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Heavy metals content of canned tuna fish

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Abstract

In this study, five heavy metals in canned tuna fish were determined after digestion by the Association of Official Analytical Chemists methods. Mercury and arsenic levels in canned tuna fish were determined by hydride generation atomic absorption spectrophotometery while cadmium and lead levels were determined by graphite tube atomic absorption spectrophotometery and tin levels were determined by flame atomic absorption spectrophotometery. The metal contents, expressed in μg g^{-1} wet weight, varied from 0.043 to 0.253 with an average value of 0.117 for mercury, from 0.0369 to 0.2618 with an average value of 0.128 for arsenic, from 0.0046 to 0.0720 with an average value of 0.0223 for cadmium, from 0.0126 to. 0726 with an average value of 0.0366 for lead and non detectable for tin. Several samples were spiked with known amounts of metals. Recoveries of the metals were in the range of 91.7 ± 2.89–99.3 ± 4.03%. The results of this study indicate that tuna fish from the Persian gulf area of Iran have concentrations well below the permissible FAO/WHO levels for these toxic metals. Their contribution to the body burden can be therefore considered negligible and the fish seem to be safe for human consumption.

1. Introduction

There is increasing concern about the quality of foods in several parts of world. The determination of toxic elements in food has prompted studies on toxicological effects of them in food. Heavy metals are considered the most important form of pollution of the aquatic environment because of their toxicity and accumulation by marine organisms. While mercury, arsenic, cadmium and lead can be tolerated at extremely low concentrations, they are extremely toxic to humans. Whilst tin is widely used for studding in canning, its toxicity is not as imperative as other heavy metals. This work was aimed at determination of arsenic, mercury, cadmium, lead and tin concentrations in canned tuna fish.

Metal pollution of the sea is less visible and direct than other types of marine pollution but its effects on marine ecosystems and humans are intense and very extensive. The toxic effects of heavy metals, particularly arsenic, mercury, cadmium and lead, have been broadly studied (Inskip & Piotrowsiki, 1985; Kurieshy & D'silva, 1993; Narvaes, 2002; Nishihara, Shimamato, Wen, & Kondo, 1985; Schoerder, 1965; Uchida, Hirakawa, & Inoue, 1961; Venugopal & Luckey, 1975).

The distribution of metals varies between fish species, depending on age, development status and other physiological factors (Kagi & Schaffer, 1998). Fish accumulate substantial concentrations of mercury in their tissues and thus can represent a major dietary source of this element for humans. Fish are the single largest sources of mercury and arsenic for man. Mercury is a known human toxicant and the primary sources of mercury contamination in man are through eating fish. Biotransformation of mercury and methyl mercury

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formation constitute a dangerous problem for human health (Inskip & Piotrowsiki, 1985).

Metal contaminations in food, especially in marine products, have been broadly investigated (Catsiki & Strogyloudi, 1999; Enomoto & Uchida, 1973; Glover, 1979; Liang, Cheung, & Wong, 1999; Martin De La Hinojosa, Hitos Natera, Cerrezo Rubio, & Reyes, 1995; Uysal, 1980; Uysal, 1990). Tuna, as a predator, is able to concentrate large amount of heavy metals. Some of them are used for biomonitoring of environmental contamination (Enomoto & Uchida, 1973; Schmitt & Brumbaugh, 1990).

In the present study, we spectrometrically evaluated the total concentrations of mercury, arsenic, cadmium, lead and tin in commercial canned fish which are frequently consumed by the Iranian population and also exported. Canned tuna fish from the Persian gulf area were used because of the heavy trafficking of oil in this region is expected to contaminate the waterway. Therefore we wish to determine heavy metal levels in the canned tuna fish. It is expected that the results of this research will assist in acquiring information about the level of toxic metals in this region.

2. Materials and methods

2.1. Apparatus

All glassware was soaked over night in 10% (v/v) nitric acid, followed by washing with 10% (v/v) hydrochloric acid, and rinsed with double distilled water and dried before using.

A Varian Model 220 atomic absorption spectrophotometer equipped with a deuterium background corrector was used for the determination of heavy metals. Lead and cadmium concentrations were determined by a graphite furnace atomic absorption spectrophotometer 110 employing pyrolytic platform graphite tubes (Moreiras & Cuadrado, 1992). Hydride generation was with a Varian model 77 with quartz tubes.

2.2. Reagents

All reagents used were of analytical reagent grade (Merck, Germany). Standard stock solutions of mercury, arsenic, cadmium, lead, and tin were prepared from Titrasol (1000 mg/l) and were diluted to the corresponding metal solution. The working solution were freshly prepared by diluting an appropriate aliquot of the stock solutions using 10% HNO_3 for diluting lead and cadmium solutions, 1 M HCl and 5% H_2SO_4 for diluting mercury solution, 7 M HCl for diluting arsenic solution and 5% HCl for diluting tin solution. Stannous chloride, for mercury analysis, was freshly prepared by dissolving 10 g in 100 ml of 6 M HCl. The solution was boiled for about 5 min, cooled, and nitrogen bubbled through it to expel any mercury impurities.

2.3. Sample preparation and digestion

Tuna, fish caught by commercial vessels from the Persian gulf of Iran, were canned as chunks at a commercial factory on land. Twenty one cans tuna (about 0.5 kg each) were used for this study. After opening, each can content was homogenized thoroughly in a food blender with stainless steel cutters. A sample were then taken and digested promptly as follows: the homogenized sample (2 ± 0.001 g) was weighed into a 0.5 l glass digestion tube, and for mercury, 10 ml of conc. HNO_3 and 5 ml of conc. H_2SO_4 were slowly added. The tube was then placed on top of a steam bath unit to complete dissolution. It was then removed from the steam bath, cooled and the solution transferred carefully into a 50 ml volumetric flask; for the reduction of mercury 5 ml $SnCl_2$ were used. For arsenic determination 2 ± 0.001 g were weighed after pre-digestion in 10 ml conc. HNO_3 mixed with 4 ml of 20% $MgNO_3$ 20% as ashing aid, dried on a hot plate and ashed in a 450 °C furnace. The ashes were dissolved in 7 ml HCl and diluted to 50 ml. For the determination of lead and cadmium, about 2 ± 0.001 g of homogenized sample were weighed into a 200 ml beaker and 10 ml of conc. HNO_3 were added. The beaker was covered with a watch glass and, after most of the sample had dissolved by standing overnight, heated on a hot plate with boiling until any vigorous reaction had subsided. The solution was allowed to cool, transferred into a 50 ml volumetric flask and diluted to the mark with distilled water. For tin, 10 ± 0.001 g of homogenized sample were weighed into a beaker and 10 ml of conc. HNO_3 were added; after boiling until the volume was reduced to about 5 ml, conc. HCl was added and heated gently until the sample bumping (from evolution of Cl_2) stopped, then the solution was allowed to cool, transferred in a 25 ml volumetric flask and diluted to the mark with distilled water.

2.4. Validation of methods

Tuna (homogenized) samples were spiked with various concentrations of heavy metals for the recovery repeatability tests and for verifing the analytical methodology. For each run, triplicate samples, spiked samples and blanks were carried through the digestion reaction. The results are shown in Tables 1–5.

2.5. Chemical analysis

Tin was determined by direct aspiration of the sample solution into the NO_2/acetylene flame. The blanks and calibration standard solutions were also analyzed in the same way as the sample solutions. Mercury and ar-

Table 1
Recovery of lead from canned tuna samples

Concentration of lead added (μg g^{-1})	Concentration of lead (μg g^{-1})	% Recovery
0.015	0.015	100
0.030	0.031	103
0.045	0.042	93

Data are mean of three samples of three replicates.

Table 2
Recovery of cadmium from canned tuna samples

Concentration of cadmium added (μg g^{-1})	Concentration of cadmium (μg g^{-1})	% Recovery
0.005	0.0049	98
0.001	0.00104	104
0.00015	0.0013	93

Data are mean of three samples of three replicates.

Table 3
Recovery of mercury from canned tuna samples

Concentration of mercury added (μg g^{-1})	Concentration of mercury (μg g^{-1})	% Recovery
0.010	0.009	90
0.020	0.018	90
0.040	0.038	95

Data are mean of three samples of three replicates.

Table 4
Recovery of arsenic from canned tuna samples

Concentration of arsenic added (μg g^{-1})	Concentration of arsenic (μg g^{-1})	% Recovery
0.005	0.0045	90
0.010	0.0091	91
0.020	0.019	95

Data are mean of three samples of three replicates.

Table 5
Recovery of tin from canned tuna samples

Concentration of tin added (μg g^{-1})	Concentration of tin (μg g^{-1})	% Recovery
10	9.98	99.8
20	20.60	103
30	28.60	95

Data are mean of three samples of three replicates.

senic were determined by the hydride generation system. The manufacturer operation procedure involves continuous addition of reductant, consisting of 0.3%NaBH4, 0.5%NaOH for mercury and 0.6%NaBH4, 0.5%NaOH, 10%KI for arsenic. The manufacturer's operating procedure consists of adding sample, reductant and acid, with the aid of argon gas, to a reaction coil; then any vapour generated is swept into the absorption quartz cell, and heated for arsenic detection. Cells were aligned in the light path of the hollow cathode lamp where the absorption was measured. Cadmium and lead concentrations were determined by graphite furnace atomic absorption spectrophotometry, employing pyrolytic platform graphite tubes, ascorbic acid and palladium for matrix modification and using the method of additions for quantification. GTA was equipped with an auto sampler and the analysis was done according to the manual instruction, optimized conditions and the method of peak area (Moreiras & Cuadrado, 1992).

3. Results and discussion

Twenty one samples of canned tuna fish were analyzed for mercury, arsenic, cadmium, lead and tin. Good recoveries of spiked samples demonstrate the accuracy of the methods (Tables 1–5).

The concentrations of mercury, arsenic, cadmium, lead and tin are presented in Table 6 with means and SD. The results indicate that the concentration varied from 0.043 to 0.253 with a mean of 0.117 μg g^{-1} for mercury, from 0.0369 to 0.2618 with a mean of 0.128 μg g^{-1} for arsenic, from 0.0046 to 0.072 with a mean of 0.0223 μg g^{-1} for cadmium, from 0.0726 to 0.0162 with a mean of 0.0366 μg g^{-1} for lead and non detectable for tin.

Statistical analysis of results by ANOVA showed no significant differences among all samples.

The levels of toxic elements in shellfish are related to age, sex, season and place (Kagi & Schaffer, 1998). It is also reported that cooking reduces the amount of some metals (Atta, El-Sebaie, Noaman, & Kassab, 1997). Moreover, the advances of new packaging technology, especially the use of cans with lacquered walls and mechanical seam, reduce or, in most cases, eliminate the leaching of heavy metals (lead and tin) into the food.

The concentrations of mercury, cadmium and lead in canned tuna fish from the Mediterranean coast are of 0.02–6.6, 0.09–0.32 and 0.18–0.40 μg g^{-1}, respectively, and are similar to our results (Voegborlo, El-Methnani, & Abedin, 1999).

Other surveys (Committee for Inland Fisheries of Africa, CIFA) showed that cadmium levels in several fish types caught in upper Austrian waters were

Table 6
Mean contents of mercury, arsenic, cadmium and lead, (μg g^{-1}) in canned tuna samples

Metal	Range	Mean	SD
Lead	0.0162–0.0726	0.0366	0.0184
Cadmium	0.0046–0.0720	0.0223	0.0193
Mercury	0.0430–0.253	0.0117	0.0575
Arsenic	0.0369–0.0261	0.1289	0.0818
Tin	Nd	–	–

Nd, not detectable.

0.10–0.13 and 0.05–0.97 μg g^{-1}. In the Northern Indian ocean, levels were higher than our values, being 0.006–0.088 μg g^{-1} (CIFA, 1992).

The concentration of lead was less than 0.05 μg g^{-1}, which was lower than other reports (CIFA, 1992).

The concentration of mercury in our study varied from 0.082–0.160 μg g^{-1}, that is lower than 0.82–1.20 μg g^{-1} (Holden, 1973) and 0.04–0.44 μg g^{-1} (Fricke, Robbins, & Caruso, 1979).

The concentrations of mercury, arsenic, cadmium and lead previously reported were 0.082–0.16, 0.037–0.262, 0.006–0.088 and 0.016–0.049 μg g^{-1}, respectively (FDA, 2000); except for arsenic, these are similar to our results.

Few comparitive data are available from the same areas but it seems that our waterways are less contaminated than industrialized country waterways. The contents of toxic metals in Persian Gulf canned tuna fish are below the permissible levels listed by the joint Food and Agriculture Organization/World Health Organization Expert Committee on food additives (FAO/WHO, 1972). Of course, more studies are needed to properly assess other sources and to compare with tolerable weekly intakes.

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