



Ligandless ultrasonic-assisted and ionic liquid-based dispersive liquid–liquid microextraction of copper, nickel and lead in different food samples



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ABSTRACT

A simple and rapid ultrasonic assisted-ionic liquid based-liquid–liquid microextraction (UA-IL-DLLME) method has been developed for the enrichment and separation of Cu(II), Ni(II) and Pb(II). A two level factorial design was used to determine the effect of key factors such as pH, volume of ionic liquid (IL), carbon tetra chloride (CCl₄) and sonication time (St). 1-Butyl-3-methylimidazolium hexafluorophosphate ([C₄MIM][PF₆]) and CCl₄ were used as an extractant and dispersant solvent, respectively. The accuracy of the proposed method was evaluated by analysing of SRM Apple Leaves 1515 certified reference material. The limits of detections (LODs) were 0.17 µg/L, 0.49 µg/L and 0.95 µg/L for Cu, Ni and Pb, respectively. The enrichment factor (EF) was 100. The method has been successfully applied for the analysis of the content of Cu, Ni and Pb in spice, vegetable and fruit samples by flame atomic absorption spectrometry (FAAS).

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1. Introduction

Heavy metals are released into water, plants, soil and food by natural and/or humans activities (Lemos et al., 2006; Mendil, Tuzen, Usta, & Soylak, 2008; Soylak & Kirnap, 2001; Onianwa, Laval, Ogunkeye & Orejimi, 2000). Some of them, including iron, zinc and copper are considered as essential for plants and animals and human beings. They play very important roles in the metabolism of human organisms (Chizzola, Michitsch, & Franz, 2003; Duran, Tuzen, & Soylak, 2008; Kandhro, Soylak, Kazi, & Yilmaz, 2014; Soylak, Tuzen, Souza, Korn, & Ferreira, 2007; Tuzen et al., 2009; Soylak, Elci, & Dogan, 1999). Some metals such as cadmium, lead and nickel have toxic roles in the human body but nickel is a moderate toxic element as compared to other transition elements. However, metals can lead to serious problems even in low concentrations, since it can cause several adverse effects on humans and animals (Manzoori & Karim-Nezhad, 2004; Soylak, Divrikli, Saracoglu, & Elci, 2007; Soylak & Turkoglu, 1999; Tuzen, Sesli, & Soylak, 2007). Toxic metals may replace the essential nutrients from human body and adjoining their sites to the vital organs (Narin & Soylak, 2003; Soylak & Elci, 2000; Kazi et al., 2008).

Several methods such as liquid–liquid extraction (LLE) (Mayer-Helm, Hofbauer, & Muller, 2006), single-drop microextraction (SDME) (Saraji & Esteki, 2008), cloud-point extraction (CPE) (Santalad, Srijaranai, Burakham, Glennon, & Deming, 2009), solid-phase extraction (SPE) (Basheer, Alnedhary, Rao, & Lee, 2009; Salarian, Ghanbarpour, Behbahani, Bagheri, & Bagheri, 2014; Soylak & Topalak, 2014; Tabani et al., 2013; Tuzen et al., 2009) and liquid-phase microextraction (LPME) (Huertas-Perez & Garcia-Campana, 2008) have been widely used for the preconcentration-separation of metal ions from different environmental, water, food and biological samples prior to their instrumental analysis. However, these techniques suffer some disadvantages including high cost, long processing time and the use of large volume of toxic reagents.

In recent years, dispersive liquid–liquid microextraction (DLLME) has been extensively used as alternative for these procedures and also used to overcome some of the drawbacks of sample preparation. It is simple, fast, and does not require large amounts of organic solvents (Behbahani, Bide, et al., 2014; Behbahani, Esrafil, et al., 2014; Behbahani, Najafi, et al., 2014; Behbahani, Sadeghi Abandansari, et al., 2014; Chen, Chen, & Li, 2010). Several experimental variables affecting the DLLME procedure were optimised. Multivariate technique has been widely used in preconcentration and separation techniques (Massart et al., 2003; Stalikas, Fiamegos, Sakkas, & Albanis, 2009).

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An ultrasonic assisted-ionic liquid based-liquid–liquid microextraction (UA-IL-DLLME) procedure for the determination by flame atomic absorption spectrometer (FAAS) of copper, nickel, and lead in different food samples has been established in the present study. The effect of variables including pH, volume of ionic liquid (IL), volume of carbon tetra chloride (CCl_4) and sonication time (St) were investigated using a full fractional design.

2. Materials and methods

2.1. Reagents and solutions

Chemical and reagents used were of high purity analytical grades (Merck, Darmstadt, Germany). During the experimental works, ultra-pure water (Millipore Milli-Qsystem $18 \text{ M}\Omega \text{ cm}^{-1}$ resistivity, Millipore, Bedford, MA, USA) was used. Nitric acid (65%, v/v) and hydrogen peroxide (35%, v/v) were obtained from Merck. Stock solutions ($1000 \mu\text{g/mL}$) of the corresponding metal ions were prepared by dissolution of an appropriate amount of nitrate salts in ultra-pure water containing 1% (v/v) nitric acid. Working standards of the corresponding metal ions were prepared by dilution of the stock standard solutions with distilled water.

1-Butyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_4\text{MIM}][\text{PF}_6]$) was purchased from Merck (Darmstadt, Germany). Phosphate buffer (pH 7.0) used for pH adjustment, was prepared with the addition of appropriate amount sodium dihydrogen phosphate and disodium hydrogen phosphate. A certified reference material CRM NIST 1515 Apple Leaves (National Institute for Standards and Technology, Gaithersburg, MD, USA) was used.

2.2. Instrumentation

Absorbance measurements were performed using a PerkinElmer Model 3110 flame atomic absorption spectrometer (FAAS) (PerkinElmer, Inc., Shelton, CT, USA), equipped with air–acetylene flame and a hollow cathode lamp. The instrumental parameter was adjusted as recommended by a manufacturer's. The final solutions containing copper, nickel, and lead were injected to the nebulizer of the flame atomic absorption spectrometer by using the micro injection method (Kandhro et al., 2014; Yilmaz & Soyak, 2014). In the micro injection method, $100 \mu\text{L}$ of the samples were injected to a mini home-made Teflon funnel that was connected to the nebulizer with capillary tubing with an Eppendorf pipette. The peak height signals were recorded.

A model Nel pH 900 digital pH meter equipped with a combined glass electrode was used for the pH adjustment.

2.3. Ligandless ultrasonic assisted-ionic liquid based-liquid–liquid microextraction (UA-IL-DLLME) procedure

10 mL of an aqueous sample solution containing $100 \mu\text{g/L}$ of Cu, Ni and Pb were introduced in a 50 mL test tube with a conical bottom; then 2.0 mL of buffer solution were added. After adjusting the pH, $150 \mu\text{L}$ of IL and $200 \mu\text{L}$ CCl_4 were rapidly injected into the sample solution with a 2.0 mL of glass syringe and the mixture was gently shaken. A cloudy solution consisting of very fine droplets of CCl_4 dispersed into aqueous sample was formed. The analytes were extracted into the fine droplets. After that, the resulting cloudy mixture was treated by ultrasonication for 3–10 min and then was centrifuged at 3000 rpm for 3 min in order to achieve phase separation. After centrifugation, the ionic liquid phase settled at the bottom of the centrifuge tube and the upper aqueous phase was decanted. Then the final volume was adjusted to $500 \mu\text{L}$ with methanol to decrease the viscosity of the ionic liquid phase. A blank sample was also treated in the same manner as the samples

were treated, but without using analytes. The analytes were determined by FAAS.

2.4. Analysis of food samples

The spice samples were purchased from a market of Karachi, Pakistan while the vegetable and fruit samples were purchased from a market of Kayseri, Turkey. 0.5 gram of food (spice, vegetable, fruit, $n = 3$) and NIST 1515 Apple Leaves sample ($n = 3$) were accurately weighed in a 100 mL of beaker. 10 mL of concentrated nitric acid (65%, v/v) and 5.0 mL of hydrogen peroxide (35%, v/v) were added to each beaker and the resulting sample solutions were heated on an electric hot plate at $100 \text{ }^\circ\text{C}$ for 2 h until clear solutions were obtained. After evaporation and cooling the samples were filtered through a $0.45 \mu\text{m}$ pore size membrane filter (Millipore Corporation, Bedford, MA, USA) into a 25 mL conical bottom flask and were diluted with distilled water. Thereafter, the pH was adjusted to the desired value and then the sample was subjected to the procedure described in Section 2.3. The final solution was analysed by FAAS for the determination of analytes.

2.5. Experimental design

The experimental data were generated using a full factorial design generated using Minitab 13.2 (Minitab Inc., State College, PA). A two level factorial design was used for evaluating the effect of four factors, more specifically pH, volume of ionic liquid (IL), volume of carbon tetra chloride (CCl_4) and sonication time (St), at two levels, low (–) and high (+). This design led to sixteen experimental runs (details in Table 1) in total (Lundstedt et al., 1998; Massart et al., 2003).

3. Results and discussion

3.1. Optimisation of experimental conditions using full factorial design

The optimisation method used in this study permitted the estimation of the principal effects of the four factors (pH, volume of ionic liquid (IL), volume of carbon tetra chloride (CCl_4) and sonication time (St)) on the % recovery of Cu(II), Ni(II) and Pb(II); the results are summarised in Supplemental Table S1.

The effect of the individual factors and their interactions were evaluated by analysis of variance (ANOVA). These were also visualised by Pareto charts using a standardised effect at a p -value of 0.05, as shown in Supplemental Figs. S1–S3. pH and IL had a considerable effect on the extraction recovery of the studied analytes. The recoveries of the analytes increased with increasing both IL and St, indicating that the interaction between IL and St was significant. The three variables [pH–IL–St] had to be operated at their highest levels (+, +, +) in order to obtain maximum recovery, as can be seen from the geometrically cube plots in Figs. 1–3. The upper right corners of Figs. 1–3 demonstrate that the highest quantitative recoveries were obtained at corresponding levels of pH = 7, Volume of IL = $150 \mu\text{L}$ and sonication time = 10 min, for all analytes. In the lower left corners of Figs. 1–3, the lowest recoveries were obtained. Overall, the optimal conditions to perform the UA-IL-DLLME method were 7.0 for pH, $150 \mu\text{L}$ for IL and 10 min for St.

Table 1
Levels and code of variable chosen for full factorial design.

Variables	Low (–)	High (+)
pH (P)	2.0	7.0
Volume of ionic liquid (IL) (μL)	100	150
Volume of carbon tetra chloride (CCl_4) (μL)	100	200
Sonication time (St) (min)	3.0	10

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