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

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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, resepctively, 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 dimethylarsonic acid (DMA), after pre-reduction of all inorganic As using potassium iodide/ascorbic acid. The accuary 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

Introduction

The adverse health risk of arsenic (As) and its widespread occurrence in the environment as well as in the food chain has raised great public concerns worldwide [1]. Therefore, a routine screening of As concentrations in food materials has become more of an urgent task for food authorities in many countries [2]. It is already well known that speciation, rather than just total As concentration is the key to fully understand the toxicity of As in food products. In the case of As determination in rice grain, several analytical techniques have been proposed such as synchrotron based X-ray spectroscopy and HPLC-ICP-MS after extraction [3]. Among all, HPLC-ICP-MS is the most frequently applied for As speciation in rice grain [4, 5]. Nevertheless, the use of HPLC-ICP-MS is disadvantaged due to the potential transformation of As species during extraction procedures. Recently, a simple extraction procedure based on hot diluted nitric acid was developed to quantitatively recover As species from rice grains without the risk of specie transformation [4]. The use of ICP-MS however is relatively expensive and may not be feasible for the analysis of large amounts of samples. Moreover, the incomplete digestion of rice grain will result in carbon rich matrix, which may potentially affect ICP-MS detection of As. The capital and running costs of HPLC-ICP-MS is also prohibitive for many food labs in developing countries and it often beyond the expertise in food laboratories. Thus, the objective of this study is to develop and verify the methodology of inorganic and total As determination in rice grains based on hydride generation atomic fluorescence spectrometry (HG-AFS).

Experimental

Chemicals and reagents

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Deionised water (ELGA 15.0 M cm^{-1}, resistivity) was used for all dilutions. $NaAsO_2$ (Sigma, 98%), $Na_2HAsO_4 \cdot 7H_2O$ (Sigma-Aldrich, 98-102%), CH_5AsO_3Na (Supelco, >98%), $(CH_3)_2As(O)OH$ (Aldrich, >99%) and arsenobetaine (Fluka, >95%) were dissolved in deionised

55 water to prepare stock solutions of 1.0 g As L^{-1}. Nitric acid (HNO$_3$) (VWR BDH Prolabo, 69% w/w)

56 and H$_2$O$_2$ (Sigma-Aldrich, 30% w/w) were taken for digestion of rice grain. Hydrochloric acid (HCl)

57 (VWR BDH Prolabo, 37% wt), KI (Sigma-Aldrich, >99%) and L-ascorbic acid (C$_6$H$_8$O$_6$) (Sigma)

58 was used to prepare the carrier solution. Sodium borohydride (NaBH$_4$) (Aldrich, 98%) was used to

59 prepare the reductant for HG and a mixed solution of K$_2$S$_2$O$_8$ (Sigma-Aldrich, >99%) and NaOH

60 (VWR BDH Prolabo) was the oxidant reagent to support UV photolysis.

61

62 Instrumentation

63 Atomic Fluorescence Spectrometry (AFS) detection was achieved with a Millennium Excalibur

64 (10.055, PS Analytical, Orpington, Kent, UK) using a boosted-discharge hollow cathode lamp

65 (Photron, Australia). The separation of the gaseous arsine from the liquid stream was performed in

66 a Type-A gas liquid separator (PS Analytical, Orpington, Kent, UK). The photo-oxidation of As

67 compounds take place in a UV cracker (PS Analytical, Orpington, Kent, UK).

68

69 Sample collection and extraction procedure

70 Rice grain of twelve different types (long grain, whole grain, japonica, indica, risotto, round-sticky,

71 long-sticky, basmati, jasmine, red, black and wild rice) were purchased in the markets and

72 supermarkets in China, Taiwan, Japan, Germany and Switzerland [4]. All rice grain was milled with

73 an ultracentrifugal mill (ZMI, Retsch, Germany). The certified NIST SRM 1568a was obtained as a

74 fine powder and was used as an experimental sample without further treatments. A 0.5 g rice

75 powder was digested with 3 mL of concentrated nitric acid in a 50 mL polypropylene vessel. It was

76 heated with heating blocks (Digi PREP Jr, SCP Science, Canada) at 100°C for an hour before the

77 addition of 1 mL H$_2$O$_2$. Thereafter, the digest was heated for another hour. After cooling the digest

78 was diluted to 30 mL with distilled water and stored until analysis. External calibration was

79 performed for quantification of As measured with HG-AFS.

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 drasticly

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].

97

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. HNO_3-H_2O_2 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 HNO_3, 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

4

107   ~80% of the total As in rice grain [9]. For total As determination, vigourous digestion techniques

108   over long periods or ashing is typically used to ensure full oxidation [8]. These pretreament

109   procedures are usually complicated and time consuming and may cause analytical uncertainties

110   especially for rice with low As concentrations. To simplify the pre-treatment, we introduced an

111   online digestion system with UV photolysis (S570U100, PS Analytical, Kent, UK) heated at

112   $100^{o}C$, which allowed effective conversion of inorganic and organic As into As(V) in the rice

113   flour digest diluted 1:9 with alkaline persulfate oxidant (3% m/v $K_2S_2O_8$ and 4% m/v NaOH) to

114   ensure the alkalinity of the sample to be ~4% (NaOH, m/v). Persulphate supports the

115   mineralisation of MMA and DMA via generation of $SO_4^{\bullet-}$ radicals under UV radiation [10]. Our

116   preliminary investigation showed the efficiency of mineralisation and oxidation of not only

117   MMA and DMA but also As(III) and arsenobetaine (AsBet) were all close to 100% under such

118   condition (Fig. 2), reflecting the validation of the method we proposed for complete conversion

119   of organic and inorganic As to As(V). Once cooled on line, the digest were further mixed with

120   0.7% w/w $NaBH_4$ and 1.2 M HCl for HG and subsequent AFS determination.

121

122   *Validation of the proposed UV-HG-AFS method for quantifying total grain arsenic*

123   The validation of the proposed procedure for the total As in rice grain was verified in several

124   ways. Firstly, we chekced the recovery of spiked DMA, the prevalent organic As in rice grain

125   and also the most difficult to decompose. Secondily, ground rice flour of NIST SRM 1568a was

126   analysed and the result compared to the certified value. In addition to this, the results of 80

127   different rice samples of various varieties were compared to ICP-MS. An excellent recovery of

128   100% was found for the NIST SRM 1568a (certified 290 ± 30 ng g^{-1} versus found 290 ± 2 ng

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},

130   n=3). Finally, UV-HG-AFS based quantification of total As in 80 rice samples are in good

131   agreement with those measured with ICP-MS in Huang et al. [4] (Fig. 4).

132

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

134 For inorganic As determination, the digest was first diluted 1:9 with reagent blank containing

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

136 minimise the DMA interference. The solution was left for 30 minutes at room temperature prior

137 to the analysis by HG-AFS to pre-reduce As(V) to As(III) to maximise the HG efficiency.

138 Scheme of the instrumental arrangement and the conditions of operation for both methods

139 proposed are detailed in Table 1 and Fig. 3. The proposed method for inorganic As in rice offers

140 an accurate screening method regardless of what DMA percentage might be present in rice grain.

141 Very few interferences are found when using the HG-AFS for As determinations [11]. We have

142 examined the interference of As analysis using HG-AFS caused by different chemical species at

143 different levels of concentrations, showing generally negiligible influences on the As recoveries

144 (Table 2). Organic substances which may cause interference with HG-AFS analysis were

145 completely decomposed after HNO_3-H_2O_2 digestion. Thus, the major concern with this method

146 is that MMA will form a hydride at approximately 20% efficiency and if present in rice a

147 positive bias for the inorganic As measurement would occur. In the 80 rice samples analysed in

148 this study using HPLC-ICP-MS and also by HPLC-HG-AFS no MMA was found, which to the

149 best of knowledge appears to be in agreement with the information reported in the literature [2].

150 An U.S. FDA survey of As speciation in 487 rice samples (mostly from U.S.) showed that

151 MMA is rarely found in rice samples independent of origins, types and treatments [12]. Arsenic

152 speciation in 121 rice of different origins and types gave an averaged percentage of MMA to

153 total As of 1.0 % [2]. At the HG conditions adopted here for MMA the error would be less than

154 0.4%. The negligible errors for inorganic As determination caused by MMA in rice has been

155 recently verified in Musil et al. [6]. Another important prerequisite is the large difference of HG

156 efficiencies between inorganic As and DMA. We have identified that in 4.8 M HCl solution, the

157 efficiency of As(III) is 100%, whereas the HG efficiency of DMA is close to zero (Fig. 1). In

158 comparison, the difference of HG efficiency between DMA and As(V) (~30%) is not so

159 remarkable which highlights the importance of the pre-reduction step using KI/L-ascorbic acid.

160 Even spiking an additional 60, 120 and 200 ng As g^{-1} DMA in NIST SRM 1568a and one

161 selected round grain rice, we observed constant values of inorganic As concentrations,

162 suggesting the correctness of our hypothesis (Fig. 5).

163

164 *Validation of the proposed HG-AFS method for quantifying grain inorganic arsenic*

165 Our newly proposed method for inorganic As in rice grain was further validated by comparing

166 the inorganic As concentrations in ERM-BC-211, NIST SRM 1568a and 80 samples of rice

167 grains of different types and origins in Huang et al. [4]. First, we have found 121.4 ± 4.8 ng g^{-1} (n

168 = 6) of inorganic As in ERM-BC-211 from two batches digested on different days, which is

169 comparable to the certificated value of inorganic As (124 ± 11 ng g^{-1}). Also, we are able to

170 measure 98.6 ± 5.6 ng As g^{-1} (n = 18) of inorganic As in NIST SRM 1568a. This was

171 performed over 18 consecutive batches of sample digests and measurements and the precision

172 found was acceptable. In addition, day-to-day precision was ensured by quantification of

173 inorganic As in NIST SRM 1568a on 7 different days with a value of 99.9 ± 4.3 ng g^{-1},

174 corresponding to a relative standard deviation of 4.3%. Although there is no certified

175 concentration of inorganic As in NIST SRM 1568a, this value is close to those from the other

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]).

177 Finally, analysis of total grain As in 80 rice samples are in good agreement with those measured

178 with HPLC-ICP-MS (Fig. 6). This approach however relies on the summation of inorganic As

179 and such the measurement uncertainty is likely to be higher than a direct selective hydride

180 measurement.

181

182 *Novelty of the proposed methods against the previous HG based methods*

183 Recently, an similar HG-AFS system was validified to quantify inorganic As and DMA in

184 fishes and waters [14], nevertheless, without consideration of the interference caused by DMA and

185 MMA. Thus, in this study, we not only validated the HG-AFS system for accurate and rapid As

186 speciation in rice grain but also carefully optimised the HG conditions to minimise such

187 interference effectively. Hydride generation at high acidity was also applied to speciation of

188 inorganic As in rice and sea food using ICP-MS detection [6]. The major drawback of this method

189 was the $^{40}Ar^{35}Cl$ interference caused by the high HCl concentration, for which a specific triple

190 quadruple ICP-MS was required to eliminate such interference. Thus, our HG-AFS method

191 performs better than the HG-ICP-MS method in terms of free of the Cl interference and a much

192 lower analysis cost. Moreover, instead of oxidising all inorganic As into As(V), our

193 quantification of inorganic As was based on reducing all inorganic As to As(III), which

194 providing higher methodical sensitivity due to approximately tripled HG efficiency of As(III)

195 than As(V) (Fig. 1).

196

Applicability of the proposed HG-AFS methods

198 Both of the newly proposed HG-AFS based methods for quantification of total and inorganic As

199 in rice grain are highly applicable to the real rice samples. Their general applicability was

200 carefully examined by analyses of 80 rice samples of different geographic origins, rice types,

201 grain sizes, cultural practices and polish treatments [2]. Perfect agreement with the results

202 obtained from HPLC-ICP-MS depicted the accuracy of our proposed HG-AFS methods and

203 highlighted the insignificant influence of the matrix from different rice samples on the HG-AFS

204 analysis. Together with the low analysis cost and short run time, it makes the proposed HG-AFS

205 method extremely ideal for food safety labs to screen total and inorganic As in rice. We

206 envision the HG-AFS method to allow more comprehensive survey on As speciation in rice for

207 the food safety agencies worldwide, even for the third countries, and to provide more efficient

208 risk assessment for people with rice as their major foodstuff.

209

210 **Conclusion**

211 We have developed two HG-AFS based methods for accurate and sensitive determination of

212 total and inorganic As in rice. For total As determination we have developed a method using

213 UV photolysis to fully oxidise all forms of As. This simplifies the sample preparation technique

214 for HG techniques and this was demonstarted using various organic As species which are

215 otherwise very difficult to decompose. The method was applied to rice grain samples and the

216 results were compared to ICP-MS. The accuracy and precsion of this approach for total As was

217 also verified using a NIST SRM 1568a. For inorganic As we have a developed a selective HG

218 method using high acid concentrations to inhibit the formation of DMA hydride which would

219 otherwise produce a postive bias to the inorganic As result. It is imperative that this procedure

220 includes a DMA quality control check to confirm that the DMA hydride formation is less than

221 5%. This is especially important for samples containing high percentage of DMA. This

222 approach was validated using DMA sample spike experiments and by running comparison

223 studies with HPLC-ICP-MS. The inorganic As method is an ideal candidate as a screening tool

224 for food labs conducting inorganic As in foodstuff. The measuremnet run is approximately 2

225 minutes per sample.

226

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Table 2. Recoveries of 2 and 10 µg L^{-1} of arsenic using HG-AFS detection in the presence of different chemical species at different levels of concentrations in 4.8 M HCl after KI pre-reduction. Mean values and standard deviations of three replicates are shown.

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

11

256 **Table 1.** Instrumental settings for total and inorganic arsenic determination in rice grain utlising

257 UV-HG-AFS and selective HG-AFS.

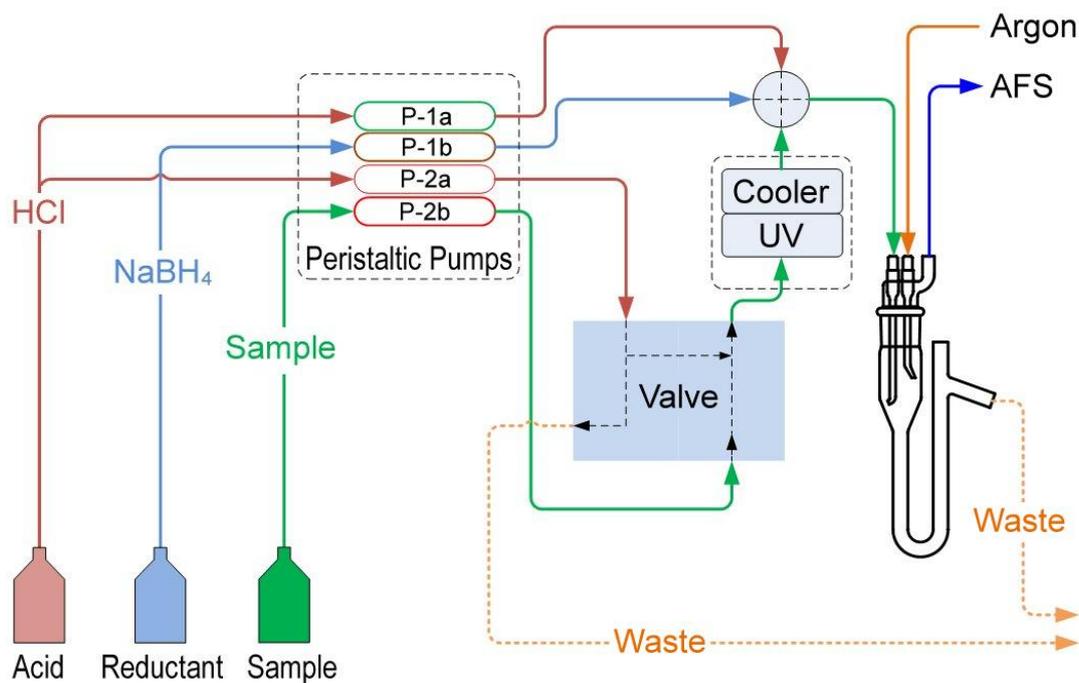| Parameters	Total arsenic	Inorganic arsenic
Carrier solution	1.2 M HCl	4.8 M HCl, 1% KI (m/v)
		0.2% L-ascorbic acid (m/v)
Reductant	0.7% NaBH$_4$ in 1% NaOH (m/v)	0.7% NaBH$_4$ in 1% NaOH (m/v)
Calibration range	$0.5 - 5$ ng mL^{-1}	$0.1 - 1$ ng mL^{-1}
Flow rate	4.5 mL min^{-1}	9 mL min^{-1}
Run time	5 min	2 min
Detection limit	3 ng g^{-1}	1 ng g^{-1}

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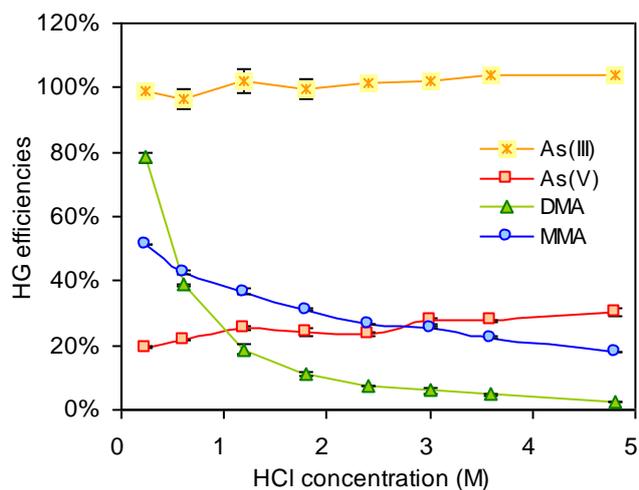
Fig. 1. Hydride generation (HG) efficiencies of As(III), As(V), MMA and DMA at different concentrations of HCl. Each 1.0 µg L^{-1} of As species was taken for efficiency examination. Mean values and standard deviations of 3 replicates are shown.

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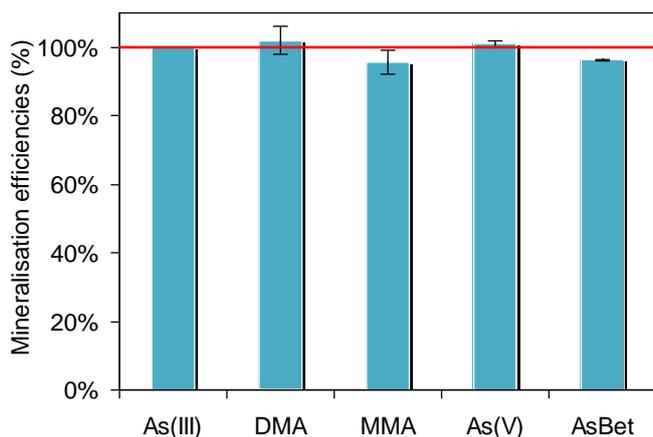
**Fig. 2.** Mineralisation efficiencies of each 20 µg As L^{-1} of As(III), As(V), MMA, DMA and AsBet by UV cracker at $100^{o}C$ in the support with $K_2S_2O_8$. Mean values and standard deviation of 3 replicates are shown.

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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).

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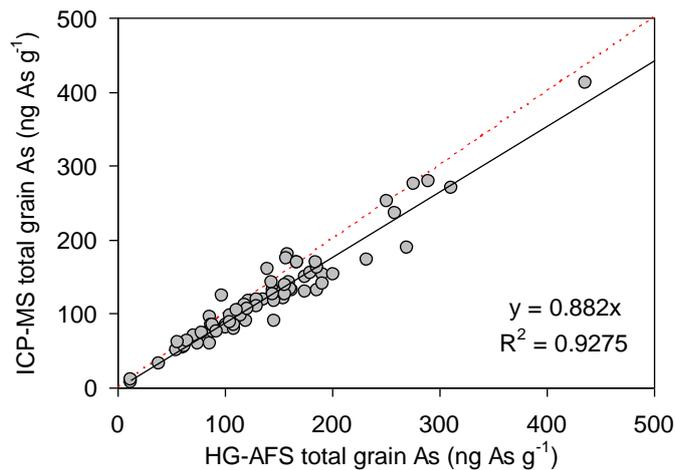
Fig. 4. The correlation between the concentration of total grain arsenic as measured by HG-AFS and ICP-MS after HNO_3-H_2O_2 and concentrated nitric acid digestion, respectively. The slope of the regression line is shown. Dot line shows the 1:1 line.

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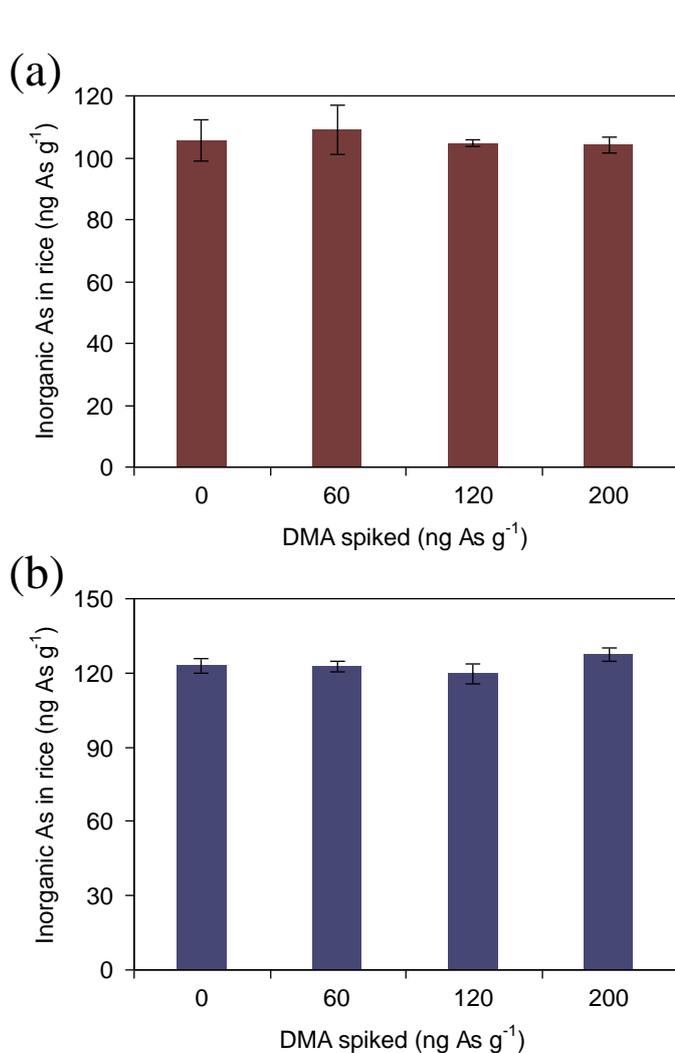
Fig. 5. Concentrations of inorganic grain arsenic in (a) NIST SRM 1568a containing high percentage of DMA and (b) round grain rice containing very low percentage of DMA, both spiked at different amounts of additional DMA as measured by HG-AFS in 4.8 M HCl solution with KI and L-ascorbic acid. Mean values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

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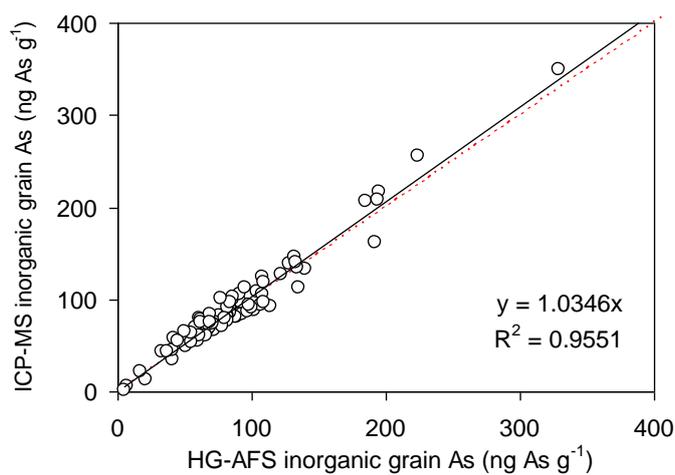
299 **Fig. 6**. The correlation between the concentration of inorganic grain arsenic as measured by HG-
300 AFS and HPLC-ICP-MS after nitric acid extraction. The slope of the regression line is shown. Dot
301 line shows the 1:1 line.