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Ion chromatography – nitrogen-sustained microwave inductively coupled atmospheric pressure plasma – mass spectrometry (IC-MICAP-MS) for arsenic speciation analysis in rice†

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The performance of a nitrogen (N_2)-sustained Microwave Inductively Coupled Atmospheric-Pressure Plasma (MICAP) – Quadrupole Mass Spectrometer (QMS) was explored as an alternative to the traditional argon (Ar) equivalent for arsenic (As) analysis in rice. Conventional Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) can be limited by Ar-based spectral interferences depending on sample matrices. Specifically, for the analysis of As, argon chloride ions ($^{40}Ar^{35}Cl^+$) can interfere with the detection of the monoisotopic $^{75}As^+$, and this interference can lead to systematic errors in As quantification. With N_2-sustained MICAP-QMS, major plasma background species are N_2-based, which eliminates the spectral interference possibility at mass-to-charge (m/z) 75 from $^{40}Ar^{35}Cl^+$. In this work, we present the first combination of the N_2-MICAP-MS with anion exchange chromatography for As speciation and quantification from several rice varieties. We used a slightly modified As-species extraction procedure per Food and Drug Administration (FDA) protocol EAM 4.11. In all rice samples, we quantified the As amount in the species arsenite (As(III)), dimethylarsinic acid (DMA), monomethylarsonic acid (MMA), and arsenate (As(V)), with detection limits of 0.26, 0.26, 0.13 and 0.22 μg kg^{-1}, respectively. We validated our experimental method with Standard Reference Material (SRM) NIST 1568b rice flour and obtained 85–110% recoveries for quantification of As from species. Speciation results were comparable to total As concentration determined by MICAP-MS. The use of N_2-MICAP-MS would allow for quantification of As in chloride containing matrices; here, we demonstrate strong matrix tolerance of the MICAP-MS for solutions with up to 1% (w/w) sodium chloride. These results suggest that the MICAP-MS is a promising approach for the analysis of As species in more complex matrices.

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Introduction

Arsenic (As) is a metalloid notorious for its toxicity. Both natural sources and anthropogenic inputs contribute to its occurrence in the environment. Exposure to As is of concern and is linked to several health-related problems.[1–5] Common entry routes into the human body include ingestion, inhalation, or dermal absorption. Two general forms of arsenic, organic and inorganic,[6] and a multitude of species[7–9] with differing toxicities[10,11] warrants the necessity to identify and quantify these As species in food, biological, and environmental samples.

Rice is a primary dietary staple for more than half of the world population.[12,13] It is an excellent scavenger for As compared to other staple crops.[14,15] Consumers are exposed to As either by consumption of grain or rice-based food products. Crowned as The World Health Organization's (WHO) top ten chemicals of major public health concern, WHO and the US Environmental Protection Agency (EPA) recommends a 10 μg L^{-1} limit for As in drinking water.[16,17] However, guidelines for rice are still in limbo. The Food and Agricultural Organization (FAO) and WHO in a joint committee for Food Standards Program on Contaminants in Foods, proposed to set a standard of total inorganic As in husked rice at 350 μg kg^{-1}.[18] A limit which is yet to be mandated by participating nations. The European Union regulation for maximum level of inorganic As (iAs) for brown rice was set at 250 μg kg^{-1}.[19] The Chinese National Food Safety Standard for Maximum Levels of Contaminants in Foods (GB 2762-2022) mandates maximum permissible limit of As in brown rice at 350 μg kg^{-1}.[20] The type of As species and its valency state in samples is responsible for the magnitude of As toxicity.[21,22] The lethality of iAs is apparent from the LD_{50} values 14, 20, 700–1800, 700–2600 respectively for As(III), As(V), MMA and DMA.[23] Thus, the determination of total As alone is insufficient to assess its damaging influence. Speciation is of paramount importance to ensure food safety and for ecological and human health risk assessment.

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While different analytical techniques such as electrochemical[24,25] or hyphenated instruments[26] exist for As speciation, to date, liquid chromatography paired with ICP-MS is the most frequently used approach.[27–29] First reported in 1980 (ref. 30) and commercialized three years later,[31] ICP-MS has evolved as a valuable asset for multielement determination at trace and ultra-trace levels owing to its high sensitivity, low detection limits, wide linear dynamic range, ability to provide isotopic information, and ease of coupling with other sample introduction systems.[32–34] Despite the widespread application of Ar-sustained ICP-MS, isobaric or polyatomic spectral interferences on isotopes arising from the sample matrix or plasma gas[35] often hinder accurate determination of elements of interest. Numerous strategies have been developed to mitigate spectral interferences for accurate elemental quantification during ICP-MS analysis,[36] such as the use of collision/reaction cells[37,38] or high resolution mass spectrometers.[39,40] Non-instrumental approaches such as mathematical corrections[41–43] or careful selection of interference-free isotopes for quantification are also common. However, drawbacks of these approaches include potential matrix dependence correction factors[44] and lack of alternative isotopes for monoisotopic elements such as As.

Over the years, several microwave-induced plasma (MIP) sources have been developed for trace-element analysis. Most of these MIPs have been used for atomic emission spectroscopy. Early MIPs, such as the Beenaker[45] cavity or Surfatron,[46] were sustained in Ar or He gas, and these low power plasmas tended to suffer from low sensitivity, low matrix tolerance, and inefficient vaporization or atomization of sample. Later, higher power N_2-sustained MIPs, such as the Okamota[47] and Hammer[48] designs, overcame many of these issues. MIPs used as an ion source for mass spectrometry are less common. The Okamota MIP was combined with MS and shown to have sensitivities and limits of detection (LODs) for most elements that were on-par with those of contemporary ICP-MS instruments.[40,48–50] The N_2-MICAP is a more recent microwave driven plasma source that was first reported in 2016 (ref. 51) and can be used to sustain a high-power plasma (1000–1500 W) in air or nitrogen. Operation details of the MICAP source have been reported.[51,52] In past research, the MICAP source has been combined with optical spectroscopy[51,53,54] or mass spectrometry.[52,55–57] This is the first report on application of N_2-MICAP ionization source combined with QMS and IC for the speciation analysis where Ar-related interferences can be a hindrance for accurate elemental analysis. The use of N_2-plasma is an effective way to eliminate interferences encountered during As analysis in high chloride content matrices *via* Ar-sustained ICP-MS. Furthermore, the ease of N_2 gas availability at reduced cost makes MICAP-MS analysis a more cost-efficient method. Cost benefit analysis was reported earlier.[52]

Experimental

All experiments described in this study were performed with Ar-sustained ICP-MS instrument (Aurora M90, Bruker Daltonics) or a prototype N_2-sustained MICAP-MS instrument (Analytik Jena, Germany). Both of these instruments have QMS and have very similar ion extraction, ion focusing, and ion detection systems.

Chemicals and reagents

Ultrapure water (resistivity 18.2 MΩ cm, PURELAB flex, Elga LabWater, UK) and trace metal grade nitric acid (HNO_3, Fisher Scientific, NJ, USA) further purified in house by sub-boiling distillation (DST-1000, Savillex Corp., MN, USA) were used as solvents for the preparation of all solutions, reagents, and standards. 12.5 mM and 135 mM ammonium carbonate ($(NH_4)_2CO_3$, Acros Organics, Fair Lawn, NJ, USA) solutions were used as mobile phase for As speciation and were prepared by dissolving the required amounts of the solute in 1% methanol (CH_3OH-HPLC grade, Fischer Scientific, Fair Lawn, NJ, USA). The pH of these solutions was adjusted to 8.7 by addition of ammonium hydroxide (NH_4OH, Fisher Scientific, Fair Lawn, NJ, USA) and/or HNO_3. Calibration standards ranging from 0.1 to 10 μg kg^{-1} in ultrapure water were prepared by serial dilution on the day of the experiment from As(III) and As(V) stock standards (As(III), As(V) Inorganic Ventures, Christiansburg, VA, USA), cacodylic acid (DMA 99% purity, Sigma-Aldrich, St. Louis, MO, USA), and MMA (99.5% purity, Chem Service Inc., West Chester, PA, USA). Arsenobetaine (AsB) standard solution NIST 3033 (National Institute of Standards and Technology, Gaithersburg, MD, USA) was used as the internal standard for all analyses. Method accuracy was validated with SRM rice flour NIST 1568b (National Institute of Standards and Technology, Gaithersburg, MD, USA). Matrix effects for As analysis were investigated with sodium chloride (NaCl, Fisher Scientific, Fair Lawn, NJ, USA) solutions from 1–10 000 mg L^{-1} in 1% HNO_3. Gas from the headspace of Dewars of industrial grade liquid Ar and liquid N_2 (Airgas Inc., USA) were used during ignition and operation of the MICAP, respectively.

Instrumentation

For As speciation analysis from rice samples, a liquid chromatography separation unit was connected to the MICAP-MS instrument. Data acquisition, processing, instrument control, and performance were monitored with Clarity chromatography software (version 8.7, DataApex, Prague, Czech Republic).

IC system

The IC system consists of AnalytikJena PQ LC S150 IC system with a PQ LC HPLC pump (model S1130) and PQ LC sample injector (model S5300) attached to a 100 μL sample loop. A Hamilton (Reno, NV, USA) PRP-X100 anion exchange column (Polyether Ether Ketone, PEEK, 150 × 4.6 mm, 5 μm particle size), was fitted to the IC system with PEEK tubing (inner diameter 0.25 mm) for separation of As species in samples studied. A Hamilton guard column (PEEK, 8 × 3 mm, 10 μm particle size) packed with the same support material was used to prevent contamination and prolong column life.

MICAP system

The MICAP ion source (Radom Corp., Pewaukee, WI, USA) system consists of a microwave (MW) magnetron powered by a 2 kV DC switch-mode power supply module (Magdrive 2000, Dipolar AB, Sweden). The magnetron generates a MW field (2.45

GHz) which is guided *via* an aluminum waveguide toward the dielectric resonator ring constructed from high density, high purity alumina (Al_2O_3). The MW field produces a bulk polarization current in the dielectric resonator, which induces a magnetic field that transfers energy to the plasma gas (*i.e.* N_2) and sustains the plasma. For plasma ignition, a small volume of Ar gas is used to aid in generation of a spark from an ignition coil to seed the plasma with free electrons. Once ignited, the plasma is sustained by N_2. A conventional ICP-MS Fassel torch (3-tube design, 20 mm outer diameter) is used to sustain and confine the MICAP, as well as inject nebulized aerosols into the plasma's base. A quartz bonnet at the end of the Fassel torch prevents backflow of hot plasma gas into the magnetron cavity; excess hot gas from the MICAP is directed through an exhaust shaft. A water-cooled copper plate sits outside the quartz bonnet to prevent MW leakage and allow 3D translation of the MICAP source. All parameters for optimal MICAP operation are controlled through ASpectMS software (Analytik Jena, Germany).

IC-MICAP coupling

A peristaltic pump was used to feed effluent from the IC column into a pneumatic nebulizer (MicroMist, Glass Expansion Inc., MA, USA) *via* PEEK tubing (inner diameter 0.25 mm). The nebulizer was combined with a double pass Scott spray chamber Peltier cooled to 3 °C. Sample aerosol was injected into the MICAP through a 2.4 mm diameter injector of a one-piece quartz ICP-MS torch (Analytik Jena).

MS system

Ions were extracted from the MICAP with a water-cooled platinum-tipped sampler cone (Analytik Jena PQMS Elite Pt, AU-109) and nickel skimmer cone in a two-stage differentially pumped extraction approach. All ion optical elements and mass spectrometer components are identical to that of the Ar-ICP-PQMS instrument (Analytik Jena PQMS Elite QMS). AspectMS was used for mass analyzer control, and to optimize ion lens voltages and plasma gas flows for maximum sensitivity. Optimum operating parameters applied for IC and MICAP-MS are summarized in Table 1.

Table 1 Operating parameters of IC and MICAP-MS for As speciation in rice samples

IC parameters	
Mobile phase	12.5 mM and 135 mM $(NH_4)_2CO_3$
Column	PRP-X 100
Elution mode	Gradient
Flow rate (mL min^{-1})	1.0
Run time (min)	10
Column temperature (°C)	30
Injection volume (μL)	100
MICAP-MS parameters	
Plasma flow (L min^{-1})	12.5
Auxiliary flow (L min^{-1})	1.20
Nebulizer flow (L min^{-1})	1.15
Sheath flow (L min^{-1})	0.25
Sampling depth (mm)	5.0
Plasma power (kW)	1.42
Pump rate (rpm)	50
Isotope measured	^{75}As
Ion optics	Optimized for highest $^{75}As^+$ intensity
Scan mode	Time resolved
Dwell time (ms)	200

Sample preparation

Collection and treatment

For As speciation analysis, eight varieties of white and colored rice (Fig. S1†) were purchased from local markets in Bangladesh. Mortar and pestle were used to pulverize the samples and each sample was dried in a laboratory oven at 70–80 °C to drive out residual water until a constant weight within 1% was obtained. The samples were cooled and preserved in pre-weighed centrifuge vials in a desiccator until further analysis.

Extraction procedure

Extraction efficiency influences quantification of As; optimization of different extraction procedures has been the focus of several studies.[58,59] Here, a mild acid hydrolysis extraction method was selected with the intention to reduce redox processes and preserve individual species. The FDA protocol described in Elemental Analysis Manual for Food and Related Products (EAM 4.11)[60] with some modifications was employed for As extraction and speciation in rice samples. In this method, approximately 1.0 g of ground rice samples were weighed with an analytical balance (ML204T/A00, Mettler Toledo, Switzerland) and then transferred into pre-weighed 30 mL PFA vials (Elemental Scientific Inc., Omaha, NE). To these sample vials, 10 mL 0.28 M HNO_3 was added followed by vortex mixing (Vortex-Genie 2T Model SI-T236, Scientific Industries, Inc., NY, USA). Vials were placed in a preheated digestion block system (Analab Model N-PLA3R-NA-1V15A, France) programmed at 95 °C for 90 min. Samples were then cooled to room temperature for 2–2.5 hours prior to addition of 6.7 g of ultrapure water. Each PFA vial's content was transferred into a 50 mL centrifuge vial and centrifuged (Eppendorf Centrifuge 5430, USA) at 3500 rpm for 10 min. Supernatant fluid was filtered through a 0.45 μm nylon syringe filter (VWR, USA) attached to a 5 mL disposable syringe and collected in a pre-weighed 50 mL centrifuge vial after discarding the first 1–2 mL to waste. Analytical blanks were prepared in the absence of rice with the identical extraction procedure.

Speciation analysis solutions

1 g of analytical blank and each rice sample extract for speciation of As(III), DMA, MMA and As(V), were weighed out in separate 15 mL centrifuge tubes. Each sample was diluted with 2 g of pH adjustment solution (pH 9.87). The pH adjustment solution was prepared by adding NH_4OH and/or HNO_3 to a 12.5 mM $(NH_4)_2CO_3$ solution until a target pH of 9.85 ± 0.05 was obtained; pH of the blank and rice extracts was adjusted to closely match that of the mobile phase. Mass added of pH adjustment solution was recorded with an analytical balance.

Arsenobetaine (the internal standard) was added to each solution to obtain a concentration of 1 μg kg^{-1}. Using a 1 mL disposable syringe, each pH-adjusted blank and rice-extract solute was transferred into individual 2 mL autosampler vials with a screw cap (Agilent 5182-0714 and 5182-0717, Santa Clara, CA, USA) by filtration through a 0.45 μm nylon syringe filter.

Total analysis solutions

Total As analysis solutions were prepared employing a similar methodology as for speciation analysis, but pH adjustment of the final solutions was not performed. To compensate for dilution, the pH adjustment solution was substituted by an equal amount of ultrapure water. Table S1† provides MICAP-MS parameters for total As analysis.

Results and discussion

MICAP-MS for arsenic analysis

A significant challenge for the analysis of As in chloride rich matrices by ICP-MS is the interference of $^{40}Ar^{35}Cl^+$ with $^{75}As^+$.[61,62] In Fig. 1, we report comparison data from As analysis in increasing concentrations of NaCl by ICP-MS and MICAP-MS. For both instruments, no appreciable matrix effect is visible until a concentration of ~0.1% w/w of the salt (NaCl). At higher salt concentration, As measurement *via* Ar-ICP-MS is overestimated owing to overlap of the $^{75}As^+$ with $^{40}Ar^{35}Cl^+$. In contrast, decreasing $^{75}As^+$ signal is observed for MICAP-MS analysis from matrix effect of easily ionized Na ions ($^{23}Na^+$).[54] In Fig. 2, we provide mass spectra (m/z 6–100) from the MICAP-MS instrument obtained during the analysis of a 1% w/w NaCl solution both with and without 10 μg L^{-1} As standard spiked into the salt solution. As seen, high $^{23}Na^+$ signal is observed; however, no interference on m/z 75 is apparent in the background MICAP-MS spectrum. While high NaCl concentration caused an attenuation

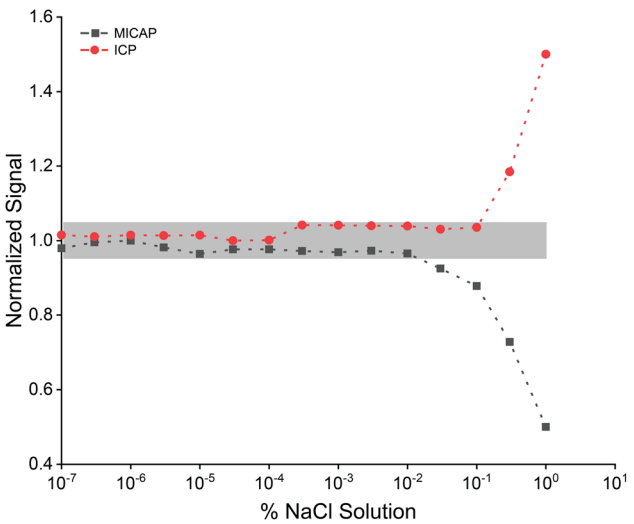

Fig. 1 ICP-MS and MICAP-MS comparison of 10 μg L^{-1} As standard in NaCl matrix to access the effect of chloride on As analysis. Shaded region shows ± 5% of the signal normalized to the As signal in 1% HNO_3 (*i.e.* with no NaCl).

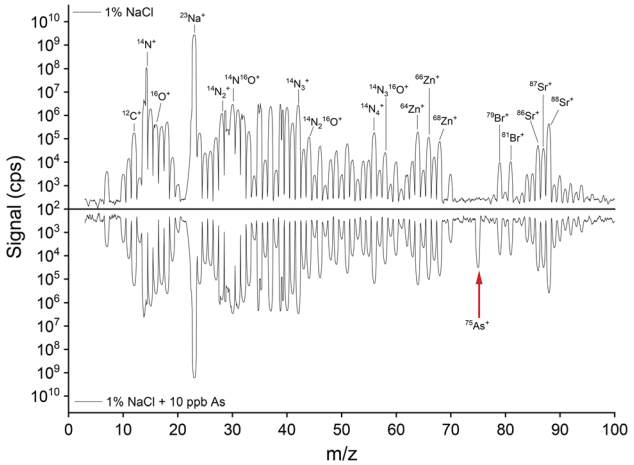

Fig. 2 Mass scan of 1% (w/w) NaCl solution in 1% HNO_3 (top figure). Bottom figure shows spectrum for 10 μg L^{-1} As standard spiked into the salt solution. High $^{23}Na^+$ signal is observed in both spectra. Other major background peaks are also labeled. Zn and, Br, Sr peaks in the mass scan are likely from trace contents of the NaCl.

Table 2 Detection and quantitation limits for As in NaCl matrix. Limits are computed using Excel STEYX function from calibration plots of 0.1–10 μg L^{-1} As in 0.0001–1% (w/w) solutions of NaCl in 1% HNO_3

NaCl concentration (% w/w)	LOD (μg L^{-1})	LOQ (μg L^{-1})
0.0001	0.18	0.55
0.001	0.17	0.51
0.01	0.16	0.49
0.1	0.14	0.43
1	0.17	0.51

of $^{75}As^+$ signals with the MICAP-MS, the detection limits (LODs) and limits of quantitation (LOQs) for As in various concentrations of NaCl solutions were unaffected, as reported in Table 2. LODs and LOQs for As were calculated as 3.3σ/slope and 10σ/slope of calibration plots in concentration range 0.1–10 μg L^{-1}, where σ represents the standard error of the responses for the analyte concentration in the regression line (coefficient $R^2 \geq 0.9998$) as determined by Excel STEYX function.

Both over- and under-estimation are detrimental to accurate As quantification. Over-estimation in ICP-MS As analysis generally arises from polyatomic $^{40}Ar^{35}Cl^+$ interfering with $^{75}As^+$ and complex procedures or mathematical corrections (described earlier) are applied for elimination or attenuation of such interferences. However, under-estimation from matrix effects during MICAP-MS analysis requires simpler measures such as matrix-matched calibration, standard addition and internal standard methods to negate effects of ion suppression on quantification.[63,64]

Method development for arsenic speciation in rice using IC-MICAP-MS

Both isocratic and gradient elutions for As speciation using different mobile phases have been reported.[29,65,66] In this study,

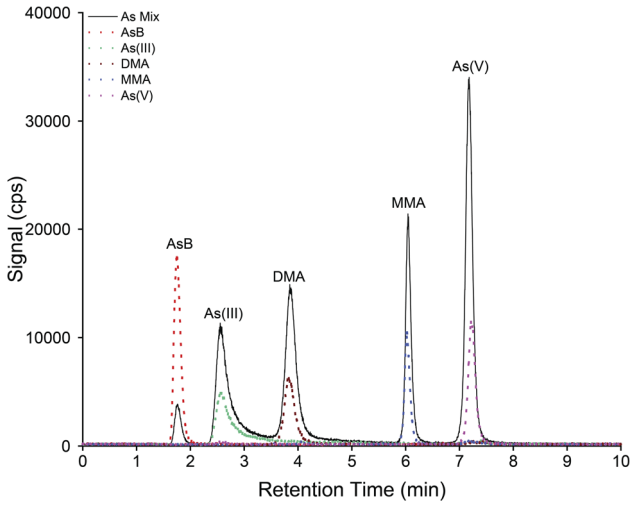

Fig. 3 Separation of As species from a multi-species mixture solution (*i.e.* "As mix") on a Hamilton PRP-X100 column accomplished with gradient elution program in Table 3. In the As mix, the concentrations of the analyte species were 10 μg L^{-1} for each As(III), DMA, MMA and As(V), which corresponds to As concentrations of 6.94, 5.35, 5.43, and 5.95 μg L^{-1}, respectively. The concentration of As in AsB was 1.0 μg L^{-1}. The overlay peaks, shown with dotted lines, are for the IC-MICAP-MS analysis of individual species to confirm retention times of the species. The concentrations are 5 μg L^{-1} for the As(III), DMA, MMA and As(V) species and 11.9 μg L^{-1} for AsB (*i.e.* 5 μg L^{-1} As as AsB).

a gradient elution was evaluated with mobile phases of 12.5 and 135 mM $(NH_4)_2CO_3$ solution in 1% MeOH. AsB was selected as the internal standard for the analysis, as it is not expected in rice.[67] The gradient method was developed using an As mix solution containing 1 μg L^{-1} AsB and 10 μg L^{-1} each of As(III), DMA, MMA and As(V). As shown in Fig. 3, baseline separation of all As species was achieved within a run time of 10 minutes using the optimized chromatographic program (Table 3). The difference in the anionic nature of the As species encourages competition with mobile phase ionic component for stationary phase sites in the anion exchange column. The quaternary ammonium functional group ($-N^+(CH_3)_3$) serves as stationary phase in the column, which interacts with negatively charged As species. The elution follows the order AsB, As(III), DMA, MMA and As(V) consistent with the species' acid dissociation constants (K_a)[65] (Table S2†) and charge states at the run buffer pH of 8.7, as has been previously reported.[59,65,68] The elution pattern was also confirmed from chromatograms of individual species under the same experimental conditions.

Arsenic species calibration

Calibration plots from 0.1–10 μg L^{-1} were constructed for each As species using standard solutions with three replicates per measurement. This concentration range spans the As species concentrations measured from the rice sample extracts. Linear response of the IC-MICAP-MS system is good with regression coefficient ≥0.9997. LODs and LOQs for each species are provided in Table 4. These values are about 1 order of magnitude higher in comparison to LODs and LOQs reported for ICP-MS,[60,69,70] which is likely due to higher *m*/*z*-non-specific background observed in the N_2-MICAP-MS.[52]

Arsenic speciation in rice samples

The experimental method developed was applied to quantify As species in SRM NIST 1568b rice flour. Recoveries for total iAs, DMA and MMA were 89, 85, and 110%, respectively (Table 5). Total iAs reported for the SRM is the sum of As(III) and As(V). This validates suitability of the method for As analysis in rice.

Table 6 shows As concentrations in several varieties of rice investigated with the optimized method. Each sample and SRM were analyzed in triplicate during the same session and analyte concentrations calculated from the integrated peak area of each species and their respective calibration plots and sample preparation. Calculation details are provided in FDAs EAM 4.11.[60] To assess possible instrument contamination, blank and calibration samples were analyzed after every three different rice varieties. All rice samples investigated show presence of As species as As(III), DMA, MMA, and As(V), except in Topa Bora, from which MMA was not detected. Contrary to reports that brown rice is usually higher in As content,[71,72] white Kotok rice was found to have the highest total As concentration. This can be attributed to the unknown source of the sample; the Kotok variety may have been produced in a higher As contaminated zone. Arsenic finds its path into rice grains *via* contaminated soil and water during irrigation.[73,74] Variability and quantity of the different species occurring in the grain is influenced by region of growth rather than rice variety.[75] Concentrations of total iAs, As(III) and As(V), in all samples studied were found to be higher than the total organic counterparts, DMA and MMA. Although a mild extraction method was employed to prevent species transformation from redox processes, As(III) and As(V) quantified in rice samples could not be individually validated owing to lack of certified standards.

Table 3 Gradient elution program for ion chromatographic separation of As species with anion exchange column PRP-X100

Time (min)	12.5 mM $(NH_4)_2CO_3$ (%)	135 mM $(NH_4)_2CO_3$ (%)
Initial	100	0
1.00	100	0
1.50	30	70
9.00	30	70
9.50	100	0
10.0	100	0

Table 4 Detection and quantitation limits of As in As species separated on PRP-X100 column using MICAP-MS. Limits were computed from calibration plots in range 0.1–10 μg L^{-1} using Excel STEYX function

As species	LOD (μg L^{-1})	LOQ (μg L^{-1})
As(III)	0.26	0.80
DMA	0.26	0.81
MMA	0.13	0.40
As(V)	0.22	0.67

Table 5 IC-MICAP-MS arsenic analysis ($n = 3$) for SRM NIST 1568b rice flour. Mean values are reported as concentration of As in each species ± standard deviation. Certified values are expressed as concentration ± expanded uncertainty at 95% confidence level. Total iAs is the sum As(III) and As(V)

	As(III)	DMA	MMA	As(V)	Total iAs
Mean (μg kg^{-1})	47.2 ± 1.7	153.7 ± 1.3	12.8 ± 0.1	34.9 ± 1.9	82.1 ± 1.8
Certified values (μg kg^{-1})	—	180.0 ± 12.0	11.6 ± 3.5	—	92.0 ± 10
% Recovery	—	85.4 ± 0.7	110.6 ± 0.4	—	89.1 ± 0.2

Table 6 Arsenic species in rice samples reported as concentration of As in each species ± standard deviation for triplicate measurements. ND = not detected

	As concentration (μg kg^{-1}) in rice					
Rice	As(III)	DMA	MMA	As(V)	Sum[a]	Total[b]
Kotok	175.8 ± 3.4	62.6 ± 0.3	6.4 ± 0.1	110.2 ± 3.6	355.0 ± 7.4	337.4 ± 2.0
Katari	57.2 ± 1.3	36.7 ± 0.4	4.1 ± 0.1	34.6 ± 0.7	132.6 ± 2.5	123.0 ± 1.0
Kala Manik	61.7 ± 0.5	8.1 ± 0.4	6.9 ± 0.6	49.6 ± 1.0	126.3 ± 2.5	145.4 ± 0.6
Hijol Digha	27.0 ± 0.5	83.1 ± 2.5	5.7 ± 0.2	66.5 ± 0.4	182.3 ± 3.6	184.8 ± 1.2
Bawla Digha	160.1 ± 1.1	70.0 ± 0.6	5.4 ± 0.1	115.0 ± 1.0	350.5 ± 2.8	321.0 ± 1.0
Maita Koral	58.2 ± 0.3	20.3 ± 1.0	4.6 ± 0.2	63.9 ± 0.7	147.0 ± 2.2	139.4 ± 1.2
Topa Bora	84.2 ± 0.6	24.1 ± 0.6	ND	122.0 ± 0.6	230.3 ± 1.8	208.2 ± 2.5
Chamara	43.0 ± 1.7	56.5 ± 0.9	1.7 ± 0.1	60.7 ± 0.5	161.9 ± 3.2	165.5 ± 1.2
NIST 1568b	47.2 ± 1.7	153.7 ± 1.3	12.8 ± 0.1	34.9 ± 1.9	248.6 ± 5.0	268.8 ± 1.7

[a] Combined value for concentration of As in As(III), DMA, MMA, and As(V) from IC-MICAP-MS analysis. [b] Total As concentration in samples as determined by direct analysis with MICAP-MS.

Total arsenic in rice using MICAP-MS

Total As in each rice sample was analyzed with MICAP-MS for comparison with total As (sum of all species) from speciation method. Total As concentration was calculated from calibration plots (0.1–10 μg L^{-1}) of As standard solutions. In each rice sample, the total arsenic concentration was in good agreement, as seen from Table 6.

Conclusion

The need to develop a robust, validated analytical and economic method for As analysis in rice grain prompted this study. Arsenic analysis is a challenging task requiring careful species extraction, speciation, detection, quantification and validation of method. We demonstrated that a N_2-sustained MICAP ionization source combined with QMS can be used to provide a fit-for-purpose analysis of As. As demonstrated in this study, spectral overlap between $^{40}Ar^{35}Cl^+$ and $^{75}As^+$, which is a typical hindrance during analysis of As with ICP-MS, is obviated using a N_2-sustained plasma source. MICAP-MS simplifies As analysis by eliminating need for tedious and often expensive procedures (collision/reaction cells, high resolution instruments, mathematical corrections) to overcome $^{40}Ar^{35}Cl^+$ interferences in chloride rich matrices. An interference free method makes MICAP-MS an attractive instrument for As analysis *versus* the traditionally used ICP-MS.

Owing to its lower operation cost, ease of gas accessibility, and design simplicity, N_2-based MICAP-MS can be a promising replacement for the Ar-based ICP-MS for elements which exhibit Ar interferences. Some potential applications of MICAP-MS are As analysis in biological samples such as nails, blood, and urine samples. The instrument could also be conveniently applied for measurements of $^{40}Ca^+$, $^{56}Fe^+$, and $^{80}Se^+$ ions which overlap with $^{40}Ar^+$, $^{40}Ar^{16}O^+$, and $^{40}Ar_2{}^+$ ions in Ar-ICP-MS. However, application of MICAP-MS for measurement of elements interfering with N_2 species *e.g.* ^{28}Si ($^{14}N_2{}^+$), ^{29}Si ($^{14}N^{15}N^+$, $^{14}N_2{}^1H^+$), and ^{30}Si ($^{15}N_2{}^+$, $^{14}N^{15}N^1H^+$, $^{14}N^{16}O^+$) remain a challenge.

Conflicts of interest

There are no conflicts to declare.

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