Food Chemistry 270 (2019) 353–358

Contents lists available at ScienceDirect

Food Chemistry

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

Analytical Methods

An alternative analytical method for determining arsenic species in rice by using ion chromatography and inductively coupled plasma-mass spectrometry

Seong Hun Son[a], Won Bae Lee[a], Donghun Kim[b], Yonghoon Lee[a], Sang Ho Nam[a,*]

[a] *Mokpo National University, Department of Chemistry, 61 dorimri, Chungkyemyon, Muangun, Chonnam 58554, Republic of Korea*
[b] *Department of Environmental Health Research, National Institute of Environmental Research, Incheon, Republic of Korea*

ARTICLE INFO

Keywords:
Arsenic speciation
Rice
Analytical method
Ion chromatography
Inductively coupled plasma mass spectrometry

ABSTRACT

Qualitative and quantitative determination of total arsenic content and arsenic species in rice is very important because rice is one of the main sources of human arsenic intake. However, extraction and determination of arsenic species in rice has been very difficult due to severe matrix interference. An alternative analytical method was developed in this study to determine arsenic species in rice by using ion chromatography coupled to inductively coupled plasma-mass spectrometry. Two internal standards were used. The first internal standard was injected before sample introduction to correct signal change with time. The second internal standard was spiked into the sample to reduce matrix interference. Using the developed method, recoveries of dimethylarsinic acid, monomethylarsonic acid, and inorganic arsenic compared to certified values (NIST SRM 1568b rice flour) were 116%, 107%, and 92%, respectively.

1. Introduction

Arsenic is known to be a highly toxic element. It has attracted considerable interest due to its universal existence and high toxicity. It has been found in water, soil, and food. Recently, it has been found that arsenic is associated with cancer (IARC, 2012). According to the World Health Organization (WHO) guideline, the permissible level of total arsenic in drinking water is 10 µg/L (WHO, 2010). The Korea Food and Drug Association (KFDA) has established the maximum contaminant level of inorganic arsenic in rice to be 200 µg/kg, as is also the requirement in Europe and China (KFDA, 2017).

Rice has been produced worldwide and is a staple food in many countries. It is known to be one of the main agricultural products with a high concentration of inorganic arsenics (Batista, Souza, De Souza, & Barbosa, 2011; Qian et al., 2010) and thus responsible for the human intake of them. In rice four arsenic forms, arsenite [As(V)], arsenate [As(III)], dimethylarsinic acid (DMA), and monomethylarsonic acid (MMA), are present with different toxicity (Ma, Wang, Tang, & Yang, 2016). The inorganic arsenics, As(V) and As(III), can be toxic and increase the risk of cancer and cardiovascular diseases (Gui-di et al., 2009; Pizarro, Roman-Silva, Gomez, Camara, & Palacios, 2013). The organic arsenics, DMA and MMA, are less toxic than As(V) and As(III) (Liu, He, Yun, Sun, & Jiang, 2013). Thus, it is important to determine both total arsenic and arsenic species present in different forms (Bushby, 1998; McSheehy, Pannier, Szpunar, Potin-Gautier, & Lobinski, 2002; Moreno, Quijano, Gutiérrez, Pérez-Conde, & Cámara, 2001). However, quantitative analysis of arsenic species in rice has been troublesome due to matrix interference (Welna, Szymczycha-Madeja, & Pohl, 2015). Rice has a complex matrix composed of hydrocarbons, protein, fat, and fiber (Torres-Escribano, Leal, Vélez, & Montoro, 2008). A standard analytical method minimizing matrix interference is needed for accurate determination of arsenic species in rice.

Arsenic extraction from rice with good efficiency preserving the original integrity of arsenic species is critical to arsenic speciation. Microwave- and heat-assisted methods are mainly used for the extraction of arsenics from rice (Narukawa, Suzuki, Inagaki, & Hioki, 2014). The microwave-assisted extraction has some advantages with its excellent and consistent extraction efficiency. However, its cost is high due to the need for expensive equipment and a high-pressure bowl. Heat-assisted extraction also has advantages, such as high sample throughput and low cost. Distilled water, trifluoro acetic acid (TFA), mixtures of methanol/water, malonic acid, nitric acid, and enzymes have been used to extract arsenic species from rice. When water is used as an extraction solvent, the extraction of inorganic species from rice takes a long time due to their strong binding to cell walls, lipids, and insoluble cellulose (Amaral, Nóbrega, & Nogueira, 2013; Ma, Wang, Jia,

---

* Corresponding author.
E-mail address: shnam@mokpo.ac.kr (S.H. Nam).

https://doi.org/10.1016/j.foodchem.2018.07.066
Received 4 December 2017; Received in revised form 4 June 2018; Accepted 11 July 2018

& Yang, 2016). TFA is a good solvent for extracting inorganic arsenic from rice by hydrolysis of starch; however, it can reduce As(V) to As(III) (Liang et al., 2010; Ma, Wang, Tang, & Yang, 2016; Williams et al., 2005). Although 50% methanol can be used for extraction, it takes a long time to obtain satisfactory extraction efficiency (D'Amato, Forte, & Caroli, 2004). Enzymes have also been used to extract arsenic species from rice; however, their extraction efficiencies vary greatly. In addition, enzymes for this purpose are very expensive (Raber et al., 2012; Sanz, Muñoz-Olivas, & Cámara, 2005; Sanz, Muñoz-Olivas, Cámara, Sengupta, & Ahamed, 2007). Malonic acid and nitric acid have also been used for arsenic extraction with excellent extraction efficiencies (Choi et al., 2016; Huang, Fecher, Ilgen, Hu, & Yang, 2012; Kubachka, Shockey, Hanley, Conklin, & Heitkemper, 2012).

The aim of this study is to develop an alternative analytical method to determine arsenic species in rice flour by inductively coupled plasma-mass spectrometry (ICP-MS) coupled with ion chromatography (IC). We identified different matrix-interfering effect on the mass signals of organic and inorganic As species. By using double internal standards, the matrix interference could be circumvented and thus the analysis accuracy could be improved. The first internal standard was injected before sample introduction to correct signal change with time. The second internal standard was spiked into the sample to reduce matrix interference. With this new and improved analytical method, arsenic speciation in rice can be successfully performed.

2. Experimental

2.1. Reagents and standards

Deionized water (DIW, 18.2 MΩ cm) from a water purification system (PURELAB CLASSIC, CLASSIC UV MK2, ELGA, USA) was used for the preparation of standard solutions, eluents, and sample solutions. Stock solutions (100 mg/kg) of arsenic species were prepared by dissolving the following reagents in DIW and storing the solutions at 4 °C in the dark: sodium metaarsenite (98%, Sigma-Aldrich, Steinheim, Germany) for As(III) stock solution, sodium arsenate dibasic heptahydrate (≥98%, Sigma-Aldrich) for As(V) stock solution, disodium methylarsenate hexahydrate (98%, Sigma-Aldrich) for MMA stock solution, sodium cacodylate (≥98%, Sigma-Aldrich) for DMA stock solution, and arsenobetain (≥95.0%, Sigma-Aldrich) for arsenobetaine (AsB) stock solution. Working solutions were prepared daily. Nitric acid (70%, Sigma-Aldrich), malonic acid (99%, Sigma-Aldrich), and hydrogen peroxide (30%, Junsei, Japan) were used to extract arsenic species. Ammonium phosphate dibasic (≥98%) purchased from Sigma-Aldrich was used as the eluent for IC.

2.2. Instrumentation

An inductively coupled plasma-mass spectrometer (SPECTRO, Germany) was used for the determination of arsenic. Its operating parameters are shown in Table 1. A GS-50 gradient pump (DIONEX, USA) equipped with an injection valve was used as the sample introduction and eluent delivery system. A Hamilton PRP-X100 analytical column (Hamilton Company, USA) was used for separation of arsenic species. The operating parameters for the IC system used herein are similar to the previous work (Taylor et al., 2012), and summarized in Table 1. A centrifuge (J2-MC, BECKMAN COULTER, USA), ultrasonicator (POWERSONIC, HWASHIN, KOREA), pH meter (725P, IST, KOREA), vortex mixer (VM-10, WISEMIX, KOREA), and hotplate (MSH-20A, DAIHAN SCIENTIFIC CO., KOREA) were also used for sample preparation.

2.3. Method validation of arsenic speciation in rice

Recently, NIST SRM 1568b (National Institute of Standards and Technology, USA) rice flour has been widely used to develop analytical methods for the determination of arsenic species in rice (Ciminelli, Gasparon, Ng, Silva, & Caldeira, 2017; Ge et al., 2016; Islam et al., 2017; Ma, Wang, Tang, & Yang, 2017; Signes-Pastor, Carey, & Meharg, 2017; Qu, Mudalige, & Linder, 2015). Herein, the NIST SRM 1568b rice flour was also analyzed to validate the analytical method for arsenic species (inorganic arsenic, DMA, and MMA). Various extraction methods were investigated for arsenic speciation in rice using the NIST SRM 1568b rice flour. Certified values for inorganic arsenic, DMA, and MMA in the NIST SRM 1568b rice flour were 92 ± 10 µg/kg, 180 ± 12 µg/kg and 11.6 ± 3.5 µg/kg, respectively.

Table 1
Operating parameters for IC-ICP-MS.

ICP-MS		
Power	1400 W	
Argon gas flow rate		
Coolant flow	12 L/min	
Auxiliary flow	2.3 L/min	
Nebulizer flow	0.8 L/min	
Nebulizer	Cross flow	
Monitor *m/z*	As 75	
IC		
Extraction method	Malonic acid	Nitric acid
Analytical column	Hamilton PRP-X100 (10 µm, 4.6 × 250 mm)	
Flow rate	1.0 mL/min	
Sample loop	100 µl	100 µl
Mobile phase	5 mM malonic acid (pH 5.6)	20 mM ammonium phosphate (pH 6.0)

2.4. Extraction method

2.4.1. Extraction with malonic acid

Approximately 1.0 g of powdered rice was combined with 10 mL of 5 mM malonic acid at pH 5.6 and agitated for 5 min. The sample was then maintained in a water bath at 80 °C for 120 min, during which the sample was sonicated for 1 min at intervals of 30 min. At the end of the procedure, the sample was sonicated again for 5 min. The sample was cooled at below 10 °C for 2 h and then centrifuged for 10 min at 3000 rpm. The supernatant was passed through a 0.45 µm nylon membrane filter. The filtrate was analyzed by IC-ICP-MS.

2.4.2. Extraction with nitric acid

A 10 mL 0.28 M HNO_3 solution was added to each 1.0 g rice powder sample and shaken for 5 min. Samples were then maintained in a water bath at 95 °C for 90 min. Afterward, samples were cooled at room temperature and centrifuged for 10 min at 3000 rpm. The supernatant was filtered with a 0.45 µm nylon membrane filter. Then, 150 µg of 1000 µg/kg AsB stock solution and 1 mL of 30% H_2O_2 were added to the filtered sample and diluted to 15 mL with DIW.

2.4.3. Description of six different methods

The concentrations of inorganic arsenic, DMA, and MMA in the NIST SRM 1568b rice flour were determined by six different methods denoted by I, II, III, VI, V, and VI. Each method can be distinguished from the others by the following two factors; One is the solvent ((i) malonic acid or (ii) nitric acid) used to extract arsenic species from the rice flour, and the other is the standardization method ((i) usage of internal standards or (ii) standard addition). In the method I, 5 mM malonic acid was used to extract arsenic species from the rice flour. For the other methods II–VI, 0.28 M nitric acid was used as their extraction solvents. The methods I and II did not employ any standardization strategies. On the other hand, As(V) or AsB were used as internal standards for the methods III–V. The method VI was based on the standard addition (Skoog, Holler, & West, 1996). Both methods III and IV used a single internal standard, and the method V employed double internal standards. In the method III, As(V) was injected as the internal standard prior to the sample introduction. In the method IV, AsB, to be