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Sushi commercialized in Brazil: Organic Hg levels and exposure intake evaluation

Esther Lima de Paiva [a], Jeanne Clécia Alves [b], Raquel Fernanda Milani [a], Bárbara Sia Boer [a], Késia Diego Quintaes [b], Marcelo Antonio Morgano [a, *]

[a] Institute of Food Technology (ITAL), PO Box 139, 13070-178, Campinas, SP, Brazil
[b] Nutrition School, Federal University of Ouro Preto (UFOP), 35400-000, Ouro Preto, MG, Brazil

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ABSTRACT

The presence of organic mercury (methylmercury) in tuna, salmon and kani sushis marketed in restaurants specialising in Japanese foods (Campinas, São Paulo, Brazil), was investigated by atomic absorption spectrometer with thermal decomposition and amalgamation. Total mercury was analyzed directly, whilst organic mercury was quantified after a previous extraction with toluene in an acid solution, assisted by microwaves. Under these analytical conditions there was no interconversion between the inorganic and organic mercury. High sensitivity was observed for organic mercury, with limits of detection and quantification of 2.0 and 6.6 μg kg^{-1}. The organic mercury contents ranged from 12 to 583 μg kg^{-1}, 6.6 to 8.2 μg kg^{-1} and no detected values, for the tuna, kani and salmon sushi, respectively. The mean proportion of organic Hg/total Hg for tuna sushi was 88%, indicating that the most toxic form of mercury, organic Hg, predominate in this food. The estimated exposure to methylmercury was made by taking into account the Provisional Tolerable Weekly Intake (PTWI 1.6 μg/kg) considering the daily consumption of 150 g and 20 g per adults (60 kg) and children (15 kg), respectively. Our results demonstrated that the consumption of tuna sushi may exceed 100% of PTWI.

1. Introduction

Fish is recognized as an important source of many essential nutrients and its consumption is widely encouraged to prevent hypertension, cancer and coronary heart disease (Sioen, Henauw, Verdonck, Thuyne, & Camp, 2007). However, fish can contain toxic elements in their tissues, such as Hg, and consequently may represent a source of human exposure to such components (Burger, Stern, & Gochfeld, 2005; Dorea & Barbosa, 2005; Morgano, Rabonato, Milani, Miyagusku, & Quintaes, 2014).

The effects of high exposure to Hg in humans include neurodevelopmental deficits (JECFA, 2004; Steuerwald et al., 2000), poor cognitive performance (Freire et al., 2010; Oken et al., 2008), increased rates of cardiovascular disease (Choi et al., 2009), and neurological and locomotion deficits (Hightower & Moore, 2003; Hites, Carpenter, Hamilton, Knuth, & Schwager, 2004). The National Health and Nutrition Examination Survey estimates that 8–15% of fetuses in the USA have excessive exposure to Hg (Trasande, Landrigan, & Schechter, 2005). Recently, the FDA (US Food and Drug Administration) and EPA (US Environmental Protection Agency) have advised pregnant women, those who may become pregnant, breastfeeding mothers, and young children to broaden the variety of fish they eat and choose those lower in Hg, restricting fish consumption to 2 or 3 servings/week (Burger, Stern, & Gochfeld, 2005).

Mercury can be found in the environment in various chemical species. All Hg species are considered toxic, but organic species such as methylmercury ($MeHg^+$) and ethylmercury are considered more toxic than elemental Hg and its inorganic species. It is well recognized that the main pathway of human exposure to Hg is through eating fish containing $MeHg^+$, which is the most common Hg species found in fish. Due to biomagnification along the food chain, $MeHg^+$ reaches maximum levels in fish at the top of the food chain, and as a result, about 90% of the total Hg present in fish can be found as $MeHg^+$ (Horvat & Gibičar, 2005).

An accurate analytical method for the determination of organic Hg species is required to assess the real toxicity of the samples (Harrington, 2000). The analysis of organic Hg is generally carried

* Corresponding author.
E-mail address: morgano@ital.sp.gov.br (M.A. Morgano).

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out using chromatographic separation techniques coupled with different detectors (Zhang, Yang, Dong, & Xue, 2012). The chromatographic separation techniques include: gas chromatography (GC) (Barst et al., 2013; Kenšová, Kružíková, & Svobodová, 2012; Nevado, Martín-Doimeadios, Bernardo, Moreno, Ropero, & de Marcos Serrano, 2011), liquid chromatography (HPLC) (Batista, Rodrigues, De Souza, Oliveira Souza, & Barbosa, 2011; Chen et al., 2013) and ionic chromatography (IC) (Shade & Hudson, 2005). The most commonly used techniques are: inductively coupled plasma mass spectrometry (ICP-MS) (Batista et al., 2011; Clémens, Monperrus, Donard, Amouroux, & Guérin, 2011), atomic absorption spectroscopy (AAS) (Naozuka & Nomura, 2011; Sarıca & Türker, 2012), atomic fluorescence spectrometry (AFS) (Nevado et al., 2011; Zhang et al., 2012), electron capture detection (ECD) (Kehrig et al., 2009; Kenšová et al., 2012), microwave induced plasma-atomic emission spectrometry (MIP-AES) (Sanz, De Diego, Raposo, & Madariaga, 2003), atomic emission detection (Kuballa, Leonhardt, Schoeberl, & Lachenmeier, 2011) and isotope dilution mass spectrometry (IDMS) (Demuth & Heumann, 2001), and for the determination of total mercury, thermal decomposition amalgamation atomic absorption spectrometry (TDA AAS) (Morgano, Milani, & Perrone, 2015).

Japanese dishes usually include tuna of various species, salmon, eel, and many other fish, as well as shrimp and crab, which may be consumed in sushi dishes as well as vegetarian varieties (Burger, Gochfeld, Jeitner, Donio, & Pittfield, 2013).

Sushi, technically referring to fish and other items served with vinegar and sticky rice (Nibble, 2012), has become a generic term often encompassing sashimi (raw fish) and several varieties of fish surrounded by rice (maki rolls), and fish over rice (nigiri). The consumption of sushi and related dishes has recently increased greatly in Brazil and other countries, with these foods being available over lunch counters, grocery stores, especially restaurants and sushi bars (Martins, 2006). Although there is a growing trend for the consumption of sushi (Issenberg, 2007), there is very little quantitative data on either the consumption patterns of sushi or the contaminants in sushi (Lowenstein, Burger, Jeitner, Amato, Kolokotronis, & Gochfeld, 2010).

Regarding to the presence of methylmercury in sushi samples commercialized in Brazil Southwest, this work aims: i) to develop and validate a quick, simple, low cost method with minimal reagent consumption; ii) to quantify organic mercury (methylmercury) in sushi samples using the technique of thermal decomposition amalgamation atomic absorption spectrometry (TDA AAS); iii) to estimate the organic mercury intake from sushi consumption and iv) to delineate an organic extract stability study.

2. Materials and methods

2.1. Instrumentation

The technique of TDA AAS using a direct mercury analyzer (DMA-80, Dual Cell, Milestone, Sorisole, Italy) was used to quantify both the total and organic mercury content of sushi samples. The organic mercury extracts were obtained via microwave extraction (Start E, Milestone, Sorisole, Italy). The samples were heated in a nickel or quartz container, making use of compressed air as the oxidant gas. A catalyst removed the combustion products and the Hg vapors were trapped in a gold amalgamator. Temperatures around 850 °C were applied for desorption, and the Hg content was quantified by determining the absorption at 253.7 nm.

2.2. Reagents and standards

Only analytical grade reagents were used in this study. The water (18.2 MΩ cm) was purified using a reverse osmosis system (Gehaka, São Paulo, Brazil) and the nitric acid using a sub-boiling distiller (Distillacid, Berghof, Eningen, Germany). Toluene (Synth, Diadema, Brazil) and a 30% HCl solution (Merck, Darmstadt, Germany) were used for the microwave extractions. A 2.5% L-cysteine solution (Sigma, Steinheim, Germany) was prepared to stabilize the organic mercury species. Certified standard solutions of mercury at 1000 mg l^{-1} (Fluka, Sigma Aldrich, Steinheim, Germany) were used to construct the analytical curves, together with a 0.5% (v/v) solution of HNO_3.

2.3. Samples

A total of 60 sushi samples were acquired from different Japanese restaurants and supermarkets located in Brazil Southwest (city of Campinas, São Paulo state), with 20 samples each of the most consumed types of sushi: 20 samples of Yellowfin tuna (*Thunnus albacares*), 20 of salmon (*Salmo salar*) and 20 of kani (a mix of fish species flavoring with crab meat). Yellowfin tuna came from the South and Southwest area of the coast of Brazil, which is included in FAO fishing area (Atlantic, Southwest). Salmon samples came from Chile coast, whilst kani were acquired from distribution centers located in the Southeast of Brazil.

The samples were separately triturated according to their specie, taking a complete dish with all ingredients, using a domestic processor to obtain a homogenized mass. The homogeneous mass samples were kept under freezing until analyses. Sample portions weight was determined experimentally as, approximately, 150 g (6 pieces of sushi).

The contribution of each sushi component (seaweed, rice, kani, and/or fish) was determined in a previous work of our group. The obtained values were, in average: 65% of rice, 30% of fish and/or kani and 5% of seaweed (Morgano et al., 2015).

2.4. Determination of total and organic mercury in the sushi samples

2.4.1. Determination of total mercury

For the determination of total mercury, the homogenized samples were weighed directly into nickel containers and the value determined using TDA AAS. According to Morgano et al. (2015) the optimal conditions for the total mercury analysis were: drying process (200 °C for 60 s) and decomposition process (600 °C for 180 s), using a 60 mg sample.

2.4.2. Determination of organic mercury

The extraction method for the organic species present in sushi samples was developed using a certified reference material (CRM) with a certified $MeHg^{+}$ value. The following parameters were optimized: the extraction temperature employed in the system assisted by microwaves; the extraction time; the concentrations of the L-cysteine solution and the volume of organic solvent (toluene) (Carbonell, Bravo, Fernandez, & Tarazona, 2009; Huang, Pan, Han, Wu, Tang, & Tan, 2012; Maggi, Berducci, Bianchi, Giani, & Campanella, 2009 and Ruiz-de-Cenzano, Rochina-Marco, Cervera, & de laGuardia, 2014).

The samples were subjected to closed extraction assisted by microwaves using an organic solvent (toluene) in an acid solution. A PFA teflon extraction vessel was weighed on an analytical balance and a 1 g aliquot of sample introduced, to which was added: 8 mL of toluene pa, 1 mL of demineralized water and 0.75 mL of a 30% (v/v) HCl solution. The vessels were sealed and transferred to a 1000 W microwave extractor which was programmed as follows: (a) room temperature to 110 °C in 10 min; (b) maintain a constant temperature of 110 °C for 5 min. After cooling, the vessels were opened and