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Analytical Methods

Speciation of organic and inorganic selenium in selenium-enriched rice by graphite furnace atomic absorption spectrometry after cloud point extraction

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ABSTRACT

A new method was developed for the determination of organic and inorganic selenium in selenium-enriched rice by graphite furnace atomic absorption spectrometry detection after cloud point extraction. Effective separation of organic and inorganic selenium in selenium-enriched rice was achieved by sequentially extracting with water and cyclohexane. Under the optimised conditions, the limit of detection (LOD) was 0.08 μg L^{-1}, the relative standard deviation (RSD) was 2.1% (c = 10.0 μg L^{-1}, n = 11), and the enrichment factor for selenium was 82. Recoveries of inorganic selenium in the selenium-enriched rice samples were between 90.3% and 106.0%. The proposed method was successfully applied for the determination of organic and inorganic selenium as well as total selenium in selenium-enriched rice.

1. Introduction

In recent years, Se-enriched rice had been introduced to the market of many countries. This raised some concerns regarding safety and quality. The selenium is an important trace element in biological and environmental systems, and it has a very narrow concentration range from sufficiency to deficiency and toxicity. Dietary reference intakes for selenium were calculated from the recommended dietary allowance (RDA) for certain groups with special physiological requirements (Food & nutrition board & institute of medicine, 2000) and established by the US Food and Nutrition Board as between 15 and 20 μg day^{-1} for infants and 70 μg day^{-1} for lactating mothers. The upper limit for safe intake is 400 μg day^{-1}.

It had been reported that the concentration for toxicity, bioavailability and reactivity of selenium depends on its chemical forms and concentrations (Besser, Canfield, & La Point, 1993). In general, the inorganic forms of selenium are more toxic than the organic forms (Gangher, Levander, & Baumann, 1966). Organic forms of selenium are more bioavailable to humans than inorganic selenium species (Rayman, Infante, & Sargent, 2008). Thus, it is much more important to determine the concentrations of organic and inorganic forms of selenium than to determine the total selenium concentration.

Procedures for the simultaneous determination of both inorganic and organic selenium species in mineral and freshwater water samples based on selective retention on anion-exchangers, have been devised (Bueno & Potin-Gautier, 2002). Effective separation of organic and inorganic selenium in selenium-enriched eggs was achieved by precipitating albumen with trichloroacetic acid (Sun & Feng, 2011). But, the extraction method of organic and inorganic selenium in selenium-enriched rice has not reported at present. Because inorganic selenium and some low molecular weight organic selenium molecules are water-soluble, extraction from both phases is necessary for separation of organic and inorganic selenium in rice. Effective extraction for speciation analysis of selenium in selenium-enriched rice is important.

A series of techniques have been reported for the determination of total selenium in selenium-enriched rice, such as inductively coupled plasma mass spectrometry (ICP-MS) (Wang & Li, 2010) and hydride generation atomic fluorescence spectrometry (HG-AFS) (Chen et al., 2002). These methods were effective for the determination of total selenium concentration, but could not provide values for organic and inorganic selenium, respectively, in rice.

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The expected organic selenium concentration in selenium-enriched rice is at $\mu g\,L^{-1}$ levels, which cannot be achieved directly using graphite furnace atomic absorption spectrometry (GFAAS). In this case, detection has to be improved by hydride generation (Shaltout et al., 2011) and/or introduction of a pre-concentration step (Tuzen, Saygi, & Soylak, 2007). The methodology of separation and pre-concentration based on cloud point extraction (CPE) had become important and practical in the last decade (McIntire & Dorsey, 1990). The technique is based on the capacity of most non-ionic surfactants in aqueous solutions to form micelles. The micelle solution separates into two phases, a surfactant-rich phase of a small volume and a diluted aqueous phase when heated to a temperature known as the cloud point temperature. The small volume of surfactant-rich phase obtained using this method allows extraction schemes to be simple, cheap, highly efficient, rapid and less toxic to the environment compared with traditional liquid–liquid extraction using organic solvents. GFAAS could, in this case, combine all the benefits associated with CPE with a sensitive instrumental technique producing a lower detection limit.

In recent years, CPE as an extraction technique prior to the GFAAS determination of Mn (Liang, Sun, & Cao, 2007), Sb (Oliveira Souza & Tarley, 2008), Cr (Sun & Wu, 2012), As (Baig et al., 2009), Sn (Zhu, Zhu, & Wang, 2006) speciation has been widely studied. There are some methods for the speciation of selenium in selenium-enriched foods, such as HG-AFS (Sun & Feng, 2011), capillary electrophoresis (CE)-ICP-MS (Zhao et al., 2011), ion chromatography (IC)-ICP-MS (Mar, Reyes, Rahman, & Kingston, 2009), high phase liquid chromatography (HPLC)-ICP-MS (Fang et al., 2009; Li, Lombi, Stroud, McGrath, & Zhao, 2010) and in situ X-ray absorption near-edge structure (XANES)(Li et al., 2010; Williams et al., 2009). However, the research on determination of selenium speciation in rice samples by CPE-GFAAS has not been reported yet.

The main purpose of this study was to develop a simple, sensitive and accurate method for speciation analysis of organic selenium in selenium-enriched rice. A new method for direct determination of inorganic and organic selenium in rice using GFAAS was developed in combination with CPE. The proposed method was successfully applied for the determination of total selenium, inorganic selenium and organice selenium in selenium-enriched rice.

2. Experiment

2.1. Apparatus

A PerkinElmer model AAnalyst 800 atomic absorption spectrometer (PerkinElmer, Massachusetts, USA) including the AS-800 autosampler (PerkinElmer, Massachusetts, USA) with Zeeman effect background correction was used with a selenium hollow-cathode lamp (General research institute for non-ferrous metals, China) as the radiation source. The optimised operating conditions for GFAAS are listed in Table 1. A HH-S11-2 thermostatic water-bath (Xiamen medical treatment electronic instrument Co. Ltd., China) maintained at the desired temperature was used in the CPE experiment. Phase separation was accelerated using a centrifuge (TDL-50B, Shanghai Anting Scientific Instrument Co. Ltd., China). An ultrasonic instrument (SK5200HP, Shanghai Kudos Ultrasonic Instrument Co. Ltd., China) was used to effectively extract water-soluble selenium in the speciation separation study. Milli-Q water purification system (Millipore Corp., Bedford, MA, USA) was used to prepare ultra-pure water with a resistivity of 18.2 MΩ cm.

Table 1
Optimum operating conditions for GFAAS.

Element	Selenium
Lamp current (mA)	12
Wavelength (nm)	196.0
Slit (nm)	2.0
Measurement mode	Peak area
Chemical modifier	0.005 mg Pd + 0.003 mg $Mg(NO_3)_2$
Graphite furnace	
Dry1 temp (°C)	110 (ramp 1 s, hold 30 s)
Dry2 temp (°C)	130 (ramp 15 s, hold 30 s)
Pyrolysis temp (°C)	800 (ramp 10 s, hold 20 s)
Atomization temp (°C)	1700 (ramp 0 s, hold 5 s)
Cleaning temp (°C)	2450 (ramp 1 s, hold 3 s)
Ar flow rate (mL min^{-1})	250 (stopped during atomizing)
Sample volume (μL)	20

2.2. Reagents

All reagents used in this work were of analytical grade or better. HNO_3 and $HClO_4$ (MOS grade, Tianjing Fengchuan Chemical Reagent Science and Technology Co. Ltd., China) were used to digest samples for the determination of total selenium.

Selenium standard working solutions were prepared from the 1000 $\mu g\,mL^{-1}$ Se(IV) standard stock solution (National Institute of Metrology, China) by serial dilution with ultra-pure water. Dithizone (Shanghai Chemicals Co., China, 2×10^{-3} mol L^{-1}) was prepared in acetone. The non-ionic surfactant Triton X-114 (Belgium, USA) used without further purification, and 10% (v/v) ethanol solution (Shanghai Lingfeng Chemical Reagent Co. Ltd., China) containing 0.1 mol L^{-1} HNO_3 was used to dilute the surfactant-rich phase. Magnesium nitrate (0.003 mg) and palladium (0.005 mg) (Shanghai Chemicals Co., Shanghai, China) were used as a mixed matrix modifier for GFAAS. A rice flour certified reference material (GBW08502, National Institute of Metrology P.R. China) was used to verify method.

Vessels used for trace analysis were kept in 50% (v/v) nitric acid for at least 24 h and washed several times with deionized water and ultra-pure water prior to use.

2.3. CPE procedures

For the CPE, an aliquot of sample (10 mL) or standard solution (pH 1) containing 0.25 mL of 1% (v/v) Triton X-114 and 0.2 mL of 2×10^{-3} mol L^{-1}dithizone, was kept in a thermostatic bath maintained at 50 °C for 20 min. Separation of the two phases was accelerated by centrifugation for 10 min at 2925×g. After being cooled in an ice-water bath for 20 min, the surfactant-rich phase became viscous and was retained at the bottom of the tube. The aqueous phase then was separated by inverting the tubes. To decrease the viscosity of the extract and ensure accurate pipetting, a 0.1 mL of 10% (v/v) ethanol solution containing 0.1 mol L^{-1} HNO_3 was added to the surfactant-rich phase. The diluted extract (20 μL) was introduced to the graphite furnace via an autosampler. Calibration was performed against aqueous standards subjected to the same cloud point extraction procedure. A blank, subjected to the same procedure, was measured in parallel with the samples and calibration solutions.

2.4. Preparation of selenium-enriched rice samples

The experiment was conducted in BuLi countryside, Changfeng county, Anhui province. The rice species used in the experiment was Jiahua-1, a widely cultivated variety in China, was used. An nutrition agent containing organic selenium was evenly sprayed onto the rice leaves, and the rice seeds harvested on October 2011. The harvested rice seeds were dried at room temperature. The husks were removed and the seeds polished.