



Determination and Safety Evaluation of Heavy Metals in Canned Fish from Liaoning Province

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The concentrations of seven heavy metal elements, *e.g.*, Cd, Cr, Cu, Fe, Pb, Sn and Zn in canned fish from Liaoning province were determined by graphite furnace atomic absorption spectrometry after using microwave digestion techniques. Relative standard deviations (RSD) were 0.76-5.65 % and recoveries were 90-110 %. The results indicated that significant difference of elemental concentrations existed among the examined fish species. The concentrations of Cr, Cu, Pb and Zn in all the examined canned fish were below the maximum levels set by food-safety law and the concentrations of Cd in canned sardines and yellow croaker were above the maximum level. The concentrations of all the heavy metals in examined canned fish were lower than provisional tolerable weekly intake, so it may be concluded that canned fish from Liaoning province were edible, but necessary to reduce intake of canned sardines and yellow croaker.

Keywords: Canned fish, Heavy metals, Safety evaluation.

INTRODUCTION

Fish is widely consumed by humans because it contains high protein content, low saturated fat, essential vitamins, trace elements and also contains omega fatty acids known to support good health¹. In particular, canned fish are one of the favorable foods because it is delicious, convenient and affordable for most working families. But the polluted water from industrial and domestic waste water leads to fish contaminated by toxic metals (cadmium, lead, *etc.*). Fish intake and accumulate these toxic metals from the polluted aquatic environments and subsequently transferred to man through the food chains as the carrier of concentrated toxicant². Toxic elements can be harmful even at low content after digesting over a long time period. The essential metals (iron, copper, zinc, tin, *etc.*) could also be harmful when the intake amounts are excessive largely³. In addition, canned fish may be contaminated by toxic elements during production, processing, transportation and storage⁴. Therefore, this study aimed to determine the concentrations of seven heavy metals, including Cd, Cr, Cu, Fe, Pb, Sn and Zn in canned fish from Liaoning province by graphite furnace atomic absorption spectrometry (GFAAS) after microwave digestion method and assess the intake safety by comparing to provisional tolerable weekly intake (PTWI) recommended by the World Health Organization/Food and Agriculture Organization (WHO/FAO) Expert Committee on Food Additives (JECFA).

EXPERIMENTAL

Concentrated nitric acid, 30 % hydrogen peroxide (suprapure quality); the standard solutions of Cd, Cr, Cu, Fe, Pb, Sn and Zn for calibration procedure were produced by diluting a stock solution of 1000 mg/L of the investigated element supplied by Institute for Environmental Reference Materials of Ministry of Environmental Protection; Double distilled deionized water was used in all experiments.

AA320N atomic absorption spectrometer equipped with GA 3202 graphite furnace system was used for determination of trace elements. Materials were digested in a MDS-2002A model closed system microwave oven. Teflon reaction vessels were used in all digestion procedures. All the plastic and glassware were cleaned by soaking in dilute HNO₃ (1:9) and were rinsed with distilled water prior to use.

Sample collection and pretreatment: The economic and representative canned fish samples were randomly purchased from retail outlets located in 14 cities in Liaoning province from January to may in 2011. There were 7 kinds of canned fish including mackerel, tuna, sardines, yellow croaker, trichiurus haumela, dace and anchovy. The edible part including muscle and soup of canned fish were homogenized using homogenizer and stored in polyethylene bottles at -20 °C.

Digestion of samples: Microwave digestion method was follows: the samples were accurately weighed out 0.5 g and then transferred to 100 mL Teflon vessels. Samples were digested

by making use of HNO₃/H₂O₂ (6:2) acid mixtures in a microwave digestion system. Digests were finally made up with deionized water to 10 mL in acid washed standard flasks. Blank digest was carried out in the same way⁵. Digestion conditions for microwave system were applied as 2 min for 250 W and 180 °C, 2 min for 0 W, 6 min for 250 W and 200 °C, 5 min for 400 W and 210 °C, 8 min for 550 W and 210 °C, vent: 8 min⁶. The operating conditions for GFAAS are specified in Table-1.

Statistical analyses: Each reported result was the average value of the three analyses. The descriptive statistics (mean, standard deviation, range) and one-way analysis of variance (ANOVA) were conducted using excel software. One-way ANOVA statistical procedure was utilized to compare the data by fish species. Results were considered significant at $P < 0.05$.

RESULTS AND DISCUSSION

After adding a certain amount standard solution to the samples, the samples were digested using microwave digestion techniques, then the concentrations of heavy metals was determined according to experimental methods. The recoveries were 90-110 %, relative standard deviation (RSD) were in the range of 0.76-5.65 %. The results were given in Table-2.

TABLE-2
AVERAGE RECOVERIES AND RSD (n = 7)

Element	Background value(µg/mL)	Added value (µg/mL)	Found value (µg/mL)	Recovery (%)	RSD (%)
Cd	0.07	0.20	0.29	110.0	5.65
Cr	0.19	0.20	0.37	90.0	4.41
Cu	2.40	2.00	4.25	92.5	2.92
Fe	22.86	20.00	42.38	97.6	0.76
Pb	0.21	0.20	0.43	110.0	3.83
Sn	0.33	0.50	0.87	108.0	2.07
Zn	16.32	20.00	35.36	95.2	1.17

Concentration of heavy metals in canned fish: The concentrations of Cd, Cr, Cu, Fe, Pb, Sn and Zn were analyzed

three times (Table-3). Each result was the average value of three analyses. The maximum levels of heavy metals set by law in China was Cd = 0.1 mg/kg, Pb = 1 mg/kg, Sn = 250 mg/kg, Zn = 50 mg/kg⁷, Cr = 2 mg/kg⁸, Cu = 50 mg/kg⁹, no limited iron levels in fish samples in China standards.

Table-3 summarized the mean concentration of the same heavy metal element was quite different among species ($P < 0.05$), e.g., the mean concentration of cadmium in seven kinds of canned fish was in the range of 0.02-0.18 mg/kg (Table-3). This may be because heavy metals absorption and accumulation of heavy metals among different kinds of fishes depends on their kinds, life habit, living environment and feeding habits¹⁰. It is also find that the mean concentrations of the different heavy metals were quite different among the same kind of fish ($P < 0.05$), but heavy metals accumulation patterns are similar, essential metals such as Fe, Cu and Zn, accumulated the highest concentrations in all kinds of the fish, whereas toxic metals such as Pb and Cd accumulated at the lowest levels. This may be because essential metals were more absorbed voluntarily by organisms than toxic metals.

The concentration levels of Cr, Cu, Pb, Sn and Zn in canned fish determined were lower than the maximum legal limits, the concentration of Cd in canned sardines and yellow croaker were 1.8 times and 1.2 times of the maximum legal limits, respectively. But this does not indicate that these two kinds of fish is unsafe, daily intake of fish for person is limited, therefore, it should be considered the individually practical daily intake of fish before making a conclusion.

Safety evaluation: The relationship between the actual metal intake amount of heavy metals and intake safety was assessed, according to provisional tolerable weekly intake (PTWI) recommended by the Joint Food and Agriculture Organization/World Health Organization (FAO/WHO) Expert Committee on Food Additives (JECFA) and weekly fish consumption by Chinese people. For example PTWI of Cd was 0.007 mg/kg body weight, so the estimated weekly intakes of Cd for a 60 kg adult were 0.42 mg. The maximum concen-

TABLE-1
GFAAS INSTRUMENT OPERATING CONDITIONS

Element	Wavelength (nm)	Slit (nm)	Lamp current (mA)	Drying		Ashing		Atomization	
Cd	228.8	0.5	10	120 °C	20s	350 °C	15s	1800 °C	4s
Cr	357.9	0.7	7	110 °C	40s	1000 °C	30s	2800 °C	5s
Cu	324.8	0.7	5	100 °C	20s	800 °C	20s	2500 °C	3S
Fe	248.3	0.2	10	100 °C	20s	450 °C	10s	2000 °C	3s
Pb	283.3	0.7	15	100 °C	15s	800 °C	25s	1800 °C	5s
Sn	286.3	0.5	7	110 °C	20s	1000 °C	20s	1800 °C	5s
Zn	213.9	0.7	10	100 °C	15S	450 °C	20s	2000 °C	5s

TABLE-3
HEAVY METAL CONCENTRATIONS OF CANNED FISH (MEAN ± STANDARD DEVIATIONS, MG/KG, WET WEIGHT)

Element	Mackerel	Tuna	Sardines	Yellow croaker	Trichiuru shaumela	Dace	Anchovy
Cd	ND	0.07 ± 0.02	0.18 ± 0.09*	0.12 ± 0.14*	ND	0.02 ± 0.00	0.07 ± 0.03
Cr	1.28 ± 0.19	0.17 ± 0.10	0.62 ± 0.15	0.15 ± 0.04	0.08 ± 0.05	0.32 ± 0.18	0.40 ± 0.20
Cu	7.39 ± 2.56	2.31 ± 0.76	1.89 ± 0.32	1.76 ± 0.24	2.01 ± 1.04	1.47 ± 0.46	3.15 ± 1.84
Fe	14.93 ± 4.77	23.60 ± 5.46	19.35 ± 3.81	30.41 ± 5.13	42.70 ± 6.25	16.75 ± 3.28	20.29 ± 3.69
Pb	0.22 ± 0.04	0.18 ± 0.02	0.05 ± 0.03	0.13 ± 0.05	0.09 ± 0.03	0.34 ± 0.10	0.11 ± 0.04
Sn	1.30 ± 0.25	0.29 ± 0.09	0.41 ± 0.36	0.74 ± 0.29	6.34 ± 2.03	0.15 ± 0.04	1.78 ± 0.44
Zn	10.64 ± 3.83	15.16 ± 4.19	11.57 ± 4.62	9.79 ± 3.25	13.41 ± 4.56	20.13 ± 3.88	14.40 ± 3.90

*out of limits

tration of Cd in all the canned fish samples analyzed was 0.18 mg/kg in sardines (Table-3) and an adult consume 0.182 kg of fish per week based on the survey data provided by Chinese total diet study¹¹, so the estimated weekly intake of Cd from canned fish for an adult was 0.33 mg, that was 7.86 % of PTWI. The results were given in Table-4.

TABLE-4
ESTIMATED WEEKLY INTAKES FOR THE
FISH SPECIES CONSUMED BY PEOPLE

Element	PTWI (mg/kgbw)	PTWI (mg)	Content (mg/kg)	Weekly intake (mg)	Percent (%)
Cd	0.007	0.42	0.18	0.33	7.86
Cr	0.0067	0.40	1.28	0.23	57.5
Cu	3.5	210	7.39	1.34	0.64
Fe	5.6	336	42.70	7.77	2.31
Pb	0.025	1.5	0.34	0.062	4.13
Sn	14	840	6.34	1.54	0.18
Zn	7.0	420	20.13	3.66	0.87

As can be seen in Table-4, Cu, Sn and Zn take up little per cent of PTWI, Cr take up much per cent of PTWI in the canned fish analyzed, but the estimated weekly intakes of the seven heavy metals analyzed were all below PTWI. But this does not indicate the estimated weekly intakes of the heavy metals were safe, because the data determined only from canned fish, other kinds of food as vegetables, fruit, grain, meat and egg also have heavy metals, it should be considered the individually practical intake of fish before making a conclusion. Thus excessive intake of canned fish (especial yellow croaker and sardine) still has potential hazards and it is necessary to reduce intake.

Conclusion

The concentrations of Cd, Cr, Cu, Fe, Pb, Sn and Zn in canned fish from Liaoning province were determined by graphite furnace atomic absorption spectrometry (GFAAS) after using microwave digestion techniques. The results indicated that the concentrations of Cr, Cu, Pb and Zn were below the maximum levels set by law, the concentration of Cd in canned yellow croaker and sardine were above the maximum levels, but lower than provisional tolerable weekly intake (PTWI) and in the tolerable range. Thus the canned fish from Liaoning province were edible, but necessary to reduce intake of canned yellow croaker and sardine.

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