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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 mol L^{-1} $HClO_4$ and silver-containing 0.15 mol L^{-1} HNO_3 were also developed.

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 mol L^{-1} 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 mol L^{-1} 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 HNO_3–H_2O_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 HNO_3 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} $HClO_4$ and Ag-containing 0.15 mol L^{-1} HNO_3 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 C_{18} 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-butanesulfonate/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 As_2O_3 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 HNO_3 (60.0%) and 2 mL of H_2O_2 (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 HNO_3 (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.

2.5. Materials

We previously reported on the arsenic speciation analysis of multiple rice samples (white and brown rice) [21–24]. To investigate extraction characteristics of arsenic species in the present study, three rice flour samples were selected, which were considered to cover a wide range of extraction and chemical species characteristics. The particle size of each sample powder was less than 100 μm diameter.

The total arsenic concentrations in sample A (polished rice, NMIJ CRM 7503-a white rice flour, certified value of total arsenic (0.098 ± 0.007) mg kg^{-1}; in this case, the figure following $\pm$ value indicates the expanded uncertainty with $k=2$; k indicates the coverage factor), and samples B and C (unpolished rice, brown rice flour) were determined by ICP-MS after microwave-assisted digestion with HNO_3–H_2O_2 (maximum temperature: 240 °C). The concentrations (hereinafter unless otherwise stated, each figure following $\pm$ indicates the standard deviation, $n=6$; n indicates the number of the measurements) for samples A, B and C were (0.096 ± 0.002) mg kg^{-1}, (0.316 ± 0.004) mg kg^{-1} and (0.618 ± 0.008) mg kg^{-1}, respectively (Table 1). To validate the analytical procedure, NMIJ CRM 7531-a (brown rice flour, certified value of total arsenic (0.280 ± 0.009) mg kg^{-1}; $k=2$) was also analyzed, and the determined arsenic concentration of (0.285 ± 0.002) mg kg^{-1} ($n=6$) was in good agreement with the certified value.

3. Results and discussion

3.1. Extraction characteristic of arsenic species

Combinations of extraction methods (extracting solvent/techniques) were used to investigate the extraction properties of arsenic species. In microwave-assisted heating extraction, the instrument was used at 90 °C, whereas the dry block heating system, used for heat block extraction, was operated at 100 °C.

The results of arsenic speciation of samples A, B and C with water/microwave extraction, water/heat block extraction, 0.0015 mol L^{-1} HNO_3/microwave extraction and 0.15 mol L^{-1} HNO_3/heat block extraction are shown in Table 1. As(III), As(V) and DMAA were detected in extracts of all three samples, but MMAA and AsB were not detected. Therefore, AsB was used as an internal standard in order to accommodate sensitivity changes during analysis resulting from physical interference because of the viscosity of the sample.

For sample A, the results for As(III), As(V) and DMAA using water/microwave extraction were in agreement with those obtained using 0.15 mol L^{-1} HNO_3/heat block extraction. And, the sum of the concentrations of extracted arsenic species agreed well with the concentration of total arsenic obtained by microwave-assisted digestion of the sample.

However, the amounts extracted from samples B and C using the water/heat block extraction method were approximately 5% lower than the total arsenic concentrations obtained by digestion of the samples. For each sample the result for DMAA agreed with those from 0.15 mol L^{-1} HNO_3/heat block extraction, but the result for inorganic arsenic was 5% lower. When 0.0015 mol L^{-1} HNO_3/microwave extraction was used, the sum of the concentrations of extracted arsenic was approximately 99% of the concentration of total arsenic from analysis after digestion. Each concentration of As (V) in the extract was close between 0.0015 mol L^{-1} HNO_3/microwave extraction and water/heat block extraction. Each proportion between the concentrations of As(III) and As(V) in the 0.15 mol L^{-1} HNO_3/heat block extraction was different from that in the 0.0015 mol L^{-1} HNO_3/microwave extraction. Probably, a portion of As(V) was changed to As(III) in the 0.15 mol L^{-1} HNO_3/heat block extraction.

To examine the possibility of occurrence of oxidation–reduction reaction due to differences of acid dissociation, the pH values of the extracts were measured. The pH values of water extractions, regardless of sample, ranged from 5.2 to 6.0, and the pH values of extracts made with 0.15 mol L^{-1} HNO_3 were approximately 1.3–1.9. There were no differences between the pH values of the extracts of samples A, B and C made with 0.15 mol L^{-1} HNO_3/heat block extraction. Thus, the change of chemical species during extraction depended on the extracting solvents and also on differences among rice flour samples resulting from, for example, sample components (coexisting substances).

3.2. Extraction efficiencies of different solvents

The efficiencies of different solvents to extract the various arsenic species, and their tendencies to alter the proportions of the arsenic species during extraction were investigated using sample B.

The following solvents were used to extract portions of sample B: (0.0015–0.30) mol L^{-1} HNO_3, (0.0015–0.30) mol L^{-1} HCl, (0.0015–0.30) mol L^{-1} H_2SO_4, (0.010–0.50) mol L^{-1} $HClO_4$, (0.10–0.50) mol L^{-1} H_2O_2, (0.010–0.50) mol L^{-1} HBr, (0.010–0.50) mol L^{-1} H_3PO_4, (0.010–1.0) mol L^{-1} formic acid, (0.010–0.10) mol L^{-1} methansulfonate acid, (0.010–2.0)% (mass fraction) tetramethylammonium hydroxide (TMAH) and (0.050–0.50) mol L^{-1} NH_4NO_3. The extracted arsenic species were analyzed by HPLC–ICP-MS. The following extraction conditions were used in each case: sample mass 0.5 g, solvent mass 2 g, heating temperature 100 °C for 2 h using the dry heating block system. The results are shown in Table 2. Water is the best solvent for suppressing or eliminating oxidation–reduction reactions; therefore, the results

Table 1
Results of As speciation of three rice flour samples.

ID	Extracting solvent	Technique	As(V) (mg kg^{-1})	As(III) (mg kg^{-1})	i-As (mg kg^{-1})	DMAA (mg kg^{-1})	Sum[a] (mg kg^{-1})	pH	Total As[b] (mg kg^{-1})	Recovery[c] (%)
Sample A	Water	Microwave	0.0130 ± 0.0005	0.0711 ± 0.0008	0.0844 ± 0.0013	0.0131 ± 0.0004	0.0975 ± 0.0014	5.30	0.096 ± 0.002	101.6
	0.15 mol L^{-1} HNO_3	Heat block	0.0133 ± 0.0005	0.0717 ± 0.0007	0.0850 ± 0.0012	0.0130 ± 0.0005	0.0980 ± 0.0017	1.32	0.096 ± 0.002	102.1
Sample B	Water	Heat block	0.0564 ± 0.0013	0.2248 ± 0.0034	0.2812 ± 0.0047	0.0186 ± 0.0010	0.2997 ± 0.0058	5.29	0.316 ± 0.004	94.8
	0.0015 mol L^{-1} HNO_3	Microwave	0.0571 ± 0.0013	0.2375 ± 0.0005	0.2946 ± 0.0017	0.0185 ± 0.0001	0.3131 ± 0.0017	4.62	0.316 ± 0.004	99.1
	0.15 mol L^{-1} HNO_3	Heat block	0.0380 ± 0.0001	0.2598 ± 0.0027	0.2978 ± 0.0029	0.0189 ± 0.0001	0.3167 ± 0.0030	1.34	0.316 ± 0.004	100.2
Sample C	Water	Heat block	0.1047 ± 0.0036	0.3923 ± 0.0047	0.4970 ± 0.0084	0.0885 ± 0.0014	0.5855 ± 0.0098	5.94	0.618 ± 0.008	94.7
	0.0015 mol L^{-1} HNO_3	Microwave	0.1054 ± 0.0036	0.4173 ± 0.0047	0.5227 ± 0.0084	0.0898 ± 0.0084	0.6125 ± 0.0098	4.53	0.618 ± 0.008	99.1
	0.15 mol L^{-1} HNO_3	Heat block	0.0656 ± 0.0035	0.4627 ± 0.0065	0.5283 ± 0.0101	0.0894 ± 0.0015	0.6177 ± 0.0116	1.91	0.618 ± 0.008	100.0

[a] Sums of the concentration of As(III), As(V) and DMAA, figure following $\pm$ indicates the standard deviation, $n=6$.
[b] Determination result after microwave-assisted digestion.
[c] (Sum/total As) × 100.

Table 2
Dependencies of extraction behaviors of As species on extracting solvents with heat block extraction method.

Extracting solvent	Concn. of extracting solvent ($mol\ L^{-1}$)	As(V) ($mg\ kg^{-1}$)	As(III) ($mg\ kg^{-1}$)	i-As ($mg\ kg^{-1}$)	DMAA ($mg\ kg^{-1}$)	Sum[a] ($mg\ kg^{-1}$)	pH (%)	Recovery[b]
HNO_3	0.30	0.0309 ± 0.0009	0.2679 ± 0.0025	0.2988 ± 0.0044	0.0188 ± 0.0002	0.3176 ± 0.0002	1.76	100.5
	0.15	0.0380 ± 0.0004	0.2598 ± 0.0026	0.2978 ± 0.0021	0.0189 ± 0.0002	0.3167 ± 0.0019	1.34	100.2
	0.075	0.0475 ± 0.0014	0.2516 ± 0.0050	0.2992 ± 0.0054	0.0190 ± 0.0002	0.3181 ± 0.0033	2.37	100.7
	0.030	0.0589 ± 0.0018	0.2359 ± 0.0071	0.2947 ± 0.0063	0.0186 ± 0.0004	0.3133 ± 0.0046	3.60	99.1
	0.015	0.0581 ± 0.0017	0.2360 ± 0.0094	0.2941 ± 0.0074	0.0188 ± 0.0004	0.3129 ± 0.0050	4.53	99.0
	0.0015	0.0571 ± 0.0034	0.2375 ± 0.0071	0.2946 ± 0.0099	0.0185 ± 0.0004	0.3131 ± 0.0061	4.62	99.1
HCl	0.30	0.0226 ± 0.0009	0.2890 ± 0.0087	0.3116 ± 0.0078	0.0187 ± 0.0006	0.3303 ± 0.0064	1.88	104.5
	0.15	0.0241 ± 0.0012	0.2693 ± 0.0081	0.2934 ± 0.0086	0.0183 ± 0.0009	0.3117 ± 0.0090	1.91	98.6
	0.015	0.0570 ± 0.0017	0.2350 ± 0.0047	0.2920 ± 0.0053	0.0185 ± 0.0007	0.3105 ± 0.0068	3.65	98.3
	0.0015	0.0548 ± 0.0027	0.2336 ± 0.0093	0.2884 ± 0.0092	0.0189 ± 0.0011	0.3074 ± 0.0105	3.75	97.3
H_2SO_4	0.30	0.0270 ± 0.0011	0.2776 ± 0.0083	0.3047 ± 0.0076	0.0186 ± 0.0006	0.3233 ± 0.0063	1.72	102.3
	0.15	0.0316 ± 0.0016	0.2688 ± 0.0081	0.3004 ± 0.0088	0.0183 ± 0.0009	0.3187 ± 0.0092	1.73	100.9
	0.015	0.0548 ± 0.0016	0.2380 ± 0.0048	0.2928 ± 0.0053	0.0185 ± 0.0007	0.3113 ± 0.0068	2.56	98.5
	0.0015	0.0554 ± 0.0028	0.2332 ± 0.0093	0.2886 ± 0.0092	0.0182 ± 0.0011	0.3069 ± 0.0104	2.68	97.1
$HClO_4$	0.50	0.0338 ± 0.0003	0.2647 ± 0.0026	0.2984 ± 0.0021	0.0188 ± 0.0002	0.3172 ± 0.0019	1.39	100.4
	0.10	0.0578 ± 0.0012	0.2396 ± 0.0024	0.2974 ± 0.0033	0.0186 ± 0.0002	0.3161 ± 0.0024	2.10	100.0
	0.050	0.0571 ± 0.0009	0.2407 ± 0.0024	0.2978 ± 0.0028	0.0189 ± 0.0003	0.3166 ± 0.0056	2.69	100.2
	0.010	0.0570 ± 0.0011	0.2476 ± 0.0025	0.2946 ± 0.0033	0.0187 ± 0.0004	0.3133 ± 0.0036	3.75	99.1
H_2O_2	0.50	0.2982 ± 0.0060	0.0003 ± 0.0001	0.2985 ± 0.0060	0.0189 ± 0.0006	0.3174 ± 0.0057	3.00	100.5
	0.20	0.2943 ± 0.0059	0.0003 ± 0.0001	0.2947 ± 0.0059	0.0191 ± 0.0008	0.3138 ± 0.0070	4.17	99.3
	0.10	0.2885 ± 0.0058	0.0057 ± 0.0005	0.2942 ± 0.0059	0.0186 ± 0.0006	0.3128 ± 0.0056	4.59	99.0
HBr	0.50	0.0293 ± 0.0006	0.2673 ± 0.0027	0.2967 ± 0.0033	0.0187 ± 0.0004	0.3153 ± 0.0036	1.45	99.8
	0.30	0.0309 ± 0.0008	0.2735 ± 0.0017	0.3044 ± 0.0039	0.0189 ± 0.0005	0.3234 ± 0.0079	1.67	102.3
	0.10	0.0339 ± 0.0013	0.2614 ± 0.0027	0.2953 ± 0.0057	0.0188 ± 0.0000	0.3141 ± 0.0044	2.25	99.4
	0.050	0.0583 ± 0.0015	0.2363 ± 0.0036	0.2946 ± 0.0045	0.0187 ± 0.0005	0.3134 ± 0.0034	2.92	99.2
	0.030	0.0562 ± 0.0015	0.2397 ± 0.0036	0.2959 ± 0.0045	0.0188 ± 0.0005	0.3147 ± 0.0034	3.81	99.6
	0.010	0.0494 ± 0.0013	0.2412 ± 0.0037	0.2905 ± 0.0044	0.0188 ± 0.0005	0.3093 ± 0.0033	4.56	97.9
H_3PO_4	0.50	0.0420 ± 0.0013	0.2456 ± 0.0074	0.2875 ± 0.0061	0.0189 ± 0.0006	0.3064 ± 0.0056	1.73	97.0
	0.10	0.0465 ± 0.0019	0.2384 ± 0.0072	0.2849 ± 0.0071	0.0194 ± 0.0006	0.3043 ± 0.0059	2.16	96.3
	0.050	0.0446 ± 0.0019	0.2395 ± 0.0082	0.2841 ± 0.0077	0.0191 ± 0.0007	0.3032 ± 0.0044	2.39	96.0
	0.025	0.0430 ± 0.0017	0.2456 ± 0.0074	0.2886 ± 0.0072	0.0193 ± 0.0004	0.3079 ± 0.0049	2.90	97.4
	0.010	0.0456 ± 0.0014	0.2325 ± 0.0070	0.2781 ± 0.0059	0.0179 ± 0.0004	0.2961 ± 0.0043	4.16	93.7
Formic acid	1.0	0.0429 ± 0.0017	0.2516 ± 0.0126	0.2945 ± 0.0094	0.0193 ± 0.0010	0.3138 ± 0.0093	2.35	99.3
	0.50	0.0464 ± 0.0019	0.2538 ± 0.0102	0.3001 ± 0.0085	0.0193 ± 0.0008	0.3194 ± 0.0078	2.55	101.1
	0.30	0.0447 ± 0.0020	0.2562 ± 0.0137	0.3009 ± 0.0105	0.0194 ± 0.0009	0.3204 ± 0.0093	2.72	101.4
	0.10	0.0485 ± 0.0024	0.2517 ± 0.0101	0.3002 ± 0.0096	0.0199 ± 0.0002	0.3201 ± 0.0054	3.14	101.3
	0.050	0.0474 ± 0.0019	0.2491 ± 0.0100	0.2966 ± 0.0084	0.0194 ± 0.0004	0.3159 ± 0.0055	3.38	100.0
	0.010	0.0425 ± 0.0013	0.1946 ± 0.0058	0.2371 ± 0.0050	0.0199 ± 0.0002	0.2570 ± 0.0030	4.63	81.3
Methansulfonate acid	0.10	0.0361 ± 0.0021	0.2673 ± 0.0025	0.3034 ± 0.0089	0.0187 ± 0.0002	0.3221 ± 0.0050	1.91	101.9
	0.050	0.0386 ± 0.0004	0.2544 ± 0.0025	0.2930 ± 0.0021	0.0198 ± 0.0002	0.3129 ± 0.0019	2.28	99.0
	0.030	0.0544 ± 0.0016	0.2459 ± 0.0049	0.3004 ± 0.0054	0.0187 ± 0.0002	0.3191 ± 0.0033	2.24	101.0
	0.010	0.0547 ± 0.0016	0.2334 ± 0.0070	0.2881 ± 0.0061	0.0186 ± 0.0004	0.3067 ± 0.0045	4.33	97.0
TMAH	2.0	0.2391 ± 0.0120	0.0581 ± 0.0029	0.2972 ± 0.0105	0.0091 ± 0.0005	0.3063 ± 0.0094	12.34	96.9
% (Mass fraction)	0.10	0.0555 ± 0.0022	0.2398 ± 0.0096	0.2953 ± 0.0084	0.0159 ± 0.0006	0.3112 ± 0.0076	5.64	98.5
	0.050	0.0444 ± 0.0018	0.2323 ± 0.0093	0.2767 ± 0.0078	0.0166 ± 0.0007	0.2932 ± 0.0072	6.13	92.8
	0.010	0.0472 ± 0.0014	0.2353 ± 0.0071	0.2824 ± 0.0060	0.0173 ± 0.0005	0.2998 ± 0.0055	5.51	94.9
NH_4NO_3	0.50	0.0503 ± 0.0020	0.1897 ± 0.0057	0.2400 ± 0.0060	0.0181 ± 0.0005	0.2581 ± 0.0050	5.31	81.7
	0.25	0.0620 ± 0.0025	0.1923 ± 0.0058	0.2543 ± 0.0064	0.0188 ± 0.0006	0.2731 ± 0.0053	5.31	86.4

	0.10	0.0472 ± 0.0024	0.1861 ± 0.0056	0.2334 ± 0.0068	0.0186 ± 0.0006	0.2520 ± 0.0053	5.46	79.7
	0.050	0.0399 ± 0.0020	0.1624 ± 0.0049	0.2023 ± 0.0059	0.0184 ± 0.0006	0.2207 ± 0.0046	4.58	69.8
HNO_3 [c]	See text	0.2988 ± 0.0030	N.D	0.2988 ± 0.0015	0.0188 ± 0.0004	0.3176 ± 0.0033		100.5
HNO_3-H_2O_2 [c]	See text	0.2969 ± 0.0059	N.D	0.2969 ± 0.0030	0.0191 ± 0.0004	0.3161 ± 0.0035		100.0
HNO_3-$HClO_4$ [c]	See text	0.2964 ± 0.0089	N.D	0.2964 ± 0.0044	0.0181 ± 0.0004	0.3145 ± 0.0039		99.5

[a] Sums of the concentration of As(III), As(V) and DMAA.
[b] Sum/total As × 100.
[c] Microwave assisted digestion method.

for each of the other solvents were compared those for water. The amounts of DMAA extracted were constant for all solvents tested (except in the case of TMAH).

When 0.0015 mol L^{-1} HNO_3 was used, the results for As(V) and As(III) were (0.0571 ± 0.0013) mg kg^{-1} (n=3) and (0.2375 ± 0.0005) mg kg^{-1} (n=3), respectively; for water extraction the results for As(V) and As(III) were (0.0564 ± 0.0013) mg kg^{-1} (n=3) and (0.2248 ± 0.0034) mg kg^{-1} (n=3), respectively, and the total extraction rate was 94.8%. The results for As(V) and DMAA agreed with each other, but that for As(III) with water extraction was lower; therefore, the total extraction efficiency was lower. When (0.075–0.3) mol L^{-1} HNO_3 was used, approximately 100% was extracted, but with increasing HNO_3 concentration, the amount of As(V) decreased and that of As(III) increased.

Extractions with HCl and H_2SO_4 were similar to those with HNO_3, with efficiencies depending on acid concentration; however, repeatability for each species was worse and analytical precisions became poorer.

Approximately 100% extractions were achieved with (0.01–0.5) mol L^{-1} $HClO_4$. No decrease in the amounts of As(V) extracted was observed for (0.01–0.1) mol L^{-1} $HClO_4$, and there was no tendency of a change in the proportions of the concentrations of As(III) and As(V).

Approximately 100% extractions were also achieved with (0.1–0.5) mol L^{-1} H_2O_2, although almost all As(III) was oxidized to As(V). Thus, inorganic arsenic was observed as As(V).

Extractions of approximately 100% were observed with (0.03–0.5) mol L^{-1} HBr, but the amount of As(V) dropped sharply at more than 0.01 mol L^{-1} HBr.

Extracted arsenic species were constant with (0.025–0.5) mol L^{-1} H_3PO_4, and it was the solvent that had the least effect on the species. However, the concentrations of As(V) were always lower than those with other solvents, and the total extraction rates were (97 ± 1)%.

Formic acid is usually an excellent solvent for organic matter, and it is used to dissolve food and biological samples [27]. In the extraction of rice flour, extraction rates of about 100% for (0.05–1.0) mol L^{-1} formic acid were observed. However, As(V) amounts were lower and As(III) amounts higher than those with other solvents; presumably a portion of As(V) was changed to As(III) in the extraction process. In addition, the influence of the solvent was large at the measurement stage; in particular, the top of the DMAA peak was split and there was a tendency to record high DMAA concentrations. Furthermore, when 1.0 mol L^{-1} formic acid was used, the retention times of the peaks of arsenic species were 30 s late compared with the case when water was used.

Methanesulfonic acid is excellent for extracting selenium compounds from biological and food samples [28,29]. At the concentrations of (0.05–0.1) mol L^{-1}, it extracted (100 ± 1)% of the arsenic in rice flour. However, the amount of As(V) decreased and that of As(III) increased with increasing acid concentration, as was the case with HNO_3.

TMAH is an alkaline reagent and its extracts will be alkaline. Therefore, the retention times of arsenic species were changed significantly when 2% (mass fraction) TMAH was used for extraction. When (0.01–0.1)% (mass fraction) were used, the peak positions did not differ from those observed when water was used. There was a tendency of increasing the concentration of As(V) with increase in TMAH concentration; oxidation of As(III) occurred under the alkaline conditions. The extraction rates of DMAA and the total extraction were reduced significantly.

In order to study the behavior of As(V) in the HNO_3 solvent, that is, to determine if the observed effect depends upon the acid concentration or the nitrate ion concentration, NH_4NO_3 was also tested as a solvent. In this case, although it was possible to extract at neutral pH, extraction rates were only 70–80%. Thus, the effect of acid concentration is a greater factor, at least, in the total extraction rate.

When the acid concentration was decreased, the nature of the solvent becomes close to water, and the extraction rates might be expected to approach those observed when water was used. However, the extraction behaviors did not always become close to water and the reason is not yet clear. Some additional work is necessary to solve the issue.

In summary, when the peak shapes of the chromatograms, extraction rates, repeatabilities and analytical precision were considered, (0.075–0.30) mol L^{-1} HNO_3, (0.050–0.50) mol L^{-1} $HClO_4$, (0.1–0.5) mol L^{-1} H_2O_2, (0.030–0.50) mol L^{-1} HBr and (0.03–0.10) mol L^{-1} methanesulfonic acid were useful because extraction rates (100 ± 1)% were achieved. However, the detected amounts of As(III) and As(V) differed under each condition.

3.3. Arsenic speciation following acid digestion

A portion of the powdered sample (0.5 g) was weighed and 7 mL HNO_3 (60.0%), 5 mL HNO_3 (60.0%)–2 mL H_2O_2 (30.0%) or 5 mL HNO_3 (60.0%)–2 mL $HClO_4$ (61.0%) were added, and a mild microwave-assisted digestion was carried out. The maximum heating temperature (200 °C) was set lower than that when the purpose of the digestion was the determination of total arsenic. The sample was then evaporated to dryness on a hot plate at 160 °C and the residue was dissolved in water. This procedure caused complete dissolution of the sample and no remainder was left. In addition, DMAA was not decomposed under these heating conditions [30]. In the three cases, the oxidizing powers of the acids were strong and all inorganic arsenic was detected as As(V). Therefore, when HPLC–ICP-MS analyses were made, only As (V) and DMAA were determined (Table 2). Thus, the results for inorganic arsenic and DMAA were similar to those obtained following HNO_3/heat block extraction.

3.4. Influence of coexisting substances and prevention of changes in the proportions of As(III) and As(V) occurring during extraction

To investigate possible components of sample A that prevented species from changing during extractions, and those of samples B and C that allowed or promoted changes, elemental analysis and amino acid analysis were carried out.

The amounts and the distributions of elements in polished rice and unpolished rice are different; many metallic elements are present in the outer layers [24]. Therefore, the concentrations of metallic elements in sample A were quite different from those in samples B and C, although there was no significant difference in the amino acid contents.

To investigate substances that might cause a change in the proportions of As(III) and As(V) during extraction, each of the following 26 elements (nitrates of Ag, Al, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn, boric acid of B or potassium salts of Cl, Br, I; 20 μg in each case) was independently added to a different 2 g portion of sample A (to give 10 mg kg^{-1}), and 0.15 mol L^{-1} HNO_3/heat block extraction was carried out. Only the addition of KI reduced some of As(V) to As(III) (Table 3). Additions of other elements (salts) produced no changes. Therefore, in the reduction of As(V) to As(III), a role of I^- was suggested. Many other substances that might cause oxidation–reduction reactions, such as vitamins and other organic compounds are contained in rice grains; therefore, other factors could also be considered as causative agents, but we focused on halides, especially I^-.

The concentrations of Cl^-, Br^-, I^-, NO_2^-, NO_3^- and SO_4^{2-} in samples A, B and C were determined by ion chromatography after alkali fusion. Br^-, NO_2^- and NO_3^- were not detected in any samples. SO_4^{2-} was found in all samples, but concentrations were about 200 mg kg^{-1} in all samples. The concentrations of Cl^- in sample A, B and C were 91.6 mg kg^{-1}, 254.4 mg kg^{-1} and 253.0 mg kg^{-1}, respectively; this could not explain the difference of tendency of As(V) reduction among the three rice samples. The concentrations of I^- in samples A, B and C were 8.38 mg kg^{-1}, 14.51 mg kg^{-1} and 20.04 mg kg^{-1}, respectively, by ion chromatography. When these amounts were compared with the results of arsenic speciation in Table 1, the extent of reduction of As(V) to As(III) increased with increasing amounts of I^- in the samples under the extraction condition of 0.15 mol L^{-1} HNO_3/heat block extraction.

The reaction of As(V) with I^- is given in Eq. (1); As(III) is produced. Thus, As(III) could be produced during the extraction process.

$$AsO_4^{3-}[As(V)] + 2I^- + 2H^+ \rightarrow AsO_3^{3-}[As(III)] + I_2 + H_2O \quad (1)$$

Therefore, to investigate the mechanism of reduction of As (V) to As(III), additional study was demonstrated by using a As (V) standard solution, an I^- standard solution and 0.15 mol L^{-1} HNO_3. When 0.5 g of sample C was subjected to 0.15 mol L^{-1} HNO_3/heat block extraction, and the extract was made up to 10 g, and if no loss and complete extraction carried out, a concentration of I^- in the extract would be 1 mg kg^{-1}. Therefore, 1 mg kg^{-1} I^- was added in a 10 ng g^{-1} As(V) standard solution. After that, 2 g of water or 0.15 mol L^{-1} HNO_3 was added. The test solutions were left without heating or those were heated at 100 °C for 2 h. Four kinds of the test solutions were made up to 10 g with water. When the concentrations of I^- in the test solutions were measured by ICP-MS, almost all amounts of added I^- were recovered from all solutions with and without heating; therefore, I^- was vaporized neither by heating nor under acidic conditions. In addition, arsenic species in the test solutions were analyzed by HPLC–ICP-MS; only As(V) was detected in all test solutions.

Table 3
Influences of iodide ions and of extracting solvent containing Ag on extraction of As.

ID	Extracting solvent	Spiked material	As(V) (mg kg^{-1})	As(III) (mg kg^{-1})	i-As (mg kg^{-1})	DMAA (mg kg^{-1})	Sum[a] (mg kg^{-1})	Total As (mg kg^{-1})	Recovery[b] (%)
Sample A	0.15 mol L^{-1} HNO_3		0.0133	0.0717	0.0850	0.0130	0.0980	0.096 ± 0.002	102.1
		KI	0.0109	0.0738	0.0847	0.0133	0.0980		102.1
Sample B	0.15 mol L^{-1} HNO_3		0.0380	0.2598	0.2978	0.0189	0.3167	0.316 ± 0.004	100.2
		KI	0.0285	0.2676	0.2961	0.0185	0.3147		99.6
	/500 μg Ag	KI	0.0441	0.2558	0.2999	0.0189	0.3188		100.9
	/4000 μg Ag	KI	0.0571	0.2424	0.2995	0.0183	0.3178		100.6
	/5000 μg Ag	KI	0.0572	0.2436	0.3008	0.0185	0.3193		101.0
	/10,000 μg Ag	KI	0.0573	0.2419	0.2991	0.0191	0.3182		100.7

[a] Sums of the concentration of As(III), As(V) and DMAA.
[b] Sum/total As × 100.

On the other hand, I^- was not detected in neither the extracts nor the residues when portions of samples A, B and C were subjected to water/heat block extraction or 0.15 mol L^{-1} HNO_3/heat block extraction. The I^- was volatilized during the extractions or subsequent steps.

When those facts were considered, it seems that I^- in the extract from rice flour was oxidized by a substance(s) present in rice flour and volatilized. And, at the oxidization/volatilization process of I^-, a part of As(V) is reduced to As(III).

Providing that the substance(s) and As(V) are competitive over I^-, it might be explained that As(V) was prevented from reducing in case of sample A containing relatively small amount of I^-. However, unfortunately, the nature of such substance(s) and the details of reaction mechanism involved are currently unclear.

But, according to the these actual phenomenon, I^- is probably involved in the reduction reaction of As(V).

Anyway, to further investigate the possibility of Cl^- and I^- suppressing the reduction, silver nitrate was added to a portion of sample B, and 0.15 mol L^{-1} HNO_3/heat block extraction was carried out (Table 3). When Ag^+ of more than 4000 μg (4000 μg/2 g=2000 mg kg^{-1}) was added, extraction of arsenic was 100% and the amount of As(V) was consistent with that from the water extraction. Besides As(V) not being reduced, the amount of extracted As(III) was increased compared with that from water extraction. Presumably As(V) was prevented from being reduced due to the reaction shown in the route (2).

$$AsO_4^{3-}[As(V)] + 2I^- + 2H^+ + \text{substance(s)} \rightarrow (\text{No reaction}) AsO_3^{3-}[As(III)] + I_2 + H_2O \quad (1')$$

+

$$2Ag^+ \rightarrow 2AgI \quad (2)$$

If no loss and complete extraction of I^- and Cl^- were realized, samples A, B and C (0.5 g each) would give 0.033 μmol, 0.057 μmol and 0.079 μmol I^-, and 1.3 μmol, 3.6 μmol and 3.6 μmol Cl^-, respectively, in the extracts. The halide content of the extract of sample B was approximately 3.66 μmol. The addition of 500 μg Ag^+ to the extracting solvent added 4.64 μmol Ag^+. However, more Cl^- than I^- is present in rice flour, and to remove the influence of I^-, it is necessary to add excess Ag^+.

When 500 μg Ag^+ (approximately 1.3 times the theoretical amount to reach complete production of silver halides) was added, suppression of As(V) reduction to As(III) was incomplete. Experimentally, the reduction of As(V) to As(III) can be completely prevented by the addition of 4000 μg Ag^+ (approximately 10 times the theoretical amount). Large amounts of Cl^- compared to I^- are present in rice flour; therefore, most Ag^+ was consumed in the reaction with Cl^- ($Ag^+ + Cl^- \rightarrow AgCl$) in practice. Excess Ag^+ was needed to fully react with I^-. Ag^+ was also likely to have been consumed by coexisting substances. Addition of excess Ag^+ did not affect any measurement of arsenic compounds. Other rice flours might contain much more halide ions. The results of this study suggested that the addition of 5000 μg Ag^+ would be appropriate to prevent reduction of As(V).

3.5. Effect of chlorine on measurement

In the measurement of arsenic by ICP-MS, it is well known that the presence of Cl^- in a sample causes an interference with m/z=75 of As^+ by forming $ArCl^+$. Therefore, there is a possibility that interference occurs when 0.05 mol L^{-1} $HClO_4$ is used as the extracting solvent and this was investigated. When 0.05 mol L^{-1} $HClO_4$ was introduced into the ICP-MS without a collision cell gas, the counts (cps) equivalent to 0.1 ng g^{-1} As^+ at m/z=75 were observed. The counts decreased with the use of He as a collision cell gas and were equivalent to less than 0.01 ng g^{-1} As^+ with a flow of 3.0 mL min^{-1} He.

In the actual experimental analysis, an ODS column was used to separate the arsenic species, and m/z=35 and m/z=75 were monitored when 0.05 mol L^{-1} $HClO_4$ was introduced. The baseline of the chromatogram obtained by monitoring at m/z=75 was comparable to the water blank. Furthermore, in the HPLC, ClO_4^- was eluted between As(V) and As(III). Thus, there were no effects of chlorine interference on the actual determination of arsenic compounds. The detection limits (3σ) of As(III), As(V) and DMAA in rice flour using the proposed system were 0.01 ng g^{-1}, 0.01 ng g^{-1} and 0.03 ng g^{-1}, respectively; the limits of

Table 4
Comparison of As speciation with different extracting solvents in heat block extraction method.

ID	Extracting solvent	As(V) (mg kg^{-1})	As(III) (mg kg^{-1})	i-As (mg kg^{-1})	DMAA (mg kg^{-1})	Sum[a] (mg kg^{-1})	Total As (mg kg^{-1})	Recovery[b] (%)
Sample A (NMIJ CRM 7503-a, certified values, k=2)		0.0130 ± 0.0009	0.0711 ± 0.0029		0.0133 ± 0.0009		0.098 ± 0.007	
	0.15 mol L^{-1} HNO_3	0.0133	0.0717	0.0850	0.0130	0.0980	0.096 ± 0.002	102.1
	0.15 mol L^{-1} HNO_3/5000 μg Ag	0.0135	0.0712	0.0847	0.0134	0.0981		102.2
	0.05 mol L^{-1} $HClO_4$	0.0138	0.0714	0.0852	0.0132	0.0984		102.5
Sample B								
	0.15 mol L^{-1} HNO_3	0.0380	0.2598	0.2978	0.0189	0.3167	0.316 ± 0.004	100.2
	0.15 mol L^{-1} HNO_3/5000 μg Ag	0.0572	0.2436	0.3008	0.0185	0.3193		101.0
	0.05 mol L^{-1} $HClO_4$	0.0571	0.2407	0.2978	0.0189	0.3166		100.2
Sample C								
	0.15 mol L^{-1} HNO_3	0.0656	0.4627	0.5283	0.0894	0.6177	0.618 ± 0.008	100.0
	0.15 mol L^{-1} HNO_3/5000 μg Ag	0.1030	0.4309	0.5339	0.0883	0.6222		100.7
	0.05 mol L^{-1} $HClO_4$	0.1042	0.4301	0.5344	0.0885	0.6228		100.8

[c](Sum/total As) × 100.

[a] Sums of the concentration of As(III), As(V) and DMAA.

[b] Determination result after microwave-assisted digestion.

quantification (10σ) were 0.03 ng g^{-1}, 0.02 ng g^{-1} and 0.10 ng g^{-1}, respectively.

3.6. Comparison study

Heat block extraction of portions of samples A, B and C was carried out with 0.15 mol L^{-1} HNO_3, Ag-containing 0.15 mol L^{-1} HNO_3, and 0.05 mol L^{-1} $HClO_4$, all of which had been shown to be useful in this study. Arsenic species were determined by HPLC–ICP-MS (Table 4). For all extracting solvents the amounts of extracted total arsenic and inorganic arsenic were consistent within the analytical precision. In addition, amounts of As(III) and As(V) extracted with Ag-containing 0.15 mol L^{-1} HNO_3 and 0.05 mol L^{-1} $HClO_4$ were in good agreement with each other. Those proportion of As(V) was higher than that from 0.15 mol L^{-1} HNO_3 extraction for samples B and C. It is likely that the As (V) proportion extracted with Ag-containing 0.15 mol L^{-1} HNO_3 and with 0.05 mol L^{-1} $HClO_4$ was not changed by reduction to As (III), and that the values for both As(V) and As(III) reflected their natural abundances. Stability of the arsenic species in extraction solutions was confirmed by keeping the solutions at room temperature for 3–5 days; there was no change of the species composition.

4. Conclusions

Various conditions for extracting arsenic species from rice flour samples were compared and the characteristics of the various species that governed their extraction were investigated. The efficiency with which DMAA was extracted depended little on the solvent, but the proportions As(V) and As(III) were significantly changed by the extracting solvents and conditions.

A heat block extraction technique using 0.05 mol L^{-1} $HClO_4$ was developed, which did not alter the arsenic species present in the sample and showed excellent reproducibility. $HClO_4$ is considered a hazard material and may therefore be subject to regulations that govern its use; however, it is thought that the dilution to 0.05 mol L^{-1} used here does not cause any safety problem. An Ag-containing 0.15 mol L^{-1} HNO_3/heat block extraction method was also developed, which prevented reduction of As (V) to As(III) and had a high extraction efficiency. This method allowed the determination of the natural abundance levels of As (V) and As(III) in rice flour.

If only analysis of total inorganic arsenic in rice flour (which might be needed for a toxicity assessment) is required, microwave-assisted digestion using acids at low temperature or 0.5 mol L^{-1} H_2O_2/heat block extraction is suitable. Under the these conditions, all inorganic arsenic will be converted to As(V) and detected as As (V). Only As(V) standard solutions will be suitable for calibration.

HNO_3/heat block extraction has a complete extraction for total arsenic in rice flour; it was tested over a wide range of samples. However, it does not allow the accurate separation analysis of As (V) and As(III), but is useful for validation of the total amounts of inorganic arsenic and other species.

Individual analysis of As(III) and As(V) in rice flour is possible using Ag-containing HNO_3 and $HClO_4$ extraction techniques.

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