Determination of Heavy Metals in Imported Canned Fish that Sold in Baghdad Markets

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Abstract

The concentrations of Pb, Zn, Hg and Cu were determined in twenty sample of canned fish, samples were collected with different origin with two meals from local markets at Baghdad city for the period (October 2012-February 2013),results of study were appeared variation in mercury concentration of canned fish between November and February .The highest concentration of mercury (0.1 mg/kg) was observed in "Hawesta" brand and "Ocean wave" " brand , the lowest average concentration for mercury 0.01ppm in "Habar","Durra" and "Sayad" brand during(Nov.2012-Feb.2013) and have not recorded any concentration for mercury in "Yasmine" brand during (Nov. 2012-Feb. 2013).The maximum level of zinc reached in November. rather than in Febreuary ,Zn concentration varied from (6.46-18.6 mg/kg) and the lowest concentration of Zn in canned fish from (0.010 - 0.370mg/kg). The results findings acceptable limit with Iraq standard.In this study we showed the concentration of copper varied from (0.073-10.216 mg/kg) .The highest concentration of copper (10.216mg/kg) was observed in "Habar" brand the lowest concentration of copper (0.073mg/kg) was observed in "Durra" brand , "Founty"and"Herring fillets" were recorded 0.19 mg/kg and 0.16 mg/kg.

Keywords: heavy metals ,canned fish ,Baghdad

تحديد المعادن الثقيلة في الأسماك المعلبة المستوردة التي تباع في أسواق بغداد

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الخلاصة

حددت تراكيز كل من الرصاص والزنك والزئبق والنحاس في عشرين عينة من الأسماك المعلبة، تم جمع عينات مختلفة المنشأ على وجبتين من الاسواق المحلية في مدينة بغداد للفترة ما بين (تشرين الاول 2012–كانون الاثاني 2013)..اظهرت نتائج الدراسةاختلاف في تركيز الزئبق في الأسماك المعلبة بين تشرين الثاني وشباط حيث لوحظ أعلى تركيز لعنصر الزئبق(0.1 ملغ /كلغ) في Ocean wave,Hawesta واقل تركيز لعنصر الزئبق (0.01 ملغ/كلغ) في "Sayad", "Durra","Habar" للفترة مابين تشرين الثاني وشباط ولم يسجل اي تركيز للزئبق في علبة السردين"ياسمين".الحد الأعلى لتركيز الزنك الذي تم التوصل إليه في تشرين الثاني بدلا من شباط، وتركيز الزنك تفاوتت من(6،46 حتي 18،6 ملغم / كغم) وأقل تركيز لعنصر الزنك في الأسماك المعلبة تراوح من(0.010 –0.370ملغم/كلغ) وكانت نتائج الدراسة موافقة للحدود المسموح بها في المواصفة العراقية.وفي

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هذه الدراسة أظهر تركيز النحاس اختلاف من (0.73−10،216 ملغ / كلغ). وقد لوحظ أعلى تركيز لعنصر النحاس(10.216ملغ/كلغ) في علبة".حبار". اما. Durra""حيث سجلت اقل تركيز لعنصر النحاس 0.073 ملغ/كلغ ،بينما لوحظ في Founty و "Herring Fillets" حيث سجل تركيز النحاس 0.16 ملغ/كلغ و0.19 ملغ/كلغ.

Introduction

Food safety is a major public concern worldwide, during the last decades, the increasing demand of food safety has stimulated research regarding the risk associated with consumption of food stuffs contaminated by pesticides, heavy metals and toxins [1].

Heavy metals, in general are not biodegradable, having long biological half-lives and having the potential for accumulation in the different body organs leading to unwanted side effects [2-4] .

The widespread of contamination with heavy metals in the last decades has raised public and scientific interest due to their dangerous effects on human health [5],this has led researchers all over the world to study the pollution with heavy metals in air, water, and foods to avoid their harmful effects and to determine their permissibility for human consumption[6,7].

Fish is widely consumed in many parts of the world because it has high protein content ,low saturated fat and also contain omega fatty acids known to support good health [8] . Degradation of lipids in fatty fish produces rancid odors [9].The risk of heavy metals contamination in meat represent with great concern for both food safety and human health ,because the toxicity nature of these metals at relatively minute concentration[10,11] . Instances of heavy metals contamination in meat products during processing have been reported [11,12].

Material and Methods

Samples of study

10 samples of canned fish were collected randomly with two groups from super stores and local markets in the city of Baghdad areas during October 2012 to January 2013 table-1.

Table 1 -.List of canned fish brands with detailed information for each of them

NO	Brand name	Batch no.	Production data	Expire data	Net weight	Note
1.	Sayad	480779	8/8/2011	8/8/2013	125GM	-Spiced sardine in vegetable oil(oil,spice,salt) -Product of Indonesia
2.	Durra		20/12/2011	20/2/2013	200GM	-Tuna solid with sunflower oil (cooked with tuna meat 70%,sunfloweroil,salt,water 30%) -Product of Thailand
3.	Founty	00A000 2	7/7/2012	7/7/2014	125GM	-Sardines in vegetable oil(sardine,oil,salt) -Product of morocco
4.	Port Clyde		8/8/2010	8/8/2014	106GM	-Port clyde sardine in soy bean oil(sardines lightly smoked,soybean,oil,salt,natural flavor smoke).
5.	Yasmine	ATSU0 024	11/3/2010	11/3/2013	200GM	-Sardin in vegetable oil(cooked sardine ,vegetaboil,salt) -Product of Thialand
6.	Tahani	3502 101001	4/11/2011	4/2/2013	425GM	-Mackerel in natural oil(water,salt,oil,mackerel) -Product of China
7.	Hawesta	0069220 01206	10/2011	12/2015	200GM	-Extra zarte herring filets in Toskana-Sauce (oil,sugar,water60%,vinegar, tomato paste,protein) -Product of Jordan
8.	Herring Fillets		7/7/2010	7/7/2014	200GM	-Herring Fillets in paprika sause(water,tomatopaste,sugar,distilledvinegar,rapeseedoil,spice,starch,bean gum). -Product ofGermeny
9.	Ocean Wave	852021 001250	2/8/2011	2/8/2013	250GM	-Light meat tuna in vegetableoil(water,oil,salt) -Product of Thialand
10.	Habar	67006w wa	3/7/2010	3/8/2013	200GM	- cuttle in tomato sause (salt,water,tomato paste) -Product of uae

PH measurement

Before the PH of food is measured, the food should be in liquid form or prepared as a puree in a blender. Distilled water may be added to aid in mixing the components thorough theninserted in pH meter (Electronic Instruments LTD).

Samples Analysis

50-100 gm of sample was taken from each canned meat with three replicate. All sample were oven dried at $(70)^0$C for 30 minute. The samples were transferred to mixer was divided into small pieces and the size of piece was 4mm., 2.5 gm of dried samples were taken, and then added 25ml of HNO_3 and heated for 30 minute, then cooled at room temperature and added (15ml con $HCLO_4$),it was heated to dry till appear of the white vapors of $HCLO_4$.

Each sample was filtered by using filter paper (42 whatman) and it was diluted with de-ionized water to complete the volume to 25 ml , each element concentration was determined by Atomic Absorption Spectrometry (Buck -Scientific FAAS/VGP 210/2005) .Mercury concentration was determined by vapor system, in Research of Food Center / Ministry of Science and Technology [13].

Statistical analysis

The data were subjected to use SPSS and statistical tests for the significant differences was used (T test) and least significant differences test LSD at ($p<0.01$) ($p<0.05$).

Results and Discussion

The Study results revealed that the highest value of pH in "Port clyde" was (7-7.11) ,While the lowest value of PH in "Durra" and "Hawesta" was 5.5 ,this difference in the values ofthe PH due to the stress of the animal before slaughtering ,the difference between the samples as a result for adding of preservatives with low pH that reflected on these meat samples [14]

Statistical analysis of the data revealedno significant different in pH value ($P<0.05$,$P<0.01$) between the samples which indicate that the value of pH is nearly equal see in table-2.

Study results were showed variation in mercury concentration between November 2012and February 2013 that related to some reasons such as the interaction mainly depend on chemical properties of the food contact material and the food stuff ,temperature at packaging during heat treatment and storage ,exposure to light ,water activity of salt and acids of the product [15].

The highest concentration of mercury (0.1 mg/kg) was observed in "Hawesta" brand and "Ocean wave" brand in November rather than in February.

"Ocean wave" and "Durra" brand, the concentration level of mercury are agreement with FDA reports that the mercury level in canned tuna is ranged between 0.1 - 0.2 ppm and it was 0.29mg/kg in Libyan canned tuna [16]

The lowest concentration level for mercury 0.01ppm in "Habar" and "Sayad" brand during(Nov.2012-Feb.2013) and have not recorded any concentration for mercury in "Yasmine" brand during (Nov. 2012-Feb. 2013) and have not recorded any concentration of Hg in "Habar" and "Founty" brand in November while " Hawesta", "Ocean wave", "Herring Fillets" and "Port clyde" does not record any concentration of Hg in February, which were agreement with [17] and [18] while [19] they showed the concentration of mercury varied from 0.01to 3 ppm exceed normal levels and [20] varied from 0.0430–0.253ppm for mercury.

Lead do not detected in fish samples, these results were agree with [17] and may be refer to the absence of these cans from the concentration of lead, which related to the toxic metals that prevent presence in the food and that causes toxicity when ingested in large amounts, in addition the effect of this metal bioaccumulation and does not show symptoms of poisoning directly, but it depends on the dose after eating

The range of copper concentration was from (0.073-10.216 mg/kg) , which were agreement with [21] ,they found the concentration of Cu in meat and fish products varied (7.18-10.01 mg/kg), while the lowest concentration of copper (0.073mg/kg) was observed in "Durra" brand , "Founty" and "Herring fillets" were observed 0.19 mg/kg and 0.16 mg/kg disagreement with[19], were found that the concentration of Cu varied from (0.001-0.01 mg/kg) in fish samples and did not agree with [22].The finding results do not exceed the acceptable limit of Iraqi standard which is 50mg/kg in canned tuna.

The maximum level of zinc reached in November rather than in February ,the study result which were agreement with [23] ,they studied the detection about heavy metals in 10 types of canned food in Turkey markets were found the Zn concentration is high (6.46-18.6 mg/kg) and agreement with [24] and [25] reported the lowest concentration of Zn in canned fish from (0.010-0.370mg/kg),which were disagreement with [26].

In Statistical Analysis explains all the differences between the heavy metals are significant (atp <0.05 & p <0.01) that shows oscillated in the concentration of these elements in each can for the study periods see in table-1.

In table-4 and table-13 it can observe that the heavy metals in each can and each period by using T test (included two element) and (L.S.D) test (included more than two element)**.**In cases that included more than two element shows that the difference between the mean of Zn and Hg higher than L.S.D (P< 0.05) (p<0.01) indicates significant different.

The difference between mean Cu and Zn are significant while the significant difference between Zn and Hg more than the significant difference between Cu and Zn which indicates that the effect of Zn concentration more than the effect Cu and Hg concentration.

Table 2- Difference between heavy metals and pH to each period at (p<0.05) (p<0.01)

Canned fish	Heavy metals	Test of variance	T-Cal.	T-table		Significant difference at α=0.05 & α=0.01
				0.05	0.01	
Habar	Hg	Unequal	-45.0333	± 4.303	± 9.925	S.
	Zn	Unequal	37.01937	± 4.303	± 9.925	S.
	Cu	Unequal	840.3805	± 4.303	± 9.925	S.
	PH	Equal	**47.76505**	± 2.776	± 4,604	S.
Tahani	Hg	Equal	24.4949	± 2.776	± 4,604	S.
	Zn	Equal	1467.086	± 2.776	± 4,604	S.
	Cu	Unequal	**-32.909**	± 4.303	± 9.925	S.
	PH	Unequal	-0.74183	± 4.303	± 9.925	N.S.
Port clyde	Hg	Unequal	34.64102	± 4.303	± 9.925	S.
	Zn	Equal	1316.601	± 2.776	± 4,604	S.
	Cu	Unequal	60.62178	± 4.303	± 9.925	S.
	PH	Equal	-1.08386	± 2.776	± 4,604	N.S.
Sayad	Hg	Equal	-30.6186	± 2.776	± 4,604	S.
	Zn	Equal	800.933	± 2.776	± 4,604	S.
	Cu	Equal	8.573214	± 2.776	± 4,604	S.
	PH	Equal	-5.94445	± 2.776	± 4,604	S.
Founty	Hg	Unequal	-27.7128	± 4.303	± 9.925	S.
	Zn	Equal	2327.015	± 2.776	± 4,604	S.
	Cu	Equal	38.72983	± 2.776	± 4,604	S.
	PH	Equal	2.44949	± 2.776	± 4,604	N.S.
erring fille	Hg	Unequal	67.54998	± 4.303	± 9.925	S.
	Zn	Equal	2308.644	± 2.776	± 4,604	S.
	Cu	Equal	75.93418	± 2.776	± 4,604	S.
	PH	Equal	**9.166562**	± 2.776	± 4,604	S.
Hawesta	Hg	Unequal	17.32051	± 4.303	± 9.925	S.
	Zn	Unequal	**220.0852**	± 4.303	± 9.925	S.
	Cu	Equal	25.71964	± 2.776	± 4,604	S.
	PH	Unequal	25.67948	± 4.303	± 9.925	S.
Durra	Hg	Equal	-106.553	± 2.776	± 4,604	S.
	Zn	Equal	1910.602	± 2.776	± 4,604	S.
	Cu	Equal	-8.57321	± 2.776	± 4,604	S.
	PH	Unequal	-0.86173	± 4.303	± 9.925	N.S.
Yasmine	Hg	Unequal		± 4.303	± 9.925	S.
	Zn	Equal	1229.644	± 2.776	± 4,604	S.
	Cu	Unequal	-36.3731	± 4.303	± 9.925	S.
	PH	Equal	**-0.16984**	± 2.776	± 4,604	N.S.
Ocean wav	Hg	Unequal	17.32051	± 4.303	± 9.925	S.
	Zn	Unequal	417.0761	± 4.303	± 9.925	S.
	Cu	Equal	40.20422	± 2.776	± 4,604	S.
	PH	Unequal	-3.07359	± 4.303	± 9.925	N.S.

Table 3- The mean and standard deviation for each sample

Canned fish	Heavy metals	28/11/2012 Mean ± S.D.	25/02/2013 Mean ± S.D.
Habar	Hg	0.0 ±0.0	0.013 ± 0.0005
	Zn	7.523 ± 0.312	0.8 ± 0.04
	Cu	10.216 ± 0.01	0.5 ± 0.02
	PH	6.31 ± 0.01	5.92 ± 0.01
Tahani	Hg	0.39 ± 0.001	0.019 ± 0.001
	Zn	9.87 ± 0.005	0.4 ± 0.01
	Cu	0 ± 0	0.19 ± 0.01
	PH	6.5 ± 0.01	6.62 ± 0.28
Port clyde	Hg	0.02 ± 0.001	0 ± 0
	Zn	13.78 ± 0.01	3.03 ± 0.01
	Cu	0.35 ± 0.01	0 ± 0
	PH	7 ± 0.173	7.11 ± 0.03
Sayad	Hg	0.013 ± 0.001	0.038 ± 0.001
	Zn	11.14 ± 0.01	0.8 ± 0.02
	Cu	0.29 ± 0.01	0.22 ± 0.01
	PH	6.2 ± 0.1	6.55 ± 0.02
Founty	Hg	0 ± 0	0.016 ± 0.001
	Zn	19.44 ± 0.01	0.44 ± 0.01
	Cu	0.69 ± 0.01	0.19 ± 0.02
	PH	6.7 ± 0.1	6.3 ± 0.265
Herring fillet	Hg	0.039 ± 0.001	0 ± 0
	Zn	19.98 ± 0.01	1.13 ± 0.01
	Cu	0.78 ± 0.01	0.16 ± 0.01
	PH	6.3 ± 0.1	5.73 ± 0.04
Hawesta	Hg	0.1 ± 0.01	0 ± 0
	Zn	24.97 ± 0.01	0.1 ± 0.01
	Cu	0.68 ± 0.01	0.47 ± 0.01
	PH	7 ± 0.1	5.51 ± 0.01
Durra	Hg	0.01 ± 0.001	0.097 ± 0.001
	Zn	16.2 ± 0.01	0.6 ± 0.01
	Cu	0.73 ± 0.001	0.08 ± 0.001
	PH	5.5 ± 0.1	6 ± 1
Yasmine	Hg	±	±
	Zn	10.35 ± 0.01	0.31 ± 0.01
	Cu	0 ± 0	0.21 ± 0.01
	PH	6.6 ± 0.1	6.61 ± 0.02
Ocean wave	Hg	0.1 ± 0.01	0 ± 0
	Zn	26.7 ± 0.01	2.5 ± 0.1
	Cu	0.52 ± 0.005	0.27 ± 0.0095
	PH	6.1 ± 0.1	6.28 ± 0.017

Table 4 - Statically Analysis of heavy metals for (Habar) with each period

A - Fish Habar 28/11/2012					
Heavy metals	Test of variance	T-Cal.	T-table 0.05	T-table 0.01	Significant difference at α=0.05 & α=0.01
Zn & Cu	Unequal	**-14.95**	± 4.303	± 9.925	S.

B - Fish Habar 25/2/2013					
Test the differences between the means					
treat.	average	L.S.D0.05	L.S.D0.01	Hg	Cu
Zn	0.8	0.051591	0.040965	0.787	0.3
Cu	0.5	0.051591	0.040965	0.487	

Zn	Cu
Mean ± S.D.	Mean ± S.D.
7.523 ± 0.312	10.216 ± 0.001

Table 5 - Statically Analysis of heavy metals for(Tahani) with each period

B - Fish Thahani 25/2/2013					
Test the differences between the means					
treat.	average	L.S.D0.05	L.S.D0.01	Hg	Cu
Zn	0.4	0.016354	0.012986	0.381	0.21
Cu	0.19	0.016354	0.012986	0.171	

A - Fish Tahani 28/11/2012					
Heavy metals	Test of variance	T-Cal.	T-table 0.05	T-table 0.01	Significant difference at α=0.05 & α=0.01
Hg & Zn	Equal	**-3339.42**	± 2.776	± 4,604	S.

Hg	Zn
Mean ± S.D.	Mean ± S.D.
0.039 ± 0.001	9.87 ± 0.005

Table 6 - Statically Analysis of heavy metals for(Port clyde)with each period

A - Fish Port clyde 28/11/2012					
Test the differences between the means					
treat.	average	L.S.D0.05	L.S.D0.01	Hg	Cu
Zn	0.4	0.016354	0.012986	0.381	0.21
Cu	0.19	0.016354	0.012986	0.171	

B - Fish Port clyde 25/2/2013				
	Zn			

Table 7- Statically Analysis of heavy metals for(Sayad) with each period

A - Fish Sayad 28/11/2012					
Test the differences between the means					
treat.	average	L.S.D0.05	L.S.D0.01	Hg	Cu
Zn	11.14	0.016354	0.012986	11.127	10.85
Cu	0.29	0.016354	0.012986	0.277	
B - Fish Sayad 25/2/2013					
Test the differences between the means					
treat.	average	L.S.D0.05	L.S.D0.01	Hg	Cu
Zn	0.8	0.025819	0.020501	0.762	0.58
Cu	0.22	0.025819	0.020501	0.182	

Table 8- Analysis of heavy metals for (Founty) with each period

A - Fish Founty 28/11/2012					
Heavy metals	Test of variance	T-Cal.	T-table		Significant difference
			0.05	0.01	at α=0.05 & α=0.01
Zn & Cu	Unequal	2296.397	± 4.303	± 9.925	S.
B - Fish Founty 25/2/2013					
Test the differences between the means					
treat.	average	L.S.D0.05	L.S.D0.01	Hg	Cu
Zn	0.44	0.025819	0.020501	0.424	0.25
Cu	0.19	0.025819	0.020501	0.174	

Zn	Cu
Mean ± S.D.	Mean ± S.D.
19.44 ± 0.01	0.69 ± 0.01

Table 9- Statically Analysis of heavy metals for(Herring Fillets) with each period

A - Fish Herring 28/11/2012					
Test the differences between the means					
treat.	average	L.S.D0.05	L.S.D0.01	Hg	Cu
Zn	19.98	0.016354	0.012986	19.941	19.2
Cu	0.78	0.016354	0.012986	0.741	
B - Fish Herring 25/2/2013					
Heavy metals	Test of variance	T-Cal.	T-table		Significant difference
			0.05	0.01	at α=0.05 & α=0.01
Zn & Cu	Unequal	118.8003	± 4.303	± 9.925	S.

Zn	Cu
Mean ± S.D.	Mean ± S.D.
1.13 ± 0.01	0.16± 0.01

Table 10- Statically Analysis of heavy metals for (Hawesta) with each period

A - Fish Hawesta 28/11/2012					
Test the differences between the means					
treat.	average	L.S.D0.05	L.S.D0.01	Hg	Cu
Zn	24.97	0.01998	0.015865	24.87	24.29
Cu	0.68	0.01998	0.015865	0.58	

B - Fish Hawesta 25/2/2013					
Heavy metals	Test of variance	T-Cal.	T-table 0.05	T-table 0.01	Significant difference at α=0.05 & α=0.01
Zn & Cu	Unequal	202.1613	± 4.303	± 9.925	S.

Zn	Cu
Mean ± S.D.	Mean ± S.D.
12.2 ± 0.1	0.47± 0.01

Table 11- Statically Analysis of heavy metals for (Durra) with each period

A - Fish Durra 28/11/2012					
Test the differences between the means					
treat.	average	L.S.D0.05	L.S.D0.01	Hg	Cu
Zn	16.2	0.01165	0.009251	16.19	16.127
Cu	0.073	0.01165	0.009251	0.063	

B - Fish Durra 25/2/2013					
Test the differences between the means					
treat.	average	L.S.D0.05	L.S.D0.01	Cu	Hg
Zn	0.6	0.01165	0.009251	0.52	0.503
Hg	0.097	0.01165	0.009251	0.017	

Table 12- Statically Analysis of heavy metals for (Yasmine) with each period

A - Fish Yasmine 28/11/2012					
		Zn			

B - Fish Yasmine 25/2/2013					
Heavy metals	Test of variance	T-Cal.	T-table 0.05	T-table 0.01	Significant difference at α=0.05 & α=0.01
Zn & Cu	Equal	12.24745	± 2.776	± 4,604	S.

Zn	Cu
Mean ± S.D.	Mean ± S.D.
0.31 ± 0.01	0.21± 0.01

Table 13- Statically Analysis of heavy metals for (Ocean wave) with each period

	A - Fish Ocean wave 28/11/2012				
	Test the differences between the means				
treat.	average	L.S.D0.05	L.S.D0.01	Hg	Cu
Zn	26.7	0.017303	0.013739	26.6	26.18
Cu	0.52	0.017303	0.013739	0.42	

	B - Fish Ocean wave 25/2/2013				
Heavy	Test of	T-Cal.	T-table		Significant difference
metals	variance		0.05	0.01	at α=0.05 & α=0.01
Zn & Cu	Unequal	38.45018	± 4.303	± 9.925	S.

Zn	Cu
Mean ± S.D.	Mean ± S.D.
2.5 ± 0.1	0.27± 0.0095

Conclusions

This study were appeared that the concentration of Hg,Cu,Zn in canned fish with acceptable limits of Iraq standard and FAO while does not record any concentration of Pb in fish samples and the concentration of Zinc more effect than the concentration of copper and mercury in canned fish.

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