



Ionic liquid ultrasound-assisted dispersive liquid-liquid microextraction based on solidification of the aqueous phase for preconcentration of heavy metals ions prior to determination by LC-UV



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ABSTRACT

Ionic liquid ultrasound-assisted dispersive liquid-liquid microextraction based on solidification of the aqueous phase was used for preconcentration of Ni^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} in natural water samples prior to liquid chromatography with UV detection. In the proposed method, the ammonium pyrrolidinedithiocarbamate was used as a complexing agent and the phosphonium ionic liquid trihexyl(tetradecyl)phosphonium bis[(2,4,4-trimethyl)pentyl]phosphinate (Cyphos IL 104) was used as an extractant. Ultrasound energy was used to disperse the extractant in the aqueous phase. After microextraction, the ionic liquid and aqueous phases were separated by centrifugation. Then the aqueous phase was frozen and the lighter than water ionic liquid phase containing metal ions complexes with pyrrolidinedithiocarbamate was separated and dissolved in a small volume of methanol prior to injection into the liquid chromatograph. Several parameters including the volume of extractant, the pH of the sample, the concentration of complexing agent, the time of ultrasound energy treatment, the time and speed of centrifugation and the effect of ionic strength were optimized. Under the optimized conditions (10 μL of Cyphos IL 104, pH = 5, 0.3% w/v ammonium pyrrolidinedithiocarbamate, 60 s of ultrasound use, 5 min/5000 rpm (2516 \times g) of centrifugation, 2.0 mg of NaCl), preconcentration factors were 211, 210, 209, 207 and 211 for Ni^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} and Pb^{2+} respectively. Linearity was observed in the ranges 0.2–75.0 $\mu\text{g L}^{-1}$ for Pb^{2+} , Cd^{2+} , Co^{2+} and 0.5–100.0 $\mu\text{g L}^{-1}$ for Cu^{2+} , Ni^{2+} . The limits of detection were 0.03 $\mu\text{g L}^{-1}$ for Ni^{2+} , 0.03 $\mu\text{g L}^{-1}$ for Co^{2+} , 0.03 $\mu\text{g L}^{-1}$ for Cd^{2+} , 0.02 $\mu\text{g L}^{-1}$ for Cu^{2+} , 0.02 $\mu\text{g L}^{-1}$ for Pb^{2+} , respectively.

The accuracy of this method was evaluated by preconcentration and determination of Ni^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} in certified reference materials (TMRain-04 and NIST 1643e) with the recovery values in the range of 97–102%. The presented method has been successfully applied for the determination of analytes in natural water samples (river and lake waters).

1. Introduction

Heavy metals are naturally occurring elements which are widely distributed in the environment. Main sources of heavy metals in the environment include industrial, agricultural, pharmaceutical and domestic effluents [1–4]. Determination of heavy metals ions in natural waters is important due to the growing ecological problems and human health concerns [1,2]. Heavy metals are also considered as trace elements because of their presence at trace concentrations in various environmental samples [1,3].

The determination of heavy metals ions at trace level is possible due to the use of sensitive instrumental techniques or preconcentration

before analysis. Various liquid phase microextraction (LPME) techniques, such as hollow fiber-based liquid-phase microextraction (HF-LPME) [5–8], single-drop microextraction (SDME) [5–7,9] and dispersive liquid-liquid microextraction (DLLME) [5–7,10–12] have been proposed during recent decades to overcome long analysis time and production of large volume of wastes. When consider classical DLLME technique, a mixture of a water-immiscible extractant and a water-miscible dispersing solvent is injected into an aqueous sample in order to obtain a cloudy solution. The analytes in the sample are extracted into fine droplets of the extractant, then the mixture is centrifuged [13,14]. The extractant phase containing the analytes is then determined mainly by employing F-AAS [15,16], ET-AAS [17–19], ICP-

Abbreviations: APDC, ammonium pyrrolidinedithiocarbamate; Cyphos IL 104, trihexyl(tetradecyl)phosphonium bis[(2,4,4-trimethyl)pentyl]phosphinate; DLLME, dispersive liquid-liquid microextraction; PF, preconcentration factor; HF-LPME, hollow fiber liquid-phase microextraction; IL-UA-DLLME-SAP, ionic liquid ultrasound-assisted dispersive liquid-liquid microextraction based on solidification of the aqueous phase; LPME, liquid phase microextraction; SDME, single-drop microextraction; VOCs, volatile organic compounds

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OES [20,21], ICP-MS [22,23], GC-MS [24], HPLC [25,26] and UV-Vis spectrophotometry [27,28] techniques. The DLLME technique is rapid, requires low volumes of the dispersing solvent and extractant, and exhibits high recovery as well as high preconcentration factor.

The application of ionic liquids (ILs) as the environment friendly extractants in order to extract heavy metals ions as well as organic pollutants has been proposed recently [29,30]. Phosphonium ionic liquid trihexyl(tetradecyl)phosphonium bis[(2,4,4-trimethyl)pentyl]phosphinate (Cyphos IL 104) has a few interesting properties such as insolubility in water, density lower than water (0.885 g mL^{-1}) and freezing point well above water freezing point [31]. Cyphos IL 104 has been used to extract of Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} and trivalent lanthanides what has been reported in the literature [32–35].

Up to now there have been published limited studies on the use of IL-DLLME/HPLC technique on the preconcentration and determination of heavy metals ions simultaneously: Cr(VI), Co^{2+} , Cu^{2+} , Ni^{2+} [36], Hg species [37], Ni^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} [38] and Cd^{2+} , Co^{2+} and Pb^{2+} [39].

There is only one literature report regarding the preconcentration with the use of the dispersive liquid-liquid microextraction based on solidification of the aqueous phase (DLLME-SAP) technique prior to chromatographic analysis [40].

This is the first report regarding preconcentration of Ni^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} by phosphonium IL-UA-DLLME-SAP prior to liquid chromatography analysis.

The aim of this study was to develop an IL-UA-DLLME-SAP procedure for preconcentration of Ni^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} prior to LC-UV detection. Phosphonium ionic liquid was dispersed into water sample with use of the ultrasound energy to form a cloudy solution; the phases were separated by centrifugation; the aqueous phase was frozen (at -18°C) and ionic liquid phase (containing metal ions complexes of pyrrolidinedithiocarbamate) was separated and next dissolved in a small volume of methanol and directly injected into the chromatograph. The developed procedure was validated using certified reference materials and applied for analysis of natural water samples.

2. Materials and methods

2.1. Instrumentation

High-purity deionized and doubly distilled water (quartz apparatus, Bi18, Heraeus, Germany) was used during this study. A pH-meter (EL20, Mettler Toledo, Switzerland) with lab pH electrode (type LE407) was used for pH measurements. A Sonopuls HD 70 ultrasonic homogenizer (70 W, 20 kHz, Bandelin, Germany) equipped with 2 mm titanium probe was used as a dispersing agent.

A centrifuge (Hettich EBA 20, Tuttlingen, Germany), with a centrifugation speed in the range from 500 to 6000 rpm (from 25 to $3622 \times g$), was used for phases separation after the microextraction procedure.

A chromatographic system (HP series 1050), which consisted of an isocratic pump and an UV detector, was used for the analysis. A reversed-phase HPLC Waters Symmetry C18 column (150 mm \times 3.9 mm I.D., 5 μm particle size) was used for separation at ambient temperature and ChemStation was used for the LC system to acquire and process chromatographic data.

2.2. Reagents and solutions

The stock solutions of Ni^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} were prepared from 1000 mg L^{-1} standard solutions (Certipur, Merck, Germany). Working standard solutions were prepared every day by diluting the stock solutions with high-purity water. As an extractant, trihexyl(tetradecyl)phosphonium bis[(2,4,4-trimethyl)pentyl]phosphinate (Cyphos IL 104, $\geq 95.0\%$) from Sigma-Aldrich (Poland) was used. As an complexing agent, ammonium pyrrolidinedithiocarbamate (APDC,

$\geq 98.0\%$) from Sigma-Aldrich (Poland) was used. The pH of the samples was adjusted using hydrochloric acid (30%, Suprapur, Merck, Germany), sodium hydroxide (30%, Suprapur, Merck, Germany) and acetate buffer (Hornik, Poland). Sodium chloride (Suprapur, Merck, Germany) was used in order to determine the effect of ionic strength on the efficiency of microextraction. Methanol (gradient grade for LC, LiChroSolv, Merck, Germany) was used as a solvent for the extractant phase prior to LC-UV analysis as well as an eluent for the mobile phase during the chromatographic analysis.

2.3. Certified reference materials and real samples

Accuracy of the analytical procedure described in this research was verified using the certified reference materials: TMRAIN-04 (a Simulated Rain Sample) supplied by Environment Canada, Burlington, Canada and NIST 1643e (Trace Elements in Water) supplied by National Institute of Standards & Technology, Gaithersburg, US.

Five natural water samples, i.e. river water (Mahanadi River, India; Mekong River, Thailand; Mahaweli River, Sri Lanka) and lake water (Tonle Sap Lake, Cambodia; Songkhla Lake, Thailand) were analysed by IL-UA-DLLME-SAP/LC-UV procedure. All natural water samples were collected into 250 mL polypropylene bottles and stored in the dark at 4°C . The samples were filtered before analysis using syringe filters (pore size $0.45 \mu\text{m}$, polytetrafluoroethylene membrane).

3. Experimental

3.1. IL-UA-DLLME-SAP technique

A 15 mL aliquot of the sample solution containing Ni^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} was transferred into a glass test tube. The pH of the sample was adjusted to 5.0 with the acetate buffer. Then 500 μL 10% w/v APDC (complexing agent) and 10 μL of Cyphos IL 104 (extractant) and 2.0 mg of NaCl (ionic strength) were added. The 2 mm titanium probe of the ultrasonic homogenizer was immersed into the mixture for 60 s (with a power of 45 W, continuous mode) and cloudy solution was formed. Afterwards, the Ni^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} were extracted into the Cyphos IL 104 phase. After that, the mixture was centrifuged for 5 min at 5000 rpm ($2516 \times g$). Next, the tube containing two separated phases was placed in a freezer at -18°C for 1 h to ensure solidification of the aqueous phase. Then, the Cyphos IL 104 phase (containing metal ions complexes of APDC) was taken up with a microsyringe and was diluted with 60 μL of methanol which was directly injected into the chromatograph.

3.2. Liquid chromatography

A 10 μL aliquot of the extractant phase was injected into the liquid chromatograph. The chromatographic parameters of separation of metals ions complexes with APDC were optimized. The mobile phase consisted of methanol/water at a ratio of 65/35 (v/v). The flow rate of the mobile phase was at 1.0 mL min^{-1} and the detection wavelength was set at 256 nm. The chromatogram of $\text{Ni}(\text{PDC})_2$, $\text{Co}(\text{PDC})_2$, $\text{Cd}(\text{PDC})_2$, $\text{Cu}(\text{PDC})_2$, $\text{Pb}(\text{PDC})_2$ complexes is presented in Fig. 1.

4. Results and discussion

4.1. Optimization of IL-UA-DLLME-SAP technique

In order to obtain a high extraction recovery, the influence of parameters such as the volume of extractant, the pH of the sample, the concentration of complexing agent, the time of ultrasound energy treatment, the time and speed of centrifugation and the effect of ionic strength were optimized by investigating a single parameter when the other parameters remained unchanged.

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