J. Food and Dairy Sci., Mansoura Univ., Vol. 3 (1): 11 - 22, 2012

DETERMINATION OF SOME HEAVY METALS IN FISH PRODUCTS

Mohamed, Sadia M. H. ; O. R. Abo Samaha ; A. A. Abdel-Nabey and M. K. M. Khalil

Food Science and Technology Dept., Faculty of Agriculture, El-Shatby, Alexandria University, Alexandria, Egypt.

ABSTRACT

This study was carried out to determine certain heavy metals (Cu, Cd, Pb, As and Hg) in twenty different samples of fish products (salted, smoked, frozen, canned and marinated) purchased from different markets in Alexandria city, Egypt during 2009, by using atomic absorption spectrophotometer technique. The results indicated that expect Pb concentrations of all fish products; Cd in frozen squid, salted mullet, salted sardine and marinated fish products were higher than the maximum permissiable levels by WHO. Expect As of frozen crab and As in canned sardine, all concentrations of Cu, Cd, Pb, As and Hg of the above fish products were below the maximum permissiable concentrations stated by the different regulatory agencies (FAO, WHO and EOSQC).

Keywords:- Heavy metals, Fish products.

INTRODUCTION

Environmental pollution represents a major problem in both developed and underdeveloped countries. Egypt is one of the countries which suffers from high biosphere pollution (air, soil and water). Many ecological changes occur in water as a result of human activities, including agricultural, industrial and municipal wastes (Atta *et al.*, 1997).

The seas and oceans, which cover 70% of the world's surface, are one of the man's great hopes for future food supplies. As human populations multiply and industrialization increases, the problems of environmental pollution become more critical. Heavy metals enter the aquatic environment naturally through weathering of the earths crust. In addition to geological weathering, human activities have also introduced large quantities of metals to local water bodies, thereby disturbing the natural balance in the ecosystem (Forstner and Wittmann, 1983).

Sea foods have essential amino acids, fatty acids, protein, vitamins and minerals. Among sea foods, fish are commonly consumed and, hence, are a connecting link for the transfer of toxic heavy metals in human being. Heavy metals have the tendency to accumulate in various organs of marine organisms, especially fish, which in turn may enter into the human metabolism through consumption causing serious health hazards (Puel *et al.*, 1987).

Fish is the major part of the human diet and it is therefore not surprising that numerous studies have been carried out on metal pollution in different species of edible fish. Industrial effluents, agricultural runoffs, transport, burning of fossil fuels, animal and human excretions and geologic weathering and domestic waste contribute to the heavy metals in the water

bodies. Heavy metals are critical in this regard because of their easy uptake into the food chain and bioaccumulation processes (Raja *et al.*, 2009).

Heavy metals acquired through the food chain as a result of pollution are potential chemical hazards, threatening consumers. At low levels, some heavy metals such as copper, zinc, iron and manganese are essential for enzymatic activity and many biological processes. Other metals, such as cadmium, mercury, arsenic and lead haven't known essential role in living organisms, and are toxic at even low concentrations. The essential metals also become toxic at high concentrations (Al-Weher, 2008).

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. Processing steps may change the concentration of heavy metals in fish before consumption (Ganjavi *et al.*, 2010).

In Egypt, fish, shellfish and fish products are considered one of the popular foods. Alexandria is one of the major industrial center, and its coast is considered one of the main summer resort and fishing area. The Mediterranean is subject to heavy discharges of pollutants from numerous industrial processes. Among these industries are leather tanning, metallic transformation, oil refineries and petroleum terminals and organic and/or inorganic chemical industries which might affect the concentration of metals in salt water fish. Many factories occur in and around Alexandria such as Egyptian Liquefied Natural Gas (ELNG), Rashpetco, Gasco, Wepco, Petroget (shipyard), Abu-Qir fertilizers, Alexandria fertilizers, National Paper and Racta company. Most of the factories wastes are discarded into the Mediterranean Sea.

To the best of our knowledge, little attention has been paid to study heavy metals pollution in some fish products. So, the present study was planned to throw light on determination of some heavy metals such as Cu, Cd, Pb, As and Hg in fish products (salted, smoked, frozen, canned, and marinated).

MATERIALS AND METHODS

Materials:-

According to sample's description as shown in Table (1) and after removing heads, viscera and fish gills, all samples were homogenized using blender (Braun type: 4262). Canned and marinated samples were homogenized with packaging solution, stored frozen at -18^{o}C in polyethylene bags prior to analysis.

Methods:-

The metal's concentration in samples were determined after digestion using AAS according to the method of Vitosevic *et al* (2007) as follow, weighted 1-3 g of sample was put into a 100 ml Kjeldahl flask and 10 ml of sulphuric acid (H_2SO_4) and nitric acid (HNO_3) (1:3) were added to the flask. After thermolysis and heating until discoloration, the solution was cooled, filtered using ashless filter paper 9.0 cm (Whatman 43) and diluted to 50 ml with deionized water.

This solution was analyzed using AAS (SHIMADZU Atomic Absorption Spectrophotometer AA-6800 where the flame unit was used together with the auto sampler SHIMADZU ASC-6100). Moisture content was determined by drying about 5g sample at 103±2 ^{o}C to constant weight as described by Less (1975).

Statistical analysis

The data was subjected to analysis of variance (Main effect ANOVA), multiple comparisons between means were carried out using LSD 0.05 test using the statistical software package "STATESTICA 8.5", StatSoft, Inc., USA (for fish products samples).

Table 1: Description of the different processed fish samples obtained from Alexandria markets

Brand	description
1-Salted samples	
A	Salted mullet.
B	Salted mullet (unknown source data).
C	Salted sardine.
D	Salted sardine (unknown source data).
2-Smoked samples	
A	Smoked herring (cold smoking).
B	Smoked herring (unknown source data).
C	Smoked sliced salmon (cold smoking).
3-Frozen samples	
A	Frozen peeled shrimp.
B	Frozen peeled shrimp.
C	Frozen giant squid fillet.
D	Frozen crab.
4-Canned samples	
A	Canned tuna meat in vegetable oil & brine.
B	Canned (Skip Jack) tuna meat in vegetable oil.
C	Canned sardine (pilchard) in soya oil with chilli.
D	Canned sardine in sunflower oil with red chilli.
E	Canned sardine (pilchard) sardine in brine.
F	Canned mackerel (*Restrelliger kanagurta*) in natural oil and brine.
G	Canned anchovies fillets in olive oil.
5-Marinated samples	
A	Marinated sardine.

RESULTS AND DISCUSSION

Salted fish products

Table (2) shows the concentrations of heavy metals namely Cu, Cd, Pb, As and Hg in salted fish samples (mg/kg; on wet and dry wt basis.).

The content of Cu (dry wt.) varied between 5.61 to 8.05 in salted mullet samples. While salted sardine samples contained Cu varied from 8.25 to 9.29 mg/kg (dry wt.).

No significant differences were found among the salted fish samples except the sample (mullet 2) which has been recorded to contain the minimum concentration of Cu (5.61 mg/kg; dry wt.). Also as shown from Table (2), Cd content varied from 1.59 to 2.15 mg/kg (dry wt.) in case of salted mullet samples with no significant differences between them. On the other hand, Cd content ranged between 2.88 to 4.38 mg/kg (dry wt.) in case of the two salted sardine samples with no significant differences between them. In general, the maximum concentration of Cd was recorded in sardine (1) sample showing a significant difference only with the two salted mullet samples.

Table (2) also showed the concentrations of Pb in salted fish samples. These values were 61.30, 33.81, 36.70 and 33.17 (dry wt.) in mullet (1), mullet (2), sardine (1) and sardine (2), respectively. It was found that salted mullet sample (1) showed the highest Pb level with a significant difference among all the other three salted fish samples. No significant differences in Pb concentrations were found between salted mullet sample (2) and the two salted sardine samples.

Table 2:Concentrations of heavy metals (mg/kg) in salted fish products*

Sample	Cu	Cd	Pb	As	Hg
Mullet (1)					
●Wwb**	3.47±0.19	0.69±0.351	26.41±1.11	1.06±0.29	0.08±0.02
●D w b***	8.05^{a}±0.45	1.59^{b}±0.81	61.30^{a}±2.57	2.47^{b}±0.76	0.19^{a}±0.04
(2)					
●W w b	2.59±0.40	1.00±0.08	15.64±0.58	0.98±0.05	0.02±0.01
●D w b	5.61^{b}±0.87	2.15^{b}±0.17	33.81^{b}±1.25	2.11^{b}±0.11	0.04^{b}±0.02
Sardine (1)					
●W w b	4.36±0.13	2.06±0.05	17.23±0.62	2.05±0.04	0.03±0.00
●D w b	9.29^{a}±0.29	4.38^{a}±0.10	36.70^{b}±1.33	4.37^{a}±0.09	0.07^{b}±0.00
(2)					
●W w b	3.72±0.18	1.30±0.34	14.96±1.50	1.85±0.07	0.07±0.01
●Dw b	8.25^{a}±0.39	2.88^{ab}±074	33.17^{b}±3.32	4.10^{a}±0.14	0.15^{a}±0.02
L. S.D	1.93	2.04	8.05	1.44	0.09

*** Data as mean ± SD**
****Wet weight basis**
*****Dry weight basis**
Means in the same column sharing the same letters are not significantly different, at 0.05 level.

The mean concentrations of As content as shown in Table (2) were 2.47, 2.11, 4.37 and 4.10 mg/kg (dry wt.) in salted mullet (1), mullet (2), sardine (1) and sardine (2), respectively. No significant differences were found between the two salted mullet samples as well as the two salted sardine samples. It can be noticed also that sardine samples had high concentration of (As) as compared to the salted mullet samples.

Data in Table (2) also showed that Hg content varied from 0.04 to 0.19 and from 0.07 to 0.15 mg/kg (dry wt.) for salted mullet samples and salted sardine samples, respectively. The data showed that no significant differences were recorded between salted mullet sample (1) and salted

sardine sample (2) and also between the other two salted samples (mullet 2 and sardine 1).

From the above results it can be concluded that heavy metals contents can be arranged in a decreasing order as follow: Pb, Cu, As, Cd and Hg, respectively.

Generally, all total concentrations of Cu found in different salted fish samples were below the maximum permissiable limit (30 mg/kg, wet wt.) regulated by FAO (1992) and limits proposed by WHO (1996); Cd content were below the maximum permissiable limit proposed by FAO (1992) (2 mg/kg) and higher than the permissiable limits proposed by WHO (1996) (0.8 mg/kg, except salted mullet (1) sample). Different salted fish products had higher concentrations of lead than the permissiable limits (2 mg/kg) proposed by FAO (1992); EOSQC (0.1 mg/kg) (1993) and (0.15 mg/kg) proposed by WHO (1996). Concentrations of As were below the maximum permissiable limit of (2 mg/kg) proposed by WHO (1996). All total concentrations of Hg of different salted fish products were below the maximum permissiable limit of 0.5 mg/kg regulated by EOSQC (1993); o.6 mg/kg proposed by WHO (1996) and FDA (2001) has set a maximum total Hg concentrations of 1 mg/kg.

Smoked fish products

Table (3) shows the concentrations of Cu, Cd, Pb, As and Hg in smoked herring and salmon samples (wet and dry wt.). The concentration of Cu was 8.08 herring (1) (mg/kg; dry wt.). On the other hand, no detected amount of Cu was observed in herring (2) and salmon. The highest concentration of Cu was found in herring (1), with a significant difference compared with all other samples.

As shown in Table (3), Cd content (mg/kg; dry wt.) varied between 0.50 to 1.60 in smoked herring samples showing a significant difference between them. On the other hand, Cd content of smoked salmon sample was 2.39 mg/kg (dry wt.) showing no significant difference with smoked herring sample (2).

The content of Pb in three smoked fish samples were: 23.86, 47.69 and 55.14 mg/kg (dry wt.) in herring (1), herring (2) and salmon, respectively. It can be noticed that smoked salmon showed the maxmium Pb concentration with a significant difference with other two smoked herring samples.

The concentrations of (As) as shown in Table (3) were 3.29, 5.91 and 1.92 (mg/kg; dry wt.) in smoked herring (1), herring (2) and smoked salmon, respectively. The highest concentration of As was found in herring (2) with a significant difference with the other samples. On the other hand, no significant difference was noticed between herring (1) and salmon with respect to their content of (As).

Data in Table (3) showed that Hg content varied from 0.06 to 0.09 mg/kg (dry wt.) in case of smoked herring samples. On the other hand, Hg content of smoked salmon sample was only 0.04 mg/kg (dry wt.). These results indicated that no significant differences were noticed between the Hg content of the studied smoked fish samples.

The Pb concentration of the smoked fish samples in the present study varied from 9.95 to 17.44 mg/kg (wet wt.). These concentrations were higher

than those reported by Adekunle and Akinyemi (2004). They showed that the mean value of Pb in processed smoked fish varied from 8.0 to 12.5 mg/kg.

The concentration of Cd and Pb (mg/kg wet wt.) in this study are not in agreement with those reported by Tansel sireli *et al.* (2006).

As a conclusion, it can be seen that heavy metal contents can be arranged in a decreasing order as follow:- Pb> Cu > As > Cd > Hg.

All total concentrations of Cu found in different smoked fish samples were below the maximum permissiable limit regulated by FAO (1992) and WHO (1996); Cd content were below the maximum permissiable limit proposed by FAO (1992) and WHO (1996). Levels of lead were higher than the permissiable limits proposed by FAO (1992) and proposed by WHO (1996). Levels of As were below the maximum permissiable limit proposed by WHO (1996). All total concentrations of Hg were below the maximum permissiable limit regulated by EOSQC (1993); WHO (1996) and FDA (2001).

Table 3: Concentrations of heavy metals (mg/kg) in smoked fish products *

Sample	Cu	Cd	Pb	As	Hg
Herring (1)					
●W w b**	3.37±0.05	0.21±0.13	9.95±0.69	1.32±0.43	0.03±0.01
●D w b***	8.08^{a}±0.11	0.50^{b}±0.31	23.86^{c}±1.65	3.29^{b}±1.03	0.06^{a}±0.03
(2)					
●W w b	N.D****	0.58±0.01	17.16±0.99	2.13±0.13	0.03±0.02
●D w b	$N.D^{b}$	1.60^{a}±0.03	47.69^{b}±2.75	5.91^{a}±0.36	0.09^{a}±0.04
Salmon					
●W w b	N.D	0.76±0.11	17.44±0.28	0.61±0.19	0.01±0.00
●D w b	$N.D^{b}$	2.39^{a}±0.33	55.14^{a}±0.87	1.92^{b}±0.59	0.04^{a}±0.00
L. S.D	0.21	0.84	6.10	2.28	0.10

*** Data as mean ± SD**
****Wet weight basis**
*****Dry weight basis**
****** N.D: below detection limit (Cu; 0.005 mg/kg)**
Means in the same column sharing the same letters are not significantly different, at 0.05 level.

Frozen fish products

Table (4) shows the values of Cu, Cd, Pb, As and Hg as mg/kg (wet and dry wt.) in frozen fish samples. Cu content in frozen shrimp sample (dry wt.) varied from N.D to 41.37 mg/kg. On the other hand, frozen squid sample had from 10.29 to 15.20 mg/kg of Cu. Frozen crab sample contained 98.41 mg/kg Cu. These result showed significant differences between the studied frozen fish sample with respect to their content of Cu. In general Cu content varied from N.D (frozen shrimp sample (2)) to 98.41 mg/kg (frozen crab sample).

As shown from Table (4), Cd content of frozen shrimp sample varied from 4.72 to 4.82 mg/kg (dry wt.) showing no significant differences between them. On the other hand, Cd content of frozen squid sample ranged between 5.24 to 7.31 mg/kg (dry wt.) showing significant differences between them. Frozen crab sample had the lowest amount of Cd (0.73 mg/kg; dry wt.). In

general Cd content varied between 0.73 mg/kg (frozen crab sample) to 7.31 mg/kg (frozen squid sample (2).

The results in Table (4) also show the concentration of Pb in the frozen fish samples. As it can be seen, Pb content in frozen shrimp samples varied between 120.86 to 123.81 mg/kg (dry wt.) showing no significant differences between them. Also, the results showed that the Pb content in frozen squid sample ranged from 50.76 to 61.20 mg/kg (dry wt.) with no significant differences between them as well. Further, the Pb content of the frozen crab sample was 37.27 mg/kg (dry wt.).

The concentrations of (As) in the frozen fish samples are shown also in Table (3). As content in frozen shrimp samples ranged between 1.99 to 6.60 mg/kg (dry wt.) showing great significant differences between them, the same trend was recorded for (As) content in frozen squid samples which varied from 2.61 to 4.64 mg/kg (dry wt.). On the other hand, higher concentration of As was found in the frozen crab sample (12.20 mg/kg).

No significant differences were noticed between the different frozen fish samples with respect to their content of Hg. The results indicated that Hg content varied between 0.06 to 0.13 mg/kg (dry wt.).

The concentrations of Cu, As and Hg in frozen shrimp were lower than those reported by Sivaperumal *et al.* (2007). While, the concentrations of Cd and Pb were higher.

Table 4: Concentrations of heavy metals (mg/kg) in frozen fish products*

Sample	Cu	Cd	Pb	As	Hg
Shrimp (1)					
●W w b**	4.39±1.12	0.50±0.11	12.79±1.92	0.70±0.11	0.01±0.00
●D w b***	41.37^{b}±10.58	4.72^{b}±0.99	120.86^{a}±18.16	6.60^{b}±1.08	0.07^{a}±0.00
(2)					
●W w b	N.D****	0.56±0.01	14.40±0.37	0.23±0.01	0.01±0.00
●D w b	$N.D^{d}$	4.82^{b}±0.04	123.81^{a}±3.21	1.99^{d}±0.12	0.11^{a}±0.01
Squid (1)					
●W w b	2.05±0.40	1.05±0.06	10.12±1.77	0.93±0.18	0.02±0.00
●D w b	10.29^{cd}±2.00	5.24^{b}±0.29	50.76^{b}±8.89	4.64^{c}±0.89	0.12^{a}±0.01
(2)					
●W w b	2.05±0.92	0.98±0.11	8.24±0.79	0.35±0.04	0.02±0.00
●D w b	15.20^{c}±6.83	7.31^{a}±0.80	61.20^{b}±5.86	2.61^{d}±0.30	0.13^{a}±0.03
Crab					
●W w b	19.76±0.08	0.15±0.01	7.48±0.26	2.46±0.05	0.01±0.01
●D w b	98.41^{a}±0.42	0.73^{c}±0.05	37.27^{b}±1.32	12.20^{a}±0.06	0.06^{a}±0.06
L. S.D	14.67	1.50	24.53	1.65	0.08

*** Data as mean ± SD**
****Wet weight basis**
*****Dry weight basis**
****** N.D: below detection limit (Cu; 0.005 mg/kg)**
Means in the same column sharing the same letters are not significantly different, at 0.05 level.

Alinnor and Obiji (2010) showed that Pb, Cd, Hg and Cu levels in frozen fish samples were 0.50; 0.05; 0.008 and 8.00 mg/kg, respectively.

Generally, all total concentrations of Cu found in the different frozen fish samples were below the maximum permissiable limit regulated by FAO (1992) and WHO (1996); Cd content were below the maximum permissiable limit proposed by FAO (1992) and WHO (1996) (except frozen squid (1) and squid (2) samples). Concentrations of lead were higher than the permissiable limits proposed by FAO (1992); EOSQC (0.1 mg/kg, on wet weight basis) (1993) and WHO (1996). Concentrations of As were below the maximum permissiable limit proposed by WHO (1996) (except, frozen crab sample). All total concentrations of Hg found in the different frozen fish products were below the maximum permissiable limit regulated by EOS QC (1993); WHO (1996) and FDA (2001).

Canned fish products

Table (5) shows the concentrations of Cu, Cd, Pb, As and Hg (wet and dry wt.) in canned fish samples. The results indicated that:-

1. The studied heavy metals can be arranged in a decreasing order as follow:- Pb > Cu > As > Cd > Hg.
2. Cd content was not detected in two canned fish samples (tuna (2) and canned mackerel).
3. Canned mackerel sample showed the highest Cu concentration (14.50 mg/kg) with no significant differences with canned sardine samples (2 and 3). While, canned tuna (2) showed the lowest Cu concentration. No significant differences were noticed between tuna (1 and 2); sardine (1) and anchovies with respect to their content of Cu.
4. Canned tuna sample (1) showed a higher mean concentration of Cd with significant differences with the other studied canned samples except, canned sardine sample (1).
5. The highest concentrations Pb were recorded in canned mackerel sample followed by canned tuna sample (2), while the lowest levels were recorded for canned anchovies followed by canned sardine sample (3).
6. Canned sardine sample (3) followed by canned tuna sample (2) were recorded to have the highest concentrations of As being 7.94 and 5.82 mg/kg (dry wt.), respectively. On the other hand, canned sardine sample (2 and 1) showed the lowest concentration being 1.26 and 1.78 mg/kg; dry wt., respectively. Canned mackerel and canned anchovies had quite similar of As with no difference between them.
7. The maximum concentration of Hg was recorded in tuna, while the lowest concentration of Hg was recorded in sardine (3) and anchovies (0.02 mg/kg dry wt.).

In accordance with the results obtained here, Aziz (1976) found that Cu, Pb and Hg content in canned sardine were: Cu, 7.084; Pb, 3028; and Hg, 2.73 mg/kg (dry wt.), the level of Cu and Pb are lower than those found in the present study, while level of Hg had higher values than those found in the present study.

Total concentrations of Cu, Cd, Pb, As and Hg in the different canned fish samples obtained in the present study are lower or higher than reported by Tahan *et al.* (1995); Voegborlo *et al.* (1999); Ikem and Egiebor (2005);

Khansari *et al.* (2005); Ashraf (2006); Ashraf *et al.* (2006); Tuzen and soylak (2007); Vitosevic *et al.* (2007); Ganjavi *et al.* (2010) and Mol (2010).

On the other hand, the results obtained here agreed well with those reported by Khansari *et al.* (2005) with respect to As concentration, Ikem and Egiebor (2005) for Cd and As concentration and Tuzen and soylak (2007) for Cu level.

All total concentrations of Cu found in the different canned fish samples were below the maximum permissiable limit regulated by FAO (1992) and WHO (1996); Cd content were below the maximum permissiable limit proposed by FAO (1992) and WHO (1996). Different canned fish products had higher levels of lead than the permissiable limits proposed by FAO (1992) and WHO (1996). Concentrations of (As) (except canned sardine (3) sample) were below the maximum permissiable limit proposed by WHO (1996). All total concentrations of Hg were below the maximum permissiable limit of regulated by EOSQC (1993); WHO (1996)and FDA(2001).

Table 5: Concentrations of heavy metals (mg/kg) in canned fish products*

Sample	Cu	Cd	Pb	As	Hg
Tuna (1)					
●W w b**	2.90±0.38	0.46±0.16	6.72±0.56	0.98±0.00	0.02±0.01
●D w b***	10.32^{bcd}±10.58	1.62^{a} ±0.55	23.90^{bc} ±1.99	3.50^{c}±0.00	0.08^{ab} ±0.02
(2)					
●W w b	2.30±0.34	N.D****	9.55±0.15	1.82±0.00	0.03±0.02
●D w b	7.34^{d}±1.10	$N.D^{c}$	30.51^{ab} ±0.49	5.82^{b} ±0.00	0.09^{a}±0.06
Sardine (1)					
●W w b	4.16±0.0.69	0.31±0.03	10.12±0.923	0.79±0.00	0.02±0.00
●D w b	9.35^{cd}±1.54	0.70^{ab}±0.07	22.73^{bc} ±3.29	1.78^{cd} ±0.01	0.04^{ab}±0.00
(2)					
●W w b	5.11±0.82	0.28±0.03	10.05±1.66	0.52±0.02	0.02±0.01
●D w b	12.36^{abc}±1.97	0.67^{b}±0. 0.08	24.31^{bc} ±4.01	1.26^{d}±0.06	0.05^{ab}±0.03
(3)					
●W w b	4.21±0.75	0.12±0.02	6.76±0.26	2.41±0.46	0.01±0.00
●D w b	13.85^{ab}±2.48	0.40^{bc}±0.08	22.25^{c}±0.84	7.94^{a}±1.51	0.02^{b}±0.00
Mackerel					
●W w b	2.69±0.32	N.D	6.47±1.26	0.53±0.26	0.01±0.00
●D w b	14.50^{a}±1.73	$N.D^{c}$	34.87^{a}±6.86	2.83^{cd}±1.41	0.03^{ab}±0.02
Anchovies					
●W w b	5.81±0.52	0.16±0.03	10.99±0.51	1.42±0.10	0.01±0.00
●D w b	10.56^{bcd}±0.94	0.30^{bc}±0.06	19.95^{c}±0.92	2.58^{cd}±1.18	0.02^{b}±0.00
L. S.D	3.93	0.51	7.98	1.86	0.07

*** Data as mean ± SD**
****Wet weight basis**
*****Dry weight basis**
****** N.D: below detection limit(Cd; 0.005 mg/kg)**
Means in the same column sharing the same letters are not significantly different, at 0.05 level.

Marinated fish product

Table (6) shows the concentrations of Cu, Cd, Pb, As and Hg in marinated sardine sample (mg/kg; dry and wet wt.). The concentrations of these metals were 9.21, 1.37, 12.16, 2.81 and 0.07 (mg/kg; dry wt.) for Cu, Cd, Pb, As and Hg, respectively.

Comparing with the other fish products studied, it can be noticed that marinated sardine sample had the lowest amount of Pb.

Total concentrations of Cu found in marinated sardine sample were below the maximum permissiable limit regulated by FAO (1992) and WHO (1996); Cd content was below the maximum permissiable limit of cadmium content proposed by FAO (1992), and higher than the permissiable limit proposed by WHO (1996). Marinated fish product had higher levels of lead than the permissiable limits proposed by FAO (1992) and WHO (1996). Concentrations of As were below the maximum permissiable limit of (2 mg/kg) proposed by WHO (1996). All total concentrations of Hg were below the maximum permissiable limit regulated by EOSQC (1993); WHO (1996) and FDA (2001).

Table 6: Concentrations of heavy metals (mg/kg) in marinated fish product *

Sample	Cu	Cd	Pb	As	Hg
Sardine					
●W w b**	5.85±0.11	0.87±0.05	7.72±1.08	1.78±0.22	0.04±0.04
●D w b***	9.21±0.18	1.37±0.08	12.16±1.70	2.81±0.34	0.07±0.07

***Data as mean ± SD**
****Wet weight basis**
*****Dry weight basis.**

As a conclusion, except Pb concentrations of all fish products (salted, smoked, frozen, canned and marinated); Cd in frozen squid; salted mullet (2); salted sardine (1 and 2) and marinated fish product were higher than the maximum permissiable levels by WHO (0.8 ppm on wet weight basis). Expect As of frozen crab, canned sardine (3), all concentrations of Cu, Cd, Pb, As and Hg of the above fish products were below the maximum permissiable concentrations stated by the different regulatory agencies (FAO, WHO and EOSQC).

REFERENCES

Adekunle, I. M. and Akinyemi, M. F. (2004). Lead levels of certain consumer products in Nigeria: a case study of smoked fish foods from Abeokuta. Food and Chemical Toxicol. 42: 1463-1468.

Alinnor, I. J. and Obiji, I. A. (2010). Assessment of trace metal composition in fish samples from Nworie River. Pakistan J. of Nutr. 9: 81-85.

Al-Weher, S. M. (2008). Levels of heavy metal Cd, Cu and Zn in three fish species collected from the Northern Jordan Valley, Jordan. Jordan J. of Biological Sci. 1: 41-46.

Ashraf, W. (2006). Levels of selected heavy metals in tuna fish. The Arabian J. for Sci. and Engineering 31(1): 89-91.

Ashraf, W.; Seddigi, Z.; Abulkibash, A. and Khalid, M. (2006). Levels of selected metals in canned fish consumed in Kingdom of Saudi Arabia. Environ. Monitoring and Assessment 117: 271-279.

Atta, M. B.; El-Sebbaie, L. A.; Noaman, M. A. and Kassab, H. E. (1997). The effect of cooking on the content of heavy metals in fish (*Tilapia nilotica*). Food Chem. 58: 1-4.

Aziz, S. L. (1976). The determination of some heavy metals in some Egyptian foods and the effect of processing and cooking operations thereon. M. Sc. Thesis, Faculty of Agriculture, Alexandria University, Egypt.

Egyption Organization for Standardization and Quality Control (E.O.S.Q.C). (1993). Maximum residue limits for heavy metals in food "Ministry of Industry" No.2360/ 1993 pp: 5 Cairo –Egypt.

Food and Agriculture Organization (FAO). (1992). Committee for inland fisheries of Africa: Report of the third session of the working party on pollution and fisheries. FAO Fish. Rep., No 471: 43p.

Food and Drug Administration (FDA). (2001). Fish and Fisheries Products Hazards and Controls Guidance, third ed. Center for Food Safety and Applied Nutrition, US Food and Drug Administration.

Forstner, U.; and Wittmann, G.T.W. (1983). Metal pollution in the aquatic environment. Berlin, Springer-Verlag. pp: 30-61.

Ganjavi, M.; Ezzatpanah, H.; Givianrad, M. H. and Shams, A. (2010). Effect of canned tuna fish processing steps on lead and cadmium contents of Iranian tuna fish. Food Chem. 118: 525–528.

Ikem, A and Egiebor, N, O. (2005). Assessment of trace elements in canned fishes (Mackerel, Tuna, Salmon, Sardines and Herrings) marketed in Georgia and Alabama (United States of America). J. Food Composition and Analysis 18: 771–787.

Khansari, F. E.; Ghazi- Khansari, M. and Abdollahi, M. (2005). Heavy metals content of canned tuna fish. Food Chem. 93: 293-396.

Less, R. (1975). Analytical and Quality Control Methods for the Food Manufacturer and Buyer. Leonard Hill Books a division of International Textbook Company limited 450Edgware Rd., London.

Mol, S. (2010). Determination of trace metals in canned anchovies and canned rainbow trouts. Food and Chemical Toxicol.

Puel, D.; Zsuerger, N. and Breittmayer, J.P. (1987). Statistical assessment of a sampling pattern for evalution of changes in Hg and Zn concentration in *Patella coerulea*. Bull. Environ. Contam. Toxicol. 38: 700-6.

Raja, P.; Veerasingam, S.; Suresh, G.; Marichamy, G. and Venkatachalapathy, R. (2009). Heavy metals concentration in four commercially valuable marine edible fish species from Parangipettai Coast, South East coast of India. International J. of Animal and Veterinary Advances 1(1): 10-14.

Sivaperumal, P.; Sankar, T.V.and Viswanathan Nair, P.G. (2007). Heavy metal concentrations in fish, shellfish and fish products from internal

markets of India vis-a-vis international standards. Food Chem. 102: 612–620.

Tahán, J. E.; Sánchez, J. M.; Granadillo, V. A.; Cubillán, H. S. and Romero, R. A. (1995). Concentration of total Al, Cr, Cu, Fe, Hg, Na, Pb and Zn in commercial canned seafood determination by atomic spectrometric means after mineralization by microwave heating. J. Agric. Food Chem. 43: 910-915.

Tansel sireli, V.; Göncuöğlu, M.; Yildirim, Y.; Gucukoglu, A. and Cakmak, O. (2006). Assessment of heavy metals (cadmium and lead) in vacuum packaged smoked fish species (Mackerel, *Salmo salar* and *Oncorhynhus mykiss*) marketed in Ankara (Turkey). E. U. J. of Fisheries & Aquatic Sci. 23: 353-356.

Tüzen, M. and Soylak, M. (2007). Determination of trace metals in canned fish marketed in Turkey. Food Chem. 101: 1378–1382.

Vitosevic, B.; Samardzic, S.; Antonijevic, V. and Jokovljevic, V. (2007). Heavy metals in some imported food products and their potential toxic implications. Medicus 8: 62-66.

Voegborlo, R. B.; El-Methnani, A. M. and Abedin, M. Z. (1999). Mercury, cadmium and lead content of canned tuna fish. Food Chem. 67: 341-345.

World Health Organization. (1996). Trace element in human nutrition and health. Geneva: WHO.

تقدير بعض المعادن الثقيلة في منتجات الأسماك

سعدية محمد هاشم محمد، أسامة راشد أبو سماحة، على أحمد عبد النبى و محمد خليل محمد خليل

قسم علوم وتقنية الأغذية – كلية الزراعة – الشاطبى - جامعة الأسكندرية – الأسكندرية – جمهورية مصر العربية

أجريت هذه الدراسة بهدف تقديرمتبقيات بعض معادن الاثار و المعادن الثقيلة والتى تشمل النحاس والكادميوم والرصاص و الزرنيخ و الزئبق فى ٢٠عينة مختلفة من منتجات الأسماك (المملحة والمدخنة والمجمدة والمعلبة والمخللة) والتى تم تجمعيها عشوائيا من الأسواق المختلفة في مدينة الأسكندرية ، خلال عام ٢٠٠٩ وذلك باستخدام جهاز(Atomic Absorption Spectrophotometer)

و أثبتت الدراسة أنه ماعدا تركيزات الرصاص فى كل منتجات الأسماك السابق الاشارة لها ،الكادميوم فى السبيط المجمد ، السمك المملح ، السمك المخلل كانت أعلى من الحدود المسموح بها بواسطة منظمة الصحة العالمية. وفيما عدا مستويات الزرنيخ فى الكابوريا المجمدة و السردين المعلب, فان كل مستويات النحاس والكادميوم والرصاص والزرنيخ والزئبق فى كل منتجات الأسماك تحت الدراسة كانت أقل من الحدود المسموح بها بواسطة بعض الهيئات التشريعية مثل هيئة سلامة الغذاء ومنظمة الصحة العالمية والمواصفات القياسية المصرية.

قام بتحكيم البحث

أ.د / مسعد عبد العزيز ابو ريه	**كلية الزراعة – جامعة المنصورة**
أ.د / محمد محمد موسى	**كلية الطب البيطرى – جامعة الاسكندرية**