

Analytical Methods

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

An accurate fast screening for total and inorganic arsenic in rice grain using hydride generation atomic fluorescence spectrometry (HG-AFS)

Bin Chen^a, Warren T. Corns^a, Peter B. Stockwell^a and Jen-How Huang,^{*b}

^a PS Analytical, Unit 3 Crayfields Industrial Estate, Orpington, BR5 3HP, United Kingdom. Fax: +44 1689 896009; Tel: +44 1689 891211; Email: bc@psanalytical.com

^b Environmental Geosciences, University of Basel, CH-4056 Basel, Switzerland. Fax: +41 61 2670483; Tel: +41 61 2670479; Email:jen-how.huang@unibas.ch

Abstract

Two novel methods based on hydride generation atomic fluorescence spectrometry for the accurate screening of total and inorganic arsenic (As) in rice grain digests in 5 and 2 minutes, respectively, are proposed here. Total As determination was achieved using online UV photolysis aided by alkaline potassium persulphate oxidation, which converted all organic As to arsenate and thus allowed quantitative hydride generation. Determination of inorganic As in rice grain was accomplished by selective hydride generation at high acidity (4.8 M HCl), which allowed ~50 times higher efficiency for hydride generation of arsenite than the prevalent form of organic As in rice, namely dimethylarsinic acid (DMA), after pre-reduction of all inorganic As using potassium iodide/ascorbic acid. The accuracy of the method was verified by (1) excellent agreement with the certified value of total As and the literature values of inorganic As in ERM-BC-211 and NIST SRM 1658a; (2) complete recovery of total As in NIST SRM 1568a spiked with additional 2 ng As g⁻¹ of DMA; (3) excellent agreement of total and inorganic As values in 80 samples of different types, origins and treatments (standing for different matrices) compared to ICP-MS and HPLC-ICP-MS measurements; (4) ~100% recovery of inorganic As in NIST SRM 1568a and a round grain rice even spiked with DMA up to 200 ng As g⁻¹. Additionally, the low data dispersion was indicated by the low relative standard deviation (~4.3%) in the day-to-day precision for quantifying inorganic As in NIST SRM 1568a on 7 different days.

Keywords Arsenic speciation · Rice grain · Hydride generation atomic fluorescence spectrometry

29 Introduction

30 The adverse health risk of arsenic (As) and its widespread occurrence in the environment as well as
31 in the food chain has raised great public concerns worldwide¹. Therefore, a routine screening of As
32 concentrations in food materials has become more of an urgent task for food authorities in many
33 countries². It is already well known that speciation, rather than just total As concentration is the key
34 to fully understand the toxicity of As in food products. In the case of As determination in rice grain,
35 several analytical techniques have been proposed such as synchrotron based X-ray spectroscopy and
36 HPLC-ICP-MS after extraction³. Among all, HPLC-ICP-MS is the most frequently applied for As
37 speciation in rice grain^{4,5}. Nevertheless, the use of HPLC-ICP-MS is disadvantaged due to the
38 potential transformation of As species during extraction procedures. Recently, a simple extraction
39 procedure based on hot diluted nitric acid was developed to quantitatively recover As species from
40 rice grains without the risk of specie transformation⁴. The use of ICP-MS however is relatively
41 expensive and may not be feasible for the analysis of large amounts of samples. Moreover, the
42 incomplete digestion of rice grain will result in carbon rich matrix, which may potentially affect
43 ICP-MS detection of As. The capital and running costs of HPLC-ICP-MS is also prohibitive for
44 many food labs in developing countries and it often beyond the expertise in food laboratories. Thus,
45 the objective of this study is to develop and verify the methodology of inorganic and total As
46 determination in rice grains based on hydride generation atomic fluorescence spectrometry (HG-
47 AFS).

49 Experimental

50 Chemicals and reagents

51 All chemicals used in this work, were of analytical reagent grade and were used without further
52 purification. Deionised water (ELGA 15.0 M cm^{-1} , resistivity) was used for all dilutions. NaAsO_2
53 (Sigma, 98%), $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma-Aldrich, 98-102%), $\text{CH}_3\text{AsO}_3\text{Na}$ (Supelco, >98%),
54 $(\text{CH}_3)_2\text{As}(\text{O})\text{OH}$ (Aldrich, >99%) and arsenobetaine (Fluka, >95%) were dissolved in deionised

1
2 55 water to prepare stock solutions of 1.0 g As L^{-1} . Nitric acid (HNO_3) (VWR BDH Prolabo, 69% w/w)
3
4 56 and H_2O_2 (Sigma-Aldrich, 30% w/w) were taken for digestion of rice grain. Hydrochloric acid (HCl)
5
6 57 (VWR BDH Prolabo, 37% wt), KI (Sigma-Aldrich, >99%) and L-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) (Sigma)
7
8
9 58 was used to prepare the carrier solution. Sodium borohydride (NaBH_4) (Aldrich, 98%) was used to
10
11 59 prepare the reductant for HG and a mixed solution of $\text{K}_2\text{S}_2\text{O}_8$ (Sigma-Aldrich, >99%) and NaOH
12
13
14 60 (VWR BDH Prolabo) was the oxidant reagent to support UV photolysis.
15

16 61

18 62 Instrumentation

20
21 63 Atomic Fluorescence Spectrometry (AFS) detection was achieved with a Millennium Excalibur
22
23 64 (10.055, PS Analytical, Orpington, Kent, UK) using a boosted-discharge hollow cathode lamp
24
25 65 (Photron, Australia). The separation of the gaseous arsine from the liquid stream was performed in
26
27
28 66 a Type-A gas liquid separator (PS Analytical, Orpington, Kent, UK). The photo-oxidation of As
29
30 67 compounds take place in a UV cracker (PS Analytical, Orpington, Kent, UK).
31
32

33 68

35 69 Sample collection and extraction procedure

36
37 70 Rice grain of twelve different types (long grain, whole grain, japonica, indica, risotto, round-sticky,
38
39 71 long-sticky, basmati, jasmine, red, black and wild rice) were purchased in the markets and
40
41
42 72 supermarkets in China, Taiwan, Japan, Germany and Switzerland⁴. All rice grain was milled with
43
44 73 an ultracentrifugal mill (ZMI, Retsch, Germany). The certified NIST SRM 1568a was obtained as a
45
46
47 74 fine powder and was used as an experimental sample without further treatments. A 0.5 g rice
48
49 75 powder was digested with 3 mL of concentrated nitric acid in a 50 mL polypropylene vessel. It was
50
51 76 heated with heating blocks (Digi PREP Jr, SCP Science, Canada) at 100°C for an hour before the
52
53
54 77 addition of 1 mL H_2O_2 . Thereafter, the digest was heated for another hour. After cooling the digest
55
56 78 was diluted to 30 mL with distilled water and stored until analysis. External calibration was
57
58
59 79 performed for quantification of As measured with HG-AFS.
60

80

81 Results and Discussion

82 *Characterisation of HG efficiencies at different HCl concentrations using AFS*

83 The HG efficiency depends on the chemical form of As in the digsted sample as well as the
84 chemical conditions used. For accurate results using HG, it is therefore important to understand
85 the chemical speciation and also to optimise the HG conditions. Our preliminary results showed
86 that the HG efficiency of As(III) is close to 100% irrespective of the acidity (Fig. 1). In
87 comparison, HG efficiencies of As(V), MMA and DMA were comparably lower (<40% in 0.6-
88 4.8 M HCl solution). The HG efficiency of As(V) was around 20-30% at the concentration
89 range of HCl investigated. In the case of MMA, its HG efficiency increased slightly with
90 increasing concentrations of HCl. Interestingly, the HG efficiency of DMA was most drastically
91 influenced by HCl concentrations with the HG efficiency of DMA decreasing with HCl
92 concentration. This data illustrates the importance of the consistency of the chemical form of
93 As species between samples and calibration standards for quantifying total As using hydride
94 generation techniques. On the other hand, the remarkable differences of HG efficiency among
95 different As species can be applied to selectively quantify inorganic As in samples such as rice
96 which do not contain appreciable quantities of MMA ⁶.

98 *Development of the UV-HG-AFS method for quantifying total grain arsenic*

99 Digestions based on hot concentrated acids with powerful oxidants e.g. HNO₃-H₂O₂ are capable
100 of complete mineralisation of organic substance in rice grain ⁷. While As(III) is completely
101 oxidised to As(V) at 100°C in a microwave oven with concentrated HNO₃, a complete oxidation
102 of MMA and DMA to As(V) requires much higher temperatures >220 °C and >280 °C ⁸. Thus,
103 the presence of MMA and DMA could potentially cause low recoveries when using HG
104 techniques unless full oxidation of As species is achieved during the sample preparation.
105 Arsenic in rice can be present in inorganic and organic forms ^{2,9}. Especially, in rice of certain
106 origin e.g. from U.S., DMA can be the most prevalent As species of all accounting for up to

1
2 107 ~80% of the total As in rice grain⁹. For total As determination, vigorous digestion techniques
3
4 108 over long periods or ashing is typically used to ensure full oxidation⁸. These pretreatment
5
6 109 procedures are usually complicated and time consuming and may cause analytical uncertainties
7
8
9 110 especially for rice with low As concentrations. To simplify the pre-treatment, we introduced an
10
11 111 online digestion system with UV photolysis (S570U100, PS Analytical, Kent, UK) heated at
12
13 112 100°C, which allowed effective conversion of inorganic and organic As into As(V) in the rice
14
15
16 113 flour digest diluted 1:9 with alkaline persulfate oxidant (3% m/v K₂S₂O₈ and 4% m/v NaOH) to
17
18 114 ensure the alkalinity of the sample to be ~4% (NaOH, m/v). Persulphate supports the
19
20
21 115 mineralisation of MMA and DMA via generation of SO₄^{•-} radicals under UV radiation¹⁰. Our
22
23 116 preliminary investigation showed the efficiency of mineralisation and oxidation of not only
24
25
26 117 MMA and DMA but also As(III) and arsenobetaine (AsBet) were all close to 100% under such
27
28 118 condition (Fig. 2), reflecting the validation of the method we proposed for complete conversion
29
30
31 119 of organic and inorganic As to As(V). Once cooled on line, the digest were further mixed with
32
33 120 0.7% w/w NaBH₄ and 1.2 M HCl for HG and subsequent AFS determination.
34

35 121 36 37 38 122 *Validation of the proposed UV-HG-AFS method for quantifying total grain arsenic*

39
40 123 The validation of the proposed procedure for the total As in rice grain was verified in several
41
42 124 ways. Firstly, we checked the recovery of spiked DMA, the prevalent organic As in rice grain
43
44
45 125 and also the most difficult to decompose. Secondly, ground rice flour of NIST SRM 1568a was
46
47 126 analysed and the result compared to the certified value. In addition to this, the results of 80
48
49 127 different rice samples of various varieties were compared to ICP-MS. An excellent recovery of
50
51
52 128 100% was found for the NIST SRM 1568a (certified 290 ± 30 ng g⁻¹ versus found 290 ± 2 ng
53
54 129 g⁻¹, n=3) and also for the DMA spikes (97%, spiked 2.0 ng g⁻¹ versus found 1.93 ± 0.7 ng g⁻¹,
55
56
57 130 n=3). Finally, UV-HG-AFS based quantification of total As in 80 rice samples are in good
58
59 131 agreement with those measured with ICP-MS in Huang et al.⁴ (Fig. 4).
60

132

1
2 133 *Development of the HG-AFS method for quantifying inorganic grain arsenic*

3
4 134 For inorganic As determination, the digest was first diluted 1:9 with reagent blank containing
5
6
7 135 4.8 M HCl and 1% m/v KI and 0.2% m/v L-ascorbic acid to ensure the high acidity required to
8
9 136 minimise the DMA interference. The solution was left for 30 minutes at room temperature prior
10
11
12 137 to the analysis by HG-AFS to pre-reduce As(V) to As(III) to maximise the HG efficiency.
13
14 138 Scheme of the instrumental arrangement and the conditions of operation for both methods
15
16 139 proposed are detailed in Table 1 and Fig. 3. The proposed method for inorganic As in rice offers
17
18 140 an accurate screening method regardless of what DMA percentage might be present in rice grain.
19
20
21 141 Very few interferences are found when using the HG-AFS for As determinations ¹¹. We have
22
23 142 examined the interference of As analysis using HG-AFS caused by different chemical species at
24
25 143 different levels of concentrations, showing generally negligible influences on the As recoveries
26
27
28 144 (Table 2). Organic substances which may cause interference with HG-AFS analysis were
29
30 145 completely decomposed after HNO₃-H₂O₂ digestion. Thus, the major concern with this method
31
32
33 146 is that MMA will form a hydride at approximately 20% efficiency and if present in rice a
34
35 147 positive bias for the inorganic As measurement would occur. In the 80 rice samples analysed in
36
37 148 this study using HPLC-ICP-MS and also by HPLC-HG-AFS no MMA was found, which to the
38
39
40 149 best of knowledge appears to be in agreement with the information reported in the literature ².
41
42 150 An U.S. FDA survey of As speciation in 487 rice samples (mostly from U.S.) showed that
43
44 151 MMA is rarely found in rice samples independent of origins, types and treatments ¹². Arsenic
45
46
47 152 speciation in 121 rice of different origins and types gave an averaged percentage of MMA to
48
49 153 total As of 1.0 % ². At the HG conditions adopted here for MMA the error would be less than
50
51
52 154 0.4%. The negligible errors for inorganic As determination caused by MMA in rice has been
53
54 155 recently verified in Musil et al. ⁶. Another important prerequisite is the large difference of HG
55
56 156 efficiencies between inorganic As and DMA. We have identified that in 4.8 M HCl solution, the
57
58
59 157 efficiency of As(III) is 100%, whereas the HG efficiency of DMA is close to zero (Fig. 1). In
60
158 comparison, the difference of HG efficiency between DMA and As(V) (~30%) is not so

1
2 159 remarkable which highlights the importance of the pre-reduction step using KI/L-ascorbic acid.
3
4 160 Even spiking an additional 60, 120 and 200 ng As g⁻¹ DMA in NIST SRM 1568a and one
5
6
7 161 selected round grain rice, we observed constant values of inorganic As concentrations,
8
9 162 suggesting the correctness of our hypothesis (Fig. 5).
10

11
12 163
13
14 164 *Validation of the proposed HG-AFS method for quantifying grain inorganic arsenic*
15

16 165 Our newly proposed method for inorganic As in rice grain was further validated by comparing
17
18
19 166 the inorganic As concentrations in ERM-BC-211, NIST SRM 1568a and 80 samples of rice
20
21 167 grains of different types and origins in Huang et al. ⁴. First, we have found 121.4 ± 4.8 ng g⁻¹ (n
22
23
24 168 = 6) of inorganic As in ERM-BC-211 from two batches digested on different days, which is
25
26 169 comparable to the certificated value of inorganic As (124 ± 11 ng g⁻¹). Also, we are able to
27
28
29 170 measure 98.6 ± 5.6 ng As g⁻¹ (n = 18) of inorganic As in NIST SRM 1568a. This was
30
31 171 performed over 18 consecutive batches of sample digests and measurements and the precision
32
33
34 172 found was acceptable. In addition, day-to-day precision was ensured by quantification of
35
36 173 inorganic As in NIST SRM 1568a on 7 different days with a value of 99.9 ± 4.3 ng g⁻¹,
37
38 174 corresponding to a relative standard deviation of 4.3%. Although there is no certified
39
40
41 175 concentration of inorganic As in NIST SRM 1568a, this value is close to those from the other
42
43 176 studies (e.g. 104.4 ± 7.0 , in Huang et al. ², 103 ± 7 in Musil et al. ⁶ and 102 ± 5 in Chen et al. ¹³).
44
45 177 Finally, analysis of total grain As in 80 rice samples are in good agreement with those measured
46
47
48 178 with HPLC-ICP-MS (Fig. 6). This approach however relies on the summation of inorganic As
49
50 179 and such the measurement uncertainty is likely to be higher than a direct selective hydride
51
52
53 180 measurement.
54

55 181
56
57 182 *Novelty of the proposed methods against the previous HG based methods*
58

59 183 Recently, an similar HG-AFS system was validated to quantify inorganic As and DMA in
60
184 fishes and waters ¹⁴, nevertheless, without consideration of the interference caused by DMA and

1
2 185 MMA. Thus, in this study, we not only validated the HG-AFS system for accurate and rapid As
3
4 186 speciation in rice grain but also carefully optimised the HG conditions to minimise such
5
6
7 187 interference effectively. Hydride generation at high acidity was also applied to speciation of
8
9 188 inorganic As in rice and sea food using ICP-MS detection ⁶. The major drawback of this method
10
11 189 was the ⁴⁰Ar³⁵Cl interference caused by the high HCl concentration, for which a specific triple
12
13
14 190 quadruple ICP-MS was required to eliminate such interference. Thus, our HG-AFS method
15
16 191 performs better than the HG-ICP-MS method in terms of free of the Cl interference and a much
17
18 192 lower analysis cost. Moreover, instead of oxidising all inorganic As into As(V), our
19
20
21 193 quantification of inorganic As was based on reducing all inorganic As to As(III), which
22
23 194 providing higher methodical sensitivity due to approximately tripled HG efficiency of As(III)
24
25
26 195 than As(V) (Fig. 1).
27

30 197 *Applicability of the proposed HG-AFS methods*

31
32
33 198 Both of the newly proposed HG-AFS based methods for quantification of total and inorganic As
34
35 199 in rice grain are highly applicable to the real rice samples. Their general applicability was
36
37 200 carefully examined by analyses of 80 rice samples of different geographic origins, rice types,
38
39
40 201 grain sizes, cultural practices and polish treatments ². Perfect agreement with the results
41
42 202 obtained from HPLC-ICP-MS depicted the accuracy of our proposed HG-AFS methods and
43
44 203 highlighted the insignificant influence of the matrix from different rice samples on the HG-AFS
45
46
47 204 analysis. Together with the low analysis cost and short run time, it makes the proposed HG-AFS
48
49 205 method extremely ideal for food safety labs to screen total and inorganic As in rice. We
50
51 206 envision the HG-AFS method to allow more comprehensive survey on As speciation in rice for
52
53
54 207 the food safety agencies worldwide, even for the third countries, and to provide more efficient
55
56 208 risk assessment for people with rice as their major foodstuff.
57

58 59 209 **Conclusion** 60

1
2 211 We have developed two HG-AFS based methods for accurate and sensitive determination of
3
4 212 total and inorganic As in rice. For total As determination we have developed a method using
5
6
7 213 UV photolysis to fully oxidise all forms of As. This simplifies the sample preparation technique
8
9 214 for HG techniques and this was demonstrated using various organic As species which are
10
11 215 otherwise very difficult to decompose. The method was applied to rice grain samples and the
12
13 216 results were compared to ICP-MS. The accuracy and precision of this approach for total As was
14
15
16 217 also verified using a NIST SRM 1568a. For inorganic As we have developed a selective HG
17
18 218 method using high acid concentrations to inhibit the formation of DMA hydride which would
19
20
21 219 otherwise produce a positive bias to the inorganic As result. It is imperative that this procedure
22
23 220 includes a DMA quality control check to confirm that the DMA hydride formation is less than
24
25
26 221 5%. This is especially important for samples containing high percentage of DMA. This
27
28 222 approach was validated using DMA sample spike experiments and by running comparison
29
30 223 studies with HPLC-ICP-MS. The inorganic As method is an ideal candidate as a screening tool
31
32
33 224 for food labs conducting inorganic As in foodstuff. The measurement run is approximately 2
34
35 225 minutes per sample.
36
37
38 226
39

40 227 **References**

- 41
42
43
44 228 1.R. Stone, *Science*, 2008, 321, 184-185.
45
46 229 2.J. H. Huang, P. Fecher, G. Ilgen, K. N. Hu and J. Yang, *Food Chem.*, 2012, 130, 453-459.
47
48
49 230 3.A. M. Carey, E. Lombi, E. Donner, M. D. de Jonge, T. Punshon, B. P. Jackson, M. L.
50 231 Guerinot, A. H. Price and A. A. Meharg, *Anal. Bioanal. Chem.*, 2012, 402, 3275-3286.
51
52
53 232 4.J.-H. Huang, G. Ilgen and P. Fecher, *J. Anal. At. Spectrom.*, 2010, 25, 800-802.
54
55
56 233 5.T. Narukawa and K. Chiba, *J. Agric. Food Chem.*, 2010, 58, 8183-8188.
57
58 234 6.S. Musil, A. H. Petursdottir, A. Raab, H. Gunnlaugsdottir, E. Knipp and J. Feldmann, *Anal.*
59 235 *Chem.*, 2014, 86, 993-999.
60
236 7.A. Raab, C. Baskaran, J. Feldmann and A. A. Meharg, *J. Environ. Monit.*, 2009, 11, 41-44.

- 1
2 237 8.W. Goessler and M. Pavkov, *Analyst*, 2003, 128, 796-802.
3
4
5 238 9.Y. J. Zavala, R. Gerads, H. Gurleyuk and J. M. Duxbury, *Environ. Sci. Technol.*, 2008, 42,
6 239 3861-3866.
7
8
9 240 10. Y. Sung-Hwan, L. Seockheon, K. Tae-Hun, L. Myunjoo and Y. Seungho, *Chem. Eng. J.*,
10 241 2011, 173, 290-295.
11
12
13 242 11. C. G. Yuan, G. B. Jiang and B. He, *J. Anal. At. Spectrom.*, 2005, 20, 103-110.
14
15
16 243 12. U. S. FDA,
17 244 <http://www.fda.gov/downloads/Food/FoodborneIllnessContaminants/Metals/UCM35246>
18 245 [7.pdf](http://www.fda.gov/downloads/Food/FoodborneIllnessContaminants/Metals/UCM35246), 2013.
19
20
21 246 13. G. Y. Chen and T. W. Chen, *Talanta*, 2014, 119, 202-206.
22
23
24 247 14. L. L. Chaparro, L. Ferrer, V. Cerda and L. O. Leal, *Anal. Bioanal. Chem.*, 2012, 404,
25 248 1589-1595.
26
27 249
28 250
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
 2 251 **Table 2.** Recoveries of 2 and 10 $\mu\text{g L}^{-1}$ of arsenic using HG-AFS detection in the presence of
 3
 4 252 different chemical species at different levels of concentrations in 4.8 M HCl after KI pre-reduction.
 5
 6 253 Mean values and standard deviations of three replicates are shown.

Species	Concentrations (mg L^{-1})	Recoveries of arsenic	
		2 $\mu\text{g L}^{-1}$ of arsenic	10 $\mu\text{g L}^{-1}$ of arsenic
Sr^{2+}	20	107.3 \pm 5.9	100.0 \pm 2.5
Zn^{2+}	1	101.7 \pm 5.5	91.0 \pm 3.1
Si^{4+}	1	94.4 \pm 3.7	102.4 \pm 1.7
Al^{3+}	1	104.6 \pm 0.8	98.9 \pm 0.8
Ca^{2+}	200	101.8 \pm 1.3	103.3 \pm 1.3
Na^+	200	104.2 \pm 1.6	100.6 \pm 1.8
K^+	200	96.3 \pm 0.7	97.6 \pm 0.7
In^{3+}	1	99.4 \pm 1.4	99.1 \pm 1.5
Ba^{2+}	1	95.2 \pm 3.1	105.9 \pm 1.4
Mg^{2+}	1	99.7 \pm 3.5	97.2 \pm 1.5
Cd^{2+}	1	100.4 \pm 0.9	97.2 \pm 0.2
Au^+	0.1	97.8 \pm 6.4	103.2 \pm 1.4
Fe^{3+}	1	99.0 \pm 0.9	100.2 \pm 0.7
Sn^{4+}	1	95.1 \pm 1.9	104.8 \pm 1.8
Ge^{4+}	1	104.4 \pm 3.0	102.1 \pm 1.1
Hg^{2+}	1	100.7 \pm 0.7	98.1 \pm 0.4
Cr^{3+}	1	101.0 \pm 1.2	98.4 \pm 0.6
Co^{2+}	1	103.1 \pm 0.7	99.9 \pm 2.0
Ag^+	1	97.9 \pm 1.8	95.9 \pm 2.3
Ni^{2+}	1	100.2 \pm 0.4	98.8 \pm 1.2
Te^{4+}	1	101.5 \pm 0.6	100.3 \pm 1.0
Sb^{3+}	0.05	107.3 \pm 1.8	97.5 \pm 1.7
Cu^{2+}	2	98.8 \pm 1.1	99.0 \pm 1.0

40 254

41

42 255

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

Table 1. Instrumental settings for total and inorganic arsenic determination in rice grain utilising UV-HG-AFS and selective HG-AFS.

Parameters	Total arsenic	Inorganic arsenic
Carrier solution	1.2 M HCl	4.8 M HCl, 1% KI (m/v) 0.2% L-ascorbic acid (m/v)
Reductant	0.7% NaBH ₄ in 1% NaOH (m/v)	0.7% NaBH ₄ in 1% NaOH (m/v)
Calibration range	0.5 – 5 ng mL ⁻¹	0.1 – 1 ng mL ⁻¹
Flow rate	4.5 mL min ⁻¹	9 mL min ⁻¹
Run time	5 min	2 min
Detection limit	3 ng g ⁻¹	1 ng g ⁻¹

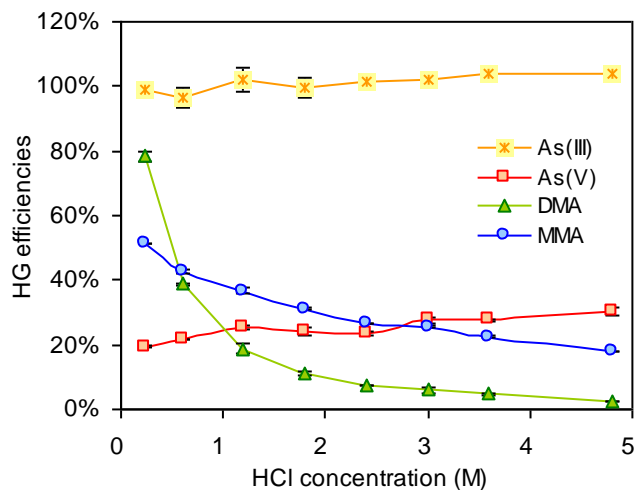


Fig. 1. Hydride generation (HG) efficiencies of As(III), As(V), MMA and DMA at different concentrations of HCl. Each $1.0 \mu\text{g L}^{-1}$ of As species was taken for efficiency examination. Mean values and standard deviations of 3 replicates are shown.

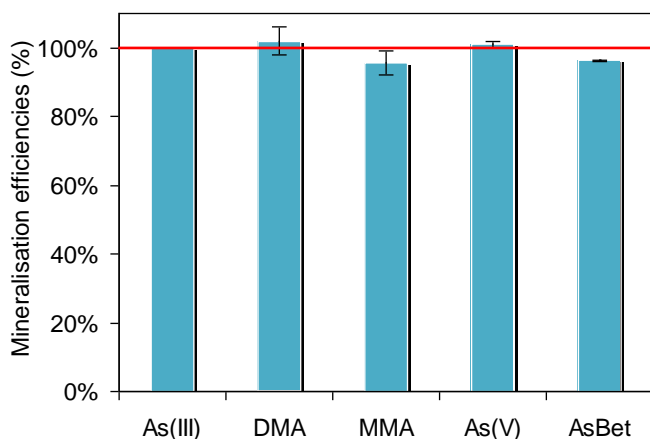


Fig. 2. Mineralisation efficiencies of each $20 \mu\text{g As L}^{-1}$ of As(III), As(V), MMA, DMA and AsBet by UV cracker at 100°C in the support with $\text{K}_2\text{S}_2\text{O}_8$. Mean values and standard deviation of 3 replicates are shown.

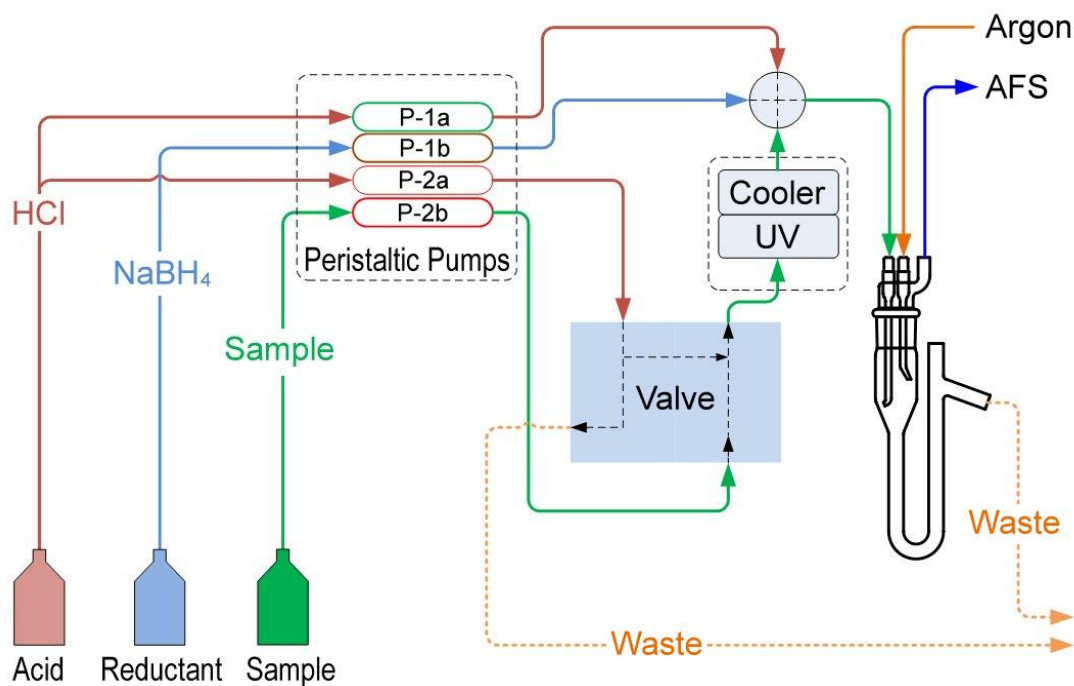


Fig. 3. Schematic presentation of the instrumental arrangement of UV-HG-AFS for total arsenic analysis and HG-AFS for inorganic arsenic analysis (when UV module is removed).

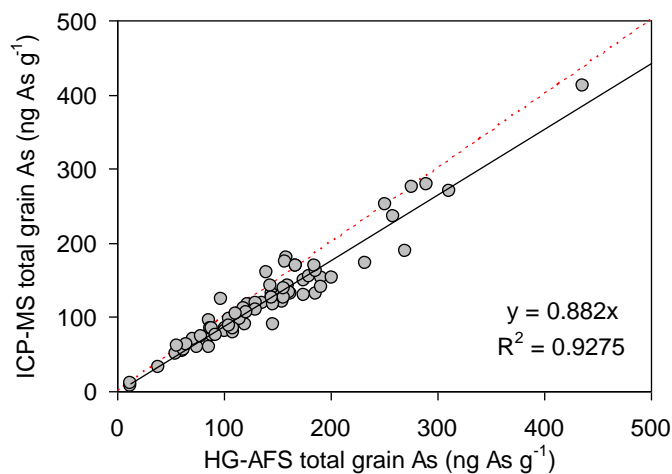


Fig. 4. The correlation between the concentration of total grain arsenic as measured by HG-AFS and ICP-MS after $\text{HNO}_3\text{-H}_2\text{O}_2$ and concentrated nitric acid digestion, respectively. The slope of the regression line is shown. Dot line shows the 1:1 line.

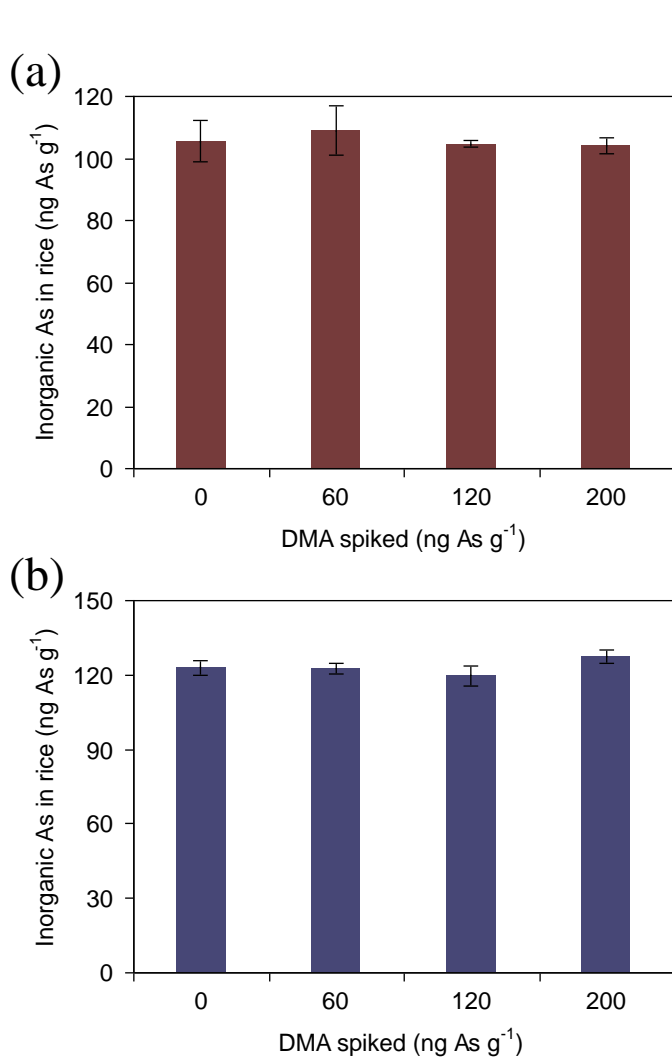


Fig. 5. Concentrations of inorganic grain arsenic in (a) NIST SRM 1568a containing high percentage of DMA and (b) round grain rice containing very low percentage of DMA, both spiked at different amounts of additional DMA as measured by HG-AFS in 4.8 M HCl solution with KI and L-ascorbic acid. Mean values and standard deviations of 3 replicates are shown.

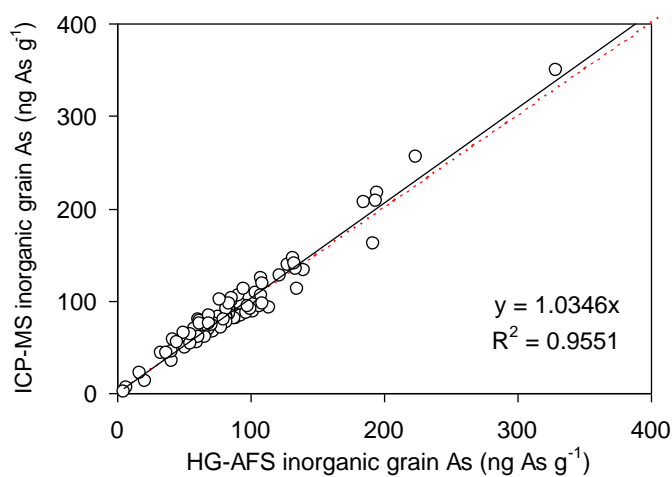


Fig. 6. The correlation between the concentration of inorganic grain arsenic as measured by HG-AFS and HPLC-ICP-MS after nitric acid extraction. The slope of the regression line is shown. Dot line shows the 1:1 line.