



Determination of total arsenic, total inorganic arsenic and inorganic arsenic species in rice and rice flour by electrothermal atomic absorption spectrometry

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ABSTRACT

The determination of inorganic arsenic species in food has become very important during the last few years, since As(III) and As(V) are considered carcinogenic and found at high concentrations in food products, such as rice. The present work describes the development of three different methods for the determination of total arsenic, total inorganic arsenic, and As(III)–As(V) in rice and rice flour food products, purchased from the local market by electrothermal atomic absorption spectrometry (ETAAS). The methods were based on the use of different selective extraction procedures and the optimization of all crucial instrumental and methodological parameters. By these new preparation procedures for the determination of arsenic species, the loss and transformation of analytes during the extraction and digestion steps was prevented. For the validation of each method, precision, accuracy, and selectivity have been assessed, as performance criteria. All developed methods were accurate and precise. The calculated recoveries ranged between 92% and 105% and the (%) relative standard deviation values, under repeatability or reproducibility conditions, were lower than 15% for all different concentration levels tested. The validated methods were applied successfully for the determination of total arsenic and total inorganic arsenic in a proficiency test organized by the International Measurement Evaluation Program (IMEP-107). The methods were also applied in rice and rice flour samples purchased from the Greek market and the obtained results indicated that in almost all samples total arsenic and total inorganic arsenic were detected at ng/g levels.

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1. Introduction

Arsenic is one of the most toxic trace elements and occurs in both inorganic and organic forms, which are found in the environment both from natural sources and from anthropogenic activities. As(III) and As(V) were deemed group I carcinogen by the International Agency for Research on Cancer (IARC) [1], and therefore the development of a fully-validated method for the determination of both organic and inorganic arsenic species is necessary.

The World Health Organization (WHO) recommended 15 µg of total inorganic arsenic (t-inAs) per body weight as a provisional tolerable weekly intake (PTWI). The main source of human exposure to As is *via* the food chain. Drinking water, or eating seafood, cereals, and algae based food products are among the commodities with the highest levels of arsenic. However, the ratio of total inorganic arsenic (t-inAs) to total arsenic (t-As) varies among the different kinds of foodstuffs [2–5]. According to a recent report published by the European Food Safety Authority (EFSA) Panel on Contaminants in the Food Chain [6], arsenic exposures from food and water across 19 European countries, using lower bound and upper bound concentrations, are estimated to be in the range 0.13–0.56 µg/kg body weight (b.w.) per

day for average consumers. In the same report, it is noted that children younger than three years of age are the most exposed to inorganic arsenic (0.50–2.66 µg/kg b.w. per day). Official studies for the estimated human exposure to inorganic arsenic in Greece are not available. However, data on the average diet for rice food products in Greece conducted by a European program called DAFNE (Data Food Network) showed that citizens consumed about 16 g of those products per person and per day, putting rice in the list as the top consumed foods in Greece [7]. Recently, some studies had been presented in literature concerning the determination of t-inAs in rice products [8–11]. In general there are two main approaches for the arsenic speciation analysis: (a) the separation of arsenic species after chromatographic separation and detection with specific detectors. These methods usually use different chromatographic techniques, such as gas (GC) or liquid (LC) chromatography with on-line detection techniques, such as mass spectrometry (MS), inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), or atomic fluorescence spectrometry (AFS) and (b) the separation of arsenic species after the selective extraction(s) based on the different chemical properties of each of the species. These methods use mainly spectrometric techniques and chemical methods for the separation of one species from the others [8–16]. Electrothermal atomic absorption spectrometry (ETAAS), hydride generation atomic absorption spectrometry (HG-AAS), inductively

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coupled plasma–mass spectrometry (ICP-MS) and high performance liquid chromatography coupled with inductively coupled plasma–mass spectrometry (HPLC-ICP-MS) are among the most used techniques. However, the lack of a standard or fully-validated method for the determination of t-inAs is of great concern. Therefore, the Directorate General for Health and Consumers (DG SANCO) of the European Commission (EC) recently requested that the European Union Reference Laboratory for Heavy Metals in Feed and Food (EU-RL-HM) evaluate the performance of European laboratories focused on the determination of total and inorganic As in rice with a view to future discussions on the need for possible regulatory measures [12]. The test item used in this exercise was rice purchased in a local supermarket which was provided by the University of Aberdeen and coded as IMEP-107.

The present work describes initially the development and the validation of two different methods for the determination of t-As, t-inAs by ETAAS. For this purpose, different extraction or digestion procedures and various (permanent and non-permanent) chemical modifiers were evaluated and optimized. Furthermore, for the first time, Pd-nanoparticles (Pd-NPs) and Pt-nanoparticles (Pt-NPs) were tested as new potential chemical modifiers for the determination of arsenic in rice and rice flour samples. Then, finally, the development of a third fully-validated method for the determination of As(III) after the reaction of As(III) with ammonium pyrrolidinedithiocarbamate (APDC) and its extraction with an appropriate organic and inorganic solvent was accomplished. This method was based on the classical extraction method proposed for the determination of As(III) in water samples [17] and was extended for the first time in food matrices. All three methods were applied for the determination of t-As, t-inAs and As(III)–As(V) in a reference sample used for the proficiency test (IMEP-107) and in rice and rice flour samples purchased from the local market.

2. Materials and methods

2.1. Instrumentation

A Perkin Elmer SIMAA 6000 atomic absorption spectrometer equipped with a transversely heated graphite atomizer (THGA) and with longitudinal Zeeman-effect background correction and an AS-72 autosampler was used. The THGA graphite furnace was equipped with an integrated L'vov platform. The THGA temperature program for all methods developed is given in Table 1. The system operation was controlled using Perkin Elmer AA Winlab, version 2.5. A Perkin Elmer arsenic electrodeless discharge lamp (EDL) at an operated wavelength of 193.7 nm and an instrument slit width 0.7 nm was used. A Perkin Elmer EDL System was used to stabilize the lamp current at 350 mA. A 20- μ L volume of the standard or sample solutions was dispensed in the graphite tube with the AS-72 autosampler. The rice and the rice flour samples were pretreated with a MARS X-Press (CEM Corporation, NC, USA) microwave oven.

Table 1
Temperature program, under the optimum conditions, for the graphite furnace for the determination of t-As, t-inAs and As (III) in rice and rice flour samples.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow rate (mL min ⁻¹)	Read
Drying 1	110	1	15	250	
Drying 2	130	15	25	250	
Pyrolysis	1100 ^{ab}	10 ^a	30 ^{bc}	250	
Atomization	2000	0	5	0	ON
Cleaning	2450	1	3	250	

^a t-As.

^b t-inAs.

^c As (III).

2.2. Materials

All chemicals were of analytical reagent grade. Ultra pure water from Millipore Direct-Q-UV water purifier (Millipore) was used. The As(V) stock standard solution (1000 \pm 5 mg L⁻¹) (H₃AsO₄ in 0.5 mol L⁻¹ HNO₃) was purchased from Merck. The As(III) stock standard solution 1000 (mg L⁻¹) was prepared by dissolving 0.1320 g of diarsenic trioxide in 100 mL of 10 M sodium hydroxide, and diluting to 100 mL with ultra pure water. An aliquot of these solutions was diluted with water to give the appropriate concentrations before use. To prepare the modifier solutions, 10 \pm 0.2 g L⁻¹ of Pd(NO₃)₂ in 15% HNO₃ (Merck), 1000 mg L⁻¹ H₂PtCl₆ in HCl (2 mol L⁻¹) (Certipur, Merck), 1% w/v of Mg(NO₃)₂ in 1% HNO₃ (High-Purity Standards), 1000 \pm 5 μ g mL⁻¹ of ZrOCl₂·2H₂O in 0.5% HNO₃ (High-Purity Standards), 1000 μ g mL⁻¹ of Ir in 2% HCl (High-Purity Standards) were used. The palladium nanoparticles (Pd-NPs; 0.58 mg Pd + 1 mg MWNs in 1 mL (1% v/v) SDS) and platinum nanoparticles (Pt-NPs; 0.42 mg Pt + 1 mg CNHs in 1 mL (1% v/v) SDS) were a gift from the National Hellenic Research Foundation [18]. Likewise, HNO₃ Suprapur 65% (Merck) and HCl 36% (Merck) were used for the extraction or the digestion of the samples. For the selective determination of t-inAs and As species, an APDC (\approx 99%, Sigma-Aldrich) solution of 1% (w/v) and an EDTA (\geq 99%, Sigma-Aldrich) solution of 5% (w/v) were prepared. For pH adjusting, HCl 1 M and NaOH 4 M solutions were prepared. 4-Methyl-2-pentanone spectrophotometric grade, (MIBK, \geq 99%, Sigma-Aldrich) was also used as an extraction solvent.

For quality assurance and accuracy estimation, the certified reference material IRMM 804, Rice flour (European Commission Joint Research Centre, Institute for Reference Materials and Measurements) and the IMEP-107 test item for the proficiency test were used.

2.3. Experimental procedures

Commercially available rice and rice flour samples of various brands and different varieties were obtained from local super markets in Lamia, Greece (in the years 2011 and 2012) and these samples were appropriately coded. The samples were milled and homogenized in a food processor, with a stainless steel cutter, and sometimes were also ground in a mortar to obtain a more representative material.

2.3.1. Determination of t-As

0.5 \pm 0.1 g of the homogenized rice or rice flour sample was weighted in PTFE vessels and 5 mL HNO₃ (65%) were added. The samples were digested with MARS X-Press (CEM Corporation, NC, USA) microwave oven after the application of a preselected program (First stage: Power = 1600 W; Ramp time (min) = 2; Hold Time (min) = 0 min; Temp (°C) = 165 and Second stage: Power = 1600 W; Ramp time (min) = 3; Hold Time (min) = 5 min; Temp (°C) = 175) and then diluted to a final volume of 20 mL with ultra pure water.

2.3.2. Determination of t-inAs

0.5 \pm 0.1 g of the homogenized rice or rice flour sample was weighted in 50 mL polystyrene centrifuge tubes and 5 mL HNO₃ 1 M were added. Then the samples were vortexed and ultrasonicated for 15 min and centrifuged at 4000 rpm for 15 min. Finally, 15 mL EDTA 0.1% (w/v) were added, vortexed and centrifuged at 4000 rpm for other 15 min. The supernatant was analyzed by ETAAS.

2.3.3. Determination of As(III)–As(V)

0.5 \pm 0.1 g of the homogenized rice or rice flour sample was weighted in PTFE vessels and 10 mL HNO₃ 1 M were added. The extraction was performed on a microwave oven MARS X-Press (CEM Corporation) with the following preselected program: First stage: Power = 800 W; Ramp time (min) = 2; Hold Time (min) = 2 min;

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