

Speciation of Six-Arsenic Species of Rice in Korea by HPLC/ICPMS

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Abstract. Determination of arsenic (As) speciation in rice is necessary because inorganic As species are more toxic than organic As. Arsenic levels of rice in Korea were determined by microwave extraction and High Performance Liquid Chromatography coupled with Inductively Coupled Plasma-Mass Spectrometry. The extraction method showed a high recovery and low Limit of Detection (LOD) and Limit of Quantitation (LOQ). Most of the As species in rice were noticed to be inorganic [Arsenite (As^{III}), Dimethylarsinic acid (DMA)]. The percentage of inorganic As/total As is 69.01 % (36.40-87.86 %). Arsenite and DMA were the major compounds in rice in Korea when compare to U.S. rice. The order and percentage of As species showed were As^{III} (56-70 %)>DMA (23-38 %)>As^V (5 %)>MMA (1 %).

Key words: Speciation, Arsenic species, HPLC/ICPMS, Rice

Introduction

Arsenic exist in forms of various chemical species (Maeda, S, 1994). In-organic arsenic species (arsenate (As^V) and arsenite (As^{III})) have been classified as carcinogenic and the methylated form, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) have been identified as cancer promoters. It is believed that arsenobetaine (AB) and arsenocholine (AC) are non-toxic (Ronkart *et al.*, 2007). Thus, it is important to separate and measure the chemical forms of As for accurate risk assessment. Arsenic speciation analysis of agricultural products, biological and environmental samples have been studied extensively (Nakamura *et al.*, 2008). Most of As-speciation analytical methods are based on chromatographic separation techniques such as High performance Liquid Chromatography (HPLC) or Capillary Electrophoresis (CE) coupled with Atomic Absorption Spectrometry (AAS) and, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The present study was to

determine the analytical method of As-species and to provide the percentage of inorganic As/total As and accurate information of human health risk assessment.

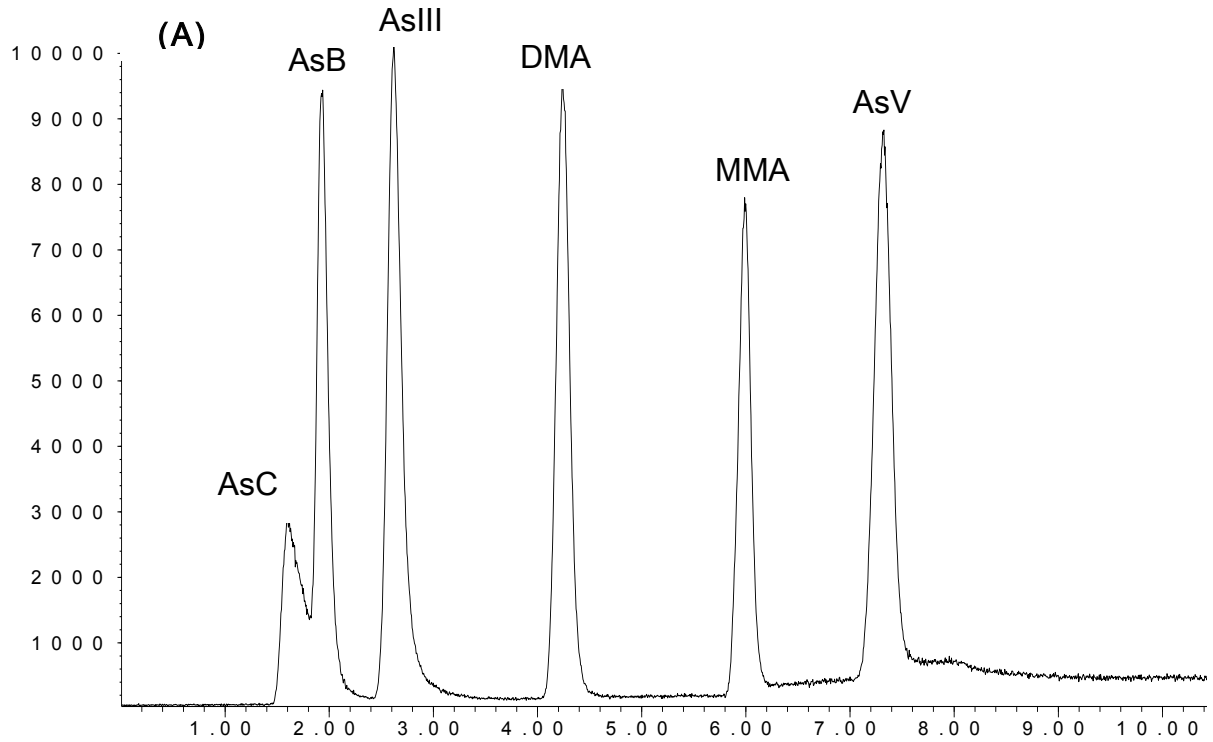
Materials and Methods

Rice samples were collected from the markets (polished rice) and mining impacted areas (mining rice) in Korea. All the samples were homogenized by grinding. The contents of total As were measured using ICP/MS after acid digestion with microwave-assisted apparatus. Arsenic species in rice samples were extracted with microwave-assisted 1 % nitric acid (Foster *et al.*, 2007). Around 0.1 g rice samples was weighed into teflon digest tube and digested with 10 mL of 1 % nitric acid at 80 °C, for 30 min. Samples were cooled to room temperature and centrifuged at 4500 rpm for 10 min. The supernatant was filtered and kept at 4°C until analysis. For quality control, the rice flour CRM, NMIJ-7513a and NIST SRM 1568a were also analyzed. Arsenic speciation was

quantified by HPLC-ICP/MS using PRP-X100 anion exchange column (250 mm x 4.1 mm i.d., 10 μ m). The gradient mobile phase was 2 mM ammonium carbonate

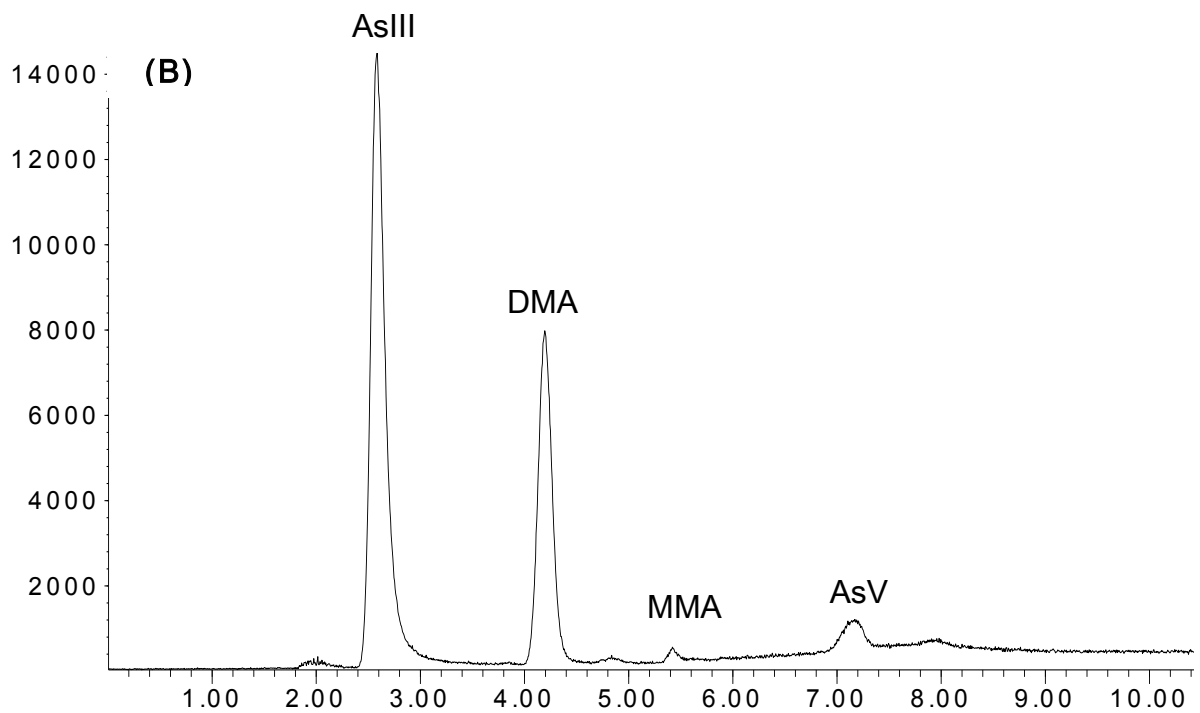
adjusted to pH 8.0 and 20 mM ammonium nitrate and, ammonium phosphate adjusted to pH 9.0.

Abundance



Time-->

Abundance



Time-->

Fig. 1. HPLC-ICP/MS chromatogram for As speciation in ((A) standard, (B) rice sample)

Results and Discussion

The HPLC-ICP/MS chromatograms of the speciation analysis of As in rice sample and standard solution are shown in Fig. 1. The order of major compounds in rice samples were As^{III}>DMA>As^V>MMA. The accuracy and precision of the method were evaluated on the recoveries of CRM and fortified samples. The recoveries of fortified rice (50 ng/g) were 96.80-111.02 %. Total As and As species results are reported in Table 1. The mean concentration of inorganic As (As^{III}, As^V) was 0.14±0.03 mg/kg in mining rice and 0.08±0.03 mg/kg in polished rice. The percentage of inorganic As based on total As was 36.40-87.86 % in mining and polished rice.

Table 1. Total arsenic and speciation results in rice samples (mg/kg)

Sam ples	As ^{III}	DMA	MMA	As ^V	InorganicAs /Total As (%)
Mining rice (n=31)	0.12 (56 %)	0.08 (38%)	0.003 (1%)	0.01 (5%)	61.34 (36.40~79.93)
Polishe d rice (n=30)	0.08 (70%)	0.03 (23%)	0.002 (1%)	0.005 (5%)	76.94 (54.50~87.86)

The concentration of inorganic As (As^{III}, As^V) increased linearly ($R^2 = 0.70$) with increasing total As concentration. Yamily (2008) reported that DMA increased linearly with increasing total As in U.S. rice. So, we recognized that rice in Korea was an inorganic As type, whereas rice from U.S. with a DMA type.

Conclusion

The method of As speciation by HPLC-ICPMS was developed which allowed the simultaneous separation by six As species. The results indicated that

microwave-assisted extraction provided good extraction efficiency. The LOD of As-speciation method was 0.1-0.5 ug/kg. Based on As speciation in rice, As^{III} and DMA were the major compounds and AsC and AsB were not found. The order and percentage of As species revealed in this study were As^{III} (56-70 %) >DMA(23-38 %)>As^V(5 %)>MMA(1 %).

Acknowledgements

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