Analytical Methods

Determination of Inorganic Arsenic in Rice by Solid Phase Extraction and Hydride Generation Atomic Fluorescence Spectrometry

Journal:	*Analytical Methods*
Manuscript ID:	AY-ART-06-2015-001434.R4
Article Type:	Paper
Date Submitted by the Author:	05-Sep-2015

Complete List of Authors:	Huang, Yatao; Institute of Agro-products Processing Science and Technology, Chinese Academy of Agricultural Sciences, Shan, Jihao; Institute of Agro-products Processing Science and Technology, Chinese Academy of Agricultural Sciences, Fan, Bei; Institute of Agro-products Processing Science and Technology, Chinese Academy of Agricultural Sciences, He, Yan; Institute of Agro-products Processing Science and Technology, Chinese Academy of Agricultural Sciences, Mei, Shuang; Institute of Agro-products Processing Science and Technology, Chinese Academy of Agricultural Sciences, Sun, Yufeng; Institute of Agro-products Processing Science and Technology, Chinese Academy of Agricultural Sciences, Lu, Jia; Institute of Agro-products Processing Science and Technology, Chinese Academy of Agricultural Sciences, Wang, Miao; Institute of Agro-products Processing Science and Technology, Chinese Academy of Agricultural Sciences, Wang, Fengzhong; Institute of Agro-products Processing Science and Technology, Chinese Academy of Agricultural Sciences,

Determination of Inorganic Arsenic in Rice by Solid Phase Extraction and Hydride Generation Atomic Fluorescence Spectrometry

Yatao Huang, Jihao Shan, Bei Fan*, Yan He, Shuangmei Xia, Yufeng Sun, Jia Lu, Miao Wang, and Fengzhong Wang*

Laboratory of Agro-products Quality Safety Risk Assessment (Beijing), Institute of Agro-products Processing Science and Technology, Chinese Academy of Agricultural Sciences, Key Laboratory of Agro-products Processing, Ministry of Agriculture, Beijing 100193, China

Corresponding Authors: Phone: +86-10-62817417. Fax: 86-10-62895382.

E-mails: fanbei517@163.com (B.F.); wfengzhong@126.com (F.W.).

Abstract

Inorganic arsenic (iAs) is a food safety concern worldwide due to its high toxicity, particularly in rice, which accumulates As more easily than other crops. Accordingly, low-cost, simple methods are needed for accurate determination of iAs in food crops. We extracted total arsenic (As) from rice using HNO_3 and then reduced arsenate (As^{5+}) to arsenite (As^{3+}) using thiourea. The combined As^{3+} was separated from organic As using polystyrene resin cartridges, and quantified by hydride generation-atomic fluorescence spectrometry (HG-AFS). This method achieved 1.1 μg/kg limit of detection, 3.6 μg/kg limit of qualification, and <6% relative standard deviation. Validation was performed using certified reference materials and conventional high-performance liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICPMS). Compared with LC-HG-AFS or LC-ICPMS, this method appears suitable for general use because of its low cost.

1. Introduction

Arsenic (As) is one of the most hazardous elements in all foods and poses high risks to consumers globally,[1] particularly in rice, as rice accumulates As more easily than other grain crops.[2] As is present in various forms with acute toxicity (LD_{50})[3] in decreasing order: arsenite (As^{3+}) (4.5 mg/kg) > arsenate (As^{5+}) (14-18 mg/kg) > monomethylarsonic acid (MMA) (700-1800 mg/kg) > dimethylarsinic acid (DMA) (700-2600 mg/kg) > tetramethylarsonium ion (Me_4As^+)(900 mg/kg) > arsenocholine (AsC) (6500 mg/kg) > arsenobetaine (AsB) (>10000 mg/kg) > trimethylarsine oxide (TMAO) (10600 mg/kg). For chronic toxicity, oral exposure to inorganic arsenic (iAs) has a number of effects, including cardiovascular, respiratory, gastrointestinal, haematological, immune, reproductive, and nervous systems, which are more harmful to health,[4] so iAs is classified as a Class ⅠA human carcinogen by the International Agency for Research on Cancer. The Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additives has determined a benchmark dose for 0.5% increased incidence of lung cancer of 3.0 μg/kg bw·day iAs (2–7 μg/kg bw·day)[5] and China has established a maximum contaminant level of 200 μg/kg for iAs in rice.[6] Thus, monitoring of iAs instead of total As in food and assessment of the resulting risks are critical.

Determinations of iAs in general includes two steps: separation of different As species, followed by quantification. As can be analysed by inductively coupled plasma mass spectrometry (ICP-MS),[7–9] graphite furnace atomic absorption spectrometry (GF-AAS),[10] hydride generation atomic absorption spectrometry

(HG-AAS)[11], or hydride generation atomic fluorescence spectrometry (HG-AFS).[12] Among these, ICP-MS typically has the lowest limit of detection (LOD); however, the cost is relatively high. HG-AFS, by contrast, can also achieve low LOD at lower cost.[13] Thus, this affordable HG-AFS method was selected in this study.

Separation of iAs from organic forms and matrix components is critical; chromatography is widely used for this purpose, HPLC-ICPMS[7,14] is the golden standard. In addition, gas chromatography (GC) [15] and capillary electrolysis (CE) [16] have been used. To simplify the process and reduce costs, non-chromatographic method may be a promising alternative. Chen et al.[17] directly determined iAs in rice grains by selective hydride generation at high acidity (4.8 mol/L HCl), which was 50 times more efficient than DMA. Solvent extraction[18] has recently been investigated for the separation of As species, but the method uses toxic chemicals and is time-consuming. Solid phase extraction (SPE) can also be used to separate the target As species with a variety of sorbents and can be operated in parallel to enhance the sample throughput[19]. Recently, a silica-based SAX sorbent was used to separate iAs from organic forms[11,13] through adjustment of the pH based on dissociation constants, which proved highly sensitive for iAs quantification. This method can be used to separate As^{5+} from organic As; accordingly, As^{3+} was oxidized to As^{5+} prior to separation.

As^{3+} also forms covalent molecular $AsCl_3$ in concentrated HCl.[20] The aim of this study was to develop a new method for separating iAs from other forms using polystyrene resin as SPE sorbent and utilizing the characteristics of $AsCl_3$, followed

by HG-AFS determination. This method is suitable for routine use because of low cost and simplicity.

2. Experimental method

2.1 Reagents and standards

Arsenite (As^{3+}), arsenate (As^{5+}), Monomethylarsonic Acid (MMA), and Dimethylarsinic Acid (DMA) were purchased from the Chinese Academy of Geographical Sciences (Beijing, China). Deionized water was made using a Milli-Q Integral Water Purification System (Millipore, Billerica, MA). $(NH_4)_2HPO_4$, KBH_4, HCL, and HNO_3 were purchased from Beijing Chemical Reagents (Beijing, China), methanol (HPLC grade) was purchased from J.T. Baker (Phillipsburg, USA). Cleanert PS solid phase column (60 mg, 3 mL) were purchased from Bonna-Agela Technologies (Tianjin, China). KOH and thiourea (analytical reagent grade) were from Beijing Chemical Reagents (Beijing, China).

The following rice flour certified reference materials (CRMs) were used: European reference material (ERM) BC211 rice flour purchased from the Institute for Reference Materials and Measurements, Joint Research Center, European Commission (Geel, Belgium); 1568b rice flour purchased from National Institute of Standard and Technologies (NIST, Boulder, CO, USA); and GBW 10043 rice flour (Chinese Academy of Geographical Sciences, Beijing, China).

Rice samples were purchased from a supermarket in Beijing, China, and were designated Nos. 1–7, and then ground into powders. All samples were stored at 4 ºC until analysis.

2.2 Instrumentation

HG-AFS (AFS8230; Beijing Titan Instrument, Beijing, China) was equipped

with an As-boosted hollow cathode lamp (193.7 nm, Beijing Research Institute of Nonferrous Metals, Beijing, China). The operating parameters for the HG-AFS are shown in Table 1. HPLC-HG-AFS (SA-20; Beijing Titan Instrument Co. Ltd., Beijing, China) with an anion exchange column (PRP-X 100, 250 mm × 4.1 mm i.d., 10 μm; Hamilton, Reno, NV, USA) was used to separate As species with 15 mmol/L $(NH_4)_2HPO_4$ (pH = 6.0, 1 mL/min flow rate) as the mobile phase and 7% HCl and 1.5% KBH_4 as the carrier solution and reductant, respectively.[12]

ICP-MS (XSERIES 2; Thermo Scientific, Dreieich, Germany) was coupled with HPLC systems (U3000; Thermo Scientific, Dreieich, Germany), and the HPLC-ICP-MS instrument was used to verify the results of SPE-GH-AFS. The column used was an anion exchange column (PRP-X 100; Hamilton), and 15 mmol/L $(NH_4)_2HPO_4$ (pH 6.0, 1 mL/min flow rate) was used as the mobile phase. The ICP-MS operating parameters were as follows: incident RF power at 1300 W, cooling Ar gas flow rate at 13 L/min, nebulizer Ar gas flow rate at 0.9 L/min, and auxiliary Ar gas flow rate at 1 mL/min. The ICP-MS was used in the collision-reaction cell with the kinetic energy discrimination (CCT-KED) mode using H_2–He as the collision cell gas (5 mL/min) to reduce $^{40}Ar^{35}Cl^+$ interference with ^{75}As. PlasmaLab Transient Time Resolved Analysis (TRA) was used as the data acquisition mode and the ion count was monitored at m/z = 75.

2.3 Determination of iAs

2.3.1 Arsenic extraction

Sample powders (1.000±0.001 g) was placed in a 50-mL polypropylene tube with 20 mL of 0.02 mol/L HNO_3. After mixing thoroughly with a vortex mixer, the tube was held in a water bath at 90 ºC for 60 min and then centrifuged at 3300g for 10 min. Finally, the supernatant was filtered through a 0.22-μm membrane, and the

solution was analysed by SPE-HG-AFS and HPLC-ICPMS.

2.3.2 SPE-HG-AFS analysis

Sample solutions were adjusted to 10.0 mol/L HCl and 0.2% thiourea, and held for 30 min. The cartridges were activated prior to installation using 3 mL of methanol and 3 mL of water. After rinsing the cartridges with 2 mL of 10 mol/L HCl, sample solutions were pumped through the cartridge at 0.5 mL/min to sequester As^{3+}. The cartridges were then rinsed with 2 mL of 10 mol/L HCl and eluted with 2 mL of water. The solutions were vortex mixed and analysed by HG-AFS. For the comparison method, the extracted solution was directly analysed by HPLC-ICPMS.

2.4 Determination of total As

Total As in the CRMs and the rice flour samples were determined by HG-AFS after microwave digestion. Smples (0.500±0.001 g) were placed in digestion vessels, and added with 8 mL of HNO_3 and 2 mL of H_2O_2. The vessels were placed on the hot block and kept at 130 ℃ for 2 h, and then heated at 145 ℃ until roughly 1 mL volume remained. After cooling, the digests were transferred to 50 mL volumetric flasks and diluted to mark with 0.5% thiourea. Following 15s vortex mixing, the solutions were measured by HG-AFS.

2.5 Method validation

Stock solutions of four As species were prepared at 0.1–50 μg/L. The linear regression equations and the correlation coefficients were obtained from the peak area ratios vs. concentration plot. The BC211, 1568b, and GBW 10045 rice flour CRMs were used to validate the method in addition to conventional HPLC-ICPMS.

2.6 Statistical analysis

Experimental data were evaluated using the statistical software SAS 9.2. Statistically significant differences were assessed using Duncan's multiple range test,

with $p \leq 0.05$ being considered significant.

3. Results and discussion

3.1 Extraction of As species from rice samples

Extraction of As species from rice samples should avoid the transformation of organic As to iAs and should simultaneously attain good extraction efficiency; therefore, the choice of the extractant is a critical factor in method development. The most commonly used extractants include dilute acid solutions, enzymes, water, and methanol solutions.[8,9,21–23] The cost of enzymes was relatively high and methanol should be removed before analysis by HG-AFS because it affects the intensity of HG-AFS. Acid extraction with HCl, HNO_3, trifluoroacetic acid (TFA), etc. is common due to high efficiency and low cost. Therefore, to select the most efficient extractant among the acids, the extraction efficiencies (ratio of all species to total As) of 0.02 and 0.1 mol/L TFA, 0.02 and 0.1 mol/L HNO_3, and 0.02 and 0.1 mol/L HCL were calculated by comparing the As species analysed by HPLC-ICPMS to total As by HG-AFS. Extraction efficiencies are also influenced by the rice species and variety.[24] Chen[13] minimized matrix effects by mixing rice samples; therefore, we similarly prepared a mixed rice sample by mixing sample Nos. 2, 4, and 5. Among the extractants, HNO_3 and TFA achieved higher extraction efficiencies than HCl (Table 2), possibly due to Cl^- competing with $H_2AsO_4^-$ for amine groups.[10] Therefore, 0.02 mol/L HNO_3 was selected as the optimal extractant.

As^{5+} in the extract should be reduced to As^{3+} first by iodide, L-cysteine, or thiourea.[21] Among these, thiourea was selected because it acts both as a reducing agent for As^{5+} and a masking reagent to eliminate interferences from transition metals.[25] The effect of the thiourea concentration was investigated over the range 0.1–

0.6% (m/v), and 0.2% thiourea in 10 mol/L HCl was found to be effective within 20 min.

3.2 Solid phase extraction

In a previous study, iAs in rice was separated from other As species by using a silica-based SAX sorbent. Based on dissociation constants,[13] only As^{5+} was retained on ion exchange sorbents at certain pH. A novel method for separating iAs from other species by SPE was developed based on the properties of covalent $AsCl_3$, which can be selectively extracted by the solvent with high recovery[18] and can also be retained by a non-polar resin. Therefore, the PS solid phase column (Bonna-Agela Technologies) was adopted. Retention of three species of As (As^{3+}, DMA, and MMA) on the PS resin at various HCl concentrations was evaluated. A series of solutions containing 50 μg/L As^{3+}, DMA, or MMA was prepared at different HCl concentrations. After elution, the eluates were analysed by HPLC-HG-AFS and the recoveries of the three As species at different HCl concentrations were calculated (Fig. 1). As^{3+} recovery increased with increasing HCl concentration, reaching a plateau at 10 mol/L HCl; DMA and MMA, on the other hand, did not retain at any HCl concentration. Clearly, retention of As^{3+} was the result of the PS resin attracting the molecular covalent compound, because formation of molecular $AsCl_3$ was enhanced at higher HCl concentrations. For maximum recovery, 10 mol/L HCl was chosen.

In the presence of certain elements, such as Sb^{3+} , DMA are also retained on the PS resins leading to substantial interfere.[17] In order to wash out other As species and interfering ions, and to maintain retention of molecular $AsCl_3$ on the PS, the columns were washed with 1 mL of 10 mol/L HCl.

$AsCl_3$ retained on the PS sorbent was eluted by hydrolysis. The elution solution should promote As^{3+} desorption from the PS resin by facilitating the following

hydrolysis reaction.

$$AsCl_3 + 3H_2O = AsO_3^{3-} + 3Cl^- + 6H^+ \quad (1)$$

From the above equation, it is obvious that water or OH^- containing eluents could promote $AsCl_3$ hydrolysis. Therefore, the recoveries of different volumes of water and 0.1% NaOH (m/v) were studied; At 1 mL, 0.1% NaOH achieved higher elution efficiency (68.9% ± 4.0%) than water (59.3% ± 5.8). At 3 mL, however, water (98.2% ± 4.0%) and 0.1% NaOH (98.1% ± 2.4%) showed identical recoveries; therefore, water was chosen as the most suitable eluent for its simplicity and low cost.

3.3 Hydride generation atomic fluorescence spectrometry

The HG procedure was critical for the determination of As, HCl and KBH_4 were used for reducing As^{3+} to arsine and producing H_2 to sustain a flame. The volume and concentration of HCl and KBH_4 were critical for the AFS intensity and stability. Based on the recommended volume by the manufacturer: 3.7 mL of HCl and 2.3 mL of KBH_4 for 1 mL of sample, the effects of HCl and KBH_4 concentrations were studied. As shown in Figs. 2 and 3, 1.4% KBH_4 and 7% HCl were considered optimal.

3.4 Method validation

The calibration curve for As^{3+} had a linear range from 0.5 to 50 μg/L with a high correlation coefficient (R = 0.9997). Based on the signals of 11 reagent blanks, the limit of detection (LOD) was 1.1 μg/kg (3σ) and the limit of quantification (LOQ) was 3.6 μg/kg (10σ). Recoveries of iAs, determined from three rice samples spiked with iAs (As^{3+}:As^{5+} = 1:1), DMA, and MMA, were 90.3–102.6% with RSDs (n = 3) of 3.1–6.3% (Table 3).

The CRMs and seven rice samples were analysed (Table 4). The results obtained by the present and conventional methods were in good agreement and were not significantly different (95% confidence level, paired *t*-test), thus verifying the high

specificity and accuracy of the developed SPE HG-AFS method.

4. conclusion

SPE coupled with the HG-AFS method for the determination of iAs achieved good selectivity with a low LOD. Operation of this method is relatively simple and can be conducted in parallel to improve throughout. With results closely agreed with those of the conventional methods, this method is applicable to routine As speciation in rice.

Acknowledgments

The authors are thankful for the support provided by the Special Fund for Supervision of Quality and Safety of Agricultural Products (Risk Assessment) from the Chinese Ministry of Agriculture (Grant GJFP2014011). The authors also thank Mr Jixin Liu and Weihong Zhang, Beijing Titan Instruments Co., Ltd., China.

REFERENCES

1 B. K. Mandal, K. T. Suzuki, *Talanta,* 2002, *58*, 201–235.

2 Y. H. Su, S. P. McGrath, F. J Zhao, *Plant Soil,* 2009, *328*, 27–34.

3 T. Agusa, T. Kunito, J. Fujihara, R. Kubota, T. B. Minh, P. T. Kim Trang, H. Iwata, A. Subramanian, P. H. Viet, S. Tanabe, *Environ. Pollut.,* 2006, *139*, 95–106.

4 EFSA European Food Safety Authority. Scientific Opinion on Arsenic in Food. Available http://www.efsa.europa.eu/en/efsajournal/doc/1351.pdf, 2009.

5 World Health Organization. *Evaluation of Certain Food Additives and Contaminants*, Technical Report Series 959, 72nd Report of the Joint FAO/WHO Expert Committee on Food Additives; WHO: Geneva, Switzerland, 2010.

6 People's Republic of China Ministry of Health. *GB 2762-2012: Maximum Levels of Contaminants in Foods of China*; Ministry of Health: Beijing, China, 2012.

7 G.Raber, N. Stock, P. Hanel, M. Murko, J. Navratilova, K. A. Francesconi, *Food Chem.,* 2012, *134*, 524–532.

8 S. Nookabkaew, N. Rangkadilok, C. Mahidol, G. Promsuk, J. Satayavivad, *J. Agr. Food Chem.,* 2013, *61*, 6991–6998.

9 R. Juskelis, W. Li, J. Nelson, J. C. Cappozzo, *J. Agr. Food Chem.,* 2013, *61*, 10670–10676.

10 S. Doker, L. Uzun, A. Denizli, *Talanta*, 2013, *103*, 123–129.

11 R. R. Rasmussen, Y. Qian, J. J. Sloth, *Anal. Bioanal. Chem.,* 2013, *405*, 7851–7857.

12 H. Yang, S. H. Dai, M. Wang, X. F. Mao, Y. T. Huang, F. H. Wang, *Anal. Lett.,*

2014, *47*, 2601–2612.

13 G. Chen, T. Chen, *Talanta,* 2014, *119*, 202–206.

14 A. A. Carbonell-Barrachina, X. Wu, A. Ramirez-Gandolfo, G. J. Norton, F. Burlo, C. Deacon, A. A. Meharg, *Environ. Pollut.,* 2012, *163*, 77–83.

15 J. C. Wuilloud, R. G. Wuilloud, A. P. Vonderheide, J. A. Caruso, *Spectrochim. Acta B,* 2004, *59*, 755–792.

16 G. Yang, J. Zheng, L. Chen, Q. Lin, Y. Zhao, Y. Wu, F. Fu, *Food Chem.,* 2012, *132*, 1480–1485.

17 B. Chen, W. T. Corns, P. B. Stockwell, J. H. Huang, *Anal. Meth.,* 2014, *6*, 7554–7558.

18 O. Muñoz, D. Vélez, R. Montoro, *Analyst,* 1999, *124*, 601–607.

19 Rasmussen, R. R., Hedegaard, R. V., Larsen, E. H., & Sloth, J. J., Anal. Bioanal. Chem., 2012, 403, 2825-2834.

20 X. Liu, T. Duan, Y. Han, X. Jia, H. Chen, *J. Anal. Atom. Spectrom.,* 2010, *25*, 206–209.

21 T. Narukawa, K. Inagaki, T. Kuroiwa, K. Chiba, *Talanta,* 2008, *77*, 427–432.

22 Y. Zhao, J. Zheng, M. Yang, G. Yang, Y. Wu, F. Fu, *Talanta,* 2011, *84*, 983–988.

23 A. H. Petursdottir, H. Gunnlaugsdottir, E. M. Krupp, J. Feldmann, *Food Chem.,* 2014, *150*, 353–359.

24 J. H. Huang, G. Ilgen, P. Fecher, *J. Anal. Atom. Spectrom.,* 2010, *25*, 800–802.

25 H. Wu,; X. Wang, B. Liu, Y. Liu, S. Li, J. Lu, J. Tian, W. Zhao, Z. Yang, *Spectrochim. Acta B,* 2011, *66*, 74–80.

Table 1 Operational parameters for HG-AFS

parameter	value
HCl concentration (v/v)	7%
HCl volume (mL)	4.7
KBH_4 concentration(m/v)	1.5%
KBH_4 volume (mL)	2.3
carrier gas (mL/min)	400
shielding gas (mL/min)	500
As-HCL current (mA)	60
PMT voltage (mV)	270
injection volume (mL)	1.0

Table 2 Extraction rates of different extractants for As speciation in rice samples (n = 3)

extractant	total As (μg/kg)	iAs[b] (μg/kg)	DMA (μg/kg)	MMA (μg/kg)	sum of species (μg/kg)	extraction efficiencies (%)
0.02 mol/L TFA		113.3 ± 6.0	40.3 ± 4.0	BDL[c]	153.6 ± 10.0	88.2 ± 5.7
0.1 mol/L TFA		115.5 ± 4.9	43.5 ± 3.3	BDL	159.0 ± 8.2	91.3 ± 4.7
0.02 mol/L HNO_3		121.8 ± 5.5	42.8 ± 4.2	BDL	164.6 ± 9.7	94.6 ± 5.5
0.1 mol/L HNO_3	174.1 ± 8.0[a]	119.5 ± 6.0	43.1 ± 4.0	BDL	162.6 ± 10.0	93.4 ± 5.8
0.02 mol/L HCl		112.0 ± 8.3	38.8 ± 5.4	BDL	150.7 ± 13.7	86.6 ± 7.8
0.1 mol/L HCl		112.3 ± 3.7	37.8 ± 4.2	BDL	150.1 ± 7.9	86.2 ± 4.5
water		98.3 ± 5.2	27.2 ± 7.4	BDL	125.5 ± 12.6	72.1 ± 7.2

[a] sample prepared by mixing rice sample Nos. 2, 4, and 5 in equal proportions.

[b] iAs was the sum of As^{3+} and As^{5+}.

[c] BDL: below the LOD.

Table 3 Recoveries of spiked iAs, DMA, and MMA

sample	amount spiked (μg/kg)			recovery (%)			RSD for iAs
	iAs[a]	DMA	MMA	iAs	DMA	MMA	%
rice	5	5	5	96.5 ± 4.1	BDL	BDL	6.3
rice	200	200	200	94.0 ± 2.4	BDL	BDL	3.8
rice	400	400	400	93.2 ± 2.9	BDL	BDL	3.1

Table 4 Analysis of certified reference materials and rice samples

sample no.	SPE-HG-AFS	HPLC-ICPMS				
	iAs (μg/kg)	iAs (μg/kg)	DMA (μg/kg)	MMA (μg/kg)	variety	place of origin
ERM BC211 rice flour[a]	119.9 ± 3.8	120.3 ± 3.2	124.1 ± 5.3	BDL	rice flour	Belgium
NIST 1568b rice flour[b]	92.9 ± 4.2	95.2 ± 3.8	177.8 ± 9.2	9.9 ± 2.0	rice flour	US
GBW10045[c]	89.1 ± 3.7	87.1 ± 4.0	21.5 ± 2.3	BDL	rice flour	Hunan, China
1	30.1 ± 2.3	29.8 ± 1.8	BDL	BDL	Japonica rice	Heilongjiang, China
2	178.8 ± 7.9	180.0 ± 5.3	40.4 ± 1.9	8.3 ± 2.5	Japonica rice	Heilongjiang, China
3	89.8 ± 3.3	92.1 ± 4.3	18.2 ± 2.9	BDL	Indica rice	Jiangxi, China
4	123.1 ± 5.2	121.8 ± 3.9	35.7 ± 3.1	BDL	Glutinous rice	Sichuan, China
5	203.2 ± 8.7	205.4 ± 7.7	41.6 ± 2.2	10.0 ± 3.1	Japonica rice	Jiangxi, China
6	57.2 ± 2.7	55.9 ± 1.8	15.2 ± 1.8	BDL	Indica rice	Guangdong, China
7	66.9 ± 2.2	65.6 ± 3.6	9.8 ± 2.6	BDL	Indica rice	Guangdong, China

[a] the certified iAs and DMA value are 124 ± 11 μg/kg and 119 ± 13 μg/kg.

[b] the certified iAs, DMA and MMA value are 92 ± 10 μg/kg, 180 ± 12 μg/kg and 11.6 ± 3.5 μg/kg.

[c] the certified total As is 110 ± 20 μg/kg.

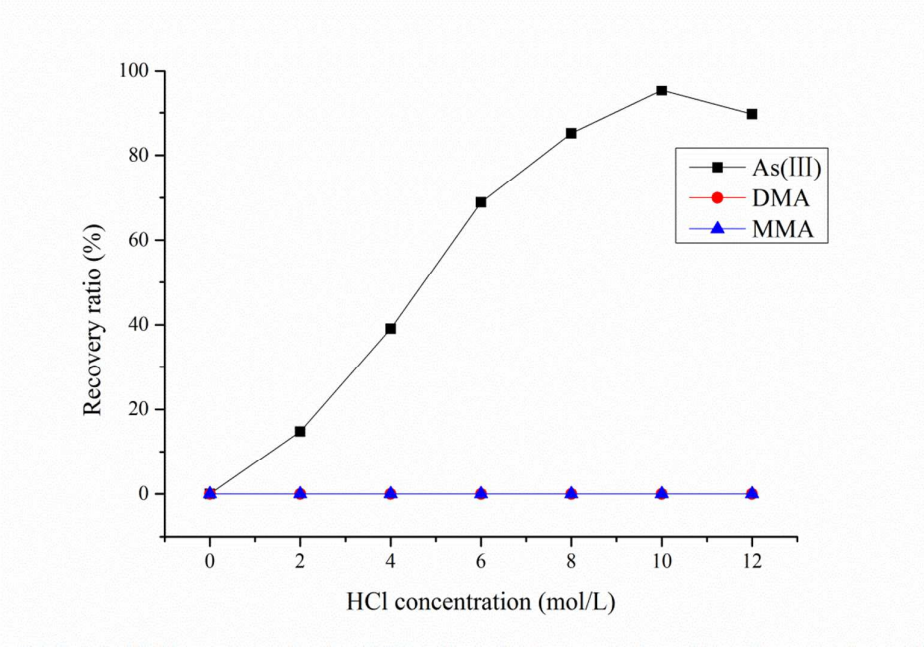

Fig. 1 Effect of HCl concentration on the recovery of 50 μg/L As^{3+}, DMA, and MMA. Sampling loading rate, 0.3 min/mL; tube rinsed with 1 mL 10 mol/L HCl; elution with 2 mL water.

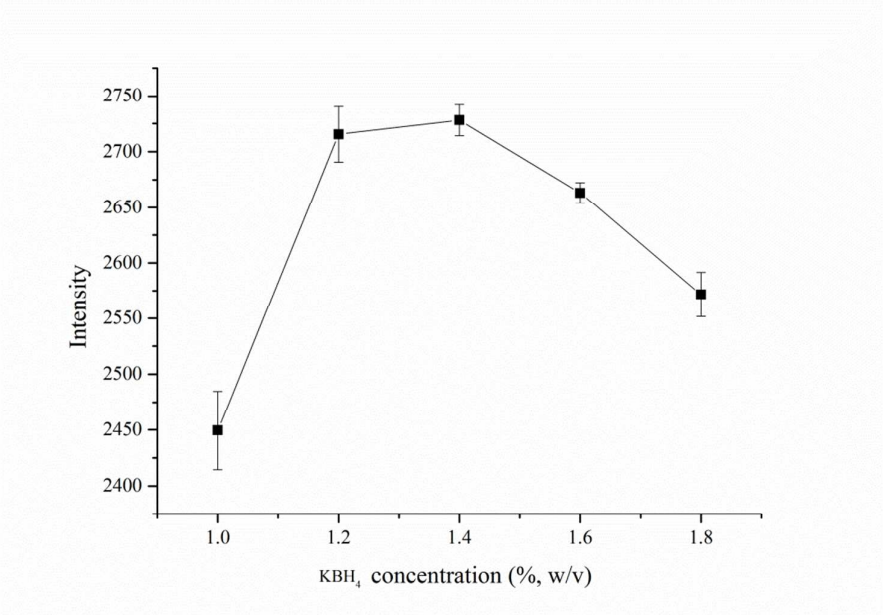

Fig. 2 Effect of KBH_4 concentration on AFS intensity (n = 3).

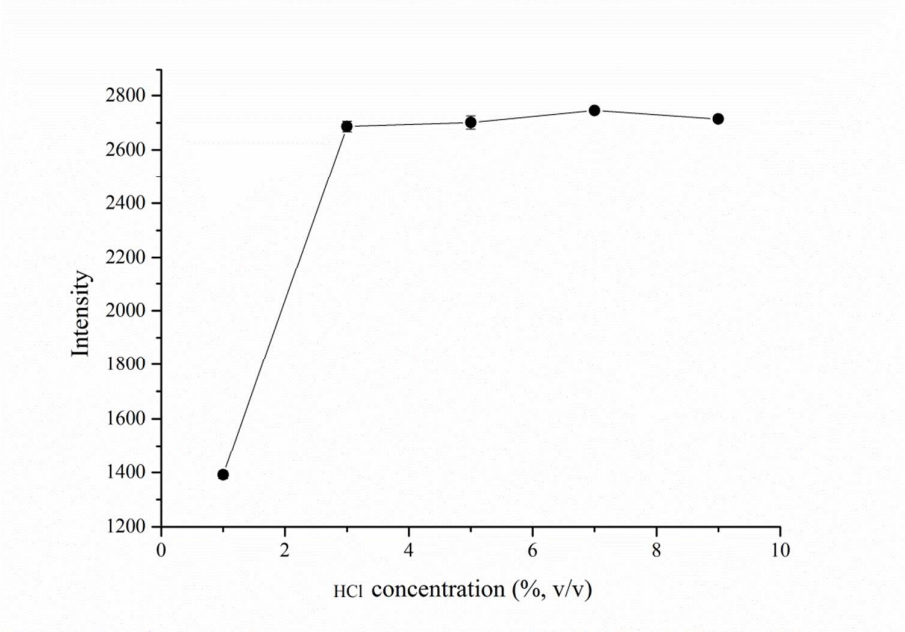

Fig. 3 Effect of HCl concentration on AFS intensity (n = 3)