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Arsenic Speciation in Rice and Rice Products using LC-ICP-MS: A Sensitive and Reliable Approach by Shimadzu.

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1. Introduction

Arsenic toxicity is a major public health concern, particularly in drinking water, leading to strict regulatory limits worldwide. While total arsenic has traditionally been measured, its toxicity largely depends on its chemical form with inorganic species Arsenite and Arsenate (As(III) and As(V)) being highly toxic and carcinogenic, and organic forms monosodium methyl arsenate (MMA) and disodium methyl arsenate (DMA) displayed in fig. 1, considered less harmful. Speciation analysis is therefore essential for accurate risk assessment.

Rice and rice-based products are of particular concern, as rice can efficiently accumulate inorganic arsenic from the environment. In response, the European Union established maximum residue levels (MRLs) for inorganic arsenic in rice under Commission Regulation (EU) 2015/1006, highlighting the need for precise speciation.

To address this, advanced techniques like liquid chromatography coupled with inductively coupled plasma mass spectrometry (LC-ICPMS) are employed. LC-ICPMS provides high sensitivity and specificity for arsenic species determination, ensuring regulatory compliance and protecting consumer health.

This study presents the effective use of Shimadzu's LC-ICPMS-2050 LF system for arsenic speciation in rice and related products.

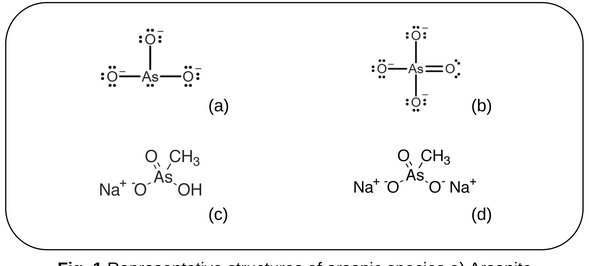

Fig. 1 Representative structures of arsenic species a) Arsenite b) Arsenate c) Monosodium methyl arsenate d) Disodium methyl arsenate.

2. Methods and Materials

The arsenite and arsenate reference standards are procured from Inorganic Ventures. Additionally, the individual reference standards for methyl arsenic acid and dimethyl arsenic acid are procured from Chem Service. Several rice and rice-based products like white rice, brown rice, rice crackers and beverage (rice based alcohol) are procured from local supermarket for studying arsenic speciation.

All standard stock solutions are prepared as specified in the LC-ICP-MS Method Package for Arsenic Speciation Analysis Type-2 by Shimadzu, Japan. Seven levels of mixed calibration standards are prepared and injected for the quantification of arsenic species. Calibration curves are generated using the external standard calibration method with a 1/I weighted regression. All samples are prepared in duplicate to verify method performance. Additionally, two spiked samples containing only inorganic arsenic standards are included to evaluate the extraction efficiency of the method.

The Shimadzu ICPMS-2050 LF, coupled with the Nexera LC series (Fig. 2), manufactured by Shimadzu Corporation, Japan, is used to separate and quantify the different arsenic species present in the samples.

Fig. 2 Shimadzu ICPMS-2050 combined with Nexera inert.

Shimadzu's LC-ICP-MS Method Package for Arsenic Speciation Analysis Type-2 facilitates rapid instrumental method optimization, enhancing throughput. The method includes all optimized instrumental parameters, reducing the burden on the user for method development. Data acquisition and processing are efficiently managed using Shimadzu's LabSolutions ICPMS TRM software, which communicates effectively with both the liquid chromatograph and the mass spectrometer.

Nishimura's extraction method[1] is used for the extraction of arsenic species. Approximately 0.5 g of milled rice sample weighed into a 50 mL polypropylene (PP) tube, and 2 mL of 0.15 M HNO_3 is added. The mixture is then vortexed and heated for 2 hours at 120 ^{0}C. The extract is further diluted with 8 mL of water and centrifuged for 10 minutes at 3500 rpm. The 1 mL of supernatant is filtered through a 0.22 µm nylon syringe filter into a PP HPLC vial. Liquid sample is diluted 10-fold with 0.15 M HNO_3. The detailed acquisition parameters are shown in Table 1.

Table 1: LC-MS method parameters.

LC System	: Nexera inert
Column	: Pentafluoro phenyl column, 250 mm x 4.6 mm; 5 µm
Mobile phase	: 0.1% Formic acid (1% methanol and 0.025% ion pair reagent solution)
Flow rate	: 0.75 mL/min
Injection volume	: 10 µL
Column temperature	: 40 ^{0}C
ICP-MS system	: ICPMS-2050 LF
Plasma torch	: Mini-torch
Skimmer Cone	: Nickel
Plasma Gas Flow rate	: 9.0 L/min
Cell Gas	: Helium

3. Results

The calibration curve spanned from 0.2 to 20 µg/L is plotted. The inorganic arsenic calibration standards met the AOAC accuracy criteria, falling within the 80–120% range. Fig. 3 shows the inorganic arsenic calibration curve and a combined chromatogram of inorganic and organic arsenic.

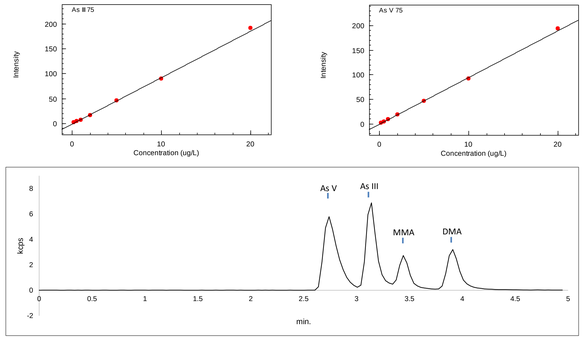

Fig. 3 Representative chromatograms for arsenics standard.

The detailed results for the quantitation of the duplicate samples and the spiked samples are shown in Table 2. Duplicate analysis shows good repeatability. The sample used for spiking already contains inorganic arsenic; therefore, to determine the exact recovery, the native concentration is subtracted from the spiked sample results.

The recovery observed ranges from 70% to 120%, demonstrating the effectiveness of the sample extraction procedure.

Table 2: Quantitative Results for Arsenic Speciation.

Sr. No	Sample Name	As III (µg/Kg)	As V (µg/Kg)	Inorganic As (µg/Kg)	As III % Recovery	As V % Recovery
1	Brown Rice_1_R1	104.00	6.97	110.97	-	-
2	Brown Rice_1_R2	98.60	8.02	106.62	-	-
3	White Rice_2_R1	31.80	ND	31.80	-	-
4	White Rice_2_R2	32.70	ND	32.70	-	-
5	White Rice_3_R1	48.40	ND	48.40	-	-
6	White Rice_3_R2	47.10	ND	47.10	-	-
7	White Rice_4_R1	61.20	ND	61.20	-	-
8	White Rice_4_R2	67.30	ND	67.30	-	-
9	White Rice_5_R1	70.10	ND	70.10	-	-
10	White Rice_5_R2	65.70	ND	65.70	-	-
11	Brown Rice_6_R1	46.60	20.20	66.80	-	-
12	Brown Rice_6_R2	47.40	21.60	69.00	-	-
13	Rice Cracker_7_R1	76.40	1.71	78.11	-	-
14	Rice Cracker_7_R2	71.50	1.09	72.59	-	-
15	Rice Cake_8_R1	112.00	0.66	112.66	-	-
16	Rice Cake_8_R2	105.00	0.77	105.77	-	-
17	Rice cereals_9_R1	41.40	3.86	45.26	-	-
18	Rice Cereals_9_R2	40.50	2.61	43.11	-	-
19	Rice based alcohol (Sake)	0.31	0.12	0.42	-	-
21	Spike_1 (50 µg/Kg)	130.00	38.90	168.90	119.8	77.8
22	Spike_2 (25 µg/Kg)	67.70	26.80	94.50	108.8	96.7

4. Conclusion

- The extraction procedure employed effectively ensures the recovery of inorganic and organic arsenic species from various sample types, including both raw and processed materials.
- A highly sensitive method based on hyphenated techniques, specifically LC-ICPMS, is developed for the speciation and quantification of arsenic using the Shimadzu ICPMS-2050 LF coupled with a Nexera inert LC system.

Reference

1) T. Nishimura, M. Hamano-Nagaoka, N. Sakakibara, T. Abe, Y. Maekawa, T. Maitani, Food Hyg. Saf. Sci. 51 (2010) 178.