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Original Research Article

Elemental characterization of Brazilian canned tuna fish using particle induced X-ray emission (PIXE)

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ABSTRACT

The elemental composition of Brazilian canned tuna fish packed in oil and brine was determined using the particle induced X-ray emission (PIXE) technique. Three different brands representative of the Brazilian market were evaluated. The metallic cans were analyzed as well. The results indicate that the canned tuna is homogeneous (average variability ~5%) inside the cans as far as elemental concentration is concerned. The data analysis reveals that the major elements present in tuna fish are Na, Cl, K, P and S with average concentration ranging from 800 to 2400 mg/kg, while Fe (14.22 mg/kg) and Zn (4.51 mg/kg) constitute trace elements. Significant variations in the elemental concentration of canned tuna across the brands were observed for most of the elements. For instance, significant higher concentrations of Mg, P, K and Zn were observed for brand P when compared to the other brands. Moreover, significant differences were observed between oil-packed and brine-packed tuna. In this case, higher elemental concentrations were obtained for oil-packed tuna. An increasing pattern in the concentration of Fe as a function of storage time was observed for two of the brands studied in this work. Finally, the results concerning the metallic cans identified two different types of cans, namely Fe-rich cans and Al-rich cans. In general, the results obtained in this work are in good agreement with previous measurements of canned tuna.

1. Introduction

Fish is well known as a healthful source of dietary proteins rich in essential amino acids, fats, vitamins and unsaturated fatty acids (omega-3) that are associated with the reduction of risk of cardiovascular diseases and neural disorders (Gladyshev et al., 2009; Jump et al., 2012). Fish is a valuable source of essential nutrients like Na, K, P and Mg, which play a key role in human health. For instance, Na participates in several physiological processes, while K is an important electrolyte that plays an important role in regulating blood pressure and in transmitting nerve impulses to muscles (Sheng, 2000). Phosphorus is an important constituent of bones and teeth and essential for the good functioning of different hormones, while Mg is important for the structure and the function of the human body and is involved in numerous metabolic reactions (Shils, 1999).

Besides macronutrients, fish constitutes a potential source of micronutrients like Fe, Mn, Zn and Cu. Indeed, iron is an essential micronutrient for humans and its deficiency on a daily dietary intake may cause anemia (Pais and Jones, 1997). Manganese is a constituent of some enzymes and is involved in a number of physiological processes (Leach and Harris, 1997). Zinc participates in numerous metabolic processes, especially those involved with the metabolism of protein, carbohydrate, fat, and alcohol (Cousins, 1996), while copper participates in the production of hemoglobin.

On the other hand, several studies have shown that the inclusion of certain fish in human diet can increase the risk of exposure to chemical contaminants. Indeed, some fish are directly exposed to water pollution and thus accumulate these contaminants (including heavy metals) in tissues like muscle and liver (Castro-González and Mendez-Armenta, 2008). For this reason, the study of trace elements and elemental composition of fresh and canned fish has gained a new impetus in the past 10 years.

The levels of trace elements in canned tuna may vary greatly according to catch location, fish size and preparation method. Several studies involving this issue have been conducted in different countries such as United States (Ikem and Egeibor, 2005; Rasmussen and Morrissey, 2007), Poland (Usydus et al., 2008), Turkey (Mol, 2011) and Iran (Ganjavi et al., 2010). The common point among these studies is the fact that they were carried out through optical-based techniques such as ICP-MS (Mol, 2011) and ICP-OES (Ikem and Egeibor, 2005) and Flame Atomic Absorption

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Spectrometry (FAAS) (Usydus et al., 2008; Tuzen and Soylak, 2007; Ganjavi et al., 2010). One of the drawbacks of these methods is that the sample preparation is somewhat complex. This problem can be overcome by techniques like PIXE (particle induced X-ray emission), which deals mainly with solid samples. PIXE is based on the induction of characteristic X-rays by energetic ions (Johansson et al., 1995). Moreover, PIXE has a truly multi-elemental capability and no prior knowledge of the elements present in the sample is required. The sensitivity of this technique (in the range of few parts per million) compares to those provided by optical-based techniques such as ICP-MS and ICP-AES (Saitoh et al., 2002). In addition, unlike optical methods, the sensitivity provided by the PIXE technique varies smoothly as a function of the atomic number.

PIXE has been widely used to characterize a great variety of materials, including foodstuff like soybeans (Medeiros et al., 2005), peanuts (Terakawa et al., 2008), wine (Kocsonya et al., 2002; dos Santos et al., 2010) and mate tea leaves (Giulian et al., 2007, 2009).

The aim of this research was to characterize canned tuna fish from Brazil through the study of the most popular brands available in the local market using the PIXE technique. In this study, tuna fish and their respective metallic cans were analyzed in order to check any possible correlation between the cans and theirs contents. Moreover, a statistical analysis was carried out in order to identify the variability of the elemental concentrations among canned tuna of different brands, moistures and date of canning. Different portions of the tuna fish inside the cans were analyzed as well, thus enabling the assessment of the homogeneity of the contents inside the metallic cans. Fresh tuna was analyzed and compared to tuna packed in cans and in sachets. Finally, the results were compared to those obtained from other studies.

2. Materials and methods

2.1. Samples

Three different Brazilian brands of canned tuna packed in brine were purchased from a local market in the city of Porto Alegre (state of Rio Grande do Sul). For each brand, tuna cans of 170 g net weight manufactured in 2007 were randomly selected from the market. It is important to note that throughout this work "*n*" refers to the number of independent samples analyzed. The brands were Gomes da Costa (G) ($n = 3$ samples), Pescador (P) ($n = 5$ samples) and Coqueiro (C) ($n = 3$ samples). Brand G constitutes the largest producer of canned tuna in Brazil. For one specific brand (C), samples of tuna canned in oil were also purchased ($n = 8$ samples). Tuna-in-oil cans were not available for brands G and P.

According to manufacturers, the following tuna species are used in the Brazilian tuna canning industry: Skipjack tuna (*Katsuwonus pelamis*) and Yellowfin tuna (*Thunnus albacores*) for brand G; Skipjack tuna, Albacore tuna (*Thunnus alalunga*), Yellowfin tuna, Blackfin tuna (*Thunnus atlanticus*), Bigeye tuna (*Thunnus obesus*), Southern Bluefin tuna (*Thunnus maccoyii*), Atlantic Bluefin tuna (*Thunnus thynnus*) and Longtail tuna (*Thunnus tonggol*) for brand P; and Skipjack tuna, Yellowfin tuna and Bigeye tuna for brand C. It is important to bear in mind that the fish species used in canning may vary according to the season and place they are caught.

Prior to preparing the samples, the external parts of the cans were thoroughly washed and cleaned with a neutral detergent (phosphate-free) and carefully rinsed with water. After opening, the moisture (brine or oil) was carefully drained from the cans.

In order to check the elemental homogeneity of the tuna inside each can, the tuna was sub-sampled in three parts: (a) the upper portion which was in contact with the lid ($n = 2$ samples); (b) the inner portion which was not in contact with the metallic parts of the can ($n = 3$ samples); (c) the lower portion which was in contact with the bottom of the can ($n = 3$ samples). Since the PIXE system requires the use of solid samples, the contents of each can had to be dried up. To that end, samples were weighed and put in a beaker inside an oven at relative low temperature (70 °C) for 2 h, thus ensuring an adiabatic thermal procedure. Once dried, the samples were homogenized and pressed into pellets of 25 mm of diameter and 2 mm thick. Eight pellets were obtained for the contents of each of the 19 cans analyzed, totaling 152 pellets.

The effects of packing on tuna fish were studied by analyzing tuna fish from brand C packed in cans and sachets. For both cases the moisture was oil. They were manufactured at the same time and the packages were stored for 30 months before opening for analysis. The sachet-packed tuna samples (brand C) were also cleaned with detergent and rinsed with water prior to opening the pack. A total of 2 packs were purchased and 4 samples were prepared.

For comparison purposes, 2 pieces of fresh tuna were purchased in different days from a local market and prepared for the PIXE measurements. In total, 5 samples of fresh tuna were prepared. For both fresh tuna and sachet-packed tuna, the samples were prepared following the same procedure used to prepare samples of canned tuna.

Finally, the metallic cans of all brands were studied as well. After opening, the cans were washed and rinsed with tap water. A visual inspection of all cans was carried out in order to check their integrity. None of them presented problems like fractures, corrosion and enamel failure, which could lead to the contamination of the tuna inside them (Kontominas et al., 2006). For each metallic can, the internal part of the lids and bottoms were analyzed. In total, 27 metallic can samples were prepared.

2.2. Instrumentation

2.2.1. PIXE

The elemental analysis was carried out at the Ion Implantation Laboratory of the Physics Institute of the Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, Brazil. A 3 MV Tandetron accelerator delivered 2 MeV protons at the PIXE station for elemental analysis. The average current was 3 nA. The chamber is completely insulated from the accelerator and therefore was used as a Faraday cup in order to obtain the total charge for each experiment. The samples (tuna pellets and metallic cans) were loaded in a ladder-type holder capable of accommodating 10 samples at the same time. The samples were positioned in the vacuum chamber using an electromechanical system and a camera for visualization. The pressure inside the PIXE chamber was of the order of 10^{-6} mbar throughout the experiments. The X-rays induced by the proton beam were detected by a Si(Li) detector placed at 135° with respect to the beam line. The overall energy resolution of the detection system was 155 eV at 5.9 keV. In order to avoid charge buildup in the samples, an electron flood gun was used in all experiments (Shubeita et al., 2005).

In order to check the presence of trace elements such as Al, Ti, Cr, Rb, Sr, Mo, Hg and Pb, high statistics PIXE measurements were also carried out using high current (6 nA) and longer irradiation times, namely two- to three-fold higher than the average irradiation time normally used during the measurements. In this way, the counting statistics and the peak-to-background ratio were improved for those elements. Three samples from each brand were analyzed in such way.

2.2.2. RBS

The Rutherford backscattering spectrometry (RBS) technique (Chu et al., 1978) was used in order to obtain the relative concentration of light (matrix) elements like C, O and N present in the tuna samples. A 1.2 MeV He^+ beam with an average current of