

Determination of Trace Elements in Canned Kilka Fish Marketed in Islamic Republic of Iran

¹V. Taghipour and ²S.N. Azizi

¹Department of Chemistry, Mazandaran University, Babolsar, Iran

²Nano and Biotechnology Research Group, University of Mazandaran, Babolsar, Iran

Abstract: Concentrations of 6 trace elements (Cu, Zn, Mn, Pb, Cr and Cd) were determined in canned kilka fish samples produced and marketed in Iran, by flame and graphite furnace atomic absorption spectrometry after microwave digestion. The accuracy of the method was corrected by standard material. The contents of investigated trace metals in canned fish samples were found to be in the range 0.62-1.74 for copper, 11.32-23.90 for zinc, 0.23-1.37 for manganese, 0.06-0.25 for lead, 0.18-0.67 for chromium and 0.02-0.07 µg/g dry wt. for cadmium, respectively. The results were compared with the literature values. According to the results of this study, the consumption of Iranian canned kilka fish of the Caspian Sea can be safe for human health in spite of possible contamination with heavy metals.

Key words: Trace elements • Canned kilka fish • Iran • Caspian Sea

INTRODUCTION

The Caspian Sea is the largest inland body of water in the world and surrounded by Iran, Azerbaijan, Russia, Kazakhstan and Turkmenistan [1]. Biologically the Caspian Sea is a special region, with endemism reaching 80% at the species level [1]. However, the biodiversity is relatively low, with the total number of species about 40% of that found in the Black Sea [2].

As a closed-environment without an outlet, various pollutants due to effluents from coastal catchment areas and leakage from offshore oil production and land-based sources, have accumulated in the Caspian Sea [2]. Several pollutants such as heavy metals are very toxic, stable and not easily biodegradable [3]. Amongst food, fish are constantly exposed to heavy metals present in polluted water. Thus, fish have been found to be good bioindicators of water pollution. These heavy metals can accumulate in their tissues in different amounts depending on the size and age of fish [4]. Consumption of fish is very popular amongst people all around the world because it has high protein content, low saturated fatty acids and high omega fatty acids content [3].

The most abundant fishes in the Caspian Sea are three small species of clupeidae known as “kilka”: common kilka, anchovy kilka and bigeye kilka. In the Iranian coastal areas of the Caspian Sea, kilka were important sources of income and protein [5]. The most part of the

caught is processed into fish meal and canned fish. Canned fishes are a popular food source in Iran. Levels of heavy metals in fish and canned fish samples have been widely reported in the literatures. However, data on trace metal levels in canned fish samples produced in Iran are very limited. The aim of this study was to determine the levels of trace heavy metals in canned fish samples.

In this study, we examined the total concentrations of 6 trace elements (Cu, Zn, Mn, Pb, Cr and Cd) in commercial canned kilka fish samples produced and marketed in Iran. It is expected that the results of this research will assist in acquiring information about the level of toxic metals in this region.

MATERIAL AND METHODS

Apparatus: All the plastic and glassware were cleaned by soaking 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 Perkin Elmer 2380 atomic absorption spectrophotometer equipped with a deuterium background corrector was used for the determination of heavy metals, lead, Chromium and cadmium concentrations were determined by a graphite furnace atomic absorption spectrophotometer 110 employing pyrolytic platform graphite tubes. Hydride generation was with a Varian model 77 with quartz tubes.

SReagents: All chemical used were of analytical reagent grade. Standard stock solutions were prepared from Titrasol (1000mg/l) and were diluted to the corresponding metal solution. The working solutions were freshly prepared by diluting an appropriate aliquot of the stock solutions. Double deionized water was used for all dilutions.

Sampling: Thirty canned kilka fish samples used for this study, were collected during from popular supermarkets in Islamic Republic of Iran.

Digestion and Chemical Analysis: The procedure used for measuring concentrations of trace elements has been described previously [6]. Freeze-dried and homogenized samples (1 ± 0.001 g) were digested with 6 ml of concentrated HNO_3 (Suprapure, Merck) and 2 ml of concentrated H_2O_2 (Suprapure, Merck) in a microwave oven with a Teflon PTFE tube. The solution was allowed to cool, transferred into a 50ml volumetric flask and diluted to the mark with double deionized water. Concentration of six trace elements (Cr, Cu, Zn, Mn, Cd, Pb) were measured with atomic absorption spectrometer (AAS). Cadmium, Chromium and Lead were determined by graphite furnace and other elements were determined in an air-acetylene flame.

Validation of Methods: Canned kilka fish (Freeze-dried and homogenized) samples were spiked with various concentrations of heavy metals for the recovery repeatability tests and for verifying the analytical methodology. For each run, triplicate samples, spiked samples and blanks were carried through the digestion reaction. The results are shown in Table 1.

RESULTS AND DISCUSSION

The recovery value were nearly quantitative ($\geq 95\%$) for the microwave digestion method. The relative standard deviations were less than 8% for all investigated elements. The student *t*-test was used in this study ($p < 0.05$). The accuracy of the method was evaluated by means of trace metals determination in standard reference material. The achieved results were in good agreement with certified values (Table 1). All metal concentrations were determined on a dry weight basis ($\mu\text{g/g}$ dry wt.) Here is Table 2.

Table 1: Recovery Of Trace Elements From Canned Kilka Samples

Element	Certified value ($\mu\text{g/g}$)	Experimental value ($\mu\text{g/g}$)	Recovery (%)
Cu	2.12	2.08 \pm 0.16	98
Zn	20.25	20.65 \pm 0.82	102
Mn	2.34	2.22 \pm 0.11	95
Pb	0.068	0.065 \pm 0.01	95
Cr	30.71	29.45 \pm 2.15	96
Cd	0.046	0.044 \pm 0.00	95

Table 2: Concentrations Of Trace Elements In Canned Fish Kilka ($\mu\text{g/g}$ dry wt.)

Element	Minimum	Maximum	Mean	Std. Deviation (\pm)
Cu	0.62	1.74	1.18	0.39
Zn	11.32	23.90	17.42	4.35
Mn	0.23	1.37	0.89	0.39
Pb	0.06	0.25	0.13	0.05
Cr	0.18	0.67	0.38	0.15
Cd	0.02	0.07	0.04	0.02

Copper is essential for good health but a very high intake can cause adverse health problems, such as liver and kidney damage [3]. The contents of investigated trace metals in canned kilka fish samples were found to be in the range 0.62-1.74 $\mu\text{g/g}$ for copper (Table 2). In the literatures, copper levels in canned fish samples have been reported in the range of 0.01-5.33 $\mu\text{g/g}$ [3], 1.10- 2.50 $\mu\text{g/g}$ [7], 7.1-45.7 $\mu\text{g/g}$ [8], 0.001- 5.02 $\mu\text{g/g}$ dry wt. in fishes collected from coastal waters of the Caspian sea [9], 0.617-3.92 $\mu\text{g/g}$ dry wt. in muscle of sturgeons in the Caspian sea [10]. There recommended daily intakes of copper is 1.5mg Cu for adult males and 3.0 mg Cu for adult femals [11]. Copper concentration in analyzed canned kilka fish samples were below the MAFF guideline value of 30 mg Cu/kg [12].

Zinc is known to be involved in most metabolic pathways in humans and zinc deficiency can lead to loss of appetite, growth retardation, skin changes and immunological abnormalities. Zinc is widespread among living organisms, due to its biological significance. The maximum zinc level permitted for fish is 50 mg/kg according to Food Codex [12]. The recommended daily intakes of zinc are 15 mg for adult males and 12 mg for adult females [11]. According to the results (Table 2), concentration of zinc to be in the range 11.32-23.90 $\mu\text{g/g}$. In the literatures, zinc levels in canned fish samples, have been reported in the range of 0.14-97.80 $\mu\text{g/g}$ [3], 7.57-34.4 $\mu\text{g/g}$ [7], 33.8-566 $\mu\text{g/g}$ [8], 12.5-201 $\mu\text{g/g}$ dry wt. in fishes collected from coastal waters of the Caspian Sea [9], 11.6-68.9 $\mu\text{g/g}$ dry wt. in muscle of sturgeons in the Caspian Sea [10].

According to FAO (1983) there is no information on the carcinogenicity of manganese. The range of manganese levels were found to be 0.23-1.37 µg/g dry wt. in canned kilka fish in this study (Table 2). Manganese levels may also be affected by food processing. Manganese contents in the literature have been reported in the range 0.01-2.55 µg/g in canned fish samples [3], 0.90-2.50 µg/g in canned tuna and anchovy fish samples [7], 1.56-3.76 µg/g dry wt. in fish samples of the middle Black sea [13] and 0.092-9.23 µg/g dry wt. in fishes collected from coastal waters of the Caspian Sea [9], 0.214-2.71 µg/g dry wt. in muscle of sturgeons in the Caspian Sea [10].

Lead is known to induce reduced cognitive development and intellectual performance in children and increased blood pressure and cardiovascular disease in adults [14]. The fact that toxic metals are present in high concentrations in fishes is of particular importance in relation to the FAO/WHO [15] standards for Pb and Cd as toxic metals. The maximum permissible doses for an adult are 3 mg Pb and 0.5 mg Cd per week, but the recommended doses are only one-fifth of those quantities.

The range of lead levels were found to be 0.06-0.25 µg/g in canned kilka fish samples (Table 2). In the literatures lead levels in canned fish samples have been reported in the range 0.09-0.40 µg/g [7], 0.0-0.03 µg/g [3], 0.0162-0.072 µg/g wet wt. [4], 0.001-0.191 µg/g dry wt. in fishes collected from coastal waters of the Caspian Sea [9] and <0.001-0.575 µg/g dry wt. in muscle of sturgeons in the Caspian Sea [10]. The maximum lead level permitted for canned fishes is 0.2 mg/kg according to the European communities [14].

Chromium (III) is an essential nutrient that potentiates insulin action and thus influences carbohydrate, lipid and protein metabolism. However, Cr(VI) is carcinogenic [7]. In this study, the range of chromium levels were found to be 0.18-0.67 µg/g dry wt (Table 2). Chromium contents in the literatures have been reported in the range 0.97-1.70 µg/g [7], 0.0-0.30 µg/g [3], 0.08-1.4 µg/g dry wt. in fishes collected from coastal waters of the Caspian Sea [9] and 0.20-0.95 µg/g dry wt. in muscle of sturgeons in the Caspian Sea [10].

Cadmium may accumulate in the human body and may induce kidney dysfunction, skeletal damage and reproductive deficiencies. The contents of investigated trace metals in canned fish samples were found to be in the range 0.02-0.07 µg/g dry wt. for cadmium (Table 2). Cadmium contents, in the literatures have been reported in the range 0.06-0.25 µg/g [7], 0.0-0.05 µg/g [3] and 0.0046-0.0720 µg/g wet wt. [4], <0.001-0.233 µg/g dry

wt. in muscle of sturgeons in the Caspian Sea [10], <0.001-0.355 µg/g in fishes collected from coastal waters of the Caspian Sea [9] and 0.01-4.16 µg/g dry wt. in fish species from Iskenderum Bay, northern east Mediterranean Sea (Turkey) [16].

Dietary standards and guideline applicable in the UK for fish have been summarized by MAFF (2000) [17] for Cd (0.2 µg/g), Cu (20 µg/g), Pb (2.0 µg/g), Zn (50 µg/g). In this present study, concentration of Cd, Cu, Pb, Zn, Mn and Cr in canned fish kilka were lower than the guideline for food or within the range of freshwater, marine fishes and fish canned from other areas, to those reported in other regions.

CONCLUSION

Therefore, according to the results of this study, the consumption of Iranian canned kilka fish of the Caspian Sea can be safe for human health in spite of possible contamination with heavy metals.

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