Determination of Inorganic Arsenic in Rice by Anion Exchange HPLC-ICP-MS

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Introduction

Long-term ingestion of inorganic arsenic by humans has been associated with development of severe adverse health effects including cancer, skin lesions, developmental effects, cardiovascular disease, neurotoxicity and diabetes [1]. Ingestion of contaminated drinking water is the most well-known cause of exposure to inorganic arsenic. However, recent reported data have indicated that elevated inorganic arsenic in rice can contribute significantly to dietary intake. Rice is generally grown under flooded conditions and accumulates As from the soil and water where As mobility is high.

Recently, toxicological risk evaluations on dietary inorganic arsenic exposure have been published by the European Food Safety Authority (EFSA) [2] and WHO/FAO Joint Expert Committee on Food Additives and Contaminants (JECFA) [1], proposing benchmark dose lower confidence limit (BMDL) values between 0.3 and 8 µg/kg body weight (bw)/day and 3 µg/kg bw/day, respectively. The dietary exposures to inorganic arsenic estimated by EFSA for average and high level consumers in Europe were within the range of the BMDL values identified, and hence little or no margin of exposure leading to possible risk to some EU consumers was one of the conclusions of the report [2]. In both reports there is a call for more accurate information on the inorganic arsenic content of foods in order to improve the assessments of dietary exposures to inorganic arsenic and furthermore it was concluded that there is a need for development of validated methods for selective determination of inorganic arsenic in food matrices, for example rice.

Experimental

In the present method, the extraction of inorganic arsenic used subsamples of approximately 0.2 g, which were weighed into microwave quartz containers and 10.00 mL of 0.06 M hydrochloric acid (Merck) in 3% hydrogen peroxide (Merck) was added. The solutions were placed in a microwave oven (Multiwave, Anton Paar, Austria) and the power was programmed to hold the solutions at 90 °C for 20 min. Using this procedure, the inorganic arsenic is extracted from the sample matrix and furthermore As(III) is oxidized to As(V), thus allowing for the determination of total inorganic arsenic as As(V). The solutions were allowed to cool to room temperature and the supernatant transferred to 15 mL plastic tubes and centrifuged at approximately 4,000 rpm for 10 min and subsequently filtered (0.45 µm) prior to analysis.

Table 1. *HPLC and ICP-MS instrument operating conditions*

HPLC	
Injection volume	25 µL
Operating pressure	45–50 bar
Mobile phase concentration	30 mmol/L $(NH_4)_2CO_3$
Mobile phase flow rate	1 mL/min
ICP-MS	
RF power	1550 W
Carrier gas flow rate	0.97 L/min
Make-up gas flow rate	0.18 L/min
Plasma gas flow rate	15 L/min
Auxiliary gas flow rate	1 L/min
Nebulizer	Concentric
Spray chamber	Water-cooled double-pass (5 °C)
Interface cones	Platinum
Mass resolution	0.8 u
Integration time	1000 ms

The determination of inorganic arsenic was done using anion exchange HPLC-ICP-MS following the chromatographic principles previously reported [3]. The column was the strong anion exchanger ION-120; 120 mm × 4.6 mm; 5 µm particles (Transgenomic, USA). The mobile phase was a solution of 30 mM ammonium carbonate (Merck, Germany) at pH 10.3 (pH adjusted with 25% NH_3 (aq), Merck) filtered through 0.45 µm prior to use. The extracts were quantified using external calibration with matched standard solutions (0.07 M HCl in 3% hydrogen peroxide). Stock standard solution (1000 mg As/L) (SCP science) was used to prepare the calibration standards.

Results

Figure 1 shows an example of a chromatogram of a rice sample used in an EU-RL proficiency test [4]. The total arsenic concentration determined in this rice sample was 0.172 ± 0.018 mg/kg and the measured result for inorganic As of 0.12 ± 0.01 mg/kg agreed well with the estimated target value at 0.107 ± 0.014 mg/kg derived from the results from all participating laboratories. For quality assurance of the method, the certified reference material NIST 1568a was analyzed. Although, this material is not certified for inorganic arsenic, it has been referenced many times in the scientific literature, where a mean concentration for inorganic arsenic at 97 ± 9 µg/kg (mean ± sd) can be calculated from 16 different publications. Using the method presented here, a concentration of 103 ± 7 µg/kg (mean ± sd, N = 3) was found for NIST 1568a, which is in good agreement with the literature values.

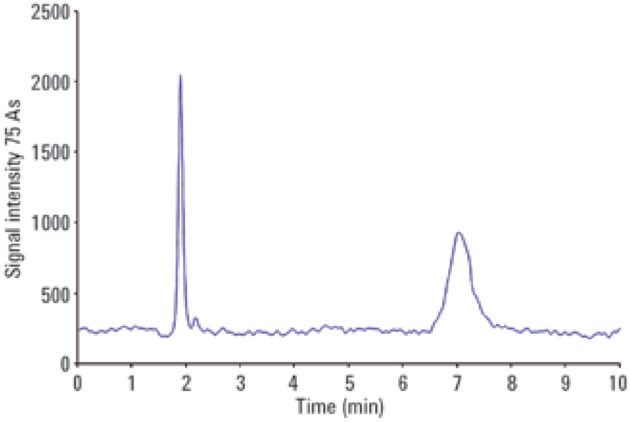

Figure 1. *Chromatogram of an extract of a rice sample used in an EU-RL proficiency test. First peak at approximately 1.9 min is DMA and the peak at approximately 7 min is As(V) = inorganic arsenic.*

Conclusions

A method for the selective detection of inorganic arsenic in rice is presented. During sample extraction As(III) is oxidized to As(V), allowing the determination of inorganic arsenic (sum of As(III) and AsV), which is separated from other arsenic compounds by anion exchange HPLC-ICP-MS. The measured results for inorganic arsenic in two reference samples agreed well with literature values.

References

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