct determination of Cr(III) and Cr(VI) at very low concentrations is always impossible because of the insufficient sensitivity of this method and matrix effects of foreign ions in water samples. As a result, preliminary species separation and preconcentration step is required before detection by FAAS.

For the speciation and preconcentration of chromium, the analytical methods reported in the literature are usually based on liquid–liquid extraction (LLE), cloud point extraction (CPE), solid phase extraction (SPE), coprecipitation, solid phase microextraction (SPME) [17] and liquid phase microextraction (LPME) [1,7,9,13–15]. Within these methods, an important effort has been shifted to the development of liquid phase microextraction methods, mainly characterized for eliminating or minimizing the time consuming, tedious and multistage operations, consumption of potentially organic solvents, production of secondary laboratory waste, necessity of large and complex laboratory equipments, which commonly faced in conventional speciation and preconcentration methods [16–18].

The biggest obstacle for the application of liquid phase microextraction methods is the utilization of environmentally friendly green solvents. The selection of the "right" solvent is the most important task not only for an effective extraction but also for the

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development green analytical methods. Because of the reasons mentioned above, the scientists focused on the search of alternative and novel solvents as separating agent. As a result of research, a new generation solvent system called deep eutectic solvents (DESs) has emerged [19,20]. A DES is generally consisting of two or more than two safe and inexpensive components that are capable of associating with each other through hydrogen bonds, to form a eutectic mixture with a melting point lower than that of each individual component [21–23].

Deep eutectic solvents (DESs) are typically formed by mixing choline chloride salt (ChCl, Vitamin B4) (e.g. cheap, non-toxic and biodegradable) with safe hydrogen bond donors (HBDs) (e.g. cheap and non-toxic urea, glycerol, sugars, carboxylic acids, etc.). When compared to organic solvents and ionic liquids used in extraction methods, DESs prepared from ChCl provide many advantages such as low price, easy to prepare by simply mixing components, no need to further purification, most of them are biodegradable, biocompatible and non-toxic [24–26]. In literature, some applications of DESs in material and organic compound synthesis, catalysis, electro-chemistry and substance dissolution have been reported [16–19]. According to our best knowledge, there is no any use of DESs as extraction solvent for speciation of inorganic analytes.

The aim of this work is the utilization of DESs as extraction solvent in ultrasound assisted-deep eutectic solvent based emulsification liquid phase microextraction method (UA-DES-ELPME) for speciation and preconcentration of Cr(III)/Cr(VI) in environmental water samples. The chromium concentration was measured by using microsample injection flame atomic absorption spectrometer. Suitable microextraction conditions for the developed method were investigated in detail.

2. Experimental

2.1. Apparatus

In order to produce nanosized and/or microsized emulsion in water phase, an ultrasonic water bath (Norwalk, CT, USA) was used. The centrifugation for phase separation was performed using an ALC PK 120 model centrifuge (Buckinghamshire, England). An Analyst 300 Model flame atomic absorption spectrometer (Norwalk, CT, USA) including air–acetylene flame and equipped with a handmade micro-injection system, which consist of a mini homemade Teflon funnel with an Eppendorf Pipette [27]. The measurements were carried with the continuous aspiration mode of FAAS. A 100 μL of extraction phase was injected to the micro-injection (microsample injection) system by using Eppendorf pipette and peak heights were recorded as signals [27]. A Sartorius PT-10 model pH meter with glass-electrode was used for pH adjustments of sample solutions (Sartorius Co., Goettingen, Germany).

2.2. Chemicals and reagents

All reagents used were of at least analytical grade and needed no further purification. Choline chloride (ChCl) (Alfa Aesar, Germany), tetrabutylamonium chloride (TBACl) (Acros, Germany) and methyltrioctylammonium chloride (MTOACl) (Sigma-Aldrich, USA) were used as quaternary ammonium salts, while phenol (Ph) and Decanoic acid (DA) (SAFC, USA) were used as hydrogen bond donors. $KMnO_4$ and sulfuric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultra pure water purified through reverse osmosis (18.2 MΩ cm, Millipore) was used as the working medium.

2.3. Synthesis of DESs

Five different DESs were synthesized as follows: (1) Mixing ChCl with Ph at different molar ratios ((molar ratios 1:2 (DES_1), 1:3 (DES_2) and 1:4 (DES_3)), (2) DES_4: Mixing 1 M of TBACl with 2 M of DA (3) DES_5: Mixing MTOACl with DA. The components of DESs were mixed in a beaker and then stirred at room temperature until a clear liquid was formed about 5 min

2.4. Ultrasound assisted-deep eutectic solvent based emulsification liquid phase microextraction

a 10.00 mL standard solution of Cr(VI) (or sample solution), 0.375 mL of 0.5 M H_2SO_4, 0.4 mL of 0.125% (w/v) sodium diethyldithiocarbamate (NaDDTC) and 450 μL of DES_2 (as water-miscible extraction solvent) were placed in a 50 mL conical bottom centrifuge tube; a homogeneous solution was obtained. 450 μL of THF was injected into the sample solution and the mixture was kept in an ultrasonic bath for 2 min leading to aggregation of DES molecules and consequently a turbid solution. At this stage, the aggregated DES droplets progressively broke into tiny droplets because of the ultrasonic irradiation involved by transient cavitation near the interface of DES droplets. The mixture was centrifuged at 4000 rpm for 10 min to accelerate the complete separation of the water phase and DES rich phase. The DES phase was situated at the bottom of the tube. The water was taken using micropipette and the volume of DES phase remain in tube was completed to 750 μL with ethanol and then an aliquot 100 μL of the solution was injected to the nebulizer of the flame atomic absorption spectrometer by micro sampling unit and absorbance value was measured. The graphical representation of the UA-DES-ELPME method was shown in Fig. 1.

2.5. Determination of chromium species

(1) Cr(VI): After the UA-DES-ELPME method, the extracted analyte concentration was directly analyzed by FAAS

(2) Cr(VI): After the UA-DES-ELPME method, the extracted analyte concentration was directly analyzed by FAAS
Total Cr: In order to determine total chromium, 5 drops of $KMnO_4$ ($0.02\ mol\ L^{-1}$) solution and 0.5 mL of H_2SO_4 ($0.5\ mol\ L^{-1}$) solution were added into 10 mL of the sample solution include Cr(VI) and Cr(III). Then, the sample solution was heated for 25 min at 60 °C for completely oxidation. After the oxidation, the UA-DES-ELPME method was applied to resulted solution and total chromium concentration was measured by FAAS.

(3) Cr(III): The concentration of Cr(III) in water samples was calculated by subtracting Cr(VI) from the total chromium.

2.6. Applications

The proposed liquid phase microextraction method was applied to tap water, two different chromium plating factory waste water (Kayseri, Turkey) and lake water (Van, Turkey) samples. Real water samples were filtered through a 0.45-μm cellulose membrane and utilized for further derivatization and UA-DES-ELPME. The certified reference water samples (TMDA-53.3 Fortified environmental water and TMDA-54.4 Fortified Lake Water) for the determination of total chromium were diluted appropriately with double distilled water prior to UA-DES-ELPME.