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SPE speciation of inorganic arsenic in rice followed by hydride-generation atomic fluorescence spectrometric quantification ☆

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ABSTRACT

Due to high toxicity, inorganic arsenic (iAs) species are the focus of monitoring effort worldwide. In this work arsenic was first extracted from rice by microwave-assisted digestion in HNO_3–H_2O_2, during which As^{III} was oxidized to As^{V}. Silica-based strong anion exchange cartridges were used to separate As^{V} from organic forms. After prereduction by iodide, iAs was quantified by hydride-generation atomic fluorescence spectrometry (HG-AFS). This method achieved 1.3 ng g^{-1} limit of detection (LOD), and 94 ± 3% and 93 ± 5% recoveries, respectively, for As^{III} and As^{V} at 100 ng g^{-1}. Validation was performed using standard reference material NIST 1568a (102 ng g^{-1}) and ERM BC211 (124 ng g^{-1}) rice flour. By eliminating chromatography, SPE speciation gained throughput and cost advantages. HG-AFS, at 10% budget and operation cost of a typical inductively-couple plasma mass spectrometer (ICPMS), proved highly sensitive and specific for iAs quantification.

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1. Introduction

Despite low (20th) crustal abundance (0.0001%), arsenic is the most significant and harmful environmental contaminant [1]. For human population, rice (*Oryza sative*) is the top source (20%) of dietary energy input and an integral part of culinary tradition in many cultures. Cultivated in flooded soils, rice takes up arsenic from irrigation water more readily than other grain crops [2]. Anaerobic rice soil was found to link to much higher shoot/soil As ratio in rice than in wheat and barley [3]. Inorganic arsenic (iAs), As^{III} and As^{V} included, in rice is an order of magnitude higher than in wheat and maize, and much higher than in foods of marine origin [4]; understandably, it has become a growing concern worldwide. Acute toxicity of iAs is much higher than its organic counterparts (Table 1) [5]. For dietary exposure, the major concern on its chronic effects is genotoxicity that may lead to cancer. As^{III} is ultimately responsible for genotoxic action; As^{V} is likely to mediate toxicity only after being reduced to As^{III}; in contrast, organoarsenicals are far less genotoxic [6]. As a consequence, the focus of regulatory monitoring is shifting from total arsenic to iAs. To estimate total dietary exposure to inorganic arsenic from drinking-water and food, the Food and Agriculture Organization/World Health Organization (FAO/WHO) has determined inorganic arsenic lower limit on the benchmark dose for a 0.5% increased incidence of lung cancer ($BMDL_{0.5}$) to be 3.0 μg/kg bw per day [7]. Acceptable iAs level in rice was set in China at 150 ng g^{-1}, and is the focus of food safety discussion in Europe and America [8].

Arsenic speciation has been extensively reviewed covering extraction, separation, and detection [9]. Currently separation is predominately fulfilled by high performance liquid chromatography (HPLC) [10] except volatile organoarsenicals, which can be separated more effectively by gas chromatography [11]. Capillary electrophoresis (CE) is a useful alternative [12]. To promote sample throughput and reduce cost, non-chromatographic approaches were developed such as cryogenic hydride trapping [13]. Based on dependence of arsine yield on hydride generation (HG) conditions, a set of linear equations were established on varied conditions [14]. After coefficients were derived from standards, individual concentrations of As^{III}, As^{V}, monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA), collectively referred to as toxicologically relevant species, can be solved from composite yields. Separation was thus completely bypassed by mathematical approach.

In addition to cleanup, SPE can also fulfill separation of target As species using a variety of sorbents [15]. By excluding HPLC and CE, throughput is improved and cost reduced. Successful applications include arsenate vs. arsenite [16], and four toxicologically

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Table 1
LD50 of arsenic species [5].

Species	Abbreviation	Formula	LD_{50} (mg kg^{-1})
Arsenite	As^{III}	$As(OH)_3$	4.5
Arsenate	As^{V}	$AsO(OH)_3$	14–18
Monomethylarsonic acid	MMA	$CH_3AsO(OH)_2$	700–1800
Dimethylarsinic acid	DMA	$(CH_3)_2AsOOH$	700–2600
Tetramethylarsonium ion	Me_4As^+	$(CH_3)_4As^+$	900
Arsenocholine	AsC	$(CH_3)_3As^+CH_2CH_2OH$	6500
Arsenobetaine	AsB	$(CH_3)_3As^+CH_2COO^-$	> 10000
Trimethylarsine oxide	TMAO	$(CH_3)_3AsO$	10600

relevant species [17,18]. More recently, iAs in aquatic animals and rice was quantified using silica-based SAX sorbent followed by atomic absorption spectrometry [19,20]. In contrast to HPLC, SPE is operated in parallel therefore sample throughput is enhanced. In this work, this SPE speciation scheme was adapted to hydride-generation atomic fluorescence spectrometry (HG-AFS) with minor modifications. HG was first developed by Marsh in 1836 to separate trace As from food matrices [21]. Its effectiveness was based on the conversion of As to highly volatile arsine, which can be completely separated from matrix interferences using a simple gas/liquid separator. Such HG approach, in addition to the use of an arsenic hollow cathode lamp as excitation source, accounts for HG-AFS' extraordinary specificity. At only 10% of instrument budget of an inductively coupled plasma mass spectrometer (ICP-MS) conventionally used for As analysis, HG-AFS is much more affordable for the majority of laboratories to perform crucial arsenic analysis. In comparison to HG-AAS, HG-AFS is intrinsically more sensitive, requires less sample solution, and provides a wider linear range [22]. In this work, HG-AFS proved fully capable of iAs-in-rice quantification yet incurred very low operation and maintenance costs.

2. Experimental

2.1. Reagents and solutions

$NaBH_4$, L-ascorbic acid, 30% H_2O_2, $(NH_4)_2CO_3$, KI, and 30% (w/v) silicone-based antifoam A were purchased from Sigma-Aldrich. Glacial acetic acid was from Fisher (Pittsburgh, PA, USA), NaOH, HCl, and HNO_3 were from Mallinckrodt (Phillipsburgh, NJ, USA). Ultra-high-purity argon and nitrogen gases were from Praxair (Danbury, CT, USA). Strata SAX cartridges (500 mg/6 mL, 55 μm, 70 Å) were purchased from Phenomenex (Torrance, CA, USA). Standard reference material (SRM) rice flour was purchased from National Institute of Standard and Technologies (NIST, Boulder, CO, USA.); and European reference material (ERM) BC211 rice flour was purchased from Institute for Reference Materials and Measurements, Joint Research Centre, European Commission, Geel, Belgium. As^{III} and As^{V} stock solutions (1000 mg L^{-1} in 2% HNO_3) were purchased from Fluka (Milwaukee, WI, USA) and Perkin Elmer (Waltham, MA, USA), respectively. Dilution to 100 μg L^{-1} was performed daily in two steps in water.

Extraction solution, 0.06 M HNO_3 – 3% (w/v) H_2O_2, was prepared by adding first about 100 mL of water to a 250 mL volumetric flask, then 937.5 μL of 70% HNO_3 and 25 mL of 30% (w/v) H_2O_2, and filling to mark with water. Equilibration solution, 0.025 M $(NH_4)_2CO_3$-0.03 M HNO_3-1.5% H_2O_2, was prepared by mixing 0.24 g $(NH_4)_2CO_3$, 187.5 μL of concentrated HNO_3, and 5 mL of 30% H_2O_2 (w/v), and finally filling with water to 100 mL. Prereduction solution, 4% KI-0.4% ascorbic acid-30% HCl-0.1% (v/v) silicone antifoam, was prepared by mixing 40 g KI, 4 g L-ascorbic acid, 1 mL of 30% silicone antifoam, and 300 mL of concentrated HCl, then filling with water to 1 L. Reagent blank solution, 2% KI-0.2% ascorbic acid-30% HCl, was prepared by mixing 20 g KI, 2 g L-ascorbic acid and 300 mL of concentrated HCl, then filling with water to 1 L. Reduction solution, 1% (w/v) $NaBH_4$-0.1 M NaOH, was prepared by dissolving 10 g $NaBH_4$ and 4 g NaOH in water and filling to 1 L with water. It was then filtered through a 0.45 μm membrane filter under vacuum, and stored in a polypropylene container with a loose cap. All the above solutions were stored at 4 °C and used within a week. Deionized (DI) water, prepared with a Barnstead E-pure system (Dubuque, IA), was used to prepare all the solutions.

2.2. Microwave-assisted digestion (MAD)

Rice samples were processed to fine powder using a small mill (Depose 203, Krups, Mexico). Aliquots of 0.25 ± 0.005 g milled rice were weighed into 100 mL Teflon microwave vessels, to which 10 mL of extraction solution was added. The vessels were then sealed and digestion was performed using a Mars-X Express (CEM, Metthews, NC, USA) microwave reaction system rated at 1200 W maximal power. The system was equipped with a RTP-300 Plus fiber-optic temperature sensor (CEM), a pressure sensor with a safety release mechanism, and a 14-position carousel that accommodated 100 mL Teflon vessels. Digestion was performed at 95 °C for 30 min. Samples were allowed to cool down to room temperature; the contents were transferred to 15 mL centrifuge tubes, which were centrifuged at 3400*g* for 15 min at room temperature.

2.3. Solid phase extraction

Supernatants (2 mL) were transferred to 15 mL centrifuge tubes and mixed with 2 mL of 0.05 M $(NH_4)_2CO_3$ solution. Following vortex mixing, the tubes were centrifuged at 3400*g* for 5 min. Next, Strata SAX cartridges were installed on a vacuum manifold, conditioned with 2 mL of MeOH, and equilibrated with 2 mL of equilibration solution. Then, the cartridges were loaded with sample solutions. Washing followed with 3 mL of 0.1 M acetic acid. At the end of washing, residual liquid must be removed by vacuum to minimize foaming in subsequent HG step. Finally, elution was carried out with 2 mL of 0.5 M HCl into 10 mL volumetric flasks.

2.4. Hydride generation

The volumetric flasks were filled to mark with prereduction solution and allowed to stand at room temperature for 50 min. In a flow-injection mode, reductant, sample and blank solutions were individually delivered by peristaltic pumps to mix in a sample valve where arsine started to form. The reaction conditions are listed in Table 2. Arsine and hydrogen gases were separated from liquid in a gas/liquid separator, and swept by ultra-high-purity argon through a Perma Pure dryer (MD-110-12FP, Farmingdale, NJ, USA) where moisture permeated through a Nafion membrane and carried away by high-purity nitrogen.

2.5. Atomic fluorescence spectrometry

A Millennium Excalibur spectrometer (P S Analytical, Kent, UK) was operated in continuous mode. Arsine was atomized in a flame supported by hydrogen that evolved from HCl-$NaBH_4$ reaction. Under excitation by an arsenic boosted discharge hollow cathode lamp (BDHCL) E033L001 (Photron, Victoria, Australia), resonance As emission at 193.7 nm was collected at 90°, isolated by an interference emission filter, and detected by a solar blind

Table 2
HG-AFS conditions.

Parameters	Values
$NaBH_4$ flow rate (mL min^{-1})	4.5
$NaBH_4$ concentration	1%
Ar flow rate (mL min^{-1})	250
Air flow rate (L min^{-1})	2.5
Sample flow rate (mL min^{-1})	4.5
KI-HCl flow rate (mL min^{-1})	9.0
BHCL primary current (mA)	27.5
BHCL boost current (mA)	35.0
Measurement mode	Peak height
Detection wavelength (nm)	193.7

photomultiplier tube (PMT). Major AFS parameters are also listed in Table 2. The instrument operations and data acquisition are controlled by Millennium software (P S Analytical).

2.6. Rice analysis

Rice samples were analyzed using a standard curve constructed daily using reagent standards. Quantification was based on peak height, and measurement was done in triplicate.

3. Results and discussion

3.1. MAD

As the first step in iAs analysis, digestion must fulfill two basic goals: quantitative iAs recovery and species conservation. Methods reported so far include acid digestion [4,23], organic solvent extraction [24,25], and enzymatic digestion [26,27] with or without assistance of heat, sonication, or microwave radiation. Unfortunately, it was observed that recoveries varied considerably among rice varieties [23]. To compromise such inevitable matrix effects, optimization of experimental conditions were carried out on a mixed rice sample from equal portions of five common rice varieties. Because of very low K_{a1} (5.1×10^{-10}), arsenous acid (As^{III}) exists predominantly as nonionic H_3AsO_3 up to pH 8, making retention on ion exchange sorbent impossible except at high alkaline pH. An obvious remedy is to oxidize As^{III} to As^{V} [19,20], which can then be quantitatively retained due to a much higher K_{a1} (5.6×10^{-3}). This approach thus only targets iAs as the sum of As^{III} and As^{V}. Because $As^{III}\leftrightarrow As^{V}$ interconversion is not an issue, relatively strong extractants such as HNO_3, HCl, and trifluoroacetic acid (TFA) can be used leading to higher recovery [23]. Selection of acids in As-in-rice extraction has been extensively discussed [23] and 0.28 M HNO_3 was considered optimal. HNO_3 was also preferred over HCl because Cl^- strongly competed against $H_2AsO_4^-$ on amine groups [20]. HNO_3 is both a strong and an oxidizing acid; its concentration affects recovery as well as oxidation–reduction equilibrium. Though preferred from extraction point of view, 0.28 M HNO_3 made it impossible to adjustment prior-loading pH adequate to retain As^{V} while maintaining low ionic strength. Consequently, HNO_3 concentration was reduced to 0.06 M in this study as a compromise between extraction and SPE retention. For the latter, both *pH* and ionic strength are crucial.

From toxicological point of view, it is acceptable internationally to quantify iAs as the sum of As^{III} and As^{V} [28]. Many oxidants prove effective to convert As^{III} to As^{V}, such as Cl_2, $KMnO_4$, O_3, and O_2 [29], among which H_2O_2 has the advantages of high oxidation potential and the lack of interfering byproducts. Fig. 1a–b shows the dependence of AFS intensity on MAD temperature and time ($n=3$) which were finalized at 95 °C and 30 min. Experimentally,

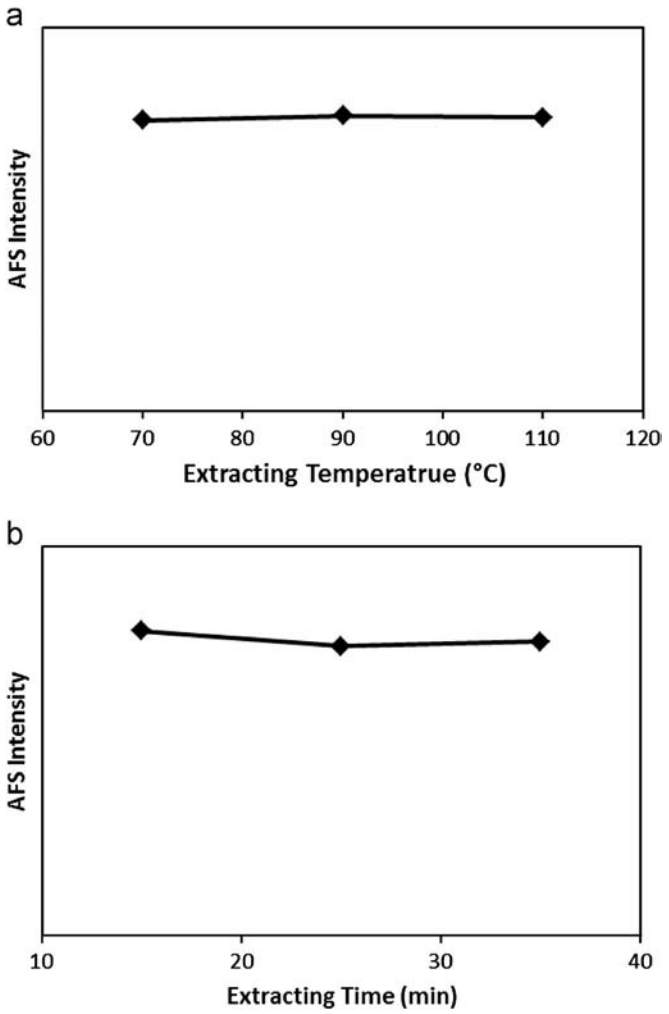

Fig. 1. Dependence of AFS intensity on MAD conditions: (a) temperature with time set at 30-min and (b) time with temperature set at 95 °C.

Table 3
Dissociation constants of As^{III}, As^{V}, MMA, and DMA [15].

Species	pK_{a1}	pK_{a2}	pK_{a3}
As^{III}	9.2	12.1	13.4
As^{V}	2.3	6.8	11.6
MMA	3.6	8.2	
DMA	6.2		

MAD was compared with 90 min digestion in water bath at 95 °C in the same medium; similar results (within 2%) indicated these two approaches were equally effective.

3.2. SPE

Separation of As^{V} from other As species is possible using ion exchange sorbents based on dissociation constants (Table 3) [15,19,30]. In theory, As^{V} retention is quantitative at pH two units higher than 2.3, it's pK_{a1}. In practice, quantitative retention of both As^{V} and MMA ($pK_{a1}=3.6$) were observed on silica-based SAX cartridge at pH 5.6; DMA ($pK_{a1}=6.2$) was only partially retained, and arsenobotaine (AsB, a trace-level contaminant in rice) was not retained [15,31]. Performance of resin-based SAX sorbents was known to be slightly inferior [30].

After MAD, excess acid must be neutralized to achieve adequate pH. Conventional buffer system could well achieve this goal but

resulting ionic strength would be too high for SAX sorbent to function properly. In this work, the sample supernatant was mixed 1:1 with 0.05 M $(NH_4)_2CO_3$, the target pH range should be 5–7.5 and ionic strength below 0.02 M. The low dissociation constants of carbonic acid ($K_{a1}=4.3\times10^{-7}$, $K_{a2}=5.6\times10^{-11}$) and ammonium hydroxide ($K_b=1.77\times10^{-5}$) lowered ionic strength yet maintained a weakly acidic pH. From this point of view, a low acid concentration in MAD was advantageous besides better species conservation. Nevertheless, due to very limited capacity of such a buffer system, the final pH may occasionally still be too acidic leading to low As^V recovery and poor reproducibility. A higher buffer capacity would inevitably result in higher ionic strength; so the final pH must be checked and, if needed, adjusted to pH ≥ 5 with dilute ammonium hydroxide. Before final elution, partially adsorbed MMA and DMA must be removed from SPE columns. Though 0.1–1 M acetic acid was reported to be effective without affecting As^V recovery [15], slight As^V loss was still observed in this laboratory with 0.5 M acetic acid. Therefore, washing was performed with 0.1 M acetic acid. Elution was possible only when As^V carried zero net charge at a low pH; so, a strong acid, HCl, was used at 0.5 M. It was observed that 1 mL was marginally sufficient (Fig. 2); to ensure quantitative elution, 2 mL was used. Antifoam A was used to minimize foaming in gas/liquid separator. If all four toxicologically relevant species must be distinguished, strong cation and anion exchange columns can be used in tandem to achieve this goal at the cost of throughput, chemicals, and labor [15,18].

3.3. HG-AFS

The efficiency of arsine conversion is, understandably, the key to achieve high recovery. Both HG rate and yield are highly dependent on As species, $NaBH_4$ concentration, and pH. In comparison to As^{III}, As^V requires strong acidic condition (pH < 1), has a slower reaction rate and a lower yield [9]. Pre-reduction of As^V to As^{III}, either by L-cysteine or KI [32], is hence necessary to achieve higher yield and higher sample throughput. When KI is used as reductant, strong acidic condition is a prerequisite, and ascorbic acid must be added to prevent formation of I_3^- by oxygen. To speed up slow As^V reduction, KI concentration can be increased [22], or temperature can be raised [33]. It was found experimentally that with 30 min reaction time, reduction efficiency increased with KI concentration, reaching 95% with 4% KI; then gradually decreased to 89% with 7% KI, probably due to solution instability. Keeping KI and ascorbic acid constant at 4% and 0.4%, respectively, reduction efficiency increased from 93% (10 min) to almost 100% (50 min), then declined to 97% (70 min). Consequently, 4% KI and 0.4% ascorbic acid were used; after mixing, samples were allowed to stand for 50 min at room temperature. Quantitative conversion was validated by data from certified reference materials (CRM). In fact, 0.1% $NaBH_4$ is sufficient to reduce As^{III} to arsine [32], but produces insufficient hydrogen to sustain a flame where atomization takes place. Without auxiliary hydrogen, 1% (w/v) $NaBH_4$ was recommended by the AFS manufacturer to render a stable Ar-H_2 diffusion flame and adequate AFS signals.

Major HG-AFS conditions used in this work were also included in Table 2. To achieve optimal performance, operation parameters must be optimized and reproducibly maintained. Dependence study on $NaBH_4$ concentration revealed that maximal AFS intensity was obtained at 1.2% (Fig. 3), however, excess hydrogen affected flame stability leading to higher noise; so 1% $NaBH_4$ and 30% HCl were finally used. Despite best efforts, other parameters and conditions may still change such as batch-to-batch fluctuation in reagent concentrations, changes of sample and reagent flow rates with fatigue of peristaltic pump tubing, and argon flow rate with time. To compensate these long- and short-term variations, a calibration curve was obtained daily with reagent standards. It is impossible to construct a matrix-match calibration curve because all rice contains arsenic; fortunately, this was usually not a problem in practice due to AFS's exceptional intrinsic specificity as validated, vide infra, by CRMs (Table 4). Typically, calibration curves yielded ≥0.998 correlation coefficients. As reported in literature, the linear range of AFS signal extends several orders of magnitude below 0.5 μg mL^{-1}; and "rollover" occurs at 1.5 μg mL^{-1} [34].

3.4. Quantitation of iAs in rice

Regardless of extraction media, efficiency and recovery are influenced by rice species and varieties [23]. To minimize such matrix effects, a mixed rice sample was used throughout optimization processes that was prepared by mixing equal portions of rice #1 through #5 (Table 4). Recoveries of As^{III} and As^V were 94 ± 3% and 93 ± 5%, respectively, obtained on different days from this mixed rice ($n=6$) spiked at 100 ng g^{-1}. The iAs contents of several domestic and imported rice samples from local markets ranged from 45 ng g^{-1} to 235 ng g^{-1} (Table 4): a brown Basmati rice at the high end and a wild black rice at the low end. Relative standard deviations (RSD) ranged from 1.1% to 5.9%. From the peak

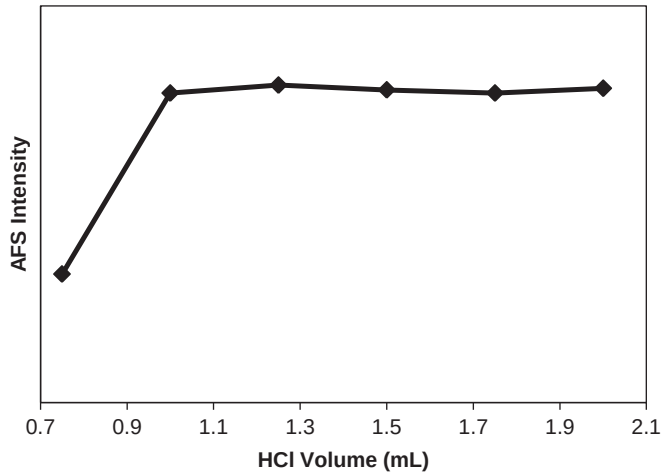

Fig. 2. Dependence of AFS intensity on the volume of 0.5 M HCl eluent ($n=3$).

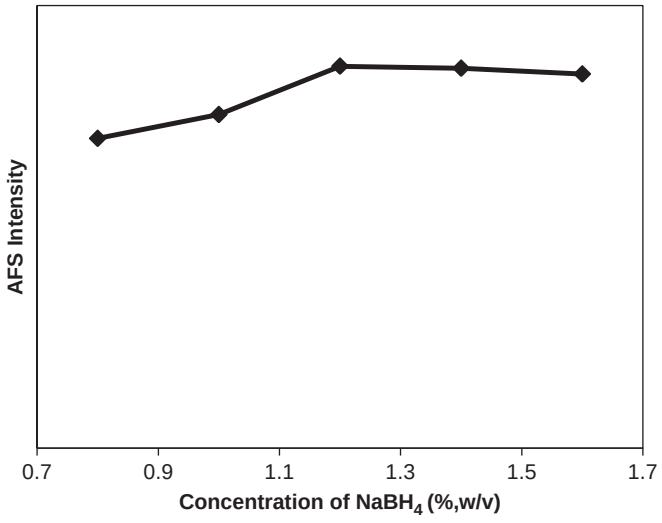

Fig. 3. Dependence of AFS intensity on $NaBH_4$ concentration ($n=3$).

Table 4
Analysis of market rice samples and certified reference materials.

#	Sample	Origin	*n*	iAs (ng g^{-1})	RSD (%)
1	Medium-grain rice	U.S.	3	74 ± 2	3.0
2	Jasmine rice	Thailand	3	77 ± 1	1.5
3	Glutinous rice	U.S.	3	66 ± 2	2.8
4	Enriched long-grain rice	U.S.	3	74 ± 1	1.1
5	Brown medium-grain rice	U.S.	3	94 ± 1	1.1
6	Basmati rice	India	3	60 ± 3	5.1
7	Matta rice	India	3	49 ± 2	5.0
8	Jasmine rice	Vietnam	3	66 ± 2	2.4
9	Brown Basmati rice	India	3	235 ± 9	3.9
10	Ponni rice	India	3	57 ± 2	4.1
11	Organic Haiga medium-grain rice	U.S.	3	83 ± 5	5.9
12	Organic Basmati rice	India	3	46 ± 1	2.6
13	Wild red rice	Thailand	3	86 ± 5	5.6
14	Wild black rice	U.S.	3	45 ± 1	2.8
15	Mixed rice (#1–5)	–	6	77 ± 5	6.9
16	NIST 1568a rice flour	U.S.	6	102 ± 5	4.6
17	ERM BC211 rice flour	Belgium	6	124 ± 2	2.0

heights of 10 reagent blanks, limit of detection (LOD) was 1.3 ng g^{-1} (3σ) and limit of quantification (LOQ) was 4.4 ng g^{-1} (10σ), rendering this method sensitive to qualify iAs in rice. So far, China established a maximum iAs level at 150 ng g^{-1} [8]; the Codex Alimentarius Committee proposed 300 ng g^{-1} and 200 ng g^{-1} for raw and polished rice, respectively [8]. Finally, validation was performed with NIST standard reference material (SRM) 1568a and European reference material (ERM) BC211 rice flour. In Table 4, the resulting iAs data obtained on multiple days agreed well with the former's consensus value (80–109 ng g^{-1}) [35] and the latter's certified value (121 ng g^{-1}).

4. Conclusion

Speciation of iAs by SPE using silica-based SAX strong anion exchange column proved effective and reliable. HG enabled complete separation of matrix interferences in solution; this unique feature, combined with AFS's intrinsic specificity and sensitivity, led to productive and low-cost quantification for iAs in rice.

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