Food Chemistry 232 (2017) 98–104

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

A simple and sensitive vortex-assisted ionic liquid-dispersive microextraction and spectrophotometric determination of selenium in food samples

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ARTICLE INFO

Article history:
Received 14 December 2015
Received in revised form 12 March 2017
Accepted 18 March 2017
Available online 1 April 2017

Keywords:
Selenium
Vortex assisted
Ionic liquid
Microextraction
Spectrophotometer
Food samples

ABSTRACT

In the present study, a novel and eco-friendly vortex-assisted ionic liquid-based microextraction method was developed for the determination of selenium in food. The microextraction method is based on the liberation of iodine in the presence of selenium; the liberated iodine reacts with I^- to form I_3^-. Anionic I_3^- reacts with cationic crystal violet dye, and the product is extracted into 1-hexyl-3-methylimidazolium hexafluorophosphate phase in the presence of Triton X-114. The proposed method is linear in the range of 2.0–70 μg L^{-1} and has a detection limit of 9.8×10^{-2} μg L^{-1}. Relative standard deviations were 3.67% and 2.89% for the five replicate measurements of 14 and 35 μg L^{-1} Se(IV), respectively. The proposed method was successfully applied to different food samples (NIST SRM 2976 mussel tissue, pepper, ginger, wheat flour, red lentil, traditional soup, cornflour, cornstarch, and garlic) after microwave digestion.

1. Introduction

Selenium is an essential element for human metabolism, but a high intake of selenium is toxic. It is a part of many antioxidant enzymes and has a unique role in converting hydrogen peroxide to a nontoxic compound (Ohki, Nakajima, Hirakawa, Hayashi, & Takanashi, 2015). Selenium deficiency is associated with reduced immune function and cognitive decline (Rybínová, Václav Červený, Hraníček, & Rychlovský, 2016). There is some important evidence for a negative correlation between the levels of selenium and the types of cancer, such as colon and prostate (Niedzielski et al., 2016). According to the World Health Organization (WHO), the maximum concentration of selenium in drinking water should not exceed 10 μg L^{-1} (Segura et al., 2015). The maximum limit for daily intake is established to be 400 μg day^{-1} (Food & Nutrition Board & Institute of Medicine, 2000).

Determination of selenium in different matrices is an important task in analytical chemistry. The toxic and deficiency levels of selenium for metabolism are rather narrow (Serra, Estela, Coulomb, Boudenne, & Cerdà, 2010). There are hundreds of research articles existing in the literature on the development of new analytical methods for the quantitative extraction of selenium (Latorre, García, Martín, & Crecente, 2013). Different sophisticated instrumental analytical techniques such as inductively coupled plasma atomic emission spectrometry (Awual, Yaita, Suzuki, & Shiwaku, 2015), inductively coupled plasma mass spectrometry (Khan et al., 2013), hydride generation atomic fluorescence spectrometry (Zhang, Fu, Fang, Feng, & Ke, 2011), ETAAS (Izgi, Gucer, & Jaćimović, 2006), liquid chromatography with tandem mass spectrometry (Zembrzuska, Matusiewicz, Polkowska-Motrenko, & Chajduk, 2014), high-performance liquid chromatography–inductively coupled plasma mass spectrometry (Jagtap & Maher, 2016; Yu-Pin, Li-Zhen, Hong-Li, & Bi-Yang, 2015), sequential injection analysis–chemiluminescence (Ezoe, Ohyama, Hashem, Ohira, & Toda, 2015), and spectrophotometry (Wen, Zhang, Li, Fang, & Zhang, 2014) are used for the detection of trace and ultratrace amounts of selenium and its species (Tuzen & Pekiner, 2015). In many cases, a sample pretreatment prior to analysis is necessary for preconcentration and/or separation of analytes. For selenium, different types of extraction processes have been developed. Vrines et al. successfully extracted volatile-alcylated selenium and sulfur compounds by using solid-phase microextraction (Vriens, Mathis, Winkel, & Berg, 2015). Escudero et al. developed a method on the basis of extraction and preconcentration of selenium with a PVC column and coprecipitation with lanthanum hydroxide, $La(OH)_3$ (Escudero, Pacheco, Gasquez, & Salonia, 2015). Another method developed by Kocot et al. is based on using graphene as solid

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http://dx.doi.org/10.1016/j.foodchem.2017.03.104
0308-8146/

adsorbents in energy-dispersive X-ray fluorescence spectrometric determination of selenium (Kocot, Leardi, Walczak, & Sitko, 2015). There also exist well-designed, interesting studies on headspace solid-phase microextraction of selenium conducted by different research groups (Shahdousti & Alizadeh, 2011; Tyburska, Jankowski, & Rodzik, 2011).

Spectrophotometric techniques are generally preferred for the determination of analytes because of their simplicity and low cost. The determination of analytes at trace levels can be achieved using a suitable complexing agent. The main drawback of the spectrophotometric method is its poor selectivity. The complex matrix components generally interfere to a large extent; therefore, in most cases, the masking of the interfering species is unavoidable (Agrawal, Patel, & Shrivas, 2009). In addition, the elimination of matrix effects and the determination of analytes present at trace and ultra-trace levels are generally performed using different separation and extraction methods. Despite the large number of studies on solid-phase extraction of selenium, liquid–liquid extraction methods are relatively simpler alternatives. Because of high consumption of organic reagents in "conventional liquid–liquid" extraction, miniaturized forms of the extraction methodologies are very popular among analytical chemists. Miniaturized extraction techniques such as liquid–liquid microextraction, cloud-point extraction, and ionic liquid (IL)-based microextraction are the comparatively new techniques for the quantitative extraction of analytes into small volumes. In microextraction techniques, only microliters of extraction reagents are used. In cloud-point extraction, generally nonionic surfactants are used, and in IL-based microextraction, ILs are used as the extraction medium. These techniques are considered to be more "eco benign", and because of the low vapor pressures of the reagents, they are much safer than the conventional extraction techniques (Rajabi, Asemipour, Barfi, Jamali, & Behzad, 2014).

In the present study, trace determination of selenium was performed on the basis of the formation of iodine in the presence of selenium. The liberated iodine reacted with crystal violet forming the reaction product. The formed complex was extracted into 1-hexyl-3-methylimidazolium hexafluorophosphate (IL), and Triton X-114 was used as the antisticking agent. The dispersion of phases was achieved by vortexing. A simple, rapid, selective, sensitive, and eco-friendly vortex-assisted ionic liquid-based microextraction (VA-IL-DLLME) method was used for the first time to determine selenium concentration in food samples.

2. Experimental

2.1. Reagents and instrumentation

Twenty-five milligrams of crystal violet (Merck, Darmstadt, Germany) was diluted to approximately 25 mL, and 3.0 mL of orthophosphoric acid was added to this diluted solution. The solution was diluted to 100 mL and mixed until the crystal violet and orthophosphoric acid were completely dissolved. The stock (1000 mg/L) Se (IV) (Sigma-Aldrich, St. Louis, MO, USA) solution was prepared by the dissolution of SeO_2. Triton X-114 (2%) was prepared and used as the antisticking agent. A KI (Merck) solution of 2 mol L^{-1} was prepared and used fresh. 1-Hexyl-3-methylimidazolium hexafluorophosphate (Sigma-Aldrich) was used as the IL without any purification or dilution.

A Mapada, series 6, spectrophotometer was used for spectrophotometric data collection. The absorbance values were recorded against reagent blanks by using a 1-cm quartz cell. A Shimadzu analytical balance was used for weighing the chemicals. Effective mixing of the test tubes was achieved using a Biosan Bio RS-24 model multirotator. Digestion of food samples was performed using a Cem Mars 6 One touch technology microwave system.

2.2. General procedure for the proposed method

An aliquot of sample or a standard solution containing predetermined amounts of selenium was introduced into a 15-mL centrifuge tube. To this, 300 μL of KI and 300 μL of crystal violet solutions were added. After dilution of the sample, Triton X-114 was introduced, and 10-min vortexing was applied to achieve the complete mixing of the solution. After addition of 100 μL of 1-hexyl-3-methylimidazolium hexafluorophosphate, the solution was strongly vortexed and became turbid. The solution was mixed using a multirotator. Centrifugation was performed at 4500 rpm for 10 min to quantitatively separate the phases. The aqueous phase was decanted, and viscous IL phase was diluted to 2 mL with absolute ethanol. The spectrophotometric measurements were performed immediately to avoid the vaporization of ethanol. The measurements were recorded against reagent blanks at 329 nm.

2.3. Microwave digestion of real samples

One gram of the food sample and 0.1 g of the standard reference material (NIST SRM 2976 mussel tissue) were placed separately in microwave tubes. To these, 8 mL of concentrated HNO_3 (65%) and 100 μL of concentrated hydrogen peroxide (30%) were added and kept overnight. The samples were digested using Cem Mars 6 One Touch technology microwave system. The excess acid was evaporated, and the samples were diluted to 10 mL with water. The selenium content of the samples was determined using the proposed method. The calibration curve was drawn using blank solutions.

3. Results and discussion

In strongly acidic medium, selenium oxidizes iodide to iodine, which immediately reacts with iodide to form tri-iodide. The tri-iodide ion forms an ion-associated complex with cationic compounds, such as crystal violet (Agrawal, Sunita, & Gupta, 1998; Agrawal et al., 2009). The ion-associated species can be extracted using an IL phase, such as 1-hexyl-3-methylimidazolium hexafluorophosphate, and the product can be strongly absorbed at 329 nm. The absorbance value is directly proportional to the concentration of selenium present. The extraction mechanism of the complex into IL phase is as follows: the positive portion of the IL molecules is surrounded by the anionic tri-iodide, and the negative portion of the IL molecules is surrounded by the cationic crystal violet. This may be the driving force for the transfer of ion-associated complex into the organic phase.

$$SeO_2 + 4H^+ + 4I^- \rightarrow Se + 2I_2 + 2H_2O$$

$$I^- + I_2 \rightarrow I_3^-$$