Slurry Sampling and HG AFS for the Determination of Total Arsenic in Rice Samples

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Abstract This paper proposes a procedure for the determination of total arsenic in rice using slurry sampling and hydride generation atomic fluorescence spectrometry (HG AFS). During optimization, water, hydrochloric acid, and nitric acid solutions were tested as extractor. Best results were found using 2.0 $mol L^{-1}$ nitric acid solutions. The slurries are prepared using 200 mg of rice sample, 5.0 mL of nitric acid solution, and sonication for 30 min. Then, an aliquot of 5.0 mL of the slurry was taken and 3.0 mL of 1.5 $mol L^{-1}$ hydrochloric acid solution and 1.5 mL of 10 % potassium iodide in 2 % ascorbic acid solution were added. After 30 min, the volume was completed up to 10 mL with ultra-pure water and arsenic quantified by HG AFS. In these experimental conditions, the method allows the determination of arsenic employing external calibration, with limits of detection and quantification of 1.1 and 3.3 $ng g^{-1}$ and precision expressed as relative standard deviation (%RSD) varying between 5.9 and 1.3 % for arsenic concentration of 0.12 and 0.47 $\mu g g^{-1}$. Accuracy was confirmed by analysis of the NIES standard reference material for rice flour, SRM 10b. This method was used to determine the arsenic content in 20 rice samples that were purchased at supermarkets in Salvador, Bahia, Brazil. The arsenic content for the three types of rice (white, parboiled, and brown) varied from 0.12 and 0.47 $\mu g g^{-1}$. Some of the samples were also analyzed by HG AFS after complete mineralization in block digester employing a reflux system (cold finger). A statistical test showed that there was no significant difference between the results obtained using slurry sampling and those obtained after complete digestion of the sample.

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Introduction

The high toxicity of arsenic is always a cause for global concern. Generally, contamination due to arsenic for humans comes from foods and drinking water (Tuzen et al. 2009; Mondal et al. 2010; Ackerman et al. 2005). However, several studies have reported also that contamination by arsenic, mercury, cadmium, and lead in plant foods has been caused by phosphate fertilizers (Jiao et al. 2012; Borges et al. 2011).

Rice being the staple food for around 50 % of the world's population contributes over 70 % of the energy and 50 % of protein as provided by their daily food intake (Fu et al. 2011). Then, methods for quantification of toxic species in rice are always opportune. Horner and Beauchemin (2012) used on-line continuous leaching and ion exchange chromatography coupled to inductively coupled plasma mass spectrometry for the speciation analysis of bio-accessible arsenic in rice. Another work evaluated the parameters: grinding and pressurized extraction with water as key points for effective and species-preserving extraction of arsenic from rice (Alava et al. 2012).

Slurry sampling is a sample preparation technique that has been much recommended for the determination of

volatile elements such as arsenic, mercury, antimony, lead, and cadmium because this offers several benefits, including reduced sample preparation time, lower possibility of sample contamination, and decreased possibility of analyte loss before analysis (Ferreira et al. 2010, 2012). Bermejo-Barrera et al. (2005) developed a method for the determination of arsenic in mussels by slurry sampling and electrothermal atomic spectrometry. A method was performed involving slurry sampling and HG AAS for speciation analysis of trace inorganic arsenic in dietary supplements (Sun et al. 2011). Recently, a method for the determination of mercury in rice was proposed, employing slurry sampling and cold vapor generation and AAS (Silva et al. 2012). Chen and Jiang (2009) employed slurry sampling and chemical vapor generation inductively coupled plasma mass spectrometry for the determination of arsenic, cadmium, and mercury in cereals. Sun et al. used slurry sampling for speciation analysis of inorganic arsenic in dietary supplements by HG AAS.

Atomic fluorescence spectrometry (AFS) is an analytical technique that has been widely used for the determination of arsenic and other volatile elements (Ferreira et al. 2011; Yin et al. 2012). The coupling of hydride generation (HG) and AFS allows determinations with low quantification limit, its instrumentation being cheaper than other conventional analytical techniques. Moreover, the combination of slurry sampling and HG AFS has allowed the development of direct methods for analysis of environmental samples, food, biological samples, etc. Qian et al. (2010) proposed a method for the analysis of ultra-trace arsenic in environmental water samples by preconcentration of TiO_2 colloid and determination by AFS.

The present paper proposed a method for the determination of arsenic in rice samples acquired in Salvador City, Brazil, employing slurry sampling and AFS.

Experimental

Instrumentation for the Determination of Arsenic by HG AFS

The fluorescence intensity of the arsenic was measured by an atomic fluorescent spectrometer (Model Lumina 3300 Aurora Biomed Inc, Canada) with a quartz tube furnace, as atomizer, and automatic ignition. Argon was used as the carrier gas. Hollow cathode lamps (HCL), with high intensity, were used as a light source. The experimental conditions are summarized in Table 1.

The slurries were sonicated in a Model USC-1850 ultrasonic bath with a (UNIQUE, Indaiatuba, S.P., Brazil) temperature controller at a frequency of 25 kHz and a power of 154 W.

The complete digestion of the rice samples was carried out using a block digester (Tecnal, Brazil), 40 channels, with a thermostat for temperature control.

Table 1 Operating parameters of the HG AFS instrument for the determination of arsenic

Parameter	Setting
Lamp primary current (mA)	80
Negative high voltage of PMT	400
Atomizer observation height (mm)	8
Flow rate of the carrier gas ($mL min^{-1}$)	400
Flow rate of the shielding gas ($mL min^{-1}$)	800
DBD applied power (W)	12
$NaBH_4$ concentration (%)	2
HCl concentration ($mol L^{-1}$)	2.0
$NaBH_4$ flow rate ($mL min^{-1}$)	1.4
Sample flow rate ($mL min^{-1}$)	4.5

Reagents and Solutions

All solutions were prepared using high-purity water that had a resistivity of 18.2 MΩ cm^{-1}. The water was obtained from a Milli-Q Plus water purification system from Millipore (Bedford, MA, USA). Analytical-grade nitric acid from Merck (Darmstadt, Germany) was double-distilled in a MILESTONE quartz distillation system.

The stock standard solutions (1.000 $mg mL^{-1}$) of As (III) were obtained by dissolving appropriate amounts of Na_3AsO_3 (Sigma, St. Loius, MO, USA) in nitric acid 0.05 % (w/v). Working standard solutions were prepared by appropriate stepwise dilution of a 1,000-$mg L^{-1}$ stock standard solution just before use.

The reducing agent was 2 % (w/v) sodium tetrahydroborate solution that was stabilized with 0.5 % (w/v) sodium hydroxide. It was also prepared daily using analytical-grade reagents from Merck and was filtered through a 0.45-μm filtration membrane. The 10 % (w/v) potassium iodide solution in 2 % (w/v) ascorbic acid was prepared by dilution of the reagents from Merck with high-purity water. The certified reference material used in the accuracy evaluation was NIES, SRM 10b rice flour, which was furnished by the National Institute for Environmental Studies, Gaitersburgh, MD, USA.

Each plastic container was washed with tap water and a diluted Extran solution, soaked in 10 % (v/v) nitric acid solution for 24 h, and rinsed three times with deionized water before it was used.

Slurry Preparation and the Determination of Arsenic by HG AFS

The rice samples were ground in a blender and then sieved through a mesh of 300 meshes. A mass of 200 mg was mixed with 5.0 mL of 2.0 $mol L^{-1}$ nitric acid solution in a volumetric flask of 25 mL. Next, the volumetric flask was placed in an ultrasonic bath for 30 min. Deionized water was

added to achieve a total volume of 25 mL. Then, an aliquot of 5.0 mL of the slurry was transferred to a 10-mL volumetric flask, with 3.0 mL of 6.0 mol L^{-1} hydrochloric acid and 1.5 mL of 10 % (w/v) potassium iodide in 2 % (w/v) ascorbic acid solution being added. After 30 min, the total volume of the flask was completed with deionized water, and this solution was taken for analysis in conjunction with the HG AFS using 2 % (w/v) sodium tetrahydroborate solution as reducing agent.

Sample Preparation Using a Block Digester (Ferreira et al. 2012)

Three selected rice samples were subjected to acid digestion to evaluate the accuracy of the proposed method. The rice samples were digested in a digester block with the addition of 2.0 mL of concentrated nitric acid and 1.0 mL of 30 % (v/v) hydrogen peroxide. The mixture was heated at 130 °C under reflux for 3 h using a digester system with a "cold finger". After complete digestion, the solutions were transferred to volumetric flasks, and deionized water was added to achieve a total volume of 10 mL. This procedure was performed in triplicate for each sample that was analyzed.

Results and Discussion

Optimization of the Experimental Conditions

The sonication time was varied from 0 to 40 min, and the results presented in Fig. 1 demonstrated a maximum extraction of arsenic for 25 min. Then, a sonication time of 30 min was selected and used for all further investigations.

Selection of the Best Solution for Slurry Preparation

Experiments were performed using three experimental conditions for slurry preparation: water, nitric acid, and hydrochloric
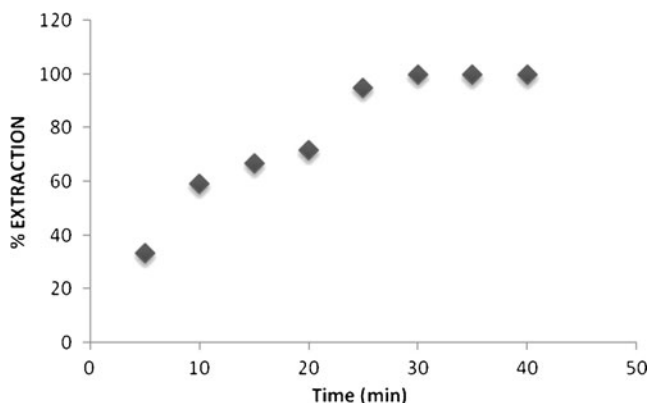
Fig. 1 Measurement of % extraction by function of sonication time of slurry sampling for arsenic determination

Table 2 Selection of liquid phase for slurry preparation

Liquid phase	Concentration (mol L^{-1})	Recovery (%)
Hydrochloric acid	1	38
	2	61
	3	62
Nitric acid	1	48
	2	98
	3	96
Water	25 °C	51
	7 °C	49

acid solutions. The acid solutions were studied in three different concentrations and the water at room temperature (25 °C) and also heated to 70 °C. The results were evaluated as arsenic recoveries, the condition being more efficient for 2.0 mol L^{-1} nitric acid solution as can be seen in Table 2.

Characterization of the Process for Analytical Determination

In order to investigate the process involved in analytical determination, several slurries of rice samples were prepared and the arsenic was quantified in these slurries and also in the liquid phases of these same slurries after centrifugation. The analytical signals obtained with the slurries are higher than the values obtained in the liquid phases, demonstrating that the extraction process under the experimental conditions of slurry preparation is not complete, and hence it was necessary to use the slurry sample for the complete recovery of arsenic by HG AAS. The results are shown in Table 3.

Validation Studies

The analyte addition technique was performed to determine the calibration technique of the method. The results

Table 3 Analytical signals for different extraction processes in As determination (n=3)

Samples	Slurry sampling	RSD (%)	Slurry and centrifugation	RSD (%)
P1	0.20±0.03	5.8	0.16±0.03	8.6
W1	0.22±0.04	4.8	0.20±0.03	6.5
B3	0.34±0.06	5.8	0.32±0.05	5.8
B4	0.22±0.02	4.1	0.17±0.01	2.8
B5	0.20±0.01	4.1	0.16±0.01	1.1
P3	0.20±0.01	2.4	0.21±0.02	4.4
W6	0.27±0.03	4.4	0.23±0.01	4.0

P parboiled rice, W white rice, B brown rice

Table 4 Determination of arsenic in rice samples using slurry sampling ($n=3$)

Samples	Added	Found ($\mu g\,g^{-1}$)	Recovery (%)
W1	0	0.19±0.02	100
	0.2	0.39±0.01	
W2	0	0.21±0.02	105
	0.2	0.42±0.04	
P1	0	0.12±0.01	95
	0.2	0.31±0.05	
P2	0	0.25±0.01	104
	0.2	0.45±0.03	
B1	0	0.13±0.01	101
	0.2	0.33±0.04	
B2	0	0.20±0.02	102
	0.2	0.41±0.05	

Confidence level of 95 %

W white rice, *P* parboiled rice, *B* brown rice

Table 6 Results obtained for arsenic in rice samples by slurry sampling ($n=3$)

Samples	Concentration ($\mu g\,g^{-1}$)
W1	0.19±0.02
W2	0.21±0.02
W3	0.28±0.03
W4	0.47±0.04
W5	0.31±0.04
W6	0.29±0.02
W7	0.13±0.02
W8	0.26±0.02
P1	0.12±0.01
P2	0.25±0.01
P3	0.23±0.01
P4	0.20±0.01
P5	0.28±0.01
P6	0.24±0.01
P7	0.23±0.01
B1	0.13±0.01
B2	0.20±0.02
B3	0.23±0.03
B4	0.22±0.02
B5	0.20±0.01

Confidence level of 95 %

W white rice, *P* parboiled rice, *B* brown rice

demonstrated that there is no matrix effect and also that arsenic can be determined using external standard calibration. The limits of detection and quantification were determined as per the recommendation of IUPAC (1978), considering a sample mass of 0.2 g. The limits obtained were 1.1 and 3.3 $ng\,L^{-1}$, respectively. Precision, expressed as the relative standard deviations (%RSD), was determined for two rice samples, being 5.9 and 1.3 % for rice samples with arsenic concentrations of 0.12 and 0.47 $\mu g\,g^{-1}$, respectively. Addition/recovery tests were developed for the evaluation of accuracy. The experiments were performed by the addition of arsenic in three rice samples of the white, parboiled, and brown kinds. The recovery values obtained varied from 95 to 105 % as can be seen in Table 4. The accuracy of the method was also confirmed by analysis of a certified reference material of rice flour, which was supplied by NIES, SRM 10b. The certified arsenic content is 0.11 $\mu g\,g^{-1}$, and the concentration found by this method was 0.12±0.01 $\mu g\,g^{-1}$.

Three rice samples were analyzed by this method and also by another procedure involving complete mineralization in

Table 5 Comparison of the average content of arsenic ($\mu g\,g^{-1}$) obtained by slurry sampling HG AFS and complete digestion HG AFS

Samples	SS[a]	RSD (%)	DB[b]	RSD (%)
White rice	0.26±0.03	5.0	0.26±0.02	3.8
Brown rice	0.28±0.03	4.5	0.23±0.03	5.0
Parboiled rice	0.23±0.01	2.2	0.24±0.01	0.3
CRM	0.11±0.01	2.7	0.12±0.01	4.9

CRM certified reference material

[a] Slurry sampling

[b] Digester block/cold finger system

digester block employing reflux system to avoid loss by volatilization. The results obtained are shown in Table 5, which demonstrated that there is no difference between the two methods proposed.

Application

The proposed method was used to determine the arsenic concentration in 20 samples of three types of rice (white, parboiled, and brown) that were purchased in supermarkets in Salvador City, Brazil, in May 2011. The arsenic content found for these 20 samples varied from 0.12 and 0.47 $\mu g\,g^{-1}$. These results are shown in Table 6.

Conclusions

The proposed method has precision, accuracy, and sensitivity for the determination of arsenic in rice. It is very opportune considering the high toxicity of this metalloid and the large consumption of this cereal in the human diet.

The arsenic contents found in the 20 samples analyzed are lower than the maximum limit permissible for this contaminant as set by the Brazilian government for foods.

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