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Analytical Methods

Ultrasound-assisted ionic liquid dispersive liquid–liquid microextraction combined with graphite furnace atomic absorption spectrometric for selenium speciation in foods and beverages

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ABSTRACT

A rapid and environmentally friendly ultrasound assisted ionic liquid dispersive liquid liquid microextraction (USA-IL-DLLME) was developed for the speciation of inorganic selenium in beverages and total selenium in food samples by using graphite furnace atomic absorption spectrometry. Some analytical parameters including pH, amount of complexing agent, extraction time, volume of ionic liquid, sample volume, etc. were optimized. Matrix effects were also investigated. Enhancement factor (EF) and limit of detection (LOD) for Se(IV) were found to be 150 and 12 ng L^{-1}, respectively. The relative standard deviation (RSD) was found 4.2%. The accuracy of the method was confirmed with analysis of LGC 6010 Hard drinking water and NIST SRM 1573a Tomato leaves standard reference materials. Optimized method was applied to ice tea, soda and mineral water for the speciation of Se(IV) and Se(VI) and some food samples including beer, cow's milk, red wine, mixed fruit juice, date, apple, orange, grapefruit, egg and honey for the determination of total selenium.

1. Introduction

Selenium is known as an essential trace element for living organisms and it has a very narrow concentration range from sufficiency to deficiency and toxicity (Sun, Liu, & Wu, 2013). Selenium is toxic at concentrations of only three to five times higher than the essential concentration. Inorganic selenium forms as selenite and selenate in water samples generally exhibit higher toxicity (up to 40 times) than organic forms (Herrero Latorre, Barciela García, García Martín, & Peña Crecente, 2013). Selenium present in different oxidation states in aqueous solution but it mostly exist in Se(IV) and Se(VI). The essentiality and toxicity of selenium depend on its concentration and chemical forms (Escudero, Pacheco, Gasquez, & Salonia, 2015). In general, inorganic species of selenium are more toxic than its organic forms, and the toxicity of Se(IV) is more than Se(VI) (Chen, Zhu, & Lu, 2015; Saygi, Melek, Tuzen, & Soylak, 2007; Tuzen, Saygi, & Soylak, 2007).

The Recommended Dietary Allowance (RDA) for selenium were calculated by the US Food and Nutrition Board as between 15 and 20 μg day^{-1} for infants, 70 μg day^{-1} for lactating mothers and 55 μg day^{-1} for adults. The upper limit for safe intake of adult is established at 400 μg day^{-1} (Food & Nutrition Board & Institute of Medicine, 2000). According to World Health Organization (WHO, 2003), the maximum permissible concentration of selenium in drinking water is 10 μg L^{-1}. Various instrumental analytical techniques such as spectrophotometry (Agrawal, Patel, & Shrivas, 2009; El-Shahawi & El-Sonbati, 2005), inductively coupled plasma mass spectrometry (ICP-MS) (Zhang, Duan, He, Chen, & Hu, 2013), inductively coupled plasma optic emission spectrometry (ICP-OES) (Welna & Szymczycha-Madeja, 2014), hydride generation atomic absorption spectrometry (HGAAS) (Sigrist, Brusa, Campagnoli, & Beldoménico, 2012), electrothermal atomic absorption spectrometry (ETAAS) (Manjusha, Dash, & Karunasagar, 2007), hydride generation atomic fluorescence spectrometry (HGAFS) (Mazej, Falnoga, Veber, & Stibilj, 2006; Stafiński, Wieczorek, & Kościelniak, 2013) have been used for the determination of selenium in different sample matrices. ETAAS is one of the most widely used techniques because of its low cost, ease of operation, high sample throughput, and good selectivity.

The concentration of selenium in water and food samples is generally lower than the detection limit of atomic absorption spectrometry. The matrix effects of some alkali, alkaline earth, some cations and anions for the determination of selenium in real samples are another problem. To solve these problems, various separation and preconcentration methods for selenium including solid phase extraction (Escudero et al., 2015; Serra, Estela, Coulomb, Boudenne, & Cerdà, 2010), solidified floating organic drop

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microextraction (Chen et al., 2015; Shabani, Dadfarnia, & Nozohor, 2013), single-drop microextraction (Fragueiro, Lavilla, & Bendicho, 2006), cloud point extraction (Sounderajan, Kumar, & Udas, 2010; Sun et al., 2013), dispersive liquid liquid microextraction (Bidari, Jahromi, Assadi, & Hosseini, 2007; Zhang et al., 2013), etc., have been widely used. Recently room temperature ionic liquids (RTILs) are interesting alternatives to organic solvents because of their unique physicochemical properties, which depend on the nature and size of their cationic and anionic constituents (Aguilera-Herrador, Lucena, Cárdenas, & Valcárcel, 2010; Pena-Pereira, Lavilla, & Bendicho, 2009).

In this study, ultrasound assisted ionic liquid dispersive liquid liquid microextraction (USA-IL-DLLME) was developed for the speciation of inorganic selenium in beverages and total selenium in food samples. USA-IL-DLLME method has some advantages such as simple, rapid, low cost, high enrichment factor and green extraction. Speciation of selenium was performed by chelation of Se(IV) with the 1-Phenylthiosemicarbazide followed by extraction with the 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [C_6MIM][Tf_2N]. The combination of 1-Phenylthiosemicarbazide and [C_6MIM][Tf_2N] was used first time for the speciation of selenium in USA-IL-DLLME method.

2. Experimental

2.1. Chemicals and reagents

All chemicals used in this study were analytical reagent grade. The standard solutions for Se(IV) and Se(VI) were obtained from Sigma–Aldrich (St. Louis, MO, USA). Stock solutions of diverse elements were prepared from high purity compounds. 1-Phenylthiosemicarbazide was obtained from Sigma (St. Louis, MO, USA) and prepared a solution dissolving 0.1 g (0.1%, w/v) in 100 mL, 20% methanol–ultrapure water. Pd and $Mg(NO_3)_2$ was used as matrix modifier obtained from Merck (E. Merck, Darmstadt, Germany). 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [C_6MIM][Tf_2N] was purchased from Sigma (St. Louis, MO, USA). 1 mol L^{-1} HCl and 1 mol L^{-1} NaOH was used for adjustment of pH values.

2.2. Instrumentation

A Perkin Elmer Analysis 700 model (Norwalk, CT, USA) atomic absorption spectrometer equipped with a deuterium background correction system and electrothermal atomizer, HGA-800 was used for selenium determination. A Se electrodeless discharge lamp (EDL) operated at a current of 200 mA and a wavelength of 196.0 nm with a spectral band pass of 2.0 nm was used. All measurements were made based on absorbance signals with an integration time of 5 s. Pyrolytic-coated graphite tubes with a platform were used. Samples of 20 μL plus 10 μL of mixture of 0.015 mg Pd + 0.010 mg $Mg(NO_3)_2$ as matrix modifier were injected into the furnace using Perkin Elmer AS-800 autosampler. The graphite furnace program for selenium determination was temperature (°C)/ramp time (s)/hold time (s) for drying 1 100/5/20, drying 2 140/15/15, ashing 1200/10/20, atomization 2200/0/5, and cleaning 2600/1/3, respectively, with argon flow rate 250 mL min^{-1}. A pH meter, Sartorius pp-15 model glass-electrode was used for measuring pH values. Nuve NF 800 model centrifuge (Turkey) was used for centrifugation. Bandelin Sonorex RK 512 CH (35 kHz) ultrasonic bath was used for USA-IL-DLLME. Milestone Ethos D (Sorisole-Bg Italy) model microwave digestion system (maximum pressure 1450 psi, maximum temperature 300 °C was used for digestion of solid samples.

2.3. General procedure

10 mL of an aqueous sample solution containing 0.5 μg L^{-1} Se(IV) and Se(VI) were introduced in a 25 mL centrifuge tube. This solution was adjusted to pH 2 using dilute HCl, then 1 mL (0.1%) 1-Phenylthiosemicarbazide and 100 μL [C_6MIM][Tf_2N] as a extractive solvent were added. The mixture was vortexed for 1 min and immediately removed to ultrasonic bath for 10 min. The extractant ([C_6MIM][Tf_2N]) was dispersed into solution and cloudy solution was formed. The analytes were extracted into the fine droplets. The cloudy solution was centrifuged at 3000 rpm for 5 min in order to archive phase separation. The content of the tube was cooled in an ice bath to increase the viscosity of the enriched phase. The bulk aqueous phase was decanted carefully by inverting the tube. The ionic liquid enrich phase was treated with 100 μL of 0.1 mol L^{-1} HNO_3 in ethanol (1:1, v/v) in order to reduce its viscosity and facilitate sample handling. A blank solution was also carried out using the same procedure without selenium added. Se(IV) and Se(VI) contents were determined by GFAAS. USA-IL-DLLME method was optimized using both reference solution and real samples.

2.4. Reduction of Se(VI) to Se(IV) and determination of total selenium

In order to reduction of selenium(VI) to selenium(IV), the optimized procedure was applied to model solutions and real samples (Ferri, Rossi, & Sangiorgio, 1998; Tuzen et al., 2007). 2 mol L^{-1} HCl was added to the samples, then the microwave program of 2 min

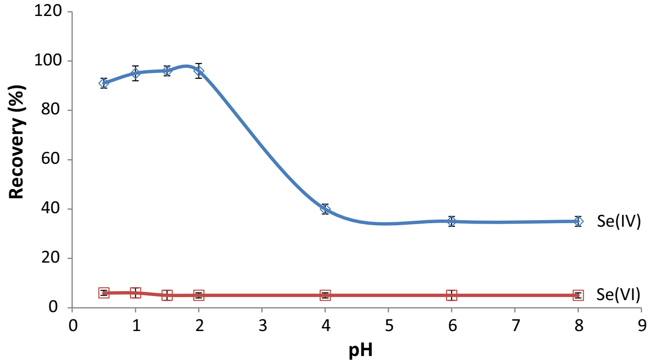

Fig. 1. Effects of pH on the speciation of Se(IV) and Se(VI): 0.5 μg L^{-1} Se(IV) and Se(VI), 1 mg 1-Phenylthiosemicarbazide, 150 μL [C_6MIM][Tf_2N], centrifugation time and rate 5 min and 3000 rpm, 15 min ultrasound extraction, room temperature, sample volume: 15 mL.

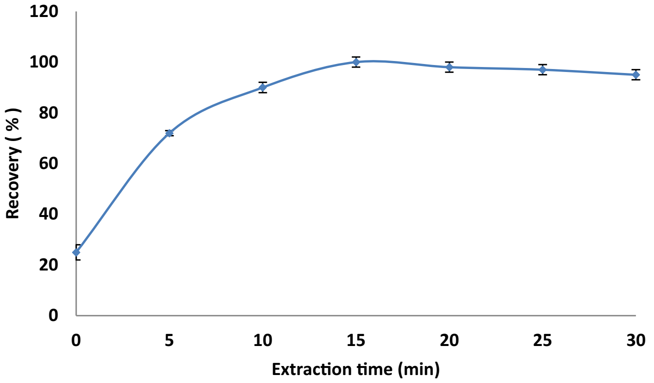

Fig. 2. Effect of ultrasound extraction time on the recovery (%) of Se(IV): 0.5 μg L^{-1} Se(IV), pH: 2, 1 mg 1-Phenylthiosemicarbazide, 150 μL [C_6MIM][Tf_2N], centrifugation time and rate 5 min and 3000 rpm, room temperature, sample volume: 15 mL.