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Analysis of Lead in Canned Foods in Markets of Benghazi-Libya

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Abstract – Canned foods are frequently consumed globally, because they are cheap and available, and the increasing concern about food safety stimulated research regarding the risk associated with the consumption of food contaminated by heavy metals. This study includes determining the concentration of lead (Pb) in different foods associated with health hazard inference in Libya. A twenty-four samples of nine brands of canned foods packaged in metal containers collected randomly from the markets during available in local markets of Benghazi-Libya.

The levels of lead usually are very low in foodstuffs, a procedure for the concentration of the element by dithizone as solvent extraction. Moreover, the pH of the sample is adjusted, and some physicochemical variables of canned food such as moisture, and ash were calculated. The concentration of selected toxic metal levels (Pb) in the foodstuffs were lower than the maximum allowable concentrations (1000µg/kg) as recommended in the China National Food Safety Standard established and by the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO). This suggests no additional health risks as well as consistency with the results.

Keywords – Health Hazard, Foodstuff Contamination, Canned Food Pollution, Heavy Metal, Lead, Benghazi- Libya.

I. INTRODUCTION

Contamination of food products by heavy metals was becoming an unavoidable problem these days. Air, soil, and water pollution contribute to the presence of harmful elements, such as cadmium, lead, mercury and arsenic in foodstuff. The occurrence of heavy metals-enriched ecosystem components, firstly, arise from rapid industrial growth, advances in agricultural chemicalization, or the urban activities of human beings. These agents have led to metal dispersion in the environment and, consequently, poor health of the population by the ingestion of victuals contaminated by harmful elements **[1]**.

The gastrointestinal tract (GIT) is exposed to various environmental pollutants, including metals that contaminate food and water and may have toxic effects on the body **[2]**.Canned foods were a war-time invention, 130 years ago, for the feeding of the troops during the Napoleonic campaign, canning requires a high degree of knowledge and scientific attention to detail. Canned foods did cause a certain amount of food poisoning, which had been improperly handled or subjected to improper storage and transport routes **[3]**. Canned foods were packed in hermetically sealed containers and are commercially sterile **[4]**.

The primary objective of food processing is to preserve perishable foods in a stable form that can be stored and shipped to distant markets during all months of the year.

Processing also can change foods into new or more usable forms and make foods more convenient to prepare. The goal of the canning process is to destroy any microorganisms in the food and prevent recontamination by microorganisms. Heat is the most common agent used to destroy microorganisms. Removal of oxygen can be used in conjunction with other methods to prevent the growth of oxygen requiring microorganisms **[5]**.

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time **[6]**. Heavy metals are naturally occurring elements and are present in varying concentrations in all ecosystems. There is a huge number of heavy metals **[7]**.

Lead can occur via food, water, soil, dust, and air. Lead exists both in organic and inorganic forms. In the environment, inorganic lead predominates over the organic lead. Exposure to the latter is generally limited to occupational settings. Organic and inorganic lead differ in terms of both toxic kinetics and toxic dynamics. Organo-lead compounds, such as tri-alkyl-lead and tetra alkyl lead compounds, are more toxic than inorganic forms of lead **[8, 9]**. Due to its long half-life in the body, chronic toxicity of lead is of most concern when considering the potential risk to human health **[10]**. Lead can accumulate in the body, primarily in the skeleton. From the skeleton, it is released gradually back into the blood stream, particularly during physiological or pathological periods of bone demineralization such as pregnancy, lactation, and osteoporosis, even if lead exposure has already ceased. Lead can be transferred from the mother to the fetus/infant through and through breast milk **[10]**. Lead affects virtually every system in the body, including the blood, the cardiovascular, renal, endocrine, gastrointestinal, immune and reproductive systems. Nevertheless, the most critical target for lead appears to be the central nervous system (CNS), particularly the developing brain, where it can cause impaired cognitive development and academic performance in children even at low exposure levels **[11]**.

Therefore, the purpose of this study was to estimate the health risks of toxic metals via consumption of canned foods to the public of Benghazi. The main objectives of this study were to determine the toxic metal (Pb) concentration levels in 24 different kinds of canned foods.

II. Experimental

2.1. Reagents and Instrumentation

All reagents were of analytical reagent grade. All glassware was soaked overnight in 10% (v/v) nitric acid followed by washing with 10% (v/v) hydrochloric acid. Acid-washed glassware was rinsed with double distilled water and oven dried before use. Double distilled water was used wherever water is specified.

AAS nov AA Model 300 flame atomic absorption spectrometer (FAAS) equipped with a

deuterium background corrector and air-acetylene burner (Unicam Analytical System, Cambridge, UK), Agilent Technologies 120 Graphite Tube Atomizer graphite atomic absorption spectrometer (GAAS) were used to estimation of lead in food cans samples.

JENWAY3150 Model for pH measurement, HG53Halogen was used to moisture and Muffle Furnace for ash estimation.

Preparation of solutions

Standard stock Solution of lead

The concentration stock solution of standard for Pb was 1000mg/l and supported by FISONS company. A series of a standard curve from (1- 5ppm) was prepared by diluting 10.00 ml of 1000 ppm of Pb stock solution up to100 ml using double distilled water (100 ppm of Pb).

Potassium Cyanide Solution

Dissolve 5.00 g KCN then diluted up to 50.00 ml using double distilled water.

Dithizone Solution

Dissolve 0.01 mg of Diphenylthiocarbaozne in 100 ml of chloroform and solution should be prepared immediately before use.

2.2. Sampling

Twenty-four varieties of canned food products were randomly collected and included ten food types such as mushroom, tomato, chickpeas, fruit, bean, pea, pineapple, corn, broad bean, and jam, which are available in local markets from Benghazi-Libya, the expiry date of the production is (2012-2016).

2.3 Sample Treatment

Wet Digestion

The samples were opened, and the contents were homogenized because it contains solid materials and liquid been mixed with an electric mixer until it became homogeneous. These materials transferred inside the vessels of polypropylene material until it starts of the chemical process of digestion, after all drying the samples in an oven at temperature 150 °C and then grind the dry samples by a mortar of porcelain to be digested. 5 g were accurately weighed out to 0.01g taken from the dry sample and placed inside size beaker 200 ml, then added to 10 ml of nitric acid Center (HNO_3) 65% and 0.5 ml of hydrogen peroxide 30% then left the sample covered to the next day with the time bottle, by the time the cup has been heated by raising the temperature gradually to 150ºC, when the amount of acid becomes less pull the cup from the surface and leaves to cool, then add 5mls of the acid centre to sample and returned to the heating surface, and continue the process of digestion until it becomes clear and upscale. After cooling the cup to room temperature, the cup contents have been filtered by a (Whatman filter paper. No.42) and transported quantitatively to 50 ml volumetric flask and complete the label's size by distilled **[12]**.

Extraction Procedure

The re-concentration of the analyst by extraction processes is as follows:

10mL of sample adjusted at 8-9.5 pH. In a 250 ml separating funnel, addition 1ml of auxiliary ligand KSCN has been added.

Prepare Dithizone then10mL was added into the sample solution; the funnel was shaken with a mechanical shaker for 30min. After the organic phase was separated from the aqueous solution, the chloroform layer was drained into another separatory funnel. A 0.05 M nitric acid 10.0 ml was pipette into the funnel, and the funnel was shaken for 40min to back-extract metal ions in an aqueous solution **[13]**.

Estimated of Pb (FAAS)

Analysis of lead of two methods calibration curve and standard addition by using the flame atomic absorption spectrometry (FAAS).

Operational Conditions of FAAS (HCl Pb, 5 mA, Acetylene / air 50 mm, 283.3 nm, Burner 9.50 mm, Slit width 0.5 nm and LOD 0.05-10).

2.3.1. Standard Calibration Curve (C.C)

For estimation concentration of heavy metal (Pb) calibration curve method was used.

1. Prepare series in 50ml volumetric flasks, 10ppm standards, lead solution by dilution with double distilled water from (0, 1, 2, 3, 4, 5) ppm using dilution law.

2. Measurement absorbance is for series, by atomic absorption spectroscopy (FAAS, GAAS then prepared calibration carve using Beers law. The calibration curves of lead as shown in fig. (1).

2.3.2. Standard Addition curve (A.C)

standard addition method is as shown.

Volum by ml of unknown	2.5	2.5	2.5	2.5	2.5	2.5
Volum by ml of Pb unknown	**0.00**	**1**.00	**2**.00	**3**.00	**4**.00	5.00

2.3.3. Preparation of Blank Solution

The procedural blank used to monitor possible contamination was prepared from the sample preparation procedure to contain the same volume of reagent used, except the canned food samples; rinse blank can be prepared from 65% (v/v) HNO_3.

2.3.4. Statistical Analysis

The value of Pb (µg/kg) was expressed as Mean ±standard deviation (s.d.). Statistical analyses were carried out using Duncan Multiple Range test **[14]**. In all cases probability level of 95% was taken as significant.

III. Results and Discussion

The results of the analysis's lead in canned foods containers collected in Benghazi-Libya.

Figure 1, shown the standard calibration curve of lead standard solution, which used to find unknown lead in canned foods.

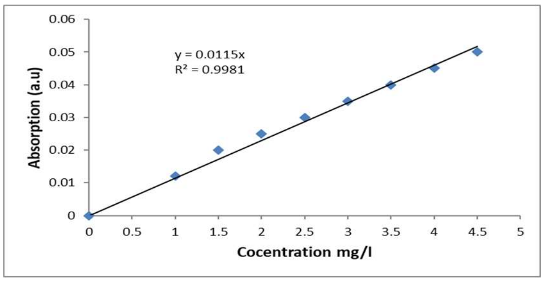

Figure 1. Calibration curve of lead standard, by flam atomic absorption spectrometry, (n=3).

Table 1. show the results, expressed as mean obtained from analysis of 24 canned foods samples (collected in Benghazi city, the expiry date of the production during 2012-2016. The table included the results of physicochemical properties, acidity, moisture content and ash content of the canned foods samples. The obtained data of acidity of samples expressed as pH is ranged from 2.30 to 6.23, moisture content expressed as % mean is raged from 5.08 to 30.21and ash content expressed as % mean is ranged from 0.11 to 7.80 as the following.

Table (1): Acidity, Moisture and Ash Content of Canned foods Product samples

Code of sample	pH	Moisture content (%)	Ash content (%)
A1	4.07	26.50%	0.80%
A2	4.22	19.10%	0.70%
A3	4.30	22.00%	0.84%
B1	3.78	5.08%	7.80%
B2	3.60	7.22%	6.70%
B3	3.90	7.21%	5.00%
C1	6.23	13.23%	1.09%
C2	6.00	7.43%	0.11%
D1	3.34	16.09%	0.13%
D2	3.40	17.01%	0.86%
E1	5.45	28.79%	1.23%
E2	5.44	12.57%	1.00%
F1	5.49	9.71%	0.23%
F2	5.53	5.59%	1.10%
G	3.46	20.23%	0.47%
H1	5.86	8.71%	0.77%
H2	5.70	8.99%	1.62%
H3	5.66	10.01%	1.55%

J1	2.47	15.10%	0.84%
J2	2.44	18.00%	0.85%
J3	2.30	8.92%	0.76%
J4	4.78	29.21%	0.88%
J5	5.34	22.04%	0.74%

3.1. pH effect on the accumulation of lead in food cans

The pH value of samples is ranged from 2.30 to 6.23, as shown in table (3) where clear that acidity of mushroom samples (A_1,A_2 and A_3) is ranging from (4.07- 4.30) an average of (4.20), while of tomato sauce samples (B_1,B_2 and B_3) is ranging from (3.60-3.90) an average of (3.76), and of chick peas samples the pH ranging from (6.00-6.23) an average of (6.115) while in fruits samples (D_1 and D_2) is ranging from (3.34-3.40) an average of (3.37), and in bean samples (E_1 and E_2) is ranging from (5.44-5.45) an average of (5.445), and in pea samples (F_1 and F_2) is ranging from (5.49-5.53) an average of (5.51), and in pineapple sample (G) is (3.46) and in corn samples (H_1,H_2 and H_3) ranging from (5.66-5.86) an average of (5.74), while in broad bean

samples (J_1, J_2, J_3, J_4 and J_5) is ranging from (2.30-5.34) an average of (3.47).

Note that all the results lead concentrations in the samples did not exceed the permitted.

value despite the low pH value in some samples in the metal packaging and thought why that material consumption Canned in time with right storage conditions. Noted pH effect on the type of packaging material on the rate of accumulation of metals in this study. Food manufacturers should avoid the use of acidic water with low pH, such foods are better bottled, or paper packaged than canned pH should be adjusted to values between 5.5 – 8.5 coupled with the use of internally lacquered containers or packaging material made up of glass, paper, and polymers **[15]**.

3.2. Moisture content effect on the accumulation of lead in food cans

Table 1. show us the moisture content of the canned foods is ranged from 5% to 29%, that is clear the moisture content of all samples less than 30% this means foods with higher moisture content might be expected to have higher water activity than dry foods, but the expectation is not necessarily correct. Products with the same water content may have very different water activities **[16]**.

3.3. Ash content on the accumulation of lead in food cans

The amount of ash contents in the canned foods expresses the amount of inorganic solids content of metals and element in food cans. Table 1. Summarized the ash content of the canned foods samples, which ranging from 0.11 to 7.80. These results are reasonable and acceptable.

3.4. Effects of lead in food packaging

First by (FAAS/C.C) where clear that concentration of metal lead in mushroom samples (A_1,A_2 and A_3) ranging from (393.8-465.6µg/kg) an average of (431.9µg/kg), while in tomato sauce samples (B_1,B_2 and B_3) ranging from (348.1-681.0µg/kg) an average of (320.9µg/kg), and in chick peas samples (C_1 and C_2) ranging from (359.5-547.5µg/kg) an average of (453.5µg/kg), while in fruits samples (D_1 and D_2) ranging from (520.2-744.9µg/kg) an average of (632.5µg/kg), and in bean samples (E_1 and E_2) ranging from (542.4-638.8 µg/kg) an average of (590.6µg/kg), and in pea samples (F_1 and F_2) ranging from (337.6- 635.3µg/kg) an average of (486.5µg/kg), and in pineapple sample (G) is (752.2µg/kg), and in corn samples (H_1,H_2 and H_3) (724.8-926.8 µg/kg) an average of (824.0 µg/kg), while in broad bean samples (J_1,J_2,J_3,J_4 and J_5) ranging from (651.0-815.2µg/kg) an average of (737.9µg/kg).

Secondly by (FAAS/A.C), note the value of lead in mushroom samples (A_1,A_2 and A_3) ranging from (140.7-153.6µg/kg) an average of (147.7µg/kg), while in tomato sauce samples (B_1,B_2 and B_3) ranging from (018.9-581.0µg/kg) an average of (310.9µg/kg), and in chick peas samples (C_1 and C_2) ranging from (174.4-359.2µg/kg) an average of (266.8µg/kg), while in fruits samples (D_1 and D_2) ranging from (510.2-761.1µg/kg) an average of (635.7µg/kg), and in bean samples (E_1 and E_2) ranging from

(541.5-631.1 µg/kg) an average of (586.3µg/kg), and in pea samples (F_1 and F_2) ranging from (537.6-610.2µg/kg) an average of (573.9µg/kg), and in pineapple sample (G) is (852.1µg/kg) an average of (852.1µg/kg), and in corn samples (H_1,H_2 and H_3) (705.2-798.0µg/kg) an average of (742.8 mg/kg), while in broad bean samples (J_1,J_2,J_3,J_4 and J_5) ranging from (612.4-804.2µg/kg) an average of (734.7µg/kg), see table (2).

Table 2. Concentration (µg/kg) of lead in canned foods packaged

Canned Foods	Code of Sample	Pb (µg/kg) /C.C	Pb (µg/kg) /A.C
Mushroom	A1	465.6±1.60	149.0±19.6
	A2	393.8±6.10	140.7±77.8
	A3	436.5±34.2	153.6±38.4
Tomato	B1	541.3±15.9	162.6±49.8
	B2	348.1±29.0	018.9±1.80
	B3	681.0±9.30	581.0±0.10
Chickpeas	C1	547.5±29.9	174.4±.41.7
	C2	359.5±52.1	359.2±0.10
Fruits	D1	520.2±17.5	510.2±0.10
	D2	744.9±46.9	761.1±0.10
Bean	E1	638.8±43.2	631.1±0.10
	E2	542.4±49.7	541.5±0.10
Pea	F1	635.3±33.0	610.2±0.10
	F2	337.6±31.3	537.6±0.10
Pineapple	G	752.2±60.1	852.1±0.10
Corn	H1	724.8±81.8	725.1±0.20
	H2	820.5±26.2	798.0±1.00
	H3	926.8±25.6	705.2± 4.50
Broad bean	J1	815.2±18.2	804.2±6.30
	J2	756.5±32.5	612.4±1.50
	J3	722.1±29.1	710.0±0.20
	J4	745.0±36.5	801.7±0.60
	J5	651.0±46.2	745.0±5.10

The results obtained for contents in the analysis of lead in canned foods packaged containers of two methods (calibration curve and standard addition by using flame atomic absorption spectrometry) (FAAS / C.C, FAAS / A.C) respectively, note that all samples were shot under the limit. But in some samples had lead concentrations were relatively high compared with the rest of the samples show in the tables (1) and (2) as follows fruits, pineapple, corn, broad and bean and D2=744.9, G=752.2, H1=724.8, H2=820.5, H3=926.8, J1=815.2, J2=756.5, J3=722.1, J4=745.0, D2=761.1, G=852.1, H1=725.1, H2=798.0, H3=705.2, J1=804.2, J2=612.4, J3=710.0, J4=801.7, and J5= 745.0, by FAAS/A.C. The results did not differ in the ways they all results showed that difference relative was allowed under (50µg/kg) **[17,18]**. The primary source of lead in canned foods is the leaching of lead from the canning. Where lead toxicity causes many diseases and symptoms such as abdominal pains, anemia, a pair bones, brain damage, anoxia, dizziness, convulsion and inability **[19]**.

IV. CONCLUSION

The levels of toxic metal such as Pb in in 24 samples of canned food items in Benghazi city, were analyzed and it potential health risks was estimated. By flame atomic absorption spectroscopy used by two methods standard curves and addition standard curve, the results show that, the lead content in cans of the packaging is low from limit recommended by (WHO) and (FAO) (1mg/kg) **[20]**. Nevertheless, some of the samples H2= 820.5, H3= 926.8 and J1= 815.2 µg /kg, respectively, by FAAS/C. C. and results of some samples were H2= 798.0, H3= 705.2 and J1= 804.2 µg/kg respectively. Noted that both samples H1 and H2 analyzed by FAAS/C.C a little higher than from samples analyzed from FAAS/A.C may be due to more accurate and sensitive. The H3 is more significant than all samples.

We can conclude that the canned foods are safe to eat for the local population. However, there are many routes for the migration of heavy metals into humans, such as food, water, air, so the potential health risks might be underestimated. In addition, although the biological indicators have been widely applied for the monitoring of environmental pollutants in health exposure risk assessments, the relationship between external and internal levels of pollutants has not yet been adequately established. Therefore, it is difficult to accurately assess the potential health risks associated with toxic metals.

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