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Total arsenic in selected food samples from Argentina: Estimation of their contribution to inorganic arsenic dietary intake

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ABSTRACT

An optimized flow injection hydride generation atomic absorption spectroscopy (FI-HGAAS) method was used to determine total arsenic in selected food samples (beef, chicken, fish, milk, cheese, egg, rice, rice-based products, wheat flour, corn flour, oats, breakfast cereals, legumes and potatoes) and to estimate their contributions to inorganic arsenic dietary intake. The limit of detection (LOD) and limit of quantification (LOQ) values obtained were 6 μg kg^{-1} and 18 μg kg^{-1}, respectively. The mean recovery range obtained for all food at a fortification level of 200 μg kg^{-1} was 85–110%. Accuracy was evaluated using dogfish liver certified reference material (DOLT-3 NRC) for trace metals. The highest total arsenic concentrations (in μg kg^{-1}) were found in fish (152–439), rice (87–316) and rice-based products (52–201). The contribution to inorganic arsenic (i-As) intake was calculated from the mean i-As content of each food (calculated by applying conversion factors to total arsenic data) and the mean consumption per day. The primary contributors to inorganic arsenic intake were wheat flour, including its proportion in wheat flour-based products (breads, pasta and cookies), followed by rice; both foods account for close to 53% and 17% of the intake, respectively. The i-As dietary intake, estimated as 10.7 μg day^{-1}, was significantly lower than that from drinking water in vast regions of Argentina.

1. Introduction

Arsenic is a metalloid that is widely distributed in the environment in water, rocks, soil and air (Smedley & Kinniburgh, 2002), contaminating plants, animals and, consequently, food consumed by humans. Drinking water and food are the primary routes of human exposure; dermal and inhalation exposures only reach greater significance in occupational environments (IARC, 2012; WHO, 2011).

Arsenic toxicity varies according to the chemical form of the element. Inorganic arsenic (i-As) compounds are more toxic than organic compounds (Hughes, Beck, Chen, Lewis, & Thomas, 2011; IARC, 1973; Leermakers et al., 2006). Most of the information on arsenic toxicity originates from studies of human exposure to high levels of arsenic in drinking water. It is assumed that As in drinking water is primarily in the inorganic forms of i-As(III) and i-As(V) (Smedley & Kinniburgh, 2002). The relationship between high levels of arsenic in drinking water and adverse health effects, including skin, bladder and lung cancer, has been well established (NRC, 2013). For non-cancer diseases, there is a well-established association between arsenic in drinking water and skin lesions (Argos et al., 2011).

Inorganic trivalent and pentavalent arsenic compounds that enter humans are rapidly absorbed in the gastrointestinal tract, and i-As(V) is rapidly reduced to i-As(III) after ingestion (Cohen, Arnold, Beck, Lewis, & Eldan, 2013). Metabolism of i-As compounds results in the generation of methylated arsenic metabolites (monomethylarsonic acid, MMA, and dimethylarsinic acid, DMA) in trivalent and pentavalent oxidation states. Pentavalent methylated metabolites are considered as detoxified i-As forms; however, the trivalent forms of MMA and DMA have been shown to be more toxic than inorganic forms (Cohen et al., 2013; Watanabe & Hirano, 2013). More complex organoarsenicals, such as arsenobetaine, arsenosugars and arsenocholine, are stable in the body and are excreted in the urine faster than the inorganic forms (Choi et al., 2010).

Except for fish and shellfish, food contains low concentrations of total arsenic. Foodstuffs of terrestrial origin, such as cereals, meats, vegetables, fruits and dairy products, contain concentrations less than 0.1 mg kg^{-1}. Rice, however, appears to be an exception, with total arsenic concentrations ranging from 0.1 to 0.4 mg arsenic kg^{-1}, and occasionally considerably higher with i-As proportions reaching up to 91% (Farías et al., 2015; Lynch,

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Greenberg, Pollock, & Lewis, 2014). Fish and shellfish have the highest total arsenic levels (2–60 mg arsenic kg^{-1} dry mass) (EFSA, 2009) but less toxic or even non-toxic organoarsenicals are widely predominant, mainly arsenobetaine (Francesconi & Kuehnelt, 2004). There are exceptions within foods of marine origin, such as the edible marine algae hijiki or hiziki, which can contain i-As compounds at concentrations greater than 60 mg kg^{-1} (FSA, 2004).

Most data reported for arsenic in foodstuffs refer to the content of total arsenic. Speciation analyses providing information about the arsenic forms or species are certainly much more difficult to perform, and more sophisticated and expensive technologies are required. A factor conversion of 70% has been suggested to estimate concentrations of i-As from total arsenic for food of terrestrial origin (EFSA, 2009). It is noteworthy that Joint Food and Agriculture Organization (FAO)/WHO Expert Committee on Food Additives (JECFA) withdrew the provisional tolerable weekly intake (PTWI) for inorganic arsenic, set at 15 μg kg^{-1} body weight, because it was no longer appropriate for health protection (JECFA, 2011). Therefore, the generation of more information about arsenic levels in food is required as well as the determination of the primary dietary arsenic contributors. Currently, data about arsenic levels in Latin American countries are scarce.

In this study, the i-As dietary intake was estimated from total arsenic data obtained by analysing 117 samples of food commonly consumed in the Santa Fe province, Argentina. A dry digestion process and an FI-HGAAS system were used to determine total arsenic levels in selected food samples.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer Model 3110 flame atomic absorption spectrometer (Connecticut, USA) was used as the detector. It was equipped with an arsenic hollow cathode lamp (Photron, Victoria, Australia) set at a 193.7 nm wavelength, 11 mA lamp current and 0.7 nm bandwidth. A Perkin-Elmer FIAS 100 flow injection hydride generation system (Connecticut, USA) with a heated quartz tube atomizer (10 mm i.d. × 160 mm length) was used for hydride generation and was coupled to the AAS. The rotation speed of the multichannel peristaltic pump and the process timing were programmed and automatically controlled by the Perkin-Elmer AA WinLab software version 3.2. PTFE tubing was used to transfer samples and solutions. Peak heights were used for the measurements of the analytical signals. FI-HGAAS instrumental and operating conditions are shown in Table 1.

Table 1
FI-HGAAS instrumental and operating conditions.

Wavelength	193.7 nm
HCl current	11 mA
Bandwidth	0.7 nm
Integration time	15 s
Read time	20 s
Carrier solution flow-rate	10.0 mL min^{-1}
Reductant solution flow-rate	5.0 mL min^{-1}
Carrier gas flow-rate (N_2)	75 mL min^{-1}
Sample loop volume	500 μL
Mixing coil length	310 mm (vol. 320 μl)
Reaction coil length I	115 mm (vol. 70 μl)
Reaction coil length II	310 mm (vol. 200 μl)
Prefill time	15 s
Fill time	10 s
Injection time	15 s

2.2. Reagents, solutions and samples

All utilized reagents were of high purity or at least of analytical reagent grade. Deionized-distilled water (resistivity 18 MΩ cm) was used to prepare all solutions in this study.

Hydrochloric acid solutions were used as carrier solutions (1.2 mol L^{-1}), and ash dissolutions (4.5 mol L^{-1}) were prepared using concentrated HCl (Carlo Erba, USA). A 0.2% (m/v) sodium tetrahydroborate solution ($NaBH_4$) was used as a reductant and was prepared daily by dissolving $NaBH_4$ (Merck, Germany) in 0.025% (m/v) sodium hydroxide (Merck, Darmstadt, Germany) to minimize its decomposition. Ashing aid suspension, which was used for the food sample mineralization, was prepared by stirring 50 g $Mg(NO_3)_2{\cdot}6H_2O$ (Merck, Germany) into 100 ml of deionized-distilled water. A 50% (v/v) nitric acid solution prepared from concentrated HNO_3 (Biopack, Argentina) was used to remove the carbonaceous residue during ashing steps. A pre-reducing solution containing 5% potassium iodide (KI) (Merck, Germany) – 5% ascorbic acid ($C_6H_8O_6$) (Merck, Germany) was used to reduce As(V) to As (III) in standard and sample solutions. Nitrogen 99.998% purity (Linde, Argentina) was used as a carrier gas to transport the generated hydride to the atomizer.

Working solutions for external calibration curves and recovery assays were made from a 5 mg L^{-1} As(V) solution prepared from a 1000 mg L^{-1} As(V) standard stock solution (Merck, Germany). Working solutions were obtained by reducing As(V) solutions to As(III) in a 1.2 mol L^{-1} HCl solution and adding 10% (v/v) pre-reducing solution. An As(V) stock solution of 5 mg L^{-1} was used for recovery assays. Reference material DOLT-3 NRC (dogfish liver certified reference material for trace metals) was used to evaluate the analytical method for determining total arsenic.

Food samples were purchased in supermarkets and commercial food stores in three cities from the Santa Fe province, which is located in the central region of Argentina. The selected samples are representative of the Argentinean diet because all foods originated from trademarks whose products are highly marketed throughout the country.

In the case of meat, round beef steak defatted, chicken breast and fish edible tissue (hake, salmon, boga and dorado) were selected. Whole cow's milk, five types of cheeses (criollo, chubut, reggianito, mozzarella and pategras) and white eggs were included for the category of milk and dairy products. As regards cereals and derivatives, three varieties of polished rice (double Carolina, parboil, long-grain), six rice-based products (crispy brown rice snacks, salted rice biscuits, sweet rice biscuits, rice cakes, brown rice cakes, rice gingerbread with chocolate), wheat flour, corn flour, rolled oats and breakfast cereals (flakes) were analyzed. Lentil, soybean, chickpea and lima bean were selected for the category of legumes. Potatoes, the vegetable the most consumed by the Argentinean population, was also included in this study; potatoes were peeled before treatment of the samples. The most of food were milled and homogenized in a food processor, sub-sampled in polyethylene bottles and refrigerated shortly until analysis. Powdered food such as wheat flour and corn flour were directly sub-sampled. Whole cow's milk was frozen just arrived to the laboratory and then thawed and homogenized in an ultrasound bath prior analysis. In the case of eggs, aliquots of mixed white and yolk were taken for each sample.

2.3. Dry ashing digestion of food samples

Digestion of food samples can be primarily accomplished by wet or dry digestion methods. Currently, wet-digestion is typically performed using a microwave with working temperatures up to 260 °C. Organoarsenicals such as arsenobetaine are not destroyed under these conditions because they require temperatures above