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ScienceDirect
Food Chemistry 101 (2007) 1378–1382
Food Chemistry
www.elsevier.com/locate/foodchem

Determination of trace metals in canned fish marketed in Turkey

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Received 14 December 2005; received in revised form 24 February 2006; accepted 24 March 2006

Abstract

The levels of trace metals of canned fish samples collected from markets in Turkey were determined by flame and graphite furnace atomic absorption spectrometry after microwave digestion. The accuracy of the method was corrected by standard reference material (NRCC-DORM-2 Dogfish Muscle). The contents of investigated trace metals in canned fish samples were found to be in the range 1.10–2.50 μg/g for copper, 7.57–34.4 μg/g for zinc, 0.90–2.50 μg/g for manganese, 10.2–30.3 μg/g for iron, 0.96–3.64 μg/g for selenium, 0.45–1.50 μg/g for aluminium, 0.97–1.70 μg/g for chromium, 0.42–0.85 μg/g for nickel, 0.09–0.40 μg/g for lead and 0.06–0.25 μg/g for cadmium. The results were compared with the literature values.

Keywords: Trace metals; Canned fish; Atomic absorption spectrometry; Turkey

1. Introduction

Fish is widely consumed in many parts of the world because it has high protein content, low saturated fat and also contains omega fatty acids known to support good health (Ikem & Egiebor, 2005). Fish are constantly exposed to chemicals in polluted and contaminated waters. Fish have been found to be good indicators of heavy metal contamination in aquatic systems because they occupy different trophic levels and are of different sizes and ages (Burger et al., 2002). Heavy metals are considered the most important form of pollution of the aquatic environment because of their toxicity and accumulation by marine organisms, such as fish (Emami Khansari, Ghazi-Khansari, & Abdollahi, 2005). Heavy metals can be classified as potentially toxic (aluminium, arsenic, cadmium, lead, mercury), probably essential (nickel, vanadium, cobalt) and essential (copper, zinc, selenium) (Munoz-Olivas & Camara, 2001). Toxic elements can be very harmful, even at low concentration, when ingested over a long time period. The essential metals can also produce toxic effects when the metal intake is excessively elevated (Celik & Oehlenschlager, 2006; Tuzen, 2003).

The ingestion of food is an obvious means of exposure to metals, not only because many metals are natural components of foodstuffs, but also because of environmental contamination and contamination during processing. Solder, used in the manufacture of cans, is a recognized source of contamination of food by lead during canning (Voegborlo, El-Methnani, & Abedin, 1999). Levels of heavy metals in fish and canned fish samples have been widely reported in the literature (Celik & Oehlenschlager, 2004; Emami Khansari et al., 2005; Karadede, Oymak, & Ünlü, 2004; Tarley, Coltro, Matsushita, & Souza, 2001; Voegborlo et al., 1999). However, data on trace metal levels in canned fish samples produced in Turkey are very limited. Canned fishes are a popular food source in Turkey. The aim of this study was to determine the levels of trace heavy metals in canned fish samples.

In this study, the levels of trace heavy metals (copper, zinc, manganese, iron, selenium, aluminium, chromium, nickel, lead and cadmium) in canned fish samples produced

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doi:10.1016/j.foodchem.2006.03.044

and marketed in Turkey were determined by flame and graphite furnace atomic absorption spectrometry after microwave digestion.

2. Materials and methods

2.1. Sampling

Canned samples of five different fish species anchovy, tuna, Black Sea bonito, sardine and *Trachurus trachurus* were purchased from popular supermarkets in Turkey during 2005.

2.2. Reagents

All reagents were of analytical reagent grade unless otherwise stated. Double deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1} resistivity) was used for all dilutions. HNO_3, H_2O_2, and HCI were of suprapur quality (E. Merck). All the plastic and glassware were cleaned by soaking in dilute HNO_3 (1 + 9) and were rinsed with distilled water prior to use. The element standard solutions used for calibration were produced by diluting a stock solution of 1000 mg/l of the given element supplied by Sigma and Aldrich.

2.3. Apparatus

A Perkin Elmer A Analyst 700 atomic absorption spectrometer with deuterium background corrector was used in this study. The operating parameters for working elements were set as recommended by the manufacturer. Selenium, aluminium, chromium, nickel, lead and cadmium in canned fish samples were determined by HGA graphite furnace, using argon as inert gas. The other elements were determined in an air-acetylene flame. A Milestone Ethos D microwave closed system (maximum pressure 1450 psi, maximum temperature 300 °C) was used.

2.4. Microwave digestion

One gramme of sample was digested with 6 ml of concentrated HNO_3 (Suprapure, Merck) and 2 ml of concentrated H_2O_2 (Suprapure, Merck) in a microwave digestion system and diluted to 10 ml with double deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1} resistivity). A blank digest was carried out in the same way (digestion conditions for microwave system applied were: 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min, respectively).

In order to validate the method for accuracy and precision, certified reference materials (NRCC-DORM-2 Dogfish Muscle) were analyzed for corresponding elements.

3. Results and discussion

The recovery values were nearly quantitative (⩾95%) for the microwave digestion method. The relative standard deviations were less than 10% 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 (SRM). The achieved results were in good agreement with certified values. The results for this study are given in Table 1. Detection limit is defined as the concentration corresponding to three times the standard deviation of 10 blanks. Detection limit values of elements, as milligrammes per litre in flame AAS were found to be 0.007 for Cu, 0.012 for Zn, 0.009 for Fe, 0.008 for Mn. Selenium, aluminium, chromium, nickel, lead and cadmium were below detection limits of flame AAS. These elements were determined by graphite furnace AAS, using different matrix modifiers.

According to the results (Table 2), the metal contents in the samples studied depend on the analyzed species. All metal concentrations were determined on a wet weight basis. The contents of investigated trace metals in canned fish samples were found to be in the range 1.10–2.50 μg/g for copper, 7.57–34.4 μg/g for zinc, 0.90–2.50 μg/g for manganese, 10.2–30.3 μg/g for iron, 0.96–3.64 μg/g for selenium, 0.45–1.50 μg/g for aluminium, 0.97–1.70 μg/g for chromium, 0.42–0.85 μg/g for nickel, 0.09–0.40 μg/g for lead and 0.06–0.25 μg/g for cadmium. According to these data, zinc has the highest concentration, followed by iron, manganese and copper.

The highest and lowest copper levels were found in canned tuna fish and canned *Trachurus trachurus*, as 2.50 μg/g and 1.10 μg/g, respectively. In the literature, copper levels in canned fish samples have been reported in the range of 0.01–5.33 μg/g (Ikem & Egiebor, 2005). The lowest and highest copper levels in Turkish canned fish samples have been found in the range 7.1–45.7 μg/g (Celik & Oehlenschlager, 2006). Copper is essential for good health but a very high intake can cause adverse health problems, such as liver and kidney damage (Ikem & Egiebor, 2005). Copper concentrations in analyzed canned fish samples were below the MAFF guideline value of 30 mg Cu/kg (FAO, 1983; MAFF, 1995). The maximum copper level permitted for fish is 20 mg/kg according to the Turkish Food Codex (Anon., 2002).

Table 1
Trace metal concentrations in certified reference material (NRCC-DORM-2 Dogfish Muscle), $N = 4$, and experimental recoveries

Element	Certified value (μg/g)	Experimental value (μg/g)	Recovery (%)
Cu	2.34	2.29 ± 0.15	98
Zn	25.6	25.8 ± 1.3	101
Mn	3.66	3.51 ± 0.20	96
Fe	142	139.2 ± 9.8	98
Se	1.4	1.35 ± 0.10	96
Al	10.9	10.7 ± 0.8	98
Cr	34.7	32.9 ± 2.9	95
Ni	19.4	18.6 ± 1.5	96
Pb	0.065	0.062 ± 0.005	95
Cd	0.043	0.041 ± 0.004	95

Table 2
Trace metal contents of canned fish samples from Turkey (μg/g), $N = 4$

Sample	Cu	Zn	Mn	Fe	Se	Al	Cr	Ni	Pb	Cd
Canned anchovy fish	1.77 ± 0.10	34.4 ± 2.7	2.50 ± 0.15	30.3 ± 1.8	1.30 ± 0.10	0.80 ± 0.06	1.70 ± 0.15	0.64 ± 0.06	0.40 ± 0.04	0.12 ± 0.01
Canned tuna fish	2.50 ± 0.12	17.8 ± 1.2	0.90 ± 0.08	14.9 ± 1.1	2.98 ± 0.25	0.45 ± 0.04	1.08 ± 0.10	0.85 ± 0.06	0.10 ± 0.01	0.08 ± 0.006
Canned Black Sea bonito	1.28 ± 0.10	8.61 ± 0.70	1.52 ± 0.13	10.2 ± 0.9	0.96 ± 0.07	0.63 ± 0.05	1.46 ± 0.13	0.42 ± 0.03	0.25 ± 0.02	0.06 ± 0.005
Canned sardine	1.96 ± 0.15	7.57 ± 0.55	2.02 ± 0.20	17.4 ± 1.3	2.77 ± 0.20	0.98 ± 0.08	0.97 ± 0.09	0.72 ± 0.06	0.09 ± 0.008	0.19 ± 0.01
Canned *Trachurus trachurus*	1.10 ± 0.10	13.2 ± 1.1	1.34 ± 0.10	12.8 ± 1.2	3.64 ± 0.32	1.50 ± 0.12	1.24 ± 0.10	0.50 ± 0.10	0.16 ± 0.01	0.25 ± 0.02

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 both the Turkish Food Codex and MAFF (Anon., 2002; MAFF, 1995). The recommended daily intakes of zinc and copper are 15 mg Zn for adult males and 12 mg Zn for adult females and 1.5–3.0 mg Cu (Anon., 1991). The highest and lowest zinc contents were found to be 34.4 μg/g in canned anchovy fish and 7.57 μg/g in canned sardine. In the literature, zinc levels in canned fish samples have been reported in the range of 0.14–97.8 μg/g (Ikem & Egiebor, 2005). The lowest and highest zinc levels in Turkish canned fish samples have been found to be in the range 33.8–566 μg/g (Celik & Oehlenschlager, 2006).

The minimum and maximum manganese levels were found to be 0.90 μg/g in canned tuna fish and 2.50 μg/g in canned anchovy fish samples. 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 (Ikem & Egiebor, 2005), 1.56–3.76 μg/g dry weight in fish samples of the middle Black Sea (Turkey) (Tuzen, 2003), and 0.05–4.64 μg/g dry weight in fish species from Iskenderun Bay, northern east Mediterranean Sea, Turkey (Turkmen, Turkmen, Tepe, & Akyurt, 2005). According to both FAO (1983) and Turkish standards (Anon., 2002), there is no information on the carcinogenicity of manganese.

Iron is a mineral essential for life and for our diets (Aktaş, 2005; Skinner, 1997). Although considered a trace mineral, diets lacking in iron can contribute to the deficiency condition known as anaemia. There is no information about maximum iron levels in fish samples in Turkish standards (Anon., 2002). Iron contents in the literature have been reported in the range 0.01–88.4 μg/g in canned fish samples (Ikem & Egiebor, 2005), 0.82–27.35 μg/g dry weight in fish species from Iskenderun Bay, northern east Mediterranean Sea, Turkey (Turkmen et al., 2005), and 9.52–32.40 μg/g dry weight in fish samples of the middle Black Sea (Turkey) (Tuzen, 2003). The lowest and highest iron contents were found to be 10.2 μg/g in canned Black Sea bonito and 30.3 μg/g in canned anchovy fish samples.

Selenium is recognized as an essential micronutrient in animals and humans, playing important biological roles as antioxidant, as a regulator of thyroid hormone metabolism or as an anticarcinogenic agent. Low concentrations of selenium can cause anomalies in organisms and high concentrations are toxic. There is no information about maximum selenium levels in fish samples in Turkish standards (Anon., 2002). Canned fish samples in this study are very rich in selenium. The minimum and maximum selenium levels were found to be 0.96 μg/g in canned Black Sea bonito and 3.64 μg/g in canned *Trachurus trachurus*. There is limited information on selenium levels in fish and canned fish.

Aluminium is not considered to be an essential element in humans. Exposure to aluminium has been implicated in a number of human pathologies including encephalopathy/dialysis dementia, Parkinson disease and Alzheimer's disease (Narin, Tuzen, & Soylak, 2004). The permissible aluminium dose for an adult is quite high (60 mg per day) (World Health Organization, 1989). There is no information about maximum aluminium levels in fish samples in Turkish standards. It is reported that maximum aluminium levels in some food samples are 15 mg/kg (Anon., 2002). Aluminium contents in the literature have been reported in the range 0.02–5.41 μg/g dry weight in fish species from Iskenderun Bay, northern east Mediterranean Sea, Turkey (Turkmen et al., 2005), and 0.032–5.346 μg/g wet weight in fish fillets baked and grilled in aluminium foil (Ranau, Oehlenschlager, & Steinhart, 2001). The lowest and highest aluminium contents were found to be 0.45 μg/g in canned tuna fish and 1.50 μg/g in canned *Trachurus trachurus*.

The lowest and highest chromium levels were 0.97 μg/g in canned sardine and 1.70 μg/g in canned anchovy fish samples. Chromium contents in the literature have been reported in the range 0.0–0.30 μg/g in canned fish samples (Ikem & Egiebor, 2005), and 0.07–6.46 μg/g dry weight in fish species from Iskenderun Bay, northern east Mediterranean Sea, Turkey (Turkmen et al., 2005). There is no information about maximum chromium levels in fish samples in Turkish standards (Anon., 2002). Chromium (III) is an essential nutrient that potentiates insulin action and thus influences carbohydrate, lipid and protein metabolism. However, Cr(VI) is carcinogenic (Ikem & Egiebor, 2005; Tuzen & Soylak, 2006).

The minimum and maximum nickel levels were 0.42 μg/g in canned Black Sea bonito and 0.85 μg/g in canned tuna fish. Nickel contents in the literature have been reported in the range 0.0–0.78 μg/g in canned fish samples (Ikem & Egiebor, 2005), and 0.11–12.9 μg/g dry weight in fish species from Iskenderun Bay, northern east Mediterranean Sea, Turkey (Turkmen et al., 2005). There is no information about maximum chromium levels in fish samples in Turkish standards. It is reported that maximum nickel level in some food samples is 0.2 mg/kg (Anon., 2002).

The lowest and highest lead levels were found to be 0.09 μg/g in canned sardine and 0.40 μg/g in canned anchovy fish samples. Lead contents (in the literature) have been reported in the range 0.0–0.03 μg/g in canned fish samples (Ikem & Egiebor, 2005), 0.09–6.95 μg/g dry weight in fish species from Iskenderun Bay, northern east Mediterranean Sea, Turkey (Turkmen et al., 2005), 0.22–0.85 μg/g dry weight in fish samples of the middle Black Sea (Turkey) (Tuzen, 2003), 0.18–0.40 μg/g in canned tuna fish (Voegborlo et al., 1999), 0.076–0.314 μg/g in Turkish canned fish samples (Celik & Oehlenschlager, 2006), and 0.0162–0.0726 μg/g in canned tuna fish (Emami Khansari et al., 2005). The maximum lead level permitted for canned fishes is 0.2 mg/kg according to the Turkish Food Codex (Anon., 2002) and European communities (Commission of the European Communities, 2001). The fact that toxic metals are present in high concentrations in fishes is of particular importance in relation to the FAO/WHO (1976) 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. Lead is known to induce reduced cognitive development and intellectual performance in children and increased blood pressure and cardiovascular disease in adults (Commission of the European Communities, 2001).

Cadmium may accumulate in the human body and may induce kidney dysfunction, skeletal damage and reproductive deficiencies. Cadmium concentrations in analyzed canned fish samples were higher than both the Turkish standards and European communities (maximum 0.05 mg Cd/kg) (Anon., 2002; Commission of the European Communities, 2001). The lowest and highest cadmium levels were 0.06 μg/g in canned Black Sea bonito and 0.25 μg/g in canned *Trachurus trachurus*. Cadmium contents, in the literature, have been reported in the range 0.0–0.05 μg/g in canned fish samples (Ikem & Egiebor, 2005), 0.01–4.16 μg/g dry weight in fish species from Iskenderun Bay, northern east Mediterranean Sea, Turkey (Turkmen et al., 2005), 0.09–0.48 μg/g dry weight in fish samples of the middle Black Sea (Turkey) (Tuzen, 2003), 0.09–0.32 μg/g in canned tuna fish (Voegborlo et al., 1999), 0.025–0.494 μg/g in Turkish canned fish samples (Celik & Oehlenschlager, 2006), and 0.0046–0.0720 μg/g in canned tuna fish (Emami Khansari et al., 2005).

The levels of some toxic elements in analyzed canned fish samples were found to be above legal limits. The level may be reduced by more careful handling practices and processing of raw materials. Canned fish samples should be analyzed more often in Turkish supermarkets with respect to toxic elements.

Acknowledgements

The authors are grateful for the financial support of the Scientific and Technological Research Council of Turkey, TUBITAK (Project No.: 104T 448).

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