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Evaluation Of (Lead (Ii), Cadmium (Ii) And Cobalt (Ii)) In Canned Foods Packaged In Glass Cans (Jam) In Benghazi Market

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Abstract:
***Background**: Canned foods are widely consumed worldwide due to their affordability and availability. However, there is growing concern about food safety, particularly regarding the risk of heavy metal contamination*
***Materials and Methods**: As a response to this concern, research has been conducted to investigate the concentrations of heavy metals in canned food samples collected from local markets in Benghazi, Libya. The study utilized flame atomic absorption spectrometry with both calibration standard curve and standard additions methods to analyze the levels of lead, cadmium, and cobalt, while graphite furnace atomic absorption spectrometry was employed with calibration standard method to analyze tin levels. Prior to analysis, the samples underwent a wet digestion process using nitric acid and hydrogen peroxide.*
***Results**: Typically, lead, cadmium, and cobalt levels in foods are extremely low. However, in this study, some samples showed higher levels of cadmium and cobalt than the permitted threshold of 50µg/kg. On the other hand, the concentration of lead in canned foods was below the allowed level of 1000µg/kg in all samples. The analysis of tin levels showed significantly high results, surpassing the allowable threshold. To further investigate the influence of pH on the mineral accumulation rate in canned foods stored in metal cans and glass containers, statistical analysis was conducted on the collected data.*
***Key Word:**Foodstuff Contamination, Canned Food Pollution, Heavy Metal, Lead, cadmium, cobalt,*

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I. Introduction

Contamination of food products by heavy metals has become an increasingly prevalent issue in recent times. The presence of harmful elements such as cadmium, lead, mercury, and arsenic in foodstuff is primarily attributed to air, soil, and water pollution. The occurrence of an environment enriched with heavy metals is primarily a result of rapid industrial expansion, increased use of agricultural chemicals, and the urban activities of human beings. These factors have led to the dispersion of metals in the environment, ultimately compromising the health of the population due to the consumption of food contaminated with these harmful elements. [1].

The human gastrointestinal tract can come into contact with different environmental pollutants, such as metals, that can contaminate the food and water we consume. These pollutants have the potential to cause harmful effects on the body. [2]

All chemicals present in the environment can enter the biological cycle and have the potential to enter the human body at any stage of its development. Among the various environmental chemicals, metals are of particular concern due to their toxicity. Some toxic metals have already reached harmful levels in the environment, especially when combined with other factors that enhance their absorption, retention, and toxicity. [3].

Our food naturally contains small amounts of various heavy metals. Some of these metals serve a biochemical purpose in our bodies, while others are unintentional contaminants. These trace metals can enter our food through agricultural practices, industrial pollution, geological sources, and food processing techniques. [4].

Canned foods were originally created around 130 years ago as a solution to feed the troops during the Napoleonic campaign. Canning process involves a significant level of knowledge and scientific precision. However, it is worth noting that during that time, improper handling, storage, and transport of canned foods did lead to instances of food poisoning. [5] Canned foods are typically placed in containers that are sealed tightly to prevent air or moisture from entering, ensuring that they are commercially sterile. [6].

The main goal of food processing is to maintain the freshness and quality of perishable foods so that they can be safely stored and transported to faraway markets throughout the year.

Processing can also transform food into new or improved forms and increase its convenience for preparation. The primary objective of the canning process is to eliminate any microorganisms present in the food and prevent subsequent contamination. Heat is the most commonly employed agent to achieve the destruction of microorganisms. Additionally, the removal of oxygen, when combined with other techniques, can be utilized to inhibit the growth of oxygen-dependent microorganisms. [7].

II. Material And Methods

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, cadmium, cobalt 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, cadmium, cobalt

To create a standard solution for elements, a concentration stock solution of 1000 mg/L was prepared for each element (lead, cadmium, and cobalt). A series of standard curves were then generated, ranging from 1 to 5 ppm for lead and 0.1 to 0.5 ppm for both cadmium and cobalt. This was done by diluting 10.00 ml of the 1000 ppm stock solution with double-distilled water to a final volume of 100 ml, resulting in a 100 ppm concentration of lead, cadmium, and cobalt in the solution.

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.

Sampling

Three samples of jam products were bought from the markets during available in local markets in local markets from Benghazi-Libya, the expiry date of the production is (2012-2016).

Sample Treatment

Wet Digestion

The samples were opened and mixed thoroughly using an electric mixer. Then, the materials were transferred into polypropylene vessels to initiate the chemical digestion process. Afterward, the samples were dried at 150 ºC and ground into a fine powder using a porcelain mortar for digestion purposes. For weighing purposes, exactly 5 g of the dried sample was measured out with an accuracy of 0.01 g and placed into a 200 ml beaker. Subsequently, 10 ml of 65% nitric acid (HNO_3) and 0.5 ml of 30% hydrogen peroxide (H_2O_2) were added to the sample in the beaker. The beaker was then covered and left undisturbed until the next day. During this time, the beaker was gradually heated up to 150ºC. As the acid level decreased, the beaker was removed from the heat source and allowed to cool. Afterwards, 5 ml of acid was added back to the sample, and the beaker was returned to the heat source. This digestion process was repeated until the sample became clear and fully digested. Once the beaker had cooled to room temperature, its contents were filtered and quantitatively transferred to a 50 ml volumetric flask. The flask was then filled to the mark with distilled water [8].

Extraction Procedure

To prepare the sample, take 10ml of the sample and adjust its pH to a range of 8-9.5 for lead (Pb) and cadmium (Cd), and at pH of 3-4 for cobalt (Co) using ammonia. Then, in a 250 ml separating funnel, add 1ml of an auxiliary ligand called potassium thiocyanate (KSCN). Next, add dithizone to the sample solution in the funnel. Shake the mixture using a mechanical shaker for 30 minutes. After that, add 0.05M nitric acid to the mixture and shake it for 40 minutes to back-extract the metal ions into an aqueous solution. [9]

Estimated of Pb (FAAS)

Analysis of metals (lead, cadmium, cobalt) Atomic Absorption Spectrometry (FASS).

Operational Conditions of FAAS for the heavy metals (Pb, Cd, Co) as shown as

Radiation Source	HCL Pb	HCL Cd	HCL Co
Lamp Current mA)	5	4	7
Fuel/ Support (mm)	Acetylene / air 50	Acetylene / air 50	Acetylene / air 50
Nebulizer (ml min1)	5	5	5
Wave length (nm)	283.3	228.8	240.7
Slit Width(nm)	0.5	0.5	0.2
Burner (mm)	9.50	9.00	9.00
LOD (ppm)	0.05-10	0.02-4	0.05-7

Standard Calibration Curve (C.C)

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

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

Measurement absorbance is for series, by atomic absorption spectroscopy (FAAS, GAAS then prepared calibration carve using Beers law. The calibration curves of lead, Cadmium, Cobalt as shown in fig. (1, 2, 3).

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
Volum by ml of Cd unknown	0.00	1.00	2.00	3.00	4.00	5.00
Volum by ml of Co unknown	0.00	1.00	2.00	3.00	4.00	5.00

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) HNO3.

Statistical Analysis

The value of Pb, Cd, Co (μg/kg) was expressed as Mean ±standard deviation (s.d.). Statistical analyses were carried out using Duncan Multiple Range test [10]. In all cases probability level of 95% was taken as significant

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III. Result

Standard Calibration Curves Method:

The results of the analysis's lead, Cadmium, and Cobalt in canned foods packaged in metal and glass containers collected in Benghazi-Libya, (2012-2016).

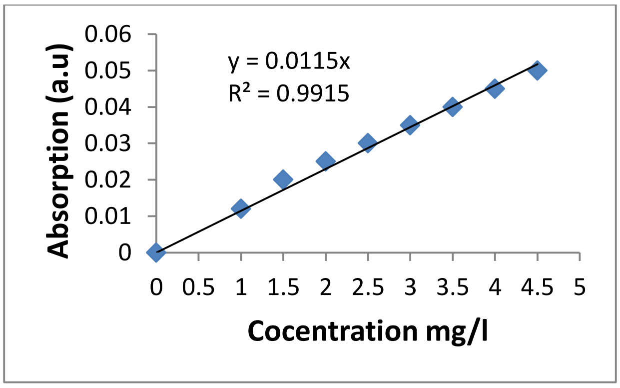

Figure (1) Calibration curve of lead standard, by flam atomic absorptionspectrometry (n=3).

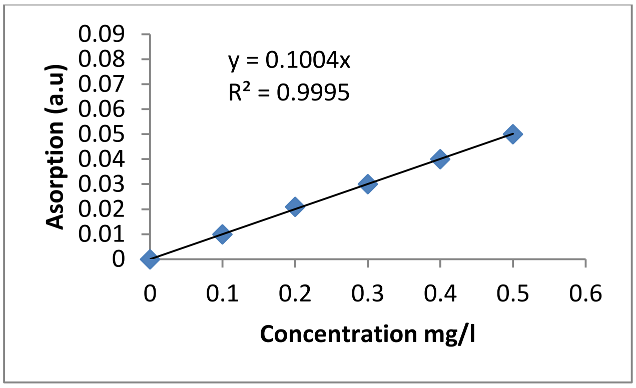

Figure. (2): Cailbration curve of cadmium standard, by flam atomic absorption spectrometry, (n=3).

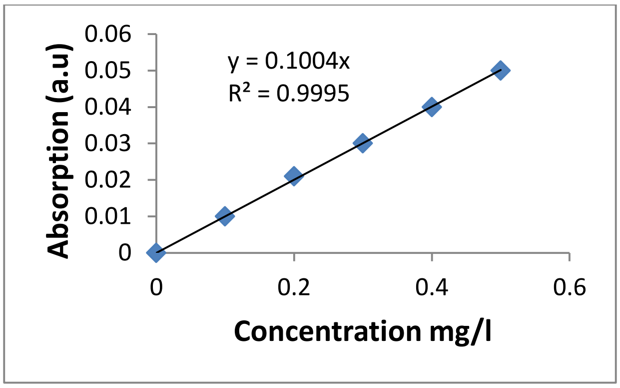

Figure. (3): Calibration curve of cobalt standard by flame atomic absorption spectrometry, (n=3).

Table 1. show the results, expressed as mean obtained from analysis of three (jam) 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 jam samples. The obtained data of acidity of samples expressed as pH is ranged from 3.69 to 3.99, moisture content expressed as % mean is raged from 0.03 to 2.67 and ash content expressed as % mean is ranged from 0.11 to 0.13 as the following.

Table (1): acidity, Moisture and Ash Content of Canned foods Products samples

Canned food products	pH	Moisture content (%)	Ash content (%)
I1	3.80	2.67%	0.13%
I2	3.99	2.33%	0.13%
I3	3.69	0.03%	0.11%

PH effect on the accumulation of metals in the glass cans (jam) by using two methods.

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 [11].

The concentration of lead in method (FAAS/C.C) were ranging from (680.3-953.6 µg/kg) an average of (827.9µg/kg), pH ranging from (3.69-3.99) an average of (3.82). And lead a range of concentration by (FAAS/A.C) were clear ranging from (589.1-850.1µg/kg) an average of (758.7µg/kg), pH ranging from (3.69-3.99) an average of (3.82) as shown in table 2.

Table(2): pH effect in glass cans of lead , cadmium, and cobalt of two methods by (µg/kg)

Code of Sample	PH	Concentration of lead		Concentration of cadmium		Concentration of cobalt	
		(FAAS/C.C)	(FAAS/A.C)	(FAAS/C.C)	(FAAS/A.C)	(FAAS/C.C)	(FAAS/A.C)
I1	3.80	953.6±0.1	837.0±0.1	52.5±0.9	37.6±0.1	1431.0±0.1	1431.2±0.6
I2	3.99	680.3±0.1	589.1±0.1	68.5±0.3	53.5±0.1	1213.4±0.1	1198.8±0.5

I3	3.69	850.0±0.2	850.1±0.1	63.2±0.1	61.7±0.1	984.0±0.5	0825.1±0.1

The affect value of pH on the concentration of lead in food samples due to glass bottles are not affected by the value of low pH, either the nutritional content in glass boxes did not affect value of pH on the concentration of lead in food samples due to glass bottles are not affected by the value of low pH.

the concentration of cadmium in canned foods by (FAAS/C.C) were clear that jam samples ranging from (52.5-68.5µg/kg) an average of (61.4µg/kg) pH ranging from (3.69-3.99) an average of (3.83). And the concentration by (FAAS/A.C) were clear ranging from (37.6-61.7µg/kg) an average of (50.9µg/kg) pH ranging from (3.69-3.99) an average of (3.82). Table (2) shows.

In the case of glass bottles, note that the cadmium concentration was below allowable internationally with this indicates that glass cans not affected by the reduced value of pH. cadmium

the concentration of cobalt in canned foods, by (FAAS/C.C) were clear that ranging from (984.0-1431.0 µg/kg) an average of (1209.5 µg/kg), pH ranging from (3.69-3.99) an average of (3.83) And range of concentration by (FAAS/A.C) from (825.1-1431.2 µg/kg) an average of (1151.7 µg/kg), pH ranging from (3.69-3.99) an average of (3.83). Table (2)

In the case of glass cans also note a high concentration of cobalt in the samples studied and were higher than allowed and believed that Cobalt element of elements present in food and also storage conditions May be bad due to its height.

Impact of glass cans on the content of (lead, cadmium, cobalt)

The lead concentration in jam samples (I1, I2, and I3) measured by FAAS/CC ranged from 680.3 to 953.6µg/kg, with an average concentration of 827.9µg/kg. Additionally, the lead concentration measured by FAAS/A.C ranged from 589.1 to 850.1µg/kg, with an average concentration of 758.7µg/kg. in Table (3)

The results were consistent in showing that there was no significant difference allowed at or below a relative difference of 50µg/kg. [12, 13]

Results for the cadmium concentration ranged from 52.5 to 68.5µg/kg, with an average concentration of 61.4µg/kg. Similarly, using the FAAS/A.C method, the cadmium concentration was found to range from 37.6 to 61.7µg/kg, with an average concentration of 50.9µg/kg.

The concentration of cadmium in jam samples exceeded the allowable limit in two ways, calibration curve and standard addition using flame atomic absorption spectrometry (FAAS/C.C, FAAS/A.C). The FAAS/C.C method showed a higher concentration of cadmium compared to the FAAS/A.C method. [13, 14] Additionally, in jam sample I3, the concentrations were 63.2 µg/kg and 61.7 µg/kg for FAAS/C.C and FAAS/A.C, respectively. Both values were equal and exceeded the allowable limit. (See table 3).

The cobalt concentration in jam samples, was determined using the FAAS/C.C method, the results showed that the cobalt levels ranged from 984.0 to 1431.0 µg/kg, with an average concentration of 1209.5 µg/kg. Additionally, the FAAS/A.C method also provided insights into the cobalt content in the jam samples, indicating a concentration range of 825.1 to 1431.2 µg/kg, with an average of 1151.7 µg/kg. as shown inTable (3)

Table (3): Concentration of lead, cadmium and cobalt in canned foods packaged in glass cans

Canned Foods	Code of Sample	Lead (Pb) (µg/kg)		Cadmium (Cd) (µg/kg)		Cobalt (Co) (µg/kg)	
		FAAS/C.C	FAAS/A.C	FAAS /C.C	FAAS /A.C	/ FAAS C.C	FAAS /A.C
Jam(cocktail)	I1	953.6±0.1	837.0±0.1	52.5±0.9	37.6±0.1	1431.0±0.1	1.4312±0.6
Jam (pieces orange)	I2	680.3±0.1	589.1±0.1	68.5±0.3	53.5±0.1	1213.4±0.1	1.1988±0.5
Jam(pieces fraises)	I3	850.0±0.2	850.1±0.1	63.2±0.1	61.7±0.1	984.0±0.5	0.8251±0.1

IV. Conclusion

Canned foods are widely consumed worldwide due to their affordability and accessibility. These findings align with the guidelines set by WHO and FAO, which prioritize food safety standards.

The study aims to analyze the concentration of heavy metals such as lead, cadmium, and cobalt in jam samples from different varieties of glass containers obtained randomly from the local markets in Benghazi, Libya. Flame atomic absorption spectroscopy was utilized to analyze the samples. Two methods, namely calibration standard curve and standard additions, were employed to measure the levels of lead, cadmium, and cobalt. The results were reported in micrograms per kilogram (µg/kg) for each element analyzed.

The concentration of lead in glass packaging for jam samples was found to be lower than the recommended limit of 1000µg/kg set by WHO and FAO, based on the analysis conducted using FAAS/A.C. However, the samples analyzed using FAAS/C.C. showed slightly lower levels, suggesting that this method may be more accurate and sensitive. In the case of cadmium concentration levels in jam samples, results obtained from two methods were compared: FAAS/S.C. and FAAS/A.S. The levels detected by FAAS/S.C. were greater than the recommended limit of 50µg/kg set by WHO and FAO. On the other hand, levels detected by FAAS/A.S. were within the recommended limit. Regarding cobalt concentration in jam samples packaged in glass, both FAAS/S.C. and FAAS/A.C. methods showed higher levels than the recommended limit of 50µg/kg set by WHO and FAO.

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