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Extraction techniques for arsenic species in rice flour and their speciation by HPLC–ICP–MS



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ABSTRACT

The extraction of arsenic (As) species present in rice flour samples was investigated using different extracting solvents, and the concentration of each species was determined by HPLC–ICP–MS after heat-assisted extraction. The extraction efficiencies for total arsenic species and especially for arsenite [As(III)] and arsenate [As(V)] were investigated. As(III), As(V) and dimethylarsinic acid (DMAA) were found in the samples, and the concentration of DMAA did not vary with treatment conditions. However, the concentrations of extracted total arsenic and those of As(III) and As(V) depended on the extracting solvents. When an extracting solvent was highly acidic, the concentrations of extracted total arsenic were in good agreement with the total arsenic concentration determined by ICP–MS after microwave-assisted digestion, though a part of the As(V) was reduced to As(III) during the highly acidic extraction process. Extraction under neutral conditions increased the extracted As(V), but extracted total arsenic was decreased because a part of the As(III) could not be extracted. Optimum conditions for the extraction of As(III) and As(V) from rice flour samples are discussed to allow the accurate determinations of As(III), As(V) and DMAA in the rice flour samples. Heat block extraction techniques using $0.05 \text{ mol L}^{-1} \text{ HClO}_4$ and silver-containing $0.15 \text{ mol L}^{-1} \text{ HNO}_3$ were also developed.

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1. Introduction

Arsenic (As) has many toxic compounds which exhibit a range of toxicities; inorganic arsenic, in particular arsenite [As(III)], is one of the most toxic forms. As the toxicity of arsenic depends upon the chemical species, it is important to determine which chemical species are present in foodstuff in addition to the total arsenic concentration. Therefore, arsenic speciation has become standard practice throughout the world [1]. Rice is a dietary staple in many countries and contributes to arsenic intake than any other Asian agricultural products [2]. To ensure that rice can be safely consumed, it is necessary to know and to monitor potentially harmful constituents. The Codex Alimentarius Commission (CAC) has stated that it is necessary to set standards for inorganic arsenic in rice, and the renewed interest in the regulation for inorganic arsenic concentration in rice (unpolished and/or polished) has resulted in using one of the analytical protocols that involved the extraction with $0.15 \text{ mol L}^{-1} \text{ HNO}_3$ for inorganic arsenic [3]. The extraction has been successfully applied to rice flour samples [4,5].

Many speciation techniques for arsenic in rice samples have been published [6–20], and we have reported the arsenic speciation

in rice flour samples after microwave-assisted extraction with water as the extracting solvent [21–24]. We have also reported a heat block extraction method using a dry heating block system with $0.15 \text{ mol L}^{-1} \text{ HNO}_3$ and water as the extracting solvents, and the method has been assessed by application to actual rice flour samples. Heat block extraction methods using HNO_3 or $\text{HNO}_3\text{--H}_2\text{O}_2$ have been also reported [25,26]. Each of these methods has its own advantages and disadvantages. When water is used as the extracting solvent, no change of chemical species is thought to occur; in particular the concentration ratio of As(III) to As(V) is not altered, and it may be possible to assess the natural abundances of these and other chemical species. However, the extraction rate of As(III) can depend on the rice sample analyzed: total arsenic extracted can range from 80% to 100% of the arsenic present. Hence, in order to achieve 100% extraction, it is necessary to optimize the extraction conditions for each sample. In addition, an extraction with water has to be followed by filtration of a highly viscous solution/suspension and therefore this process is difficult to be carried out.

Using acid extraction, it is possible to extract approximately 95–100% of the total arsenic present in many rice flour samples. Also, the method is versatile and easy to use. However, it has been found that chemical species are changed during the extraction processes in many cases. In acid extraction, it is difficult to individually determine the original concentrations of As(III) and As(V), and they must be considered together as inorganic arsenic (i-As). However,

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apparent concentrations of As(III) and As(V) can be measured separately, and the inorganic arsenic concentration is calculated as the sum of the measured concentrations of As(III) and As(V). However, in spite of the possible changes in the oxidation states, the concentrations of As(III) and As(V) have sometimes been reported directly. The usual direction of changes during HNO₃ extraction is from As(V) to As(III), which is more toxic and toxic risk may thus be overestimated.

In this study reported here, we have investigated the extraction characteristics and extraction efficiencies for arsenic species in rice flour samples using several different solvents and conditions, and suitable extraction technique for inorganic arsenic in rice flour containing both As(III) and As(V) was investigated. And, heat block extraction techniques using 0.05 mol L⁻¹ HClO₄ and Ag-containing 0.15 mol L⁻¹ HNO₃ were developed.

2. Experimental

2.1. Instruments

An ICP-MS (7500c, Agilent, Tokyo, Japan) equipped with a micromist nebulizer (100 µL type) and a Scott spray chamber (2 °C) was used. Typical operating parameters for the ICP-MS were as follows: incident rf power was 1600 W, outer Ar gas flow rate 15 L min⁻¹, intermediate Ar gas flow rate 0.9 L min⁻¹, carrier Ar gas flow rate 0.7 L min⁻¹ and make-up Ar gas flow rate 0.4 mL min⁻¹. The ICP-MS was usually operated with He as the collision cell gas (3 mL min⁻¹) to reduce some polyatomic molecular interferences. The total arsenic concentrations in the samples were determined by ICP-MS.

Arsenic species were separated by HPLC and directly introduced into the ICP-MS. A CAPCELL PAK C₁₈ MG column (250 mm × ID 4.6 mm, Shiseido Ltd., Tokyo, Japan) was used with the mobile phase containing 10 mmol L⁻¹ sodium 1-butanefulfonate/4 mmol L⁻¹ malonic acid/4 mmol L⁻¹ tetramethylammonium hydroxide/0.05% methanol (pH 3.0) at a flow rate of 0.75 mL min⁻¹. The exit of the HPLC column was connected to the nebulizer of the ICP-MS with PEEK tubing.

A heating block system (Digi PREP, SCP Science Inc., Canada) was used for heat-assisted extraction and a Mars X microwave system was used for microwave-assisted extraction. An MSL 1200-mega (Milestone MLS, Leutkirch, Germany) was used for microwave-assisted digestion to decompose the samples.

The acids and other reagents used were of ultra-pure and/or PMA-grade (Kanto Chemical Industries Ltd., Tokyo, Japan). Ultra-pure water purified with a Milli Q-Labo filter (Nippon Millipore Ltd., Tokyo, Japan) was used throughout.

An ion chromatograph DX-500 (Dionex, Sunnyvale, CA, USA) equipped with an Ion Pac AG20 and an Ion Pac AS20 columns (Dionex) was used to measure the concentrations of halides in solutions.

2.2. Standards and reagents

The Japan Calibration Service System (JCSS) arsenic standard solution (ca. 1000 mg L⁻¹) was used as the source of calibration standard solution (Kanto Chemical Co., Inc., Tokyo, Japan). A JCSS arsenic standard solution was made from As₂O₃ powder, and As (V) was certainly not detected in the JCSS arsenic standard solution used. Therefore, the JCSS arsenic standard solution was used as the As(III) source standard solution.

The As(V) certified reference material (NMIJ CRM 7912-a), the dimethylarsinic acid (DMAA) certified reference material (NMIJ CRM 7913-a) and the arsenobetaine (AsB) certified reference material (NMIJ CRM 7901-a), supplied by the National Metrology

Institute of Japan/National Institute of Advanced Industrial Science and Technology (NMIJ/IST), (Tsukuba, Japan), were used as the source standard solutions. The concentrations of all standard solutions are SI traceable.

A monomethylarsonic acid (MMAA) solution was prepared from a commercially available reagent after its purity evaluation (moisture, C, H, O, Br and Cl elemental analysis and impurity arsenic compounds) had been carried out. It was dissolved in water to prepare an in-house standard solution containing ca. 1000 mg kg⁻¹ as As.

Working mixed standard solutions [(0.5–20) ng g⁻¹ as As] were prepared daily by mixing the stock solutions and diluting with water. AsB was used as the internal standard during the analyses.

2.3. Total analysis procedure

A portion of sample powder (0.5 g) was weighed precisely and transferred to a perfluoroalkoxy (PFA) vessel to which 5 mL of HNO₃ (60.0%) and 2 mL of H₂O₂ (30.0%) were added. The operating program of the microwave system was as follows: the samples were heated at 200 W for 5 min in the 1st step, 300 W for 5 min in the 2nd step, 500 W for 10 min in the 3rd step, and 600 W for 5 min in the 4th step, and then cooled to room temperature. The vessel containing the dissolved sample was placed on a hot plate to evaporate the sample to dryness. The residue was dissolved with 0.6 g of HNO₃ (60.0%) and then made up to 30 g with water. After appropriate dilution, the resulting solution was used for the determination of total arsenic by ICP-MS employing an external calibration method. Blank tests for the procedure were also performed.

Factors for converting between dry mass and wet mass were obtained by measuring the mass losses after drying portions of the samples at 135 °C in an oven for 90 min. The correction factor was also used in the arsenic speciation analyses.

2.4. Arsenic speciation

Arsenic species were extracted from the rice flour samples using a heat-assisted extraction technique with different extracting solvents. A portion of a rice flour sample (ca. 0.5 g) was accurately weighed into a 10 mL glass tube with a cap and 2 g of extracting solvent were added. The tube was capped and placed in a dry heating block system at 100 °C for 2 h. After cooling, 1 g of a 50 ng g⁻¹ AsB standard solution and 7 g of water were added (total liquid phase: 10 g).

The tube was centrifuged at 3500 rpm for 10 min and the liquid phase was then passed through a 0.45 µm syringe-type polyvinylidene difluoride (PVDF) membrane filter. The filtrate was analyzed by HPLC-ICP-MS using an external calibration method.

Blank tests were performed to investigate possible arsenic contamination; none was detected.

Arsenic species were also extracted from the rice flour samples using a microwave-assisted extraction technique with a range of extracting solvents. A portion of a rice flour sample (ca. 1.0 g) was accurately weighed into a PFA vessel with a cap and 10 g of extracting solvent were added. The capped vessel was placed in a microwave system at 90 °C for 30 min. After cooling, the sample was transferred to a 15 mL polypropylene (PP) tube, and the tube was centrifuged at 3500 rpm for 10 min; the liquid phase was then passed through a 0.45 µm syringe-type PVDF membrane filter. The filtrate was analyzed by HPLC-ICP-MS using an external calibration method.

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